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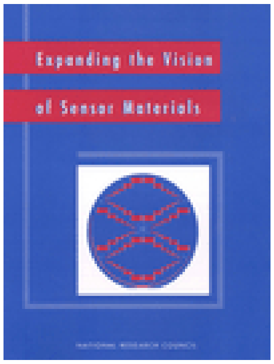

Expanding the Vision of Sensor Materials

Committee on New Sensor Technologies: Materials and Applications, Commission on Engineering and Technical Systems, National Research Council

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THE NATIONAL ACADEMIES
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Expanding the Vision of Sensor Materials

COMMITTEE ON NEW SENSOR TECHNOLOGIES:
MATERIALS AND APPLICATIONS
NATIONAL MATERIALS ADVISORY BOARD
COMMISSION ON ENGINEERING AND TECHNICAL SYSTEMS
NATIONAL RESEARCH COUNCIL

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NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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PREFACE

Sensors have become pervasive and essential in the modern industrial world. Applications range from sophisticated industrial processes to common consumer products. In many respects, the manufacturing industry has led the use of advanced sensors in monitoring and controlling its industrial processes. In most cases, these sensors are based on well-established technologies that sense external factors, such as process temperature, and basic product characteristics, such as imperfections, thickness, and weight. The application envelope of advanced sensor technologies is being extended. Today, on-line sensing of material properties, combined with real-time control, is making the goal of self-directed, intelligent processing a reality.

During the 1980s, many National Materials Advisory Board (NMAB) reports identified sensor technology as a critical area that would spur advancements in materials processing. These reports covered a range of topics, notably bioprocessing (NRC, 1986a), heat treatment (NRC, 1989a), integrated processing systems (NRC, 1992), metals processing (NRC, 1989b), nondestructive evaluation (NRC, 1986c), refining (NRC, 1986b), and welding (NRC, 1987). This report originated from a desire to synthesize the requirements described in previous NMAB reports and to develop a generalized research and development approach through which important sensor material needs could be satisfied.

Many efforts are under way to advance the state of the art of sensor technology and to apply what is already known to solve current problems. Most of this work is stimulated by the expectation of significant end results. It is often highly desirable that these sensors be mounted at the location of concern, placed in a remote location, or embedded as a component of a structural element. Simultaneously, the materials development community is investigating a wide assortment of novel materials that can lead to desired solutions to very difficult sensing requirements. Advances in materials technologies and the ability to precisely "engineer" material properties and behavior offer a wide possibility for developing new sensor materials. This work requires close collaboration with other technical disciplines, such as solid state physics and electrochemistry.

The Committee on New Sensor Technologies: Materials and Applications was comprised of 9 specialists with expertise in chemical sensor technology, engineering applications of sensor technology, materials science and engineering, microelectronic and photonic technology, and nondestructive evaluation. The committee also added two technical advisors with expertise in intelligent manufacturing and in the detection of hazardous chemicals. The committee met seven times between March 1992 and May 1993. Invited presentations by experts from industry and government provided relevant information regarding applications for advanced sensor technology and sensor development issues.

The objectives of this study by the committee were threefold:

- review the state of the art of sensor technologies;
- identify novel sensor materials that could benefit the manufacture and operation of advanced systems for the Department of Defense and the National Aeronautics and Space Administration; and
- identify research and developments efforts that could accelerate the development and incorporation of these emerging sensors in particular applications with potentially high payoff.

A comprehensive review of the state of the art of sensor technologies would be an enormous undertaking. The committee chose to provide a bibliography of recent publications that present the state of the art of sensor technologies. Since there is no commonly accepted taxonomy of sensor technologies, the bibliography contains some overlaps between the different sensor areas. The committee identified a crucial barrier that has impeded development of advanced sensor materials: the communication mismatch between the sensor application community and the research and development community. The committee determined that the attributes of an "ideal" sensor material can only be considered within the context of an application area that establishes the material's requirements. Hence, there can be no absolutes for an "ideal" sensor material. This conclusion results in the definition of significant issues for the materials developer concerned with novel sensor materials: What are the appropriate applications to address? What are the critical needs for sensor materials? And where are the fundamental understandings that provide foundations for development?

In order to provide a tool to address these crucial issues, the committee developed a strategy that exploits a common framework for describing both sensing system applications and sensor technologies. The uses and research needs for novel sensor materials arise from matching available and potential technologies with the applications. The committee has provided examples of applying this framework to selected sensor materials and application areas. These examples are not meant to be an inclusive list but rather are representative of the process of identifying the state of the art in an application area, examining the role and need for sensors, and describing opportunities for materials development. The committee also developed overall conclusions and recommendations concerning future directions for sensor materials research efforts through generalizing the experiences in the application areas examined.

The committee considered several titles for this report. *Expanding the Vision of Sensor Materials* was selected because it captures the essential message of this report: there is a need for multidisciplinary efforts to identify and prioritize sensor needs, so that materials developments can be targeted towards requirements.

Any comments or sugestions that readers of this report wish to make can be sent via Internet electronic mail to **nmab@nas.edu** or by fax to the NMAB at (202) 334-3718.

Nicholas Eror, *Chair*

Committee on New Sensor Technologies: Materials and Applications

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EXECUTIVE SUMMARY

DEFINITIONS AND ISSUES

Sensor technology is a rapidly growing field that has significant potential to improve the operation, reliability, serviceability, and utility of many engineering systems. Advances in materials science and engineering have paved the way for the development of new and more capable sensors. U.S. industry is experiencing shorter innovation cycles, growing technical complexity of its products, and increased costs in conducting and commercializing research and development (R&D). The nature and scope of commercial R&D programs in sensor technologies, including sensor materials, are largely determined by these market drivers plus the potential size of the available market. The trend is toward the development of materials tailored to specific, or targeted, applications rather than toward fundamental R&D without a specific application-focus (i.e., toward materials development driven by "market pull" as opposed to "technology push"). However, technology-driven, leading edge research is vitally important, since the results from these efforts have the potential to create entirely new products and markets.

Two categories of sensors and sensor materials development can be distinguished: high-volume, low-cost sensors and low-volume, high-cost sensors. In the case of sensors for mass market applications, clearly defined R&D strategies have frequently been identified and implemented. Often, the selection and development of materials for niche market applications do not originate from a logical, top-down strategy but rather from a serendipitous combination of technical and commercial considerations. Such innovative developments have led to major breakthroughs in "pathfinding" applications and have served as a means to gain much needed operational experience with a new technology. Exceptions to this generalization of development approaches include niche markets, such as well-defined defense applications.

Advancing the sensor technology state of the art has been limited by the lack of a widely accepted language for describing sensor needs and performance. Potential users of sensor technology often speak a different technical language from the sensor technologists involved in developing sensors. In response, the Committee on New Sensor Technologies: Materials and Applications prepared a communication tool that employs a common set of descriptors to map sensor application requirements to sensor technology attributes, and vice versa. This tool can provide guidance in identifying opportunities for sensor materials development and application areas in which materials can be further exploited.

MATERIALS FOR SENSORS: IDENTIFYING NEEDS

A considerable body of published work relates to the vast topic of sensor technologies. The committee compiled an extensive bibliography of the recent literature to document the state of the art. A review of the literature indicates that there is at present no common language concerning the definition and classification of sensors. The domain of endeavor is very broad and encompasses all technical disciplines. Sensors can be categorized in a number of different ways, most notably by either their chemical composition or their principle of operation.

To address this lack of standardization and to establish a solid framework for its own analysis of the field, the committee defined the basic terms associated with sensor technology. A *sensing element* is the fundamental transduction mechanism (e.g., a material) that converts one form of energy into another. A *sensor* supplies a usable output in response to a specific measurand (input) in a predictable way; a sensor's physical configuration includes the sensing element together with its physical packaging and external connections (e.g., electrical or optical). A *sensor system* is a sensor and its assorted signal processing hardware (analog or digital) with the processing either in or on the same package or discrete from the sensor itself.

The diversity of sensor technologies and applications and the resulting diversity of materials needs led the committee to conclude that the concept of an "ideal" sensor material is inadvisable. It is frequently possible to fulfill a given sensing need by more than one type of sensor. Thus, identification of the "best" sensor material should only be done within the context of a specific application.

SUMMARY OF CASE STUDIES

Since the present report could not realistically provide a comprehensive list of research opportunities for the entire field of sensor materials, a "case study" method was used to illustrate the different driving forces and considerations that affect the development and incorporation of new sensor technologies. Examples of sensor materials technologies were synthesized from two applications areas (manufacturing, and structural monitoring and control) and two sensor technology categories (long-wavelength infrared sensors and chemical sensors).

Manufacturing

Intelligent processing can reduce product variability, optimize use of processing facilities, and decrease costs. As defined by the committee, intelligent processing involves event-based control of process variables. Sensors are currently the weak link in intelligent processing. They must perform reliably in hostile manufacturing environments and provide data that permit accurate representation in time and space of the changes occurring as the material is processed.

Intelligent (self-directed) processing of aerospace structural polymeric composites (e.g., thermosetting resin systems) is an illustrative example. In this case, the state of cure of the polymer is determined, and then the process variables are adjusted to achieve the most efficient cure cycle. There is a significant need to improve sensor materials and technologies for this application, notably by directly measuring the molecular structure of the polymer to more precisely determine the degree of cure. Laser-fiberoptic sensor technology has considerable potential in this regard.

The fabrication and processing of complex semiconductor materials is an important and expanding industrial endeavor. There is a significant need for in situ diagnostics to permit precise on-line process control during epitaxial growth of electro-optical thin films. The manufacture of low-cost, reproducible, uniform, and tailorable structures needs noninvasive sensors to measure film thickness, composition, interlayer sharpness, and other properties. Notable opportunities exist for optical sensing technologies (e.g., ellipsometry, laser-induced fluorescence, and fiberoptic probes) that can significantly improve the processing of complex semiconductor devices.

Structural Monitoring and Control

"Smart" structures that incorporate active materials are emerging as an important broad-based discipline. A step toward the development of such "smart" structures is the incorporation of sensor systems that provide accurate information describing the state of a structure at any given time throughout its life cycle. This life-cycle management approach has the goal of combining the traditional fabrication and customer-use periods of a product.

The availability of advanced sensors and actuators, together with developments in signal processing, communication, and control technologies, has led to a surge of interest in smart structural materials systems that can adapt to an ill-defined, changing environment. Important issues include evaluating the long-term performance of sensors used for in-service monitoring, understanding the sensor/host interactions for embedded-sensor applications, and focusing on improved long-term reliability of sensors for in-service environments.

Long-Wavelength Infrared Sensors

The sensing of electromagnetic radiation is essential for a wide variety of activities. Sensing radiation in the long-wavelength infrared (LWIR) window (spectral region with a wavelength of 8 mm to 14 mm) allows detection of unilluminated objects that are approximately at room temperature. Infrared sensors are attractive because they are non-contracting and can quickly sense a temperature change over an area. This capability is important for applications such as measuring part temperature, detecting process defects, enabling night vision, and identifying chemical species.

There are three materials strategies—at different levels of maturity—for obtaining high-efficiency photodetector LWIR sensors.

- Mercury cadmium telluride (MCT) compounds. The quality of LWIR MCT has improved over the last decade, and continued incremental improvements may eventually yield temporally stable, uniform detector arrays for LWIR applications. However, materials instabilities still result in major challenges.
- Artificially structured materials with tailored band gaps based on multiple-quantum-well devices (e.g., GaAs/AlGaAs system). The theoretical sensitivity of these sensors is lower than that of MCT; however, because of superior response uniformity, arrays of these structures already exhibit performance exceeding that of MCT detector arrays for selected applications. These materials can be produced using real-time sensor-based process controls developed for GaAs.
- Artificially structured materials with tailored band gaps based on strained-layer superlattice structures (e.g., those that exploit In [As, Sb] alloys). The fundamental detectivity limit of these materials is higher than that of MCT. It is the least mature of the technologies, and substantial improvements in performance appear to be possible, since no fundamental limitations have emerged as obstacles.

Chemical Sensors

The committee defines chemical sensors as devices or instruments that determine the detectable presence, concentration, or quantity of specific chemical substances (analytes). Arguably the most severe limitation on current chemical sensor technology is the inability to obtain a selective response to a target analyte, given the millions of known molecular species, the variations in environmental conditions (presence of water, etc.), and the variations in analyte amount or concentration by factors of 10^{23} or greater. Applications of chemical sensors include monitoring manufacturing processes, environmental sensing, and health monitoring.

Direct-reading selective sensors, such as electrochemical sensors, detect species in the gas or liquid phase. They achieve molecular selectivity through interaction at the sensor-sample interface. This selectivity depends on recognition of the size, shape, or dipolar properties of the analyte by molecular films, phases, or "receptor sites," with resultant selective binding, absorption, or permeation of the analyte. Selectivity of direct-reading chemical sensors can be enhanced through the development of analyte-specific films, membranes, and coatings. Miniaturization of these sensor systems could lead to compact, lightweight, portable monitoring systems.

As an alternative, analyte selectivity can be addressed by using sensors that incorporate preliminary sample separation steps, such as chromatography and electrophoresis. Conventional analytical chemistry methods, such as mass spectroscopy, may then be used if the analysis can be performed fast enough and the equipment is significantly compact and inexpensive. Miniaturized and integrated platforms that incorporate both separation and detection systems would be preferable.

GENERAL CONCLUSIONS

Trends in Sensor Technology

Current sensor development is trending toward increased complexity in sensor systems. The greater flexibility and lower cost of advanced, integrated electronic technology allows signal processors to be reduced to a microelectronic chip; however, from the perspective of the end user, the sensor system appears simpler.

The principal technical drivers for sensor development are becoming enabling/supporting technologies other than materials technology. Most recent advances in sensors have not originated from the synthesis of new transduction materials; they have been due to sensor technologies not heavily dependent on transduction materials and to innovations that have significantly decreased the cost of a sensor system.

Networking of large sensor systems can provide improved spatial and temporal sampling in low-cost, low-maintenance systems. A network of sensors can provide data to a central processor that monitors performance or helps characterize defects. Also, the individual outputs from an array of sensitive but moderately selective transducers can provide a composite indication that is both sensitive and selective.

Sensor R&D lends itself to dual use and commercialization efforts. Sensors are an enabling technology with a wide spectrum of applications.

R&D Strategy

Few programs have existed to develop sensors solely for the sake of advancing sensor technology. Historically, sensor research and development efforts have been funded as an adjunct to large application programs that required sensors. A new approach will require the implementation of a research planning process that addresses the needs of a broad set of users and applications.

A generally accepted framework to describe both sensor application requirements and sensor performance capabilities is needed. A common set of descriptors for use by sensor users, suppliers, and researchers was identified by the committee as the most important step in facilitating the identification of sensor materials R&D opportunities and in accelerating the development and use of advanced sensor technologies.

Experience in establishing centers of excellence for sensor development provides useful guidelines for improving sensor R&D strategy. Essential characteristics include: a multidisciplinary approach with emphasis on teamwork; capabilities ranging from an initial proof of concept through engineering prototypes; focus on selected sensor technologies for a broadly defined range of applications; and strong linkage to industry to guide the general relevance of the research.

Opportunities in Materials R&D

Sensor materials include all materials required by the sensing system. These materials encompass those required by the transducer, package, and leads.

Sensor materials R&D can be divided into two main categories: the development of new materials and materials engineering for particular applications. These two categories frequently require very different approaches to materials R&D.

High payoff opportunities for new sensor materials in the near term will come primarily from R&D on existing materials rather than synthesis of new compositions of matter. The committee identified fundamental research on new compositions of matter as the highest risk element of sensor materials R&D programs, although this approach also offers the highest potential payoff. Exploiting materials developed for purposes other than sensing can lead to rapid sensor technology advancements at relatively low cost and risk.

Materials processing science will be the foundation for developing affordable sensor materials. Materials synthesis and processing will facilitate the transfer of innovations in materials science to commercially viable products.

Universities and federal research laboratories play a critical role in conducting frontier research. Universities are well positioned to conduct frontier research and to use such programs as vehicles to educate students. Federal research laboratories generally sponsor frontier research and conduct a portion of the research in-house to keep abreast of the leading-edge technologies. Long-term commitment to such research is essential to remain technically competitive internationally.

GENERAL RECOMMENDATIONS

R&D Strategy

In the view of the committee, focused programs in which sensors are treated as a separate field of endeavor, as opposed to an adjunct to larger programs, will significantly accelerate the development and use of advanced sensors. The R&D approach aimed at satisfying high payoff opportunities in sensor technology should emphasize the multidisciplinary integration of existing technologies for specific or generic applications.

The committee recommends use of a communication tool to facilitate interdisciplinary communication in the identification of research opportunities and needs for sensor systems and technologies. A standard terminology is needed to describe sensing requirements and technology attributes. The communication tool and descriptors should form the basis for an evolutionary methodology that can be augmented and refined for use by specific research groups and applications.

Organizations undertaking sensor R&D programs should maintain a broad research base with critical core competencies. These organizations should possess, or have access to, expertise from all technical disciplines involved in the sensor technology under investigation. To give a sense of relevance and urgency to any applied R&D program, a customer or end user with a specific implementation need should be identified and charged with demonstrating the potential payoff in a joint effort with the developer.

R&D programs that develop sensor materials should focus on selected classes of materials. In view of the diverse range of sensor materials and the high costs of fabrication facilities for many advanced sensor materials, the committee recommends that specific R&D programs set priorities for selected classes of materials rather than attempting to encompass a very broad range of endeavor.

Priorities in Materials R&D

The committee recommends that sensor materials R&D be pursued in three main areas. In order of decreasing priority these are

- development of processing techniques for existing sensor materials;
- assessment and development of sensing capabilities in existing materials that have properties not yet exploited for sensor applications; and
- fundamental investigation of novel sensing approaches, such as using multiple physical responses to a sensing phenomenon and new compositions of matter.

ORGANIZATION OF THE REPORT

The report is divided into three parts. Part I, "Definitions and Issues," has two chapters that provide the basic definitions used throughout the report and suggests approaches to planning and conducting research and development in sensor materials. The basic definitions and discussion of the state of art are contained in Chapter 1. The generic framework and suggested approaches to sensors R&D is the subject of Chapter 2.

Part II, "Materials for Sensors: Identifying Needs," has four chapters that contain the illustrative examples of opportunity areas for sensor development. Topics discussed are manufacturing (Chapter 3), structural monitoring and control (Chapter 4), LWIR sensors (Chapter 5), and chemical sensors (Chapter 6). R&D opportunities in sensor materials that arose from these case studies are highlighted at the end of each chapter.

Part III, "Opportunities, Conclusions and Recommendations," contains two chapters that summarize the materials development opportunities that originated from the illustrative case studies described in Part II, as well as generalized conclusions and recommendations that resulted from the committee's synthesis of the material in parts I and II. Chapter 7 is a synopsis of the material development opportunities from Part II. Chapter 8 discusses the committee's general conclusions and recommendations.

In addition, there are seven appendices, which contain more detailed information on the sensor terminology and technologies that are discussed in the report.

PART I:

OVERVIEW DEFINITIONS AND ISSUES

Life is a permanent possibility of sensation.

Robert Louis Stevenson

The value of the North American sensor market in 1990 was estimated to be $1.6 billion, and it is predicted to grow to $4.2 billion by the turn of the century (Thome, 1992). According to one estimate, the world sensor market in 1992 was $7.15 billion; if it grows at an eight percent per year rate, it will approach $13 billion by 1999 (Defense Base Forecast, 1993). In addition to constituting an important market in their own right, sensors have a significant impact on many areas, such as manufacturing, the development of consumer goods, environmental monitoring and regulation, and national security. There are obvious economic and social benefits to developing improved sensors and sensor materials, and over the past decade there have been significant advances in certain areas of sensor technology, such as the manufacture of complex silicon-based sensor systems. However, some of the fundamental materials challenges associated with sensing have received far less attention from the materials community.

During the 1980s, a number of National Materials Advisory Board studies addressed a variety of issues for advanced materials processing, including the availability of sensors for process control (NRC, 1986a,b,c, 1987, 1989a,b, 1992). Additional development of sensors and sensor materials was consistently identified as a requirement for enhanced materials processing. On the same theme, a National Research Council report on chemical and biological sensor technologies identified a requirement to develop coating and membrane materials to improve the performance of chemical microsensors (NRC, 1984). Similar materials needs were identified during the course of the present study, suggesting that progress in developing improved sensor materials for certain applications has been relatively slow.

In the course of its deliberations, the committee noted that progress in developing new sensor technologies and materials has been hampered in part by the difficulty of communicating sensing requirements and the capabilities of existing sensor technologies across the diverse technical disciplines involved in sensor research and development (R&D). For this reason, some basic definitions and possible approaches to sensor R&D are discussed in the two chapters of Part I prior to discussion of specific sensor technologies and materials requirements in Part II.

Chapter 1, "Introduction to Sensors," provides the basic definitions and background material for the remainder of the report. Chapter 2, "Interdisciplinary Strategy," discusses the recent trends in sensor development and issues in developing an R&D strategy for a program in sensor technology and suggests an approach for identifying opportunity areas for sensor research.

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INTRODUCTION TO SENSORS

History has shown that advancements in materials science and engineering have been important drivers in the development of sensor technologies. For instance, the temperature sensitivity of electrical resistance in a variety of materials was noted in the early 1800s and was applied by Wilhelm von Siemens in 1860 to develop a temperature sensor based on a copper resistor. The high resonance stability of single-crystal quartz, as well as its piezoelectric properties, have made possible an extraordinarily wide range of high performance, affordable sensors that have played an important role in everyday life and national defense. More recently, a new era in sensor technology was ushered in by the development of large-scale silicon processing, permitting the exploitation of silicon to create new methods for transducing physical phenomena into electrical output that can be readily processed by a computer. Ongoing developments in materials technology will permit better control of material properties and behavior, thereby offering possibilities for new sensors with advanced features, such as greater fidelity, lower cost, and increased reliability.

As noted in the preface, the Committee on New Sensor Technologies: Materials and Applications was asked to identify novel sensor materials that could benefit the manufacture and operation of advanced systems for the Department of Defense and the National Aeronautics and Space Administration and to identify research and development (R&D) efforts that could accelerate the development and incorporation of these emerging sensor materials in particular applications with potentially high payoff. To provide a foundation for its recommendations in these areas, the committee began by assessing the current status of sensor technologies. Early in this assessment, the committee found that applications, not materials, drive new sensor development. Therefore the committee identified a conceptual framework that could relate sensor materials to application needs within which the importance of particular sensor materials could be determined.

Given the extensive body of published work relating to the broad, multidisciplinary subject of sensor technologies, the committee prepared a summary bibliography drawn from the recent literature (Appendix A). The bibliography includes review articles, books, and monographs relating to the wide range of sensor technologies. These references can form a basis from which a more detailed study of any particular sensing technology, principle, or application can be initiated. Several key journals dealing with sensing have been included in the bibliography; they are suggested as starting points for investigating the most recent developments and trends in sensor technologies. Additional information is available from the reference list at the end of each chapter.

Despite the extensive published literature that treat the fundamentals of sensor technology, considerable ambiguity exists in sensor definition and classification, as illustrated by a recent buyer's guide for sensors in which two lists of sensor suppliers are provided, one based on properties sensed and the other on technologies used (Sensors, 1992). The latter list includes both physical phenomena (for example, acoustic, electrochemical, Hall effect and infrared sensors), and material types (such as bimetallic, fiberoptic, thick-and thin-film, and zirconium oxide sensors).

Understanding the physical or chemical effects that yield useful transduction is important in selecting and designing sensors. However, these effects by themselves are usually not sufficient to establish an unambiguous sensor classification, since typical sensors may use more than one effect. A simple example is a diaphragm pressure gauge. The diaphragm uses one form of mechanical energy to create another (pressure generates displacement and strain); however, the creation of an electrical signal from the displacement or strain can be accomplished using many approaches. The diaphragm could be made of a piezoelectric material, in which the air would induce an electrical charge; an inductive or capacitive effect could be employed to measure the charge related to the strain and the deflection and thereby infer the pressure. Thus understanding all of the possible field effects and features of transducer materials behavior provides the most complete set of sensor design options.

In order to accelerate the incorporation of emerging sensor materials in new applications, it is critically important that the sensor materials community be able to readily identify sensing needs that candidate materials could fulfill.

DEFINITIONS

The formal study of sensor technology is plagued by ambiguity in definitions and terminology. This evolving field of endeavor is extraordinarily broad with nearly every scientific and technical discipline playing an important role. Thus, it should not be surprising that there is no unanimous concept of a sensor. Given the impossibility of presenting a universally accepted definition for sensors, the committee used terms and definitions that are generally accepted in the current technical literature to provide the basis for discussion in this report.[1] (A complete tutorial on sensors and their transduction principles is beyond the scope of the present report.)

The terms "sensor" and "transducer" have often been used as synonyms. The American National Standards Institute (ANSI) standard MC6.1 defines a transducer as "a device which provides a usable output in response to a specific measurand" (Instrument Society of America, 1975). An output is defined as an "electrical quantity," and a measurand is "a physical quantity, property, or condition which is measured." In 1975, the ANSI standard stated that "transducer" was preferred to "sensor." However, the scientific literature has not generally adopted the ANSI definitions, and thus currently "sensor" is the most commonly used term. Therefore, the term "sensor" will be used throughout this report.

The committee recognizes that, for the purpose of this report, the output of a sensor may be any form of energy. Many early sensors converted (by transduction) a physical measurand to mechanical energy; for example, pneumatic energy was used for fluid controls and mechanical energy for kinematic control. However, the introduction of solid-state electronics created new opportunities for sensor development and control, with the result that sensors today almost exclusively produce an electrical output for use in such applications as computer-based controls, archiving/recording, and visual display. This need for electrical interfacing is causing a broadening in the definition of a sensor to include the systems interface and signal conditioning features that form an integral part of the sensing system. With progress in optical computing and information processing, a new class of sensors, which involve the transduction of energy into an optical form, is likely. Also, sensors based on microelectromechanical systems may enable fluidic elements to operate as controls and actuation devices in the future. Thus the definition of a "sensor" will continue to evolve.

The definition of a sensor does not precisely define what physical elements constitute the sensor. For example, what portion of a thermocouple is the sensor? Is it solely the bimetallic junction? Does it include the wires used for transmission purposes? Does it include any packaging or signal processing? On the basis of information in the current technical literature, the committee chose to adopt the following definitions:

Sensor element: The fundamental transduction mechanism (e.g., a material) that converts one form of energy into another. Some sensors may incorporate more than one sensor element (e.g., a compound sensor).

Sensor: A sensor element including its physical packaging and external connections (e.g., electrical or optical).

Sensor system: A sensor and its assorted signal processing hardware (analog or digital) with the processing either in or on the same package or discrete from the sensor itself.

In order to describe and characterize the performance of a sensor, a large and specific vocabulary is required. Several excellent references, which provide a basic review of transducer characteristics, are cited in the bibliography (Appendix A). Table 1-1 lists some of the characteristics important for describing a sensor and its static and dynamic performance. (Most of the characteristics listed under "static" are also important for dynamic measurements.) Sensor characteristics will be discussed in greater detail in Chapter 2 in the context of a set of "descriptors" used by the committee to provide a common framework for sensor technologists and users. Appendix B contains a definition for each of the sensor descriptors used in this report.

TABLE 1-1 Selected Sensor Characteristics

Static	Dynamic
Accuracy	Dynamic error response
Distortion	Hysteresis
Hysteresis	Instability and drift
Minimum detectable signal	Noise
Nonlinearity	Operating range
Selectivity/Specificity	Repeatability
Sensitivity	Step response
Threshold	

TRANSDUCTION PRINCIPLES[2]

Lion (1969) introduced a classification of principles according to the form of energy in which sensor signals were received and generated, which yielded a matrix of effects. Table 1-2 lists the six energy forms or signal domains generally encountered with examples of typical properties that are measured using those energy forms.

Table 1-3 (Göpel et al., 1989), contains the most common transduction principles, excluding biological and nuclear effects, and illustrative physical phenomena. The table demonstrates some interesting complexities in definitions. For example, a device that converts electrical energy into mechanical energy, such as by piezoelectricity (which may be considered a sensor by definition), is more generally termed an output transducer or an actuator rather than a sensor. Clearly then, the appropriate use of "sensor" or "actuator" is not based on physics but instead on the intent of the application.[3] Classifying the signal domains in the manner shown in Table 1-3, while not precise, demonstrates that understanding the physics of the application is vital to selecting the appropriate sensor scheme, materials, and design. It is one method of visualizing the transduction principles involved in sensing.

A rigorous attempt at classifying sensors was undertaken by Middlehoek and Noorlag (1982), in which they represented the input and output energy

TABLE 1-2 Sensor Energy Forms

Energy Forms	Example Measurands
Mechanical	Length, area, volume, all time derivatives such as linear/angular velocity, linear/angular acceleration, mass flow, force, torque, pressure, acoustic wavelength and acoustic intensity
Thermal	Temperature, specific heat, entropy, heat flow, state of matter
Electrical	Voltage, current, charge, resistance, inductance, capacitance, dielectric constant, polarization, electric field, frequency, dipole moment
Magnetic	Field intensity, flux density, magnetic moment, permeability
Radiant	Intensity, phase, wavelength, polarization, reflectance, transmittance, refractive index
Chemical	Composition, concentration, reaction rate, pH, oxidation/reduction potential

TABLE 1-3 Physical and Chemical Transduction Principles.

Input (Primary) Signal	Output (Secondary) Signals					
	Mechanical	Thermal	Electrical	Magnetic	Radiant	Chemical
Mechanical	(Fluid) Mechanical effects; e.g., diaphragm, gravity balance. Acoustic effects; e.g., echo sounder.	Friction effects; e.g., friction calorimeter. Cooling effects; e.g., thermal flow meter.	Piezoelectricity. Piezoresistivity. Resistive. Capacitive. Induced effect.	Magneto-mechanical effects; e.g., piezomagnetic effect.	Photoelastic systems (stress-induced birefringence). Interferometer. Sagnac effect. Doppler effect.	
Thermal	Thermal expansion; e.g., bimetallic strip, liquid-in-glass and gas thermometers. Resonant frequency. Radiometer effect; e.g., light mill.		Seebeck effect. Thermo-resistance. Pyroelectricity. Thermal (Johnson) noise.		Thermo-optical effects; e.g., liquid crystals. Radiant emission.	Reaction activation; e.g., thermal dissociation.
Electrical	Electrokinetic and electro-mechanical effects; e.g., piezoelectricity, electrometer, and Ampere's Law.	Joule (resistive) heating. Peltier effect.	Charge collectors. Langmuir probe.	Biot-Savart's Law.	Electro-optical effects; e.g., Kerr effect, Pockels effect. Electro-luminescence.	Electrolysis. Electro-migration.
Magnetic	Magneto-mechanical effects; e.g., magnetostriction, and magnetometer.	Thermo-magnetic effects; e.g., Righi-Leduc effect. Galvano-magnetic effects; e.g., Ettingshausen effect.	Thermo-magnetic effects; e.g., Ettingshausen-Nernst effect. Galvano-magnetic effects; e.g., Hall effect, and magneto-resistance.	Magneto-optical effects; e.g., Faraday effect, and Cotton-Mouton effect.		

Input (Primary) Signal	Output (Secondary) Signals					
	Mechanical	Thermal	Electrical	Magnetic	Radiant	Chemical
Radiant	Radiation pressure.	Bolometer. Thermopile.	Photo-electric effects; e.g., photovoltaic effect photo-conductive effect.	Photo-refractive effects. Optical bistability.		Photo-synthesis; e.g., dissociation.
Chemical	Hygrometer. Electro-deposition cell. Photo-acoustic effect.	Calorimeter. Thermal conductivity cell.	Potentiometry. Conductimetry. Amperometry. Flame ionization. Volta effect. Gas sensitive field effect.	Nuclear magnetic resonance	Emission and absorption Spectroscopy. Chemi-luminescence. Photo-chemical effects.	

Source: Göpel et al., 1989.

only as the transduction principle and disregarded any "internal" or compound transduction effects that may have taken place. In addition, they included two other types of sensors: self-generating and modulating. They referred to self-generating and modulating as fundamental transduction principles to be included in a chart such as Table 1-3, thereby creating a third dimension. A sensor based on a modulating principle requires an auxiliary energy source; one based on a self-generating principle does not. No standard convention has been established in the technical literature as to whether a modulating sensor should be classified as "passive" or "active"; both terms are used in the literature. Therefore, the committee adopted the terms "self-generating" and "modulating" to avoid any confusion that could arise from the use of "passive" and "active."

In order to more clearly depict the sensor taxonomy approach adopted by the committee, Appendix C contains several simple examples that depict the sensor taxonomy. They were drawn from previous National Materials Advisory Board reports on materials processing. The examples in the appendix include thermocouple, transducers, scale of measured properties, and typical constraints.

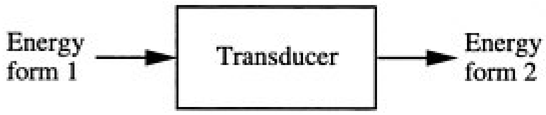

FIGURE 1-1 Self-generating sensor.

A comparison of Figures 1-1 and 1-2 illustrates schematically the difference between a self-generating sensor and a modulating sensor. An example of a self-generating sensor is a piezoelectric pressure sensor. In this case, the mechanical energy form (strain or pressure) creates electrical signal (an electrical charge) as a result of the fundamental material behavior of the sensor element. An example

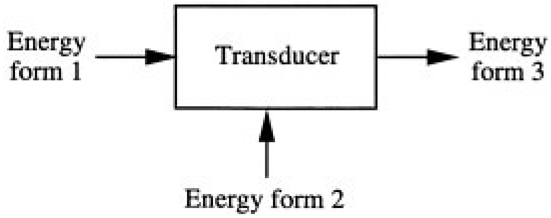

FIGURE 1-2 Modulating sensor.

FIGURE 1-3 Self-generating piezoelectric pressure sensor.

of a modulating sensor is a fiberoptic magnetic-field sensor in which a magnetostrictive jacket is used to convert a magnetic field into an induced strain in the optical fiber. The resulting change in the gauge length of the fiber is measured using interferometry (i.e., the strength of the magnetic field is inferred). Schematic representations of a piezoelectric pressure sensor and a fiberoptic magnetic-field sensor are depicted in Figures 1-3 and 1-4, respectively.

Often sensors incorporate more than one transduction principle; thus, sensors can be conveniently classified simply by their input energy form or signal domain of interest. The committee adopted a sensor taxonomy for this report that is based on the input energy form or measurand as a practical engineering-oriented approach that provides insight into selecting sensors technologies for applications. This approach, however, does not emphasize the underlying mechanisms to the extent that a more science-based taxonomy would; this limitation is particularly telling when multiple response interactions occur. Nor does this approach lead to rapid identification of low-cost sensors, sensors that exploit a particular type of material, etc. Therefore, alternative sensor taxonomies are also useful.

In addition, research efforts should be directed at improving the understanding of multiple physical responses to a sensing phenomena. For instance, it has been shown that reaction of certain gases on a surface can be effectively measured with a novel sensing approach that uses the differential thermal expansion of a bimetallic material and changes in heat capacity and thermal conductivity of the sensor elements (Gimzewski et al., 1994).

Other possible classification methods for sensors include:

- physical or chemical effect/transduction principle;
- measurand (primary input variable);
- material of the sensor element;
- application;
- cost;
- accuracy; and
- output signal domain.

ANATOMY OF A SENSOR

Sensors, in their most general form, are systems possessing a variable number of components. Three basic components have already been identified: a sensor element, sensor packaging and connections, and sensor signal processing hardware. However, there are additional components to certain sensors. The fiberoptic magnetic-field sensor illustrated schematically in Figure 1-4 is an example of a common sensor that uses "compound" sensors to transduce a magnetic field into an electric signal. There are numerous technologies available to convert a magnetic signal into an electrical signal; however, application constraints (cost, environmental effects, packaging, etc.) strongly influence the actual physical design of a sensor and the selection of sensor materials and technologies.

The anatomy of a complete sensor system is shown in Figure 1-5. Technological components in current sensor systems include:

- sensor element(s) and transduction material(s);
- interconnection between sensor elements (electrical and/or mechanical) input "gate";

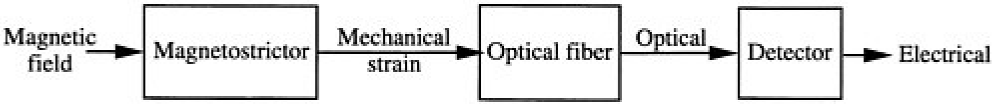

FIGURE 1-4 Modulating fiberoptic magnetic field sensor.

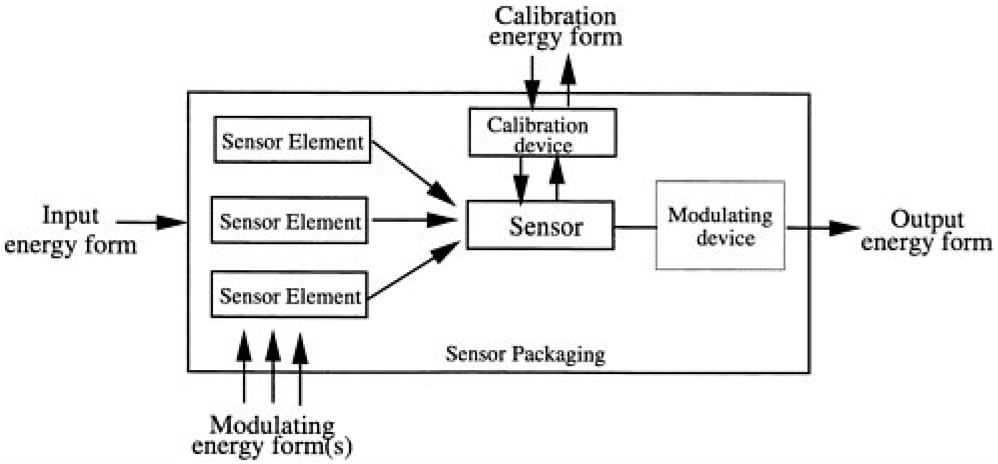

FIGURE 1-5 Anatomy of a sensor system.

- output "gate" and interconnection;
- packaging;
- modulating input interconnects;
- calibration device;
- calibration input/outputs;
- output signal modifying device (amplifier);
- output signal processing (for smart sensors); and
- actuators for calibration

The scope of hardware elements is indicative of widening definition of a sensor attributable to advances in silicon micromachining, micropackaging, and microelectronics. It is clear from the preceding discussion that modern sensors are much more than a transduction material. Opportunities for introducing new materials in sensors thus arise from three areas: (1) sensor transducer mediums (material); (2) sensor packaging materials; and (3) electronic (signal processing) devices and readouts. This report focuses attention on the sensor transducer medium but recognizes the importance, and in some instances dominance, of materials requirements for the other portions of a sensor system.

Many recent advances in sensors have not come from the synthesis of new transduction materials (except perhaps for chemical sensors) but rather from microelectronic innovations in low-cost, large-scale manufacturing of interconnections, microelectronics, and micromachining that have allowed more complex sensor systems to be formed using well-known sensor elements.

SMART SENSORS

One of the most important advances in sensor technology in the last ten years has been the focused development of smart sensors. The definition of "smart" and "intelligent" sensing can be debated. In general, it is difficult to identify any features in a smart sensor that parallel intelligence in natural systems; however, the terms have become cemented in the technical jargon. The basic tenet of smart sensors is that the *sensor complexities must be concealed internally and must be transparent to the host system*. Smart sensors are designed to *present a simple face to the host structure via a digital interface*, such that the complexity is borne by the sensor and not by the central signal processing system. This report does not address specific technologies associated with smart sensing but instead presents the concept and identifies where and why opportunities exist for new sensor materials as well as for the utilization of existing materials that have not traditionally been used for sensing applications.

The basic requirement for a smart sensor is that it be a system with dedicated "on-chip" signal processing. Realization of this concept simply means that electronic (or optical) signal processing hardware is dedicated to each sensor and miniaturized to the point that it becomes a part of the sensor package. Figure 1-6 provides a schematic representation of a smart sensor that employs "on chip" signal processing within a sensor package. With reference to Figure 1-5, a smart sensor would include the sensor, interface circuit, signal processing, and power source.[4] The subsystems of a smart sensor include:

- a primary sensing element;
- excitation control;
- amplification (possibly variable gain);
- analog filtering;
- data conversion;
- compensation;
- digital information processing;
- digital communications processing; and
- power supply.

The primary sensor element within a smart sensor may not be made of a conventional transducer material. Nonlinear and hysteretic materials, previously discarded as being too unreliable or unstable for sensing applications, may now be applied in a sensor that contains its own dedicated microprocessor; the need to burden a central processor with a complex constitutive model or filtering algorithm is thereby avoided. Applications can be envisioned that exploit the inherent memory or hysteresis of nonlinear materials to reduce the signal processing workload for example, "record" peak temperature.

The principal catalyst for the growth of smart-sensing technology has been the development of microelectronics at reduced cost. On-chip actuators for self-calibration and mechanical compensation may be created using micromachining techniques or thin-film technologies. Many silicon manufacturing techniques are now being used to make not only sensor elements but also multilayered sensors and sensor arrays that are able to provide internal compensation and increase reliability. It is difficult to predict the future in smart sensing, as the new applications will be driven by the availability of new sensing materials, an improved understanding of the transduction characteristics of "old" materials, and manufacturing techniques for microactuators, microsensors, and microelectronics. It is clear, however, that the smart-sensing concept creates new opportunities for using novel materials for sensors. The smart-sensing concept makes it possible to avoid the constraint of the paradigm

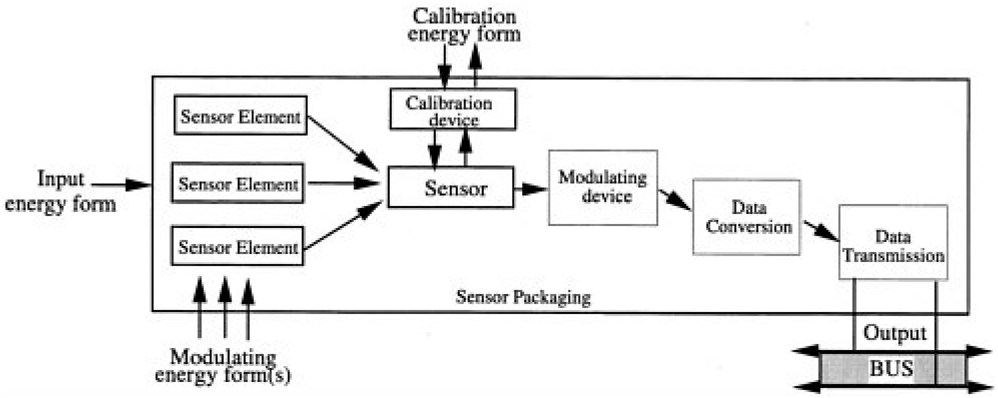

FIGURE 1-6 Schematic representation of a smart sensor.

that sensor elements must be linear and noise-free; however the cost of the added electronics must be considered in the sensor system design analysis.

Potential advantages of the smart-sensor concept include:

- lower maintenance;
- reduced down time;
- higher reliability;
- fault tolerant systems;
- adaptability for self-calibration and compensation;
- lower cost;
- lower weight;
- fewer interconnections between multiple sensors and control systems; and
- less complex system architecture.

These advantages of smart sensors are application specific. There is certainly justification for many applications in distributing the signal processing throughout a large sensor system so that each sensor has its own calibration, fault diagnostics, signal processing, and communication, thereby creating a hierarchical system. Innovations in sensor technology have generally allowed a greater number of sensors to be networked or more-accurate sensors to be developed or on-chip calibration to be included. In general, new technology has contributed to better performance by increasing the efficiency and accuracy of information distribution and reducing overall costs. However, these performance enhancements have been achieved at the expense of increased complexity of individual sensor systems. Currently, the practical utility of smart sensors seems to be limited to applications that require a very large number of sensors.

SUMMARY

The field of sensor technology is extremely broad, and its future development will involve the interaction of nearly every scientific and technical discipline. The basic definitions and terminology in this chapter have been presented to establish some consistency in discussions of sensor applications and technologies, since considerable ambiguity exists in sensor definitions and classifications. In the remainder of the present report, a sensor classification system based on the measurand, or primary input variable, is used. The committee acknowledges that alternative systems of sensor taxonomy may be useful in particular circumstances, but for the purposes of the present study, the aforementioned scheme was adopted as the most practical option. In order to accelerate the incorporation of emerging sensor materials in new applications, it is critically important that the sensor materials community be able to readily identify sensing needs and to target those physical phenomena that candidate materials could sense.

The definitions of the terms "sensor," "sensor element," and "sensor system" given above have been adopted by the committee in order to facilitate coherent and consistent analysis of sensor technologies. Many modern "sensors" are in fact sensor systems, incorporating some form of signal processing. Integration of sensor functions into a "black box" system in which the technical complexity is effectively hidden from the user is a growing trend in sensor development. Of particular interest is the smart sensing concept, which creates new opportunities for using novel materials in sensors, for instance by removing the constraint that sensor elements be linear and noise-free (although the cost-effectiveness of such an approach would depend on the application). Since modern sensors encompass much more than a transduction material, there are many opportunities for introducing new materials in sensor systems, although this report focuses on transducer materials.

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NOTES

1. The following references contain more detailed information: Göpel et al., 1989; Middlehoek and Noorlag, 1982; and Instrument Society of America, 1975.

2. Transduction is sometimes referred to by the materials community as a physical or chemical effect.

3. Some materials exhibit a reciprocal behavior; for example, in a piezoelectric material a mechanical stress generates an electrical charge and vice versa.

4. There are many examples in the technical literature of smart sensors in which the modulating energy source is discrete from the sensor package/chip.

2

INTERDISCIPLINARY STRATEGY

The Committee on New Sensor Technologies: Materials and Applications, as noted in Chapter 1, was asked to identify novel sensor materials that could benefit the manufacture and operation of advanced systems and to identify R&D efforts that could accelerate the development and incorporation of emerging sensor technology in particular applications. In identifying such *R&D opportunities for new sensor materials,* the committee concluded that the critical technical issue in sensor technology is satisfying the functional requirements of the application. The diversity of sensor technologies and applications and the resulting diversity of materials needs lead the committee to conclude that the *concept of an "ideal" sensor material is inadvisable*. It is frequently possible to fulfill a given sensing need with more than one type of sensor. Thus, identification of the "best" sensor material can only be done within the context of a specific application. Furthermore, judgments regarding the critical importance of particular materials will quickly become outdated as sensor technology and materials research advance. Therefore, the committee focused its effort on developing a conceptual framework that relates sensor materials to sensor applications and can be used to examine a wide range of application needs against technological capabilities.

The committee believes that this framework approach will not be quickly outmoded. It can be used to aid analysis and to foster communication between sensor users and sensor technologists and thus facilitate identification of R&D opportunities and strategies. In preparing its report, the committee used the framework to explore sensor applications relevant to its task and important classes of sensor materials. Illustrative R&D opportunities for sensor materials or sensor technologies that emerged from these explorations are derived in each chapter and collected in summary form in Chapter 7. More general conclusions and recommendations that emerged from developing the framework and the overall exercise of applying it are presented in Chapter 8.

SENSOR TECHNOLOGY DRIVERS

U.S. industry is experiencing shorter innovation cycles, growing technical complexity of its products, and increased costs in conducting and commercializing R&D. These trends have important implications for sensor development. Weyrich (1993) observed that material developments tailored to specific targeted applications ("market pull") are increasingly dominating basic innovation ("technology push") developments. The committee concurs with this observation; current sensor R&D is primarily application-driven rather than technology-driven. However, the "market pull" and "technology push" drivers for sensor development are interdependent and can constructively complement each other. For example, a new material that creates markets by means of a new application triggers the demand for further materials enhancements. Conversely, mass production can lead to reduced manufacturing costs and, via a learning curve, to improved materials technology, thereby facilitating further materials development.

The interdependence of "market push" and "technology pull" developments is illustrated by the example of silicon semiconductor sensors. Mass market applications such as smoke detectors, automotive exhaust sensors, and personal blood sugar and cholesterol monitors are driving the development of integrated silicon-based systems incorporating sensing and data processing functions that are low-cost, lightweight, and user-friendly. The increased availability of low-cost personal monitors will likely lead to increased demand for chemical microsensors, such as carbon monoxide sensors that provide warning of accidental poisoning in vehicles and homes.

The committee identified three primary market drivers for the development of new or improved sensors and related materials:[1]

1. economic, such as end user demand for a product with a competitive advantage (for example: better, faster, cheaper);
2. regulatory, such as user demand spurred by a government-mandated requirement (for example: environmental and safety monitors, automotive emissions control);
3. unique government requirements, typified by Department of Defense or Department of Energy needs in energy, the environment, and defense, or National Aeronautics and Space Administration needs for space exploration and advanced civil aircraft.

Based on production volume, current sensor production can be divided into two general categories. High volume, low-cost sensors produced for mass markets (such as automotive exhaust sensors and smoke detectors) can be distinguished from low-volume, high-cost items produced for specialized niche market applications (such as intelligent processing of materials and vibration damping of space structures).

The nature and scope of R&D programs in sensor technologies, including sensor materials, are largely determined by the market drivers mentioned above plus the potential size of the total available market. In the case of sensors for mass market applications, clearly defined R&D strategies have frequently been identified and implemented. For example, current materials research is addressing some of the shortcomings in the oxygen sensor used in the exhaust systems of modern automobiles (Hughes et al., 1991).[2]

In contrast, evidence from a number of case histories considered by the committee indicates that the selection and development of materials for niche market applications oftentimes did not originate from a logical, top-down strategy but rather from a timely combination of technical, commercial, and government considerations, including availability of, and constraints on, federal grants and support for small businesses. Such innovative developments have historically led to major breakthroughs in "pathfinding" applications and have served as a means to gain much needed operational experience with a new technology. For example, extremely sensitive chemical sensors [3] are the result, in part, of a confluence of scientific discovery, as described below.

- In the course of research on sputter deposited ZnO on a silicon subtrate to make surface acoustic wave devices, researchers observed that they had difficulty keeping the resonant frequency constant during the humid summer months. A researcher recognized that changes in the humidity level in the laboratory were inducing the frequency changes. This led to the development of an improved humidity sensor.
- Early quartz crystal micro-balances were used to measure the thickness of sputter-deposited films. Researchers developed the idea of using quartz crystal balances for chemical sensing as well as the idea of using a coating to selectively absorb mass. These efforts have led to extremely sensitive chemical sensors that are based on porous coatings, such as ZnO. Such sensors that can detect water vapors at a concentration of 1 ppb will be a very important technology for future integrated circuit manufacture.

Clearly, there are exceptions to this generalization of development approaches for niche market applications, particularly in the case of strategic defense-related applications for which precise, application-specific technical requirements can be defined and for which market factors are of secondary importance.[4]

Currently, most sensors for high-volume applications are manufactured by large companies, whereas niche market opportunities are primarily exploited by small companies (UNIDO, 1989). The development of certain sensor-related technologies may also be limited to large organizations capable of sustaining a substantial R&D investment. For example, the high costs of producing silicon sensor prototypes result in only large companies being able to start new sensor projects that require innovative silicon fabrication technology. However, this situation may be changing as mechanisms are established that provide industry access to expensive, highly capable research facilities. Indicative of this trend, many universities are forming liaisons with industry, and federal laboratories are being encouraged by legislation to negotiate Cooperative Research and Development Agreements with industry. Such mechanisms could be of particular benefit to small innovative companies during the R&D phase.

However, small manufacturing companies generally do not have facilities to mass-produce integrated circuits (ICs) and thus tend to concentrate on low-volume specialty products. This niche focus can be viewed either as a commercial opportunity or as a problem. The huge variety of available sensing principles allows the niche market approach to be successful in many cases (UNIDO, 1989), but it may be difficult for a single company to show an acceptable return on investment in sensor R&D when the available market is small and fragmented (NRC, 1989). In any case, the existence of a large number of small companies, each committed to the development of a somewhat different type of sensor, can challenge the sensor practitioner attempting to make a choice between several candidate sensor systems for a given application.

TRENDS IN SENSOR DEVELOPMENT

Following a review of recent developments in sensors and sensing materials, the committee made several observations that provide the basis for suggesting a strategy for sensors R&D, in particular for identifying development opportunities in sensing materials.

Current sensor development is trending toward increased technical complexity in sensor systems. As noted above, growing technical complexity requires adaptability in the approach to materials R&D. This observation is particularly pertinent to the development of increasingly complex and sophisticated sensor systems, such as smart sensors that incorporate dedicated, on-chip signal processing. The committee concurs with the observation that the physics, technology, and mathematical aspects of smart sensor systems are so interwoven that "there is a need for a well-focused, well-directed, concentrated research program to devise widely applicable, accurate, and relatively inexpensive smart sensor systems" (UNIDO, 1989). This reinforces the need for an interdisciplinary strategy for identifying needs and developing sensor technologies. Thus the materials community must be able to work as full partners within the multidisciplinary team.

The principal technical drivers for sensor development may come from enabling/supporting technologies other than materials technology. Most recent advances in sensors have come not from the synthesis of new transduction materials (except perhaps for chemical sensors) but from innovations in low-cost, large-scale manufacturing of interconnections, microelectronics, and micromachining that have allowed more-complex sensor systems to be formed incorporating well-known sensor materials. Mallon (1993) observes that "the revolution in electronics … is reinventing the sensor industry and how it serves its customers." Some of the technical advances that have led to the rapid growth of electronics are materials-and processing-related; for example, micro-machining. However, many significant technical drivers for sensor development are not in the field of materials science and engineering, and there is a need to relate sensor development to advances in diverse technical fields.

It is sometimes possible to advance the state of the art in sensing technology by leveraging materials developed for non-sensing applications. A notable recent materials-related sensor development is the use of fiberoptic sensors for chemical, mechanical, and biological applications. Optical fiber development has been supported by the communications industry, since it offers the capability of high data rates and multichannel operation at speeds several orders of magnitude higher than that possible with copper cable. Needed improvements in purifying and doping techniques for silica glass began as a materials development effort, with the goal of reducing light loss in the fiber, but rapidly evolved into a processing issue in the quest for consistently long fibers with low optical loss. The cost per meter fell rapidly as usage increased, and the advantages of small size and weight, low power, and extremely low sensitivity to electromagnetic fields were attractive to the sensor community. As a result, by the middle 1980s, an average of one new fiberoptic sensor application per week was being submitted for patent protection.

Sensor technologists obtained significant benefit by leveraging fiberoptic materials developed for non-sensing applications. A new set of material development needs was subsequently defined, based purely on the perceived sensor attributes rather than on the original communications requirements. In particular, the ability to bring high-power optical energy to the measurement site within a narrow bandwidth and coherency generated a need for fibers with controlled refractive indices, polarization-maintanence, and temperature stability.

The example of optical fibers illustrates that leveraging and exploiting materials developed for purposes other than sensing can lead to sophisticated sensor technologies. The overall cost (and risk) of such development would be significantly less than that of developing new compositions of matter.

Experience in establishing centers of excellence for sensor development provides useful guidelines for the development of a revised sensor R&D strategy. Four common characteristics can be identified in the sensors R&D conducted at several major centers for sensor technology:

1. A multidisciplinary approach is adopted, with emphasis on teamwork. Those centers located at universities also expose students to a multidisciplinary environment which enhances their educational experience.
2. Capabilities exist to develop sensors from an initial research concept through engineering prototypes to fielded systems (vertical integration). Laboratories possessing such a broad research base can readily address the root cause of problems and issues that arise during development. They would be limited in effectiveness if they participated in only a portion of the development process.
3. Efforts are focused on selected sensor technologies for a broadly defined range of applications in line with the core competencies of the organization. No attempt is made to cover the entire field of sensor technology and the associated diversity of sensor materials. These organizations have access to expertise from the many technical disciplines involved in sensor technology.
4. Strong linkage to industry is actively encouraged and pursued. Contact with industrial and end users aids these institutions in insuring the general relevance of their research areas. Since industry's needs oftentimes tend to be very specific and narrowly defined, these centers specialize in transferring general knowledge that can subsequently be applied to solve specific problems.

Universities play a critical role in conducting frontier research. Frontier research can be defined as leading edge research that does not have a particular application in mind, or does not expect to be commercialized within the foreseeable future (e.g., within 10 years). While industrial research centers are having increasing difficulty in justifying such research, universities are well positioned to conduct frontier research and to use these programs as vehicles to educate students.

In the view of the committee, focused programs in which sensors are treated as a separate field of endeavor, as opposed to an adjunct to larger programs, will contribute significantly toward accelerating the development and use of advanced sensors.

PLANNING SENSOR TECHNOLOGY RESEARCH

Current interest in initiating R&D programs directed specifically toward sensor development results from potentially high economic and technological benefits from incorporating improved sensors for a number of applications. Several examples are presented in Part II (chapters 3 to 6) of this report.

In the experience of the committee, an R&D strategy that maintains an applications-focused research base is necessary to accelerate sensor development. The successful characteristics described above for the sensor centers of excellence should be emulated.

The need to improve the planning of sensors R&D derives from multiple factors:

- interest in accelerating the product innovation cycle;
- the increasing complexity of product technology; and
- increased costs in conducting and commercializing R&D.

The fact that much sensor development has taken place as an adjunct to larger programs in areas such as materials processing, equipment maintenance, or control systems is due in large measure to the relative "newness" of the field compared to many of the other technical disciplines.[5]

Due to their multidisciplinary nature, R&D programs in sensor materials frequently do not usually fit neatly into conventional areas of materials science and engineering (e.g., ceramic materials, metallurgy, nondestructive evaluation, etc.). As will be seen in Part II, sensor materials development draws on a wide variety of disciplines, such as solid-state physics, crystal growth, materials science, processing science, materials modeling, and device engineering. In many cases, highly specialized technical expertise is needed. For example, the use of organometallic vapor-phase epitaxy techniques to grow III-V semiconductor materials requires not only an understanding of physics, crystal growth, and processing issues but also an in-depth knowledge of the complex chemistry of organometallic precursors. Therefore, the materials research community must broaden its perspective in order to fully participate in sensor technology research.

The committee identified several different approaches to planning R&D for sensor materials. One is *reactive* planning, based on the assumption that the future needs will be incremental changes from past needs. At the other end of the spectrum is *proactive* planning which attempts to project a future that is not a linear extension of the past.

A third approach is one that is *technology-driven,* which strives to achieve optimum performance from technology, attempting to add practical application constraints only in the late stage of development. This approach contrasts with a fourth *needs-driven* approach that focuses planning on well-defined requirements and then exploits current technologies or researches new materials or materials physics that may have potential to meet the defined requirements.

Figure 2-1 is a two-dimensional grid depicting the intersection of these four strategies. From a practical viewpoint, most planning efforts encompass elements of each of these strategies, although certain styles usually predominate.

In the opinion of the committee, "market pull" (i.e., needs-driven) is likely to remain the dominant driver in planning future R&D in sensor materials, given the ever shorter innovation cycles and the importance of identifying high-payoff opportunities likely to yield a high return on investment. However, technology-driven leading-edge research should not be neglected, since its results have the potential to create entirely new markets over a period of time.

Reactive planning is frequently perceived as being lower risk than a proactive approach because

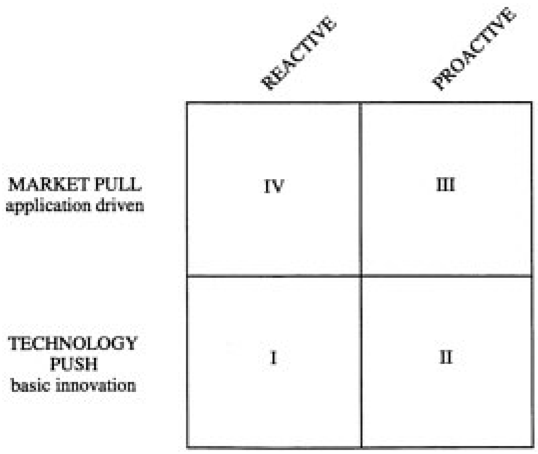

FIGURE 2-1 R&D strategy grid.

it is based on recent experience. However, history has shown that past experience is no guarantee of the future, and despite steady incremental enhancements based on a reactive approach to R&D planning, a technology may become obsolete as a result of new developments. Thus, vacuum tube manufacturers were unable to survive the transformation to transistors and integrated circuits. Under certain circumstances then, reactive planning carries a very high risk.

Proactive planning relies on estimating future needs and, as such, involves higher risk. For example, significant resources may be directed toward a project that will not be successful, notably if demand is reduced due to introduction of an alternative technology or if an attempt is made to rush an immature technology to production. Nonetheless, proactive planning can result in large improvements in capability. The likelihood of failure can be reduced by incorporating a realistic assessment of technical risk as part of the planning strategy.

IDENTIFICATION OF R&D OPPORTUNITIES

Some general goals for improving sensor performance and utility have been identified by the committee. These objectives, which form the basis for current research trends, include miniaturization, low power consumption, low cost, improved detection limits, high sensitivity and specificity, and utility at high temperature or in otherwise hostile environments. Diverse materials-related issues must be addressed to meet performance goals associated with these general trends. In the case of miniaturization, for example, improvement of optical sensors will require progress in semiconductor processing technology. In contrast, the development of a miniaturized mechanical sensor for strain measurement may require the use of advanced metallurgical techniques.

A Common Language

During the course of the committee's discussions of R&D opportunities in sensor materials, it became clear that the processing of advanced sensor technology has been limited by the lack of a well-accepted language for conveying sensor needs and performance requirements. In the experience of the committee, potential users of sensor technology often use different technical terms than those involved in researching and developing sensors. In response, the committee has suggested a set of descriptors that can characterize both sensor application requirements and sensor technology attributes, as schematically depicted in Figure 2-2.

A list of the principal descriptors is presented in Table 2-1. (Appendix B contains the definitions of each descriptor in terms that are nonspecific to a particular discipline.) In preparing this table the committee applied two main criteria. First, the descriptors were chosen to provide a comprehensive, though not necessarily exhaustive, means of describing required performance specifications and sensor attributes. Second, the descriptors were selected to allow unbiased evaluation of candidate sensor technologies, since the descriptors themselves should not a priori favor the selection of a particular sensor or technology.

Referring to Table 2-1, the first six descriptors (i.e., transduction, transduction mode, measurement scale, implementation, reliability, and acquisition mode) are discriminators based on a predefined list of key characteristics for each descriptor that help place the particular sensing task or sensor system within a series of well-defined groups. Each parameter listed as a characteristic is quantifiable to facilitate direct comparisons among different sensor technologies. Table 2-1 is also known as a "framework."

The last two descriptors (i.e., constraints and economic considerations) are more subjective than the other descriptors; some subcategories, such as development cost, may be difficult to quantify with a high degree of confidence. Nevertheless, "constraints" and "economic considerations" are often important considerations in determining the suitability of a sensor technology for a particular task. In some cases, these two descriptors may be of overriding importance in selecting cost-effective sensor technologies for an application.

Comparison of Requirements and Technology Attributes

A major advantage of using a common set of descriptors is that it facilitates the matching of sensing

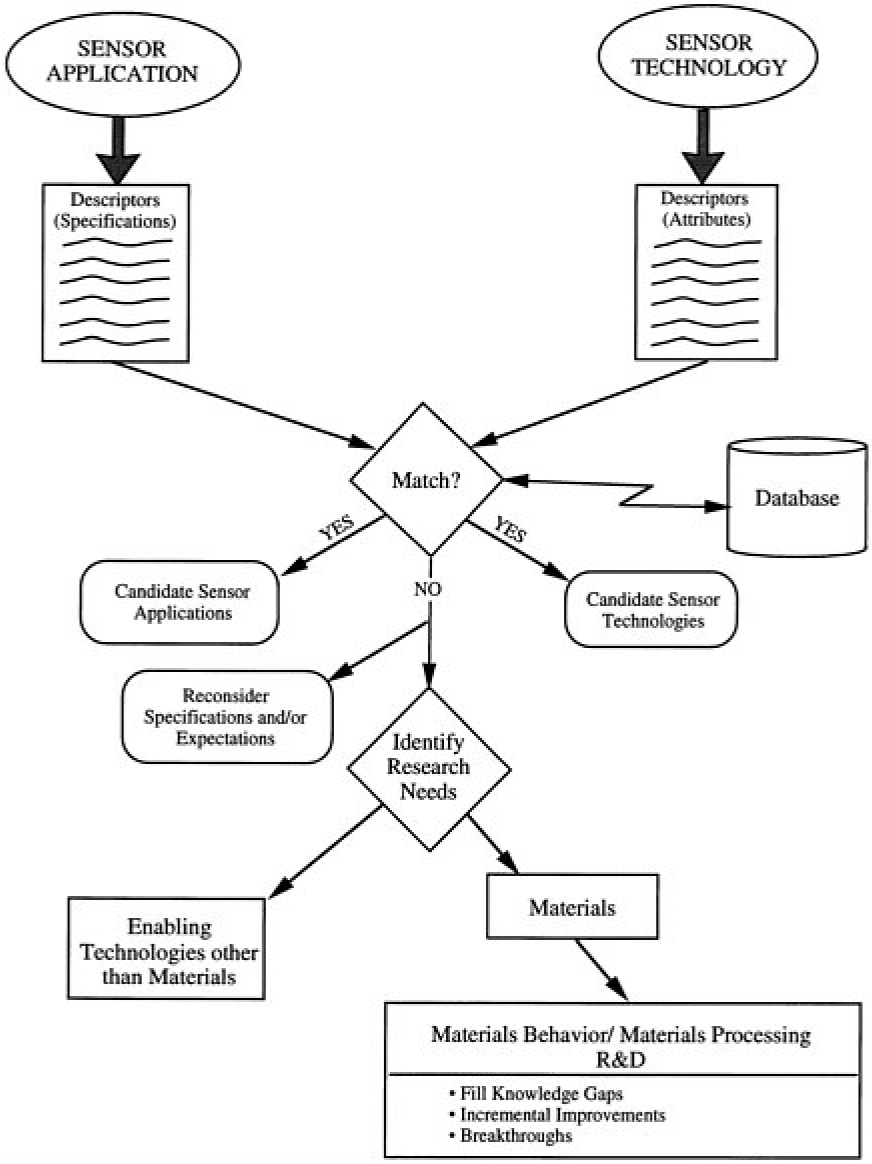

FIGURE 2-2 Sensor communication tool for comparing application requirements and technologies.

TABLE 2-1 Key Sensor Descriptors

- TRANSDUCTION
  - Self-Generating
  - Modulating
- TRANSDUCTION MODE
  - Direct (with respect to Measured Parameter)
  - Indirect (Infers)
- MEASUREMENT SCALE
  - Nano, Micro, Milli, Macro
- IMPLEMENTATION
  - Scale
  - Single Point
  - Integrating
  - Array
  - Format
  - Integrated Signal Processing
  - Multi-Channel
  - Multiplexing
  - Mode
  - Noncontact vs. Contact
  - Remote
  - In Situ
  - Invasive vs. Noninvasive
  - Nondestructive vs. Destructive
- RELIABILITY
  - Lifetime
  - Multiuse vs. Single
  - Calibration vs. Accuracy Drift
- ACQUISITION MODE
  - Continuous vs. Discrete
  - Threshold/Peak
  - Integrating
- CHARACTERISTICS
  - Response Time
  - Sensitivity
  - Resolution
  - Range
  - Linearity
  - Limit of Detection
  - Selectivity
  - Accuracy
  - Repeatability (Precision)
- CONSTRAINTS
  - Packaging
  - Size
  - Weight
  - Hermeticity
  - Isolation
  - Thermal
  - Electromagnetic
  - Mechanics
  - Chemical
  - Optical
- ECONOMIC CONSIDERATIONS
  - Development
  - Acquisition
  - Manufacturing
  - Life Cycle

requirements to the capabilities of existing sensor technologies as illustrated in Figure 2-2. Information about the particular sensor application is depicted on the left in terms of requirements, and information about a candidate sensor technology (technology attributes) for addressing that application is shown on the right. These branches reflect two of the general approaches to sensor technology R&D, namely, application-driven selection of a sensor technology and technology-driven advances in sensing capability.

In the application-driven use of this tool, the descriptor attributes are selected for the application of interest. Candidate technologies are then compared against this list to determine how well they "match"; that is, how closely they meet the requirements of the application. Such comparisons provide the basis for sensor selection and trade-off decisions (i.e., giving up an aspect of the requirement to gain something else). If there is a very good match, some evaluation of sensor performance may still be necessary to establish that the available technology meets the requirement. If the match did not provide sufficient performance for the application, the shortfalls may provide the basis for significant, focused research needs.[6] The use of the descriptors in characterizing a sensing problem permits concurrent "top down" and "bottom up" approaches by the practitioner and sensor scientist and enhances the ability of both to make an informed assessment of the technical problems requiring investigation in order to meet a given sensor requirement.

In the technology-driven use of this tool, the descriptor attributes are selected based on the capabilities of the technology. The goal is to use this framework to identify application areas in which the technology would be useful. Therefore, application needs can be compared against this list of technology attributes. The result of the match can guide further specialization of the sensor technology. This case is further discussed below.

In practice, the process of completing the framework and performing the match requires considerable technical expertise and judgment. For example, the identification of a particular sensor application and candidate sensor technologies will likely require significant interaction between the sensor users who understand the problem domain and the sensor technologists who know what the technology can provide. Not all the descriptors may be appropriate in every instance. Moreover, technological advances and new requirements may warrant adding descriptor terms and categories. Nonetheless, the committee believes that this concept of a common framework is an important basis and will remain useful.

R&D Needs

When a sensor technology need has been identified using the process described above, the nature of the R&D necessary to rectify this deficiency must be understood. Figure 2-2 envisages two principal areas for sensor technology R&D: materials and other enabling technologies. The former category is the subject of the present study. The latter category would include technologies required for the implementation of a given sensor material or system—for example, compact, lightweight cryogenic cooling systems or rugged computer hardware for harsh operating environments. Such developments were not considered in the current study, although they may depend on materials R&D.

The use of the descriptors in identifying and highlighting specific deficiencies in existing technologies provides useful information on which to base a preliminary evaluation of technical risk. The committee identified three broad categories of development risk:

1. low risk, involving relatively minor modifications to existing sensor systems, with incremental expansion of the existing sensor performance envelope;
2. low to medium risk, based on proven technical concepts. A typical example might involve the redesign of an existing sensor system to meet implementation constraints; and
3. medium to high risk, requiring the investigation of new or unproven concepts. Long-term R&D on new concepts in materials, packaging, physics, and chemistry for sensing fall into this category.

The experience of committee members indicates that research leading to incremental improvements has an important role, particularly in the integration of sensor devices. Nonetheless, the most significant high-payoff research opportunities[7] are likely to fall into the second and third risk categories described above.

Research opportunities in sensor materials are discussed in Part II. *However, it must be emphasized that the purpose of the present report is not to provide a comprehensive list of research topics in sensor materials but rather to give representative examples, together with a rational basis for identifying materials research needs within the context of state-of-the-art materials science and engineering for sensors.*

Database

An added advantage of using a common framework with descriptors is that they can be used to establish a database of information on sensor applications and sensing technologies. Experience with particular sensor systems and technologies for a variety of applications can be characterized and captured in terms of generic descriptors. Thus, valuable "handbook" data would be available for future users that integrates sensor data and requirements from different sources in a coherent and comprehensible fashion.

The information in the sensors database on candidate technologies and previous applications (presented in terms of descriptors) could also establish the degree of match/mismatch between available technologies and requirements. In this way, quantitative data based on actual experience can be incorporated into the comparison process in addition to the specification data provided by sensor manufacturers and suppliers and information on technology attributes. The efficacy of the comparison process should increase as experience is gained with the process.

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NOTES

1. Requirements associated with these market drivers are discussed in Part II (chapters 3 to 6) in the context of selected examples.

2. Although R&D requirements for sensing materials have often been clearly defined for mass market applications, the large amount of funding required for implementation often remains an issue (NRC, 1993). For example, the cost of establishing a high volume wafer fabrication line for silicon sensor research has been estimated at more than $200 million (Thome, 1992).

3. Chemical sensors have been developed with sensitivities on the order of parts per billion (ppb).

4. See, for example, Longshore (1993) for a discussion of infrared detector materials.

5. Sensor technology has only been identified as an independent field of R&D for about 20 years.

6. In instances where mismatches between attributes and specifications occur, it may also be necessary to reconsider priorities given to the particular performance specifications that could not be met. This process ensures that the expectations of the potential sensor user are realistic and that advances in sensor technology to meet those expectations are actually required.

7. High-payoff areas for sensor research and development have been defined by the committee as those areas which, if successful, will have a major impact leading to a large return on investment.

PART II:

OVERVIEW MATERIALS FOR SENSORS— IDENTIFYING NEEDS

> *When you can measure what you are speaking about, and express it in numbers, you know something about it; but when you cannot measure it, when you cannot express it in numbers, your knowledge is of a meager and unsatisfactory kind…*
>
> *Lord Kelvin*

Sensors are widely used in many different applications, and sensor technology has become a basic enabling technology in many instances. The rapid increase in the interest in sensors has been driven by numerous applications, such as intelligent manufacturing processing,[1] in which sensors can provide a large benefit. In addition, sensors are of great importance in safety-related areas, with applications ranging from assessing the integrity of aircraft to monitoring the environment for hazardous chemicals.

Selected examples of sensor applications and types of sensors were chosen to illustrate the different driving forces and considerations discussed above: technology push, commercial market pull, military applications, life-cycle management, and regulatory demands. These illustrations are not intended to be comprehensive. Rather, they are relevant examples from which the committee identified general conclusions concerning research needs in sensor materials and the rapid development of sensor technologies for high-payoff applications. Each example describes an application, discusses the key technical issues pertaining to the use of sensors, and identifies key sensor material needs. Each sensor-type example describes the physical phenomena being sensed, a taxonomy of the different sensor types, and sensor materials issues related to the application. Of necessity, these cases are simplifications of reality. For instance, sensor needs are introduced as if each sensor were an independent entity, although in reality many applications require arrays of sensors or fusion of information obtained from many different types of sensors. Also, the level of technical detail for each example differs according to the domain being discussed.

New types of sensors are made possible with new materials that are produced using advanced processing technologies. To a greater extent than this technology push, market pull is driving increased activity in sensors. The primary market needs can be categorized as economic, regulatory, and unique government requirements.[2] Economic motivations for improved sensor materials and technology include reducing the cost of product manufacture, increasing a product's functionality at low additional cost, and improving the quality of the product. These motivations also improve product competitiveness. For example, the quality, safety, and comfort of automobiles have been greatly enhanced by the many sensors incorporated into the operation of modern vehicles (Shepard, 1992). Similarly, the cost of manufacturing and the frequency of defects in automobiles have been dramatically reduced by the increased use of sensors during manufacture. An equally important economic driver is the development and incorporation of sensors into products that aid in extending usable life. Examples include sensors for engine oil that monitor the integrity of motor oil in an engine, allowing a user to change oil only when it is necessary due to lubricant degradation, and sensors that can detect corrosion or metal fatigue in older aircraft in lieu of more expensive externally applied inspection procedures.

Sensors have been essential in satisfying a profusion of government-mandated regulatory requirements which include such applications as measuring chemical effluent from factories and exhaust gases from automobiles. These sensors can also have significant economic impact and effect on the quality of life.

Government agencies have many unique, wide-ranging sensor needs. The military has been on the leading edge of applying sensor technologies to improve its operational capability. For instance, because of extensive media coverage, the general public is now well aware of "smart" weapons used during the recent Persian Gulf conflict. Sensors were used to develop necessary information about the target, and once the weapons were launched they were guided to the target in real time by other types of on-board sensors. A very demanding need for new sensors is represented by National Aeronautics and Space Administration's Earth Orbiting Satellite program, which has the goal of monitoring changes in chemical composition and temperature of the earth's atmosphere (Zorpette, 1993). In this case, new materials and technologies will be required to provide sensors that possess the needed sensitivity in the spectral regions of importance. The reduction in the size of the military forces and the resulting closing of military bases have led to a requirement for sensors capable of monitoring the clean-up and disposal of numerous toxic organic compounds, chemical warfare agents, and obsolete munitions. Sensors will be required for on-line control to manufacture low-volume specialty components or ultra-high-performance military aircraft. Without sensor-based control for these specialized needs, the cost per unit would very likely be prohibitive.

Because of the diversity of sensor technologies and applications and the resulting diversity of materials needs for sensors, it is frequently possible to satisfy a given need with more than one type of sensor. A key finding of this committee is that an "ideal" sensor material does not exist apart from the context of a specific application. This fact has a significant effect on planning R&D of sensor materials and systems. To accelerate sensor development, an R&D strategy that maintains a broad applications-driven research base is necessary. This requires the identification and support of critical core competencies. As will be seen in the following chapters that contain examples of sensor applications and sensor materials, sensor development draws on a wide variety of technical disciplines—from physics to engineering and from chemistry to materials science to process engineering. The diverse nature of sensor technology development requires an interdisciplinary culture. It further requires an applications focus on selected sensor technologies and materials. Risk, scientific and technological impact, and advancement of a knowledge base for sensors must be considered in order to identify the most promising opportunity areas that can have a major impact and lead to a large return on investment.

The first two chapters of this part contain illustrations of applications that dictate sensor requirements as well as the resultant impact on sensor materials. Chapter 3, "Selected Sensor Applications in Manufacturing," first discusses the role of sensors in dynamically tailoring the curing cycle of advanced polymeric composites to achieve superior properties at reduced cost. The chapter concludes with several examples of leading edge applications of sensors in the production of micro-electronic components. Chapter 4, "Selected Sensor Applications for Structural Monitoring and Control," moves the application domain to the service environment. It discusses selected examples of the emerging use of sensors to make structural components more "intelligent."

The last two chapters of this section address two quite different classes of sensors. Chapter 5, "Long Wavelength Infrared Sensors," discusses sensors that provide "night" vision in the long-wavelength infrared (LWIR) regime. The advantages and limitations of three materials options are considered in the context of fundamental considerations that derive from an understanding of basic physics, manufacturability, and the application domain. The chapter explains how some of the ideas presented in Chapter 3 could be applied to produce these sensors at much lower cost. The next chapter, Chapter 6, "Chemical Sensors," develops a taxonomy for this broad sensor class, describes some promising applications areas (e.g., the detection of toxic chemicals in the environment), and highlights the key materials challenges.

Each of these chapters concludes with a wrap-up of sensor material needs. These recommendations are presented within the context of the information discussed in the chapter. They are illustrative of the analytical approach recommended by the committee. They are not intended to be considered as the most important material needs in the entire universe of sensor technology. Chapter 7 in Part III contains a summary of these illustrative sensor material needs.

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NOTES

1. The world sensor market is projected to grow at an annual rate of more than 8 percent (i.e., doubling in about 9 years), driven in part by intensified global manufacturing competition. At this rate, the market will reach $13 billion by 1999 (Defense Base Forecast, 1993).

2. Although beyond the scope of this report, sensors for health care and biomedical applications are of increasing importance. Key areas would include chemical sensors for consumer health monitors (e.g., for glucose and cholesterol) for home use, bio-compatible materials for use with implants and prostheses, and chemical sensors to facilitate research in the human genome project.

3

SELECTED SENSOR APPLICATIONS IN MANUFACTURING

Practitioners of manufacturing have always employed sensors. The earliest sensors included the experienced eyes of a blacksmith helping to guide the shaping of a steel sword and the vernier calipers of a medieval artisan used to measure the critical dimensions of an architectural icon. As the technological sophistication of the manufactured products has increased, so has the complexity of the process required for manufacture. To a significant extent, manufacturing has been in the fore-front of incorporating advanced sensor technology. For example, the current revolution in computer-integrated manufacturing has been enabled by advanced sensor technology.

An increasingly competitive global market-place has demonstrated the high cost of "inspecting-in" quality (i.e., the cost to assess the quality of the product after it has been manufactured and then "fix" or remake those parts that do not meet the required quality level). Consequently, quality must be an integral element of the manufacturing process, necessitating that the process be under control, either through constant monitoring using appropriate sensors or by withdrawing the product for inspection at intermediate manufacturing stages. In many instances today, manufacturing process sensors are the limiting capability that defines the best possible product performance and reliability.

The traditional manufacturing approach involved calibrating the equipment at the start of the operation with the expectation that it would continue to perform satisfactorily over a certain period of time. In this approach, sensors monitor process parameters, such as temperature, gas pressure, and composition. However, as the sophistication and complexity of materials processing increase, sensors will be needed to directly monitor changes in the product, such as grain size growth during processing; location of nucleation sites in epitaxial grown thin films; and chemical composition, morphology, and nanoscale thickness of fiber interface coatings for ceramic and metal matrix composites. In addition, on-line control of processes is highly desirable when the use and generation of toxic or hazardous chemicals is involved. In some cases, the component may be so sophisticated that manufacturing it reproducibly would not be possible without in situ sensors to provide on-line measurement and feedback for real-time process control.

An understanding of the process based on first principles or empirical study is highly desirable for manufacturing complex components. This approach provides an understanding of the interdependence between the various processing steps and can result in the development of qualitative and quantitative models for in situ model-based control. For example, variations in the product that would be caused by variations in a given process parameter, such as temperature, can be calculated; the process could then be adjusted to accommodate these variations. Furthermore, the combination of process models and sensor-based on-line control permits downstream processing steps to be tailored to accommodate irregularities in the current (or preceding) step. Such "feed-forward" control optimizes the process window for each individual process step, resulting in intelligent materials processing of a high-quality product at high-yield production rates.

Many of the recent advances in control technology have been made possible by rapid progress in information processing. Real-time control is only possible when the time constant for the measurement and analysis is commensurate with the time scale of the process itself. In the past, process monitors were necessarily confined to measurements of primary parameters, such as temperature and pressure. The massive computing power afforded by modern computer workstations now allow in situ, real time measurement (assuming the appropriate sensor technology is made available) of parameters that were not feasible in the past. With computational performance doubling about every two years, even more precise real-time control will become the standard practice of the future.

As is evident from the preceding discussion, sensors are crucial in a wide variety of manufacturing situations. Sensors that cost-effectively measure critical material behavior and guide a process to achieve desired properties would greatly enhance the process productivity and yield. For manufacturing, this is often the most important, yet most elusive, process improvement.

The remainder of this chapter extracts examples of current needs in sensor materials by examining needs from the high end of manufacturing: intelligent processing of materials and manufacturing of products that require a multitude of interdependent steps. The next section discusses sensor needs that arise from the self-directed curing of high-value polymeric composites. The following section broadly surveys the manufacture of optoelectronic components (integrated circuit and optoelectronic devices) in order to identify key sensor needs. The combination of these examples then serve to define key research objectives for sensor materials, which are summarized in the final section.

INTELLIGENT PROCESSING OF ADVANCED MATERIALS

Different terminology has been used to describe intelligent processing, including *closed-loop* (involving sensor feedback) and *real-time* requiring dynamic adjustment of control variables. Although closed-loop and real-time are necessary, intelligent processing also requires knowledge about the material and the process to enable a self-directed control system. In short, a *self-directed* system generates a control path in response to changes in material behavior that are denoted as process events, as opposed to some pre-established schedule of process parameters. Intelligent processing systems exemplify a process control strategy whereby process events regarding material changes, such as chemical-state change, flow, deformation, and growth, are continually evaluated for dynamic adjustment and prediction of process parameters that affect product quality metrics, which include process repeatability, process yield, and consistent properties.

Discrete part production, as opposed to the coordinated control of multiprocess manufacturing, is typically the domain of intelligent processing. Processes such as machining, welding, and forging typically involve either a priori or a posteriori control strategies. Although the metrics are very similar, intelligent processing is distinguished from conventional a priori and a posteriori processing by the in situ control system autonomy used in achieving these metrics, as depicted in Figure 3-1.

In a priori processing systems, control actions for variables such as process temperature and pressure are based on the results of a model (that may have been developed by empirical trials), which are used to generate a predicted schedule of process

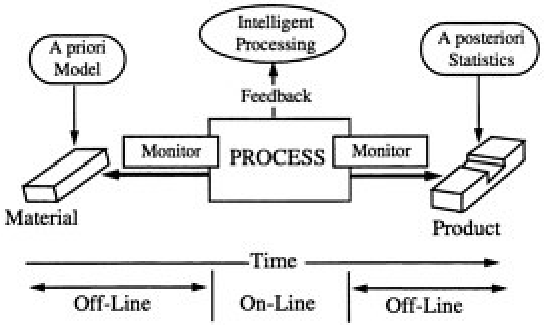


FIGURE 3-1 Intelligent versus conventional processing.

events; e.g., a time-temperature profile. In a posteriori statistical process control, attention is focused on monitoring a process to collect statistics. These statistics are used for process evaluation in order to eliminate or reduce undesirable variability. Reduction of process variability is accomplished by modifying either the process or those product features that are the causes of the variability.

Intelligent processing systems depart from predefined process models and statistics by using sensed information to self-direct the process via an event-based control strategy. Event-based implies the use of sensed information to denote the occurrence or prediction of an event for which adaptation (i.e., on-line decision making or conflict resolution) of some control variable may be required. The use of sensed information, such as in situ material behavior, to effect continual adaptation of these variables is the basis for the term *self-directed* as it is applied to intelligent processing (LeClair, 1991). Self-directed control can be used in conjunction with process models or in lieu of them if sufficient empirical information exists to construct the necessary rule-bases or neural networks.[1] In summary, intelligent processing is process control by objectives rather than control by following prescribed parameters.

Applications of intelligent processing vary widely and range from the processing of thin-film engineered materials[2] to the processing of polymers and polymeric composites, metals, and ceramics for bulk structural applications. In almost every application to date, intelligent processing has been applied to introduce a new material or process or to achieve a step-change improvement in an existing process that has been plagued by quality problems.

General Sensor Issues

A key issue raised in past reports of the National Materials Advisory Board (as referenced in the Preface) is that sensors are the weak link in intelligent processing. There are fundamental concerns about the capability of other available sensors to perform in a noisy or adverse manufacturing environment, compounded by real-world constraints that include:

- *short time constants*: sensing very rapid, localized changes or large gradients in a material over several hours of processing;
- *chemical change monitoring*: sensing the nonlinear behavior of one or more simultaneous chemical reactions and associated by-products;
- *point measurement*: sensing critical points, rates, and changes in rates within a complex three-dimensional product shape; and
- *inferred measurement:* sensing parameters of interest that are not directly measurable (i.e., inferred parameters require the establishment of constitutive relationships to those parameters that can be directly measured).

Intelligent processing of polymeric matrix composites offers a clear illustration of the challenges posed by these issues and benefits that could result from advances in sensor materials and technology.

Sensors for Intelligent Processing of Structural Polymeric Composites

Structural polymeric composites are critically important to sustaining U.S. aerospace and defense superiority. The potential market for these materials, by the end of the century, is projected to be 90,000 metric tons, a sixfold increase in tonnage since 1986, with a tenfold increase in worldwide employment to 200,000 people (AIA, 1991). Improvements in the manufacture of products that use these materials will help in the realization of such projections.

A polymeric composite typically has two primary microstructural components: a polymer material and reinforcing fibers. Two different generic types of polymers are used: thermosetting (the traditional choice) and thermoplastic (the more recent choice). Thermosetting polymers are initially low-viscosity liquids that can flow into a mold or around fibers. During the course of processing, thermosets react to increase molecular weight and viscosity, eventually becoming highly cross-linked, insoluble, infusible materials. On the other hand, thermoplastics are fully polymerized materials that melt and flow upon application of heat. Thermoplastics are processed well above their glass transition temperatures or melting points (if the material is semicrystalline) to reduce the melt viscosity and allow flow and to promote adhesion to the fibers.

The fibers in the composite are the component that provides the desired high stiffness and strength properties that make the material useful for structural applications. The polymer matrix protects the fiber, serves as a medium to transfer load between the fibers, and stabilizes the fiber when subjected to compression loading.

A composite structure is typically made by stacking layers of pre-impregnated ("prepreg") material[3] in prescribed directions on a tool form, compressing the stack, and then curing or consolidating the composite. In the case of high-performance thermosetting resins, the curing process requires the application of heat and pressure. For small-lot production, this curing step is usually accomplished in a large pressure vessel called an autoclave. Alternative processes, such as resin transfer molding, are preferred for higher-volume mass production.

Consolidation of a thermoplastic resin does not require autoclave but does require the application of energy, such as heat. In addition, new composites are being developed that consist of blends of thermosets and thermoplastics; in these materials, curing and consolidation occur simultaneously and interactively to produce complex microstructures possessing functionally gradient material properties that can be tailored to optimize specific strength, processability, etc.

Intelligent processing can improve the resultant properties of composite components. The discussion that follows examines the technologies required to fully implement intelligent processing with emphasis on the most critical sensor requirements.

Thermosetting Polymer Matrix Composites

At the present time, most of the structural polymeric composites used in the aerospace industry consist of a high strength/high stiffness fiber (e.g., graphite, boron, or aramid) embedded in a thermosetting organic-resin matrix binder (e.g., epoxy, bismaleimide, polyimide, polyester, or cyanate ester). These resins are complex chemical formulations with batch-to-batch chemical variations.

Until recently, the conventional processing strategy for thermoset polymer composites was based on a priori models. These models cannot account for variations in material chemistry, part geometry, autoclave sizes and heating patterns, and tolling materials. As a consequence, they assume "one size fits all" and are developed for the worst-case processing conditions. Hence these models specify a safe (i.e., protracted) cure cycle.

In contrast, intelligent processing senses the state of the material during cure. The development of these models requires the definition of events that denote the changes in material state, e.g., flow, deformation, growth, etc. A processing system is also required that is empowered (through a model or set of condition-action relations) to adjust the process parameters in response to changes in the materials state to achieve desired end-use properties.

The first steps in developing an intelligent processing system are the mapping of these desired end-use properties to the actual material parameters that can be sensed and the processing variables that can be controlled. Some properties (such as residual stresses; void volume; and fiber location, volume, and orientation) can be inferred from engineered relationships with parameters that can be sensed in situ, while other properties (such as part strength and modulus) depend upon other engineering relationships to determine properties that cannot now be measured in situ.

Identifying "need-to-be-sensed" parameters can be accomplished through a review of available models of the process[4] or by developing a mapping of properties to parameters and to variables. This mapping, depicted in Figure 3-2, is often referred to as an "influence diagram." It relates process control variables to in situ material behavior to resultant material properties.[5] It can serve to identify and prioritize relationships needed for self-directed process control as well as establish sensing technology requirements (LeClair and Abrams, 1989).

In the next step, a process engineer must assess available sensor technologies that can provide the necessary information either directly or indirectly. To accomplish this assessment, the framework developed in Chapter 2 can be used as a guide to list and detail the necessary parameters for evaluating

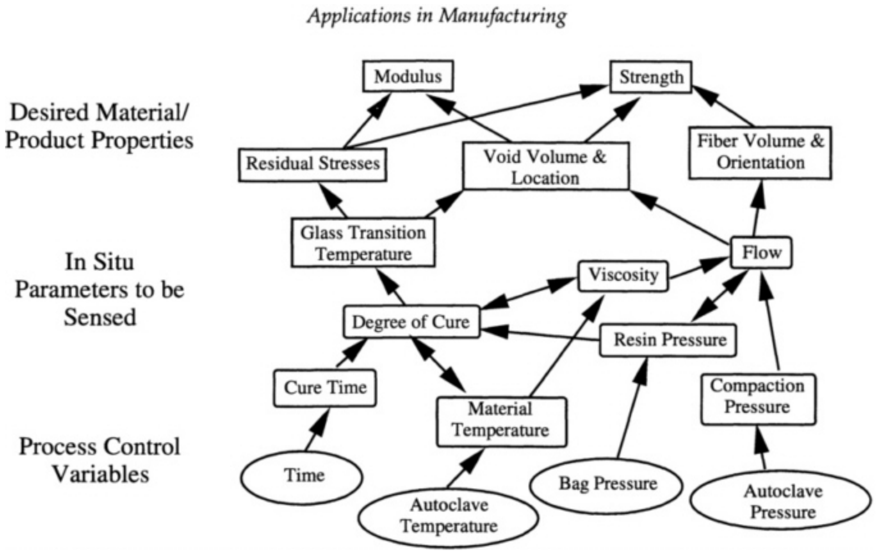


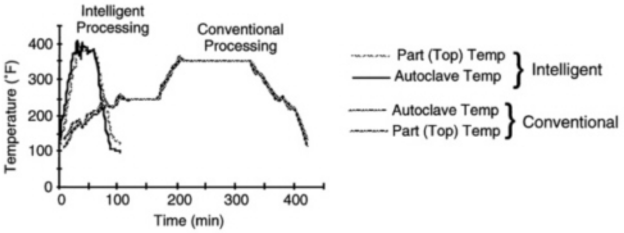
FIGURE 3-2 Influence diagram for curing of polymer composites.

and comparing different sensor technologies. With these descriptors, the process engineer can describe the range, tolerance, and limits of the sensing requirements and identify one or more candidate sensor technologies, and their respective capability and constraints.

Performance estimates and benefits of intelligent manufacturing can only be validated in a true manufacturing environment. One example is provided by the U.S. Air Force for an application that produces polymer composite replacement parts for the A-10 aircraft. In this case, sheet metal aluminum parts for the leading edge of the aircraft wing are being replaced with a hybrid carbon and aramid fiber/epoxy-resin composite to improve performance and extend the useful life of the aircraft. Initially the composite replacements were cured using a conventional (i.e., a priori model) cure cycle. But in 1990, the Air Force's Sacramento Air Logistic Center implemented an intelligent processing system that achieved full cure in 1.5 hours versus 7 hours required for the conventional approach; that is, a 70 percent reduction in cure time. The intelligent manufacturing system was originally implemented using the polymeric material temperature (as measured by a thermocouple) as the basis for estimating the degree of cure. Figure 3-3 displays the results for the initial implementation. Autoclave temperature profiles during cure are presented for both approaches along with the resultant test values of selected material properties. This data confirmed that intelligent processing could produce parts with strength values statistically equivalent to those conventionally processed (Warnock and LeClair, 1992).

Even though this initial implementation was quite successful, it was not without difficulty. For instance, the thermocouple signal was "noisy" and hence many data points were needed to clearly establish the trendline. To identify various levels of candidate improvements, the framework presented in Chapter 2 was applied to relate sensing needs (e.g., resin temperature) to the currently available sensor technology (e.g., thermocouple); the results of this comparison are summarized in Appendix D. Some of the thermocouple shortfalls can be partially ameliorated, but nonetheless, a new sensor technology was clearly needed. For example, autoclave temperature does not directly relate to the degree of resin cure (i.e., extent of the formation of cross-linked polymer bonds).

The new sensor technology should be able to



Mechanical Properties	Intelligent Processing	Conventional Processing
0° Tensile Strength	273 ksi	260 ksi
Modulus	21 Msi	21 Msi
90° Tensile Strength	8.2 ksi	7.5 ksi
Modulus	1.6 Msi	1.4 Msi
0° Tensile Strength	251 ksi	245 ksi
Modulus	20.9 Msi	21 Msi
90° Tensile Strength	5.25 ksi	5.27 ksi
Modulus	1.3 Msi	1.31 Msi
0° Compressive Strength	228 ksi	231 ksi
Shear Strength	15.5 ksi	14.7 ksi

FIGURE 3-3 Intelligent processing of composite repair components.

measure microscopic properties (e.g., physical, mechanical, chemical) in situ while minimizing the number of different sensors required for intelligent processing. Ideally, a new sensor technology should be as convenient, practical, and inexpensive to implement as a thermocouple.

One such multiuse technology which addresses both the limitation of thermocouples and the need for more microscopic property monitoring is photon scattering fiberoptic sensing, as described in Appendix D. Photon-scattering sensor technology[6] uses the energy and momentum distribution in the scattered photon flux to extract a wealth of useful and interpretable information regarding the physical and chemical nature of the material being processed. Suitable electromagnetic radiation scattering measurements (i.e., Rayleigh, Brillouin, and Raman scattering) can theoretically provide a direct measurement of material properties that include bulk modulus, thermal diffusivity, sound attenuation factor, sonic speed, heat capacity ratio, chemical composition, bulk viscosity, shear viscosity, and the free energy of mixing (Maguire and Talley, 1995). The scattered flux can be detected by the receiving optical fiber at any given angle, and transported at the speed of light to a remote spectrometer.

Near-infrared Raman spectroscopy, using fiber optics to provide a relatively simple optical contact with the material, can allow direct determination of the degree of cure. As an example, an epoxy-amine material[7] has a Raman spectral peak at 1,250 cm^{-1} resulting from the vibration of the polymer's epoxide ring structure and another one at 2,870 cm^{-1} arising from the stretching of C-H bonds. During cure, the number of the C-H bonds does not change significantly, while the number of epoxide groups notably decreases. Therefore, the 2,870 cm^{-1} peak can be used as an internal standard to determine the degree of change in the 1,250 cm^{-1} peak over time (Maguire and Talley, 1995). In this case, the ratio of the two peaks at time, *t*, can be represented as:

$$R(t) = \frac{I_{1250cm^{-1}}(t)}{I_{2870cm^{-1}}(t)}$$

The degree of cure, α, can be defined as:

$$\alpha(t) = \frac{R(t=0) - R(t)}{R(t=0) - R(t=\infty)}$$

This parameter, α, is a measure of the degree of cure related to a direct material phenomenon (Maguire and Talley, 1995).

For example, Figure 3-4 compares a near infrared fiberoptic Raman spectrograph for an uncured and cured sample of an epoxy-amine. From this spectrum it is apparent that $R(t=0)$ is about 0.7. After five hours of curing, R (t=5 hrs) has fallen to about 0.3.

Through a series of such measurements, the state of cure can quickly be determined. As indicated in Appendix D, Table D-3, expansion of the photon-scattering fiberoptic sensing into the Rayleigh and Brillouin regimes can provide additional useful information and could serve as the basis for an advanced noncontacting multifunctional

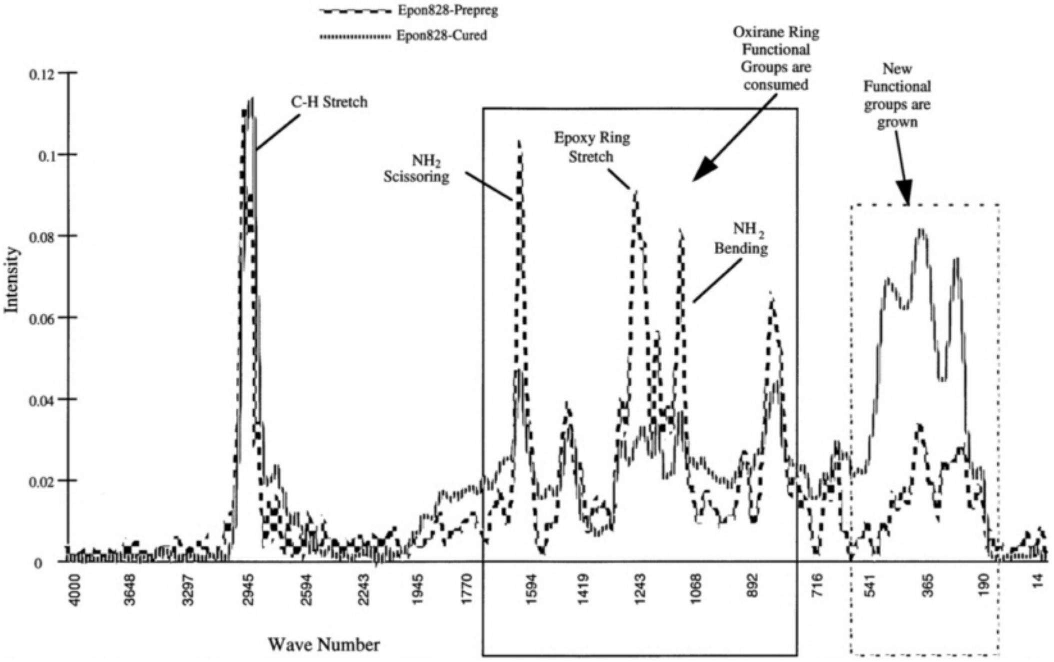


FIGURE 3-4 Fiberoptic Raman spectrograph (FORS) of pre-and post-cured bismaleimide-isocyanate (adapted from Maguire and Talley, 1995).

sensor array useful in many intelligent processing applications. Continued research and development of multiuse sensor technology will provide crucial enabling science and understanding for addressing these intelligent processing sensor opportunities.

The last section of this chapter discusses research needs and opportunities for photon-scattering sensor technology.

Thermoplastic Polymer Matrix Composites

Future systems, ranging from aircraft parts and printed circuit boards to applications that must survive in the rigors of space, will require further innovation in intelligent processing, particularly in the development of low-cost out-of-autoclave[8] composite fabrication techniques and new material systems such as components made of thermoplastic matrix composites. A newly developed out-of-autoclave technique involves the use of a unique energy transduction mode known as direct electric heating, that is, passing a current through the carbon reinforcing fibers (Miller and Van den Nieuwenhuizen, 1993). Electric heating of the fibers provides for a versatile temperature source capable of accommodating complex parts possessing varying curvature and laydown angles. It can produce a high strength, low void content composite. In the discussion that follows, processing needs, together with the unique hardware for part lay-up, are discussed to identify requirements for new sensor configurations.

Direct electric resistance heating uses electric current to heat the graphite fiber prepreg near the laydown point while the material is in the form of prepreg tape that is fed to a tape head that applies pressure and electrical power via metallic pads. A

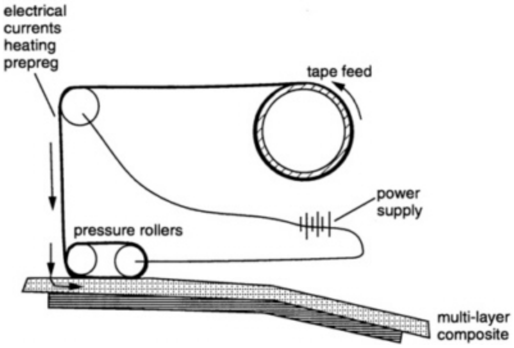


FIGURE 3-5 Direct electric heating for thermoplastic graphite composite tape consolidation.

schematic of this approach is depicted in Figure 3-5. The process requirement consists of raising the temperature of the high-performance thermoplastic matrix at the hot zone or interface between the part and tape.[9] The forming of the thermoplastic is achieved by pressing the part and tape together for continuous "wetting" contact and allowing the interface to cool so that the tape adheres to the part (Anderson and Grant, 1991; Cirino et al., 1991).

Thermoplastic material part quality is defined by the resultant physical properties, such as ultimate strength, void content, and elastic modulus. However, in-process measurements of some of these quantities (e.g., ultimate strength) cannot be directly obtained, since their measurement requires part destruction (University of Delaware, 1989).

Void content, a commonly used measure of laminate quality, can be measured by x-rays, ultrasonic pulses, or determination of local electrical or by thermal conductivity using infrared sensors. Controlling void content during the process requires measuring both temperature and pressure in real-time during processing and making appropriate adjustments. Thus, temperature must be measured; if it begins to exceed the prescribed range, the tape head pressure can be adjusted accordingly across the face of the tape head to bring the temperature back in line.

The issues and resulting sensor development opportunities as a result of these needs are summarized in the last section of this chapter.

SENSORS FOR ELECTRONICS MANUFACTURING

Electronics has become the largest single industry in the world, with a projected worldwide market of $2,000 billion by the year 2000, including U.S. revenue in excess of $400 billion and a job base in excess of 2.9 million employees. Integrated circuits (ICs) based on semiconductor materials are the enabling technology for the diverse range of functions, such as logic, memory, and control, that are required for today's electronic products. The national economy and infrastructure, including the manufacturing and service sectors, rely to a large degree on the information processing afforded by ICs. The future of the U.S. economy and its national security are directly linked to the health of the domestic microelectronics and electronics industry.

In addition to the rapid growth of silicon-based IC industry, advances in the understanding of compound semiconductors, typified by gallium arsenide (GaAs), have led to major progress in optoelectronics. Advances in materials control offered by new growth techniques and increasingly precise sensors have enabled the development of new types of "band-structure-engineered" materials that are leading to major new areas of optoelectronics as they are incorporated into devices. These devices range from laser diodes to optical fibers (which form the basis of optical communication) to fiber-based nonlinear optics, lasers, and optical amplifiers pumped by strained quantum-well lasers. The marriage of optoelectronics and microelectronics could lead to optoelectronic integrated circuits that enable such advances as massively parallel optical interconnects for high-speed computing and communications applications.

Integrated Circuit Manufacturing

The increasing complexity of microelectronics has caused a dramatic escalation in the cost of semiconductor production facilities. New production facilities for volume manufacture now cost approximately $1 billion. This cost is driven by the complexity of today's ICs and the sophistication of the processing equipment required for their manufacture. As the technology advances, the costs for future factories to produce the next generations of technology are anticipated to be even greater. Because of the major capital investment required to survive in this highly competitive industry, new approaches are required to increase the productivity of semiconductor factories. These approaches will make extensive use of sensor technologies to provide increased understanding and control of the various manufacturing processes.

Without extremely stable and well-characterized processes, it is not possible to obtain an acceptable final product without employing either sensors that monitor the process steps along the way or sensors to measure the state of the product at intermediate phases of the manufacturing sequence. The advancement of semiconductor manufacturing toward more and more complex structures, requiring smaller and smaller feature sizes, is rapidly leading to the convergence of the two cases.

A few observations serve to illustrate the complexity of IC manufacturing. Manufacture of a typical IC, such as a 16-megabyte dynamic random-access memory chip, requires in excess of 400 distinct process steps involving different types of materials. Typical process steps include ion implantation and annealing to control the electrical properties of the semiconductor, metal deposition for electrical contacts, metal patterning based on lithography and etching for interconnects, and dielectric deposition and patterning for insulation between the layers of multilevel metal interconnect required to carry the signals from the individual electrical components in the circuit. The inexorable march to higher and higher density requiring smaller and smaller feature sizes has advanced to the point that today's circuits have feature sizes below 1 μm; feature sizes for advanced devices and circuits are currently 0.35 μm.

The manufacturing complexity is typified by the fact that an IC contains several layers of these 0.35-μm interconnects separated by insulators, and these layers must be aligned within a small fraction of the 0.35-μm line width. Further, to achieve the performance required, the chemical compositions of all parts must be controlled with enormous precision, and the cleanliness of the process maintained at unparalleled levels. For example, a particle with a diameter of about one-tenth the minimum feature size can ruin the entire IC. Since the size of a typical IC is 2 cm × 2 cm, this implies that sensors must be developed to detect less than one 35 nm particle per 4 cm^2.

Another consequence of the steady advance of IC technology to smaller feature size is that the composition of the semiconductor must be controlled over a 10-nm scale and the composition of the dielectrics on a 5-nm scale. This control will require increases in the understanding of materials science and control of the process steps to produce the necessary feature sizes with required absolute interface and compositional control. It is also evident that the complexity of structural control for IC manufacturing will approach that for artificially structured materials discussed below.

Low-cost, sensitive, and reliable sensors are required to increase the rate of learning in process tool development, reduce the time to market for process equipment, improve tool and process control, improve process yield, and reduce defects (SIA, 1994). Increased use of real-time in situ sensors is driven by economics for these applications. Sensors are the critical elements in closed-loop process control and are necessary for detecting process problems when they occur, so that corrective action can be taken immediately. Sensors are also required to improve first-pass success when introducing process variations. For example, accurate control of even such commonly used processes as rapid thermal processing and plasma deposition and etch requires new sensor materials and approaches. And environmentally conscious manufacturing will require recycling and reuse of chemicals, not only for waste minimization but also for cost reduction. Typical sensor needs for these applications are discussed in the last section of this chapter.

Processing of Artificially Structured Semiconductors

The complexity of the semiconductor systems that are spawning development of artificially structured compound semiconductors requires major improvements to sensor materials and technologies for volume manufacture. In many cases, the technology requires that the microstructures be tailored at the atomic level in order to attain precise control of the resultant electronic properties.

The control required for low-cost volume manufacture of the artificially structured materials, such as those that form the basis of the LWIR detectors (which are themselves sensors, discussed in Chapter 5), necessitate the development of in situ sensors for intelligent on-line process control. Small numbers of devices with the desired performance can be demonstrated in a research environment. However, without real-time control the process cannot be scaled up at high yield to produce devices in which the composition is consistently controlled to a fraction of a percent, the dopant concentration controlled to parts per billion, and the thickness controlled to an atomic layer.

Techniques for characterizing epitaxial device structures have long provided crucial feedback to crystal growers as they try to develop and optimize growth processes. Techniques such as x-ray diffraction, secondary-ion mass spectrometry, reflection ion and optical spectroscopy, and photoluminescence permit one to determine thickness, composition, and quality of even very complicated multi-layered structures quickly and precisely. Many of these techniques have conventionally been performed off-line.

Over the past few years, there has been a considerable effort to bring as many as possible of these characterization techniques into the crystal-growth reactor itself. The motivation has been two-fold: to gain an increased understanding of the complex science of crystal growth and to improve the precision, quality, and technology of crystal growth for manufacturing.

Improvements in crystal growth of semiconductor materials will require the development of a full panoply of surface-sensitive structural, chemical, and optical diagnostic sensors. These sensors must be compatible with contamination-free manufacturing environments that include rotating wafers and harsh chemicals. Among the more promising of these diagnostics are optical transmission spectroscopy (the basis for a recent technique for measuring wafer temperature) and reflectance spectroscopy (recently applied to the growth of complex vertical-cavity surface-emitting laser structures).

There is currently a limited understanding of the relationship between processing parameters and the final product. As a result, process control requires measurement of both the chemical composition of the gases in the growth chamber and the composition and thickness of the material being deposited. The development and application of new types of sensors will lead to increased understanding of the relationship between the gas phase and the resulting solid to permit the development of algorithms for on-line control. R&D of in situ diagnostics is being pursued intensively in many laboratories throughout the world. Advances in techniques and development of new techniques will undoubtedly yield important advances in manufacturing technology over the next several years.

Noteworthy among applications are molecular beam epitaxy and chemical vapor deposition processes for epitaxial growth of electro-optical thin-films for semiconductors, detectors, etc. Spurred by the growth in new high-bandwidth wireless and optical fiber communication, advanced semiconductor processing has become a very active area of intelligent processing research because of the potential size of the worldwide market. These epitaxial growth processes require sensors for control of layer thickness, alloy concentration, interface sharpness, composition, etc., to enable low-cost, reproducible, uniform, and tailorable structures. Research in new sensor materials and technologies for molecular beam epitaxy and chemical vapor deposition includes work on reflection mass spectrometry (Brennan et al., 1992; Chalmers and Killeen, 1993; Chalmers et al., 1993); desorption mass spectrometry (Evans et al., 1993a, b), and ellipsometry (Patterson et al., 1992). The focus of these research efforts has been in developing non-invasive sensor technologies to sense and control the thickness (down to one atomic layer) of films, especially "superlattice" structures; a key sensor materials issue arising from the need for an optoelectronic modulator is discussed in the last section of this chapter.

SENSOR MATERIALS NEEDS IN MANUFACTURING

Curing of Thermosetting Resins

As previously discussed, a specific sensor suite for monitoring the curing of thermosetting resins has been developed but has several shortcomings. The principal opportunities to improve sensor materials and technologies include measuring more microscopic properties while reducing the number of separate sensors required for intelligent processing, and increasing the range of materials that a sensor technology can accommodate. Multiuse sensors provide an important method for addressing these intelligent processing sensor opportunities.

Photon-scattering intrinsic sensor technology (described in Appendix D) has the potential to satisfy many of these needs cost-effectively. The near-term research opportunity is to use photon-scattering sensor technology to increase the range of properties that laser-fiber optics can accommodate for multiproperty sensing (e.g., resin temperature, viscosity, degree of cure, degree of surface stress). The advantages of this technology include small size, ruggedness, survivability in hostile and inaccessible environments, simplicity of construction, ability to monitor multiple parts at one time in an autoclave, and low cost.

Laser-fiberoptic sensor technology has been demonstrated to perform in situ chemical analysis of polyimide and epoxy to determine degree-of-cure and infer the molecular weight during processing (Maguire et al., 1992). This accomplishment in laser-fiberoptic sensing technology has enabled the intelligent processing of new polyimide composites that are more difficult to process and for which conventional sensing of physical parameters such as temperature and viscosity has been insufficient. Since laser-based fiberoptic sensing has great potential, a comparison of this sensor technology against the multiproperty sensing requirement is contained in Appendix D.

Just ten years ago, the ability to use photon scattering as the basis for an industrial sensor-based control technology would not have been possible, and it is noteworthy that the current use of this technology is due to advances in four related areas:

- the invention of robust low-cost lasers to provide a ready source of photons;
- low-loss optical fiber, developed for the telecommunication industries, to allow the transport of photons over exceedingly long distances;
- the development of sensitive strained superlattice infrared detectors (discussed in Chapter 5) to enable the detection of the scattered "heat" flux with unprecedented sensitivity; and
- the massive increase in computational capability that has taken place over the last ten years to allow these powerful individual technologies to be suitably combined.

Consolidation of Thermoplastic Resins

For intelligent processing of thermoplastic structural composite parts, void content sensing is currently the most common measure of laminate quality. Void content can be measured by a number of techniques, including x-rays, ultrasonic pulses, and determination of local electrical or thermal conductivity using infrared sensors. The choice of a technique for in situ process monitoring is governed by factors such as speed of response, cost, and reliability. The use of x-ray techniques requires complex, costly, shielded equipment and a diagnostic system that must compute the control response within 100 milliseconds. The development of such a system would be a substantial undertaking.

For ultrasonic sensors, the main issues are essentially those of implementation: that is, how to couple the energy produced by the ultrasonic transducer into the newly laid-down hot tape and how to detect the reflected signal. A suitable cooled, miniature transducer would be required; this would necessitate modification of existing transducer designs. The detector required to receive the reflected signal information would involve the development of a sensor array, suitable low-attenuation coupling greases or gels (which would not interfere with laying down the next layer of prepreg), and a fast multiple-channel signal processor. For this sensing solution, the limitations imposed by transduction mechanics essentially define the operating parameters.

The use of thermal conductivity measurements with an infrared scanner is an attractive option. The presence of voids changes the rate of cooling of the newly laid-down tape and a thermal image of the part shows the void areas as hot spots. The sensor does not need to contact the part. Optical access to the part is required, however. A commercially available scanning thermal imager ("pushbroom" array) can be used. The primary implementation issues are optical access and processing speed. An optical fiber that conducts suitable infrared energy and could be built into or attached to the tape-laying head, with perhaps direct fiber bonding to a detector, is required. For this sensing solution, process geometrical constraints would be of major importance.

In order to control void content in real-time during the process, both temperature and pressure must be controlled. Thus, temperature must be accurately measured, and if too high, pressure must be adjusted across the face of the tape head. This leads to a requirement for local point measurements of pressure, implying an array of transducters at pitch spacing of less than 2.54 mm (0.1 inch). Conventional technology allows this to be done with an array of pressure tubes attached to miniature pressure transducers. But this process is bulky, the time constant is too slow (due to tube gas path), and tube blockage by molten matrix material is likely. A pressure-conductive matrix pad, which backs the metallic electrical pressure shoe, is geometrically compact and digitally simple (computationally), but it is thermally limited in currently available versions.

The measurement of modulus as a control parameter is currently not possible, due to the non-isotropic nature of the material and the thermal gradients in the parts. The best indirect approach is to measure the speed of sound (which is directly related to modulus). Other measurement concepts, such as the determination of molecular bond strengths of the matrix material at the interface, appear possible but are of unknown feasibility. Thus there is a requirement for the development of a matrix modulus sensor.

Manufacturing Integrated Circuits

Accurate control of even such commonly used processes as rapid thermal processing and plasma deposition and etch requires new sensor materials and approaches. For example, the back surface emission technique for measuring and controlling temperature in today's rapid thermal processing equipment leads to error of as much as 50¹C to 200¹C in temperature. The new long-wavelength infrared sensors, discussed in Chapter 5, could be important for more accurate measurement and control of this temperature.

Improved sensors that monitor gas and chemical purity/cleanliness are of major interest. Gas analyzers, mass controller calibrators, chemically selective sensors, and particle detectors are all essential to maintaining the required process cleanliness. Also, environmentally conscious manufacturing will require recycling and reuse of chemicals, not only for waste minimization but also for cost reduction. Chemical generation and reuse will require sensors that can detect impurities at the part per billion level for on-line monitors of chemical purity. These are typified by the chemical sensors discussed in Chapter 6.

Processing of Artificially Structured Semiconductors

A high-priority requirement is the development of noninvasive sensor technologies to sense and control the thickness (down to one atomic layer) of films, especially "superlattice" structures. The use of optical technologies (such as ellipsometry, laser-induced fluorescence, and fiberoptic probes) as an energy transduction medium is rapidly growing in capability and popularity. A material issue relevant to all optical technology is the optoelectronic modulator. It is the interface between optical and electronic components and is the key optoelectronic component for fiberoptic communications. The material currently used in optical modulators is lithium niobate, but its cost is prohibitively high.[10] Recently, the French have identified "molecular" optoelectronics research as a potential solution, since molecular materials would reduce the bottle-neck and allow the wide-scale application of optical fibers. Interestingly, one of the processing techniques for growing molecular optoelectronic films is a variation of molecular beam expitaxy—organic molecular beam epitaxy.

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NOTES

1. In practice an event-based controller will necessarily use a combination of models and rules to manage the multiple, conflicting, and often nonlinear aspects of a manufacturing process.

2. These include advanced electro-optical materials for semiconductors, detectors, etc.; interface materials between composite fibers and resins; and coatings for corrosion and lubrication.

3. Prepreg material consists of reinforcing fibers embedded in a polymeric resin matrix, usually in strip or sheet form.

4. Progress has been made in the development of time-temperature-transformation isothermal cure diagrams for thermosetting polymeric materials so that at least rudimentary process models can be readily constructed (for example, see Gillham, 1986).

5. The quality and usefulness of an influence diagram, which is typically constructed by a process engineer (possibly with a process operator), is highly dependent on available material knowledge and experience with the process. Control variables identify the alternative means of adapting the process in terms of varying mass/energy input and output. In situ material behavior refers to those parameters that capture chemical and physical changes in the material during processing. Desired material properties primarily relate to customer-established product-quality metrics. In situ material behavior specifies the candidate "need-to-be-sensed" information.

6. In the committee's opinion, photon scattering sensor technology is an excellent example of how research which was classified as "pure science" some 10 years ago now provides the basis for a powerful new sensor technology.

7. Epon 828 resin mixed with V-40 curing agent.

8. Out-of-autoclave fabrication involves using mechanical methods instead of heated high-pressure air to form and consolidate the material to the desired geometric configuration and strength.

9. The current generation of thermoplastic materials is processed up to 800 ¹F.

10. Better optoelectronic modulators are also enabling for advancements in volatile memories that provide durable and reversible displays and for nonvolatile memories used to store data.

4

SELECTED SENSOR APPLICATIONS FOR STRUCTURAL MONITORING AND CONTROL

Advanced sensors and actuators, together with exponential improvements in computer technology, are causing a surge of interest in the development of "intelligent" structures and equipment. Scientists and engineers are investigating materials systems that are capable of monitoring condition, changing shape, controlling vibrations, accommodating changes in the environment. Numerous applications are possible that range from the mundane to the exotic (Ramamurthy, 1992). They include automotive springs, smart skins on aircraft, smart bridges, improved biomedical devices, and advanced military systems. The shorter-range interests address incorporation of sensors into systems that monitor structural performance throughout the life cycle. The long-range goal is the deployment of active systems that are able to autonomously adapt in response to a change in the environment. These technologies offer the potential of substantive advancements for better, more reliable structures.

Within a product's total life cycle, sensors can play a significant role during manufacture and customer use. Sensors are able to monitor manufacturing operations and ensure that the final product meets its design specifications, as discussed in Chapter 3. Throughout use, sensors could perform many important functions such as monitoring the condition and performance of the product, controlling use, and aiding in maintenance and repair decisions.

LIFE-CYCLE MANAGEMENT

Life-cycle management (LCM) has the ultimate goal of integrating the fabrication and customer-use-periods, in order to create a birth-to-death concept of product design. Three major considerations are pushing the implementation of LCM:

1. reduction in operating costs through optimizing maintenance procedures and avoidance of premature component replacement;
2. enhanced product safety in the face of product liability requirements; and
3. product life extension.[1]

Four disparate applications (condition monitoring of equipment, control and condition monitoring of aeronautical jet engines, structural monitoring of test prototypes, and structural monitoring during operation) are discussed below to illustrate the broad range of current LCM applications and associated sensor technology requirements.

Condition Monitoring of Equipment

Preventive maintenance is commonly employed in industry to reduce the probability of equipment failure. In line with this approach, maintenance actions are typically scheduled on the basis of operating time without regard to whether the equipment actually needs specific maintenance or repair. Condition monitoring is a more "intelligent" approach, which detects impending problems early

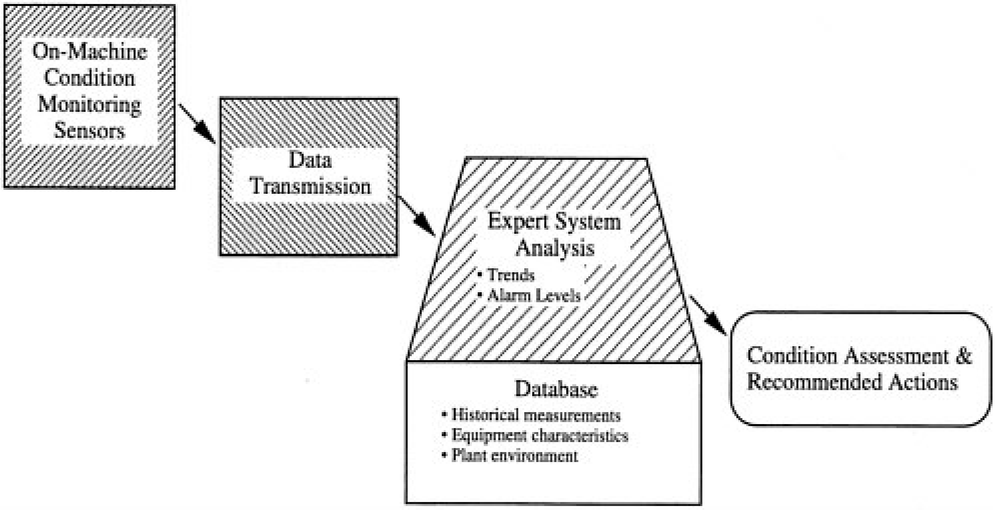


FIGURE 4-1 Factory equipment condition monitoring system.

enough to allow corrective maintenance actions to be prioritized and scheduled during noncritical time periods. Properly designed and implemented, such systems can reduce unnecessary work, allowing concentration on the most important maintenance and repair actions.

In the design of a typical installation, components to be monitored are identified and measurement points designated. Sensors are specified in terms of functional requirements, so that a variety of sensor options are available. This "open architecture" strategy is based on the premise that suitable sensors are commercially available.[2] These systems typically employ sensors that target one or more equipment degradation modes. They then provide early warning of an impending problem when signs of degradation begin to appear. The sensor framework described in Chapter 2 can be used very effectively in developing a core set of sensor specifications and in comparing the attributes of candidate sensors.

Condition monitoring requires periodic polling of the sensors and analysis of the data. Increasingly, the analysis is facilitated by computerized expert systems. A basic assessment compares the value of a parameter with an established alarm level.[3] A higher level of analysis examines the trendline of the data to estimate when future maintenance actions may be necessary. In addition, an automated diagnostic tool can aid in determining the root cause of equipment problems; accuracy can be enhanced by fusing the readings from multiple sensors.

The architecture of a typical automated equipment condition monitoring system is depicted in Figure 4-1. The core of this architecture is an expert system that analyzes the inputs from a distributed network of sensors. Such a condition-monitoring system is being used to monitor turbomachinery and other expensive rotating equipment (e.g., that used for electrical power generation). This equipment has well-characterized warning signs of impending failure. Failures typically result from misalignment of the rotating elements, imbalance, antifriction bearing defects, and mechanical looseness. A vibration sensor monitors each machine, since a change in a machine's vibration level is usually indicative of a change in the machine's performance, perhaps as a result of deterioration that will lead to failure (Voegtle and Bever, 1992).

Control and Condition Monitoring of Aeronautical Jet Engines

Modern jet (gas turbine) engines that power today's aircraft are very complex, highly engineered systems. The centerpiece of these engines is rotating turbomachinery that is built and maintained to very exacting standards. Engine operation is well understood at the macro level. Hence, even the most sophisticated jet engines developed for front-line military fighter aircraft can be controlled by monitoring and adjusting relatively few critical engine parameters. In order to accomplish this, jet-engine technologists have been among the leaders in implementing sensor-based control technology.

Advanced jet engines use an electronic digital control to manage engine operation and performance. These controls are more capable and reliable than the hydromechanical control they replaced. For instance, through March 1993, approximately 788,000 flight hours had been accumulated by digital controls installed on F100-PW-220 engines; during this period, 19 controls were removed for reported problems. This unscheduled removal rate of 1 per 41,500 engine flight hours is a factor-of-five improvement over the previous generation of hydromechanical controls (Khalid, 1994).

The electronic digital control receives engine sensor and actuator position feedbacks, processes these signals with its control logic, and sends commands to drive engine effectors to provide optimum engine and aircraft performance. The basic control parameters are engine pressures and total airflow, which are derived from the engine sensor inputs. An overview of a typical control system, along with sensed parameters, is indicated in Figure 4-2. Also shown are typical engine-control interfaces with the engine's hydromechanical components that control main gas-generator fuel flow, augmentor[4] sequencing, exhaust nozzle position, augmentor ignition, and bleed air.

A more advanced control is being used by the Air Force's F-22 Advanced Tactical Fighter engine (F119-PW-100 engine). Two full-authority digital electronic controls (FADECs) are employed, each with its own dedicated set of sensors. They operate "dual active," with both channels continuously active and performing identical functions. Each FADEC also communicates with the aircraft's flight-control system. Each channel provides half the control output; if one channel fails, the other channel assumes full authority.[5] Cross-channel communication allows sensor values to be compared between FADEC channels.

These electronic digital controls employ a number of different sensors to detect engine speeds, temperatures, pressures, and actuator/valve positions. The control's ability to accurately sense these critical parameters is important so that the control can recognize when engine limits are being approached, and appropriate accommodations can be made in fuel flow scheduling. The sensors must

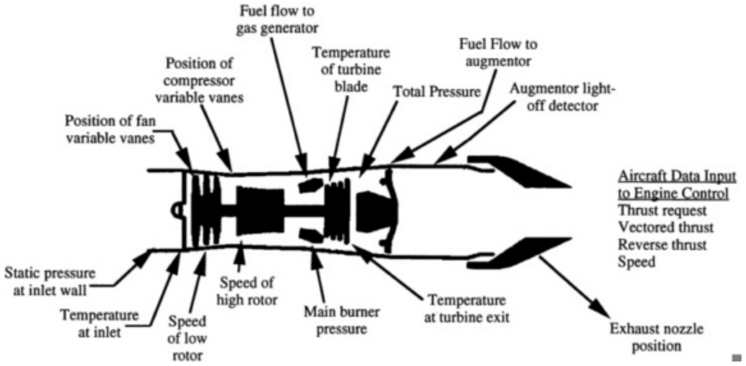


FIGURE 4-2 Jet engine digital control system.

have high reliability and repeatability in a severe environment. Some examples of sensors that are currently used include:

- a magnetic pickup sensor to measure engine fan speed;
- thermocouples to measure engine gas temperature, as well as fuel, oil, and hydraulic fluid temperature;
- an optical pyrometer to measure temperature of a rotating set of turbine blades;
- pressure transducers to measure gas pressures, such as inlet and burner pressures;
- strain-gauged diaphragm sensors to monitor oil, fuel, and hydraulic pressure;
- linear and rotary variable differential transducers to measure actuator and valve positions; and
- an ultraviolet light photodetector to monitor the thrust augmentor flame.

A significant advantage of a digital control is that it can be readily integrated with an engine diagnostic system to continuously assess the health of the engine. Table 4-1 summarizes the key storage functions of an onboard engine diagnostic system. Figure 4-3 is a simplified block diagram depicting how the diagnostic system interfaces with the engine control for the F100-PW-220 engine mentioned above (Khalid, 1994). When a control system fault or an anomalous engine event is detected, the pertinent aircraft and engine conditions are stored in memory for later use by maintenance technicians. Also, a fault indicator is set on an aircraft status panel to alert maintenance personnel that a problem occurred in flight. A significant payoff has resulted from being able to quickly isolate faults, at a high confidence level, that are quite difficult to duplicate on the ground.

The reliability and maintainability of the digital electronic jet-engine control systems are sufficiently high to have allowed their certification by the Federal Aviation Administration and successful transition to commercial aircraft engines.

Advanced architectures for future control systems are being developed that have potential benefits in terms of lower cost and weight. Distributed control architectures that utilize engine-mounted smart sensors and actuators that communicate to the propulsion system controller through high-speed optical data bus are being studied (Skira and Agnello, 1991). The sensors and actuators can be

TABLE 4-1 Functions of a Jet Engine Diagnostic Unit

Function	Typical Stored Parameters
Engine event detection	Low-pressure turbine rotor speed High-pressure turbine rotor speed Turbine airfoil over-temperature Hot start Engine stall Augmentor blowout or mis-light
Engine performance determination	Fuel flow Engine pressures Mach number Thrust-level request
Life-usage data collection	Engine operating time Engine flight time Hot section time
Control-system fault detection	Electronic control faults System faults

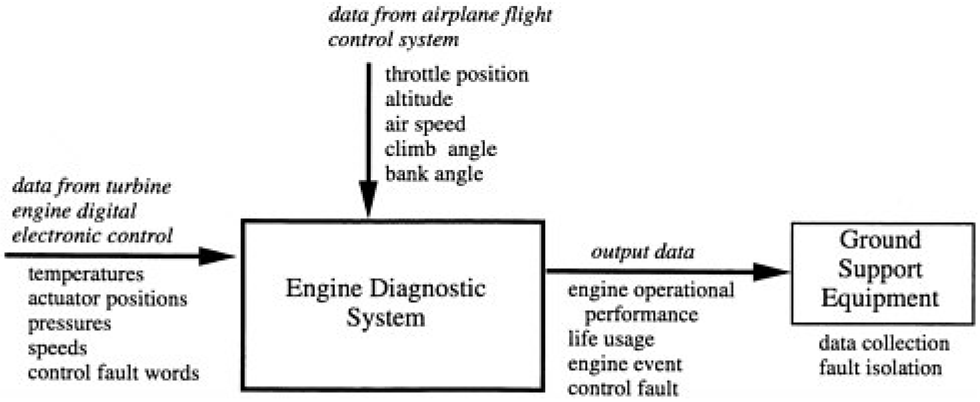


FIGURE 4-3 Jet engine engine diagnostic system.

copackaged with electronic modules to provide signal conditioning directly at the source. These "smart" devices will have the ability to provide their own environment/temperature compensation, use built-in test features to assess their health, compute necessary engineering units conversion, resolve actuator position requests from the engine controller, and perform actuator loop closures. Use of these smart devices would eliminate the need for point-to-point wiring for sensors and actuators at extended distances from the engine controller and would, in turn, greatly reduce engine harness weight (Tillman and Ikeler, 1991).

The use of smart sensors and actuators for jet-engine control is currently limited by the availability of mature high-temperature electronic components that can withstand the engine operating environment.[6] As this technology advances, smart devices will increasingly appear in engine applications.

One of the most challenging turbine-engine sensor requirements is measuring the gas temperature as it exits the combustor and enters the turbine. As engine temperatures have increased, the durability and performance limit of engine temperature sensors are an issue. Thermocouples are commonly used for engine temperature sensing, but their lifetime above 1100 ^{1}C (2000 ^{1}F) decreases rapidly. Since the first-stage turbine in advanced engines currently operates above this temperature, the temperature sensor has been moved downstream to a cooler environment. The turbine inlet temperature is then estimated using an empirically derived relationship.

However, this approach results in inaccuracies. For instance, it does not take engine-to-engine variations into account, nor does it compensate for engine operational changes due to normal "wear and tear." In addition, future-generation turbines are expected to have turbine inlet temperature well above 1650 ^{1}C (3000 ^{1}F), which renders the thermocouple approach unusable (Bird et al., 1990). On the latest advanced military engines, an optical pyrometer that measures turbine blade temperature is used to improve the accuracy of the turbine inlet temperature.

An improved temperature sensor that can provide accurate temperature measurement over a broad temperature range is under development. It uses an opaque coated sapphire rod to act as a near-blackbody cavity. A fiberoptic guide collects the radiation emitted from the sapphire rod and transmits it to a photodetector as shown in Figure 4-4. The resultant voltage is proportional to the engine temperature (Bird et al., 1990). This sensing technology will be an advancement, but it suffers from materials temperature limitations of the sapphire rod and silicon carbide housing that restrict the upper end of temperature measurement to about 1650 ^{1}C (3000 ^{1}F). Thus, although this technology

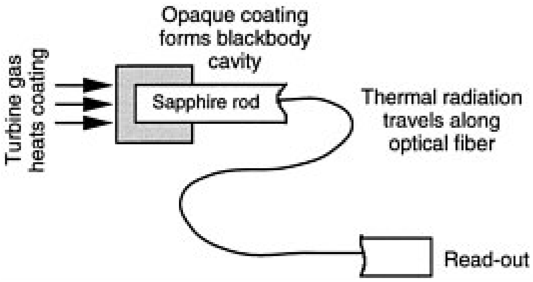


FIGURE 4-4 Fiberoptic high temperature sensor.

offers an advancement beyond thermocouples and will probably be adequate for commercial jet engines for the foreseeable future, it does not represent the "ultimate" solution.

Another temperature-sensing approach, which is much less mature, involves exciting the molecules in the gas path with a laser; the resulting spectra can be calibrated against temperature over a broad range. Using this method, it may be possible, in the long run, to monitor the temperature at the exit of the combustion chamber directly, providing an even greater opportunity for exact engine control. This sensing method has the added advantage of being nonintrusive (Eckbreth and Stufflebeam, 1985; Hall and Eckbreth, 1984).

Structural Monitoring During Validation Testing

Oftentimes particularly difficult sensing needs arise during the development of a testing program that is necessary to validate an innovative engineering design of equipment. When the overall program involves public safety concerns as well as the expenditure of considerable resources, there is a heightened interest in ensuring that the design is correct. Design models offer a list of parameters that should be monitored to validate the design assumptions and calculations, and these in turn establish the sensor requirements. Frequently, there are a multitude of sensor candidates, none of which exactly "fits the bill."

As an example of sensor needs during a development program, the National Aerospace Plane (NASP) program, a joint effort of the U.S. Air Force and the National Aeronautics and Space Administration had advanced far enough that planning for the flight-safety validation testing of critical airframe components was initiated (Lockheed, 1988). NASP's flight envelope is substantially different from conventional experience; for instance, it will cruise in the range of Mach 6 to Mach 12.[7] (Conventional passenger jets cruise well below the speed of sound at Mach 0.7. Even supersonic military fighters usually do not exceed Mach 2, and then only for a limited time.) NASP's mission profile will result in aerodynamic heating of some sections of the airframe to peak temperatures on the order of 1650 ¹C (3000 ¹F) for a large fraction of flight duration, in excess of 1 hour. In addition, aerodynamic and aerothermal loads will be significantly larger than those of previous aircraft experience and will experience significant transients. This hypersonic flight regime demands that the testing program be able to rapidly simulate changing aerodynamic and thermal loading on structural components and establishes instrumentation needs for monitoring the test conditions and the resultant structural response.

Validation testing methods include wind-tunnel, shock-tunnel, and structural simulations. Both static (e.g., normal, side, axial forces, and related moments) and dynamic (e.g., pitch, yaw, and roll damping) measurements are required. Measurement of static surface pressures are important for structural panel proof testing, engine inlet evaluation for propulsion system performance, and assessment of aerodynamic interactions. Dynamic pressure measurements are required for analysis of acoustic problems, panel flutter, and unsteady flow phenomena. Knowledge of actual surface heat transfer rates and temperature distributions is critically important to structural survivability and integrity.

Structural engineers determined that strain measurement at elevated temperature was the prime requirement, followed by heat flux and structural temperature measurement. Instantaneous nonintrusive flow diagnostics measured at a point, across the plane, and in the entire three-dimensional field were also judged very important. Two additional daunting sensor requirements were identified: rapid thermal mapping of entire components or structural elements and measurement of pressure fluctuations in an aerodynamic flow close to a surface in a high-temperature environment. As a first step in developing an appropriate sensor suite, all possible sensor technologies were identified. Table 4-2 lists a generalized set of sensing concepts for four of the key parameters. Evaluation of each of these sensor options was a significant undertaking. The framework presented in Chapter 2 could be used to develop a structured approach that examines each option against the requirements and determines the gaps in capability. These gaps could then serve as the basis for sensor development efforts.

TABLE 4-2 Initial Sensor Options for NASP Ground Simulation Testing

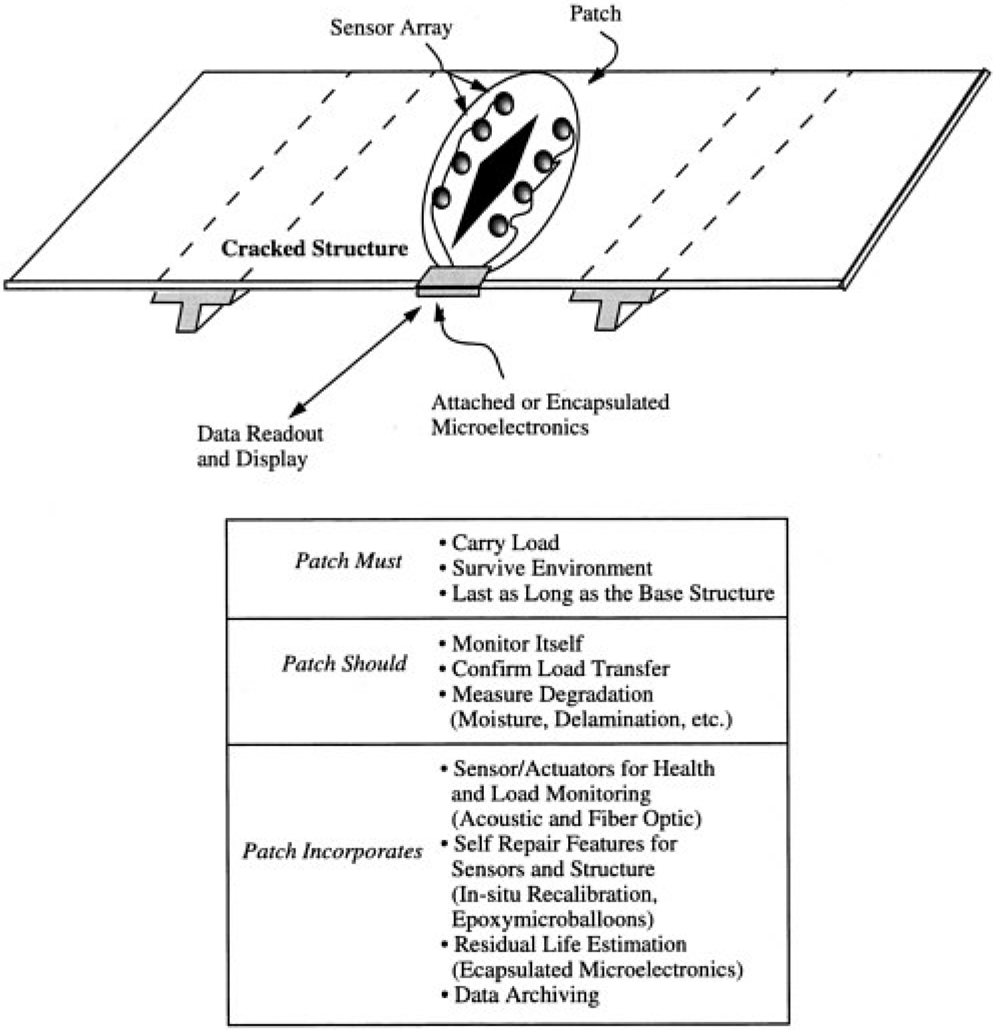
Parameter	Sensor Options	
Pressure	absorption/ scattering/ fluorescence	fiber optic laser
	bourdon tube	piezoelectric
	capacitance fluidic	semiconductor
		strain gauge
Temperature	acoustic	laser Raman/ fluorescence
	antiStokes Raman	phase change paint
	spectroscopy	resistive element
	fluid expansion	semiconductor
	infrared radiation	thermoelectric
	isotope radiation	thermal phosphor
Velocity	drag force	laser particle
	hot film	pitot pressure
	hot wire	ultrasonic
	ionization	velocimetry/ Doppler/time
	laser fluorescence/ Doppler/fiberoptic	
Strain	capacitance	laser speckle
	foil	resistive wire
	carbon filament	thin film
	fiberoptic	ultrasonic

Structural Health Monitoring

Structural health monitoring involves the evaluation of a structure's capability to carry useful load. Structural health monitoring is being given greater emphasis as a result of the interest in extending the life of equipment and facilities as long as possible (Gerardi and Hickman, 1992; Rotherford and Westerman, 1992). This evaluation can be done passively (e.g,, through deflection or distortion measurement), actively (e.g., analyzing ultrasonic response), or by inference (e.g., examining time history of load cycles). Of these three techniques, the active approach is the most desirable, since the signal-to-noise ratios of the measurement are typically high, and sensors can target the critical areas where precursors to serious damage or failure are expected to originate. On the other hand, this approach typically adds cost and complexity to the structure's design, and benefits would not accrue until later in the life cycle.

Monitoring the integrity of structures is a high-interest application of this technology. Early detection of fatigue cracks in metallic structure can allow relatively inexpensive repairs to be made, rather than replacing or extensively repairing structural components. In the case of aircraft (or bridges, etc.), the cost of replacement (in terms of capital cost and loss of use) is extremely high, and patch-type repairs are universally made. Once the repairs are made, continued monitoring can provide a high degree of confidence in continued structural integrity. How to effectively monitor the degradation of structures is currently an active area of research, with many different sensor approaches under exploration. Several of the approaches are discussed below.

The Air Force has a need to repair fatigue cracks in aluminum structural components of C-130 transport aircraft. A current repair process uses composite boron/epoxy patch. After repair, the component strength greatly exceeds that of the original aluminum structure. However, if the epoxy interface weakens or delaminates over time, the patch effectiveness can eventually degrade to the point of uselessness. The Air Force must therefore assess the integrity of this patch over an expected 20-year lifetime, as schematically depicted in Figure 4-5. The example sensor technologies described below



Patch Must	• Carry Load • Survive Environment • Last as Long as the Base Structure
Patch Should	• Monitor Itself • Confirm Load Transfer • Measure Degradation (Moisture, Delamination, etc.)
Patch Incorporates	• Sensor/Actuators for Health and Load Monitoring (Acoustic and Fiber Optic) • Self Repair Features for Sensors and Structure (In-situ Recalibration, Epoxymicroballoons) • Residual Life Estimation (Ecapsulated Microelectronics) • Data Archiving

FIGURE 4-5 Embedded sensors in a composite repair section.

are not a comprehensive list of the many different sensor methods that could be employed to accomplish this task but are representative of sensor approaches that have been or are being applied to satisfy this particular requirement.

Two different approaches have been used: embedded fiberoptic sensors[8] (passive) and ultrasonic transmission (active). If the strains exceed preset values, the sensor could issue an alert (Pollack, 1992). Embedding fiberoptic probes for strain measurement in epoxy was found to be difficult. First, the interface between the fiber and the epoxy was unreliable, and intermittent separation occurred. Second, moisture was absorbed over time in the epoxy and ultimately permeated to the silica fiber; this caused surface microcracks that resulted in light loss and eventually fiber breakage. A materials development effort resulted in improved reliability and survivability for the optical fibers due in part to the development of hermetic coatings for the fibers. System reliability was also improved through better connectors and electronically simpler processing systems.

The ultrasonic approach involved attaching transducers to the structure in order to generate ultrasound waves around and through the patched area.[9] If the bond degrades or the patch deteriorates (e.g., through cracking, delamination, modulus changes) the ultrasonic pulse spectrum will also change. Problems of implementation included finding a way to couple sufficient pulse energy into the structure and to securely attach the transducers for long-term environmental survivability. Energy coupling was achieved by two methods: (1) using wires as acoustic waveguides to direct ultrasonic energy into specific portions of the patch and surrounding structure and (2) developing piezoelectric and electrostrictive wafers capable of generating ultrasonic energy that could be adhesively bonded to the structure. Most significant in this latter case was the application of the tape casting process that enabled routine production of these ceramic wafers with thicknesses down to 5 mils.

In addition to fatigue cracks, a significant cause of gradual structural debilitation in aircraft is metallic corrosion. Visual inspection by trained technicians has traditionally been the detection method of choice. However, corrosion normally occurs in areas of the aircraft that have restricted access and thus are difficult and expensive to inspect visually. Several solutions have been proposed, although none has yet been demonstrated to be fully cost effective. One method involves the continuous monitoring of the environment (e.g., detecting the presence and concentration of moisture, corrosive chemicals [NaCl] in the air, corrosion by-products) and then using this data in a computerized analysis program to estimate the likelihood of corrosion. The computer would then cue the inspection process, identifying when and where to look for indications of incipient corrosion. Such monitoring could be performed by chemical sensors, which have considerable promise (see Chapter 6). However, these sensors must be able to survive for many years in the operational environment, detecting the critical corrosion precursors. Further maturation of chemical sensor technology is necessary before this approach becomes feasible. Other sensor solutions include a variety of nondestructive evaluation techniques, such as conductivity measurement, capacitance thickness measurement, neutron adsorption, and high-resolution radiography.

A most promising near-term inspection system is the High Resolution Real Time Radiographic system that is being developed by the U.S. Air Force. The unique part of this system is the development and use of scintillating doped optical-fiber matrix screens coupled to solid-state charge-coupled device video camera chips. This replaces conventional photographic-film recording media and enables images of much higher resolution at much lower dosage of x-ray illumination.

Video spectroscopy is emerging as an important sensing method for this application. It involves remote inspection of a part using a vision system that can image the corroding surface in any part of the optical spectrum, from ultraviolet to infrared. Corrosion products can be observed and the extent of damage characterized by analysis of the image's optical spectrum. For this method to be effective, the optical system must be able to view a remote area over a wide bandwidth. Moreover, it may be necessary to illuminate the area with a pulsed laser. These requirements have led to the development of an image translation system that employs a coherent bundle of flexible optical fibers with a very broad passband. Both materials development and innovative equipment design are crucial to the advancement of this technique.

SMART MATERIALS AND STRUCTURES

Smart materials and structures are defined in the literature in many different ways. Smart materials are primarily distinguished by being able to perform both sensing and actuating functions.

Newnham (1993) provides definitions of the degrees of "intelligence" of smart materials.

- Passively smart materials respond to external change without external control.
- Actively smart materials utilize a feedback loop enabling them to function like a cognitive response through an actuator circuit.
- Very smart materials sense a change in the environment and respond by altering one or more of their property coefficients, turning their sensing and actuating capabilities, i.e., materials with built-in learning functions are smarter than those without learning.
- "Intelligent" materials integrate the sensor and actuator functions with the control system.

The success of engineering is ultimately measured by the ability of a structure or component to perform its intended function without failure; oftentimes these structures must operate in an environment that was not fully known or defined at the beginning. Traditional design practices use a philosophy of "defense in depth." This dictates that a system incorporate numerous reinforcements, redundant subunits, and backup systems that add mass and cost to ensure safety in an uncertain environment. This typically results in conservative designs that require considerable human effort to postulate and analyze all possible contingencies, the application of more resources than required to implement the structure, and the consumption of additional energy to produce and maintain the structure.

The ultimate goal of "intelligent" materials systems is to be able to adapt to an unpredictable operational environment. In the long term, the conventional "defense in depth" design philosophy could become outmoded.

The significant effort in developing the theories, simulations, and hardware implementations for the control of machines, as discussed earlier in this chapter, has spurred the development of smart structures. Modern control approaches, including adaptive control and neutral networks, are finding widespread use. However, the tremendous number of sensors, actuators, and associated power sources that are required for smart structures do not lend themselves to conventional, centrally processed computer architectures. A distributed architecture appears to have significant advantages. Further discussion of actuators and signal processing, communication, and controls is beyond the scope of the present report. The bibliography contains references for further information on these topics (Wada et al., 1990; Crawley and de Luis, 1987; Rogers and Robertshaw, 1988).

Sensing is a critical function within smart material systems and structures. Damage control, vibration damping, acoustic attenuation, and intelligent processing all require accurate information provided by sensors to describe the state of a structure. Sensing capabilities can be added by externally attaching sensors or by incorporating them within the structure's material during manufacture. Sensing materials used for this purpose include optical fibers and piezoelectric materials, possibly in conjunction with "tagging" particles.

Optical fibers can be used either extrinsically or intrinsically in sensing, as explained in Appendix D. When used extrinsically, the optical fiber is not itself a sensor; it merely transmits light. Intrinsic sensing relies on changes in the light transmission characteristics of the optical fiber. The use of optical fibers to perform intrinsic sensing in smart structures was first investigated in 1979 at the National Aeronautics and Space Administration's Langley Research Center. In this early research, optical fibers were used to measure strain in low-temperature composite materials. (Measures, 1989a,b; Hickman et al., 1990). The work in "smart skins" (as it was then called) provided a catalyst for the development of a variety of fiberoptic sensors. Interferometric, refractometric, blackbody, evanescent, modal domain, and time-domain sensors were investigated for use in nondestructive materials evaluation, in-service structural health monitoring, damage detection and evaluation, and composite cure monitoring. Researchers examined the use of fiberoptic sensors as magnetic field sensors, deformation and vibration sensors, accelerometers, and sensors in propulsion systems. Resistance to adverse environments and immunity to noise from electrical or magnetic disturbances are among the many advantages of fiberoptic sensors (Claus, 1991).

Piezoelectric materials have found widespread use as sensors in intelligent material systems. Piezoelectric ceramics and polymers produce measurable electrical charges in response to mechanical stress. Recently piezoelectric materials have been used to simultaneously actuate and sense. For example, when bonded as a patch to a structure and powered by an alternating voltage, these materials induce structural vibrations that in turn modulate the current flowing through the patch. The current flowing through the piezoelectric transducer can be divided into two parts, one due to the actuation function and the other due to the sensing function that is representative of the mechanical strain. The primary advantage of controlling structures with colocated velocity feedback is that such systems are inherently stable at all frequencies.

Piezoelectric polymers, such as polyvinyldene fluoride (PVDF), are used in many sensing applications. PVDF can be formed as thin films and bonded to many surfaces. Uniaxial films, which are electrically poled in one direction, can measure strain along one axis, while biaxial films can measure strain in a plane. The g-constants, which represent the voltage generated in response to a mechanical strain, are typically 10 to 20 times those of piezoceramics. PVDF film also produces an electric voltage in response to infrared light; the pyroelectric coefficient defines this relationship. As a sensor, it behaves like a strain gauge, but does not require a conditioned power supply. The output signal is also typically greater than an amplified strain gauge signal. This high sensitivity is due to the thinness of the typical PVDF film (˜ mil). Even a very small extensional force creates a large strain because of the small cross-sectional area. Specially shaped PVDF sensors have also been used as modal sensors for monitoring particular modes of vibration of structural elements such as beams, plates, and cylinders.

The sensitivity of PVDF films to pressure changes has been utilized in tactile sensors that can read the Braille alphabet and distinguish different grades of sandpaper. Tactile sensors with ultrathin (200–300 μm) PVDF films have been proposed for use in robotics.[10] The pyroelectric effect, which allows piezoelectric polymers to sense temperature, limits their use of these types of sensors to lower temperature ranges (Lovinger, 1983; Tanaka, 1981; Amato, 1989; Carlisle, 1986).

One of the key factors limiting the application of ceramic sensors, such as a piezoelectric, is their brittle nature and low tensile strength. These limitations can be overcome to an extent by combining ceramics with polymer materials. The development of electroceramic composites offers two distinct advantages: overcoming the limitations of brittle ceramics and tailoring properties to suit specific needs. The piezocomposite consists of long, thin piezoceramic rods, poled along their axis, held parallel to each other and perpendicular to the faces of the plate by a piezoelectrically passive polymer, as shown in Figure 4-6. In this configuration, the thin rods can expand or contract laterally at the expense of the softer polymer even though the plate as a whole is restrained. This results in an increased bandwidth and higher sensitivity, which allows the external high-frequency uniaxial strain of the ultrasonic waves to be effectively coupled electrically within the rod composite.

Piezocomposite materials are widely used in hydrophones and medical ultrasonic transducers and have improved sensitivity and mechanical performance compared with the traditional piezoelectric ceramics (Vest, 1991). A good example of this is the 1–3 piezoelectric transducer composite pulse-echo transducer used in medical diagnostic imaging (Newnham, 1986; Newnham and Ruschau, 1991; Newnham et al., 1978). Polymers containing piezoelectric powders have also been investigated

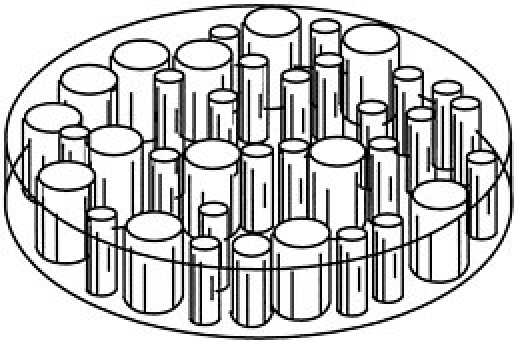


FIGURE 4-6 Piezocomposite structure.

for use as sensing materials. Piezoelectric paint and coatings are being developed that can be applied to complex shapes to provide information about the state of stress and health of the underlying structure.

Passive and active tagging are sensing techniques that involve adding taggant particles to materials. Embedded particles that are piezoelectric, magnetostrictive, electrostrictive, or magnetic can be used to provide inherent information about the in-process or in-service state of adhesives and polymers. Tagging offers the advantage of distributed in-situ sensing, which is not possible with many types of sensors. If the material system is properly designed, the tagging particles will have a minimum adverse effect on the properties of the host material (Clark, 1991, 1992; Zhou et al., 1993).

Passive techniques involve sensing the distribution of the particles. The earliest literature regarding tagging for nondestructive evaluation is a patent in which ferromagnetic particles were added to concrete structures containing nuclear waste to monitor the integrity of the structures. Another example of a passive technique is adding magnetic particles to an adhesive and then employing an eddy current probe to detect voids in a tagged adhesive bond.

Active tagging involves exciting the sensing particles and measuring the response of the host material. Applying an alternating magnetic field to a polymer tagged with magnetic particles and measuring the resulting force is an example of active tagging. Applications of passive and active tagging techniques include characterization of adhesive bonds, cure monitoring, intelligent processing, nondestructive materials evaluation, damage detection, and in-service health monitoring.

The tagging technique is now being investigated for nondestructive evaluation applications in composites, in adhesive bonding layers, and even in intelligent manufacturing processes. Some of the preliminary research involves using active ferromagnetic tagging to determine the complex modulus of polymer specimens using magnetostrictive tagging particles to detect delamination in thermoplastic composites, using active ferromagnetic tagging particles to monitor the curing process of composite specimens and using ferroelectric particles to monitor adhesive bonds. Using the tagging method for nondestructive evaluation usually requires the selection of the appropriate sensor particles, determination of the quantity of particles, preparation of the proper transducers (to pick up signatures resulting from the tagging particles), and the proper interpretation of the measured signal. Current knowledge of the above factors and issues is limited, and the investigations are in the preliminary stages. Although the investigations so far have demonstrated great potential for both the active and passive tagging techniques for nondestructive evaluation, much further development and research is required to make them competitive with the well-developed existing nondestructive evaluations methods.

SENSOR MATERIALS DEVELOPMENT OPPORTUNITIES IN STRUCTURAL MONITORING AND CONTROL

The technology required for structural monitoring and control is still evolving. Sensors constitute an enabling technology, as do the other elements of the system, such as computer processing, actuators, and controls.

Sensor technology can be viewed as falling into one of four categories, listed in decreasing order of maturity (Lockheed, 1988):

1. proven, off the shelf, and commercially available;
2. proven, but requiring validation in the service environment over the extended operational envelope;
3. new concepts currently undergoing laboratory development; and
4. new concepts proposed with undetermined applicability and difficulty of implementation.

For the near term, the critical issues are engineering-related. For any given measurement requirement that typically arises for condition monitoring, there usually are a great many sensing options from categories (1) and (2) above. A critical challenge is to assess these different options against the requirements, so that the most appropriate selections can be made. The framework described in

Chapter 2 can be used very effectively to specify the requirements for a sensor technology and then serve as a framework to compare different sensors. If no candidate sensor meets all of the requirements, then a development effort can provide incremental improvements to the technology. Such developments often require innovative equipment design or enhanced computer analysis programs, as well as materials improvements. An example is video spectroscopy to examine hard-to-inspect structures for signs of corrosion. Flexible optical fibers with a broad passband were required (conventional optical fibers do not transmit infrared radiation), as well as a very capable image translation system.

LCM has somewhat different requirements for sensors than those associated with the manufacturing process discussed in Chapter 3. The most challenging additional sensor needs for in-service monitoring relate to the following three areas:

- Requirement for very long sensor lifetimes with high reliability;
- Sensor information displayed in an user-friendly format; and
- Sensor-product integration.

The lifetimes of sensors used in manufacturing operations can be relatively short, and frequent opportunities normally exist for sensor calibration, maintenance, and reliability checks. In contrast, in-service performance-monitoring sensors must have a lifetime that exceeds that of the product; this can translate into tens of years of reliable, maintenance-free use in uncontrolled environments. Despite the use of accelerated aging tests, there is a lack of confidence regarding sensor performance over a lifespan of twenty years or longer. As a result, the development focus of sensor suppliers is beginning to change from one dominated by sensitivity and resolution enhancement to issues of long-term reliability and calibration. However, this change in strategy is not easy to make, particularly considering the fact that the typical major developers and suppliers of sensors are small businesses supporting niche market applications. About half of all commercially available sensors have been fielded within the last five years; thus the long-term reliability track record is incomplete.

A major problem encountered in LCM is the lack of field experience in using many of the relevant sensors. Sensors within a manufacturing environment are typically used by skilled personnel in a relatively controlled setting. However, once the product is sold, the sensor readout must be readily interpretable by maintenance technicians who may be relatively unfamiliar with that particular sensor.

There is a general concern about avoiding interference of the sensor with the performance of the product. For instance, if the sensor is embedded in the structure, degradation of the structural strength could result (Davidson and Roberts, 1992). The sensor may also become detached during service, reducing its effectiveness or possibly causing total failure of the sensor. Design approaches to integrate the sensor with the product must be developed by detailed analysis, test results, and experience in the service environment.

LCM is expected to continue to provide a technology pull for incremental materials development efforts that are needed to solve the myriad of problems that arise as sensors are incorporated into structures that must satisfactorily endure their environment. The need for long sensor lifetimes with high reliability in the operational environment requires sensors that are inherently stable and have very high operational reliability, which may result in sensing solutions that do not directly depend on materials for transduction. An example is turbine temperature sensing. Thermocouple technology is being eclipsed by a completely different sensor technology: one that acts as a blackbody cavity. But this technology also has materials-related limitations that will eventually restrict its application. The high-temperature sensing technology of the future will measure molecular spectra.

LCM and smart materials have many similar sensor requirements. Fiber optic sensors, both intrinsic and extrinsic, are very important, and their potential has yet to be fully exploited. Chemical sensors, possibly used in conjunction with fiber optics, have significant potential for the future (see Chapter 6). Piezoelectric polymers, piezoelectric ceramics, and piezoelectric composites offer advantages for strain measurements. Smart materials have the added requirement for actuation, and these piezoelectric materials can do "double duty." Active and passive taggants placed in structures offer the possibility for low-cost in situ sensing; their potential is only beginning to be explored.

In the long term, the full potential of intelligent material systems cannot be achieved unless appropriate sensors are available (Amato, 1992). Existing sensor technology is often less advanced than required for many of the envisioned smart structures applications. However, major advances in control technology are also needed; a discussion of these is outside the scope of this report, but Appendix A contains appropriate references.

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NOTES

1. In addition to the obvious benefit of being able to use a product longer, there is a secondary benefit of reducing environmental impact by postponing the disposal of the product and the production of its replacement.

2. This approach also facilitates testing of candidate sensors and allows ready insertion of new sensors.

3. Alarm levels are usually first set on the basis of industry standards or manufacturer recommendations. However, these often are adjusted to take the peculiarities of the service environment into account.

4. Fighter aircraft use an augmentor, also known as an afterburner, to provide a very quick increase in thrust. Usually this boost is on the order of 50 percent. The augmentor burns fuel in a separate stage after the turbine, and is not very fuel-efficient.

5. In the event of dual sensor failure, the control's software uses an on-board model of the engine's operation to synthesize the value of the parameter.

6. A National Materials Advisory Board study is under way that addresses materials for high temperature semiconductor devices. Publication is expected by mid-1995.

7. Mach numbers are multiples of the speed of sound. Thus, Mach 1 is the speed of sound, Mach 6 is a velocity that is six times the speed of sound.

8. Optical fiber sensor technology is discussed in Appendix D of this report.

9. A piezoelectric driver supplies an impulse to the structure, and the transducers pick up the transmission through the patch and surrounding structure.

10. For example, a skin-like sensor with temperature-and pressure sensing capabilities can be used in different modes to detect edges, corners, and geometric features or to distinguish between different grades of fabric.

5

LWIR SENSORS

The sensing of electromagnetic radiation is very important for a wide variety of activities. The utility of radiation sensors in the visible region[1] is large, because the atmosphere absorbs weakly in this wavelength range, allowing information to be obtained about distant objects. The near infrared and the LWIR regions[2] also exhibit particularly low atmospheric absorption and thus offer high potential for long-range observation sensors.

Sensing radiation in the LWIR allows detection of unilluminated objects that are at room temperature. This capability is pivotal to several specialized applications. For instance, efficient detection of LWIR is an enabling capability for night vision, and LWIR sensors are extremely valuable for a variety of reconnaissance applications. Temperature is also a critical parameter for many manufacturing applications (see Chapter 3). Infrared sensors are advantageous because they are non-contacting and can sense a temperature change over an area very quickly. These same characteristics can be used to detect defects, such as voids, because their thermal characteristics are different from those of the matrix. In addition, LWIR detectors with appropriate characteristics could also be valuable for chemical detection, since many molecular vibrations have characteristic resonant frequencies in this energy range.

Well-defined infrared sensor needs exist in the 8–14 µm spectral region. The Department of Defense has made substantial investments in materials research for applications in LWIR sensors, due to DoD requirements for reconnaissance and night vision capabilities. For example, the military has a need to track large numbers of ballistic missiles and their associated warheads; this dictates requirements for very discriminating sensors. In this type of application, performance is of paramount importance, and cost is a significant, albeit secondary, factor. However, a key issue for future development of widespread infrared sensing technology is consideration of the price/performance tradeoff. Many applications of LWIR are far more price sensitive than the DoD example (e.g., civilian law enforcement).[3] In those cases in which ultra high performance is not needed, the ease and reliability of processing and compatibility with conventional silicon electronics become important considerations, since these factors strongly affect the cost.

Many strategies can be used to detect LWIR. Bolometric approaches, in which the incident radiation heats a detector element and causes a measurable quantity to change (e.g., resistance or capacitance), are the simplest and usually the least expensive. Bolometers can operate at room temperature and are useful for certain applications, such as those in which an integrating detector is needed. A low-cost[4] night vision camera is reportedly available; it is based on 240 by 336 individual microbolometers fabricated on a micromachined silicon chip (Technology Advances, 1993). Bolometers rely on a second-order effect, and this results in fundamental performance limitations of bolometric detection; for example, high sensitivity tends to impose slow response (Westervelt et al., 1991).[5] For applications requiring high sensitivity, photo-detectors (which directly convert individual photons into either an electrical voltage or current) are generally the superior choice.

LWIR PHOTODETECTORS

Photodetectors can achieve their theoretically maximal (i.e., background-limited) performance with a fast response time. These solid-state devices are used for many applications because of potentially excellent (Göpel et al., 1992):

- geometrical registration and stability;
- signal-to-noise ratio and dynamic range;
- optical, electrical, and mechanical robustness; and
- compactness and compatibility with solid-state circuitry.

Most LWIR detectors of interest are made from semiconductor materials. Detection occurs when a photon is absorbed and a carrier is excited from the filled valence band into the conduction band. Schematic diagrams of typical band structures for two different semiconductors are shown in Figure 5-1 and 5-2. The longest radiation wavelength that can be efficiently absorbed is determined by the size of the band gap.[6] Figure 5-1 depicts a direct-gap material (e.g., MCT), in which the radiation can be absorbed directly, whereas Figure 5-2 depicts an indirect bandgap material (e.g., silicon), for which momentum cannot be conserved when the photon is absorbed unless lattice vibrations (phonons) are also excited. Direct bandgap materials can absorb radiation whose energy is close to the band gap more efficiently than indirect gap materials (Sze, 1981).

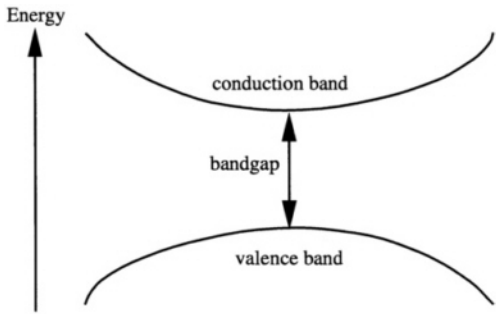

FIGURE 5-1 Direct bandgap semiconductor.

No semiconductor material can absorb radiation efficiently unless the wavelength of the absorbed light is short enough that the photons have sufficient energy to excite carriers across the band gap. Thus, an important issue in developing materials suitable for infrared sensing at long wavelengths is tuning the band gap to be small enough for the wavelength of interest to be efficiently absorbed. An LWIR sensor must detect objects whose temperature is close to ambient (about 300 K). Since a temperature of 15 ^{1}C corresponds to a radiation wavelength of 10 μm, the search for improved infrared sensor materials involves finding materials with band gaps less than about 130 meV. No binary alloy has a band gap in the 130 meV range that is needed to make efficient LWIR detectors.

The materials challenges involved in making high-efficiency sensors increases markedly as the wavelength of interest increases. Given that no binary material is suitable for use as an LWIR detector material, different strategies have been used to obtain a material with the "right" bandgap. Three such materials strategies for obtaining high-efficiency infrared detectors are discussed below: MCT (mercury-cadmium-telluride) III-V multiple-quantum-well devices, and III-V strained-layer superlattices. The last two strategies involve man-made,

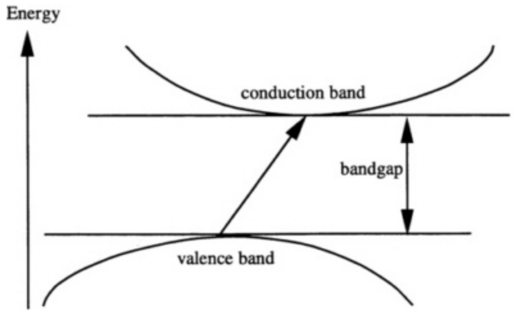

FIGURE 5-2 Indirect bandgap semiconductor.

artificially structured crystals; their manufacture requires atomic-scale control of the growth process (see "Sensors for Electronics Manufacturing" in Chapter 3).

Appropriate characteristics required of the sensors are described in terms of descriptors in Chapter 2 (and are explained in more detail in Appendix E). Several of these are particularly important for unbiased comparisons of performance between different infrared sensors technologies (Göpel et al., 1992):

- sensitivity, as measured by specific detectivity, D^*;
- resolution, or noise-equivalent temperature i.e., the smallest temperature difference that can be resolved);
- range, or spectral response (i.e., how the detectivity depends on wavelength);
- response time; and
- thermal constraint, in terms of operating temperature.
-

From a materials and processing perspective, significant issues are involved in addressing the list of sensor descriptors discussed in Chapter 2. In terms of minimizing the acquisition cost of LWIR sensors, a key consideration is the selection of a materials system that is inherently producible. The performance-related "figure of merit" that is usually employed for individual detectors is D^*, a measure related to the inverse of the smallest detectable signal. Generally, achieving high detectivity requires reducing all nonradiative causes of carrier excitation and recombination. Strong coupling between the incident radiation and the carriers promotes high detectivity because radiative processes occur faster than nonradiative ones, which makes them more likely to be dominant. In addition to intrinsic sources of nonradiative recombination, recombination can occur at defects; these can often-times be reduced or eliminated through improved processing of the detector material.

As a general rule, the performance of a given detector can be improved by cooling, since nonradiative carrier excitation and many recombination processes can be suppressed by lowering the temperature.[7]

Imaging applications require multiple sensors in an array format (Scribner et al., 1991). These arrays are usually processed using semiconductor processes; this imposes stringent requirements on materials stability and uniformity as well as on processing control. For example, "dead" pixels clearly degrade the image. Even small differences between the individual detectors that make up the pixels of an array degrade the image. For a single detector, D^* is clearly a relevant figure of merit. However, for arrays of detectors the performance can be limited by spatial noise (i.e., detector nonuniformity[8]). Material stability is an important component of the array uniformity issue. To some extent, nonuniformity can be corrected by calibrating each sensor in the array and then multiplying the output response by a correction factor. This approach increases processing overhead, and detector response can drift, which causes the correction to degrade. Drift can arise from changes in the composition of the detector material (e.g., loss of mercury from MCT due to the high vapor pressure of mercury) or from so-called "$1/f$ noise." The origin of $1/f$ noise is poorly understood, but it appears to be associated with defects in the material. In addition, noise sources can arise at sample surfaces, in which case surface passivation is extremely important.

The typical performance figure of merit for arrays is the noise-equivalent temperature, which is the smallest temperature difference that can be resolved. Nonuniformity is particularly important under conditions of substantial illumination and for staring (i.e., fixed-position) arrays. Arrays can have a million or more sensors (or pixels), and such large arrays require high data rates to read the response from each sensor; this places strong constraints on correction algorithms.

Another key consideration involves the coupling of the detectors to the data processing portion of the sensor. Since the data processor and the detector materials are different (data processors are usually silicon-based), mismatches in mechanical response due to different coefficients of thermal expansion can lead to detector array operability problems.

As mentioned previously, there are at least three materials strategies for producing LWIR sensors and each is at a different level of maturity. Currently, the performance of LWIR sensors implemented in MCT is limited by materials processing issues that are based on fundamental materials characteristics. The technology of sensors based on multiple III-V quantum-well materials is less mature but has benefited from the large investment by the electronics industry in gallium-arsinide technology. This investment has resulted in rapid progress and has made it possible to produce arrays with performance comparable to, or in some cases better than MCT arrays. The new strained-layer superlattice materials are the least mature of the three technologies. In principle, their technical characteristics should be superior to those of MCT and the cost much less. Results to date show considerable promise. However, substantial investment in materials processing improvement will be necessary to determine whether this superior performance can be achieved in practice. The status of each of these LWIR sensor materials technologies is summarized below.

LWIR Detectors Based on MCT

An early successful strategy for obtaining a material with a band gap of about 130 meV was to search for a material with three constituents (ternary alloy) possessing a bandgap of the appropriate value. This led to the consideration of $Hg_xCd_{1-x}Te$, which is a combination of the semiconductor, CdTe (1.6 eV band gap) and the metal, HgTe (0 band gap). The band gap in mercury-cadmium-telluride thus can be continuously tuned between 0 and 1.6 eV by altering the cadmium concentration. In this system, a cutoff wavelength of 10 µm corresponds to $x = 0.23$. High-quality bulk material can only be obtained by alloying materials with similar lattice constants. MCT is the only bulk ternary system that is a combination of two lattice-matched materials in which bandgap tuning to the desired region has been found to be possible. The materials characteristics of mercury-cadmium-telluride are such that single detectors operating at 77 K can attain background-limited performance for detection of 10-µm radiation. The properties leading to high detectivity include the direct gap (leading to a large absorption cross-section) and high mobility carriers. The principal drawbacks of mercury-cadmium-telluride arise because the material is extremely difficult to manufacture reproducibly at the composition of interest. Indeed, individual detectors of mercury-cadmium-telluride with high D^* were demonstrated in the early 1960s. Despite more than 30 years of extensive effort, the technology for manufacturable, low-cost arrays with high sensitivity in the LWIR region and good uniformity remains elusive, although considerable progress has been made (Balcerak et al., 1992; Kilby, 1994). Problems include the difficulty of maintaining homogeneous stoichiometry, as well as concentration drift, because of the high vapor pressure of mercury.[9] The cutoff wavelength (related to the band gap of the material) is highly dependent on the cadmium concentration; typical variations in D^* of about 15 percent for mercury-cadmium-telluride in the 10-µm region have been reported (Norton, 1991). Such a large variation leads to poor array performance as discussed earlier. Growing defect-free material necessary for reducing nonradiative carrier recombination is difficult. The material has poor radiation hardness (i.e., radiation induces defects, which degrade performance) and is soft, which makes it susceptible to mechanical damage during the many processing steps. Surface leakage currents are a problem, so that passivation is also an important issue. Generally speaking, the requirements for homogeneity and freedom from defects become more stringent as the wavelength detected increases.

The difficulties associated with mercury-cadmium-telluride have been attacked via sophisticated materials processing techniques, including MBE, organometallic vapor-phase epitaxy (Hicks, 1992), metal-organic chemical-vapor deposition, and liquid-phase epitaxy. Sensors for in situ control of melt temperature and pressure for manufacture of mercury-cadmium-telluride focal-plane arrays via liquid phase epitaxy are under development. Research areas include eddy current analysis, resistance temperature devices for precision temperature control, fiberoptic retractable probe for pressure, and energy dispersive spectroscopy for composition (Castro et al., 1992). Materials quality has improved over the last decade, and continued incremental improvements may eventually yield temporally stable, uniform detector arrays for LWIR applications. However, at the present time, major materials and processing challenges remain.

LWIR Detectors Based on Multiple-Quantum-Well Superlattice Structures

Another strategy for obtaining a material with the desired band gap for LWIR detection is to artificially create one. Semiconductor heterostructure devices can be constructed with quantum-well potentials engineered to have cutoff wavelengths in the 10-μm range. Such devices are composed of materials whose absorption spectra are tunable, because the energy levels of the bound states depend on both the depth and the width of the well. They rely on photon-induced transitions of electrons from the ground state of a quantum well to the conduction-band continuum or to a level very close to the continuum. Electrons excited in this manner are then collected using an applied voltage to yield a photo-conductive detector. Figure 5-3 is a schematic diagram of a square potential well.

Quantum-well heterostructures are constructed using alternating multiple epitaxial layers of materials with different bandgaps (Levine, 1993). The Fermi level of the structure is continuous, so that the conduction and valence bands of the different materials have a relative offset. These structures can be created so that the carriers that are doped into them effectively "see" a square potential well. Gallium arsenide (GaAs) and aluminum-gallium-arsenide ($Al_xGa_{1-x}As$) are well suited for making heterostructures, since they have different band gaps and are lattice-matched over the entire aluminum concentration range. Aluminum-gallium-arsenide is used for the barriers, gallium-arsinide for the quantum wells.

For the infrared detectors of interest here, thick barriers (about 50 nm) of aluminum-gallium-arsenide separate thin gallium-arsinide layers (about 5 nm). To a very good approximation, the energetics of the carriers are well described by considering a single square potential well whose width, *l*, is the thickness of the gallium-arsinide layer and whose depth is determined by *x*, the fractional amount of aluminum in the aluminum-gallium-arsenide layers. The energy of the bound states in the wells can be adjusted by changing the amount of aluminum in the barrier (increasing the barrier height) or by changing the width of the gallium-arsinide regions (changing the barrier width).

The design of the quantum-well structure, the doping of the gallium-arsinide layers (needed so that there are carriers available to absorb the radiation), and coupling between the incident radiation and the carriers in the heterostructure must be considered in the design of infrared detectors. First, the height and width of the wells must be designed so that the energy separation between the bound state in the well and the continuum current-carrying states is the desired value. Of the several ways of designing the quantum wells, the combination of well width and depth is adjusted to optimize the detector characteristics. The carrier concentration must be large enough to provide substantial optical absorption but not so high that the carrier Fermi energy becomes too large; in practice the detectivity of the devices is optimized for silicon doping in the gallium-arsinide of about 2×10^{18} cm^{-3}. The performance is not highly sensitive to the carrier concentration.

The separation between quantum wells must be large enough that the tunneling between them is negligible and background noise (i.e., dark current) minimized to avoid degrading specific detectivity, *D**. For separations greater than 50 nm, the dominant noise process involves either carriers tunneling or being thermally activated into the conduction band. Since the quantum wells are separated by large distances, it is crucial that the absorption cross-section of the carriers in each well is large. Heterostructures with approximately 50 quantum wells that are separated by aluminum-gallium-arsenide barriers with width of about 50 nm are currently used.

Optimizing the coupling efficiency of the devices

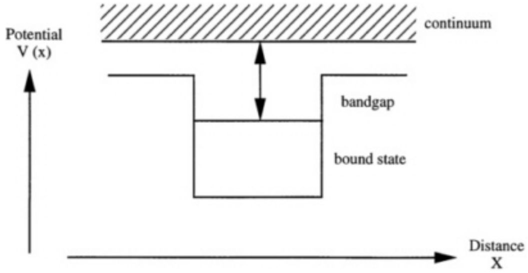

FIGURE 5-3 Square well potential.

is important, because the matrix element for optical absorption of radiation propagating normal to the plane of the layers of the heterostructure is zero. Either the geometry or the polarization of the light must be altered for the radiation to excite carriers. A properly designed metal grating (which can be realized using standard lithographic techniques) has been shown to yield over 90 percent quantum efficiency even for unpolarized light (Andersson and Lundqvist, 1991).

Another key issue for high detector performance is that the carrier recombination rate should be as small as possible. In the gallium-arsenide superlattices, the effective carrier lifetime is given by $t/2v$, where t is the device thickness and v is the limiting carrier velocity, which for these heterostructures is about 10^7 cm/s. The observed values of v are somewhat lower than would be predicted assuming energy loss caused only by electronphonon interactions (Kinch and Yariv, 1989). At this juncture it is not clear whether this discrepancy arises because of electron-electron interactions or because of recombination in the gallium-arsinide regions. Minimizing the recombination is non-trivial: on one hand, reducing the width of the quantum wells causes the carriers to spend less time in the gallium-arsinide regions, thus reducing the recombination probability; on the other hand, for small widths, the imperfect nature of the interface at the well edges causes scattering which increases the recombination probability.

To date, quantum-well detectors have achieved a specific detectivity, D^*, of greater than 10^{10} at 77 K for 10-μm radiation. This value is a factor of about three lower than the maximum obtainable background-limited value (assuming a 300 K background and a hemispheric field of view). Further substantial improvements in detectivity require increasing the carrier lifetime, which is beyond current understanding.

The quantum-well infrared detectors discussed here all generate a photocurrent when exposed to radiation (i.e., they are photo-conductive) and thus require an externally supplied bias voltage. In principle, a photovoltaic detector is preferable to a photo-conductive detector; the maximum theoretically attainable D^* for a photovoltaic detector is larger by a factor of `2, a bias voltage is not needed, and a photovoltaic detector usually dissipates less energy.[10] Recently, a quantum-well structure with a blocking layer was shown to exhibit photovoltaic response but with a quantum efficiency of less than 1 percent (Wu et al., 1992). In this case, the photovoltaic response arose only from a few quantum wells near the blocking layer, so it is uncertain if this type of detector can be improved to the point where the performance is comparable to the photoconducting quantum-well detectors or to mercury-cadmium-telluride.

In summary, present individual gallium-arsinide/aluminum-gallium-arsenide heterostructure detectors operating at 77 K have a specific detectivity, D^*, for a hemispheric field of view which is about a factor of 3 lower than the background-limited value. However, because of superior uniformity, arrays of these structures already exhibit performance exceeding that of mercury-cadmium-telluride detector arrays for selected applications.

LWIR Detectors Based on Strained-Layer Superlattice Structures

Desired band gaps for LWIR detection can be artificially created in semiconductor heterostructures by employing lattice strain to cause major changes in electronic and optical properties of the material. Significant materials and processing issues are involved in the growth and processing of strained-layer superlattice (SLS). A typical structure designed to have no net strain consists of three principal regions:

- a crystalline substrate of bulk crystal;
- a buffer layer made up of an alloy with a graded composition, so that the lattice constant varies from that of the substrate to that of the SLS to be grown; and
- the SLS.

The buffer layer is engineered to provide a transition from the substrate crystalline lattice constant to the average lattice constant of the SLS and must be sufficiently thick so that the equilibrium lattice constant at the final composition constant is determined by the accumulation of misfit dislocations. In the strain-relief buffer, the lattice constant is graded by gradually changing the composition of ternary materials grown over a thickness of a few micrometers.

The SLS grown on the buffer layer consists of many alternating thin (≤30 nm) single crystal layers with lattice constants that are alternately larger and smaller than the average constant. Thus, each layer of the SLS is elastically strained. The alternating strains deflect dislocations that originated in the graded layer to the edge of the wafer. The dislocations tend to be confined to the first few layers of the SLS to produce high-quality, dislocation-free material in the upper layers. This structure is shown schematically in Figure 5-4 in which the average lattice constant is greater than that of the substrate. The grid width represents a unit cell dimension (not to scale in Figure 5-4.) The lattice spacing changes in the plane of the epitaxial strained-layer structure are accompanied by a change in the lattice spacing perpendicular to the layer to maintain a constant unit cell volume. Thus, crystals with cubic equilibrium structures undergo a tetragonal distortion. This tetragonal distortion can be used to engineer major changes in the electronic and optical properties of the layers (Osbourn, 1986).

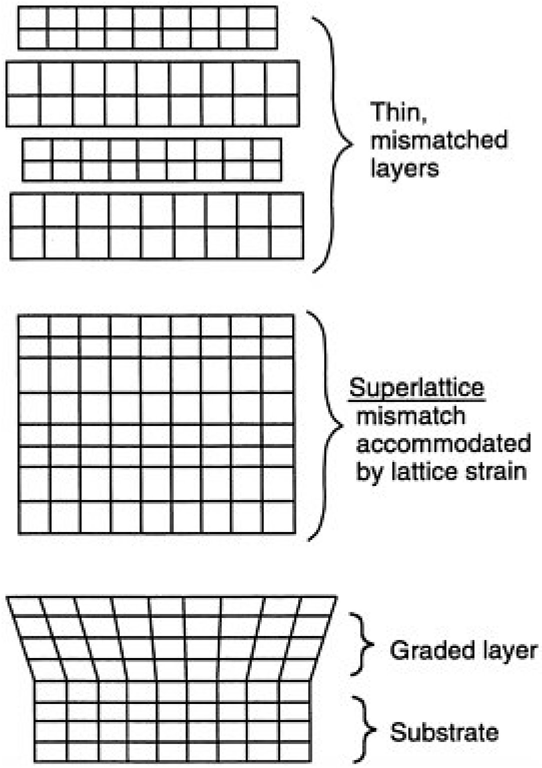

FIGURE 5-4 Nanoscale cross-section of strained layer superlattice material.

SLSs grown in the indium-arsenide-antimonide [In(As,Sb)] materials system currently offer the best route for developing SLS LWIR detectors. Historically, indium-arsenide-antimonide was the first III-V compound semiconductor materials system in which photovoltaic detectors were demonstrated at wavelengths beyond those possible in bulk III-V alloys, and thus significant effort had been directed toward the development of detectors and arrays of photodiodes for infrared imaging systems in the indium-arsenide-antimonide materials system. Indium-antimonide (InSb) infrared detector technologies, based upon p-n junction photodiodes or metal-insulator-semiconductor detector structures grown on indium-antimonide substrates, are widely used for medium-wavelength infrared applications. Indium-antimonide detectors typically operate at 77 K and have maximum detectivity at a wavelength near 5-µm. Indium-antimonide detector arrays are usually hybridized with silicon readout electronics to construct high-resolution imaging systems. Indium-arsenide detectors have also been developed and are commercially available. Because the spectral range of indium-antimonide detectors is not well matched to any infrared transparent atmospheric windows, these detectors have received little attention.

Devices based on ternary alloys of In(As,Sb) offer longer-wavelength performance than either indium-antimonide or indium-arsenide; however, development of bulk devices based on In(As,Sb) alloys is limited by the absence of any binary III-V crystal with the appropriate lattice constant. Growth of bulk alloys on a substrate with a significantly different lattice constant leads to high dislocation densities and microcracks which severely limit the device performance. Even if high-performance devices could be developed in these bulk alloys, the cutoff wavelength would be limited to less than 9-µm at 77 K. The minimum band gap corresponding to this 9-µm limit occurs near the $InAs_{0.4}Sb_{0.6}$ alloy composition.

Osbourn recognized that SLS of indium-antimonide/InAsSb could permit infrared detector development for operation in the spectral region of interest for atmospheric applications of about 10 µm (Osbourn, 1984). Furthermore, high-quality SLS structures can be artificially grown by using a strain-relief buffer between the InSb substrate and the active layers of the device to accommodate the lattice mismatch.

An important feature of antimony-rich InSb/InAsSb SLS is that it exhibits Type II band alignment in which the electron and hole potential wells are located in different layers on the SLS. For this type of band alignment, the lowest-energy, longest-wavelength transition occurs for an electron excited to the conduction band of an InAsSb layer, leaving a hole in the valence band of an InSb layer. The transition is direct in momentum-space but indirect in real space. Because the very low electron effective mass in InSb allows penetration of the wave function into the barrier layer, the transition has a large absorption cross-section. Furthermore, electrons and holes excited in this manner physically separate into different layers of the crystals, which results in anomalously long lifetimes for the charge carriers. The unique solid-state physics features of this SLS materials system make high-efficiency detectors possible.

Type II behavior is infrequently observed in III-V materials, but it has important implications for LWIR detectors. Specifically, the band gap between the InAsSb and InSb layers decreases with increasing arsenic content in the InAsSb layer of the SLS. The band gap of InSb/InAsSb SLS structures goes to zero at an arsenic content of about 25 percent; because the energy levels are affected by strain and quantum size effects, the exact composition at which the band gap vanishes depends on the details of the structure.

As a point of interest, the ability to tailor the band gap throughout the LWIR spectral region permits the fabrication of detectors with very long wavelength response. To date, detectors that exhibit response out to 18 µm have been demonstrated. However, major materials and processing development will be required before arrays are available with spectral response at this wavelength. Materials with spectral response at this wavelength are pushing the limit of stability and are difficult to grow on InSb substrates, where the entire structure is in tension if the buffer layer is not completely relaxed.

Although the InSb/InAsSb materials system has not yet been extensively developed, it offers important advantages in infrared detector performance compared with mercury-cadmium-telluride. In addition to the III-V compound semiconductors being much more robust materials than the II-VI compound semiconductors, they offer a major advantage over bulk alloys in that the band gap is controlled by different properties in the two systems. For mercury-cadmium-telluride, the band gap is determined by the bulk alloy composition. The effective masses, m^*, of the electrons and holes are intimately connected to the band gap, and m^* approaches zero as the band gap approaches zero. The small effective mass results in large tunneling currents in photovoltaic detectors. These tunneling currents result in noise in the detector, which severely limits detector performance. Since tunneling is temperature independent, the performance is degraded at all temperatures. In a Type II SLS, however, the band gap is determined by the band offset by the two layers. Thus, the band gap can be driven to very low values without concomitant decreases in the effective mass of the charge carrier. Decoupling the band gap and the effective mass eliminates the limiting feature of bulk alloy systems for very long wavelength operation.

High-quality InSb/InAsSb SLSs have been grown both by molecular beam epitaxy and metal-organic chemical vapor deposition (Dawson, 1989; Biefeld, 1986). Both photovoltaic and photoconductive detectors have been fabricated using such materials. As noted in the discussion of quantum-well detectors based on gallium-arsinide/AlGaAs, photovoltaic detectors are preferable in principle to photoconductive detectors because they offer higher detectivity and do not require a bias voltage. To date, however, because of $1/f$ noise, the detectivities of SLS photovoltaic detectors operated at video frequencies are lower than those composed either of mercury-cadmium-telluride or of gallium-arsinide/AlGaAs quantum wells.

The SLS detectors made to date display substantial zero-illumination current which can be reduced by surface passivation. However, the passivated devices display large $1/f$ noise, which limits the frequency region where high detectivity is obtained to frequencies greater than 100 kHz (Kurtz et al., 1990). Video imaging typically samples at frequencies on the order of 100 Hz, so that substantial reduction of the $1/f$ noise is needed before these detectors are an attractive option for these applications. The origin of the $1/f$ noise is unknown; it may be related to the surface passivation, or it could reflect the presence of threading dislocations in the SLS.

Photovoltaic detectors operating at 10 µm that have been made from InSb/InAsSb SLS structures have demonstrated a D^* of 4×10^{10} operating at 100 kHz at 77 K (Kurtz et al., 1990). Detectors have also been demonstrated in the InSb/InAsSb SLS system that operate at longer wavelengths. At these longer wavelengths, the theoretical detectivity of InSb/InAsSb SLS infrared detectors exceeds that of MCT detectors that have the same long-wavelength limit.

MATERIALS DEVELOPMENT OPPORTUNITIES FOR LWIR PHOTODETECTORS

In evaluating LWIR sensor materials, many factors arise in addition to the value of the band gap. Some of these factors include those based on solid-state physics principles. In these cases, theoretical calculations can be made regarding a material's expected best performance and theoretical limitations. The performance of a sensor cannot surpass that determined through an understanding of the fundamental physics. For example, fundamental limitations include carrier interaction, absorption cross-section, and electron-phonon couplings, as well as material stability.

In practice, maximum theoretical performance is rarely attained for large LWIR arrays due to the realities imposed by the materials synthesis and processing operations. In many cases, final performance is limited by materials issues. These issues form the basis for materials research opportunities. Materials processing plays a critical role in all of these strategies. For example, detector performance is extremely sensitive to defects and inhomogeneities that are not "fundamental" but can be pervasive unless the materials growth and processing is extremely well controlled. Improvements in LWIR sensor materials will thus depend to some extent on the development of LWIR and other sensor technologies that can be used for intelligent process control (e.g., as discussed in Chapter 3). This is particularly true for those processes that involve artificially structured materials where manufacture requires atomic scale control of the growth process.

Cost is not a fundamental physical limit, but it does impose significant practical constraints in most cases. To control the acquisition cost of LWIR sensors, a key consideration is the selection of materials systems that are inherently robust and producible. In terms of operating costs, materials that do not require significant post-processing of their outputs to provide a uniform response are preferable, as are sensors that do not readily degrade in performance over time.

Examples of specific materials R&D needs for the three LWIR photodetector materials systems discussed in this chapter are summarized below. It should be noted that LWIR bolometers can present attractive alternatives to photodetectors for certain applications, and the committee encourages continued development of those systems.

MCT

The quality of LWIR MCT has improved over the last decade, and continued incremental improvements may eventually yield temporally stable, uniform detector arrays for LWIR applications. However, materials instabilities result in major materials and growth challenges.

Very sophisticated materials-processing techniques are being employed to produce low-defect LWIR material. These processes can only be effective if there are available sensors for in situ process control. Sensors that detect melt temperature and pressure of the constituent elements (especially mercury) during liquid-phase epitaxy processing are under development. Sensors developed for in situ process control can be applied to molecular beam epitaxy organometallic vapor-phase epitaxy, and metal-organic chemical vapor deposition processing.

Growth of MCT is made more difficult by a paucity of suitable lattice-matched substrates. The most commonly used substrate is cadmium-telluride, which is expensive and difficult to produce in the large sizes needed for arrays. Development of a low-cost, producible alternative material to cadmium-telluride for substrate use represents a high-risk, high-payoff research opportunity. Another high-payoff, but high-risk, approach is the development of materials processing techniques for growth on nonlattice-matched substrates.

Multiple-Quantum-Well Materials

The background-limited performance of LWIR sensors based on multiple quantum well technology is inferior to that of mercury-cadmium-telluride. Currently, individual gallium-arsinide-AlGaAs heterostructure detectors have a specific detectivity of about one-third that of the fundamental limit. Because of superior response uniformity, arrays of these structures already exhibit performance exceeding that of MCT detector arrays for selected applications despite the higher theoretical detectivity of mercury-cadmium-telluride. These materials are producible using process controls developed for gallium-arsinide.

Further improvements in detectivity of quantum-well detectors involve improving the efficiency of the optical coupling of the incident radiation to the detector material and increasing the carrier lifetime. Several promising approaches are under way to improve the optical coupling efficiency, but the definitive solution has not yet been found. At this time, it is not clear how to increase carrier lifetime, and thus this is an area requiring basic research.

SLS Materials

From consideration of the fundamental physics, this materials system offers many attractive advantages for LWIR applications. SLS is the least mature of the three technologies. Thus, substantial improvements in realized performance should be possible if adequate effort is devoted to the technology, since there appears to be no fundamental limitations. Major materials and processing issues remain to be resolved for the manufacture of low-cost, high-performance detector arrays in this materials system. For example, the development of surface passivation is extremely important to device performance.

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NOTES

1. The visible portion of the electromagnetic spectrum extends from violet (wavelength of about 0.38 µm) to red (about 0.78 µm).

2. The near-wavelength infrared region comprises wavelengths of 3–5 µm, the medium-wavelength infrared region wavelengths of 5–7 µm, and the long-wavelength infrared region, 8–14 µm.

3. It is doubtful if this sensor technology will be widely used in civil applications, regardless of its performance, unless it is relatively inexpensive. Generally speaking, it is easier and less expensive to produce sensors with shorter cutoff wavelengths and lower sensitivity.

4. In this context "low-cost" means less than $1,000, as opposed to the usual $50,000.

5. NASA's Jet Propulsion Laboratory has recently reported the development of a bolometer that uses electron-tunneling to achieve microsecond response times.

6. The band gap is the minimum energy needed to excite a carrier from the valence band to the conduction band.

7. Comparisons between different detector technologies must therefore be made at a given operating temperature.

8. Definitive statements about nonuniformity are difficult to make, because nonuniformity can be corrected to some extent by computerized signal processing.

9. While the temperature of the material can be controlled during detector use, process temperatures are more difficult to control.

10. However, this latter consideration does not appear to be important for the photo-conductive detectors discussed here.

6

CHEMICAL SENSORS

The ideal chemical sensor is an inexpensive, portable, foolproof device that responds with perfect and instantaneous selectivity to a particular target chemical substance (analyte) present in any desired medium in order to produce a measurable signal output at any required analyte concentration. Such ideal chemical sensors, however, are far from reality in spite of enormous advances over the past decades. Chemical sensors in actuality are complex devices, generally optimized for a particular application. Appendix F summarizes some of the chemical sensor formats of current interest.

The committee defined chemical sensors as devices or instruments that determine the detectable presence, concentration, or quantity of a given analyte. The complexity of a chemical sensor application is related to the technical difficulties associated with these determinations and with the specific nature (i.e., elemental or molecular) of the chemical substance to be analyzed. Given the huge number ($>10^6$) of known molecular substances, molecular sensing typically relies on recognition of molecular structure or associated reactivity; this recognition aspect is called selectivity. Sensitivity and limit of detection relate to the quantity or concentration of the element or molecule to be analyzed (the analyte). The quantity of analyte present in a sample can have a dynamic range of greater than 10^{23}, and chemical sensors are commonly required to detect 10^{-9} molar concentrations or less. Thus, the challenge of attaining the needed sensitivity in chemical sensing is comparable to that of achieving the needed selectivity.

The sensitivity and selectivity aspects of chemical sensing are affected by the phase, dimensional, and temporal aspects of the desired determination. The analyte can be present in a gas, liquid, or solid phase on various dimensional scales ranging from bulk volumes of liters to picoliters, or surface layers from nanoscopic to monomolecular scale. It may also be persistent or transitory. A further set of requirements can originate from a need for repetitive measurements of the analyte over long times (e.g., days, months) or at multiple and perhaps remote locations, such as in environmental analysis and personal monitoring.[1] The design of chemical sensors also requires appreciation of the needed degree of quantitative reliability (precision or accuracy). Finally, economic resources and constraints can affect the design and strategy of any sensing task in many different ways.

The capability of chemical sensing technology is substantial and has grown steadily over the past several decades, but it has been outpaced by the needs and diversity of chemical measurements. Materials limitations are prominent among the existing limitations of chemical sensors. The following discussion outlines the various chemical sensor types and strategies for further development, with emphasis on those areas in which materials needs are especially evident.

It is not practical within the context of the present report to address the entire known range of chemical sensing principles, methods, and applications; the general bibliography on chemical sensing (Appendix A) contains a more complete exposition. This chapter develops a taxonomy for this broad sensor class, describes some promising application areas (e.g., the detection of toxic chemicals in the environment) and highlights the key materials challenges. The discussion of chemical sensor types is divided into two sections:

- direct-reading, selective sensors (e.g., electrochemical sensors, optical fibers); and
- sensors that use a preliminary chromatographic or electrophoretic sample separation step followed by sensitive, but not necessarily selective, detection.

TRADE-OFFS IN CHEMICAL SENSOR DESIGN

The characteristics of a sensor developed for a given application are strongly shaped by the requirements of the application and by existing sensor science and technology. Using the descriptors developed in Chapter 2, limiting features of many existing chemical sensors include:

- selectivity;
- sensitivity;
- limit of detection;
- response time[2]; and
- packaging size.[3]

A direct-reading chemical sensor functions by detecting and rapidly responding to the presence or concentration of an analyte at some interface between the sensor and the sample matrix containing the analyte. This idealized form of chemical sensor is the most demanding, since the sensor must be selective toward the desired analyte; that is, it must be unresponsive to other, perhaps quite similar, chemical substances (interferants) that may be present in the sample matrix. Considerable potential exists to enhance the selectivity of direct-reading chemical sensors by the use of novel materials. (Requirements and possible future trends are discussed in the following section.)

The large investment involved to achieve high selectivity for large numbers of different analytes with direct-reading chemical sensors is often impractical, and this customarily leads to compromises in the requirements. The trade-offs typically involve constraining the context, or environment, of the sensing application and specifying the normally expected quantity or concentration of the target analyte, as well as that of potentially likely interfering species.

In the absence of adequate selectivity, several different types of compromise are normally encountered:

Sensors with limited selectivity. Such sensors may be acceptable in a controlled environment, such as a manufacturing site, where the nature and range of interferants is known and the normally expected quantities or concentrations of target analyte and interferants can be specified with confidence.

Mathematical deconvolution of multiple responses from arrays of imperfectly selective sensors. An array of sensors can be employed, with each sensor in the array having a different but known (calibrated) level of response to each analyte or interferant in the sample mixture. Then appropriate mathematical approaches (e.g., pattern recognition, a topic of "chemometrics") may permit extraction of the desired analyte response from the fusion of responses from the multiple sensors, (Newman, 1993; Grate et al., 1993; Haswell, 1992; Brown et al., 1992).

Separation of the analytes from the sample matrix, followed by sensing of individual analytes with sensitive but nonselective sensors. In this case, a large number of different analytes in a sample are separated into pure components. A nonselective detector can then be used to detect the pure components. Separation by modern techniques of chromatography and electrophoresis is an extremely powerful and enabling technology for analysis of complex chemical mixtures. (Manz et al., 1993; Harrison et al., 1993a, b). When combined with a suitable detector and electronic support packages, separation-based sensors (i.e., not truly "direct-reading") can nonetheless potentially provide an analysis system with response times approaching those of many direct reading sensors but with greatly enhanced effective selectivity. Miniaturized, total analytical systems are a relatively new area of research in analytical chemistry, but their development could significantly supplement the capabilities of existing direct reading sensors. Numerous materials issues in designing and fabricating miniaturized separations-based analytical systems are considered later.

Conventional analytical chemistry techniques and instruments at a central laboratory site. This traditional mode of chemical analysis remains necessary whenever:[4]

- alternative sensors lack the required technical capabilities;
- correlation of multiple kinds of analytical measurements is required to obtain the needed information; or
- site-centered sensing is economically infeasible compared with the cost of a central laboratory, due to the large number of sites of interest, short sensor lifetimes, or high sensor unit cost.

The above discussion applies to the sensing of samples in the gas or liquid phase. Chemical sensing within solid samples, and of their surfaces, is particularly difficult and, in the former case, not well-developed technology. As a result, the overwhelming majority of solid-state analytical problems are addressed by traditional laboratory approaches. Chemical sensors adaptable to solid-state problems are a frontier topic of substantial importance and challenge.

DIRECT-READING, SELECTIVE CHEMICAL SENSORS

The operation of a direct-reading, selective chemical sensor is based on the existence of a selective recognition event that results in a change in a measurable parameter. Selected transduction parameters and generic device types are summarized schematically in Figure 6-1.

In most cases, the response of the sensor-sample interface to the presence of analyte within the

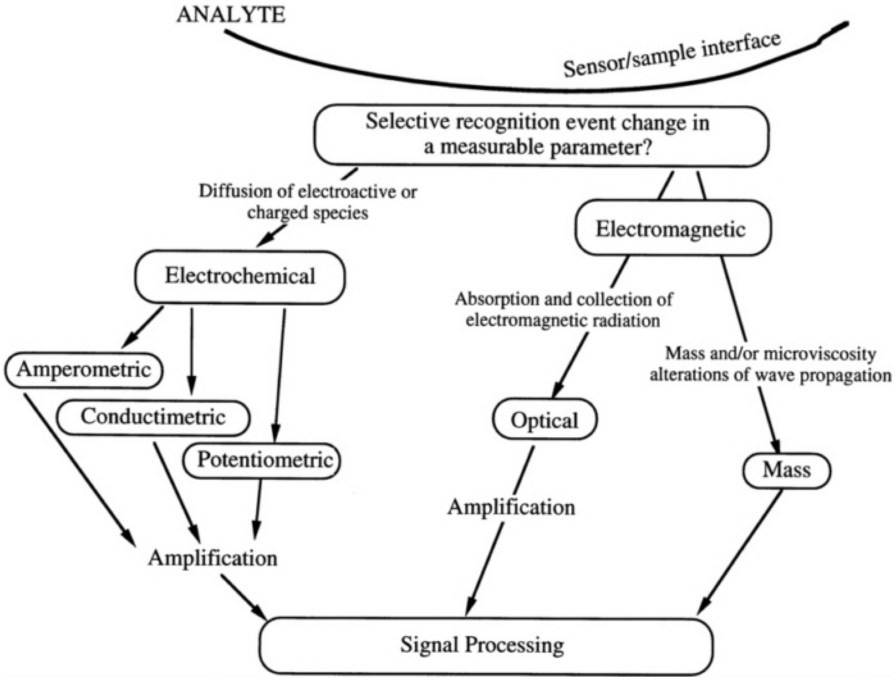

FIGURE 6-1 Direct-reading, selective, chemical sensors.

sample relies on some form of chemical reactivity of the analyte. The design of molecular selectivity for analytes typically involves a delicate choice of the sensing chemistry and associated materials. Chemical reactivity can involve a very wide range of chemical phenomena, including:

- *Recognition of size/shape/dipolar properties of molecular analytes by molecular films, phases, or sites*. These can be bioreceptor sites, structures allowing molecular recognition or host-guest interactions, or ceramic or other materials with templated cavities. The molecular recognition leads to selective, strong binding or absorption of analyte to the sensor material.
- *Selective permeation of analyte in a thin-film sensor*. If the binding or permeation of analyte is reversible, the sensor film can be re-used (i.e., recycled) in repeated measurements. Irreversible binding of analyte to the sensor, or side reactions with interferants, can stoichiometrically consume the sensor material, shortening its useful lifetime.
- *Catalytic reaction cycle of the sensing materials,* which results in analyte consumption.

The most important materials-related factor leading to enhancements of direct-reading chemical sensors is the choice of materials employed to elicit stable selectivity of interaction with the target analyte. Material needs for this class of sensors are summarized in the last section of this chapter.

SENSORS WITH SAMPLE SEPARATION

Chromatographic or electrophoretic separation in chemical analysis has classically not been considered to be a "chemical sensor." However, the difficult analyte selectivity issue of direct-reading sensors can be avoided by using a chromatographic or capillary electrophoretic format. In this case, a mixture of analytes flowing under pressure, or under an electrical gradient, are separated as a result of localized environmental interactions which can then be detected as they flow sequentially past the detector (sensor).

The enormous power of column chromatographic and capillary electrophoretic separations, together with their potential for miniaturization as analytical systems, demands that these areas be considered in any trade-off with chemical sensors. The key issue is the response time scale of chemical sensors relative to the time scale for the separations-based approach. If the chemical separation is not very difficult, it is often possible to design the chromatographic or electrophoretic experiment such that the moving phase segment can be shortened to produce separation and detector response within a few minutes or even fractions of a second. This scenario is analogous to using a direct-reading sensor with a relatively slow response time.

There are wide variations in the sensitivity, selectivity to structure, and cost of the numerous different kinds of detectors employed in column chromatographic and capillary electrophoretic experiments. An important consideration for sensor systems with sample separation is amenability of the detector system (detector, supporting appurtenances, control and measurement electronics) to miniaturization. Detector systems for which miniaturization appears most readily achievable or likely to yield the greatest benefits include:

- thermal conductivity;
- electrode, amperometric;
- fluorescence (laser induced);
- surface acoustic wave (SAW) device;
- mass spectrometry; and
- ionic conductivity.

These detectors are relatively low cost, except for mass spectrometry. However, mass spectrometry is the most powerful of the sensitive and structurally selective detectors, and in combination with a preceding chromatographic or electrophoretic separation step, it is probably the most generally applicable chemical analysis system currently available.

Recalling the definition of an ideal chemical sensor, the requirements of portability, ease of fabrication, and low cost would seem to be incompatible with a sensor requiring a preceding separation step or a complex detector like a mass spectrometer. However, inadequately explored research avenues offer the potential for chromatographic and electrophoretic instruments that are simple, miniature, and portable. This general problem is discussed in the following section.

SENSOR MINIATURIZATION, SIMPLIFICATION, AND PLATFORMS

The foundation for chemical sensing often originates with analytical studies using bulky, complex instruments. Transforming the results of these studies into a useful chemical sensor generally requires some miniaturization of the sensor and supporting instrumentation. Miniaturization frequently involves simplification and some degradation of sensor performance. Examination of low cost, miniaturized platforms on which sensor devices can be fabricated is stimulated by the potential economic advantages that could result from more timely forms of monitoring. Recognition of the potential importance of low-cost, miniaturized sensor platforms has been gradually growing. Both separations-based (chromatographic, capillary zone electrophoretic) and direct-reading (fiberoptic, surface acoustic wave device, amperometric) sensors have been demonstrated in on-chip formats (Terry et al., 1979; Manz et al., 1990, 1991; Harrison, 1993a, b; Murray et al., 1989; Monnig and Jorgenson, 1991; Seitz, 1984; Wolfbeis, 1985; Angell, 1987; White, 1987; Wohltjen, 1984; Grate et al., 1993; Frye and Martin, 1991; Ballantine and Wohltjen, 1989; Morita et al., 1988; Aoki et al., 1988; Chidsey et al., 1986; Tonucci et al., 1992; Seiler et al., 1993) Substantial research investments remain to be made before the significant promise of these approaches can be realized for chemical sensors. Given the advantages of existing lithographic technologies and potential-associated economies of scale, much of the existing work has employed either silicon or silica (SiO_2) as platform materials for the sensor system. Polymeric platforms may offer some economic advantages for chemical sensors, but the research base in this area is more limited.

A number of separation and sensor systems have been built on potentially mass-producible platforms:

- gas liquid chromatography and high-performance liquid chromatography separation systems;
- capillary-zone electrophoresis separation systems;
- fiberoptic sensor systems;
- piezoelectric effect-based mass sensors, such as SAW devices; and
- electrochemical, amperometric sensors.

Some of these systems have received little or no attention with respect to microfabrication, despite the potentially substantial dividends that would result from miniaturization. A number of general fabrication/miniaturization issues have been identified by the committee; information and relevant references are summarized in Table 6-1.

Mass spectrometry is perhaps the most prominent of the tools that could potentially revolutionize separation-based, miniaturized chemical sensor systems. Improvements in inexpensive mass analyzers with a truly portable format have the potential to revolutionize approaches to chemical sensing based on combinations with high-speed gas or liquid chromatography or with capillary electrophoresis. Miniaturization would almost certainly degrade the mass analyzer resolution, but even a low-resolution capacity would find many applications and would offer benefits in multiplexing. Key issues include:

- miniaturization of vacuum systems for the mass analyzer and of supporting electronics for detector read-out, mass scanning, and data reading; and
- fabrication of an on-wafer mass analyzer, such as a quadrupole or ion trap device, that uses lithographic or micromachining technology.

SENSORS FOR TOXIC CHEMICALS

Applications of sensors to detect chemical toxins fall into a variety of contexts. Toxicity commonly refers to potential consequences of exposure on human health and safety. Toxins are generally taken as being fabricated chemicals, and this assumption is reflected in regulations governing toxin monitoring. However, there is a growing awareness, felt keenly in risk-assessment issues, of the potential importance of "natural" toxins (Ames et al., 1990). Toxicity can also refer to effects on any biological system (not necessarily human) and to influences on nonbiological systems, such as the ozone layer.

TABLE 6-1 Chemical Sensors: Miniaturization/Fabrication Trends

SENSOR TYPE	REQUIREMENTS/REMARKS
Gas liquid chromatography	Examples known (Terry et al., 1979; Manz et al., 1990) of silicon wafer with lithographically defined sample introduction, column, and detector; 2 times 6 mm liquid chromatography detector channels
High performance liquid chromatography	Micropumps and valves reported (Shoji et al., 1988) Adaptable to injection flow analysis (Ruzicka and Hansen, 1984) Miniaturized liquid chromatography requires micropump and microsample injectors to accommodate small sample sizes Simple on-wafer mass analyzer device possible for molecular mass-sensitive detection?
Capillary zone electrophoresis	Examples known of channels etched in silicon with oxide, nitride coatings (Harrison et al., 1993a); also, 10 mm × 10 mm × 2 cm long channels micromachined into glass wafers (Harrison et al., 1993b) with >40,000 plates and separation times ~ 10 seconds Small sample volume injection possible with crossing channels and independent electric field gradient control (Harrison et al., 1993b) Most work done with silica microcapillaries which are readily used in shortened forms for high speed separations (Monig and Jorgenson, 1991) Multiple channels, combination of CZE with flow injection analysis, and reagent derivatization channels possible (Manz et al., 1991; Manz et al., 1993) Submicron channels may be possible (Tonucci et al., 1992) Requires electrically insulated channel, since samples move under electric field gradient Improve micromachining for reagent derivatization tracks, avoiding cross-channel leakage and improving control of surface chemical interactions with sample; (separation can be enhanced by interactions between sample and stationary phase)
Fiberoptics	Submicron fibers and photopolymerized molecular coatings possible (Tan et al., 1992; Barnard and Walt, 1991) Spatially defined sensor positions
Piezoelectric effect-based mass sensors	Deposition of surface acoustic wave electrode patterns becoming standard Possible exploration of new forms of mechanical excitation of piezoelectric material
Electrochemical amperometric	Examples known of three and four Au and Pt electrode electrochemical cells and interdigitated arrays lithographically defined on silicon, with micron-scale electrodes and electrode-electrode spacings (Morita et al., 1988; Aoki et al., 1988; Chidsey et al., 1986) Many amperometric formats are improved by miniaturization, close electrode spacing (Morita et al., 1988) Fabrication of microelectrodes (micron and nanometer scale electrodes) necessary (Wightman and Wipf, 1989) Need to improve low cost, disposable electrochemical cell-on-chip designs

Monitoring of toxic chemicals for benefits to human health and safety is illustrated by two examples: (1) workplace or occupational environmental monitoring and (2) on-site monitoring of chemical warfare agents, precursors, and degradation products under the Chemical Weapons Convention.[5] These examples serve to illustrate differences in design and selection of chemical sensors and existing materials constraints within the general context of toxic chemical monitoring. Many of these ideas and technologies for improved chemical sensing can be applied to other types of environmental monitoring.

Environmental Monitoring

The following discussion shows that the requirements identified for general chemical sensing (i.e., improved chemical selectivity and miniaturization of separations-based sensor systems) apply equally to environmental monitoring. However, two additional factors significantly influence the development of chemical sensors for environmental monitoring: the requirement for a complex monitoring strategy covering the transport of toxic chemicals from source to human exposure and the influence of regulatory requirements.

The general pathways for transport of toxic materials from their sources to produce human exposure, with potential ensuing absorption, metabolism, and adverse health effects, are summarized in Figure 6-2. This figure provides a framework for design of an environmental sensing strategy and assessment of the hazard level. Specifically, sensing can be aimed at determining the level or activity of toxins in the emission source; in the media into which the toxin is incorporated en route to human exposure (the transport medium); and at the point of human exposure, including possible consequences of exposure. Monitoring of the emission source, the transport medium, and the point of human exposure may be necessary for a comprehensive plan designed both to assess hazard and to exert control on the emission sources in order to achieve hazard reduction. Typical problems in occupational exposure monitoring include:

- dermal exposure monitoring;
- air-purifying respirator end-of-service-life indicators;
- personal monitors for aerosols;
- biological monitoring (blood, urine, breath);
- personal/area monitors for gases and vapors; and
- soil/groundwater monitoring.

For a given toxin analyte, chemical sensors differing in sensitivity, selectivity, or other characteristics may be required to monitor the emission source, the transport medium, and individual exposure. The toxin concentration is typically greater, at the source than after dispersal in a transport medium; and the complexity of, and potential interferences in, the transport matrix (e.g., air, water, soil, skin, biological fluid sample) can vary widely. The physical and chemical properties of the analyte and its immediate environment (airborne vapor, contained in solid or liquid aerosol, chemically or photochemically reactive and decaying into substances of differing toxicity, radioactive, ionic, acidic, lipophilic, etc.) are also influential in the choice and design of a suitable sensor.

Regulatory requirements influence environmental chemical sensing design, particularly at the point of human exposure. Such requirements can specify detection of the approach to some designated exposure limit over a short time span, over a

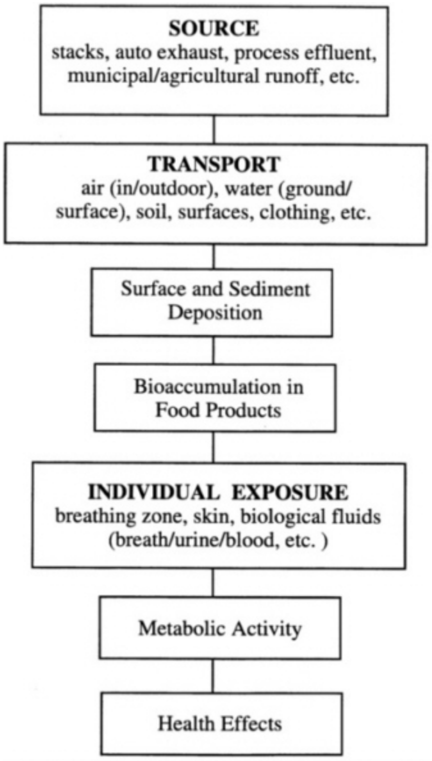

FIGURE 6-2 Schematic pathway for human exposure to toxic materials.

typical work day, or over some longer period. Regulatory requirements are set by governmental agencies having differing jurisdictions and differing approaches to monitoring, including the Environmental Protection Agency, the Food and Drug Administration, the Occupational Safety and Health Administration, and the American Conference of Governmental Industrial Hygienists.

There emerge from the regulatory requirements detailed lists of toxic chemical exposure limits, time scales permitted for such exposure, and often a recommended analytical method or reference method (see, for example, Environmental Protection Agency, National Ambient Air Quality Standards). Overlaid on such requirements is the prioritization imposed by the need to monitor different types of hazards in the face of finite economic resources. In a practical sense, the materials needs of environmental chemical sensors are substantially influenced by the nature of governmental regulation. Success in meeting regulatory needs at low cost will reduce the need to make hard-pressed choices among regulatory priorities. Despite the pressure of regulatory requirements, not all research on environmental chemical sensors is driven by regulation. A significant amount of basic work on environmental sensing is under way in universities and in industrial laboratories.

Thus sensing of environmental chemicals is a substantial, complex challenge that dictates several key requirements that affect sensor technology:

- The difficulties in attaining adequate selectivity of sensor response to the desired toxic analyte apply to environmental monitoring as well as to other types of chemical sensing.
- Environmental sensing requirements further justify the emphasis on miniaturization of chemical sensors, particularly for use in mass-producible formats. Small size and weight, together with low cost, offer a number of advantages, including:
    - — attaching the sensor to the individual (lapel, belt) to provide a more accurate and realtime indication of worker exposure to particularly severe toxins;
    - — redundant sensors to compensate for sensor failure or poisoning;
    - — improved portability; and
    - — lower power requirements, resulting in longer unattended field use and easier access in certain sampling situations.

Chemical Weapons Detection

Implementation of any chemical weapons treaty depends upon the existence of the necessary technology to monitor and verify compliance. A critical issue is the need for on-site inspection of factories and facilities suspected of making chemical warfare agents or precursors (Ember, 1993), and the associated requirement to detect the presence and amount of specified toxic chemicals. In contrast to the case of occupational environmental monitoring discussed above, sensor units for chemical weapons treaty verification will likely be custom units produced in very small numbers (e.g., tens of units). A unit acquisition cost on the order of $10,000 would probably be acceptable. However, the issues of selectivity and sensitivity are similar for chemical weapons detection and workplace monitoring. For example, Schedule II compounds (chemicals with limited dual use) are complex organic molecules without a distinctive characteristic that allows easy and rapid identification. In addition, these compounds can be masked by, or mistaken for, other organic compounds that may be present in higher concentrations (NRC, 1993). Limits of detection on the order of 1 part per billion are required (i.e., high sensitivity) together with high selectivity in order to avoid incorrect sensor response to common, legitimate chemicals, such as pesticides.

An example specification for the detection of Schedule II compounds is presented in Table 6-2 in terms of the descriptors identified in Chapter 2. The committee identified a number of candidate sensor types that could potentially meet the requirements presented in the table:

- gas chromatograph-mass spectroscopy;
- ion mobility spectrometer;
- patch chemical reactions showing color change;
- fiberoptic and related methods;
- electrochemical sensors;
- acoustic-wave chemical sensors; and
- immunochemical assays.

TABLE 6-2 Sensor System Needs for Verification of a Chemical Weapons Treaty (Schedule II Compounds)

DESCRIPTORS	SENSOR SPECIFICATIONS
CHARACTERISTICS	
Response time	Can be > 10 seconds; < 1-minute response and recycle time desirable
Sensitivity	Detection of toxins at nonlethal levels (approximately 1 ppb in gas phase)[a]
Resolution	Approximately 1 ppb in air for selected compounds
Range	From 1 ppb to 1 part per thousand
Linearity	Sensor nonlinearities can be corrected by microprocessor
Limit of detection	1 ppb
Selectivity	High: must not give incorrect response to common and legitimate chemicals (e.g., pesticides)
Accuracy	Detection at 1-ppb level may be sufficient
Repeatability (precision)	Repeatability of measurement must be such that the sensor system does not indicate the presence of target compound when it is there in concentrations lower than 0.1 ppb
CONSTRAINTS	
Packaging	
Size	Hand held, less than 1 cubic foot
Weight	Less than 5 pounds
Hermeticity	Must survive rain; "sports-type cassette player" level of packaging
Isolation	
Thermal	-10 °C to +50 °C
Electromagnetics	Human ambient (power lines, transformers)
Mechanical	Must survive drop test from 10 feet
Chemical	Will be hand held, sampling vapors; must survive normal human environments of humidity, air, environmental chemicals, and poisons
Optical	Not applicable
ECONOMIC	
Acquisition	Unit cost could be fairly high (~$10K), since only a few custom units (about 10) will be made[b]
Development	In the absence of suitable commercial products, up to $10M will be spent over 5 years to develop sensor system
Manufacturability	Not applicable
Life cycle	Total number of units too small for problem
RELIABILITY	
Lifetime	2 years, multiuse on inspection tours, hundreds of cycles
Calibration	Once per month or before each country tour.[c]
ACQUISITION (data)	Discrete, with about 10 seconds between readings; internal data storage, possibly with encryption, with data sent to a microcomputer later
IMPLEMENTATION	
Scale	Array or alternative detector scheme for measurement over a large area
Format	Chemical sensor array or other detector scheme will feed information to microprocessor[d]
Mode	Hand held unit with small pump for sampling vapor
TRANSDUCTION	No specification made
TRANSDUCTION MODE	No specification made
MEASUREMENT SCALE	No specification made

[a] A detailed list of compounds and required sensitivities is not yet available. There may be a requirement that no chemical interpretation need be made by the operator in the field; that is detection of a pattern of chemical responses and data reduction into a pattern recognition program would provide a judgment that chemical weapons are being manufactured in the vicinity or that the treaty is being violated in some other way.

[b] Other treaty scenarios include the possibility that industrial plants will require permanently installed units to avoid potential loss of proprietary information. Only information about detected violations would leave the site.

[c] Expensive recalibration, including factory recalibration, is acceptable, given the small number of units and the political implications of poor sensor performance.

[d] A decision will be made on whether to challenge an inspected facility based on some chemical information score, such as a ten-step indicator, with zero indicating no possibility of chemical weapons production and 10 indicating sublethal concentrations of the chemical agent itself.

A discussion of the use of the communication tool in identifying candidate technologies for chemical weapons detection is presented in Appendix G. The matrix shown in Table 6-3 summarizes the results of comparing specification requirements and attributes of candidate sensing technologies using the descriptors. Anticipated problems in meeting specification requirements with available technologies have been marked "X," and particularly desirable features of the candidate systems have been marked with a "+." Use of the descriptor terminology and approach developed in Chapter 2 is extremely useful in conducting a comparative evaluation of different technologies.

An analysis of the data in Table 6-3 indicates that:

- no single candidate technology can fulfill all the specified requirements for detection of Schedule II compounds;
- existing sensor technologies are inadequate in several areas, most notably selectivity; and
- there may be a very fine distinction between desirable attributes.

The framework tool developed in Chapter 2 can be useful in identifying general areas (sensitivity, selectivity, etc.) for development of sensors to meet specific application needs and in highlighting potentially significant development costs. However, the committee noted that, for a given application, additional descriptors may be needed, such as one that summarizes the status of sensor development. Such a descriptor would permit the identification of technology deficiencies in particular areas, allowing the user to make a better estimation of the likely cost to bring a particular sensor technology up to the required performance level.

TABLE 6-3 Candidate Sensing Technologies for Detection of Chemical Warfare Agents

	CANDIDATE SENSING TECHNOLOGIES						
DESCRIPTOR	GC-MS	Ion Mobility Spectrometer	Patch Test	Fiberoptic	Electrochemical	Acoustic Wave Chemical	Immunochemical Assays
Response time			X				X
Sensitivity	+	X		X		X	+
Resolution			X				+
Range			X				
Linearity							
Detection limit		X				X	
Selectivity	+	+			X	X	+/X
Accuracy	+		X			X	
Repeatability	+						
Constraints							
Packaging	X	X		+			+
Isolation				+			
Economic							
Acquisition	X						X
Development				X		X	X
Lifecycle							
Reliability							
Lifetime			X		X		X
Calibration					X	X	X
Acquisition (data)							
Implementation							
Scale							
Format					+	+	

Key: X (potential) problem in meeting specification; + desirable attribute

MATERIALS DEVELOPMENT OPPORTUNITIES FOR CHEMICAL SENSORS

Most chemical sensor applications have been based on a broad background of measurement principles and chemical reactivity developed through research in analytical and other branches of chemistry. Many fundamental ideas, devices, and materials have been adapted from other sciences and technologies (Murray et al., 1989):

- Inexpensive *optical fibers* from the communications industry have been applied in spectroscopically based direct-reading sensors and near-field microscopy (Betzig et al, 1991).
- *Lithographic patterning technology* widely used in the manufacture of modern microelectronics has been exploited to fabricate miniaturized electro-chemical devices such as interdigitated array electrodes, microelectrodes, and chemically sensitive field-effect transistors and to form patterned electrodes on surface acoustic wave (SAW) devices.[6] (Kepley et al., 1992; Ricco and Martin, 1992; Martin et al., 1990).
- Materials research has resulted in *advanced piezoelectric materials* that are employed as micro-positioners; these materials have enabled new forms of microscopy, like scanning electrochemical, scanning tunnelling, and atomic force microscopy. The availability of these micropositioners is also critical for chemical sensing on an extremely small dimensional scale (Snyder and White, 1992).
- Ultrasensitive light detection using *charge coupled devices,* which were developed for astronomy, is under active consideration for detection of laser-induced fluorescence from extremely small populations of molecules.

Research in the above areas involves applying new technologies to analytical chemistry and chemical sensor research. It is intrinsically multi-disciplinary, with contributions from analytical chemists, materials scientists, electrical engineers, and professionals in other fields. At the initial stages of research, the interest is generally focused on exploring and proving the principles by which a new technology can be applied to measure a chemical substance. Open access to specialized equipment and facilities, such as those required for lithographic patterning, can be crucially important to foster interest and progress as applications to specific practical analytical and chemical sensing measurements start to appear.

As previously mentioned, the most important materials-related opportunities to improve direct-reading chemical sensors involve the choice of materials employed to elicit stable selectivity of interaction with the target analyte. Table 6-4 summarizes materials needs for direct-reading chemical sensors. Nearly all the requirements are presented in terms of material functionality rather than material type (e.g., ceramic, polymer, semiconductor) to avoid inappropriate assumptions based on existing solutions.

Limitations of the existing chemistry or technology can become apparent at any stage during sensor development. Table 6-5 summarizes some key materials challenges for various chemical sensor technologies. The most frequent materials limitation for chemical sensors probably relates to the chemistry required to fashion an adequately selective response to the target analyte. Considerable potential exists to enhance the selectivity of direct-reading chemical sensors by the use of novel materials. One strategy to address this is the development of miniaturized high-speed separations-based sensors. These have the potential for avoiding difficulties in molecular selectivity but present major challenges in improving detector sensitivity.

Miniaturized total analytical systems are a relatively new area of research in analytical chemistry, but their development could greatly supplement the capabilities of existing direct reading sensors. The numerous materials issues in designing and fabricating low-cost, miniaturized separations-based analytical systems include:

- coatings and films with improved properties for enhanced sensor performance (e.g., chemical selectivity, chromatographic efficiency, stability under electric field gradients, electrocatalysis efficiency);
- materials that enhance detector sensitivity and increase performance range (fiber optics);

TABLE 6-4 Materials Needs for Selective Direct-Reading Chemical Sensors

Material Forms	Applications	Functional Requirements	Possible Mechanisms
Membranes	Amperometric, conductimetric, potentiometric electrochemical sensors	Analyte selectivity Stability	Analyte binding or partitioning Permselectivity Catalytic reactivity Sensing electrode arrays
Coatings/Thin Films	Amperometric, conductimetric, potentiometric electrochemical sensors Optical fibers and waveguides Piezoelectric devices Surface acoustic waves	Analyte selectivity Stability	Analyte binding or partitioning Enzyme or antibody properties Sensing electrode, optical fiber, waveguide arrays Permselectivity Electrocatalytic activity Changes in light propagation or luminescence Viscoelastic changes
Bulk Materials	Amperometric and electrochemical sensors	Analyte selectivity Stability	Solid or polymer electrolytes with selective binding sites
Fibers (optical)	Optical fibers and waveguides	Extended operational wavelength range	Improved near- and extended-infrared transparency and reflection

- fiberoptic materials with improved performance in the near-infrared and infrared spectral regions;
- technologies for cost-effective miniaturization of sensor systems;
- on-chip formats for practical applications of miniaturized sensor systems; and
- chemical sensor systems with increased ruggedness, reliability, and control.

Research efforts directed at determining which chemical sensing technologies are practical and should be developed for high-volume home and personal wellness applications are expected to have particularly high payback.

New materials can lead to improvements in the selectivity of direct chemical sensors. The development of fast, miniaturized chromatographic and capillary electrophoresis systems with detectors that are senstitive to chemical structure is important for both general chemical sensing and for the more specific case of environmental monitoring. In the latter case, the requirement to monitor a given analyte over a wide range of concentrations and in a variety of environments places particularly stringent requirements on chemical sensor sensitivity and selectivity. The need to meet and possibly redefine regulatory requirements for monitoring toxins is also an important driver in the development of environmental chemical sensors. Mass-producible sensor formats are particularly important for occupational environmental monitoring in view of the need for low-cost compliance with regulatory requirements.

The detection of chemical weapons is a specific type of environmental sensing. The following materials areas have been identified by the committee as important in developing candidate sensor technologies to meet requirements for chemical weapons detection:

- fiberoptic coatings with improved chemical selectivity, for example, selective analyte absorption (a polysiloxane film has been shown to respond

TABLE 6-5 Materials Challenges for Chemical Sensors with Sample Separation

SENSOR TYPE	MATERIALS NEEDS
Gas liquid chromatography	Stationary phase coatings with improved chromatographic efficiency on silicon channel walls
High performance liquid chromatography	Materials to enhance sensitivity of detectors for gas and solution column eluent Improved design and materials for fusing of microchannel roof
Capillary zone electrophoresis	Improved design and materials for fusing of microchannel roof Materials for better and miniaturized detectors Improved breakdown and insulation characteristics of silica and of oxide and nitride coatings on silica
Fiber optics	Improved fiber materials for near-infrared and infrared regions Materials to enhance detector performance in near-infrared and infrared regions Improved fiber coatings for enhanced selectivity to target sample species Improved solid-state lasers for laser-induced fluorescence detection
Piezoelectric-based mass sensors	Materials for improved coating selectivity Better understanding of mass response of alternative mechanical excitations in contact with liquid and viscous media
Electrochemical amperometric sensors	Achieve selectivity through molecular coatings, film coatings on electrodes, or chemically modified electrodes (Murray, 1992) Electrode coatings with improved electrocatalytic rate, selectivity, and stability Improved chemical ruggedness of metal electrode patterns

to di-isopropyl-methylphosphonate, but the sensitivity, resolution, and detection limit are inadequate, and selectivity is unsatisfactory, since the material responds to most organic solvents);

- new membranes and electrode coatings to obtain improved chemical selectivity with electro-chemical sensors; and
- chemically selective films that undergo changes in mechanical and electrical properties following analyte sorption (SAW devices).

These materials requirements are very similar to some identified previously as being important in improving the selectivity of other direct-reading chemical sensors. It should be noted that selectivity is specific to a particular compound or class of compounds. Thus, specialized materials are required for detection of Schedule II compounds, and these materials will likely differ from those developed to detect toxic chemicals encountered in environmental health monitoring.

Little potential for dual-use applications (or other secondary applications) is anticipated for coatings developed for the detection of chemical warfare agents. Nonetheless, the general lessons learned in developing chemically selective materials (understanding the role of electrical and chemical forces on surface and interfacial phenomena, molecular characterization of ion-specific membranes and modified surfaces with catalytic or enzymatic properties, etc.) can be broadly applicable and should be of help in designing materials to meet particular functional requirements.

The possibility exists of leveraging generic miniaturization techniques, including materials and processing technologies developed for mass market applications, in order to further develop compact, lightweight hand-held sensor systems for chemical weapons detection. Miniaturization techniques of particular interest include methods relating to supporting electronics and protective packaging.

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NOTES

1. This may require portable sensors that add another aspect of complexity to the problem.

2. Response times are commonly in the millisecond-to-second range for direct-reading sensors. Response times for separation-based systems are longer but can be less than 1 minute.

3. Within a sensor system, the sensor element is frequently smaller than the supporting electronics.

4. It is likely that a large fraction of chemical sensing needs will continue to be met by traditional analysis.

5. International Convention on Prohibition of the Development, production, Stockpiling, and Use of Chemical Weapons, and on Their Destruction.

6. Appendix F describes in more detail several chemical sensor platforms based on this technology.

PART III:

OVERVIEW OPPORTUNITIES, CONCLUSIONS, AND RECOMMENDATIONS

Judging from current uses and development efforts in sensor technologies, the committee expects increased use of advanced sensors in the manufacture and operation of major aerospace and military systems, commercial products, and infrastructure applications.

Traditionally, major sensor research and development efforts have been funded by various application programs that require specific sensor technology. The committee believes that a new era of sensor research and development is emerging in which the significant benefits of advancements in sensor technology will be rapidly adopted by multiple applications rather than focusing on specialized niches.

The committee anticipates that technological advances involving materials for sensing applications will, in some cases, result in more capable and more complex sensor systems. However the complexity will be "hidden" from the end user. For example, highly integrated sensor systems incorporating advanced signal processing and fusion from multiple sensor inputs will involve a high degree of internal complexity, although the user would have a simplified task of applying the sensor since the subsystem details are packaged together within the sensor system.

It is clear that a multidisciplinary approach to sensor technology R&D and to sensor application engineering is critical. Advancing the field of sensor materials, for example, is quite difficult unless specific requirements are known. Many of the sensor system materials needs include portions of the system other than the transducer.

Part III provides the committee's conclusions and recommendations regarding what could be done to accelerate the introduction of new sensor materials into applications. Chapter 7 contains a synopsis of the broad range of materials development opportunities that were presented in the case studies discussed in the four chapters of Part II. The decision process for sensor development involves both a categorization of sensor needs and a maturity/risk assessment of potential technologies. Three broad categories of risk can be identified:

- *low-risk*: incremental extension of an existing sensor's performance envelope (e.g., the development of a cooled, miniature ultrasonic transducer that is needed to measure in situ void content during the consolidation of thermoplastic resins);
- *medium-risk*: redesign of existing sensor system to satisfy new implementation constraints. Chemically selective sensors to monitor gas purity during semiconductor processing, if the nature of the impurities are known, would be a medium risk sensor materials need. Another example is the redesign design of an existing pressure sensor to accommodate the geometrical constraints imposed by a prepreg tape-laying head.
- *high-risk*: a new materials solution to replace an inadequate materials solution or to support an entirely new concept of measurement (e.g., finding a superior optoelectronic modulator material to replace

lithium niobate; also high risk is the development of multiproperty sensors based on photonscattering technology).

Chapter 8 synthesizes the material presented in parts I and II in terms of general conclusions and recommendations.

7

SENSOR MATERIALS R&D OPPORTUNITIES

This chapter synopsizes the sensor materials R&D needs and opportunities that were identified in the examples presented in the four chapters of Part II: Chapter 3, "Selected Sensor Applications in Manufacturing"; Chapter 4, "Selected Sensor Applications for Structural Monitoring and Control"; Chapter 5, "LWIR"; and Chapter 6, "Chemical Sensors."

These opportunities are illustrative of a process of matching technologies to needs to determine application opportunities and of matching needs to technologies to determine gaps in capabilities. They are not prioritized and are only representative of the cases examined by the committee.

SELECTED MANUFACTURING APPLICATIONS

Curing of Thermosetting Resins

Sensors currently used to monitor the curing of thermosetting resins have serious shortcomings. The principal opportunities lie in developing sensor systems that can measure, in real time, several different microstructural parameters of the curing materials without requiring a number of separate sensors. Such multiuse sensors would enable low cost intelligent processing of a range of polymeric composites.

Photon-scattering sensor technology has the potential to satisfy many of these needs cost-effectively. The near-term research opportunity involves extending this technology, using laser-fiber optics, to measure changes in several key parameters during cure such as resin temperature, resin viscosity, degree of cure, and amount of surface stress. The materials challenges result from applying this sensor system in a severe manufacturing environment.

Consolidation of Thermoplastic Resins

Void content sensing is currently the most common measure of laminate quality for thermoplastic structural composite parts. Void content can be measured many different ways, including x-rays, ultrasonic pulses, and local electrical or thermal conductivity gradients. Thermal conductivity, as measured with an infrared scanner, is an attractive option. The presence of voids affects the cooling rate of the newly laid down tape, and thus a thermal image of the part indicates void areas as hot spots. This sensor approach is noncontacting and does not interfere with the process.

A commercially available scanning array thermal imager of sufficient resolution may be suitable. The primary implementation issues arise from considerations of optical access and processing speed. The fiber optics must be able to conduct infrared energy without severe loss. Various geometrical and environmental constraints imposed by the process equipment configuration and operation will be of paramount importance in the sensor design.

To allow control of consolidation processes in real-time, both temperature and pressure must be accurately measured during processing. Temperature could be measured by the infrared scanner mentioned above. Point measurements of pressure must be made at small intervals. A pressure-conductive matrix pad would be geometrically suitable and possess a fast enough response time; but its operating temperature range would have to be enhanced through use of temperature-resistant materials and/or coatings.

Manufacturing Integrated Circuits

Accurate control of rapid thermal processing and plasma deposition and etching requires advanced sensor materials and approaches. For example, the back surface emission technique for measuring and controlling temperature in today's rapid thermal processing equipment can lead to temperature errors as much as 200 ¹C. LWIR sensors could provide superior temperature measurement capability.

Improved sensors to monitor gas and chemical purity/cleanliness are of major interest. Gas analyzers, mass controller calibrators, chemically selective sensors, and particle detectors are all essential to maintaining the required process cleanliness. Environmentally conscious manufacturing requires recycling and reuse of chemicals, not only for waste minimization but also for cost reduction. Chemical generation and reuse will require sensors that can detect impurities at the part-per-billion level for on-line monitors of chemical purity.

Processing of Artificially Structured Semiconductors

A high-priority requirement is the development of noninvasive sensor technologies to sense and control the thickness (down to one atomic layer) of films, especially "superlattice" structures. The use of optical technologies (such as ellipsometry, laser-induced fluorescence, and fiberoptic probes) as an energy transduction medium is rapidly growing in capability and popularity.

A material application critical to all optical technology is the optoelectronic modulator, which serves as the interface between optical and electronic components. The material currently used in optical modulators is lithium niobate, which is extremely costly. A lower cost replacement represents a significant materials development opportunity.

SELECTED STRUCTURAL MONITORING AND CONTROL APPLICATIONS

Sensors constitute an enabling technology for this application area, although specific requirements are still evolving for many specific applications. For the near term, the critical materials issues are oriented at solving particular implementation problems.

Condition Monitoring

Condition monitoring applications generally enjoy an abundance of available sensing options. The challenge is to assess these options against the requirements, so that the most appropriate selections can be made. Incremental improvements to these sensor technologies can involve materials improvements. An example is video spectroscopy used to examine hard-to-inspect structures for signs of corrosion. Flexible, broad-passband optical fibers would be required to allow all the measurements to be made effectively.

Life-Cycle Management

Life-cycle management (LCM) has several challenging sensor needs for in-service monitoring that are affected by sensor materials selection: very long sensor lifetimes with high reliability, and integration of the sensor with the product. LCM will provide a technology pull for incremental materials development efforts that are needed to solve the profusion of problems that arise as sensors are incorporated into structures.

Smart Materials

LCM and smart materials have many similar sensor requirements. Fiberoptic sensors, both intrinsic and extrinsic, are very important, and their potential has yet to be fully exploited. Chemical sensors, possibly used in conjunction with fiber optics, have significant potential. Piezoelectric polymers, ceramics, and composites offer advantage for strain measurements. Smart materials have the added requirement for actuation, and these piezoelectric materials can do "double duty." Active and passive taggants placed in structures offer the promise of low-cost sensing; their potential is only beginning to be explored.

LWIR PHOTODETECTORS

LWIR sensor materials must satisfy a multitude of criteria in addition to their wavelength sensitivity. The performance of a sensor cannot surpass that determined through an understanding of a material's fundamental limitations, which include such factors as carrier interaction, absorption cross-section, and electron-phonon couplings, as well as material stability. In practice, maximum theoretical performance is rarely attained for large LWIR arrays due to the limitations of the materials synthesis and processing operations. For example, detector performance is extremely sensitive to defects and inhomogeneities that are not "fundamental" but which can be ubiquitous unless the materials growth and processing is extremely well controlled. Improvements in LWIR sensor materials thus depend to some extent on the development of LWIR and other sensor technologies that can be used for intelligent process control. This is particularly true for those processes that require atomic scale control during the growth process.

Cost is not a fundamental physical limit, but it does impose significant practical constraints. A key consideration is the selection of materials systems that are inherently robust and producible. In terms of operating costs, materials that provide sensors with a uniform response are preferable, as are sensors whose performance does not degrade over time.

Examples of specific materials R&D needs for the three LWIR photodetector materials systems (mercury-cadmium-telluride, multiple-quantum-well, and strained-layer-superlattice) are summarized below. In addition, LWIR bolometers offer attractive alternatives to photodetectors for certain applications, and the committee encourages continued development of those systems.

MCT

The quality of LWIR (MCT) has improved over the last decade, and continued incremental improvements may eventually yield temporally stable, uniform detector arrays. However, materials instabilities result in major materials and growth challenges. Very sophisticated materials-processing techniques are being employed to produce low-defect LWIR material. These processes can only be effective if there are sensors for in situ process control. Sensors that detect melt temperature and pressure of the constituent elements (especially mercury) during liquid-phase epitaxy processing are under development. Sensors developed for in situ process control can be applied to molecular beam epitaxy organometallic vapor-phase epitaxy and to metal-organic chemical vapor deposition processing.

Growth of MCT is made more difficult by a paucity of suitable lattice-matched substrates. The most commonly used substrate is CdTe, which is expensive and difficult to produce in large sizes needed for arrays. Development of a low-cost, producible alternative material represents a high-risk, high-payoff research opportunity. Another high-payoff, high-risk opportunity is the development of processing techniques for growth on nonlattice-matched substrates.

Multiple-Quantum-Well Materials

The background-limited performance of LWIR sensors based on multiple-quantum-well technology is lower than MCT. Arrays of GaAs/AlGaAs heterostructures exceed the performance MCT arrays for selected applications due to their superior response uniformity. Further improvements in detectivity of quantum-well detectors will require higher efficiency in the optical coupling of the incident radiation to the detector material and an increase in the carrier lifetime. Several promising approaches are under way to improve the optical coupling efficiency, but the definitive solution has not yet been found. At this time, it is not clear how to increase carrier lifetime, and thus this is an area requiring additional basic research.

SLS Materials

From consideration of the fundamentals, this materials system offers many attractive advantages for LWIR applications. It is the least mature of the three technologies. Thus, substantial improvements in realized performance appear to be possible if adequate effort is devoted to the technology, since there appear to be no fundamental limitations. Major materials and processing issues remain to be resolved for the manufacture of low-cost, high-performance detector arrays in this materials system. For example, the development of surface passivation is extremely important to device performance.

CHEMICAL SENSORS

Most chemical sensor applications have been based on a broad base of measurement principles and chemical reactivity developed through research in different branches of chemistry. Chemical sensor research has also adapted many fundamental ideas, devices, and materials from other sciences and technologies, such as: inexpensive optical fibers from the communications industry, lithographic patterning technology widely used in the manufacture of modern microelectronics, advanced piezoelectric materials, and ultrasensitive light detection using charge coupled devices.

Selective Direct-Reading Chemical Sensors

The most important materials-related opportunities to improve direct-reading chemical sensors involve the choice of materials employed to elicit stable selectivity of interaction with the target analyte. Table 6-4 summarizes materials needs for direct-reading chemical sensors.

Chemical Sensors with Sample Separation

Limitations of the existing chemistry or technology can become apparent at any stage during sensor development. Table 6-5 summarizes some key materials challenges for various chemical sensor technologies employing sample separation. The most frequent materials limitation for chemical sensors probably relates to the chemistry required to fashion an adequately selective response to the target analyte. One strategy to address this is the development of miniaturized high-speed separations-based sensors. These have the potential for avoiding difficulties in molecular selectivity but present major challenges in improving detector sensitivity.

Miniaturized, total analytical systems are a relatively new area of research in analytical chemistry, but their development could greatly supplement the capabilities of existing direct reading sensors. The numerous materials issues in designing and fabricating low-cost, miniaturized separations-based analytical systems include:

- coatings and films with improved properties for enhanced sensor performance;
- materials that enhance detector sensitivity and increase performance range;
- fiberoptic materials with improved performance in the near-infrared and infrared spectral regions;
- technologies for cost-effective miniaturization of sensor systems;
- on-chip formats for practical applications of miniaturized sensor systems; and
- chemical sensor systems with increased ruggedness, reliability, and control.

Environmental Monitoring

New materials can lead to improvements in the selectivity of direct chemical sensors. The development of fast, miniaturized chromatographic and capillary electrophoresis systems with detectors that are sensitive to chemical structure is important for environmental monitoring. The requirement to monitor a given analyte over a wide range of concentrations and in a variety of environments places particularly stringent requirements on chemical sensor sensitivity and selectivity. The need to meet regulatory requirements for monitoring toxins is an important driver in the development of environmental chemical sensors. Low cost sensor formats are particularly important for occupational environmental monitoring.

Detection of chemical weapons is a specialized type of environmental sensing. The following materials needs are important in developing suitable candidate sensor technologies for these applications: fiberoptic coatings with improved chemical selectivity; new membranes and electrode coatings to obtain improved chemical selectivity with electrochemical sensors; and chemically selective films that undergo changes in mechanical and electrical properties following analyte sorption.

The possibility exists of leveraging generic miniaturization techniques, including materials and processing technologies developed for mass market applications, in order to further develop compact, lightweight, hand-held sensor systems for environmental and chemical weapons detection. Miniaturization techniques of particular interest include methods relating to supporting electronics and protective packaging.

8

GENERAL CONCLUSIONS AND RECOMMENDATIONS

The general conclusions and recommendations contained in this chapter, relating to sensor research and development, are the result of the committee's analysis of the illustrative examples and discussion contained in parts I and II of this report. Specific sensor materials development opportunities derived from the illustrative examples of Part II are summarized in Chapter 7.

CONCLUSIONS

Trends in Sensor Technology

Current sensor development is tending toward increased complexity in sensor systems. The greater flexibility and lower production cost associated with advanced, integrated electronic technology allows computer processing that once required large and sophisticated signal processing systems to be reduced to a microelectronic chip; for example, smart sensors have transduction, signal amplification, filtering, and other processing on a single substrate. However, from the perspective of the end user, the sensor system now appears simpler even with its increased functionality and internal complexity.

The principal technical drivers for sensor development may come from enabling/supporting technologies other than materials technology. Most recent advances in sensors have not originated from the synthesis of new transduction materials (except perhaps for chemical sensors) but from innovations in low-cost, large-scale manufacturing of interconnections, microelectronics, and micromachining. Many advanced sensor techniques, such as photon-scattering and laser acoustic technologies, require materials developments to support particular implementations, not the sensor transducer.

Networking of large sensor systems can provide improved spatial and temporal sampling in low-cost, low-maintenance systems. A network of sensors distributed throughout a large structure can provide data to a central processor that monitors performance or aids in locating and characterizing structural defects. In other cases, such as chemical sensing, the individual outputs from an array of sensitive but only moderately selective transducers can provide a composite indication that is both sensitive and selective with regard to a target chemical species.

Sensor research and development lends itself to dual use and commercialization efforts. Sensors are an enabling technology, applicable to a wide spectrum of uses. To be effective, it requires identification of potential uses and assessment of the degree of suitability. For example, sensor systems developed for structural health monitoring of an aging military aircraft or for other vehicle monitoring applications can be exploited in some form by the commercial aircraft and automotive industries. Chemical sensors used for detection of chemical warfare agents have numerous possible non-DoD applications in areas such as environmental and health monitoring. Also, infrared sensors, traditionally developed for military applications such as reconnaissance, are finding uses in materials manufacture, intrusion detection, and chemical detection systems as they become affordable.

R&D Strategy

Few programs have existed to develop sensors solely for the sake of advancing sensor technology. Historically, sensor research and development efforts have been funded as an adjunct to large application programs that required sensors. A concentrated effort to support the advancement of sensors and the development of new or improved sensor materials will require the implementation of an effective research planning process that addresses the needs of a broad set of users with related applications.

There is a need for a generally accepted framework to describe both sensor application requirements and sensor performance capabilities. The establishment of a common set of descriptors for use by sensor users and suppliers and for researchers in the diverse disciplines associated with sensor development was identified by the committee as the most important step in facilitating the identification of sensor materials R&D opportunities and in accelerating the development and use of advanced sensor technologies.

Experience in establishing centers of excellence for sensor development provides useful guidelines for improving sensor R&D strategy. Four characteristics appear to be essential: a multidisciplinary approach with emphasis on teamwork; capabilities ranging from an initial proof of concept, exploratory and developmental research through engineering prototypes; focus on selected sensor technologies for a broadly defined range of applications in line with the core competencies of the organization (i.e., not attempting to cover the entire field of sensor technology and the associated diversity of sensor materials); and strong linkage to industry to guide the general relevance of the research.

Opportunities in Materials R&D

Sensor materials R&D can be divided into two main categories: the development of new materials, and materials engineering associated with implementation constraints for particular applications. These two categories frequently have very different approaches to materials R&D. New sensor materials are often targeted at very innovative, high payoff applications for which the requirements are ill defined. In contrast, materials engineering issues, such as longevity, resistance to a hostile environment, and incorporation in a host structure, are associated with sensor implementations in defined applications with relatively well-known requirements.

High-payoff opportunities for new sensor materials in the near term will come primarily from R&D on existing materials rather than synthesis of new compositions of matter. The committee identified fundamental research on new compositions of matter as the highest risk element of sensor materials R&D programs, although this approach also offers the highest potential payoff. Experience has indicated that the introduction of new materials has created many new and exciting opportunities for sensors. Nonetheless, the development time for a commercially available sensor based on a new composition of matter may well be greater than ten years, indicating that, although the opportunities are enormous, the associated costs will likely be high.

Exploiting materials developed for purposes other than sensing can lead to rapid sensor technology advancements at relatively low cost and risk. As a case in point: fiberoptic sensors are now commonly employed in many applications. Optical fiber development was supported by the communications industry; performance was greatly improved and cost decreased rapidly as usage increased. The sensor community very creatively took advantage of these materials without the need to support a major development activity of the fibers.

Materials processing science will be the foundation for developing affordable sensor materials. Materials synthesis and processing will facilitate the transfer of innovations in materials science to commercially viable products. Numerous existing materials could be incorporated in commercial sensors if the material could be produced at low cost in the needed configurations and quantities.

Universities and federal research laboratories play a critical role in conducting frontier research. Frontier research can be defined as leading-edge research that is conducted without a particular application in mind or does not expect to be commercialized within the near or intermediate term (e.g., within 10 years). While industrial research centers are having increasing difficulty in justifying such research, universities are well positioned to conduct such research and to use such programs as vehicles to educate students. Federal research laboratories, including the military laboratories, generally sponsor frontier research and conduct a portion of the research in-house to keep abreast of the leading-edge technologies. Long-term commitment to such research is essential to maintain a stable effort.

RECOMMENDATIONS

R&D Strategy

In the view of the committee, focused programs in which sensors are treated as a separate field of endeavor, as opposed to an adjunct to larger programs, will contribute significantly toward accelerating the development and use of advanced sensors. The primary R&D approach to exploit high-payoff opportunities in sensor technology should be the multidisciplinary integration of existing technologies (e.g., transducer materials, signal processing, and packaging) for specific or generic applications. This will allow for aggressive investigation of new sensor technologies from a system perspective. Frontier research activities should therefore be closely coordinated with in these applied R&D programs.

The committee recommends use of a communication tool to facilitate interdisciplinary cooperation and the identification of research opportunities and needs for sensor systems and technologies. A standard terminology is needed to describe sensing requirements and technology attributes. The communication tool and descriptors should form the basis for an evolutionary methodology that can be augmented and refined for use by specific research groups and applications.

The committee recommends that the communication tool be used in conjunction with additional information on technical risk[1] and potential payoff in developing a decision-making methodology to guide sensor materials R&D. Guidelines to facilitate such R&D planning could include the following steps:

- a systematic approach to identifying research opportunities based on a comparison of requirements to available technologies;
- realistic assessment of technical risk and challenges;
- an estimate of potential benefits; and
- effective communication of sensing needs and capabilities across the diverse technical disciplines involved in sensor development.

Organizations undertaking sensor R&D programs should maintain a broad research base with critical core competencies. Because the emergence of sensors as a field is the result of the convergence of activities from physics, chemistry, materials science, and engineering, a multidisciplinary approach to R&D is particularly important, both in identifying opportunities for future development and in conducting R&D in the field of sensor technology.[2] Thus, organizations undertaking R&D programs in sensors should possess, or have access to, expertise from all technical disciplines involved in sensor technology. To give a sense of relevance and urgency to any applied R&D program, a customer or end user with a specific implementation need should be identified and charged with demonstrating the potential payoff in a joint effort with the developer.

R&D programs that develop sensor materials should focus on selected classes of materials. In view of the diverse range of sensor materials and the high costs of fabrication facilities for many advanced sensor materials, the committee recommends that specific R&D programs focus on selected classes of materials, such as semiconductors or ceramic-based materials, rather than attempting to encompass a very broad range of endeavor.

Priorities in Materials R&D

The committee recommends that sensor materials R&D be pursued in three main areas. In order of decreasing priority these are:

- development of processing techniques for existing sensor materials;
- assessment and development of sensing capabilities

in existing materials that have properties not yet exploited for sensor applications; and

- fundamental investigation of novel sensing approaches, such as using multiple physical responses to a sensing phenomenon and new compositions of matter.

The committee recommends that this prioritization be used as a guide in allocating resources, with the highest priority category receiving the largest share in aggregate. The lowest priority would also receive resources, although in aggregate not at the same levels as the categories above it.

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NOTES

1. Sensor risk analysis, defined as the probability of sensor failure multiplied by the cost of not using the appropriate sensor, can provide a meaningful metric.

2. An earlier National Materials Advisory Board report (NRC, 1986) reached a similar conclusion in the context of electrochemical sensor development:" Sensor technology is multidisciplinary, both in the assembly and characterization of the sensing element and in the fitting of the element into the specific system in the field. Manufacturers of instruments often do not have specialist teams with adequate breadth to develop novel techniques into commercial devices. As a consequence, there are missed opportunities in the conception of new methods as well as poor transfer to the marketplace of those concepts that do arise."

APPENDIX A

BIBLIOGRAPHY OF SENSOR TECHNOLOGY

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APPENDIX B

SENSOR TECHNOLOGY GLOSSARY

DEFINITIONS AND EXPLANATIONS OF DESCRIPTORS AND OTHER TERMS

accuracy.	*See* **characteristics of sensors—accuracy.**
acquisition of data [continuous versus discrete, threshold/peak, integrating].	How information from a sensor is to be processed. The use of computer control requires digitized input, which converts continuous, discrete, threshold/peak, and/or integrating sensor information into digital information. *See* discussion of this descriptor in Chapter 2.
analyte.	A chemical species targeted for qualitative or quantitative analysis.
attenuation.	A decrease in the amplitude of a signal as it passes through any part of the measurement system.
background-limited performance.	A situation in which the signal is weak relative to the background noise.
bandwidth.	The range of frequencies over which the measurement system can operate within a specified error range.
breakdown.	Failure of a material resulting from an electrical overload. The resulting damage may be in the form of thermal damage (melting or burning) or electrical damage (loss of polarization in piezoelectric materials).
characteristics of sensors	
accuracy.	The degree of correctness with which the measuring system yields the "true value" of a measured quantity, where the "true value" refers to an accepted standard, such as a standard meter or volt. Typically described in terms of a maximum percentage of deviation expected based on a full-scale reading.
limit of detection.	The smallest measurable input. This differs from resolution, which defines the smallest measurable change in input. For a temperature measurement, this would provide an indication of the lowest temperature a sensor could generate an output in response.
linearity.	The degree to which the calibration curve of a device conforms to a straight line.
range.	The difference between the minimum and maximum values of sensor output in the intended operating range. Defines the overall operating limits of a sensor.
resolution.	The smallest measurable change in input that will produce a small but noticeable change in the output. In the context of chemical separations, defines the completeness of separation.
response time.	The time it takes for the sensor's output to reach its final value. A measure of how quickly the sensor will respond to changes in the environment. In general, this parameter is a measure of the speed of the sensor and must be compared with the speed of the process.
selectivity.	The ability of a sensor to measure only one metric or, in the case of a chemical sensor, to measure only a single chemical species.

sensitivity.	The amount of change in a sensor's output in response to a change at a sensor's input over the sensor's entire range. Provides an indication of a sensor's ability to detect changes. For some sensors, the sensitivity is defined as the input parameter change required to produce a standardized output change.[1]
conformance.	The closeness of a calibration curve to a specified curve. Equipment that is in conformance is in compliance with specifications, industry standards, or other guidelines.
constraints.	*See* discussion of this descriptor in Chapter 2.
isolation.	How much a device must be isolated from various disturbances or effects which compromise information integrity or sensor reliability. For example, electromagnetic isolation provides immunity to interference from electromagnetic radiation. This improves the overall quality (and therefore accuracy) of a sensor signal.
packaging.	How the packaging material or design limits the environments in which the sensor can be used.
cross-sensitivity.	The influence of one measurand on the sensitivity of a sensor another measurand.
crosstalk.	Electromagnetic noise transmitted between leads or circuits in close proximity to each other.
detectability.	*See* **characteristics of sensors—limit of detection**.
distortion.	Inaccuracy in a reproduced or amplified signal, such as shifted frequencies, unequal delays, or unequal change in amplitude ratios of the components of an output signal.
drift.	Gradual departure of the instrument output from the calibrated value. An undesired slow change of the output, which is not a function of the measured quality.
dynamic characteristics.	A description of an instrument's behavior between the time a measured quantity changes value and the time the instrument obtains a steady response.
dynamic error.	The error that occurs when the output does not precisely follow the transient response of the measured quantity.
economic factors.	(*See* discussion of this descriptor in Chapter 2.)
acquisition cost.	The cost to purchase the sensor technology.
development cost.	The investment required to develop the technology.
life-cycle cost.	The cost of acquiring and maintaining the technology over its useful life.
maintenance cost.	The investment in resources to maintain the sensor technology.
manufacturability.	The cost-effectiveness of a sensor technology.
eddy current.	Electrical current induced in a conducting material by a variation of magnetic flux.
electrode.	A conductive element used to emit, collect, or control the movement of electrons or ions in an electric field.
efficiency.	In the context of chemical separations, a measure of the ability to separate.
end points.	The output values at the upper limits of the sensor's range.
error.	The difference between the measured value and true value.
ferroelectric material	A dielectric material made from molecules containing dipoles (asymmetric distributions of electrical charge) which spontaneously align.
free impedance.	The impedance at the input of a transducer when the impedance of the load is made zero.
frequency response.	Two relations between sets of inputs and outputs. One relates frequencies to the output-input amplitude ratio; the other relates frequencies to the phase difference between the output and input.
gain.	The ratio of the amplitude of an output to input signal.
grounding.	Creating an electrically conductive path to the earth or some other conducting body at zero potential with respect to the earth.
hysteresis.	The difference in the output when a specific input value is approached first with an increasing and then with a decreasing input. This phenomenon occurs in ferroelectric materials and results in irreversible loss of energy through heat dissipation.
impedance.	The complex ratio of a force-like quantity (force, pressure, voltage, temperature, or

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[1] For a discussion of acoustic sensor sensitivity, see Vig, J.R. 1991. On acoustic sensor sensitivity. IEEE Transactions on Ultrasonics, Ferroelectrics, and Frequency Control 38(3):311.

	electric field) to a corresponding related velocity-like quantity (velocity, volume velocity, current, heat flow, or magnetic field strength).
implementation	(*See* discussion of this descriptor in Chapter 2.)
format (integrated signal processing, multichannel, multiplexing).	The manner in which a number of sensor signals over time or space are mixed.
mode (contact vs. noncontact, remote, in situ, invasive vs. noninvasive, nondestructive vs. destructive).	The measurement of a property involves selecting the best combinations of alternatives depending on material, process, and/or product constraints.
scale (single point, integrating, array).	The size of a sample area or volume used to determine the desired property. Sensor measurement of a property or state of the material may be at a point or aggregated over a large area.
inductance.	That property of an electric circuit which tends to oppose change in current in the circuit.
industrial noise.	Electrical disturbances created by an industrial environment, such as 60-Hz noise from AC power lines or sporadic noise from changes in power consumption.
instability.	The tendency to behave in an unpredictable, changeable, or erratic manner.
interchangeability error.	The error observed when a sensor is replaced by another sensor when the quantity being measured is identical.
isolation.	*See* **constraints—isolation**.
lag.	The time delay required for a system to completely respond to a change in the input signal.
leakage.	The loss of all or part of a useful agent, as of the electric current that flows through an insulator of the magnetic flux that passes outside useful flux circuits.
life (lifetime).	The length of time the sensor can be used before its performance changes.
linearity.	*See* **characteristics of sensors—linearity**.
magnetometer.	An instrument used for measuring the intensity and/or direction of a magnetic field.
magnetostrictive material.	A material that changes dimension in the presence of a magnetic field or generates a magnetic field when mechanically deformed.
measurand.	A physical quantity, condition, or property that is to be measured.
measurement scale (macro, milli, micro, or nano).	The amount of sample or measure being sampled. Sensor measurement of a property or state of the material may be at a nano (or atomic) level or at various increasing levels of granularity for which the macro (bulk or global) level is the highest. *See* discussion of this descriptor in Chapter 2.
microsensors.	Sensors having dimensions in the range of 10^{-7} to 10^{-3} meters, as is typical of solid-state sensors employing silicon microtechnology.
minimum detectable signal.	See **characteristics of sensors—limit of detection**.
noise.	Meaningless stray signals and electrical disturbances in a measurement signal that decrease accuracy of the measurement.
nonlinearity.	Lack of constant proportionality between two parameters over a range of measurement.
offset.	The output signal of the sensor when the measurand is zero.
operating temperature range.	The range of temperatures over which a sensor can be used with a specified maximum error. *See* **characteristics of sensors—range**.
output impedance.	The ratio of output voltage to the short circuit current of an instrument.
overall performance.	The performance of the entire system, which takes into account the contributions from all of the components of that system.
overshoot.	The amount an indicator or system goes beyond its steady-state value before returning to the steady-state value.
phase angle.	The difference in the phase relationship of the current and voltage expressed as the angle between the vectors representing the two.
phase shift.	A time difference between the input and output signals.
piezoelectric material.	A ferroelectric material in which an electrical potential difference is created due to mechanical deformation, or conversely, in which the application of a voltage causes dimensional changes in the material.
precision.	The degree of reproducibility among several independent measurements of the same true value under specified conditions.

Q factor.	A rating, applied to coils, capacitors, and resonant circuits, equal to the reactance divided by the resistance. The ratio of energy stored to energy dissipated per cycle in an electrical or mechanical system.
range.	*See* **characteristics of sensors—range**.
reactance.	The component of the impedance of an electric circuit, not due to the resistance, which opposes the flow of an alternating current.
reliability. (life, multiuse vs. single, calibration vs. accuracy drift).	How well a sensor maintains both precision and accuracy over its expected lifetime. Also includes the robustness of the sensor. *See* discussion of this descriptor in Chapter 2.
repeatability.	The exactness with which a measuring instrument repeats indications when it measures the same property under the same conditions.
resistivity.	The resistance of a material expressed in ohms per unit length and unit cross section.
resolution.	*See* **characteristics of sensors—resolution**.
resonant frequency.	The frequency at which the sensor has maximum output.
response time.	*See* **characteristics of sensors—response time**.
selectivity.	*See* **characteristics of sensors—selectivity**.
sensing element.	The part of a transducer that is in contact with the medium being measured and that responds to changes in the medium.
sensitivity.	*See* **characteristics of sensors—sensitivity**.
signal-to-noise-ratio.	The ratio of the output signal with an input signal to the output signal with no input signal.
smart sensor.	A sensor in which the electronics that process the output from the sensor, and forms the modifier, are partially or fully integrated on a single chip.
span.	The difference between the highest and lowest scale values of an instrument.
specificity.	*See* **characteristics of sensors—selectivity**.
step response.	The response of a system to an instantaneous jump in the input signal.
strain gauge.	An element (wire or foil) that measures a strain based on electrical resistance changes of the gauge that result from a change in length or dimension strain of the wire or foil.
thermistor.	A temperature-measuring device, which contains a resistor or semiconductor whose resistance varies with temperature.
thermocouple.	A temperature-measuring device, which contains a pair of end-joined dissimilar conductors in which an electromotive force is developed by thermoelectric effects when the joined ends and the free ends of the conductors are a different temperatures.
threshold.	The smallest input signal that will cause a readable change in the output signal.
time constant.	The time it takes for the output change to reach 63 percent of its final value.
transduction (self-generating or modulating).	The conversion of the signal to be measured into another, more easily accessible form. Source of energy for transmission of the sensor signal. (*See* discussion of this descriptor in Chapter 2).
transduction mode (direct or indirect).	How the sensor acquires the desired information from the material. In general, this parameter is an indication of the ability of the sensor signal to provide information regarding a material property or state of interest. *See* discussion of this descriptor in Chapter 2.
transient response.	The response of the sensor to a step change in the measurand.

APPENDIX C

AN ILLUSTRATIVE SENSOR TAXONOMY

The discussion of a taxonomy for sensors that was presented in Chapter 1 was necessarily brief. This appendix applies those somewhat theoretical concepts to specific examples drawn from past reports of the National Research Council's National Materials Advisory Board that addressed various sensor applications (NRC, 1986a,b,c, 1987, 1989a,b, 1992). For example, Figure C-1, based on a 1989 report (NRC, 1989a) graphically depicts the classification, presented in Chapter 1, in which sensors are classified on the basis of the energy form in which signals are received and generated (mechanical, thermal, electrical, magnetic, radiant, or chemical) and by the nature of the transduction effect (self-generating or modulating).

Figure C-2 applies the example taxonomy to a thermocouple. The figure indicates that in the general case, both input and output signals can be in any one of these six forms of energy, giving rise to a six-by-six matrix of primary (input) and secondary (output) signals, as summarized in Table 1-3. Following the approach of Middlehoek and Noorlag (1982), self-generating and modulating signals may be treated as fundamental transduction principles, creating a third dimension to the six-by-six matrix. As discussed in Chapter 1, some confusion then arises from the use of the terms "passive" and "active" for modulating sensors. For this reason, the designations "self-generating" and "modulating" are preferred to describe, respectively, sensors that do and do not require an auxiliary energy source to produce an output signal. For example, as shown in Figure C-2, a thermocouple is a self-generating transducer, since a change in temperature is converted directly into an electrical signal that can be measured. In contrast, the mechanical energy input to a strain gauge is modulated or converted to an electrical signal (Figure C-3) through the use of a piezoresistive element made of wire or metal foil. Deformation of this element as a result of a tensile or compressive force results in a change in electrical resistance. The various signal energies that are used in modulating transducers include photoconductive, magnetoresistive, thermoresistive, electrically conductive, or piezoresistive ones.

Figure C-4 illustrates the correlation between the form of the sensor signal and sensor sensitivity,

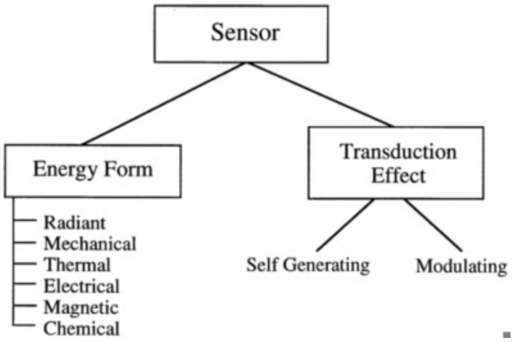

FIGURE C-1 Basic sensor taxonomy.

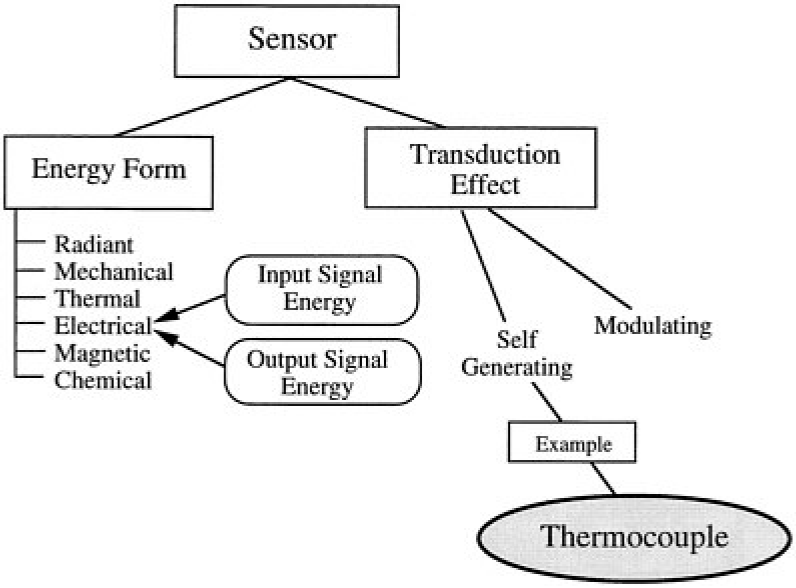

FIGURE C-2 Example of thermocouple transducer.

based on the magnitude of the energy change to be detected. For example, the detection of chemical signals is generally less than the measurement of chemical bonding or binding energies, which are likely to be in the range of 0.025 volt. In contrast, the energies associated with thermal signals are significantly greater, corresponding to wavelengths and intensities in the thermal energy spectrum. Similarly, sensing of radiant, electrical, and magnetic signals requires the detection of energies in the relevant parts of the electromagnetic spectrum. For example, the long-wavelength infrared detectors discussed in Chapter 5 depend upon the use of semiconductor materials that can efficiently absorb radiation in the wavelength band of 8 to 14 microns; this requirement necessitates the use of sensor materials with band gaps less than about 130 MeV.

Figure C-5 shows that sensitivity requirements for sensors used in materials processing depend not only upon the signal energy magnitude and form, as discussed above, but also on the scale of the material property to be measured. In the case of metal processing, the properties of interest can range from nanostructural features, such as point defects and dislocation densities, through microstructural features (phase transformations, grain size) to millistructural and macrostructural properties such as tensile strength. The selection and design of an appropriate sensor depends upon an understanding of the scale of measurement and sensitivity required for the proposed application. The communication tool presented in Chapter 2 offers an effective means for matching the measurement scale of the application with the capabilities of candidate sensor technologies. In the polymer matrix composite processing example discussed in Chapter 3, sensing requirements to determine part quality are based on the determination of bulk properties. In contrast, the in situ diagnostic techniques under development to monitor the fabrication of band-structure-engineered semiconductor materials depend on the determination of materials properties at nanostructural and microstructural scales.

Figure C-6 illustrates some of the practical constraints associated with sensor applications for materials processing. These constraints apply regardless of the signal form or transduction type. For example, there is frequently a requirement for sensing

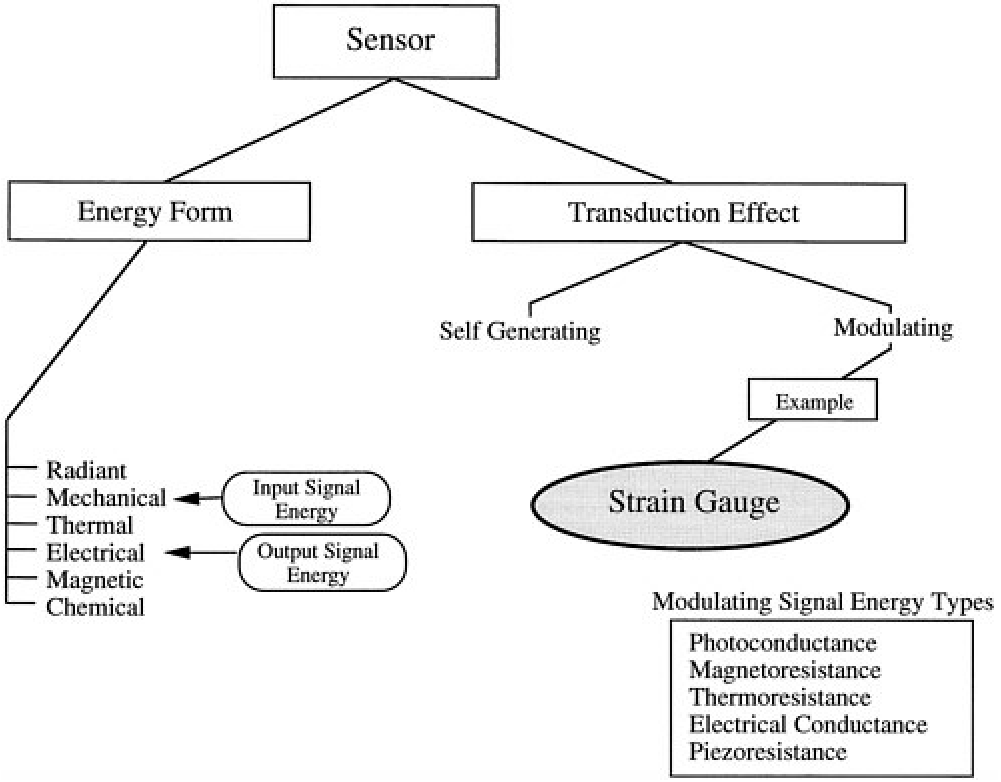

FIGURE C-3 Example of strain gauge transducer.

to be conducted in a noninvasive fashion such that the presence of a sensor does not perturb the fabrication process. Applications of this type are discussed in Chapter 3 in the context of intelligent processing of polymer matrix composites, and the requirement for noninvasive monitoring of composite cure is identified as a major driver for the development of new sensor types. The use of optical sensing technologies is particularly promising for such noninvasive sensing applications.

Another important constraint for sensing applications is the availability of reliable, low-cost sensors. As noted in Part II of the report, the availability of such sensors is critical in order to accelerate the incorporation of advanced sensors in practical applications, including materials and component manufacture. Low-cost, reliable sensors are also needed for structural control and health monitoring and for environmental sensing applications, such as personal health monitoring. In the case of structural health monitoring, practical requirements for long-term reliability may be far more challenging than those associated with materials manufacture.

The issue of measurement time and sensor response time (Figure C-6) is considered in Chapter 3 in the context of intelligent processing of structural polymer matrix composites. It is noted that, in practical applications, sensors with short time constants are required in order to detect very rapid, localized changes in the matrix resin system during composite cure or to detect large gradients in material

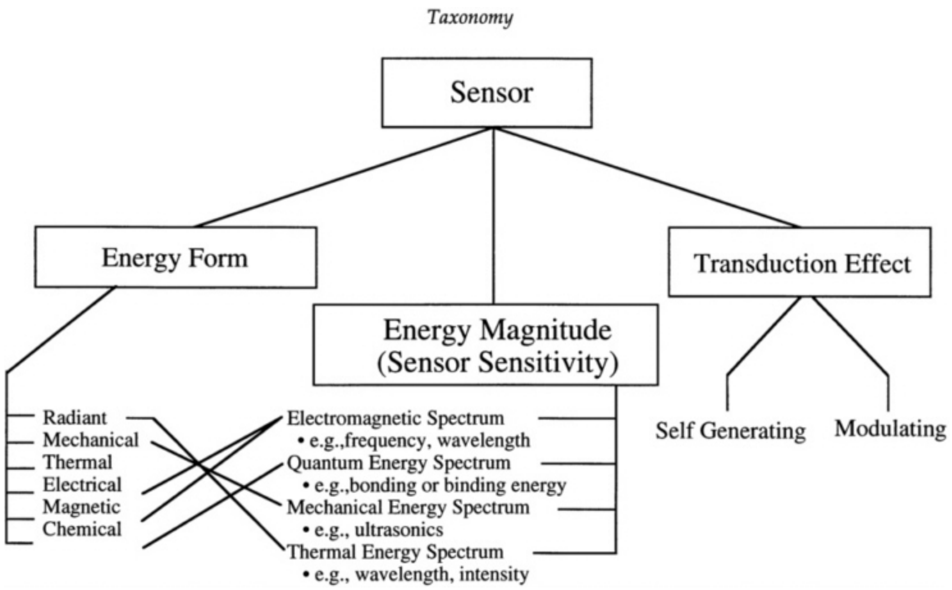

FIGURE C-4 Correlation between transducer energy form and sensitivity.

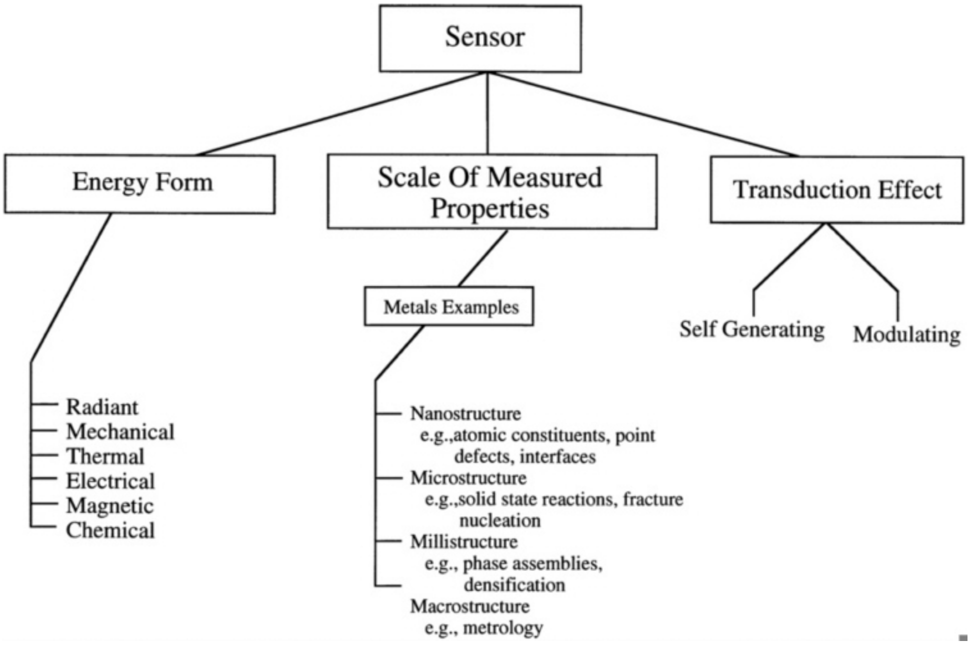

FIGURE C-5 Correlation of sensor sensitivity with property measurement scale.

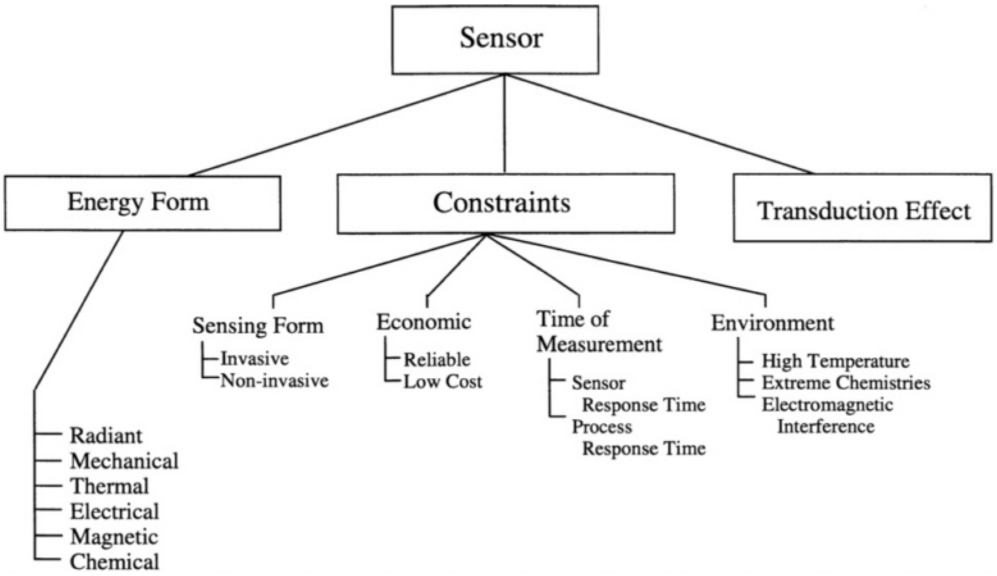

FIGURE C-6 Illustration of typical constraints on sensor applications.

properties over a processing time of several hours. Thus, the sensor response time must be short enough to provide an accurate and "instantaneous" representation of the material during processing, thereby permitting modifications to be made to the composite cure parameters in real time in order to optimize the process for final material quality and efficient use of processing facilities. If the sensor response time is long compared with the process response time, changes to the material processing parameters cannot be achieved effectively on-line, and intelligent processing is not feasible.

A further constraint on sensors for materials processing arises from the hostile manufacturing environment in which such sensors must operate. Processing is frequently performed at elevated temperatures (up to 900 °F or 480 °C for advanced thermosetting polymer matrix composites), and the chemical environment associated with processing may tend to attack the material of the sensor (exposure to polymer resins and their precursors may result in degradation of sensor performance). Thus, the sensors used to monitor process changes must be robust and capable of performing reliably under elevated temperature and chemically aggressive conditions. In addition, sensors must be insensitive to electromagnetic interference effects, for example, in an autoclave during processing. Some of the major constraints associated with monitoring the temperature of polymer-matrix composite resin during cure are summarized in Appendix D, Table D-1.

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APPENDIX D

SENSOR TECHNOLOGY FOR MONITORING POLYMER CURING

In the past, the progress of cure for thermosetting polymers has been estimated from the measurement of a single, easily monitored parameter, such as resin temperature. As discussed in Chapter 3, such an approach has deficiencies that limit the extent to which intelligent processing can be accomplished. A new sensor technology is needed that can measure several different microscopic properties and thus provide a direct, accurate measure of the extent of cure.

This appendix points out the limitations of using temperature sensing alone to estimate the degree of cure and provides background information on a new approach that exploits fiber optics to provide multiproperty sensing.

SINGLE PROPERTY SENSING

As noted in Chapter 3, intelligent processing of structural polymer materials has benefited from the use of thermocouples to sense material (resin) temperature during the cure process. Although the thermocouples can be used noninvasively by inserting them into excess material areas (i.e., areas that will be later removed when fitting the cured part to an aircraft structure), they still require insertion by an autoclave operator, which is an impediment to high-volume manufacturing applications. An alternative method is to insert a thermocouple into the tooling used to hold the material to obtain a specific geometry, but the thermocouple still requires frequent replacement due to corrosion and thermal cycle fatigue of the autoclave environment.

Thermocouples have a slower than desired response time. Also, since they are made of metal alloys, thermocouples are affected by electromagnetic radiation, such as interference arising from heating elements within an autoclave. This reduces the signal-to-noise ratio and hence the sensing resolution, repeatability, and sensitivity.

A more detailed characterization of thermocouples as a sensor technology is captured in Tables D-1 and D-2 below. These tables provide the basis for evaluating thermocouples as a sensor for the specific need and further help identify particular limitations that may be overcome by alternative sensing technologies. The discussion that follows addresses one such alternative technology and its inherent opportunities, some of which will require further research and development to realize.

MULTIPROPERTY SENSING

Optical fibers are an attractive alternative for sensing applications because of their high sensitivity, ability to resist adverse environments, and their immunity to noise from electrical or magnetic disturbances and ground loops. Fiberoptic sensors are classified in several different ways. One categorization differentiates between those that are intensity versus phase modulated. The intensity of the received light through the fiber is a function of the phenomenon being measured with *intensity modulated*

TABLE D-1 Key Descriptors for Temperature Sensing during Polymer Composite Curing

Descriptor	*Sensing Need*: Resin Temperature	*Sensor Technology*: Thermocouple
Transduction	Self-generating. Not adversely affected by electrical noise during cure.	Self-generating. Affected by electrical and process noise.
Transduction mode	Direct.	Direct.
Measurement scale	Macro (bulk).	Macro (bulk).
Implementation scale	Single point / aggregation over area.	Single point.
Format	Processing over time for velocity and acceleration.	Single point over time, differentiated for velocity and acceleration. Multichannel or multiplexing not required.
Mode	Contact or noncontact.	Contact.
	Remote. Driver is low cost.	Remote.
	In situ. Driver is low cost.	In situ.
	Noninvasive. Key constraint is product shape.	Invasive.
	Nondestructive. Must not compromise product integrity.	Nondestructive if suitably positioned in part or in material
Reliability	Multiple use, long lifetime: 100 to 1000 parts.	Typically not reusable if used invasively. Standard grade can last for hundreds of process cycles. If structurally strengthened (at increased cost), could last for years. Calibratible[a].
Acquisition	No special requirements.	Provide continuous information; no threshold, peak, or integration for data acquisition.
Characteristics response time	1–5 s.	5–25 s based on diameter of wire.[b]
sensitivity	1ºF (at ambient) to 5ºF (at 900ºF). [0.6ºC (at ambient) to 2.8ºC (at 482ºC)].	Typically 1ºF (ambient) to 5ºF (at 1500ºF to 2300ºF) [(Typically .6ºC (ambient) to 2.8ºC (at 815ºC to 1260ºC)]
resolution	1ºF (0.6ºC).	Limited to approx. 1ºF (0.6ºC).
range	Ambient to 900ºF (482ºC).	See Table D-2.
linearity	95% over above range.	Nonlinear[c]
limit of detection	±5ºF (±2.8ºC).	±1ºF (±0.6ºC)
selectivity	Constant, ambient to 900ºF (482ºC).	N/A
accuracy	Within 5ºF, ambient to 900ºF (within 2.8ºC, ambient to 482ºC).	Standard grade: 10% over 500ºF (278ºC) range[d]
Precision Constraints	High repeatability desirable; not critical.	95–100% repeatability over specified use range.
packaging size	Ideally approx. equal to diameter of reinforcing fiber.	0.04–0.25 inch diameter.
weight	Not applicable.	Not applicable.
hermeticity	Not applicable.	Not applicable.
isolation		
thermal	Up to 900ºF (482ºC).	Not applicable.
electromagnetic	Isolated for use in autoclave.	Very important: affects accuracy and overall performance.
mechanical	Robust-daily handling.	Possible problems in harsh conditions or production environment (e.g., excessive handling).
Chemical	Must withstand exposure to polymer resins.	Shrouded for protection from environmental conditions.
Optical	Not applicable.	Not applicable.
Economic factors	Acquisition cost < $1 amortized over lifetime of 100 to 1000 parts. Maintenance cost ≤ $0.10 over sensor life.	Little or no development required. Acquisition cost < $5, can be amortized over lifetime. Maintenance cost for resin temperature sensing ≤ $0.10 over sensor life.

[a] Thermocouples must be calibrated on a regular basis if accurate results are required.

[b] Thermocouple response times start at 1 to 5 s depending on mechanical configuration for a diameter of 0.040 in and increase to 25 s for a diameter of 0.25 in (Marlin Manufacturing, 1989).

[c] Thermocouples are nonlinear devices. Their output (in millivolts) does not generally map linearly to a temperature. However, over certain ranges thermocouples can be nearly linear. The specific process requirements determine whether a thermocouple's output is "good enough" without linearization.

[d] Stated accuracy implies that any reading over the entire range of a thermocouple may deviate from the true temperature by 5° F (2.6°C).

sensors; for example, microbend sensors rely on this type of modulation.

Phase modulated sensors compare the phase of light in a sensing fiber to a reference fiber in an interferometer. This technique requires the use of monomode fibers. Phase modulation is much more accurate than intensity modulation and can be used over a wider dynamic range. However, phase modulated sensors are almost always more expensive since the electronic processing equipment must be very sophisticated.

Another classification that is used is *interferometric* or *non-interferometric*. This distinction depends on whether principles of interferometry are used in the sensing.[1] The operating principle of interferometric sensors is straightforward. A single light wave is split into two parts that travel down different arms, one of the arms is subjected to the external parameter (e.g., strain or pressure) which needs to be measured, and the other arm is isolated from it. The two parts are then combined, causing interference fringes because of the phase difference between the two arms. Photodetectors convert the resulting light signal to an electrical signal for further processing.

There are three classical fiberoptic interferometers: Mach-Zehnder, Michelson, and Fabry-Perot.

- The Mach-Zehnder interferometer relies on a change in the length of the sensing arm to cause a relative phase change between the two light waves at the point they are recombined.
- The Michelson interferometer operates on the same principle except that the two arms are not combined at the end but have mirrored ends that reflect the light back. This eliminates the need for a second coupler (a fiber optic coupler is analogous to a beam splitter in traditional optics).

TABLE D-2 Temperature Ranges of Thermocouple Materials

Thermocouple Wire Alloy	ANSI Type	Temperature Range[a]
Copper-constantan	T	330 °F to 660 °F (116 °C to 345 °C)
Iron-constantan	J	32 °F to 1400 °F (0 °C to 760 °C)
Chromel-constantan	E	32 °F to 1600 °F (0 °C to 870 °C)
Chromel-alumel	K	32 °F to 2300 °F (0 °C to 1260 °C)
Nicrosil-nisil	N	32 °F to 2300 °F (0 °C to 1260 °C)

[a] From Marlin Manufacturing, 1989; the upper temperature limit is not continuous duty.

- In the Fabry-Perot interferometer, two partial reflectors are placed in one optical path, and the difference between the two reflected signals is an indication of the strain between the two reflectors. The Fabry-Perot interferometer allows the tailoring of the gauge length (the length of the sensor across which the measurement is taken), and obtaining discrete strain information.

Fiberoptic sensors are often classified into two major classes: *intrinsic* and *extrinsic*. Extrinsic sensors depend on some effect that is external to the fiber. For example, it is possible to design sensor systems that monitor chemical changes using extrinsic approaches. For example, the common red-blue litmus test for acidity can be monitored photometrically using fiber optics, and this has given rise to a reliable class of low-cost pH meters. More generally, specific chemical reactivity can be engineered into a supporting substrate which is then supported at the tip of a fiber device and illuminated by a fiberoptic transmitter and monitored photometrically by a fiberoptic receiver. In this way, a whole class of highly sensitive low-cost sensors can be constructed. While such approaches are interesting from an academic point of view and hold promise in the industrial and environmental field, they have certain drawbacks. Their use depends on being able to locate the appropriate chemical reactivity on the tip of the fiber. A key limitation derives from the fact that this type of extrinsic sensor is usually quite bulky and somewhat fragile.

An intrinsic optical sensor depends on some physical phenomenon that is inherent to the propagation of electromagnetic waves through a dense medium. Intrinsic optical sensors are of two types: physical and spectroscopic. The physical type involves the sensing of phenomena by measuring variations in the refractive index, fluorescence (Bur and Wang, 1991; and Bur et al., 1994) or equivalently the optical path length. As a case in point, it is well known that the application of pressure or stress to a material (such as residual stresses created during the processing of polymer composites) causes a small but measurable change in the refractive index; for example, the piezo-optic coefficient of glass fibers is $\tilde{}50\times10^{11}$ Pa^{-1}. If an optical fiber is imbedded in another medium, the optical inhomogeneity associated with a stress applied to the medium will cause increased scattering in the vicinity of the stress. This effect is used in a class of sensor where a light pulse from a laser is transmitted into the optical fiber and the backscatter from the optical inhomogeneity is measured as a function of the delay time relative to the incident pulse.

While there are many variations in the details for implementing this sort of device, it typically involves the construction of a miniaturized Fabry-Perot interferometer on the fiber end and the construction of a simple fringe counting system to monitor changes in the optical path length. If a reactive resin is allowed to fill the cavity, then the sensor effectively monitors the changes in refractive index as the material cures. Similarly, if the cavity is filled with a standard medium, the temperature (but not the viscosity) can be inferred from the fringe count as the sensor is heated. These types of sensors are commercially available and represent a useful addition to sensor technology. It should be noted that a measurement of the refractive index or flourescence of polymer material during processing essentially provides a phenomenological description of the curing process, and the actual chemical and physical states of the resin must be inferred from the measurement.

The other type of intrinsic fiberoptic sensor is the spectroscopic variety. This class of sensor is by far the more powerful but is the least well developed. In this case, the optical fiber is used only as a conduit to transport laser photons to the material being processed and the scattered light from the material to the analytical equipment. The sensor relies on the photon scattering phenomena to monitor materials behavior at the molecular level. Since this area is at an early stage of development, it is perhaps worthwhile reviewing briefly the underlying principles of operation based upon a system developed at Southwest Research Institute (Maguire and Talley, 1995). The material may be solid, liquid, or gas, and the fiber may be embedded within the body of the material or merely make optical contact with the surface. In either case, the material under investigation is bombarded with a flux of monochromatic coherent photons. These photons excite the various translational, rotational, and vibrational eigenstates of the material and undergo quasielastic and inelastic scattering over a range of momentum transfers.

It is worth pointing out distinctions between Fourier transform (FT) mid-infrared absorption, FT near-infrared absorption, and FT near-infrared Raman. As a practical matter, the mid-infrared absorption technique is not amenable to remote implementation because at present there are no optical fibers that have good transmission characteristics in this spectral region. The near-infrared absorption technique can be remotely implemented and commercial instrumentation is available.

A recent paper (George et al., 1991) reported a careful study of the curing of an epoxy resin using FT near-infrared absorption. The paper concluded that this was a useful technique but did have several drawbacks. The major limitation arises from the fact that absorption arises from overtones and combinations of the fundamental stretching and bending frequencies of functional groups containing hydrogen atoms. This has the unfortunate consequence that the bands are somewhat weak, broad, and sometimes overlapping. From a spectroscopic point of view, this certainly complicates the analysis and is undesirable. A useful rule of thumb in applied spectroscopy is that the most information is obtainable from strong, sharp, well-resolved, nonoverlapping lines. As was illustrated in Chapter 3, this is precisely what is afforded by the Raman technique, where the experimentally observed full width at half height is typically on the order of 1 cm^{-1} as opposed to near infrared absorption values of order 200 cm^{-1}.

The information content of the scattered photon flux is represented by a power spectrum, as detected by an intrinsic fiberoptic sensor. An incident photon with a particular wave vector, frequency, and polarization is incident upon a piece of material. The scattered photon also has a characteristic wave vector, frequency, and polarization and is detected at some angle to the incident radiation, as shown in Figure D-1. The modulus of the scattering vector is variable and is defined by the wavelength of the laser, the refractive index of the medium, and the scattering angle. It is an easy matter to change the scattering angle in a fiberoptic sensor so as to probe a range (spectrum) of wave numbers.

A few points are noteworthy about the scattered intensity. First, it is inversely proportional to the fourth power of the wavelength. Therefore, doubling the frequency from the visible region (˜500 nm) to the near infrared (˜1000 nm) will decrease the scattered intensity by a factor of about 16. Also, the scattered intensity falls off inversely as the square of the distance (*R*) between the scattering center and the detector. Because of the small diameter of the optical fiber, *R* can be kept small for typical fibers; this results in an order-of-magnitude increase of the solid angle. This enhancement of the optical efficiency for the fiberoptic approach more than offsets the losses associated with optical transmissions through the fiber.

All of the useful physiochemical sensor information is contained in the Fourier transform of the optical dielectric correlation function. For large frequency shifts (500 cm^{-1} to 4,000 cm^{-1}) the fiberoptic spectra have been recorded for a number of materials including an epoxy and bismaleimide-isocyanate resin for structural aircraft applications. Here

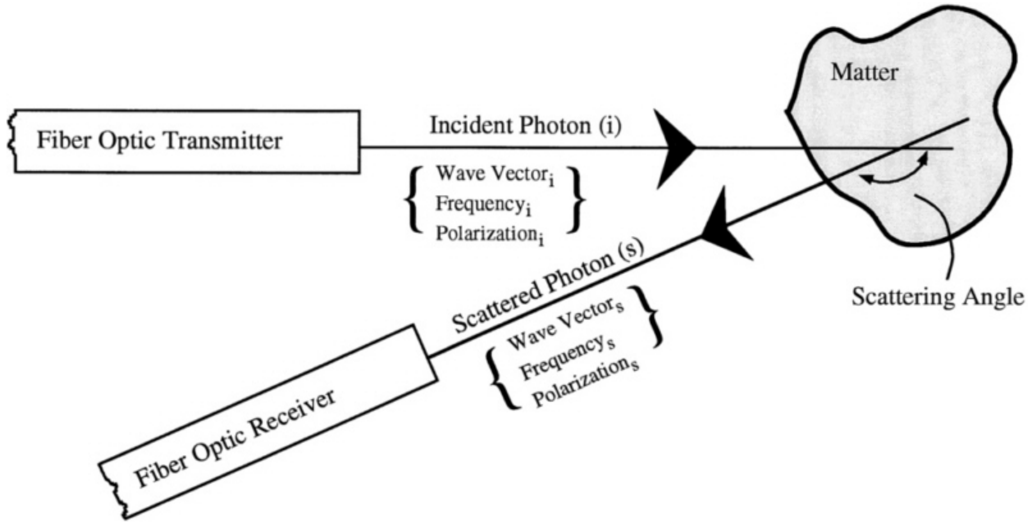

FIGURE D-1 Fiberoptic photon scattering detection.

TABLE D-3 Key Descriptors for Multi-Property Sensing during Polymer Composite Curing

Descriptor	*Sensing Need*: Multi-Property Sensing	*Sensor Technology*: Laser/Fiberoptic Technology
Transduction	Self-generating:	Self-generating:
	-high information content	-near-term research required
	-remote multiplex analysis	-near-term research required
	-not affected by electrical noise	-not applicable
	-multiproperty sensing capability.	-near-term research required.
Transduction mode	Direct.	Direct (visible & infrared analysis).
Measurement scale	Macro (bulk) through nano.	Macro (bulk) through nano
Implementation scale	Single point/sphere of ~100 µm to full aggregation over area of part.	Single point, sphere of ~100 µm. Near term research required for area information.
Format	Processing over time for velocity and acceleration.	Single point over time, differentiated for velocity and acceleration. Autocorrelation near term research required.
Mode	Contact or noncontact. Remote. In situ. Noninvasive. Nondestructive. Must not compromise product integrity.	Contact or noncontact. Remote. In situ. Noninvasive. Nondestructive.
Reliability	Multiple use, long lifetime; i.e., 100 to 1,000 parts.	Typically reusable, Comparable to thermocouple reliability. *See* Table 3-1.
Acquisition	No special requirements.	Provide continuous information. Near-term research required for pulsed information. No threshold, peak, or integration for data acquisition. Mode dependent. Total intensity determined using: -photodiode Brillouin -Fabry-Perot Raman -monochromator -Michelson interferometer.
	Temperature	Temperature
Response time	1–5 s.	1–500 s.
Sensitivity	0.6°C (1°F) (at ambient)-2.8°C (5°F) (at 900°F).	0.06°C [over -273°C (-459°F) to 2500°C (4532°F)].
Resolution range	100. 16°C–482°C (60°F–900°F)	10-1. -273°C to 2500°C.
Linearity	Not applicable.	Not applicable.
Limit of detection	Not applicable.	~1% of actual temperature.
Selectivity	Constant, (over -273°C to 2500°C).	Constant, from -273°C to 2500°C.
Accuracy	Within 2.8°C (over range from ambient to 482°C).	~1% of actual temperature.
Precision	High repeatability desirable but not critical.	~95% repeatability over specified range of use.
	Chemical Analysis	Chemical Analysis
		Key research need: Measure molar concentrations of oligomers using depolarized Raman scattering.

Descriptor	*Sensing Need*: Multi-Property Sensing	*Sensor Technology*: Laser/Fiberoptic Technology
	Viscosity	Viscosity *Key research need*: Determine reorientation/relaxation using depolarized Raman scattering.
	Longitudinal Kinematic Viscosity	Longitudinal Kinematic Viscosity *Key research need*: Measure Rayleigh/Brillouin scattering using Krypton laser.
	Heat Capacity Ratio	Heat Capacity Ratio *Key research need*: Determine with Nd: YAG laser using Rayleigh/Brillouin scattering.
	Sound Attenuation Factor	Sound Attenuation Factor *Key research need*: Measure using Brillouin scattering via Fabry Perot interferometer/spectrum analyzer.
	Adiabatic Sound Speed	Adiabatic Sound Speed *Key research need*: Determine using Brillouin scattering via Fabry Perot interferometer/spectrum analyzer.
	Thermal Diffusion	Thermal Diffusion *Key research need*: Determine using Rayleigh scattering via optical homodyne/optical heterodyne.
	Isothermal Compressibility	Isothermal Compressibility *Key research need*: Determine using Rayleigh scattering.
CONSTRAINTS		
Packaging size	Ideally approx. equal to diameter of reinforcing fiber.	0.10–0.25 mm diameter.
Weight	Preferably no heavier than one reinforcing fiber.	No heavier than one reinforcing fiber.
Hermeticity	Varies.	*Near term research need*: Improve sensor packaging.
Isolation	Up to 482ºC (900ºF).	Up to 2500ºC (4532ºF).
Thermal	Isolated for use in autoclave.	No need for shielding.
Electromagnetic	Robust: daily handling.	Possible problems in harsh conditions or production environment (excessive handling).
Mechanical		
	Must withstand exposure to polymer resins.	*Near term research need*: Improve sensor packaging.
Chemical		
Optical		Requires quality optics/micro-optics.
ECONOMIC	Acquisition cost < $1, to be amortized over 100 to 1,000 parts.	Acquisition cost is unknown.
	Maintenance cost ≤ $0.10 over sensor life.	Maintenance cost is unknown. Substantial research and development required.

the various absorption frequencies are clearly evident and allow a fairly complete analysis of the material.

Far more information is contained in these signals than has been extracted to date. For example, deconvolution of the Raman spectra will yield line widths from which the viscosity of the curing resin may be deduced. Similarly, the Rayleigh-Brillouin spectrum contains information on the adiabatic sound speed, acoustic attenuation coefficient, thermal diffusion, and a number of other parameters; but here again, no work has been done to extract this information for composite materials. It should be noted that our ability to detect spectra of this type is of relatively recent origin. Typically, observation of the Rayleigh-Brillouin and Raman scattering from materials was restricted to transparent materials of fairly high optical purity. This restricted the methodology to research studies in the laboratory. Despite the wide recognition that the application of such powerful approaches would provide a breakthrough in "sensor" technology, the promise was not realized for two reasons. First, real materials have fluorescent impurities that can completely mask the Raman signal. The standard way to overcome fluorescence is to go to longer excitation wavelength. However, in the red and near infrared, detector efficiency falls off markedly. It was not until the development of the indium-gallium-arsenide-strained superlattice detectors that the sensitivity in this spectral region increased to the point where inelastically scattered (Raman) near-infrared photons could be detected.

The near-term research opportunity is to use photon scattering sensor technology to increase the range of properties which laser-fiberoptics can accommodate for multiproperty sensing, such as resin temperature, viscosity, and degree of cure. Given the potential of laser-fiberoptic sensing, the framework tool developed in Chapter 2 has been used to develop an evaluation of future research opportunities. The results are summarized in Table D-3.

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NOTE

1. Most fiberoptic sensors rely on interferometry for converting the phase shift information into an electrical signal.

APPENDIX E

FIGURES OF MERIT FOR INFRARED PHOTODETECTORS

The key figure of merit that is usually employed is the specific detectivity D^*, which describes the smallest detectable signal (Accetta and Shumaker, 1993). D^* can be viewed as a measure of the temporal noise in the detector. D^* is defined through the following procedure.

1. Define the responsivity, R, for photodetectors as the ratio of the root mean square output voltage to the input signal power of the root mean square.
2. Define the noise-equivalent power (NEP) in watts as the incident flux required to give output voltage equal to the noise voltage:
   $NEP = V_n / R$ (watts),
   where V_n is the RMS noise voltage
3. The detectivity is given by:
   $D = 1/NEP$ (W^{-1})
4. The specific detectivity, D^*, is the detectivity D for a 1-Hz bandwidth and a 1-cm^2 area:

$D^* = D\,(A\times\Delta f)^{1/2}\ W^{-1}\ cm.\ sec^{-1/2}$

D^* is independent of the detector area, A, and bandwidth, Δf, if the noise is proportional to $(A\times\Delta f)^{1/2}$. This area dependence is found if radiation fluctuations dominate the noise or if A is varied by connecting together several small identical detectors; the bandwidth dependence is found if the spectral response is flat over the relevant frequency range. The specific detectivity, D^*, is a normalized measure related to the inverse of the smallest signal that can be detected.

Noise from the background places a fundamental limit on detectivity. A background limited photodetector with a wavelength-independent response at 300 K has a D^* of 1.8×10^{10} W /(sec$^{1/2}$ cm) for a hemispheric field of view.

For a single detector, D^* is clearly a relevant figure of merit. In order to maximize D^*:

- reduce all noise except for unavoidable radiative background noise; and
- increase the quantum efficiency as much as possible.

The typical figure of merit for arrays is the noise-equivalent temperature difference which is the smallest temperature difference that can be resolved. Typical error-correction algorithms that calibrate by illuminating the array uniformly at two different temperatures eliminate inhomogeneity caused by linear time-independent and spectrally independent variations. However, non-linearities in the detector response, variations in the spectral response between detectors, and temporal variations (drifts and $1/f$ noise have all been shown to lead to residual spatial nonuniformity that under many operating conditions is substantially larger than the temporal noise described by D^*. Spatial noise cannot be averaged out by time integration (Mooney et al., 1989). Therefore, nonuniformity is particularly important under conditions of substantial illumination and for staring arrays, because the large data rates place strong constraints on correction algorithms.

The operating temperature is an important consideration. Refrigeration becomes more costly and difficult as the operating temperature is lowered. For many applications the detector operating temperature should be high enough so that relatively low-cost refrigeration (such as liquid nitrogen at 77 K) can be used. This requirement of 77 K operation eliminates the possible use of extrinsic silicon detectors, which must be cooled to less than 30 K, from many applications.

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APPENDIX F

ACOUSTIC WAVE DEVICES FOR CHEMICAL SENSING

This appendix describes several types of chemical sensors that are based on acoustic wave formats. There are many other formats being developed for chemical sensing, as discussed in Chapter 6, "Chemical Sensing."

SURFACE ACOUSTIC WAVE DEVICES

Surface acoustic wave (SAW) devices are simple, rugged sensors that consist of a piezoelectric substrate and two patterned electrodes to launch and detect acoustic waves. The surface is covered with a coating that sorbs selected chemicals present in the environment. As an acoustic wave travels from one electrode to the other, the presence of molecules sorbed on the coating changes the velocity and attenuation of the SAW. Measurements of these changes can be used to indicate the identity and concentration of a specific chemical species in the environment.

By using coatings with selective absorption properties, investigators are developing sensors that can detect specific chemical species for both gas-phase and liquid-phase environments (Kepley et al., 1987). Typically, durable oxide-based coatings that are chemically modified to provide the required sorption characteristics are used. An important area of materials research is the development of coatings for particular chemicals. Another area of current materials research is the development of coatings that selectively sorb ionic species from solution for use in applications such as monitoring electroplating processes or waste streams for toxic species such as chromium, cadmium, or lead.

Polymer coatings that absorb a wide variety of chemicals have been found to be ideally suited for monitoring the highly regulated ozone-depleting chlorinated hydrocarbons. Simultaneous measurement of the wave velocity and attenuation can be used to identify a chemical species and its concentration.

SAW devices are fabricated from piezoelectric materials, typically quartz. SAWs rely on two interdigitated transducers—one to launch and the other to detect a wave that travels from one end of the device to the other. Each transducer is composed of many pairs of photolithographically defined fingers, and each finger is only a few micrometers wide. SAW devices operate in the 100-MHz-frequency regime.

The SAW is extremely sensitive to tiny mass changes and is capable of detecting 100 picogram/cm^2, which corresponds to a sensitivity to less than 0.01 monolayer of carbon. The velocity and the attenuation of acoustic waves result from changes in surface mass in SAW devices. Measuring both these properties simultaneously helps determine the nature and cause of the sensor response. However, the motion of the SAW is subject to extreme damping in liquids. As a result, applications are confined to the gas phase.

Typical applications of SAW devices are monitoring of volatile organic compounds in effluents on-line for environmentally conscious manufacturing and in waste-monitoring and remediation. The sensitivity and versatility of SAW sensors permit this technology to be engineered into many industrial processes, improving productivity and reducing environmental emissions.

A recent application of SAW sensors is the selective detection of organophosphates, which are a common class of chemical warfare agent. The detection of these chemicals was made possible by the recent development of thin films of self-assembled monolayers as the active surface of SAW devices. The sensitivity of this film/SAW device combination endows the sensor with immunity to interference from water vapor and common organic solvents while providing sensitivity in the part-per-billion concentration of organophosphates. As a result, arrays of such sensors with appropriate coatings can be used to detect the production of chemical weapons.

ACOUSTIC PLATE MODE SENSORS

The material of choice for acoustic plate mode sensors is quartz because of its low coefficient of thermal expansion. These sensors are typically made from ST-cut quartz, with mode propagation along the x-direction of the crystal. The plates are lapped to the desired thickness, and both sides of the plates are optically polished. Input and output transducers are defined on the face of the crystal to which the sensitive coating has been applied. The transducers are formed using evaporated metal films and standard photolithography techniques. Standard metallization, typically gold on chromium, is used. Dimensions of the quartz plate are not critical; typical dimensions are 23 mm × 7.6 mm × 0.5 mm.

Different transducer geometries are used to excite different modes (Martin et al., 1989). In all cases, the transducer finger dimensions scale with periodicity d: finger and width separation are $d/4$, while finger length is $50d$, where d is selected based on the desired mode to be excited. Typical mode frequencies are 100 or 150 MHz for $d = 50$ and 32 µm, respectively. There are advantages to operating at higher frequencies; the sensitivity increases as the square of the operating frequency. This in creased performance is available until the increased complexity of high-frequency operation or the increased fabrication complexity due to decreased dimensions of the photolithography outweigh the advantages.

QUARTZ CRYSTAL MICROBALANCE

The quartz crystal microbalance (QCM) is based on a resonant mode in a bulk crystal. The performance of these sensors relies on the changes in frequency as a result of mass loading on the surfaces. QCM sensors can also measure density-viscosity product in liquids as described below. The sensors are typically circular with about a 10:1 ratio of diameter to thickness; the precise dimension is determined by the desired operating frequency. Typical operating frequencies are about 5 MHz (Martin et al., 1991).

Electrodes are formed by evaporation of a chromium adhesion layer followed by evaporation of gold. A large electrode covering the center one-fourth of one side serves as ground, and a radio frequency electrode of one-half the diameter is deposited on the other side of the plate. The active area is determined by the area of the smaller electrode, since the radio frequency field is confined primarily to the quartz region beneath this electrode.

The resonance decreases in frequency and peak intensity and broadens as the QCM is loaded by the density-viscosity product of the liquid in which it is immersed. Because the admittance of the unloaded device can be measured precisely and because the behavior under loading can be calculated in detail, the QCM readily gives the product of the viscosity and density of the liquid. The QCM has a wide variety of applications that range from monitoring the viscosity-density product for oil or other liquids during refining or processing, measurement of degradation of jet fuels in high-temperature environments, to monitoring the life of motor oil in automobile engines.

CATALYTIC GATE SENSORS

Catalytic gate sensors refer to sensors based on silicon integrated circuit technology. The best known example is the hydrogen sensor that is fabricated from a metal-oxide—semiconductor field-effect transistor. The sensor consists of a silicon base, a thin silicon dioxide insulating layer, and a metallic outer layer that catalytically decomposes H2 or other hydrogen-containing molecules. The initial demonstration used palladium metal (Hughes et al., 1992; Lundström 1981; Lundström and Söderberg, 1981; Keramati and Zemel, 1982; Ruths et al., 1981). When hydrogen-containing molecules adsorb on the palladium surface, a fraction of the molecules decompose to release hydrogen atoms that diffuse rapidly through the palladium electrode to the underlying oxide layer. The atoms are trapped at interface states between the metal and the oxide, changing the amount of charge trapped at the interface which in turn changes the bias voltage in the channel between the source and drain and thus the gain in the transistor.

This type of sensor is fabricated using standard silicon integrated-circuit processing technology, with the exception of the catalytic gate. These sensors are extremely sensitive and can accurately measure hydrogen concentrations down to parts per billion. Such sensitivity is important in development of technologies to measure and control impurities in integrated circuit fabrication. Although palladium was used in the earlier demonstrations of these devices, PdNi alloys have proven to be more robust. PdNi alloys are capable of reversible behavior after exposure in 100 percent H_2 atmosphere, whereas pure palladium irreversibly forms a palladium hydride (Hughes and Schubert, 1992). Optimum alloy sensors for hydrogen detection, as well as development of alloy systems to detect other species, are an area of active materials research.

Recent extensions of this type of sensor technology have included adding resistors formed from hydrogen absorbing material, such as PdNi, to detect high concentrations of hydrogen. This capability is important if one wishes to use these sensors to detect explosive concentrations of H_2. Combining the two sensors on the same device and adding temperature sensing and control permits detection of hydrogen over a wide range of concentrations in gases under adverse environmental conditions. Since the sensors are fabricated using standard microelectronics techniques, further addition of integrated circuits on the sensor chip provide "smart" sensors; such sensors measure hydrogen concentrations and can also conduct signal processing, calibration, and output buffering, as well as initiate some action based on the measurement result.

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APPENDIX G

CANDIDATE SENSOR TECHNOLOGIES FOR DETECTION OF CHEMICAL WEAPONS (SCHEDULE II COMPOUNDS)

Candidate technologies have been identified by attempting to match the descriptors presented in Table 6-3 to available sensor systems. For the sake of clarity, only fatal shortcomings (indicated by *) and other descriptors deemed worthy of particular consideration are included in the following discussion. Additional descriptors may be necessary for detailed description of the status of development and the cost to implement the technology.

Gas chromatography-mass spectrometry systems currently provide the standard for sensitivity measurements and will fulfill requirements. However, as indicated in Table G-1, existing systems are too large, heavy, and expensive to meet needs.

Current ion mobility spectrometer systems can only detect part-per—million levels of very electronegative or electropositive species. These systems are not sufficiently sensitive for treaty verification, although they could be useful in battlefield conditions. The comparison of several available attributes for these systems to the requirements is shown in Table G-2.

Patch-test chemical reactions exploit selective chemical reactions that are irreversible and result in color changes. They are reported to be sensitive to selected Schedule II compounds in the parts-per-billion range. Their response time is slower than required, as shown in Table G-3.

Fiberoptic micromirrors use reliable communications technology to measure reflectance of sensor coating on the end of a cleaved fiber. The reflectivity can be changed by the analyte, by changes in the thickness of the sensing film, or by a change in refractive index. The sensor is very small and light and is immune from electrical interference. A poly-siloxane film has been shown to respond to di-isopropyl-methylphosphonate (DIMP).

TABLE G-1 Key Descriptors for Gas Chromatography-Mass Spectrometry

Descriptor	Requirements (Specification)	Available (Attributes)
Constraints-packaging (size, weight)	Hand held, volume < 1 cubic foot, weight 2.3 kg (5 lb).	Too large and heavy; survey mobile analyzer on two-wheeled cart weighs ~ 80 kg.
Economic-acquisition	Unit cost ~ $10,000.	~$50,000 for portable mass spectrometer; $130,000 for rugged, portable GC-MS.
Characteristics-response time	< 1-minute response and recycle.	Can be as low as 1 minute.

TABLE G-2 Key Descriptors for Ion Mobility Spectrometer

Descriptor	Requirements (Specification)	Available (Attributes)
Constraints-packaging (size, weight)	Hand held, volume < 1 cubic foot, weight 2.3 kg (5 lb).	Hand held unit resembling toolbox, ~1 foot long, weighing 20 kg (44 lb), with no vacuum pump required.
Characteristics-response time	< 1 minute response and recycle.	1 minute.

TABLE G-3 Key Descriptors for Patch-Test Chemical Reactions Showing Color Change

Descriptor	Requirements (Specification)	Available (Attributes)
Characteristics-response time	< 1-minute response and recycle.	About 1 minute, but unit is nonreusable.

TABLE G-4 Key Descriptors for Fiberoptic Sensors

Descriptor	Requirements (Specification)	Available (Attributes)
Characteristics-response time	< 1-minute response and recycle.	Approximately 1 minute at low concentrations.
Characteristics-sensitivity	Approximately 1 part per billion in gas phase.	1 ppm of DIMP.
Characteristics-resolution	Approximately 1 part per billion in air.	Change in reflectivity of 0.01% can be observed with prototype apparatus, corresponding to ~1 ppm of DIMP.
Characteristics-range	From 1 thousand to 1 part per billion.	Large dynamic range observed: 1 ppm to 100 part per billion for DIMP.
Characteristics-limit of detection	1 part per billion.	Approximately 1 part per million using polysiloxane film.
Characteristics-selectivity	*High.	Selectivity is poor; sensors respond to most organic solvents.
Characteristics-accuracy	Detection at 1 part per billion level may be sufficient.	± 10 percent.
Economic-acquisition	*Unit cost of ~$10,000 acceptable.	No commercial units available.
Economic-development	Estimate that up to $10 million could be spent over 10 years to develop sensor system.	Considerable development of coatings required for chemical selectivity.

Table G-4 contains a comparison of requirements versus available technology. This technology currently suffers from low selectivity and high cost.

Electrochemical sensors are available for chemical analysis, including ion selective electrodes for solvated (usually in water) analytes, amperometric analysis for both gas and liquid phases, and biosensor systems. Electrochemical sensors are amenable to array designs. The chemical selectivity issues are similar to those for fiberoptics, as depicted in Table G-4.

The basic technology for surface acoustic wave (SAW) sensors involves the use of small, thin plates of a piezoelectric material, often quartz, with evaporated metal electrodes for applying radio frequency signals (see Appendix F). Chemically sensitive films on the piezoelectric material have their properties altered by the adsorption of molecules of interest. Often the mass of adsorbed molecules is measured, but subtle changes in the mechanical and electrical properties of the films are also detected. SAW sensors can exhibit high sensitivity; in some cases a thousandth of an adsorbed monolayer of analyte can be detected. Considerable research and development has gone into developing SAW technology, notably highly selective chemical coatings, for sensitive and selective sensors for nerve agents and their precursors and degradation products. The technology is amenable to array designs for pattern recognition. Table G-5 compares requirements versus available technology. This technology currently suffers from variable selectivity.

TABLE G-5 Key Descriptors for Acoustic Wave Chemical Sensors

Descriptor	Requirements (Specification)	Available (Attributes)
Characteristics-response time	< 1-minute response and recycle.	1-10 seconds, reversible.
Characteristics-sensitivity	Approximately 1 ppb in gas phase.	1 ppm commonly, potentially 1 ppb with preconcentration hardware.
Characteristics-range	From 1 part per thousand to 1 part per billion (ppb).	Good dynamic range.
Characteristics-limit of detection	1 ppb.	Potentially approximately 1 ppb.
Characteristics-selectivity	*High.	Highly variable, but promising in a few cases.
Characteristics-accuracy	Detection at 1 ppb level may be sufficient.	Frequency shifts can be read to 1 part in 10^9, which translates to 1 part per million out of a signal from a concentration of 1 part per thousand.
Constraints-packaging (size, weight)	Hand held, volume < 1 cubic foot, weight < 5 lbs (2.3 kg).	With electronics, about the size of a pager; complete system (including computer for data acquisition) potentially suitcase sized; weight 5-10 kg for entire portable system.
Economic-development	Estimate that up to $10 million could be spent over 10 years to develop sensor system.	Some custom units are now available; there is substantial development research activity.

TABLE G-6 Key Descriptors for Sensors Using Immochemical Assays

Descriptor	Requirements (Specification)	Available (Attributes)
Characteristics-response time	< 1 minute response and recycle.	10 minutes to 2 hours; involves wet chemical steps; unattended, fieldable assay that can be remotely placed does not exist.
Characteristics-sensitivity	Approximately 1 ppb in gas phase.	Parts per trillion in best laboratory-based design.
Characteristics-resolution	Approximately 1 ppb.	Can be ~1 ppb.
Characteristics-range	From 1 part per billion to 1 part per thousand.	Can be designed for parts per trillion, or any higher level.
Characteristics-limit of detection	1 ppb.	Parts per trillion.
Characteristics-selectivity	High.	Extremely high; potentially a drawback, since slight changes in chemical structure of agent being manufactured could make kit obsolete.
Constraints-packaging (size)	Volume < 1 cubic foot.	Threshold assay field units can consist of credit card sized platform & several cigarette sized reagent vials; more precise assays require larger unit.
Economic-development	*Unit cost ~$10,000.	~$50,000-100,000 for antibodies; and $100,000 for assay kit development.

Immunochemical assays[1] offer high selectivity and sensitivity through the use of antibodies raised against specific nerve agents or classes. (Many different types of antibodies are now available from many biotechnology companies.) The assay sensor uses these antibodies in one of several schemes in which the attachment of the antibody to the target molecule (e.g., nerve agent) results in a series of chemical reactions that produce a detectable change in the final sample. As indicated in Table G-6, the main shortcomings of the current generation of these sensors involves slow response time and high cost.

NOTE

1. The term "assay" refers to the steps the technician must take and the reagents that must be used to get the final result. Wet chemical steps are usually involved, and there are no unattended, fieldable assays that can be remotely placed. Assays for at least one nerve agent, soman, have been developed.

APPENDIX H

BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

NICHOLAS G. EROR, JR. is Professor and Chairman of the Materials Science Department at the University of Pittsburgh. He received his B.S. and M.S. degrees from Yale University, and his Ph.D. in materials science from Northwestern University. His current research activities are primarily in the area of advanced ceramic materials, including dielectrics and high temperature superconductors. He is a member of the American Ceramic Society, the National Institute of Ceramic Engineers, and American Association for the Advancement of Science.

SUSAN N. COPPERSMITH is a Distinguished Member of the Technical Staff at AT&T Bell Laboratories. She earned her B.S. from Massachusetts Institute of Technology, and her M.S. and Ph.D. in physics from Cornell University. Her research interests are in theoretical condensed matter physics, notably the study of disordered materials. She has also served on the Defense Science Study Group of the Institute for Defense Analyses.

PETER D. DEAN is Senior Staff Scientist at Lockheed Missiles and Space Company. He received his B.S. and M.S. in engineering from the University of Adelaide (Australia), and his Ph.D. in applied science from the University of Southampton (U.K.). In his current position he is responsible for instrumentation and sensor system development for a variety of advanced aerospace applications. His experience and research interests include sensors for non-destructive evaluation, strain measurements in advanced composites, sensing techniques for hypersonic vehicles, and smart structures. He is a member of the American Institute of Aeronautics and Astronautics, the American Institute of Artificial Intelligence, and the Society of Photo-optical Instrumentation Engineers.

ROYCE W. MURRAY is Kenan Professor of Chemistry at the University of North Carolina, Chapel Hill where he has spent his entire professional career after receiving his Ph.D. in analytical chemistry from Northwestern University. His research interests are in electroanalytical chemistry, including surface chemistry, instrumentation, and electroactive polymers. He is a member of the NRC's Board on Chemical Sciences and Technology, and a past chairman of the Air Force Office of Scientific Research (AFOSR) Advisory Board in Chemistry under the Commission on Physical Sciences, Mathematics, and Applications. Dr. Murray is a member of the National Academy of Sciences, the Japanese Society for the Promotion of Science, and the American Chemical Society, and editor of the journal *Analytic Chemistry.*

PAUL S. PEERCY is Director of Microelectronics and Photonics at Sandia National Laboratory. He previously managed the Compound Semiconductor and Device Research and the Ion Implantation and Radiation Physics Research Departments at Sandia. He received his Ph.D. in physics from the

University of Wisconsin, Madison. His research interests include the electronic band structure of semiconductors, ferroelectric and structural phase transitions in solids, ion implantation and ion beam analysis of solids, laser-solid interactions, and advanced sensors. He is a fellow of the American Physical Society, IEEE, and AAAS. He is a member of the Materials Research Society. He is currently chairman of the Division of Materials Physics of the American Physical Society, and a Councilor of the Materials Research Society.

CRAIG A. ROGERS is Director of the Center for Intelligent Material Systems and Structures, and Professor of Mechanical Engineering at Virginia Polytechnic Institute and State University. He received his Ph.D. in mechanical engineering at Virginia Tech. He had previously worked for Bell Telephone Laboratories in Holmdel, NJ. His research interests include the use of sensors for acoustic and vibration control, damage detection in advanced composite structures, and control of composite processing. He is editor-in-chief of the *Journal of Intelligent Material Systems and Structures,* and editor-in-chief of Cambridge University Press *Materials Science and Engineering Book Series.*

DONALD R. SADOWAY is Professor, Materials Engineering, at Massachusetts Institute of Technology. He received his B.A.Sc., M.A.Sc., and Ph.D. in metallurgy from the University of Toronto. His research interests are in high temperature physical chemistry and electrochemistry, notably the electroprocessing of metals in molten salts. He was a member of the National Materials Advisory Board committee on On-Line Control of Metal Processing. He is a member of the American Institute of Metallurgical Engineers, the Electrochemical Society, the International Society of Electrochemistry, and American Association for the Advancement of Science.

JOHN R. THOME is Director of Manufacturing for the Motorola Corporation, where he was previously Advanced Manufacturing Research Manager for the Mobile Division. His responsibilities include the optimization of existing processes, and the introduction of new manufacturing processes throughout Motorola. He received his M.S. in chemistry from Marquette University. His interests and experience include the application of sensor techniques for robotics, machine vision, and electronics manufacturing. He is a past national president of International Society for Hybrid Microelectronics.

JAMES W. WAGNER is Professor in the Materials Science and Engineering and Biomedical Engineering Departments at Johns Hopkins University. Prior to joining the faculty of JHU, he was an electronics engineer with the Food and Drug Administration. He received a B.S. in electrical engineering from the University of Delaware, and an M.S. in clinical engineering and a Ph.D. in materials science and engineering from the Johns Hopkins University. His research interests are in optical sensing methods, notably the use of holographic, interferometric, and related techniques for the non-destructive characterization of materials. Dr. Wagner coordinates sensors research at the JHU Center for Nondestructive Evaluation.

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STEVEN LECLAIR is currently chief of manufacturing research at the Air Force's Wright Laboratory Materials Directorate. Prior to his appointment to the Materials Directorate in 1993, he was a visiting research scientist for the BF Goodrich Company. Previous assignments included a position as project manager for the Air Force's Integrated Computer Aided Manufacturing program and technical director of manufacturing research within the Air Force Materials Laboratory. He received a B.S. in industrial technology (electronics) from the University of Wisconsin; a B.S. in electrical engineering, and a M.S. and Ph.D. in industrial engineering, from Arizona State University. His research interests are in intelligent material processing and feature-based design for manufacturability.

ROBERT HUGHES, is a Distinguished Member of Technical Staff in the Microsensor Department at Sandia National Laboratories. He previously managed the Microsensor Division and a number of other groups since joining Sandia in 1966. He received his Ph.D. in physical chemistry from Stanford University in 1966. Currently his research in sensor science emphasizes the use of silicon microelectronics in both chemical sensing and radiation sensing. He is a fellow of the American Physical Society.