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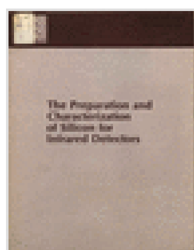

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Professor, Aeronautical and Astronautical Engineering
University of Illinois Urbana
101 Transportation Building
Urbana, IL 61801

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[illegible]cutive Director

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- Device process-induced contamination.

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Recommendations for meeting the materials requirements as specified in the charge to the committee have been made in each pertinent chapter.

Materials requirements for high-speed, high-sensitivity IR detectors as specified in the charge are significantly beyond the present capability of crystal growth technology. The preparation of ultrahigh-purity polysilicon can be achieved in principle by upgrading or modifying present purification procedures. However, the preparation of both ultrahigh-purity and homogeneous uncompensated In-doped single-crystal silicon, either by Czochralski growth or by float-zoning, with the established procedures is impossible. Substantive modifications of conventional crystal-growth procedures and the development of appropriate alternative approaches to silicon crystal growth, now in the research stage, are mandatory to meet the materials requirements. Process-induced contamination must be significantly reduced if the stringent property requirements are to be maintained through devide fabrication. At the present level of research and development, it cannot be expected that high-speed, high-sensitivity, silicon-based IR detectors will be available for use in the foreseeable future.

THE PREPARATION AND CHARACTERIZATION OF SILICON FOR INFRARED DETECTORS

Report of
The Committee on the Preparation of
Ultrahigh-Purity, Low-Boron Silicon

NATIONAL MATERIALS ADVISORY BOARD
Commission on Sociotechnical Systems
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The 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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DEDICATION

The NMAB Committee on the Preparation of Ultrahigh-Purity, Low-Boron Silicon dedicates its report to the late Mrs. Elizabeth (Beth) H. Tarrants, who functioned as liaison representative and competently as well as graciously assisted the staff officer and the committee in early stages of the study program. Beth, Supervisory Physicist at the Air Force Materials Laboratory at Wright-Patterson Air Force Base, supplied much needed background information on the study topic to the committee. Her strong background in chemistry gave her deep insight into crystal growth processes and placed her in a highly respected position among her peers. Beth was one of the first scientists to recognize the potential problems caused by a limited U.S. capability to produce adequate silicon for sensitive IR detection devices, and it was through her insight and dedicated efforts that a program was initiated to develop a domestic source. Fortunately, she did see her work leading to the implementation of an automated pilot line for IR-type silicon crystal growth with maximum control of all manufacturing phases. The committee members and the liaison representatives from the various government agencies regret her passing and that she cannot share in the product of this study program.

ABSTRACT

Materials and processing requirements for IR-type silicon were analyzed and defined. The status of the related processing technology was reviewed and deficiencies were identifed. The major subjects addressed are:

- Device needs.
- Materials characterization.
- Preparation of polycrystalline silicon.
- Preparation of single-crystal silicon.
- Device process-induced contamination.

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PREFACE

The NMAB Committee on the Preparation of Ultrahigh-Purity, Low-Boron Silicon was formed at the request of the Department of Defense and the National Aeronautics and Space Administration. Its charge was:

> To assess the status of the production technology for ultra-high-purity silicon to determine its capability to produce silicon with a boron impurity content in the $10^{11}/cm^3$ range. Various approaches to silicon production and purification will be investigated which have the potential to yield a material suitable for high-sensitivity infrared detectors used in surveillance and reconnaisance systems. Processing technology will be identified which can ensure appropriate purity control and uniformity through all production stages; from the single crystal through device processing. A survey of the status of analytical techniques and materials characterization procedures will be included for impurities other than boron which interfere with device performance. Recommendations will be made as to where R&D efforts should be directed to meet materials requirements for infrared devices.

It should be noted that the original charge, which focused exclusively on materials requirements for intrinsic silicon detectors, was considered too restrictive. Upon recommendation by the committee, the charge was modified to include both the materials requirements for extrinsic detectors and the crystal growth and processing steps that follow polysilicon production. Thus, single crystal growth, doping procedures, and basic device processing are covered in appropriate chapters of this report. (A significant number of the recommendations made in this report have the objective of obtaining a reliable supply of high-purity infrared-detector-grade silicon. No judgment is provided on the merits of this objective relative to other approaches to obtaining infrared detectors with equivalent performance based on alternative electronic materials.)

Early in its deliberations the committee recognized that the preparation of infrared-grade silicon is of concern to agencies other than those sponsoring this study. The committee thus invited representatives from all interested government agencies to participate (see liaison representatives on committee roster).

To provide the best available answers to all questions raised, inputs were also obtained from recognized scientists and process engineers in the pertinent areas. The issues are dealt with in various chapters, each of which was the responsibility of one or two members of the committee. All committee members contributed to all chapters of this report.

It is of interest to examine briefly the status of electronic materials processing in the United States through an analysis of activities related to crystal growth. The publication record of industrial, government, and academic laboratories indicates that basic and applied research as well as long-range development have been noticeably reduced over the past several years. Deficiencies in materials processing capabilities are acknowledged and attributed in part to a lack of sufficient market incentives to attract industry action, to corporate policies in a declining economy, to inadequate government support, and to government policies as they relate to sponsored research. While government and industry share the responsibility for the status of our processing potential, additional factors must not be overlooked. One of the most important of these consists of the inability of the materials science and engineering community to establish meaningful and sustained lines of communications with the government and with corporate management.

Many individuals over the years have voiced their concern about the long-range consequences of industrial electronic materials research that reflects expediency rather than long-range corporate and national interests. The desirable advancement of processing technology for bulk electronic materials is impeded, moreover, by traditionally poor interaction between the materials and device processing communities. This deficiency originates largely in as-yet uncertain, unexplored, and frequently disputed correlations between deficiencies in starting materials (silicon wafers, for example) and the yield and performance of devices. As a consequence, it has become expedient in device fabrication to suppress adverse effects of materials deficiencies in substrates to the extent possible through modifications of device processing steps. This approach to a large extent is responsible for the inadequate attention paid to the production of electronic materials in bulk form and thus for the fact that crystal-growth technology has become a limiting factor on desirable advances in several areas of device technology.

The primary deficiency of crystal-growth technology is its largely empirical basis, which reflects a significant gap between theory and experiment in crystal growth and impurity segregation. While processing procedures so far have satisfied the materials requirements for device fabrication, they are found to be increasingly inadequate for many devices now in the development stage. The supply picture for adequate electronic materials is tenuous and is complicated by the need for foreign imports and rèliance on foreign technology (large-diameter silicon growth by float-zoning) to meet domestic production requirements.

It is of interest to consider the need for significant advances in processing technology as perceived by industry and the government. The solid-state device development sector generally considers advances in crystal-growth technology desirable but not mandatory. The prevailing attitude is that the emerging needs will somehow be met. This study shows that the status of crystal growth technology in the United States is inadequate to meet the requirements of projected DoD- and NASA-related device technology and that advances beyond the state of the art are mandatory to preserve national interests. The findings of this study suggest strongly that the solid-state industry should examine the long-term consequences of its present research and development effort, that the government should examine its attitude and policies toward sponsored industrial research, and that it is in the national and corporate interest that both cooperate in the formulation of a viable national materials policy.

August F. Witt, Chairman
Committee on the Preparation of
Ultrahigh-Purity, Low-Boron Silicon

ACKNOWLEDGMENTS

This study was conducted by a committee of technical experts incorporating the viewpoints of the manufacturer, designer, and user. Committee members acted as chapter coordinators responsible for combining the inputs from the committee and guest contributors. The numerous suggestions made by the liaison representatives are gratefully acknowledged. They normally lend guidance to study panels, but, in this study, their expertise in specific areas provided valuable background data to the committee.

Scientists and process engineers from IBM, Texas Instruments, Western Electric, Wacker-Chemitronic, and Shin-Etsu made significant contributions to this report. Acknowledgement is made to E. L. Kern and other members of the Hughes technical staff who supplied valuable unpublished technical data on recent crystal-growth developments. Of particular help were technical inputs and discussions from J. A. Baker of Monsanto. Special acknowledgment is given to the participants in the two-day workshop held at the National Academy of Sciences. A listing of the participants and their topics is given in Appendix B.

The committee, and particularly its chairman, wish to express their sincere appreciation to George Economos, staff officer of NMAB, for his support and contributions as well as for his patience during the preparation of this report. The assistance provided by Maria Kneas, secretary to the staff officer, is sincerely acknowledged.

Committee on the Preparation of Ultrahigh-Purity, Low-Boron Silicon

Chairman

AUGUST F. WITT, Professor of Materials Science, Department of Materials Science and Engineering, Massachusetts Institute of Technology Cambridge, Massachusetts

Members

KENNETH E. BENSON, Supervisor, Semiconductor Materials and Analytical Support Group, Bell Telephone Laboratories, Allentown, Pennsylvania

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ROBERT N. HALL, Signal Semiconductor Branch, Signal Electronics Laboratory, General Electric Company, Schenectady, New York

GEORGE E. STILLMAN, Professor of Electrical Engineering, University of Illinois, Urbana, Illinois

Technical Advisor

EDWARD L. KERN, Project Manager, Solid State Products, Industrial Products Division, Hughes Aircraft Corporation, Carlsbad, California

Liaison Representatives

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PATRICK HEMENGER, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio

CHARLES SAHAGIAN, RADC/ESM, Hanscom Air Force Base, Massachusetts

RICHARD A. REYNOLDS, Materials Sciences Offices, Defense Advanced Research Projects Agency, Arlington, Virginia

JOHN R. CARRUTHERS, NASA Headquarters, Washington, D.C.

BERNARD RUBIN, NASA Headquarters, Washington, D.C.

W. MURRAY BULLIS, Electronics Technology Division, National Bureau of Standards, Washington, D.C.

HOWARD LESSOFF, Electronic Materials Technology, Naval Research Laboratory, Washington, D.C.

THOMAS R. AuCOIN, Materials Synthesis, USA ERADCOM, DELET-ESY, Ft. Monmouth, New Jersey

JEROME PERSH, Staff Specialist for Materials and Structures, Office of Deputy Under Secretary of Defense for Research and Engineering (ET), The Pentagon, Washington, D.C.

NMAB Staff

GEORGE ECONOMOS, Staff Officer

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Chapter One

SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

1.1 Present Production and Supply of High-Purity Polysilicon for IR Devices

The sole producer of high-purity silicon for infrared (IR) detectors in the United States is Dow Corning. The material, although adequate for device fabrication, suffers from excessive boron and carbon contamination. The supply is based on the selection of polycrystalline rods of exceptional purity from electronic-grade silicon production; it is considered tenuous, being afflicted with uncertainties concerning both quality and quantity.

Noteworthy in the supply situation is the fact that the silicon-purification process used by Dow Corning (involving trichlorosilane) (Bishoff, 1964) appears to be not as readily amenable to a significant reduction of boron contamination as the silane purification process. Accordingly, Dow Corning does not consider processing modifications aimed at reducing the residual contamination level. In contrast, Japanese manufacturers, focusing on better control and exploitation of known technology, anticipate the production of improved IR-type silicon in the near future.

In view of the limited market for IR-type silicon, it is recommended that:

- the short-term supply within the United States be stabilized, in view of the limited market, by giving the manufacturing industry adequate financial incentive to continue production;

- efforts should be made to establish the nature and origin of all contaminating elements in IR-type polysilicon;
- industry should be encouraged to adopt, in the design of new processing facilities, purification procedures that yield silicon of increased purity; and
- stockpiling by government agencies (or the private sector) of electronic-grade polysilicon should not be considered in spite of the tenuous supply situation.

The last item obviously would be taken care of if domestic and foreign sources are given the incentive to modify their facilities to yield IR-grade material. Moreover, large-scale stockpiling must be considered a potential impediment to efforts aimed at achieving improved purification procedures.

1.2 Production of Ultrahigh-Purity Polysilicon for IR-Devices (Boron Content $10^{11}/cm^3$)

No certain assessment of the gap between present processing capabilities and the specified materials requirements can be made at this time. Quantitative chemical analyses of raw, ultrahigh-purity polysilicon are missing, and the precise materials requirements for high-speed, high-sensitivity IR detectors, particularly as far as contamination by elements other than boron is concerned, are still to be determined. The limited evidence available suggests, however, that the materials requirements specified in the charge to the committee cannot be met today with established U.S. processing technology.

It is recommended that the development of an ultrahigh-purity polysilicon production capability of required capacity be pursued so as to make it an operation which is parallel to but independent of large-scale, electronic-grade polysilicon production. The trichlorosilane purification process, used for conventional polysilicon

production, should be considered together with alternative approaches such as the silicon tetrachloride and the silane processes for their potential in reducing residual contamination in silicon to below the levels specified. Particular emphasis should be placed on the removal of boron, carbon, and oxygen from silicon.

It is strongly recommended that polysilicon production and silicon crystal growth be vertically integrated to minimize overall contamination in single crystals.

Implicit in the development of ultrahigh-purity polysilicon processing facilities is the availability of reliable, quantitative analytical techniques for measuring all impurities at the concentrations of concern. It is essential that appropriate techniques be identified and developed to make them applicable to industrial production.

In establishing support for the research and development required to make IR-type silicon production a stable activity, it must be recognized that at present there is little economic incentive for private industry to serve the market represented by the IR-detector community. The IR-type silicon supply can be stabilized only through a commitment of funding adequate to support the needed research and production capability with assurance of long-term continuity for the program.

1.3 Silicon Single Crystal Growth

The crystal-growth procedures used to produce intrinsic and extrinsic silicon are marginally adequate to meet the requirements for the present generation of IR devices. The same growth procedures are considered inadequate, in terms of contamination and composition control, for the projected generation of devices, including monolithic focal-plane arrays. Specifically, uncontrollable longitudinal and radial macro- and microsegregation inhomogeneities adversely affect performance in extrinsic devices and reduce significantly the effectiveness of neutron transmutation doping for the compensation of boron contamination in intrinsic devices.

Considering the quality of the best contemporary silicon crystals and the gap between theory and experiment in crystal growth, it is likely that advances in crystal-growth technology, rather than the development of improved silicon purification procedures, will control the rate of advance in IR-device technology. Despite this it is very unlikely that an intensive research effort in the area of crystal growth will lead in the near future to the production of ultrahigh-purity or heavily doped silicon single crystals that approach the desired theoretical degree of chemical and crystalline perfection.

With this premise, it is recommended that research and development be focused on the following problems: (a) identification and reduction of primary growth-induced silicon matrix deficiencies which adversely affect device performance and fabrication; (b) indentification and reduction of crystal-growth-related contamination; and (c) development of alternative nonconventional approaches to the production of improved intrinsic and extrinsic IR-grade silicon single crystals.

1.4 Materials and Process Characterization in Silicon IR-Device Technology

Materials and process characterization as practiced by the evolving silicon IR-device technologies in all processing phases up to device fabrication, is highly deficient and must be considered a rate-determining factor for projected advances. Existing inadequacies arise from the stringent purity requirements with impurity concentrations which are below the measurement capabilities of the characterization techniques now used. Advanced materials-characterization techniques with the capability of providing the required quantitative information at the concentrations of concern are complex research instruments which require professional expertise for both acquisition and interpretation of meaningful data. Considering the modest market for IR-type silicon, industry considers the expense associated with the acquisition and use of such characterization facilities unjustifiable. It is noteworthy that the precise impurity content of polycrystalline silicon rods is as yet unknown and that only sporadic attempts have been made to characterize quantitatively the silicon-crystal growth process and associated phenomena.

To provide a basis for a comprehensive approach to the characterization of IR-type silicon, which is considered a prerequisite for a satisfactory device technology, it is recommended that:

- A dialogue be established (through a series of workshops) between experts in advanced methods of electronic materials characterization, IR-device physicists and engineers, the scientific and engineering community concerned with silicon single crystal growth, and experts in polysilicon preparation. The dialogue should focus on familiarizing the materials-processing community with the status of advanced characterization techniques and on providing to experts in characterization the precise analytical requirements for IR-device technology. Analytical approaches meeting, or considered capable of meeting, the requirements are to be identified and efforts initiated to develop appropriate facilities which can be operated reliably in production.

- Sponsored work in IR-device development and fabrication should include a strong materials characterization component to establish cause-and-effect relationships between materials properties and device yield and performance. Considering the importance of IR-device development, it is recommended that the capabilities of NBS, the national laboratories and academia be applied to the development of standarized analytical approaches.

1.5 Contamination Associated With IR-Device Processing

The full extent to which process-induced contamination limits the performance of silicon infrared detectors is as yet not well established. Available data suggest that contamination in finished devices significantly exceeds residual contamination in unprocessed high-purity wafers. While it appears feasible to produce silicon crystals with adequate purity control, it is unlikely that this degree of purity can be maintained through device processing unless major improvements in the processing environment can be achieved or cleaner

alternative processing techniques are established. Reduction of process-induced contamination is mandatory and must be pursued with at least the same intensity as the problem of producing ultrahigh-purity silicon in single crystal form.

With the development of appropriate characterization techniques, it is recommended that:

- the effects of process-induced contamination on device yield and performance be ascertained;

- the primary sources of interfering contamination be identified; and,

- steps be undertaken to reduce such contamination to below tolerance limits.

REFERENCE

Bishoff, F., "Method for Producing Pure Silicon", U.S. Patent No. 3,146,123 issued to Siemans Aktiengesellschaft, August 25, 1964.

Chapter Two

INTRODUCTION

The development of intrinsic infrared (IR) detectors has resulted in a need for high-resistivity silicon with a purity control significantly exceeding that required for most conventional silicon devices. The demand for IR-type silicon, however, was and can be expected to remain small in the foreseeable future because of the materials limited consumer market. Thus, it is not surprising that the major commercial silicon suppliers are reluctant to establish the special processing facilities necessary to meet the tight property specifications. Demands are met marginally at present by a limited number of foreign and domestic suppliers of electrical-grade silicon who circumvent the need for special polysilicon preparation facilities by designating a limited number of silicon reactors at ultrahigh-purity reactors and by vacuum zone refining selected polycrystalline rods. When all factors are considered, the supply situation for IR-type silicon may best be described as tenuous.

The materials problems of silicon IR detector technology are analogous to those of solid-state device technology in general. The IR materials problems, however, are complicated by the need for technical advances beyond the state of the art in the light of a rather limited potential production volume. Thus, the established solid-state device industry, which is best qualified to make the needed advances, will commit its resources to the task only if it can be convinced that the required research and development effort will benefit its primary device market or if adequate economic incentive is given. There are strong indications that industry considers neither condition as being met at this time.

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Chapter Three

BACKGROUND TO THE STUDY

The need for silicon IR detectors has created a requirement for a reliable high-yield source of high-purity materials. Both undoped "intrinsic" and "extrinsic" detectors require starting material with background impurities reduced to at least the low $10^{11}/cm^3$ range.* This means that the boron concentration must be reduced by a factor of up to 100 below that in electronic-grade polycrystalline silicon.

3.1 Intrinsic Detectors

Silicon detectors sensitive to 1.06 IR radiation are made from p-type material with resistivity in either the 9,000-20,000 ohm-cm or the 15,000-30,000 ohm-cm range, depending on the application of the device processing, which results in erratic and generally low yields. Moreover, the resulting detectors usually had high noise and marginally high dark currents. The observed instability during device processing is frequently attributed to (a) changes in the donor/acceptor compensation ratio caused by shifts in the location of impurities within the lattice;

(b) diffusion of impurities into the device; (c) formation of complexes involving impurities such as oxygen; or (d) creation of ionized crystallographic defects. Available analytical techniques cannot distinguish between these possibilities. Therefore, the occurrence of all possible phenomena must be reduced by (a) using starting material with donor concentrations much lower than the residual boron concentration; (b) improving materials and device processing in terms of cleanliness; (c) reducing oxygen and carbon contamination to below $10^{15}/cm^3$; and (d) growing a material that has a low or zero dislocation density and has no other extended crystallographic defects such as twin lamallae and the like.

The specified requirements precipitated a materials improvement program based on trichlorosilane ($SiHCl_3$) with extremely low boron content obtained through distillation (Crossman and Baker, 1977). This $SiHCl_3$ is used to produce polysilicon which is vacuum float-zone refined into single crystals (high-purity boules) (Kern et al, 1977). The most significant impurity remaining in this silicon is boron; most other contaminants are removed during vacuum float-zoning, either by volatilization or by segregation and freeze-out in the tang. Atomic boron does not evaporate significantly from silicon, and its segregation coefficient is so near unity that it cannot be removed effectively by zone refining. The $SiHCl_3$ purification procedure results in silicon with (a) boron concentrations in the range of $5 \times 10^{11} - 1 \times 10^{12}/cm^3$; (b) compensation ratios of five or more; and (c) low dislocation densities. The material thus obtained has improved stability during device processing and the devices exhibit improved performance.

*Common terminology in crystal growth: $10^{11}/cm^3$ (or $10^{11}cm^{-3}$) = 10^{11} atoms per cubic centimeter.

At present, however, neither the production of polysilicon of the required purity nor the multiple vacuum float-zone procedures are under complete control, even though needs can be met on a selective basis. That is, material of the required purity must be selected from each of the two processes--it represents a relatively small fraction of the output of each. Because silicon of the specified purity is essential to a number of DoD and NASA systems, the need to review the established processing technology and identify means of improving the availability and reliability of this material is felt to be critical.

3.2 Extrinsic Detectors

Silicon doped with selected impurities is being developed as a substrate for monolithic focal plane arrays (MFPAs) which will be sensitive at longer wavelengths in the IR region (Sclar et al, 1977). For example, indium- and gallium-doped silicon are sensitive in the 3-5 mm and 8-14 mm regions, respectively. The interest in these silicon devices is based on the intent to build monolithic arrays that will include charge-coupled device (CCD) structures for signal integration and readout in addition to data processing. These arrays will be the key elements in real-time imaging systems for terrestrial, airborne, and space applications. The orderly development of the MFPA concept depends largely on processing developments leading to economic yields of suitable extrinsic (doped) silicon. The material must satisfy detector-oriented specifications uniformly over the entire area of the large wafers that are necessary for fabricating monolithic circuits efficiently in automatic processing equipment (Sclar et al, 1977). Furthermore, as with the intrinsic 1.06 mm detectors, the property specifications must be maintained through device fabrication, which necessarily involves high-temperature processing steps.

At present, the major limiting property of the material is the responsivity, the key operational parameter. The responsivity depends on several parameters, including the majority carrier lifetime, dopant concentration, concentrations of "shallow" impurities such as boron, and

on carrier mobility. Unwanted impurities and the shallow energy levels they exhibit are the basic cause of most problems with device performance. Boron, for example, causes a high dark current if left uncompensated. Boron can be compensated using nuclear transmutation doping (NTD) (Meese, 1979), if its concentration is low and it is uniformly distributed.

Another problem observed in indium-doped silicon is the X-level. This level is shallower than the energy level of indium and thus degrades the materials' responsivity at the operating temperature (Baron et al, 1979). The effect of the X-level is to lower the maximum temperature for background-limited operation Si:In MFPA's by as much as 15K. Recent evidence strongly suggests that the X-level is due to a substitutional indium, substitutional carbon-pair complex (Baron et al, 1979). Reduction of carbon contamination should therefore reduce the X-level concentration. Other impurities such as aluminum apparently introduced along with the major dopant element, are also encountered. These impurity problems can be controlled to some extent by compensation, but during array processing, the charge carrier balance is upset and the responsivity degrades dramatically because of rearrangement of the impurities.

The fundamental areas requiring attention are: (a) control of the dopant concentration and distribution (which includes uniform distribution of the unavoidable background boron); (b) reduction of residual impurities from all sources to less than one part in 10^{11}; (c) examination of less familiar dopants to obtain close matching of spectral response to the mission (Vydyanath et al, 1979; Sclar, 1976, 1977); (d) exploitation of new crystal-growth procedures for incorporating dopants in silicon; and (e) optimization of material properties for different detector configurations. As with the intrinsic devices the purity of the starting material and the crystal-preparation procedures are critical to reliable production of uniform and highly sensitive detectors.

3.3 Foreign Technology and the Availability of Ultrapure Silicon

The sources of ultrapure silicon for infrared detector applications are limited to the "trailend" of a distribution of purity levels associated with large-scale production of semiconductor-grade silicon. Reliance on such sources has resulted in uncertain supply and dependence on all available sources, both foreign and domestic. Consequently, an examination is required of the influence of foreign technology on the availability of ultrapure silicon and the techniques by which supply can be assured to meet anticipated demands strategically important to the United States.

3.3.1 Supply Picture

Silicon processing technology comprises four steps: chlorination of metallurgical-grade silicon to produce $SiHCl_3$; purification of $SiHCl_3$ by fractional distillation; production of pure polysilicon by chemical vapor deposition (involving hydrogen reduction processes); and growth of single crystals from the polysilicon (Matlock, 1977). Complications in the supply of silicon are exacerbated by the interrelations between foreign and domestic suppliers who license the technology as well as market the silicon.

Sources of Polysilicon: Worldwide production capacity for semiconductor-grade polycrystalline silicon is about 2,400 metric tons annually (1977 estimates, R.I. Scace, National Bureau of Standards, private communication). Almost all of this silicon is produced by the trichlorosilane process patented by Siemens in Germany. The boron contamination in polysilicon at levels of $10^{12}/cm^3$ is believed to be due primarily to inadequacies in the trichlorosilane process. Refinements or modifications of established processing technology aimed

at reducing this boron contamination apparently are not attractive to suppliers because of the small and uncertain market for IR-type silicon. Nevertheless, several silicon suppliers produce a range of polysilicon that extends to about 1 x 10^{12} boron/cm^3 when prepared in single-crystal form. These supplier are: Dow-Corning, U.S.; Topsil, Denmark; Wacker-Chemitronic, Federal Republic of Germany; and Shin-Etsu, Japan. Of these Dow-Corning is the only U.S. supplier selling polysilicon in the specified purity range.

The supply of low-boron silicon is controlled by the demand, which, while increasing, remains only a fraction of one percent of total silicon production. This quantity can be obtained from the tail end of the conventional semiconductor-grade silicon production line, but reliance of this source involves certain complications:

A. Suppliers do not maintain an inventory of tail end materials, and silicon suitable for IR detector fabrication is sold as semiconductor-grade silicon unless there is a specific order for the detector-grade materials.

B. The supply of conventional semiconductor-grade silicon is subject to significant market perturbations. When demand is strong, as at present, silicon suppliers are reluctant even to consider small-volume specialty orders.

Sources of Single Crystals: The supply of single crystals of low-boron silicon is rather limited, reflecting demands, and is complicated by special processing requirements. The complications involve the uncertain supply of polycrystalline rods suitable for growth by float-zoning as well as the requirement for crystals of 25 mm diameter, about one third the size of commercial electronic-grade material. Consequently, growth float-zoned, IR-type silicon has been funded thus far as an independent, specialized operation at four domestic corporations: Hughes Industrial Products Division; Westinghouse; Rockwell International; and Texas Instruments. The commercial producers are:

A. Domestic: Hughes Industrial Products Division
Rockwell International
Texas Instruments (for internal use only)

B. Foreign: Wacker-Chemitronic (FRG)
Topsil (Denmark)*

The best commerically available material contains 5-6 x 10^{11} boron/cm^3. The best IR-type silicon single crystal known to have been produced to date has a boron content "estimated" at 3 x $10^{11}/cm^3$.

In view of the uncertainties in the supply of IR-grade silicon, different courses of action have been considered by various government agencies. Thought was given to using U.S. government procurement to create an artificial demand so that enough IR-grade silicon could be stockpiled to meet the needs of the next several years. The Federal Preparedness Agency (FPA) concluded, however, that the usage was too small for stockpiling and that the Department of Defense should stockpile for its own needs. It has also been suggested that the U.S. Customs Service include IR-grade silicon on its list of strategic materials. Such an action would initiate reporting activities by the Customs Service which would continuously provide data on current production quantities and estimates of future supply.

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*Wholly owned by Motorola.

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Chapter Four

DEVICE NEEDS

Intrinsic and extrinsic infrared photodetectors require silicon with very low concentrations of total extraneous impurities to achieve maximum sensitivity. The intrinsic detectors are reverse-biased, p-n junctions (actually, p-intrinsic-n, or PIN detectors); the extrinsic detectors are cooled, impurity-doped photoconductors. High-purity silicon is needed for intrinsic detectors to obtain wide depletion regions for high quantum efficiency at relatively long wavelengths ($\lambda = 1.06$ μm). It is needed for extrinsic detectors to minimize dopant-compensating impurities and other majority impurities with smaller ionization energies that decrease the desired device sensitivity.

4.1 Intrinsic Detectors

The performance specifications generally given for system applications of PIN or avalanche photodiodes (and for any other photodetector) are the wavelength to be detected, λ, the quantum efficiency at the operating wavelength, $\eta(\lambda)$, and the noise-equivalent power (NEP), i.e., the minimum optical power required to obtain a given signal-to-noise ratio in a 1 Hz bandwidth.

The modulated optical power (P_o) required to obtain a power signal-to-noise ratio, S/N, with a PIN detector (Stillman and Wolfe, 1977) is given by

$$P_o = \frac{2h\gamma B}{\eta}\left(\frac{S}{N}\right)\left(1 + \left[1 + \frac{I_{eq}}{qB(S/N)}\right]^{\frac{1}{2}}\right)$$

where

$$Ieq = I_B + I_D + 2kT_{eff}/qR_{eq}$$

In these expressions, Hn is the photon energy, B is the bandwidth, I_B is the photocurrent resulting from background radiation, I_D is the dark current, and T_{eff} and R_{eq} are the effective noise temperature and resistance of the load resistor and amplifier combination, respectively.

For ultimate sensitivity of these detectors, it is essential that the term $I_{eq}/qB(S/N)$, be negligible with respect to unity and for many applications it is possible to do this even though the required bandwidth is relatively small. When this term is negligible, the only limiting factor is the quantum noise associated with the optical signal itself, and

$$P_o = \frac{4h\gamma B}{\eta}\left(\frac{S}{N}\right)$$

For a specified photon energy, bandwidth, and a signal-to-noise ratio, P_o can be minimized only by making the quantum efficiency, η, as close to unity as possible. Even for applications where $I_{eq}/qB(S/N)$ is not negligible it is still important to have $\eta \approx 1$. This requirement places rather severe restrictions on the silicon used for these devices when the operating wavelength is 1.06 µm.

For low to moderate electric fields, the absorption coefficient, α, for silicon at 1.06 µm is only about 13 per cubic centimeter. A device that has a perfect anti-reflection coating on the front surface and is thick enough that reflections from the back of the device are insignificant, has a quantum efficiency given approximately by $\eta \approx 1 - e^{\alpha d}$ where d is the thickest of the depletion or "intrinsic" region in the PIN structure. Thus, for a quantum efficiency of 50 percent the thickness is

approximately 0.053 cm, while for 99 percent it is about 0.35 cm. For wide bandwidth applications, the transit time through thick depletion layers is a limiting factor, but for small bandwidths it is not a significant limitation. However, the requirement for depletion of thick layers at relatively low reverse-bias voltages limits the impurity concentration (net doping level) and/or the resistivity of the silicon used for these devices. For an "intrinsic" silicon layer with uniform net doping ($N = N_D - N_A$), the depletion width at an applied voltage, V, is given by $d = \varepsilon V/2\pi q N^{1/2}$ µm (or $3.64 \times 10^3 (V/N)^{1/2}$cm). The net impurity concentrations and resistivity required in silicon to obtain several different values of quantum efficiency for reverse-bias voltages of 50 and 500V are given in Table 1. It is clear that high quantum efficiency at 1.06 µm places severe requirements on the resistivity of silicon used for these applications, and it will be virtually impossible reliably to obtain quantum efficiencies $\geq$90 percent of this wavelength. If reflection from the back contact is taken into account, the net doping required can be larger by a factor of $\sqrt{2}$ and the resistivity can be lower by a factor of $1/\sqrt{2}$; however, the resistivities values required for $\eta \gtrsim 90$ percent are still not attainable consistently.

Table 1. Required Net Doping Concentrations in Silicon for 1.06 µm Intrinsic Detectors

Internal Effective η (%)	Required Depletion Width d (cm)	Bias Voltage (Volts)	Net doping for given d at the specified bias voltage (cm^{-3})	Required N-type resistivity ρ_N (Ω-cm)	Required P-type resistivity ρ_p (Ω-cm)
50	0.053	50	2.35×10^{11}	21,000	59,000
		500	2.36×10^{12}	2,100	5,900
90	0.180	50	2.04×10^{10}	240,000	670,000*
		500	2.04×10^{11}	24,000	67,000
95	0.230	50	1.25×10^{10}	410,000*	1,100,000*
		50	1.25×10^{10}	41,000	110,000
99	0.350	50	5.4×10^{9}	910,000*	2,500,000*
		500	5.4×10^{10}	91,000	250,000

*The intrinsic carrier concentration and resisitivity at 300K are about $1.5 \times 10^{10}/cm^3$ and 3×10^5Ω-cm respectively, so reduced temperatures would be necessary to achieve these values.
SOURCE: Committee data.

4.2 Extrinsic Detectors

For intrinsic detectors the only adjustable material parameter that directly affects device performance is the net carrier concentration. In contrast, for extrinsic detectors the ionization energies and the relative and absolute concentrations of the donor and acceptor species are critical to the spectral response, responsivity, noise, response time, and required operating temperature. The ionization energy of the majority impurity species controls the long wavelength cutoff and the wavelength of peak response.

The quantum efficiency of an extrinsic photodetector, including the effects of multiple reflections from its parallel front and back surfaces, is given by

$$\eta = \frac{(1-R)(1-e^{-\sigma_i N_i d})}{(1-Re^{-\sigma_i N_i d})}$$

where R is the reflectivity, σ_i is the majority impurity absorption cross-section at the wavelength of interest, N_i is the concentration of neutral impurities, and d is the thickness of the detector. The detector's operating temperature must be low enough so that the concentration of neutral uncompensated majority impurities, N_i, is not limited by thermal ionization. The shallower the impurity level, the lower the necessary operating temperature. For a given impurity level (and therefore fixed σ_i), the quantum efficiency will be maximized when (1) the majority impurity concentration is made as large as possible without introducing the effects of impurity band conduction, and (2) the concentration of compensating impurities is as small as possible. (The response time of the detector is strongly influenced by the concentration of compensating impurities, but for the monolithic focal plane arrays of interest in this study the response can be quite slow and intentional compensation is unnecessary to adjust this parameter.) If there is negligible compensation, it is also important that there be no majority impurities with shallower energy levels present since this would require a reduced operating temperature.

The sensitivity of an extrinsic photoconductive detector can be limited by noise effects from the contacts, or pickup from the surface or the amplifier. If these sources of fluctuations can be eliminated or reduced sufficiently, the ultimate sensitivity will be determined by generation-recombination noise from both thermal generation and background radiation. For a given background condition, it is possible to determine the required detector temperature for background-limited operation. If there are additional uncompensated shallower majority impurities, the temperature required to obtain background-limited performance will be much lower than that needed in the absence of these shallower impurities. The required temperature may be so low that it can not be obtained for many applications. Thus, for optimum performance of an extrinsic photoconductive detector it is important to minimize the concentration of all impurities, other than the desired majority dopant that determines the spectral response of the detector.

Although the general material requirements for extrinsic silicon photoconductive detectors are well understood, it is difficult or impossible to specify the increase or decrease in sensitivity with a change in the concentration of compensating impurities or shallower impurities for arbitrary conditions because of the wide variety of operating conditions and possible impurity levels. To gain appreciation for the materials requirements for highest performance of these devices it is informative to consider the situation for In-doped silicon (Si:In) extrinsic detectors.

The detectivity normalized to unit area and unit bandwidth, jD*, is a widely used figure-of-merit for these detectors. $D_{pk}^*(T,Q_B)$, the normalized detectivity at the wavelength of peak response for operating temperature T and background photon flux Q_B, can be written as (Sclar, 1976):

$$D_{pk}^*(T,Q_B) = \frac{D_{pk}^*T_o, Q_B(0)}{\left(\frac{p(T)}{p\ Q_B(0)} + \frac{Q_B}{Q_B(0)}\right)^{1/2}} \quad \text{cm Hz}^{1/2}\text{W}^{-1}$$

where

$$D_{pk}^*\left[T_o, Q_B(0)\right] = \frac{\lambda_{pk}}{2hc}\left[\frac{\eta}{Q_B(0)}\right]^{1/2} \text{cmHz}^{1/2}\text{W}^{-1}$$

is the usual expression for background-limited peak detectivity. (Note that a given background flux $Q_B(0)$ will determine the operating temperature T_o required to achieve background-limited operation.) In this expression, p(T) represents the thermally excited hole concentration at temperature T, and $p\left[Q_B(0)\right]$ is the optically excited hole concentration resulting from the absorbed background flux, $Q_B(0)$.

The total hole concentration for some arbitrary absorbed background flux, Q_B, in terms of a background flux $Q_B(0)$ is

$$p(T,Q_B) = p(T) + \frac{Q_B}{Q_B(0)}\, p\left[Q_B(0)\right]$$

Thus, if $p(T) << \left[Q_B(0)\right]$, the peak D* for an absorbed background photon flux Q_B is degraded from the background limited D* at T and Q_B (0) only by the factor $\left[Q_B(0)/Q_B\right]^{1/2}$. Also, for a fixed background condition and a single compensated acceptor level with an

ionization energy ΔE, the D* will vary nearly exponentially with $\Delta E/kT$ in the temperature range where $p(T) > p(Q_B)$ since p(T) will vary exponentially with $\Delta E/kT$. Figure 1 shows the variation of D_{pk}^* with temperature for several different impurities in silicon and a 300K background flux from a 60° field of view (FOV). (The absorbed photon flux depends on the value of ΔE.) Since ΔE increases for impurities from left to right in the figure, it is clear that the smaller ΔE, $\Delta E(eV) = \frac{1.24}{\lambda_{pk}(\mu m)}$, the lower the temperature must be to achieve background-limited detectivity. This is a fundamental limitation for this type of detector.

The compensation ratio will affect the behavior somewhat, since $p\,Q_B(0) = \eta \frac{Q_B(0)\gamma}{d}$, where $\gamma = [B(N_D+p)]^{-1}$ is the lifetime of the optically excited carriers, B is a recombination coefficient, N_D is the concentration of compensating donors, and p is the free hole concentration. However, this effect is not very significant for detectors with small compensation ratios. Similarly, the compensation of the majority impurities can reduce h by reducing the number of neutral majority impurities, N_i, but for $N_A = 10^{17}/cm^3$, because of indium doping and $N_D \lesssim 10^{13}/cm^3$, this changes N_i only by 0.01 percent or less, which makes this effect also quite insignificant.

A much more serious effect on the temperature required for background-limited operation occurs when there are additional shallower majority impurities such as boron. In this case p(T) is determined by the energy level of both impurities and the temperature must be significantly lower to freeze out the holes on the shallower acceptor levels. Figure 2 shows an energy diagram of Si:In with compensating phosphorus (P) donors and residual boron (B) acceptors. If the concentration of P donors can be adjusted to equal the concentration of B acceptors, the performance of the detector will be nearly the same as if the P and B impurities were not present.

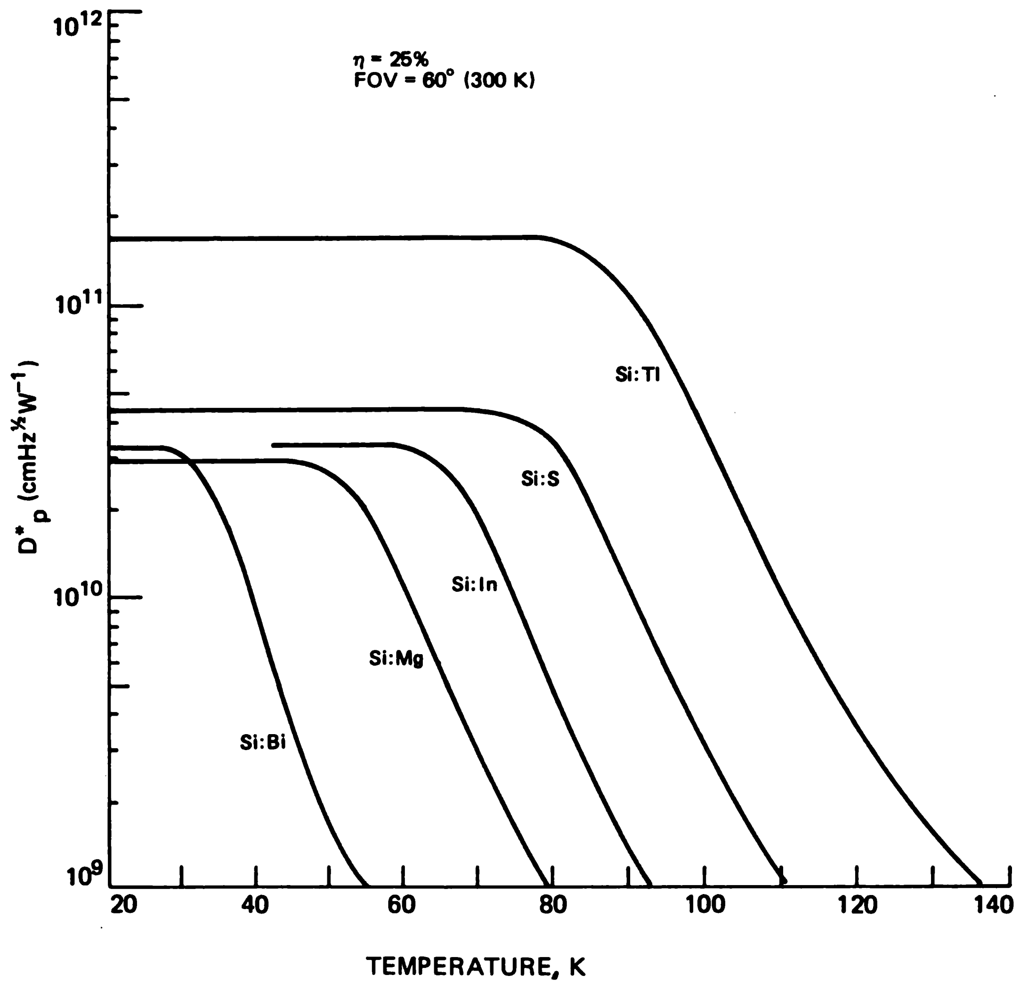

Figure 1. Theoretical detectivity curves for intrinsic silicon detectors with different dopants. (after Sclar, 1976)

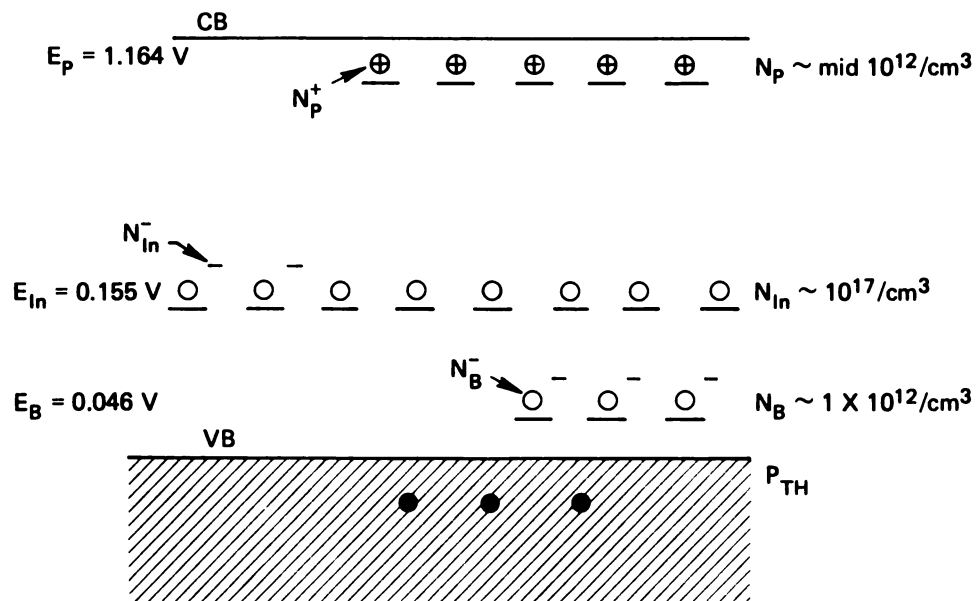

Figure 2. Schematic energy diagram of Si:In containing boron and compensating phosphorus impurities. (Presentation to the committee by R. N. Thomas, Westinghouse, 1979)

The compensation of the P donor concentration in principle can be achieved in a very controlled and adequately uniform way using transmutation doping; however, the concentration of B throughout the crystal is not sufficiently well known or sufficienty uniform to permit accurate compensation of the residual boron throughout the crystal. Slight overcompensation is necessary to eliminate all of the shallow uncompensated boron acceptors so that the temperature for background-limited operation is not drastically reduced. The penalty for this overcompensation is a slight decrease in λ, caused by a decrease in the concentration of neutral indium acceptor, and a slight decrease in the photocondutive lifetime, $\gamma = [B(N_P - N_B - p)]^{-1}$, where N_P and N_B are the concentrations of the phosphorus donor and boron acceptor respectively. If the residual boron concentration could be reduced below the background-generated hole concentration, $p(Q_B) = \eta Q_B \gamma / d$, the effects of the free carriers due to the boron would be negligible. For the 60° field-of-view of a 300K background and $\eta = 25\%$, $\gamma \approx 10^{-6}$ sec, η_{pk} 5.0 µm, $p(Q_B) \approx (0.25) \sin^2\left(\frac{\Theta}{2}\right) (2 \times 10^{-16} (10^{-6}) 0.5\text{cm} = 1 \times 10^{10}/\text{cm}^3$. Thus, for this background the net hole concentration should be much less than $1 \times 10^{10}/\text{cm}^3$. Since it is probably not feasible to reduce the boron concentration below this level, some form of compensation will continue to be necessary to keep the background-limited operating temperature of In-doped extrinsic Si photodetectors as high as possible.

There are two problems potentially more serious than the residual boron in high purity, float-zoned, single crystal silicon used as source material. The first is contamination by significant amounts of boron during the indium doping in either Czochralski or vacuum float-zoning of the indium-doped crystal. This problem presumably can be solved through purification of In as discussed in the following chapters. The second problem is the appearance of "X" levels associated with In acceptors. The ionization energy of the In "X" level is shallow enough to cause the same problem as discussed above for residual boron. Figure 3 shows the variation of D^* with temperature of three samples with different concentrations of the "X" level. As expected from the previous discussion, the operating temperature can be higher while still achieving

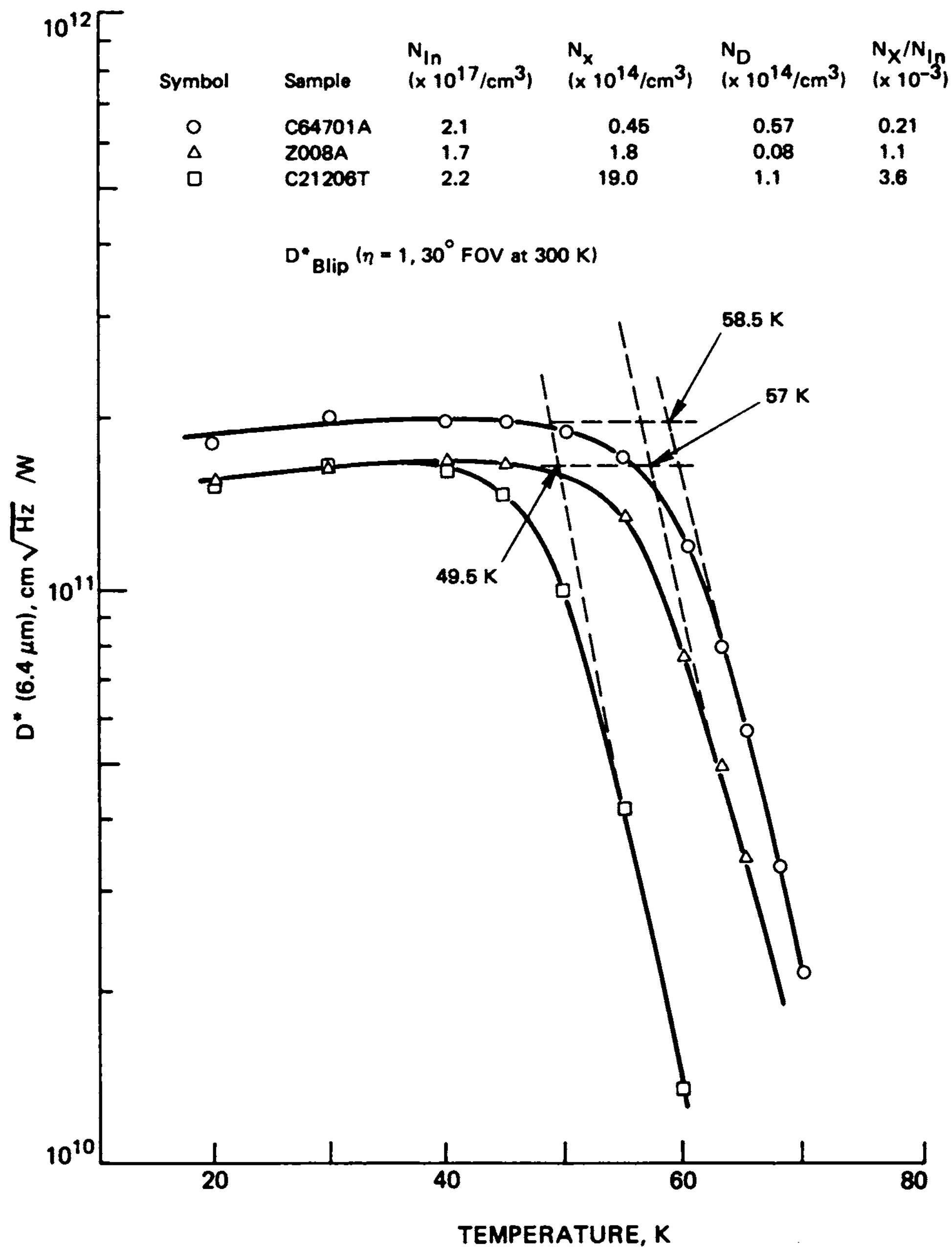

Figure 3. Variation of detectivity with concentration of X levels. (Presentation to the committee by J. Baukus, Hughes Research Laboratories, 1979)

background-limited operation for samples with lower concentrations of the "X" impurity levels. Behavior similar to that shown in Figure 3 is observed for samples with varying concentrations of uncompensated residual boron.

The origin of the "X" level has recently been identified as an In-C substitutional pair (Baron et al, 1979). Reversible changes in the "X" level concentration can be obtained by annealing at temperatures between 650°C and 850°C, with annealing at the higher temperature causing large reductions in the concentrations of the "X" level because of dissociation of the In-C substitutional pair at this temperature. While high-temperature annealing can reduce the concentration of the "X" level by nearly an order of magnitude the remaining concentration of the "X" level at the In-doping range useful for extrinsic photoconductors (N_{IN}>$10^{17}/cm^3$) is greater than $10^{13}/cm^3$. This concentration causes a decrease in the temperature for background-limited operation of Si:In detectors from about 60-70K (Figure 1) to about 49.5K (Figure 3) -- a considerable penalty to pay in the capacity of the required cooling system. (The different quantum efficiencies and field-of-view for the two figures, η =0.25, 60°FOV in Figure 1 and η = 1, 30°FOV in Figure 3 nearly cancel, but the different peak response wavelengths used permit only a rough qualitative comparison between these two figures.) If the identification of the "X" level as Si-C pair complex is correct, it is clear that it is just as important to reduce the residual carbon content of the doped Si as it is to reduce the residual boron content.

4.3 Detector Material Requirements

4.3.1 Intrinsic Detectors

The primary material requirement for high-quantum-efficiency, reverse-biased PIN detectors is low and uniform net impurity concentration. Because of the efficiency of the vacuum zone refining technique in effectively removing all impurities except boron, a reduction of the boron content in the starting material to the $10^{10}/cm^3$ level could lead to a significant improvement in the yield of suitable high-resistivity material with an increase in resistivity from the currently attainable ~20K Ω-cm to ~3x10^3 Ω-cm at room

temperature. Compensation techniques such as transmutation doping, Li-drifted diffusion, etc., should also be effective in producing material of the required resistivity, particularly if the distribution of the residual boron can be made more uniform.

4.3.2 Extrinsic Silicon:Indium Detectors

Under present conditions, reduction of residual boron in the high-purity polycrystalline starting material probably would have little effect on the yield of extrinsic silicon:indium material for monolithic focal plane array detectors, since there appears to be some evidence that larger amounts of boron are added along with indium during the doping process. This problem can be solved by improving the purity of the indium used for doping the extrinsic crystals. A more serious problem for these detectors is the presence of large concentrations of "X" levels. The concentration of these levels changes considerably during the high temperature processing steps used in fabricating monolithic focal plane arrays which makes it virtually impossible to compensate for the number of these shallower levels through transmutation doping. Limited evidence suggests that for extrinsic Si:In detectors, a reduction of the X-level concentration through reduction of the residual carbon in the crystal is as important as the reduction of the residual boron. Removal or reduction of residual carbon may well be an even more difficult problem, since carbon in silicon is electrically neutral and therefore not readily detectable at very low concentration.

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Chapter Five

CHARACTERIZATION OF HIGH-PURITY SILICON

5.1 Status of Materials Characterization in the Silicon Producing Industry

Polycrystalline silicon produced commercially in the United States and Europe for device fabrication is routinely characterized by the producer through resistivity measurements on test samples grown into single-crystal form. Information on residual impurity content is normally extracted from these measurements with the aid of the Irvin curves. Single crystals and ultimately wafers are routinely subjected to dislocation density measurements (Sirtl etch analysis) and are spot-checked for radial composition variations through four-point probe resistivity measurements. More recently, these routine characterization steps have been complemented on demand by IR absorption spectroscopy to determine primarily the oxygen and carbon content in single crystals.

Many consider this characterization procedure restrictive and deficient, but it must be pointed out that it evolved over the years through cooperation between producers and consumers and is considered adequate by the device industry. New characterization requirements (such as the analysis for swirl defect and spreading resistance measurements for microsegregation analysis) which are sensitive to sample preparation and to some extent problematic in data interpretation are customarily established by a "round robin" approach under the guidance of ASTM and with the cooperation of NBS.

The recent emergency of demand for ultrahigh-purity, low-boron silicon for IR devices required modifications of processing procedures and exposed deficiencies and limitations in the routine characterization techniques. For these reasons "polyrods" of appropriate dimension are either shipped directly (without characterization) by the producer to the

consumer and analyzed by him, or alternatively, after vacuum float-zoning, are analyzed by resistivity measurements and then shipped. The burden of proper materials characterization rests at this time with the consumer.

The silicon producing industry realizes the deficiencies in the present polysilicon characterization procedures. However, because of an increased and steadily increasing demand for silicon, there is no economic incentive for additional capital investment in characterization. The conventional silicon device market, occasional complaints notwithstanding, appears to be satisfied with the status. The specialty market, including IR device technology, becomes a liability for the silicon-producing industry because its low volume offers little chance for profits.

5.2 Characterization in Silicon Device Research and Technology

Recent years have seen the emergence of a large number of new and potentially very powerful characterization techniques such as scanning electron microscopy/electron beam induced current (SEM/EBIC), deep level transient spectroscopy (DLTS), and others. These new approaches, however, have thus far been applied to conventional silicon technology only to a limited extent.

The absolute contamination levels of polysilicon and the sources of this contamination by and large are still unknown; the contribution of crucible materials, dopant charge, and carrier gases to the impurity level of single crystals are virtually unexplored. The exception is oxygen and carbon contamination, which has been studied on a macroscale but which cannot yet be determined and studied on a microscale. Only limited work has been done on charactrization of the crystal growth process itself in spite of the fact that it is recognized directly to control impurity incorporation and macro- and microsegregation as well as defect formation. Significant efforts, involving most sophisticated techniques, have been made in wafer characterization as well as in the characterization of defect formation and contamination associated with

isolated device-processing steps such as oxidation and junction formation. These efforts notwithstanding, a quantitative understanding of the defect structure in raw silicon wafers and of growth-induced contamination and defect formation is still missing.

An analysis of the electronic materials processing community reveals a pronounced tendency of individuals and research groups to focus on one or at most a very limited number of characterization techniques. This attitude is understandable because the methods that could advance this technology generally require expensive equipment and always require expertise to facilitate, calibrate, and extract meaningful information from the raw data. At the same time the attitude is unfortunate because even the most reliable of the characterization methods currently available fall far short of providing sufficient information to accelerate the development of an understanding and control of the impurities and defects that influence detector performance. A case in point is the common reliance on the Hall measurement. This technique, in the view of a number of experimentalists in the field, offers the most relevant information, but it has limitations which, if overlooked, may lead to erroneous results and subsequently to wrong conclusions. The capabilities and limitations of the Hall and other applicable methods are outlined in Appendix A.

Clearly no one characterization technique can provide the sensitivity and spatial resolution desired for all species of interest. It is also clear that no such unique technique will be available in the foreseeable future. It is necessary therefore, to recognize the key capabilities of individual methods and to derive the comprehensive quantitative information sought by the intelligent use of a combination of techniques. For certain specific contaminants of interest, adequate characterization techniques are already available and are currently employed, but development is needed to simplify the analytical procedures and to make the interpretation of results less ambiguous. Other methods,

offering major potential advantages over the techniques used currently, require considerable development of some of the fundamental aspects for their capabilities to be fully realized, accepted, and utilized.

The fact that comprehensive silicon characterization procedures for all phases of device processing are still lacking can be attributed only in part to adequate techniques. Some factors contributing significantly to any melt-growth process, is a nonequilibrium matrix. The properties of this matrix must be expected to change during processing and the final (probably) metastable device configuration depends largely on the original defect structure, the composition on a microscale, and the thermal history through device processing. Variations of any of these parameters, even on currently ignored scales, may have significant effects on the gradually evolving electronic properties. This problem can be demonstrated, for example, by subjecting apparently identical wafers (according to accepted characterization procedures) to device processing. It is found that the yield and performance of the resulting devices vary both within each wafer and from wafer to wafer. Moreover, comprehensive materials characterization in silicon-device technology demands the cooperation and interaction of the silicon producer, the materials community in the device industry, and the device-processing community. Such cooperation and interaction to date are virtually nonexistent.

It is conspicuoüs that several of the most advanced materials characterization techniques to emerge in recent years were developed in conjunction with device research. Most of these techniques have yet to be applied to silicon technology in general and to device fabrication in particular. The existing situation in device technology, a benign neglect of substrate characterization, has a multifaceted background: (a) in epitaxial (bipolar) device fabrication the material deficiencies in substrates are generally considered largely inconsequential, while in MOS and CCD technology, on the other hand, the relationships between most process-induced defects and substrate deficiencies, and between defects and device yield and performance, are still to a large extent unsolved research problems; (b) the facilities required for comprehensive

materials characterization are not automated enough at this stage to permit their use on production lines and the required cooperative interaction between research and production personnel is largely missing.

5.3 Characterization Requirements for IR Detector-Grade Silicon

Other sections of this report provide evidence that the performance of both intrinsic and extrinsic IR detectors is strongly affected by impurities at concentrations of $10^{12}/cm^3$ and less. Both the yield and performance of devices, moreover, are adversely influenced by macroscopic and microscopic variations in dopant concentrations, which are expected to be particularly important in monolithic focal plane arrays. IR device characteristics are also influenced by crystalline defect structures in the starting crystal and/or introduced into the single-crystal lattice during device processing. The exact nature of the specific effects of impurities and crystalline defects on device performance is obscured by complex interactions. While the importance of understanding and controlling contaminants and defect structure has been recognized for some time, there are many unresolved questions regarding the sources of contaminants, the effectiveness of the various purification procedures, the requirements of the polycrystalline starting material and the single crystal prior to device processing, and the influence of processing conditions on the presence of contaminants.

The lack of quantitative information on these issues attributed largely to the unavailability of materials characterization techniques with adequate sensitivity and spatial resolution. It should be pointed out, however, that such characterization methods are indeed available for many of the species of interest. But for the most part, these methods are cumbersome and, when exercised at their maximum sensitivity and resolution, require skilled personnel for data interpretation. Moreover, all of these techniques require calibration, which imposes major problems and introduces significant uncertainties at the concentrations of interest. Most importantly, the required techniques at present are used almost exclusively in research and are not amenable to use in production.

5.4 Primary Characterization Techniques and Approaches for Silicon IR Device Technology

The evaluation of applicable characterization techniques requires detailed knowledge of materials, of the range and sensitivity of various analytical instruments, and of the reliability of the data interpretation process. This section provides a short survey of the techniques involved and the types of results expected from technique. Appendix A provides additional details for each technique.

The comprehensive matrix characterization of IR detector-grade silicon is severely complicated by the diverse nature of the defects of concern and by their concentratons which range at the low end from 10^{12} to $10^{10}/cm^3$. Since no one analytical approach covers the spectrum of required capabilities, comprehensive characterization requires a facility with many diverse, complementary techniques. While the semiconductor industry maintained some comprehensive characterization facilities geared to the needs to conventional device fabrication, few organizations can afford to maintain a facility that meets the extreme requirements of IR detector development work. Individual investigators will be forced by necessity to focus on limited areas of development. A comprehensive picture of the nature of defects in silicon and of their effects on the yield and performance of devices will emerge ultimately through synthesis of analytical results obtained in various laboratories.

Any general review of the salient advantages and disadvantages of specific characterization methods includes an element of subjectivity introduced by the experience and needs of the reviewer. In discussing the various techniques with recognized experts, it is found that analytical results that are easy for one to interpret may be difficult for another, and that wide variations are encountered in the willingness of individuals to accept the limitations of different methods. In Appendix A, an attempt has been made to indicate the effort needed for sample preparation and the effort and time required by the measurement. Even though the sources of these comments are experts in the field, the issue of effort involved must be considered subjective. It should be

noted that essentially all of the measurements must be made as a function of temperature and/or at very low temperatures, primarily because of the very low defect concentrations of concern for IR-detector silicon.

The degree to which a measurement method may be considered standardized in research use involves some subjective interpretation based on experience and need. The application of a widely used, commercially available measurement apparatus can go from a routine procedure that is generally accepted to one that is difficult to interpret as the impurity concentrations of interest decrease or the effect of interfering species present increases. For measurements of impurities such as boron in silicon within the concentration range of interest for IR-detector silicon, it must be stated that all methods used require very skilled personnel for operation and data interpretation and that several of the applicable instruments must be considered research instruments. Under these circumstances the formulation of generalizations regarding capabilities and limitations of characterization methods is difficult and perhaps even hazardous. Nonetheless, in an attempt to bring attention to the salient features of the various techniques, and to come to some logical recommendation on areas that could be usefully developed, the following comments are offered on the potentially most useful characterization techniques.

5.4.1 Hall Measurements

The key feature of the Hall measurement is that it provides a quantitative, essentially direct measure of the concentration of the majority carriers. For this reason it is commonly employed to calibrate other methods. Since only electrically active species are measured, the results may be related directly to device performance. Within the uncertainties of the value of the r-factor (which is a function of the carrier concentration), constants determined at relatively high impurity levels can be employed at lower levels. A major drawback of the Hall effect for absolute measurements is the uncertainty in the value of the r-factor. A further drawback is the need for a standard

chemical/mechanical surface treatment to avoid carrier depletion effects by surface charges. The measurement of low carrier concentrations from different contributing species requires skilled personnel for data interpretation.

Hall measurements have been widely used and accepted in the semiconductor industry. Their usefulness is greatest in the characterization of materials for devices in which the majority carrier of interest is at concentrations well above the level of residual or unwanted impurities. There appears to be a tendency to make some unjustified extrapolations from such measurements to the characterization of materials of concern for IR-detectors. At the impurity levels of interest here, and in the presence of compensating species and species with similar energy levels, the interpretation of Hall data becomes very difficult and ambiguous. The main application in the detector field has been in the selection of the polycrystalline silicon expected to be suitable for device fabrication. At this point, the need to grow a single crystal specifically to accommodate the characterization technique constitutes a major practical disadvantage and a potential source of error.

While a number of investigators in the field employ the Hall method extensively, for the reasons outlined above it cannot be considered adequate for characterizing detector-grade silicon.

5.4.2 Fourier Transform IR Spectroscopy

The major advantage of IR spectroscopy for applications in the detector field is that the concentrations of the electrically inactive carbon and oxygen can be measured. At present, there is no other satisfactory choice for determining these important constituents. The detection limits for carbon and oxygen at present are given as 2 to 10 x 10^{15} and 1 to 10 x 10^{14}atoms/cm^3, respectively; these limits are considered inadequate for IR-detector fabrication, according to recent findings. In principle, all shallow impurities in silicon can be observed. The samples can easily be prepared in a manner that does not

alter the nature of the material, and no electrical contacts are required. Single-crystal material is not required. A major drawback is the relatively large sample volume required, which increases with decreasing concentration and prevents the study of impurity distribution on a microscale. As with most of the other techniques discussed, IR spectroscopy must be calibrated against other absolute measurements, and skill is required to interpret data at the levels of impurities of interest in detector work.

Infrared spectroscopy is a versatile, well known, and widely employed technique. The marriage of IR spectroscopy and the Fourier transform technique increases its sensitivity significantly. A practical problem is the high cost of the Fourier transform equipment.

5.4.3 Deep-Level Transient Spectroscopy

Deep-level transient spectroscopy (DLTS) stands alone in its ability to measure deep-level impurities at the concentration range of interest for silicon-detector work. Since the shallowest impurities cannot be observed, DLTS must always be employed in conjunction with other methods or the samples must be doped specifically to compensate for this deficiency. Single-crystal material is required, and Schottky barriers must be fabricated. One commonly finds that for the expert practitioners involved in DLTS measurements, data collection is relatively refined but simple. On the other hand, those less familiar with the technology will have to put considerable effort into establishing this capability. DLTS certainly cannot be considered a routine measurement for detector work and it requires special skills. For obtaining information on the influence of crystalline defect structures on device performance, the marriage of DLTS with scanning electron microscopy in the electron beam induced current mode (SEM/EBIC) has proved very productive.

5.4.4 Photothermal Ionization Spectroscopy

Photothermal ionization spectroscopy (PTIS) is very effective for identifying shallow impurities in the concentration range of interest for silicon detector work. For quantitative measurements, the absorption

cross-sections must be determined. Since the measurement should not be influenced by the crystal line character of the sample, PTIS is applicable at all purification steps. The key experimental disadvantage is that contacts of low noise at low temperatures are required.

Photothermal ionization spectroscopy has not received the attention that seems warranted in the IR-detector field. With the appropriate skills, the method is relatively simple, and the analysis is rapid when used in conjunction with the Fourier transform technique. Here again, weface the practical limitation of cost, and there needs to be some consideration of the extent to which the technique is compromised if it is not employed in conjunction with the Fourier transform technique.

5.4.5 Photoluminescence

For detecting shallow impurities at very low concentrations, photoluminescence (PL) appears to offer a potential similar to that of PTIS, with the advantage that electrical contact to the sample is not required. Using semiconductor detectors, it may be possible also to determine the deep-level impurities. Single-crystal material is normally required for PL, but since the area of measurement is small ($\sim 100\ \mu m^2$), it may be feasible to make measurements within a single grain of polycrystalline material. The small area of measurement also provides the capability of investigating compositional homogeneity. PL at present is very much a research stage, and more development work is needed for it to become a routine method. Capture cross-sections of the impurities of interest must be measured if the method is to be employed for quantitative measurements. While quantitative dopant and impurity analyses of IR-grade silicon with PL have been reported in the open literature, the short-term outlook suggests that its primary use is for qualitative rather than quantitative work. The fundamentals of the PL method are less well understood than those of most other techniques.

Both photothermal ionization spectroscopy and photoluminescence require further development if they are to be widely employed for the development of IR detectors. The potentials of these two methods warrant further effort; for both methods, fundamental studies are required to

make the measurements quantitative. More detailed information is needed on the effective cross-sections, and a more complete understanding of interfering effects must be developed. To establish PTIS as a useful technique, it will be necessary to establish experimentally that the crystalline nature of the sample does not influence the measurement. This particular aspect is rather important in the identification of the sources of impurities, the identification of effective purification procedures, and the characterization of polycrystalline silicon. With PL, it may be possible to measure impurity concentrations within an individual grain of polycrystalline material because of the small sample required. The minimum grain size feasible, grain proximity effects, etc., should be further defined. The PTIS method so far has been applied more extensively in the analysis of germanium than of silicon. The limitations and capabilities for the analysis of silicon should be further investigated. The small sample required and the freedom from the requirement for low-temperature contacts make PTIS particularly attractive. The technique will not be generally accepted, however, without a more detailed understanding of the basic mechanisms involved. It is recommended that recognized experts in the use of PL and PTIS in characterization investigate the possible advances that can be expected from further development.

5.5 Recommendations

5.5.1 Development of a Realistic Perspective of the Capabilities and Limitations of Analytical Techniques

In principle, the capabilties and limitations of the various characterization techniques are uniquely defined by the underlying physical processes. Existing uncertainties in limitations reflect inadequate understanding of the processes involved, limitations in instrumentation, improper specimen pareparation, or interference by processes other than the one considered. Thus, many characterization problems encountered are symptomatic of the state of development of the particular approach to characterization and become a function of the research environment involved.

The outline presented of the capabilities and limitations of materials characterization methods in the current state of development, therefore, is far from complete and is not generally applicable. Moreover, when expert experimentalists in characterization, even those active and knowledgable in more than one method, do not agree on existing capabilities and limitations, it is not possible to develop a complete perspective. This is the case with the users of these methods, and it is often the case that one method is favored and its limitations accepted without attempting to take advantage of the capabilities of less-well-known techniques. This situation arises because much of the apparatus is expensive and not readily available, and specific skills must be developed with the expenditure of considerable time and effort. This situation could be improved by several approaches:

1. The organization of workshops designed to bring together practitioners in device design and fabrication, instrument manufacturers, and individuals concerned with materials characterization. The characterization experts could thus become more familiar with specific needs and real-world experience with currenty employed analytical methods. The experts in device fabrication in turn could be exposed to an expanded spectrum of less-well-known characterization techniques. Such workshops could be sponsored by the interested government agencies or by the various professional societies.

2. The distribution of sets of silicon samples selected from the various purification, crystal growth, and device processing steps to experts for state-of-the-art characterization by various techniques. The samples selected should be both poly- and single-crystalline. Sample sets should be distributed both to investigators versed in several characterization techniques and to a number of experts in a single characterization method. Analysis of the results would contribute significantly to the development of a realistic perspective of the capabilities of the various chracterization techniques as used by the experts in the field. This approach, for example, would provide a base of information for further development of particular powerful techniques.

3. All sponsored work pertaining to IR-device development and fabrication should include a strong materials characterization component. This procedure could insure the advancement of pertinent characterization techniques and contribute to the establishment of as-yet-unknown cause and effect relationships between materials deficiencies and device yield and performance. Such knowledge ultimately could remove much of the empirical element in materials processing.

4. The expansion of present activities of the National Bureau of Standards or another neutral institution should include standardization of analytical approaches and procedures. Existing funding limitations of NBS demand that interested government agencies sponsor programs relevant to the advancement of specific device development. But NBS involvement can benefit many programs and activities simultaneously and thus provide for cost-effective research, development, and production in industry

5.5.2 Further Development of Specific Characterization Methods for IR Materials Research

The foregoing recommendations of further discussion among experts of detectors and characterization, and round-robin analyses of selected sample sets, are designed to highlight areas where additional development in characterization techniques would be useful. Certain recommendations, however, can be made on the basis of information already available.

Hall measurements are based on a mature technology, and no fundamental advances can be anticipated. Measurements are being made successfully within the carrier concentration range of interest for IR detectors (10^8-$10^{11}/cm^3$). There is little possibility that the effort associated with these measurements or with interpreting the data can be significantly decreased. Commercial automated equipment that minimizes the effort is available. Interpretation of the data could be made less ambiguous, however, if the dependence of the r-factor on the impurity concentration, temperature, and magnetic field could be further

characterized. It is anticipated that the Hall method will remain in use in its current form and that its replacement will depend on the development of less laborious techniques.

Infrared spectroscopy is also a mature technology, and within its inherent limitations can be used effectively in the current state of development. Fourier transform IR spectroscopy is well developed and commercially available. For the common dopants, measurements are already being made at concentrations of $\sim 10^{11}$ atoms/cm^3. The present detection capability carbon and oxygen (10^{14}-10^{15} atoms/cm^3), however, is considered inadequate for the IR-type silicon. The development of this method should be in the direction of increased resolution and of making the analysis at the lower concentrations more routine and less dependent on the availability of highly skilled personnel.

Chapter Six

POLYCRYSTALLINE SILICON PREPARATION

High-purity polycrystalline silicon is used for growing single crystals, either by float-zone (FZ) or Czochralski (CZ) methods. As described in Chapter 4, the purity requirements for infrared detectors are even more stringent than those for conventional semiconductor devices. This is particularly true of traces of boron, since this element has the lowest ionization energy of the acceptor impurities and therefore has the most serious adverse effect on the operating temperature of infrared detectors.

The purity requirements of the starting material are more stringent for intrinsic ($\sim$1.06μm) detectors than for extrinsic detectors, which are intended for longer wavelength operation, because the latter involve the addition of specific dopant elements and crystal growth methods that are likely to introduce contaminants exceeding those in the starting material. This chapter will be concerned with the preparation of polysilicon for intrinsic IR detectors. Present requirements are that boron not exceed $5 \times 10^{11}/cm^3$ (corresponding to a resistivity of 30,000 ohm-cm). Boron for projected applications should ultimately not exceed the $10^{10}/cm^3$ range.

Impurities other than boron in polysilicon appear less critical. Phosphorus can be removed by segregation and evaporation during multiple FZ regrowth. Other donor and acceptor elements, including heavy metal contaminants are generally not observed. Carbon, which may be introduced from traces of hydrocarbons that survive the distillation process, is not by itself electrically active. It may, however, give rise to X-levels as noted earlier, or produce secondary effects by serving as a nucleus for other defects during device processing. Carbon therefore should be held below $\sim 10^{15}/cm^3$ after the polysilicon is converted to single-crystal form.

It should be noted that, while attempts hve been made to determine quantitatively the impurity contents in IR-type silicon single crystals, the exact impurity contents in polycrystalline material are as yet unknown. Known methods of chemical analysis are not sensitive enough for the evaluation of polysilicon. Current practice is to grow a FZ crystal and determine the boron level from resistivity measurements of portions of the crystal that have experienced different numbers of zone passes. This determination requires more than just a measurement of resistivity, since crystal defects or deep-level impurities can cause misleading results. It generally involves fitting the measured resistivity or Hall effect data to net impurity profiles calculated using the known distribution coefficients for the impurities (primarily boron and phosphorus) assumed to be present during successive zone passes. This method for evaluating the quality of polysilicon assumes implicitly that impurities are not introduced during the loading or operation of the float-zone furnace. It is likely that some of the techniques described in the preceding chapter have adequate sensitivity for quantitative analysis of residual impurities in IR-type polysilicon.

6.1 Status of Polysilicon Preparation

High purity polysilicon is made by three different methods based on the distillation of SiH_4, $SiHCl_3$ or $SiCl_4$ and subsequent reduction to silicon. Each method has been shown to be capable of meeting the purity requirements stated above, and it is not clear which has the greatest potential for further improvement. U.S. production is based entirely on $SiHCl_3$; only a small fraction of world production of semiconductor-grade polysilicon is based on the other two compounds.

More than 2400 metric tons per year of polysilicon are produced from $SiHCl_3$, principally by Dow-Corning in the U.S. and Wacker-Chemitronic in the Federal Republic of Germany. In recent years, Dow-Corning has evaluated production runs of polysilicon and has set aside material of exceptional purity to meet the needs of crystal growth for IR detectors. This material has been used by Hughes, Rockwell, and Texas Instruments to grow high-purity FZ-silicon crystals, and it is generally regarded as

being of high quality and good consistency. It is not clear whether Dow-Corning will continue this practice because of the economics of handling the small amounts of material and the special diameters of polycrystalline rod required by IR detector manufacturers.

Topsil (Denmark) produces polysilicon from $SiCl_4$ and is able to achieve boron levels of 7 to 9 x $10^{11}/cm^3$. Reduction by a factor of 10 is believed possible through redesign of the reactor. An advantage of working with $SiCl_4$ rather than $SiHCl_3$ is the greater separation of boiling temperatures of the boron-containing compounds, which makes the purification process more efficient. Topsil, now wholly owned by Motorola, could supply polysilicon made in Denmark to the U.S. market.

Komatsu is the only manufacturer producing silicon by reduction of SiH_4. Advantages of this process are that it uses no chlorine with its corrosive properties, and that the SiH_4 is distilled and reduced at much lower temperatures than with the other methods, making contamination easier to avoid. A disadvantage is the hazard associated with the high flammability of SiH_4. Union Carbide is developing a manufacturing process for low-cost, polysilicon based on SiH_4 for the Low-Cost Solar Array Project for making photovoltaic cells (Breneman et al, 1978). This work could result in a supply of high-purity SiH_4 that could be used to produce IR detector-quality polysilicon. Laser purification offers a selective means of removing traces of boron-containing impurities from SiH_4, as discussed in Section 6.2.

There thus appear to be several processes capable of producing polysilicon containing less than 5 x $10^{11}/cm^3$ boron. Problems to be overcome include resolution of the question of whether residual impurities in the FZ single crystal material came from the polysilicon or are associated with the zoning process. A further concern is whether industry demand can provide sufficient economic incentive to produce the small quantities and special forms of polysilicon needed by the IR detector market. More drastic measures evidently will be necessary to achieve another order of magnitude reduction in residual boron.

6.2 Alternatives

Polysilicon is manufactured by one major supplier and is converted to single-crystal form by another, making it difficult to determine the sources of residual impurities. Significant improvements in yield and purity will almost certainly require that both processes be carried out within a common organizational structure to facilitate the elimination of sources of contamination. The organization also should be closely associated with the manufacture of semiconductor-grade polysilicon, or single crystal silicon so it will have first-hand knowledge of these production processes. It must be recognized that the cost of the silicon produced in such a vertically integrated facility would necessarily be rather high because of the special care and equipment required relative to the small volume of material produced.

Laser purification of SiH_4 is another tool available for eliminating boron and phosphorus from polysilicon. (Clark and Anderson, 1978). Because the laser radiation is absorbed by the impurity species to which it is tuned, its effectiveness remains high or even increases as the degree of purification increases, contrary to most methods of purifications.

Several other processes may be considered for preparing high-purity polycrystalline silicon. The iodide process is effective in eliminating boron in silicon (Rubin, 1958), but it suffers from low yield and there is limited experience with scale-up of the laboratory process. Chromatographic purification is another tool that can be applied (R.J. Starks, Eagle-Picher Co., presentation to the committee, January 1979). It can selectively eliminate impurities in a gaseous intermediate such as SiH_4 or $SiHCl_3$. While these approaches may prove useful, the present outlook is that further purification can best be achieved by refining the processes now in use.

6.3 Recommendations

One of the first questions to be resolved is to what extent residual impurities are being introduced by the float-zone apparatus used to produce the single-crystal silicon. The design and operation of FZ furnaces should be studied to see how to further develop them for operation under vacuum as well as inert gas atmosphere conditions. This can best be done as vertically integrated effort in which the furnace studies are carried out in close cooperation with the manufacture of the polysilicon.

The highly sensitive detection methods described in Chapter 5 should be explored for the evaluation of polysilicon. Measurements of fluorescence radiation and photothermal ionization spectroscopy appear particularly effective for this purpose.

Laser purification has been demonstrated to be effective for the elimination of boron and phosphorus from SiH_4 (Clark and Anderson, 1978). Continuation of these studies should be encouraged, particularly if a domestic source of semiconductor-grade SiH_4 emerges, such as that under investigation by Union Carbide.

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Chapter Seven

PREPARATION OF SILICON IN SINGLE CRYSTAL FORM

The preparation of silicon-based IR detector devices requires matrices of utmost perfection and composition control. It is therefore worthwhile to review briefly the status of the two primary crystal growth techniques and analyze the requirements for the growth of intrinsic and extrinsic, heavily In-doped silicon.

7.1 Czochralski Crystal Growth

While the principles of crystal pulling by the Teal-Little technique (modified Czochralski) are well understood, it is important to recognize that the process is as yet conducted strictly on an empirical basis. Operator know-how affects significantly the quality of the single crystal matrices obtained, and advances in growth procedures are largely noncommunicable. Dislocation-free, single crystals can readily be grown; however, vacancy cluster formation, which frequently leads to complications during device processing, is prevalent. Achievement of composition control (i.e., compositional homogeneity) is rather limited. Depending on the distribution coefficient of the dopant element involved, longitudinal macrosegregation, radial segregation and microsegregation constitute problems affecting to varying extents both wafer and device yield as well as device performance for a multitude of device codes.

The primary drawback of the Czochralski technique for producing IR-type silicon is excessive contamination. Required melt confinement (quartz liners) results in unavoidable oxygen contamination of silicon at levels of about $10^{17}/cm^3$ (Figure 4). Moreover, contamination by hot zone constituents (heater elements, heat shielding, crucible support and the like) often raises the overall contamination by electrically active elements into the $10^{13}/cm^3$ range.

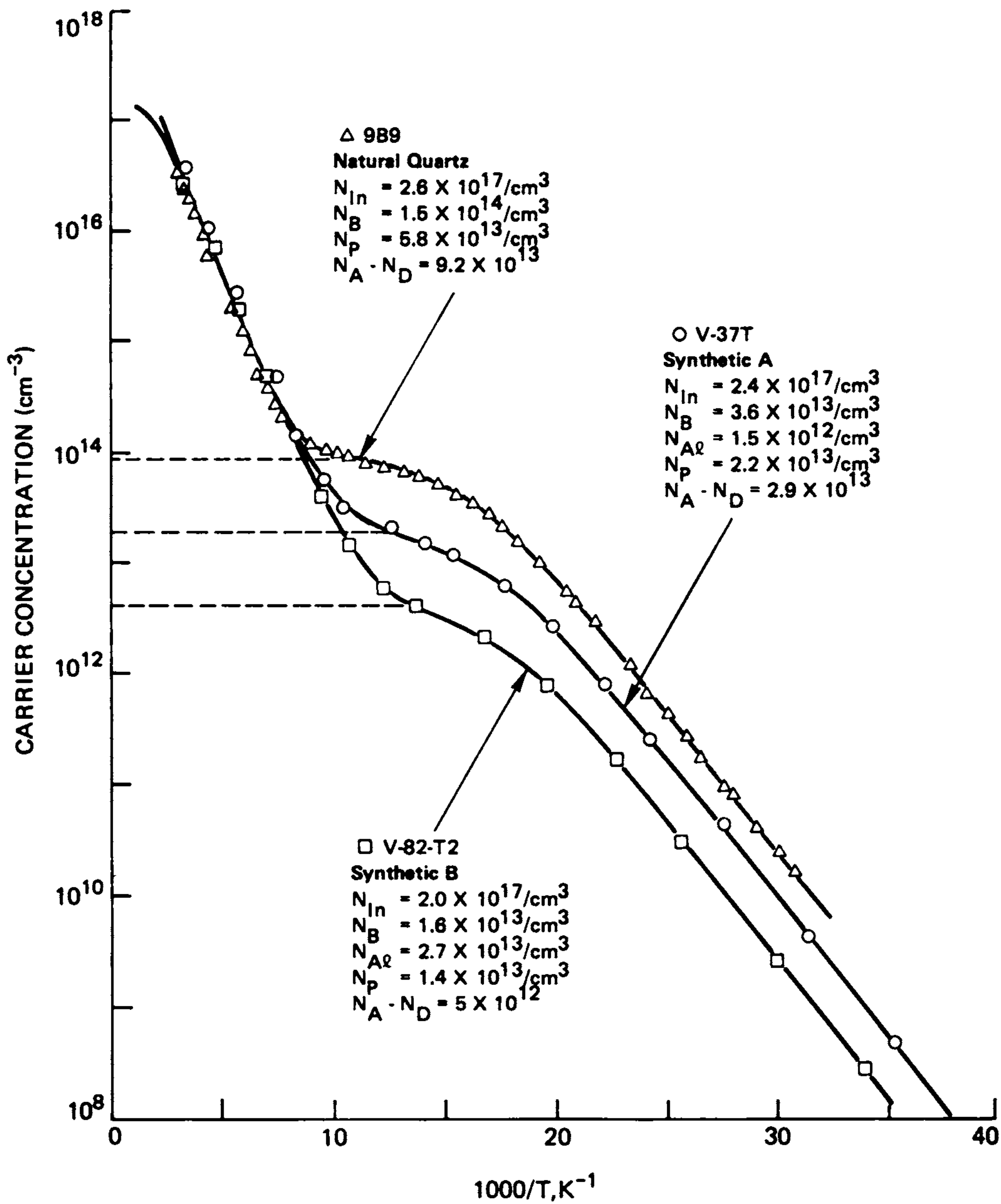

Figure 4. Carrier concentration versus reciprocal temperature for tang end samples from Si:In crystals pulled from natural quartz and synthetic quartz crucible - Type A: ~1500 ppm wt OH^-; Type B: ~5-10 ppm wt OH^-. (Presentation to the committee by R. N. Thomas, Westinghouse, 1979)

An analysis of the quality of silicon produced by Czochralski technique in the United States, Japan, and Germany did not confirm the frequent contention that silicon produced in the latter two countries is significantly superior. Several U.S. users of silicon acknowledged, however, that some narrow specifications are met more readily by Japanese producers. And it is generally agreed that Japanese processing capabilities are in a stage of development (significant integration of research with production) that makes it very likely that Japan in the near future will establish absolute superiority in silicon processing technology.

7.2 Float Zoning

Float-zoning, like crystal pulling, is largely an empirical process whose development has been neglected in the United States over the years. Until recently, virtually all float-zoning of large diameter crystals (d $>$ 3 in) in the United States was done with licensed (Siemens) facilities.

The primary advantages of float-zoning over Czochralski pulling consist of the establishment of a nonconfined melt zone and the possibility of using the same process for purification as well as for crystal growth. As with crystal pulling, a dislocation-free growth mode can readily be established. While the extent of macrosegregation is less than in Czochralski growth, control of radial segregation and particularly of microsegregation are bigger problems. Process-induced contamination in float-zoning is significantly reduced with the virtual absence of oxygen.

It is generally acknowledged that Germany and Japan are significantly more advanced in the "art and science" of large diameter silicon float-zoning than is the United States. No evidence suggests that the U.S.S.R. is industrially competitive in this crystal growth technique.

7.3 Status of Silicon Growth for Intrinsic and Extrinsic IR Detectors

The requirements of silicon matrices for use as intrinsic and extrinsic IR detectors with optimized performance (see Chapter 4) are well defined: single crystals of near theoretical crystalline perfection, free of contamination (intrinsic detectors in the 1.06 μm range) and with maximized and uniformly distributed indium as electrically active dopant (p-type extrinsic detectors in the 3 to 5 μm range). Since the best starting material available for single crystal growth contains residual boron in the low $10^{12}/cm^3$ range, the primary effort in the growth process consists of preventing further contamination, establishing dislocation-free growth without excessive point defect formation, and achieving uniform indium incorporation at the highest possible concentration. The efforts have led to the fabrication of useful devices. However, the material produced falls significantly short of meeting the theoretical specifications (outlined above) and does not approach the amended specifications now being considered. From available reports, it must be concluded that growth-induced contamination, defect formation, and significant macro- and microsegregation are encountered which lead to relatively low yields of useful wafer material as well as in low yields of devices with unknown performance characteristics.

7.3.1 Growth Induced Contamination

Growth induced contamination in float-zoned and pulled material can be attributed in principle to volatile species generated at the high temperature within the growth chamber and/or to contamination carried into the melt with the dopant element. Quantitative studies of growth-induced contamination and its exact origin are as yet missing. Limited experimental evidence for Czochralski growth confirms that impurity out-diffusion from quartz crucible liners and volatile impurities from conventional hot-zone materials contribute significantly to melt contamination (Figures 4 and 5). In the presence of active elements such as oxygen, significant evaporation of silicon from the melt

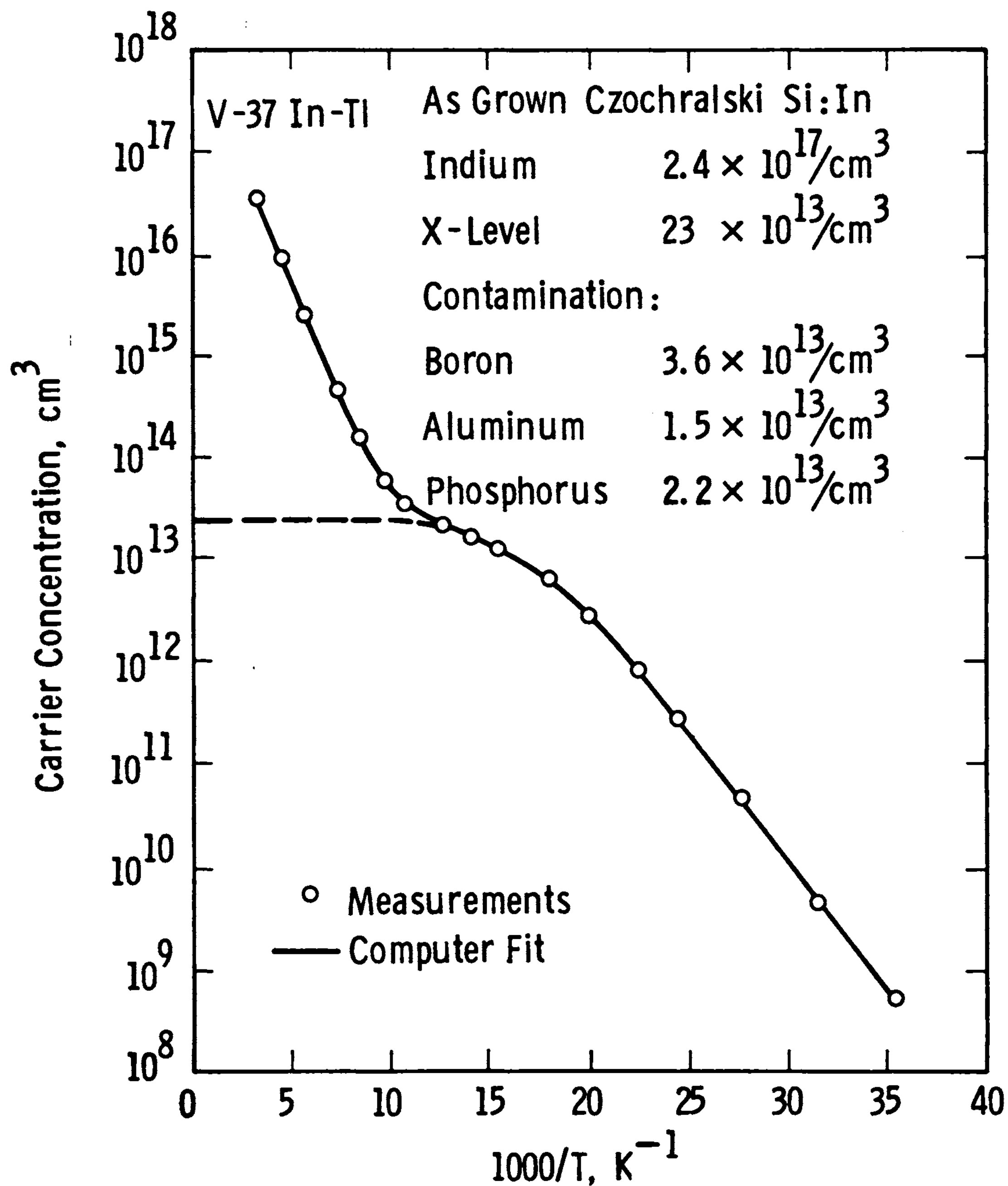

Figure 5. Thermal carrier concentration as a function of reciprocal temperature for typical Czochralski Si:In showing characteristic residual impurity contamination. (Presentation to the committee by R. N. Thomas, Westinghouse, 1979)

takes place, leading to the buildup of highly adsorbing deposits within the growth chamber. Any particles of these deposits, which are carried by the ambient gas stream back into the melt, will lead to noticeable contamination.

It has been shown that adverse side effects of p-type impurities in intrinsic material can be eliminated by compensation through neutron transmutation doping. The usefulness of this approach is limited, however, because the contamination is high overall and is nonuniform both axially and radially.

The effects of contamination on the peak responsivities of extrinsic Si:In detectors made from Czochralski and float-zoned material are compared in Figure 6. The data establish the superiority of the float-zone process for the production of intrinsic IR-type silicon. It should be noted, however, that the material thus obtained suffers from pronounced and largely uncontrollable axial resistivity (composition) fluctuations (Figure 7) and from the presence of the so-called "X-level", which adversely effect device yield and device performance respectively.

Finally, it should be pointed out that even in float-zoning, the "cleanest" growth technique available, the risk of extraneous contamination is rather severe. A particle of only 10 μm diameter is sufficient to contaminate a 0.5-kg charge to unusable levels. The need to avoid contamination imposes clean-room procedures on the entire operation. For example, the polycrystalline silicon rod must be contacted only with noncontaminating materials such as mylar, and all mechanical processes, such as sawing, grinding, etc., are to be avoided prior to growth. Even the use of electronic-grade solvents in the preparation of seed material may give rise to excessive contamination.

7.3.2 Indium Doping of High-Purity Silicon

High-speed and high-responsivity extrinsic indium-doped silicon detectors require uniform, highest possible doping levels (in the $10^{17}/cm^3$ range) with a minimum background impurity level. The latter

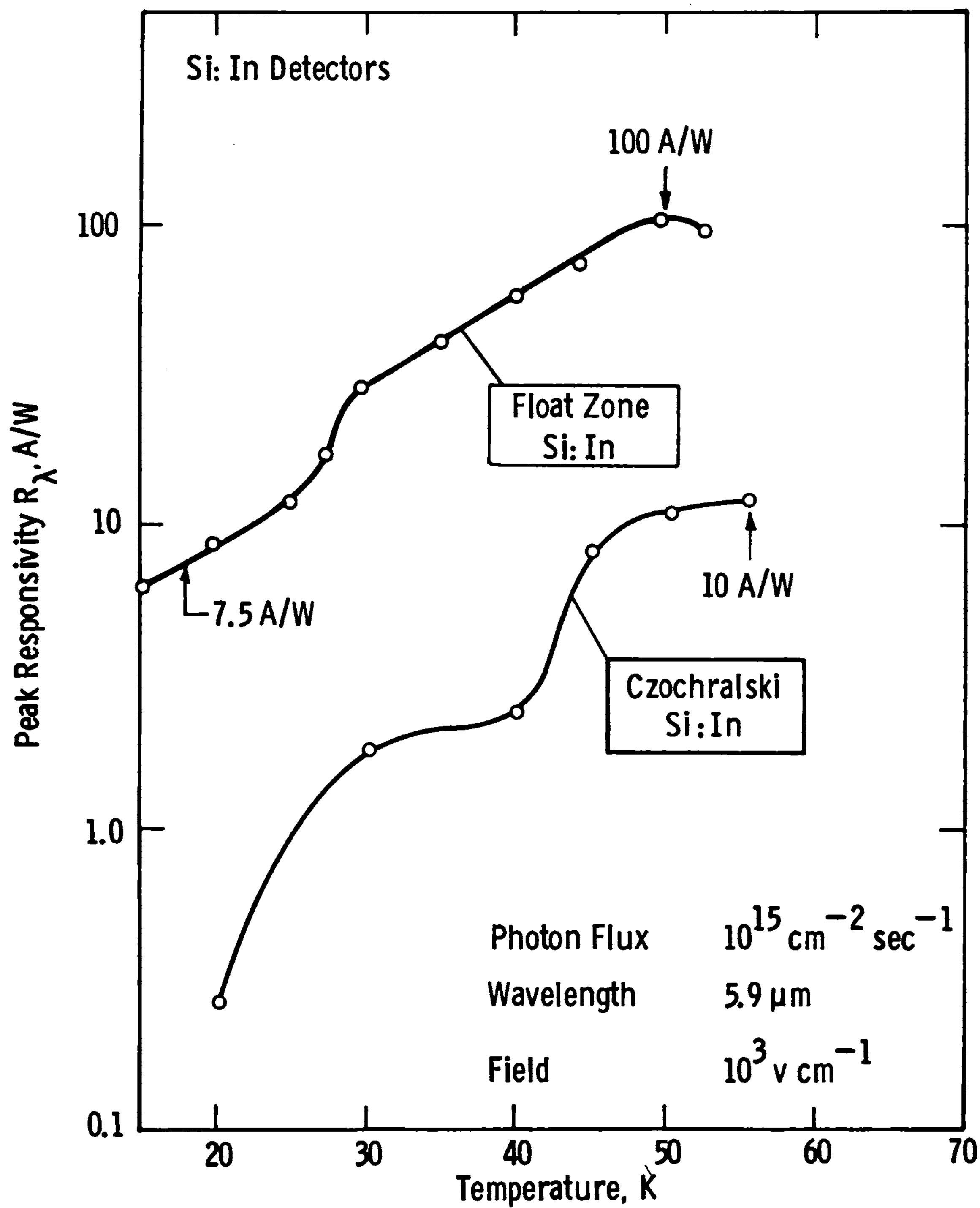

Figure 6. Comparison of peak responsivity for Si:In detectors made from float-zone and Czochralski Si:In. (Presentation to the committee by R. N. Thomas, Westinghouse, 1979)

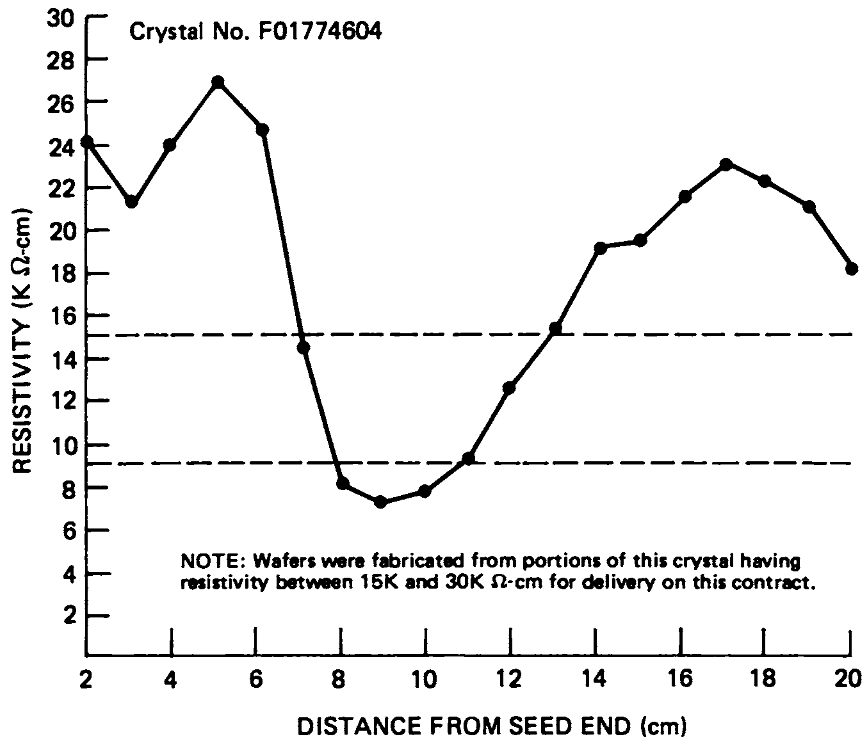

Figure 7. Axial resistivity profile of float-zoned intrinsic silicon. (Courtesy E. Kern, Hughes, 1979)

requirement suggests the same clean operation as for growth of intrinsic silicon with a major complication arising from the fact that the distribution coefficient of indium is rather small ($k_c \approx 4 \times 10^{-4}$). As a consequence, large amounts of dopant in the melt are required to achieve the desired indium level in the silicon matrix and the problem of melt contamination through the dopant material is enhanced significantly, particularly for boron. (Boron contamination of 1 ppm in indium will increase the residual boron in the final grown silicon crystal from its $10^{12}/cm^3$ level to a concentration of about $10^{15}/cm^3$ and thus render the material useless for device purposes.) While there is no concrete evidence for boron contamination of indium at the indicated level, the possibility of indium as a major source of boron contamination cannot be ignored.

In view of complications arising during float-zoning from the required high indium concentrations in the melt, the maximum doping level achievable by float-zoning of silicon is somewhat lower than desirable and lower than that achievable by Czochralski growth. During silicon growth by float-zoning, the incorporation of indium in the axial direction can be made acceptably uniform on a macroscale. The indium concentration in the axial direction, however, is invariably nonuniform on a microscale and also nonuniform in radial directions. These unavoidable composition fluctuations arise from turbulent free-melt convection, driven by destabilizing thermal gradients in the floating zone, and by rotation-induced variation in growth rate. The turbulent melt convection leads to time-dependent boundary conditions at the growth interface, prevents uniform dopant incorporation and reduces the maximum achievable doping level. A further complication of dopant incorporation (radial segregation) must be expected as a result of unavoidably nonplanar growth interface morphologies during float-zoning. Evidence for microsegregation inhomogeneities can be obtained from axial and longitudinal resistivity profiles with spatial resolution of better than 20 μm.

A comparative analysis of the growth of extrinsic indium-doped silicon by the Czochralski technique and by float-zoning leads to the following conclusions. Float-zoning does not permit doping at the same high level as Czochralski growth; it leads, however, to significantly lower background contamination. The "X-level" concentration is at the same high level in both types of material. Macrosegregation in float-zoned material is reduced significantly, but the extent of microsegregation is increased. Considering the development of integrated focal plane arrays, heavy atom gettering (required to reduce the effects of device processing-induced contamination) can be achieved through dissolved oxygen in Czochralski grown material only. At this stage in the development of intrinsic and extrinsic detector fabrication, both background contamination and compositional matrix nonuniformity are major processing problems.

7.3.3 Crystal Defect Formation

Recent advances in both Czochralski pulling and float-zoning make it possible to grow single crystals with diameters up to 5 in. in dislocation-free mode. Thus, growth of intrinsic, dislocation-free silicon is not a major problem. The formation of excessive vacancy concentrations and associated vacancy cluster formation has not been investigated to the extent desirable, and their effects on device processing and performance are still unknown.

Dislocation densities in the range of $1000/cm^2$ for heavily In-doped silicon are in line with the developed lattice strain, and further improvements appear unlikely.

7.4 Conclusions on the Status of Industrial Silicon Crystal Growth

It is worthwhile to reiterate that industrial crystal growth from the melt, the basis of most solid state technology, is still without an adequate scientific foundation and therefore is conducted on a largely empirical basis. The extent of our ignorance of the facts is well demonstrated in textbooks which state that optimum growth conditions in crystal pulling are achieved through slow pull rates, minimized thermal gradients along the crystal axis, and the establishment of a convex crystal-melt interface. On the other hand, empirically determined industrial melt-growth conditions yielding dislocation-free silicon involve high pull rates, large thermal gradients along the growth axis, and, in most instances, concave crystal-melt interfaces. Silicon crystal pulling is conducted conventionally with seed rotation at about 20 rpm and with simultaneous counterrotation of the crucible at about 5 rpm. There is no rational justification for these particular rates of rotation other than tradition.

Approaches to segregation control during industrial melt growth are few and at best sporadic. Attempts to account quantitatively for the observed macro- and microsegregation behavior are limited and generally based on one- (or at best, on two-) dimensional analyses, using of steady state theory. Studies on nonsteady state segregation and fluid flow behavior in Czochralski and float-zone configurations have been initiated only recently. These studies, however, are limited in scope and number.

Research and development in growth systems design has been aimed at increasing the silicon output. New facilities operate with larger charges and yield crystals of steadily increasing diameter. Efforts are being made to design facilities for growth of up to 6 in. diameter dislocation-free crystals. The originally conceived growth configurations traditionally have been scaled up without adequate consideration of heat- and mass-flow control, recognized as the dominant quality determining parameters. Similarly, hot-zone design and crystal diameter control have been approached without considering adverse side effects on purity control and segregation, respectively. While a significant amount of research on growth of silicon has been conducted, the evidence suggests that virtually none of the reported results have been considered so far in the design of growth systems.

The status of slicon growth technology must be viewed in the proper perspective. Available commercial facilities are capable "in principle" of satisfying the materials requirements for conventional device fabrication. On the other hand, it must not be overlooked, as it frequently is, that requirements for the newer generations of devices are met only with low and steadily decreasing yields. It is concluded that crystal growth facilities now operating are far from being optimized with regard to purity control, segregation behavior, and crystalline perfection of the material obtained. U.S. technology is internationally competitive in Czochralski growth; it is not competitive with West Germany and Japan in crystal growth by float-zoning.

Realistically, the materials requirements for silicon IR devices as specified several years ago must be considered somewhat beyond the capability of crystal growth technology, although they are met at low yields, with the established crystal growth procedures. The currently specified materials properties--involving boron contamination below $10^{11}/cm^3$, reduced carbon contamination, and improved radial resistivity characteristics--are significantly beyond the state of the art.

An analysis of industrial processing technology indicates that crystal growth-related deficiencies in bulk materials have generally been ignored whenever possible. Alternatively, adverse effects of substrate deficiencies on device processing and performance, where identifiable, have been suppressed by modifying device processing procedures. As a consequence, only minimal efforts have been made to advance bulk crystal growth technology. This study reveals clearly that the projected materials requirements for silicon IR device technology cannot now be met. Considering the present fundamentally empirical approach to crystal growth and the complexity of the processes involved, significant progress is unlikely without a major sustained effort. Some evidence suggests that Japan is in the best position to make significant advances in bulk crystal growth technology in the near future.

7.5 Alternative Approaches and New Techniques

7.5.1 Solution Growth of Indium-Doped Silicon

The retrograde solubility of indium in silicon suggests the growth of indium-doped silicon from indium as a solvent with a temperature gradient as the driving force. The feasibility of this approach has been demonstrated through the "gradient transport solution growth process" developed by M. W. Scott (Honeywell, 1979). The process reportedly yields significantly increased doping levels, improved dopant uniformity, and decreased background contamination. In a modification of this technique involving the application of an electric field, increased rates of growth at even decreased temperatures should be obtainable. For obvious reasons this technique is not suitable for growing intrinsic material.

7.5.2 Cold Crucible Technique

The advantages of the Czochralski technique without the complications of quartz crucibles can be established with the skull melting technique, which involves high frequency induction heating of silicon in a water cooled crucible-like structure. While this approach is not expected to provide major advantages in growing of extrinsic material (microsegregation effects are expected to be pronounced), it has potential for growing intrinsic silicon. In the present state of development, materials grown with cold crucible techniques do not exhibit the degree of crystalline perfection obtained by the conventional growth techniques.

7.5.3 Integrated Polysilicon Synthesis and Crystal Growth

Integrating the synthesis of starting materials, which are contamination-sensitive, with the crystal growth process has been pursued recently in a variety of III-V systems. This approach to the production

of IR-type silicon matrices seems not only feasible, but may well be necessary considering the low production volume and the purity requirements, which exceeds significantly that of conventional device grade material. Integrated facilities eventually should yield silicon of higher purity at lower cost and eliminate the uncertainty associated with reliance on polysilicon producers for ultrahigh-purity starting material.

7.5.4 Growth in Reduced Gravity Environment

Preliminary and to some extent inconclusive results of crystal growth experiments performed by NASA in a reduced gravity environment suggest that semiconductor single crystals can thus be obtained without direct melt confinement and without convection. Should these findings be confirmed through more extensive and more conclusive experimentation, the growth conditions achievable would have to be considered optimized in every respect. Contaminaton from confinement would be eliminated and steady state segregation conditions leading to compositional homogeneity on a micro- and macroscale could be achieved. IR-type silicon is not required on a tonnage scale -- the existing needs for intrinsic and extrinsic materials could be met in space in a laboratory scale facility.

7.6 Recommendations

The following recommendations are aimed at advancing the industrial melt growth capabilities in general and growth of IR-type silicon for device fabrication in particular:

1. Mandatory Research in Government Sponsored Production Contracts

   Government contracts involving the industrial production of IR-type silicon (or any other electronic material) in single crystal form for device fabrication should have a stipulated requirement for a crystal growth research program (preferably sponsored jointly by government and industry) at a level of about 20 percent of contract funding. An alternative approach would be to provide the right price and let the industry provide its own R&D. All crystal growth production should be documented with precise data on growth conditions and yield.

The research portion of such production contracts, to be negotiated for specifics prior to contract award, should focus on quantifying the growth process and on establishing correlations between controllable growth parameters and crystal properties of concern. The research should be conducted jointly by research and production personnel and should involve actual production facilities. If the industrial contractor lacks adequate research facilities and/or personnel, an interactive research program with an academic institution or the National Bureau of Standards, for example, should be considered. Basic research results should be made available for unrestricted publication.

2. Nonrestrictive Patent Rights

To provide incentives for industrial involvement in advancing silicon crystal growth technology, although it is a policy matter beyond the scope of this study, consideration should be given to changing existing government policies so as to permit granting industry unrestricted patent rights to innovative advances resulting from production and research contracts with the government.

3. Assessment of Level of R&D Effort

A standing committee or some similar mechanism should be established to examine annually the level of scientific effort associated with government contracts involving the production of electronic materials. It should have access to crystal growth related research data compiled by all DoD and NASA sponsors.

4. Interactive Involvement of Government Laboratories

Since industry in many instances is unable or unwilling to commit its primary research resources to essentially nonconsumer activities (growth and characterization of IR-type silicon, HgCdTe, InP, In:SB, and the like), it is in the national interest to examine

the research potential of the laboratories of the various DoD and NASA agencies. The situation should be studied by another standing committee; if indicated, the capabilities of these laboratories should be strengthened (1) through a sustained research commitment to crystal growth and characterization and (2) through interactive programs with industry, centers of excellence in academia, the National Bureau of Standards, and/or national laboratories.

5. Vitalization of Interactive Academic Research

Crystal-growth-related research in universities, which at present is rather limited in scope and quality, must be vitalized and expanded to comprise, in a cooperative mode, expertise in materials science, solid state physics, fluid dynamics, and electrical and chemical engineering. Considering the need to eliminate empiricism from crystal growth technology, as well as the desirability of establishing cause-and-effect relationships between materials properties and device yield and performance, government sponsored programs in universities should be interactive with related industry to the extent possible. On the other hand, major efforts should be made to encourage and facilitate industry-sponsored academic research. It is self-evident that the success of any attempt to advance crystal growth significantly from its present state will depend in the long run on the availability of competent research staff.

6. Accelerated Transition from Research to Development

It is conspicuous that processing technology, in its efforts to meet the demands for electronic materials in single crystal form, leans excessively on conservative growth methods. Efforts should be made to carry available alternative approaches expeditiously from the research to the development stage.

7. Exploration of the Potential of Silicon Crystal Growth in Reduced Gravity Environment

Considering the explicit requirements for IR-type silicon--low contamination, crystalline perfection, and composition control--it is suggested that the potential of crystal growth in a reduced gravity environment be examined more closely. This recommendation is considered in basic agreement with the conclusions reached by the STAMPS* Committee, which, while critical in its overall analysis of materials processing in space, recognized potential merits of this environment for controlling contamination and composition in crystal growth.

8. Research Areas to be Pursued

Identifiable areas of research which must be pursued if the submitted property specifications for IR-type silicon are to be achieved comprise:

- Development of analytical approaches to the quantitative characterization and analysis of the crystal-growth process in production type facilities.

- Investigation of segregation associated with Czochralski growth and float-zoning: (a) experimental establishment of

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*Scientific and Technological Aspects of Materials Processing in Space

quantitative correlations between prevailing growth conditions and the resulting micro- and macrosegregation behavior; (b) development of a quantitative framework for segregation under nonsteady state conditions; (c) optimization of growth process control with segregation uniformity as the primary objective.

- Study of growth-induced contamination: (a) identification of contaminating elements, their origin, mode of transfer into the melt, and dynamics of accumulation; (b) furnace and hot-zone design, with the objective of minimizing melt contamination; (c) investigation of the dynamics of X-level formation and of approaches to suppressing or reducing it.

- Systematic investigation of the relationships between growth-induced matrix deficiencies and device problems, device performance characteristics, and device yields.

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Chapter 8

DEVICE PROCESSING-INDUCED CONTAMINATION

It is likely that ultrapure silicon can be produced and adequately characterized in the foreseeable future. Existing processing capabilities make it very unlikely, however, that such material can be processed into devices such as silicon focal plane arrays without a significant increase in the level of residual impurities. Limited information presented at the NMAB workshop suggests that the achievement of contamination-free processing of ultrapure silicon will require as much or more development effort than the preparation of the crystals.

In this chapter, the need for work to assess the severity of the processing problems is pointed out. Also discussed are the processing steps that are known to lead to contamination. Some suggestions are offered on areas where development is needed to reduce process contamination.

8.1 Status of Process-Induced Contamination

It is difficult to determine process-induced contamination quantitatively and it is equally difficult to determine the exact point in a process when the contamination is introduced. Because of the adverse effects of contamination, the semiconductor industry must continue to provide a better total processing environment to make more reliable and more complex circuitry. Some of the most probable known sources of contamination are involved in slice fabrication and device processing.

8.1.1 Slice Fabrication

After a silicon crystal is grown, it is shaped into slices for device processing. The shaping operations (Bonora, 1977) are essentially

"dirty" and can contribute to increasing the residual impurity density in the silicon during subsequent device-processing steps (i.e., oxidations, diffusions, etc.).

Listed in Table 2 are the primary shaping operations, their purpose, probable source of contamination, and most likely contaminants. It is obvious that many processing steps are involved in the early stages of preparing the silicon for device processing, and all of these steps can lead to contamination.

TABLE 2. Sources of contamination during silicon shaping operations

OPERATION	PURPOSE	PROBABLE SOURCE OF CONTAMINANT	PROBABLE OR TYPICAL CONTAMINANT
Grinding	Control diameter of slices	Abrasive, binder holding abrasive, coolant	Cu, Cr, Fe, Ni, Co.
Sawing	To shape silicon into slice form of required thickness	Metallic binder holding diamonds to saw blade, blade body	Cu, Cr, Fe, Ni, Co.
Lapping	To control thickness of slice	Abrasive, lapping fixtures and lubricant	Ta, Cu, Fe, Ni, Al
Edge Rounding	To control shape of silicon slice edge to reduce chipping (i.e., particulate contamination)	Abrasive and binder, coolant	Cu, Ni
Etching	To remove mechanical damage from shaping operations	Chemical etch	Cu, Au
Polishing	To produce surfaces suitable for device processing	Polishing slurry, mounting fixtures polishing pads	Cu, Cr, Au, Co, Ni, Fe, Ta

SOURCE: Panel compilation

The contamination from the mechanical shaping operations (i.e., grinding, sawing, lapping, and edge rounding) is greatly reduced during the chemical etching process. Although this process is used primarily to remove defects created by mechanical damage during the shaping operations (e.g., see Buck and Meek, 1970, and Vieweg-Gutberlet, 1979, for a discussion of mechanical damage depths and methods of detection), it is also very effective in removing contamination from these processes. After the wafers are chemically etched, they are polished with a silica sol or suspensions of silica (i.e., particle size 0.001-0.004 μm) in aqueous alkaline (pH 10-12) solutions. The impurities normally found in these polishing solutions are listed in Table 3. These impurities, if left on the silicon, are only partially removed in the various slice cleaning processes. (See Amick, 1976, and Toliver, 1975, for a description of various cleaning processes commonly used in the semiconductor industry for polished silicon slices.) After these final clearing steps, the slices are ready for device processing.

TABLE 3

MAJOR IMPURITIES IN SILICA SOLS
AND SUSPENSIONS USED TO POLISH SILICON SLICES

Impurities	Concentration PPM
Fe	30-200
Cu	0.2-4
Mn	0.3-3
V	0.1-1

8.1.2 Device Processing

The silicon slices are processed into devices by a series of repeatable steps, which include oxidation, photolithography, diffusion, and/or implantation, gettering, and metalization. Table 4 shows typical processing sequence for an intrinsic PIN detector. Also, some complex detectors require epitaxial layers which are grown generally by high temperature chemical vapor deposition. Cleaning steps normally follow each process step; thus, complex device wafers may be cleaned up to 100 times during the fabrication process. Each of these cleaning steps potentially can add unwanted contamination.

TABLE 4

TYPICAL PROCESSING SEQUENCE FOR INTRINSIC REVERSE-BIASED PIN DETECTORS

1. Clean
2. Initial Oxidation $\sim$900-1000°C
3. Photolithography and Patterning
4. Clean
5. Boron Diffusion $\sim$1000°C
6. Remove Boron Glass
7. Oxidize (pre-implant oxide $\sim$1000A)
8. Boron Implant
9. Clean
10. Oxidize $\sim$900-1000°C
11. Photolithography and Patterning
12. Phosphorus Diffusion (850-1100°C)
13. Photolithography and Patterning
14. Clean
15. Metalize
16. Package

All of these process steps can lead to levels of contamination that degrade detector performance. As documented by reports at the NMAB Workshop (R. Newman, Rockwell International, and R.N. Thomas, Westinghouse, Presentation to the Committee, January 1979), high temperature processes such as oxidation diffusion and epitaxial growth can increase the background impurity levels to the range of $10^{14}/cm^3$.

Process-induced impurities can originate from many sources as previously described. However, the major contributors are the high-temperature oxidation and diffusion furnaces. For more detailed information on this source of contamination, see for example, Amick, 1976, and Mayo and Evans, 1978.

8.2 Possible Techniques for Reducing Process-Induced Contamination

The semiconductor industry relies primarily on in-process gettering (Seidel, 1976) to control process-induced contamination. This method no doubt, will continue to play a dominant role in device processing. The use of impure chemicals in all steps of device processing must be considered one of the primary sources of contamination. Work in American Society for Testing and Materials Committee F-1 on Electronics is to define particulate levels in electronic-grade chemicals, while chemical specifications are being developed by the Semiconductor Equipment and Materials Institute, (Pat Westley, Executive Secretary), Mountain View, CA 94034. These efforts should aid in improving the quality of needed chemicals. While progress in this direction is being made, automated chemical cleaning techniques such as those described by Oswald (1976) must be developed to realize the benefits of improved chemicals.

Techniques for removing particulate matter from silicon wafers such as scrubbing (Seltzer, 1975) and automated inspection systems (Oswald and Munro, 1974), should aid in reducing and controlling contamination. The development of low-temperature processing procedures for oxidations and diffusions should be seriously considered for reducing contamination. Low-temperature (~750°C), high-pressure oxidation (Katz and Kimerling, 1978; Katz and Howells, 1978) certainly has shown promise for this purpose.

Ion implantation (Sansbury, 1976) followed by low temperature or laser annealing are process steps with potential for further improvement. It should be noted that ion implantation can also introduce unwanted impurities, and, moreover, can lead to defect formation; its use must be carefully evaluated. Plasma processing also should be considered as a possible low-temperature process with reduced contamination. However, plasma processing, like ion implantation, must be carefully evaluated, because it also can increase rather than decrease contamination.

8.3 General Conclusions

Present silicon processing technology, starting with the very first stages of mechanical shaping, can introduce contamination levels exceeding the allowable limits for infrared-sensitive, high-responsivity focal plane arrays. It is extremely important to recognize that the processing of ultrahigh-purity silicon needs major development efforts. The development of sensitive, reliable, and standardized characterization techniques and of improved materials and processing techniques will greatly enhance the capability of making and processing ultrahigh-purity silicon and, no doubt, will lead to more advanced electronic devices.

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APPENDIX A

CHARACTERIZATION TECHNIQUES APPLICABLE TO HIGH-PURITY SILICON

(An extension of Chapter 5, Section 5.4)

This section is intended to present the generally accepted characteristics for bulk, surface, and thin-film analysis techniques (Tables A.1 and A.2) applicable to ultrahigh-purity silicon for IR device application. It also includes an in-depth analysis of the most relevant characterization methods.

A.1 Advanced Characterization Techniques Covered

The characterization techniques selected as being the most appropriate for IR detector materials are:

- Hall measurement.
- Fourier Transform Infrared Spectroscopy.
- Deep Level Transient Spectroscopy (DLTS) (also referred to as the transient capacitance method).
- Photothermal Ionization Spectroscopy (PTIS).
- Photoluminescence (PL).

While the Hall measurement might be considered conventional in that it is commonly available and used in semiconductor industry, it is included among the advanced characterization techniques for several reasons: it has been employed for measurements within the concentration range of interest, and the analysis of the results falls more in the area of research than routine analysis. Also, it is commonly used to calibrate other methods and therefore serves as a frame of reference.

TABLE A.1. Survey of Methods for Bulk Analysis

Method	Coverage	Optimum* Sensitivity (ppms)	Typical Sample Weight (mg)	Analysis: Bulk	Surface	Destructive	Chemical Handling	Standard Used	Accuracy (Error Factor)	Time Required (Hours)
Mass Spectrometry	Nearly Complete	0.001-1	100	Yes	Yes	Yes	No	No	3	2
	Simultaneous							Yes	1.2	10
Emission Spectrography	70 Elements	0.01-100	10	Yes		Yes	No	No	3	1
	Simultaneous				Yes	Yes	Special	Yes	1.1	10
Atomic Absorption	70 Elements	0.01-100	10	Yes		Yes	Yes	Yes	1.02	0.5
	One at a Time				Yes	Yes	Special			
Wet Chemistry	Complete	1-1000	100	Yes		Yes	Yes	Yes	1.001	5
	One at a Time				Yes	Yes	Special			
Activation Analysis	75 Elements	0.001-100	1000	Yes		No	No	No	1.2	>10
	One at a Time							Yes	1.05	>10
	Matrices				Yes	Yes	Special			
X-Ray Fluorescence	All Elements with Z > 22	10-100	100		Yes	No	No	Yes	1.1	0.5

SOURCE: R. E. Honig, Internal Publication of the RCA Laboratories

*Sensitivity depends on element and specific set up.

TABLE A.2. Survey of Methods for Surface and Thin Film Analysis

Method	Probe Diameter μm	Sampling Depth μm	Sampling Depth Atomic Layers	Optimum* Detection Sensitivity (ppm atomic)	Reproducibility (%)	Coverage of Elements	Special Features
X-Ray Fluorescence Spectrometry	10^4	3-100	10^4- $3 \cdot 10^5$	1-100	±1	Nearly Complete ($Z > 9$)	Quantitative: Nondestructive, Insulators
Electron Probe Microanalysis	1	0.03-1	10^2- $3 \cdot 10^3$	100-1000	±2	Complete ($Z > 4$)	Quantitative: "Nondestructive"
"EDXRA": Energy-Dispersive X-Ray Analysis	0.1	0.03-1	10^2- $3 \cdot 10^3$	100-1000	±2	Nearly Complete ($Z > 9$)	Small Probe, Speedy
Solids Mass Spectrography	10-100	1-10	$3 \cdot 10^3$ -$3 \cdot 10^4$	0.01-10	±20 ±2	Nearly Complete	Semi-Quantitative: Ion-Sensitive Plates Electrical Readout
Ion Scattering Spectrometry	10^2-10^3		1	100-1000	±20	Nearly Complete (No H, He)	Semi-Quantitative: In-Depth Conc. Prof. Insulators
Secondary Ion Mass Spectrometry	10^3		3	0.1-100	±2	Nearly Complete	Semi-Quantitative: In-Depth Concentration Profile
Ion-Probe Microanalysis	1-300		10-1000	0.1-100	±2	Nearly Complete	Semi-Quantitative: Three-Dimensional Conc. Profile
Auger Electron Spectrometry	25-100		2-10	0.01-0.1%	±20	Nearly Complete (No H, He)	Semi-Quantitative: Three-Dimensional Conc. Profile
"Sam": Scanning Auger Microanalysis	4-15		2-10	0.1-1%	±20	Nearly Complete (No H, He)	Semi-Quantitative: Three-Dimensional Conc. Profile. Two-Dimensional Auger Images
"XPS": X-Ray Photoelectron Spectroscopy ("ESCA")	10^4		2-10	1%	±20	Nearly Complete (No H, He)	Semi-Quantitative: Valence States
Electron Diffraction: Transmission	0.01-1	0.1			±1	Crystalline Only	Spatial Distribution of Small Crystallites
Electron Diffraction: Reflection	10		6				

SOURCE: R. E. Honig, Thin Solid Films *31*, 89 (1976)
*Sensitivity depends on element and specific set up.

A.2 Literature on Advanced Characterization Techniques

It is beyond the scope of this report to describe in detail the methods to be discussed. To partially compensate for this and to lead the reader to at least one description of the technique, the following references are listed in which a description may be found of each of the methods. There is no implication that these are the first or primary references.

REFERENCES

Hall Measurement

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Deep Level Transient Spectroscopy/Transient Capacitance

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Photoluminescence

Tajima, M., "Determination of Boron and Phosphorus Concentration in Silicon by Photoluminescence Analysis," Appl. Phys. Lett. 32 (11), p. 719-721, 1978.

Hammond, R.B., McGill, T.C., and Mayer, J.W., "Temperature Dependence of the Electron-Hole-Liquid Luminescence in Si," Phys. Rev. B13, p. 3566-3575, 1976.

SEM-Charge Collection Microscopy

(While this method of characterization is not explicitly discussed in the report, it is pointed out that the combined use of DLTS and SEM/EBIC is an extremely useful method to examine and correlate impurities in the defect structure and the electrical activity of the defect structure.)

Kimerling, L.C., Leamy, H.J., Benton, J.L., Ferris, S.D., Freeland, P.E., and Rubin, J.J., "Analysis of Impurity Distributions and Defect Structures in Semiconductors by SEM-Charge Collection Microscopy," in Semiconductor Silicon 1977 (Proceedings of the Third International Symposium on Silicon Materials Science and Technology), H.R. Huff and E. Sirtl, Editors, The Electrochemical Society, Inc., Princeton, N. J., 1977.

A.3 Overview of Analytical Techniques Which are Considered Suitable for IR-Type Silicon Characterization

Following are overviews in outline form of the five characterization techniques assessed. These overviews are not meant to be exhaustive. The emphasis has been on considerations that make them practically useful for the further development of silicon for IR detector application. One may find some redundancy in various parts of the outlines, which results from developing headings designed to cover the very different features of the five methods. There may also appear to be some contradictions in the various statements; they result from assembling the views of investigators in a field where there is, indeed, difference in opinion. An attempt has been made, however, to balance the judgment of the various investigators into a coherent picture.

A.4 HALL MEASUREMENT AS A FUNCTION OF TEMPERATURE (4-300K)

A.4.1 General Considerations

- Advantages: Fundamental

- the physics of the measurement is well understood.

- provides a quantitative determination of the majority type impurities and ionization energies (provided their ionization energies fall near the fermi level at a temperature within the range of the measurement).

- provides a determination of the net compensation.

- compared with other methods the Hall measurement is relatively direct and is commonly used for calibration of the other (less direct) methods.

- provides data which can be related to device behavior.

- Advantages: Practical and Experimental

  - method well known, available in many laboratories and widely employed particularly for the characterization of silicon with one or a few dopants commonly at carrier concentrations higher than used for detector silicon.

- automated commercial equipment is available.

- useful for a large number of dopants and residual impurities (see under specific comments).

- samples can be prepared with room or moderate temperature processing.

- Limitations: Fundamental

  - a key limitation is that the analysis of data requires that N_{Ai}, N_{Dc}, E_i be extracted by computer curve fitting to theoretical expressions.

  - the degree to which this method is an absolute measurement depends on knowledge of the degeneracy factor (g) of impurity and r-factor ($\gamma \approx 1$ assumed); the r-factor is a function of the dopant density and temperature of the sample; this can be suppressed only at very high, generally unavailable magnetic fields.

  - the analysis of the data is difficult if not impossible in the presence of different impurities with nearly identical energy levels.

- Limitations: Practical and Experimental

  - the technique requires precision instrumentation.

  - the measurement is relatively slow and tedious.

  - the establishment of ohmic contact to high resistivity samples which are to be measured at low temperatures is difficult.

- surface inversion in high resistivity samples is a problem; methods for the stabilization of the surface properties with a chemical and mechanical surface treatment have not been standardized.

- there is uncertainty in the temperature dependence of some of the basic parameters.

A.4.2 Specific Considerations for Hall Measurement

- Lowest Limit of Detection

  - already realized: there is some disagreement among the various investigators; as low as 10^8 atoms/cm^3 has been claimed; there is no disagreement at $\sim 10^{11}$ atoms/cm^3 for the majority carriers.

  - potential: possibly 10^7 atoms/cm^3 for the majority carriers; sample impedance is the limitation.

  - which elements can be measured: electrically active elements, defects and complexes, including essentially all shallow acceptors and donors of interest (if not compensating), as well as information bearing on the X-level.

  - interference effects for elements of interest: there is some discussion among investigators on this point; it is difficult to be certain of P donors if B dominates.

  - capability for C and O: cannot detect C (electrically inactive). Oxygen may produce donors when sample is annealed.

- capability for deep levels: effective for the measurement of deep levels; for very deep levels competition from intrinsic generation makes the measurements difficult.

- Method of Calibration

  - essentially self-calibrating, with reservations stated under fundamental limitation heading.
  - commonly employed to calibrate other methods.

- Can Constants Developed at Relatively High Impurity Levels be Reliably Used at Low Levels?

  - not a consideration in Hall measurement, except to note that the r-factor depends on the impurity concentration.

- Sample Preparation Required

  - contacts must be made with care to the high resistivity material; may be temperature dependent.

  - surface treatment important to control surface inversion effects in high-resistivity samples.

  - samples can be prepared at moderate temperatures; ion implantation (followed by standard anneal) frequently used.

- Minimum Sample Size

  - ~0.6 cm x 0.6 cm x 0.05 cm if the Hall pattern is produced by cavitation; otherwise the size limited only by available photolithographic techniques.

- Typical Time Required for the Measurement and Interpretation

  - ~1 day per sample measurement time; one solution is to run overnight with automated equipment.

  - ~10-15 min. terminal time on a minicomputer for interpretation.

- Areas Where Further Development is Needed

  - the development of detailed knowledge of the r-factor as a function of temperature, impurity concentration, and magnetic field is needed for more absolute interpretation of the data.

  - a better determination of effective mass as a function of temperature is needed.

A.5 Fourier Transform Infrared Spectroscopy

A.5.1 General Considerations

- Advantages: Fundamental

  - the physics of the measurement is well understood.
  - use of the technique does not require detailed modeling and complicated analysis of the data.

  - identity of impurities can be established.

  - if the optical absorption cross- ections are known, the method provides a direct measure of impurity density.

  - accurate energy resolution is possible.

- the impurity need not be electrically active (this can be a disadvantage in relating results with device performance).

- in principle, the method is sensitive to all impurities and defects of interest, including carbon and oxygen.

- with intrinsic illumination: compensation can be measured semiquantitatively

- Advantages: Practical and Experimental

  - the high sensitivity of this technique results from a combination of the optical advantages of the Fourier transform technique and the digital advantages of computer signal averaging.

  - no electrical contacts are required.

  - the method is nondestructive.

  - no above-room-temperature treatment is required for sample preparation.

  - the apparatus is commercially available.

- Limitations: Fundamental

  - quantitative information depends on how accurately the optical absorption cross-section is known.

  - the sensitivity is limited by lattice absorption.

  - the sensitivity for deep level impurities is severely limited due to the small cross-section for optical absorption of these impurities.

- does not specifically identify electrically active species.

- the sample concentrations measured are average over relatively large volumes (for pure samples, see comment on sample length below).

- Limitations: Practical and Experimental

  - calibration is difficult and ambiguous; the method is commonly calibrated against Hall or resistivity measurements for the electrically-active impurities.

  - for the analysis of high-resistivity material, the samples must be 1 cm in thickness.

  - the samples must be optically polished.

  - the Fourier transform spectrometer is expensive (for the most versatile equipment which is necessary to take full advantage of the technique, the cost is ~$100,000).

A.5.2 Specific Considerations for Fourier Transform IR Spectroscopy

- Lowest Limit of Detection.

  - already realized: generally reportred to be $\sim 1x10^{11}$ atoms/cm^3 for B, As, and P; $\sim 10^{12}$ atoms/cm^3 in heavily In-doped material.

  - potential: the consensus among a number of investigators is that the limit has probably already been reached for "practical" measurements.

  - elements of interest demonstrated: all group III and V elements, as well as O and C can be measured.

- interference effects for elements of interest: there are no serious interference effects for net impurities, but there is a problem for total impurities when boron and phosphorus are present at a level $\sim 10^{15}$ atoms/cm^3; resolution of the two lines is a problem. There is some interference with H_2O lines originating from the apparatus and sample surface. High dopant concentrations (e.g., In) may interfere with residual impurities below the 10^{12} atoms/cm^3. Minority dopants can be seen if sample is flooded with above-bandgap illumination. A large lattice absorption line nearly coincides with a carbon line.

- capability for C and O: carbon $2\text{-}10 \times 10^{15}$ atoms/cm^3.
  oxygen $1\text{-}10 \times 10^{14}$ atoms/cm^3.

- capability for deep levels: questionable, there is some potential if concentration is high enough.

- Method of Calibration

  - calibration with resistivity or Hall measurements, by IR measurement of sample with a known concentration.

  - constants for C and O have been developed using vacuum fusion and neutron activation.

- Can Constants Developed at Relatively High Impurity Levels be Reliably Used at Low Levels?

  - yes, for acceptor concentrations $\gtrsim 10^{15}$ atoms/cm^3; in heavily compensated material line broadening results.

- Sample Preparation

  - optically polished surfaces are required (better than 1 cm).

  - since no contacts, junctions, or oxide layers are required, no above-room-temperature processing is required.

- Minimum Sample Size

  - ~1 cm diameter, 0.5-1 cm thick, depending on impurity level.

- Typical Time Required for Measurement and Interpretation

  - typically ~1 hr. for the measurement exclusive of sample preparation and cool-down (this depends on the resolution sought and range of wavelength investigated); 15 min. for interpretation with proper equipment.

- Areas Where Further Development is Needed

  - the method, with equipment currently available, can be usefully applied to many of the current problems.

  - the development of derivative techniques could yield increased sensitivity.

  - further noise suppression in the IR detector would be useful.

A.6 Deep Level Transient Spectroscopy (DLTS) (Also Referred to as the Transient Capacitance Method)

A.6.1 General Considerations

- Advantages: Fundamental

  - the concentration of deep levels ($E > 0.1$ eV) originating from both impurities and defects can be measured.

  - deep levels can be observed in the presence of shallow ionized impurities (within limits, see specific considerations).

  - concentrations of deep levels as low as 10^{10} atoms/cm^3 can be measured.

- Advantages: Practical and Experimental

  - the method is essentially self-calibrating for comparative measurements.

  - structure in the data contributes to ease of interpretation.

  - measurements can be made on completed devices.

  - the equipment can be relatively simple.

  - the measurement can be relatively rapid after establishing the procedure with the appropriate skill levels.

  - the output is in a form that can be handled by sophisticated data recording techniques.

- Limitations: Fundamental

  - shallow acceptor or donor levels, e.g., B, P ($E \lesssim 0.1$ eV) cannot be detected except at very low temperatures.

  - the shallowest of levels present cannot be observed.

- Limitations: Practical and Experimental

  - the technique requires the use of thermal/mechanical processes associated with the fabrication of a device structure (if p-n junctions are used). Thus it may be difficult to separate the effects of the processing procedures from the fundamental materials properties; high-temperature processing is avoided by the use of Schottky barrier structures with a sacrifice in information content and sensitivity.

  - ohmic contacts are required.

  - sample contact resistance influences measurement.

  - the change in sample resistance with temperature must be determined by an independent measurement and included in the analysis, or background doping is needed that dominates deep levels to a resistivity which is relatively independent of temperature.

  - must have good temperature measurement and control equipment.

  - interpretation of the DLTS spectra is difficult; identification of a specific element or defect is difficult; as many as 25 spectra may be required to completely characterize a sample.

  - particularly in high-resistivity samples (>100-200 Ω-cm) correct capacitance values may be difficult to determine.

A.6.2 Specific Considerations for DLTS and Transient Capacitance Analysis

- Lowest Limit of Detection

  - already realized: 10^{11}-10^{10} atoms/cm^3; this is a function of the level of background doping (shallow levels). present - the current capability is 10^{-4} of background doping.

  - potential: 10^9-10^{10} atoms/cm^3 with a capability of 10^{-4} of the background doping.

  - elements of interest demonstrated: most heavy metals, complex point defects, and radiation-induced defects can be measured.

  - note that with the requirement that $E_B \gtrsim 0.1$ eV, common dopants are excluded.

- Interference Effects for Elements of Interest

  - if too many deep levels are present, it may be difficult to resolve them.

  - knowledge of activation energies and capture cross-sections may not be enough to differentiate between various trap complexes.

  - deep levels may be present in amounts which result in variation of the sample resistance with temperature.

  - capability for deep level impurities: this is probably the most appropriate method for the measurement of deep level impurities, within the limitation stated above.

- Method of Calibration

  - the method is commonly calibrated by the measurement of a known standard using other methods.

- Can Constants Developed at Relatively High Impurity Levels be Reliably Used at Low Levels?

  - possibly, this needs further investigation.

- Sample Preparation

  - see Limitations: Practical and Experimental.

  - sample must be specially prepared to contain shallow defects (e.g., boron) in order to study the deeper levels (e.g., In).

- Minimum Sample Size

  - the sample size is the area needed for device processing (100 μm diameter).

- Typical Time Required for Measurement and Interpretation

  - measurement time: 4 hrs. or less.

  - interpretation time: possibly days.

- Areas Where Further Development is Needed

  - a good deal of experimental development has taken place in recent years; it is not clear that further developments in the fundamental aspects of the technique are indicated.

- high-frequency (20-30 MHz) capacitance meters are not commercially available.

- develop theory for low-temperature measurements in order to get information on majority impurities.

- develop a practical procedure for interpreting data when there are large changes in resistivity with temperature.

A.7 Photothermal Ionization Spectroscopy (PTIS) (also referred to as Photothermal Photoconductivity and Photoelectric Spectroscopy)

A.7.1 General Considerations

- Advantages: Fundamental

  - for the analysis of shallow impurities in relatively pure crystals:

    - the sensitivity is excellent (the sample serves as the IR detector, and the electrical signal is directly available).

    - the method provides identification of impurities present.

    - an estimation of the degree of compensation is possible using band-edge illumination.

    - an estimation of impurity ratios is possible.

  - donors and acceptors can be simultaneously identified.

- Advantages: Practical and Experimental

  - using the Fourier transform technique, the method is relatively fast.
  - the measurements are relatively easy to make.
  - the sample size and shape are not critical; no optical flats are required.
  - the method may not depend on the single-crystal character of the sample.

- Limitations: Fundamental

  - it is difficult to extract quantitative information using this method; independent calibration is necessary.
  - the sensitivity drops rapidly with the "depth" of centers.
  - broadening and overlapping of excited states is a problem above $N \approx 10^{16}$ atoms/cm^3 in silicon.
  - for analyses of minority dopants, sample must be flooded with above-bandgap radiation; this gives an added background and limits detectivity.

- Limitations: Practical and/Experimental

  - the high impedance of the very pure samples leads to problems with microphonics, noise, etc.
  - the absorption cross-sections are not well known; this influences the accuracy of determining the ratio of impurities.

- ohmic contacts at low temperature are required.

- the equipment (assuming use of the Fourier transform method) is expensive.

A.7.2 Specific Considerations for Photothermal Ionization Spectroscopy

- Lowest Limit of Detection

  - already realized: total impurity levels of 10^{11} atoms/cm^3 have been observed in Si (in Ge, impurities to a level as low as 10^7 atoms/cm^3 have been observed).

  - potential: there exists some uncertainty on this point; the optimistic estimate is that the detection of 10^6 shallow levels per cm^3 should be possible in Si in relatively pure uncompensated material.

  - elements of interest demonstrated: boron and phosphorous have been measured in Si.

  - interference effects for elements of interest: at higher doping levels, overlapping of excited states may result in interference effects.

  - capability for C and O: this method is not capable of detecting C or O directly.

  capability for deep-level impurities: the sensitivity decreases with the "depth" of the impurities, thus this is not the method of choice for deep-level impurities.

- Method of Calibration

  - the measurement is calibrated by Hall measurements.

- Can Constants Developed at Relatively High Impurity Levels be Reliably Used at Low Levels?

  - constants developed at impurity levels less than 10^{14}-10^{15} atoms/cm^3 can be used at the lower levels.

- Sample Preparation Required

  - good low-noise contacts, which are usable at low temperatures (15-25K) must be made; this requires diffusion at elevated temperatures or ion implantation followed by an anneal.

- Sample Size

  - small, $\sim$1 mm^3.

- Typical Time Required for Measurement and Interpretation

  - the measurements and interpretation are relatively rapid, typically less than an hour (exclusive of sample preparation), depending on the resolution desired.

- Areas Where Further Development is Needed

  - measurement of absorption cross-sections would considerably contribute to the accuracy of establishing the ratio of impurities present in order to make the technique more quantitative.

  - need to develop a mechanism of interaction when compensating impurities are present in order to make the technique more quantitative.

- experimentally establish the influence of crystalline perfection on quantitative impurity measurements.

A.8 Photoluminescence (PL)

A.8.1 General Considerations

- Advantages: Fundamental

  - in principle, all shallow impurities in the sample can be identified; neutralization of impurities occurs automatically so the method is sensitive to impurities regardless of compensation.

  - the method is useful for making quantitative comparisons between impurities within a sample.

- Advantages: Practical and Fundamental

  - no contacts are needed, thus high temperature processing during sample preparation is avoided.

  - high sensitivity is realized in a small volume probed (~100 μm on a side); therefore, impurity profiling is practical and it may be possible to make useful measurements within the individual grains of polycrystalline materials.

  - the measurements are rapid (after cool down).

  - the equipment is relatively inexpensive, about $25,000 (assuming the availability of liquid helium).

- Limitations: Fundamental

  - cannot detect C or O directly; can, however, measure C and O quantitatively after exposure of the sample to known amounts of radiation.

- at high concentrations ($\gtrsim 10^{17}$ atoms/cm^3 or more for deeper impurities) lines broaden and may overlap; capture processes will be affected.

- the physics of the PL process is not completely understood.

- Limitations: Practical and Experimental

  - the free-exciton-capture cross-sections need to be measured.

  - the measurements are done at a low temperature (4K).

  - high concentrations of deep levels may make it difficult to observe shallow levels at low concentrations.

  - large numbers of lines make the interpretation of data difficult (at present).

  - the photoluminescent quantum efficiency is low, and therefore the signal is low and the S/N ratio is a problem in practical application.

  - the experimental apparatus is relatively difficult to set up (alignment of optics, etc.).

A.8.2 Specific Considerations for Photoluminescence

- Lowest Limit of Detection

  - already realized: there is some discussion among investigators on the low limit of detection already realized; the range reported is 10^9 to 10^{11} atoms/cm^3 for both B and P.

- potential: here again there is some discussion, the range stated as 10^7 to 10^{10} atoms/cm^3 for both B and P; improvement could come as the result of the use of shaped samples, better detectors, and long wavelength excitation illumination.

- elements of interest demonstrated: essentially all shallow impurities can be detected and some deep levels.

- line positions are catalogued for B, Al, Ga, In, Tl, Sb, P, As, Bi.

- interference effects: interference depends on the possibility of excitation tunneling and on the relative excitation capture cross-sections for different impurities; quantitative results do not exist for either process.

- high concentrations of deep levels may make it difficult to observe the shallower levels.

- capability for deep levels: deep levels can be observed using semiconductor detectors in place of the more commonly employed photomultiplier tubes; in general, however, this is not the favored method for deep levels.

- Methods of Calibration

  - initially exciton-capture cross-sections must be measured using samples characterized by some other technique. With these data, however, no more calibration is necessary since the concentration is obtained from the ratio of two luminescence lines--no absolute measurement is necessary after the cross-sections are known.

- Can Constants Developed at Relatively High Impurity Levels be Reliably Used at Low Levels?

  - exciton capture cross-section measured at 10^{14}-10^{15} atoms/cm^3 should be reliable for low concentrations. Effects of high impurity densities will probably not show up until 10^{17} atoms/cm^3. 10^{15} atoms/cm^3 is probably quite safe.

- Sample Preparation Required; Sample Temperature; Temperature Dependence

  - samples are lapped and etched to remove surface damage. During the experiment the sample is at liquid helium temperature (~4K). The exciton-capture cross- ections are temperature-dependent though it is thought that the dependence saturates below about 10K -- this is not known conclusively. However, maintaining a stable temperature of 4.2K (boiling point of liquid He at 1 atm.) is quite feasible.

- Minimum Sample Size

  - having a large thermal mass is desirable for temperature stability but probably not critical at the low excitation intensities ($\lesssim$100 mW) used in the high purity material. Wafers, 1 cm or less on a side (~10 mm^3), have been used at these intensities with no problem.

- Typical Time Required for Measurement and Interpretation

  - after the sample has cooled down and the optics aligned, recording a spectrum takes probably no more than one-half hour and typically a few minutes. The interpretation requires only a ratio of two line intensities to be found for each

impurity and the result multiplied by a constant to obtain the impurity concentrations. Starting from a warm dewar, several hours are needed to cool down.

- Areas for Further Development

  - the exciton capture cross-sections of the various impurity atoms need to be measured to extend the quantitative capability of the method.

  - an understanding of the effects of impurity saturation by free exciton-capture needs to be developed (these first two areas can be addressed by a systematic study of exciton decays).

  - the investigation of the temperature dependence of the exciton capture cross-sections and a development of the mechanisms involved could contribute to the quantitative capability of the method.

  - research into the possibility of extending the technique to the analysis of deeper levels could prove to be worthwhile.

  - experimentally investigate the usefulness of measurements made within small grains.

APPENDIX B

WORKSHOP PARTICIPANTS*

The committee held a two-day limited workshop at the National Academy of Sciences in Washington, D.C., on January 23-24, 1979, to get inputs from other experts. Invited participants (limited in number because of the size of the meeting room and the time available for each speaker) made short informal presentations on innovative and possibly unproved technologies applicable to high-purity silicon preparation and characterization. Not all inputs are specifically identified in the report; however, the committee gratefully acknowledges all contributors for the stimulating and thought-provoking impact they had on the committee's deliberations. The meeting agenda below lists the participants together with the topics presented.

* Attendees who made no direct presentation were A. L. Bement, Jr. of DARPA, C. Duggar of National Science Foundation, and W. F. Holden of Naval Materiel Command

Tuesday, January 23, 1979

Session A: BACKGROUND OF NEEDS FOR HIGH-PURITY SILICON
W. Frederick, Session Chairman

This session dealt with the government agency needs for high purity silicon and set the stage for specific inputs to answer various questions regarding the availability of proper materials.

1. Air Force Needs and Requirements--W. Frederick, Air Force Materials Laboratory, Wright-Patterson Air Force Base, Ohio

2. DARPA, Specification and Projected Needs--R. Reynolds, Defense Advanced Research Projects Agency, Arlington, Virginia

3. Air Force Systems Command, Needs--R. Fabrie, Air Force Systems Command, Washington, D.C.

4. DARCOM, Projected Needs--F. Michel, DARCOM Headquarters, Alexandria, Virginia

5. NASA, Needs and Specifications--J. Carruthers, NASA Headquarters, Washington, D.C.

Session B: FOREIGN TECHNOLOGY
J. Carruthers, Session Chairman

Experts discussed the state of the art of off-shore capabilities compared to the United States.

1. European Technology--J. Guldberg, Topsil, Denmark (division of Motorola)

2. Russian Technology--J. Wenckus, CERES, Waltham, Massachusetts

3. Japanese Technology--J. Carruthers, NASA Headquarters, Washington, D.C.

4. Miscellaneous Technologies--A. Witt, Massachusetts Institute of Technology, Cambridge, Massachusetts

Session C: POLYSILICON PREPARATION AND CHARACTERIZATION
R. Hall, Session Chairman

People concerned with polycrystalline high-purity silicon preparation, purification and evaluation made contributions.

1. High Purity Silicon Poly Preparation and Impurity Detection Techniques--J. A. Baker, Monsanto (formerly Dow-Corning Corp.), St. Peter, Missouri

2. High Purity Silicon Poly Production Capability--C. Hahn, Dow-Corning Corp., Hemlock, Michigan

3. Preparation of Silicon from Silane--W. Breneman, Union Carbide, Sisterville, West Virginia

4. Preparation of High-Purity Silicon from Purified Silicon Tetrachloride--J. Guldberg, Topsil, Denmark

5. Preparation of High-Purity Silicon by the Iodide Process--B. Rubin, NASA Headquarters, Washington, D.C.

6. Chromatographic Technique for Purification--R.J. Stark, Eagle-Picher, Inc., Miami, Oklahoma

7. Laser Purification of Silane--J. H. Clark, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

8. Preparation of Low Boron Silicon from Purified Silane and Measurement of Boron Concentration--R. Lutwack, Jet Propulsion Laboratory, Pasadena, California

Session D-1: SINGLE CRYSTAL PREPARATION AND CHARACTERIZATION
G. R. Cronin, Session Chairman

Session D was separated into two sections in order to cover in more detail some recent developments. Some overlap and out-of-sequence presentations occurred due to the presentors' coverage area.

1. Silicon Crystal Prepartion and Evaluation at TI--G. R. Cronin, Texas Instruments, Inc., Dallas, Texas

2. Neutron Activation Analysis for Impurities in Silicon--G. B. Larrabee, Texas Instruments, Inc., Dallas, Texas

3. Silicon Crystal Preparation and Evaluation at Hughes--E. L. Kern, Hughes Aircraft Corporation, Carlsbad, California

4. Silicon Crystral Characterization--J. Baukus, Hughes Research Laboratories, Malibu, California

Session D-2: ADVANCED CHARACTERIZATION METHODS
G. W. Cullen, Session Chairman

This section of Session D is a late afternoon continuation of the session dealing primarily with characterization techniques.

1. Photothermal Ionization Spectroscopy (PTIS) of Impurities in Pure Silicon and Germanium--E. E. Haller, Lawrence Berkeley Laboratory, University of California-Berkeley

2. Analysis of Defects and Impurity Distributions in Semiconductors by SEM-Charge (Transient Junction Capacitance) Collection Microscopy--L. C. Kimerling, Bell Laboratories, Murray Hill, New Jersey

3. Detection of Impurities by the DLTS Technique--M. W. Scott, Honeywell Corporation, Materials Sciences Center, Bloomington, Minnesota

4. Exiton Photoluminescence Techniques--S. A. Lyon, Princeton University, Princeton, New Jersey

5. Exciton Luminescence for the Characterization of High-Purity Silicon --R. B. Hammond, Los Alamos Scientific Laboratory, Los Alamos, New Mexico

6. Impurities in Indium, A Major Dopant for Silicon--C. E. T. White, Indium Corporation, Utica, New York

Wednesday, January 24, 1979

Session E: CONTAINER MATERIALS AND DOPANTS

R. M. Burger, Session Chairman

1. Cold Crucible Technology and Its Application to Ultra-High-Purity Silicon--J. F. Wenckus, CERES Corporation, Waltham, Massachusetts

2. High Purity Indium Supply Capability--S. C. Liang, Cominco American, Inc , Spokane, Washington

3. Impurity Sources in Crystals and Crystal Growth--E. L. Kern, Hughes Aircraft Corporation, Carlsbad, California

4. Impurities Identification and Measurement by the Hall Effect--J. Baukus, Hughes Research Laboratory, Malibu, California

5 Container Studies in the Solar Cell Program--G. W. Cullen, RCA, Princeton, New Jersey

6. X Defect Studies--M. W. Scott, Honeywell Corporation, Materials Sciences Center, Bloomington, Minnesota

Session F: DEVICE NEEDS AND PRODUCT RELIABILITY

K. E. Benson, Session Chairman

1. IR Device Specification--E. L. Kern, Hughes Aircraft Corporation, Carlsbad, California

2. Processing of Extrinsic Devices--R. N. Thomas, Westinghouse R&D Center, Pittsburgh, Pennsylvania

3. Influence of Materials Processing on Device Behavior -- R. Newman, Rockwell International, Anaheim, California

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