Database Needs for Modeling and Simulation of Plasma Processing

DETAILS

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and
Plasma Science Committee
Board on Physics and Astronomy
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Preface

In the spring of 1994 the Plasma Science Committee and the Committee on Atomic, Molecular, and Optical Sciences of the National Research Council (NRC) established a panel to organize and conduct a workshop on database needs in plasma processing of materials. This activity was motivated by the NRC report *Plasma Processing of Materials: Scientific Opportunities and Technological Challenges* (National Academy Press, Washington, D.C., 1991), prepared by the Panel on Plasma Processing and Materials under the auspices of the Board on Physics and Astronomy, which pointed out the need for an improved database to enable more quantitative modeling of plasma reactors and processes, especially in the area of integrated circuit manufacturing. The beneficial product of such modeling would be a more competitive and responsive microelectronics industry that serves both defense and civilian markets.

The primary purpose of the workshop, held April 1 and 2, 1995, in Washington, D.C., was to bring together experts with the goal of developing a prioritized list of database and diagnostic needs based on their potential impact on plasma processing technology. This report summarizes the findings of the workshop.

Each of the members of the Panel on Database Needs in Plasma Processing headed an ad hoc group that helped draft a subset of the report, based on input from the workshop participants. The panel thanks the members of these groups for their assistance: P.B. Armentrout, University of Utah; E. Aydil, University of California, Santa Barbara; K.H. Becker, The City College of the City University of New York; R. Buss, Sandia National Laboratories; M.W. Chase, National Institute of Standards and Technology; L.G. Christophorou, Oak Ridge National Laboratory; J.M. Cook, Lain Research Corporation; D. Ernie, University of Minnesota; K.P. Giapis, California Institute of Technology; M.F. Golde, University of Pittsburgh; I.P. Herman, Columbia University; P. Ho, Sandia National Laboratories; R. Johnsen, University of Pittsburgh; Y.-K. Kim, National Institute of Standards and Technology; H. Sawin, Massachusetts Institute of Technology; D.W. Setser, Kansas State University; S. Srivastava, Jet Propulsion Laboratory; W. Tsang, National Institute of Standards and Technology; R.J. Van Brunt, National Institute of Standards and Technology; C. Woods, University of Wisconsin; J. Wormhoudt, Aerodyne Research Inc.; and M. Zachariah, National Institute of Standards and Technology.

In view of the fact that the primary use of data on plasma processing is in technology development in industry, special efforts were made to ensure that there was extensive industrial participation in the workshop, both in breadth and depth. The panel owes a particular debt of gratitude to the following individuals for their active participation in the workshop and for critiquing and improving drafts of the report: Kaihan A. Ashtiani of Materials Research Corporation; Andrew D. Bailey HI of Plasma and Materials Technologies; Joel M. Cook of Lam Research Corporation; Frederick Dill of IBM T.J. Watson Research Center; Vincent Donnelly of Lucent Technologies Bell Laboratories; Erik Egan of Motorola; Sychi Fang of Intel Corporation; David Fraser of Intel Corporation; Abe Ghanbari of Materials Research Corporation; R.A. Gottscho of Lain Research Corporation (formerly of AT&T Bell Laboratories); Michael Hartig of Motorola/Sematech; Les Jerde of Tegal Corporation; Andrew Labun of Digital Equipment Corporation; Michael Mocella of Dupont; Joseph Proud of GTE; Vivek Singh of Intel Corporation; Vikram Singh of Lam Research Corporation; M. Surendra of IBM T.J. Watson Research Center; Alexander Voschenkov of Lain Research Corporation; and Jody Wormhoudt of Aerodyne Research.

The scope of this report is substantial, covering industrial needs for better plasma process engineering, the current state of the art in plasma modeling, and the various supporting databases and diagnostics techniques that underlie and complement modeling and simulation. The report is intended for a variety of audiences: academic and government laboratory researchers, industrial engineers and scientists, and technical program managers at federal agencies. Although it emphasizes industrial and technological applications, the report raises many challenging questions involving fundamental science that underlies the technological applications, and these challenges should appeal to many in the basic science community as well as to technologists. The fundamental science disciplines to which this report is most relevant include, but are not limited to, plasma science and atomic, molecular, and optical science.

The panel notes that this report has been preceded by several excellent reports that address similar and/or complementary issues from somewhat different perspectives. The Semiconductor Industry Association (SIA), for example, prepares periodic "roadmaps" of industrial needs and potential solutions to guide technology development in critical areas of semiconductor manufacturing. SIA's second such report (*The National Technology Roadmap for Semiconductors*, SEMATECH, Austin, Tex., 1994) contains numerous insights regarding the role of future plasma processing in semiconductor manufacturing. In 1995 SEMATECH published an important supplement to the SIA roadmap; titled *Technology Computer-Aided Design (TCAD) Roadmap: Supplement to the National Technology Roadmap for Semiconductors*, it contains a chapter on equipment modeling, including plasma equipment modeling and the database needs for this application. In 1994 SEMATECH published *White Paper for a Chemical Kinetics Database to Support Integrated Circuit Manufacture*, a report that focuses primarily on modeling and simulation for thermal chemical vapor deposition (CVD) processes and that contains much useful information and valuable insight on the proper approach to developing an equipment modeling database.

As noted above, plasma processing was specifically addressed in the 1991 NRC report *Plasma Processing of Materials*, which provided the primary motivation for the present activity. In 1995, the NRC published in the Naval Research Laboratory Series a report titled *Plasma Processing and Processing Science* (National Academy Press, Washington, D.C.). Also published in 1995 was a comprehensive NRC report entitled *Plasma Science: From Fundamental Research to Technological Applications* (National Academy Press, Washington, D.C.). All of these previously published reports contain useful, often additional, and sometimes conflicting information relevant to the goals of this report. Readers are advised to examine the earlier reports as well, to obtain historical perspective and a broader base of opinion.

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Executive Summary

The 1991 National Research Council (NRC) report *Plasma Processing of Materials: Scientific Opportunities and Technological Challenges*[1] included a projection that worldwide semiconductor sales would double from $50 billion in 1990 to $100 billion in 1995. In fact, total sales worldwide for semiconductors passed $140 billion during 1995, nearly triple the 1990 level.[2] Companies that supply plasma equipment to the semiconductor industry have experienced similar, if not greater, rates of growth. Plasmas in one form or other are used in about 30% of all semiconductor manufacturing processing steps, and about the same fraction of processing equipment is plasma-based in a typical microelectronics fabrication facility.[3] An important trend accompanying this growth in the industry is the fact that the capital cost of constructing a new microelectronics fabrication facility is similarly escalating and is now on the order of $1 billion or more.[4] Estimates are that over 60% of this capital cost is for processing equipment, including plasma equipment. Processing equipment design, optimization, and control therefore take on added importance, because equipment depreciation accounts for a significant part of the price of a chip.

In spite of its high cost and technical importance, plasma equipment is still largely designed empirically, with little help from computer simulation. Plasma process control is rudimentary. Optimization of plasma reactor operation, including adjustments to deal with increasingly stringent controls on plant emissions, is performed predominantly by trial and error. There is now a strong and growing economic incentive to improve on the traditional methods of plasma reactor and process design, optimization, and control. An obvious strategy for both chip manufacturers and plasma equipment suppliers is to employ large-scale modeling and simulation. The major roadblock to further development of this promising strategy is the lack of a database for the many physical and chemical processes that occur in the plasma and especially at surfaces. Although a complete set of data for all gas phase and surface processes for all species present in the plasma is not necessary for many applications, the current lack of detailed information concerning the vast majority of processes and species is the major factor limiting the effectiveness of models.

Given the reality of inevitably limited resources, and the often considerable investments that must be made to measure and/or compute collision cross sections, reaction rate coefficients for gas phase reactions, and surface chemical rates at surfaces exposed to plasma, some priorities must be established. These priorities are discussed below, and the report's recommendations on priorities constitute one of the main results of the study.

FINDINGS

1. The integrated circuit (IC) manufacturing industry remains in its historical pattern of rapid technological change, and this pattern has begun to seriously challenge plasma equipment suppliers to continue the trend toward ever higher performance/cost ratios. Plasma processing tools are, in most cases, designed and optimized empirically. Real-rune control of plasma processes has not been adopted by the industry. Further improvements in performance by means of empirical adjustments will soon reach a point of diminishing returns, if they have not already.
2. Control of processes in plasma reactors must occur on length scales that range from tens of angstroms to tens of centimeters and time scales that range from seconds to tens of hours. Loss of control at any point in this spectrum of length and time scales can result in reduced yields of components and therefore significant economic losses. For example, precise control of transistor gate and metal wiring levels across the entire chip is necessary to manufacture microprocessors at the highest speeds. Loss of this control over etching precision produces slower microprocessors and a loss of hundreds of dollars per chip. Obviously, across-wafer control is equally important to maintain high yields and therefore high profitability.

3. Models of low-temperature, nonequilibrium plasmas, especially for the description of physical phenomena, have developed rapidly in the last 5 years. Computing power per unit cost continues to increase rapidly. However, few of the currently available plasma models can be easily used by process engineers. Although attempts have been made to model plasmas with realistic chemistries, the parameter space that can be addressed is limited. Only a handful of studies have been made that attempt to validate models of plasma processes with industrially relevant chemistries. Models that attempt to link the relevant length scales (from tool scale to feature scale to atomic scale) are just now emerging. Simulations can be no more accurate than the data and assumptions on which they are based. The lack of fundamental data for the most important chemical species is the single largest factor limiting the successful application of models to problems of industrial interest.
4. Heterogeneous (surface) processes are at the heart of plasma materials processing technology, but are in many cases much less well understood than are gas phase processes. Numerous etching and deposition profile evolution simulations are used in industry. These simulations generally use empirically derived rate coefficients that must be refit to experimental data whenever conditions change. Experimental diagnostics and modeling of plasma-surface processes based on first principles are rudimentary and require much development. Surfaces exposed to plasmas are often strongly modified by intense ion, photon, and radical species bombardment. Therefore, not only are the chemical and physical processes themselves strongly perturbed by plasma exposure, but in addition, the surfaces upon which the processes take place are unconventional in their structure and composition.
5. Electron collision cross section data are second only to data on heterogeneous processes in their importance to plasma processing. These data are sketchy at best for most species of interest, although some key species, such as SiH_4 and CF_4, have received considerable attention. Little information is available for dissociation products or for species in excited states. Recent progress in computational methods based on quantum scattering offers the possibility that the costly and time-consuming experiments may be augmented or even replaced by large-scale computation.
6. There now exists a wealth of sensitive radiative and laser-based techniques that permit species concentration and temperature measurements in processing plasmas. All spectroscopic diagnostic techniques depend on a database of atomic and molecular parameters. A comprehensive spectroscopic database is important to enabling unambiguous identification of a particular species in the plasma or on the surface. Spectroscopic measurements are usually the first step in measuring a rate coefficient or in testing a model prediction. The spectroscopic database therefore serves a dual role to provide both qualitative and quantitative information. Although the spectroscopic database is far from complete, especially for surface species, data are available in the literature that are relevant to plasma processing. However, these data are scattered throughout the technical and scientific literature, and in some cases their accuracy is in doubt. The ready availability and ease of spectroscopic database manipulation and storage will stimulate the development of new diagnostic techniques and the wider application of existing methods.
7. The database for ion-molecule and neutral-neutral chemistry varies considerably. For some species and reactions, the data are good. This is especially true for the cases in which there is overlap with processes occurring in the upper atmosphere or in some cases in chemical vapor deposition processes. In other cases, however, most notably for etching processes, there are few data available.
8. Thermochemical data are sketchy for many species of interest in plasma processing. These data are important in helping to establish boundaries for reaction pathways and for estimating reaction rate coefficients. Techniques, both experimental and computational, are generally available to obtain these quantities, but few efforts are under way at present to meet these needs.

CONCLUSIONS

1. The major potential benefits of plasma modeling for chip manufacturers are better control over plasma processes, minimization of resources that would otherwise be devoted to optimizing plasma

processes, and possibly minimization of problems associated with undesirable emissions such as greenhouse gases and ozone depleters.

2. The major potential benefits of plasma modeling to plasma equipment suppliers include more rapid and efficient development of new tools that meet increasingly stringent process requirements, optimization of designs before fabrication of prototype tools, and development of robust, real-time process control schemes for their tools.
3. The main roadblock to development of plasma models that will have these industrially important uses is the lack of fundamental data on collisional, reactive processes occurring in the plasma and on walls bounding the plasma. Among the most important missing data are the identities of key chemical species and the dominant kinetic pathways that determine the concentrations and reactivities of these key species, especially for the complex gas mixtures commonly used in industry.
4. The lack of a central location to collect, analyze, and disseminate the data that are currently available, or that will be available in the future, is a serious problem.
5. Large numbers of materials and chemistries are used in plasma processes for integrated circuit manufacturing. Given the reality of inevitably limited resources, it is necessary to establish priorities that encourage development of relevant data for only a few of the most important chemistries, both currently and for the next 5 to 10 years.

RECOMMENDATIONS

1. Federal funding agencies should make greater and more systematic efforts to support development of an improved database for plasma modeling. In addition, given the direct benefits an improved database would provide for both semiconductor manufacturers and plasma equipment suppliers, organizations set up by industry to promote integrated circuit manufacturing and the semiconductor equipment industry should participate in supporting targeted database development. Greatest emphasis should be placed on surface processes because of their centrality in the technology and because this is the area in which in general the least is known. However, the other database needs outlined in the main text of this report—electron-collision processes, spectroscopic/radiative processes, ion-neutral and neutral-neutral chemistry, and thermochemistry—are also important and need considerable work if the models are to achieve their potential impact industrially. Computational approaches to providing database information, using ab initio electronic structure codes as well as semiempirical methods, should be encouraged.
2. A spectrum of plasma models should be developed, aimed at a variety of uses. One set of codes should be developed to provide a compact, relatively fast simulation that addresses plasma and surface kinetics and is useful for process engineers. Convenient user interfaces would be important for this set of codes. A second set of codes would include more sophisticated algorithms and higher dimensionality, and would be more useful for equipment design. Development and testing of models that meet these needs should be supported. Careful validation of the codes by systematic comparison to the results of experiments needs to be undertaken. As learning and resources allow, some development effort should focus on fully three-dimensional plasma, electromagnetic, and neutral transport codes. The degree of chemical complexity to be included will vary depending on the availability of data, the goals of the modeler, and the available computational resources.
3. The following chemistries and materials should have a high priority in database development. The panel chose these systems because the applications are currently important and are anticipated to continue to be important for at least the next 5 years and quite probably beyond that:

a. *Polycrystalline silicon etching in chlorine-containing gases and bromine-containing gases*. This set (of materials and chemistries) is commonly used in the etching step to define the gate electrode in field effect transistors. Control of this step is crucial in maintaining optimum device performance, and since at endpoint this step involves exposure of the increasingly thin gate dielectric, concern about damage and reliability is considerable for this step.

b. *Silicon dioxide etching in fluorocarbon-containing gases mixed with gases such as* O_2, H2, CO, He, and Ar. In back-end-of-the-line (BEOL) processes, one is mainly concerned with making the metallic interconnects inside a silicon dioxide insulator. The number of interconnect levels is rising, and the number of steps that involve contact (to the active device regions) and vias (from one level of metalization to the next) will increase accordingly. Concern here is with anisotropy, selectivity, and uniformity, as well as with contamination. These gases are also used to clean chambers that have been coated with dielectric films (silicon dioxide and silicon nitride) from previous steps using chemical vapor deposition (CVD). In addition, since many of the gases that are used for dielectric etching are currently of environmental concern because they are greenhouse gases (e.g. C_2F_6), an opportunity exists to minimize their use, remediate them as effluents, or even to replace them outright, if effective models of dielectric etching can be developed.

c. *Silicon dioxide deposition through plasma-enhanced chemical vapor deposition (PECVD), using mixtures of* SiH_4, N_2O, and O_2 or SiH_4, O_2, Ar, and TEOS (tetraethoxysilane). For the same reasons that oxide etching will continue to play an important role in BEOL processing as the number of interconnect levels increases, deposition of the intermetal dielectric will be a key process.

4. At least one data center should be established to archive, evaluate, and disseminate the existing and future database for models of plasma materials processing in integrated circuit manufacturing. The archived database should include kinetic pathways, mechanisms, and comparisons of models to the results of experiments. This structure would provide a framework for iterative improvement of the database. Full advantage should be taken of emerging electronic data acquisition technology exploiting rapid access through the Internet and the World Wide Web. Although individual companies will no doubt develop proprietary databases, the goal sought with the establishment of the data center is to serve the entire community interested in plasma modeling and diagnostics.

REFERENCES

1. National Research Council, *Plasma Processing of Materials: Scientific Opportunities and Technological Challenges* (National Academy Press, Washington, D.C., 1991).
2. *Semiconductor International*, May 1996, p. 83.
3. National Research Council, *Plasma Processing of Materials: Scientific Opportunities and Technological Challenges* (National Academy Press, Washington, D.C., 1991).
4. Semiconductor Industry Association, The National Technology Roadmap for Semiconductors (SEMATECH, Austin, Tex., 1994).

1

Industrial Perspectives

INTRODUCTION

The main purpose of this report is to highlight the opportunities for more rapid and effective development of plasma process modeling and simulation as an engineering tool in the semiconductor manufacturing and plasma equipment supplier industries. It is intended for a variety of audiences: academic and government laboratory researchers, industrial engineers and scientists, and program managers at federal funding agencies. The scope of the report is substantial, coveting the industrial needs for better plasma process engineering, the current state of the art in plasma modeling, and the various supporting databases and diagnostic techniques that underlie and complement modeling and simulation. The report begins with this chapter on industrial perspectives to emphasize the primary purpose of this activity: to serve the needs of industrial suppliers and users of plasma process equipment. The need to maintain this industrial perspective is a recurring theme of this report.

The potential for using modeling and simulation to benefit industrial users of plasma processes and equipment has never been greater. Computational costs continue to decrease steadily, and in the last several years, considerable progress has been achieved in establishing the major modeling strategies that are necessary to achieve practical industrial objectives. Nevertheless, low-temperature plasma processing science is a relatively young field, and has not therefore received the in-depth, sustained attention that is required to have a significant, timely impact in industry. This situation is perhaps most evident in the area of the database for physical and chemical processes in plasma materials processing. The data that are currently available are often scattered throughout the scientific literature, and assessments of their reliability are usually unavailable. The goals of this report include identifying strategies to add data to the existing database, to improve access to the database, and to assess the reliability of the available data. In addition to identifying the most important needs, this report assesses the experimental and theoretical/computational techniques that can be used, or must be developed, in order to begin to satisfy these needs.

A major complication in this process is the fact that industry uses a large variety of gases and materials in plasma processes and equipment. Since time and resources are always limited, one must make choices regarding which chemical systems to examine carefully. Experiments are expensive and time-consuming, and therefore it may be necessary to augment these measurements of fundamental data with theory. Computational techniques are useful, but may require careful testing since the methodologies are sometimes not fully mature. The panel has attempted to develop a compromise between the competing needs for breadth and depth in the database, recognizing that needs change as industry evolves. The recommendations presented here will therefore require updating, probably within 3 to 5 years of the publication of this report.

PLASMA PROCESSING FOR SEMICONDUCTOR MANUFACTURING

The semiconductor industry and related industries such as flat panel display manufacturing are growing rapidly. In the semiconductor industry, worldwide revenues grew from $50 billion to $140 billion from 1990 to 1995.[1] Projections are that a similar rate of growth will persist at least through the end of the decade, and probably longer. Plasma processing is one of the key technologies in this industry, accounting for ˜ 30% of all process equipment in a typical wafer fabrication facility and a similar percentage of process steps. These include etching, deposition, cleaning, and stripping. The current level of annual sales for plasma equipment is on the order of $3 billion to $4 billion, with increases projected to match the rate of growth of the industries it serves.[2] Projections are that by the end of the decade, sales of equipment for plasma etching, cleaning, physical vapor deposition (PVD), and chemical vapor deposition (CVD) will reach $10 billion.[3] An important trend in the industry is the rapidly escalating cost of capital equipment, and the growing share of equipment costs (now about 60%) in the total cost of a state-of-the-art fabrication facility (currently about $1.5 billion).[4]

The projected changes in integrated circuit technology anticipated in the 1994 roadmap of the Semiconductor Industry Association (SIA) are given in Table 1.1. The historic trend of a doubling in device density every 1.5 years or so will continue. New generations of technology are introduced every 3 years, fueled by information age demands that continue to explode. Notably, the introduction of 0.25 μm technology overlaps the introduction of the next jump in wafer size to 300 mm diameter in 1999. Part of the reason for the exceptional rate of growth in the semiconductor industry has been the dramatic and steady rise in performance per unit cost. In order that this trend in the performance/cost ratio continue, the next-generation developments listed above must be accomplished with a corresponding increase in manufacturing efficiency.

TABLE 1.1 Changes in Silicon Integrated Circuit Technology Projected to 1999

	1990	1993	1996	1999
Critical dimension (μm)	0.8	0.5	0.35	0.25
DRAM capacity (Mbits)[a]	4	16	64	256
MPU/logic clock speed (MHz)[b]	25-40	50-200	140-350	240-500
Wafer size (mm)	150	150-200	200	200-300
Defect density (no./cm^2)	0.2	0.1	0.05	0.03
Interconnect levels	2-3	34	4-5	5-6

[a] DRAM = dynamic random access memory. [b] MPU = microprocessor unit.

SOURCE: A. Voshchenkov, Workshop on Database Needs in Plasma Processing, Washington, D.C., April 1-2, 1995.

Increasing manufacturing efficiency will require a significant increase in the sophistication and effectiveness of process control, among other changes. For example, as critical dimension (CD) decreases, the control of the CD must be to within 0.03 μm. Even though the wafer diameter will increase, etching rate and selectivity nonuniformity across the wafer must in some cases be kept to less than 2%. During etching, an important control variable is the angle of the microfeature sidewall with respect to the surface. Control of this profile angle is sought to within 3 degrees. Another important processing variable in MOSFET (metal oxide semiconductor field effect transistor) manufacturing is related to the thin (< 80 Å) gate oxide between the gate electrode and the active device region below it. During the etching step in which the gate electrode is defined, and when gate oxide may be exposed to the plasma, selectivity must be high enough to keep gate oxide loss to less than 15 Å. This is only 4 to 5 atomic layers.

From the industrial perspective, plasma processing, especially plasma etching, is often seen as being unusually difficult to understand and control.[5] Although some of the general mechanisms of the plasma are known—such as the role of chemical interactions with radicals such as F or C1 atoms, the role of sidewall passivation in preserving etch anisotropy, and the fact that positive ion bombardment of surfaces has a mechanical sputtering role—many details remain obscure. Interactions between plasma species and the walls bounding the discharge are complex and depend on surface temperature, surface and bulk composition, and other variables that are empirically observed to change with time, but are not well understood. The goals of plasma etching, including high rate, selectivity, uniformity, minimal damage to the underlying nascent electrical devices, minimal chemical residue contamination, minimal particulate deposition, and microfeature critical dimension control, sometimes depend in subtle ways on the plasma quantities. Moreover, these processing objectives are commonly difficult to achieve simultaneously. For example, there is often a conflict between etch anisotropy (enhanced by more energetic ion bombardment) and selectivity (degraded by more energetic ion bombardment, since most solid materials sputter at about the same rate).

Measuring fundamental plasma quantities is challenging, especially in industrial plasma tools with limited access for diagnostic instruments and rudimentary sensors. Most often, one must develop empirical correlations between observed process characteristics such as etching rate, uniformity, and selectivity, and design and operating variables such as chamber shape and materials, applied power, gas pressure, composition of the inlet gases, and substrate temperature. There are many of these parameters in a plasma etching tool. The tendency to view plasma etching as " an art rather than a science, more black magic than engineering,"[6] can be attributed largely to the murky relationship between the output of a plasma tool and its operating and design characteristics. In order to develop a manufacturable plasma process, engineers must carefully balance the competing process objectives, selecting process operating conditions (and tool type) so that the trade-offs are reasonably satisfied. In addition, this optimization must occur in a region of parameter space that is as large as possible. That is, if some set of operating conditions yields acceptable process results, but a very small change in gas pressure or wall temperature (for example) results in unacceptable process characteristics, the "operating window" is too narrow and the process will be ill suited to an industrial operation. Finding the right combination of operating conditions usually involves a tedious search of a large parameter space, unaided by theory or computation and guided only by intuition and/or experience.

Partly in response to the challenges of etching high-aspect-ratio features, plasma equipment manufacturers have introduced in the last several years new plasma tools capable of operating at relatively low gas pressures, usually between several millitorr and several tens of millitorr. It is thought that the lower operating pressures improve etched feature profiles—for example, anisotropy—by minimizing collisions between bombarding ions and neutral molecules in the sheaths. However, lower operating pressures tend to reduce etching rates, lowering wafer throughput and increasing the cost of operating the equipment (part of the cost of ownership). In order to raise rates in spite of the reduced gas pressure, the newer tools have been designed to sustain a higher plasma charged-particle number density—typically on the order of 10^{11} to 10^{12} cm^{-3}. Perhaps more importantly, these newer tools (high density, low pressure) have at least partly separated power deposition into electrons to maintain plasma density (the source power) from power deposition into ions bombarding the substrate (the bias power). It should be noted that in addition to decreasing the frequency of ion-neutral collisions in the sheath and therefore increasing ion velocity anisotropy at the processed surface, these newer tools operate with considerably different ratios of ion flux to neutral flux bombarding the substrate, and with different neutral species impacting the surfaces. The latter effect is due to higher plasma densities—both neutral and ionic species in the high-density plasmas tend to be more highly dissociated, no doubt affecting the plasma chemistry. For example, fluorocarbon gases commonly used in dielectric film etching are considerably more dissociated into atomic F than is the case in more conventional tools. This has caused problems with selectivity between silicon dioxide and silicon and has necessitated other changes in tool operation (or design) to counter this effect. Some observers have noted that the chemistry in high-density plasmas, originally thought to be simpler and "cleaner" than in conventional tools, is perhaps simply different, still requiting careful balancing to meet all objectives.

Other effects are observed in high-density tools that are not observed in conventional tools. For example, in high-density plasmas, the flux of positive ions to the walls, and the return flux of neutral species, represent an internal recirculating mass flow of a magnitude similar to that of the gas flow entering and leaving the chamber due to pumping. The effects of this internal recirculation on processing are not known at present. In sum, because of the relatively new conditions experienced in high-density plasma tools, it is fair to say that modifications are needed to some of the established wisdom gleaned from years of experience with conditions of lower plasma density and higher gas pressure.

The combination of rapidly changing process objectives (see, e.g., Table 1.1) and a rapidly changing technology (e.g. the shift to low-pressure, high-density plasma tools) compounds the challenges for manufacturers and users of plasma processing equipment.Plasma processes have been successful in meeting the processing needs of many aspects of the semiconductor manufacturing industry.However,to keep up with the projected acceleration in the industry,plasma equipment design,optimization,and control must become more efficient.Plasma equipment suppliers that are able to meet the accelerating demands will win market share over their competitors both domestically and abroad.Chip manufacturers better able to optimize,maintain,and control their plasma tools will enjoy an advantage in productivity and therefore profitability.This advantage will in turn translate into more capable and affordable electronics for the civilian and defense sectors.In the rest of this chapter the panel outlines the opportunities that modeling and simulation offer to chip manufacturers and to plasma equipment suppliers to meet these goals.

PLASMA EQUIPMENT SUPPLIER PERSPECTIVES

Equipment suppliers design plasma process chambers,with the associated pumping,gas handling,wafer handling,and control software and hardware.In addition,plasma equipment suppliers develop process chemistries to meet the needs of their chip manufacturing customers,often in a collaborative effort.As silicon technology evolves toward the gigabit era in the next millennium,the requirements listed in Table 1.1 will place increased demands on the design of both new chambers and process chemistries.The choice of plasma tool design,process gas chemistries,and operating conditions (the operating window)must satisfy these criteria over a reasonable range of conditions.A major concern is the rune it takes to design a new plasma process chamber and to select the appropriate process chemistries and operating conditions.Plasma-induced contamination and damage are always a concern and must be kept to an absolute minimum,if not eliminated altogether.

The major problems with plasma processing technology from the point of view of the tool supplier can be summarized as difficulties in tool design,tool optimization,and tool control.Historically,and currently,plasma process equipment has been designed and optimized largely empirically.Designers have relied on experience, intuition,and estimation to develop the next generation of tools.Process control strategies have lagged behind the standards seen in other industries.Mostly,control has focused on simply maintaining constant mass flow of reactants,constant pressure in the chamber,constant wafer temperature,and constant radio-frequency power to the discharge.The wafer-to-wafer and batch-to-batch drifts that are well known to all users of plasma process equipment have not been addressed,or they have been dealt with by more frequent (and costly)chamber cleaning and wall conditioning.

The general consensus is that the traditional method of meeting the requirements listed above,namely empirical trial and error,is encountering a point of diminishing returns.One view of the overlapping roles that modeling and simulation can play is illustrated in Figure 1.1.The “modeling design engine”includes virtual prototyping of equipment,real-time process control,and process design.Virtual prototyping is the use of modeling to determine the location and size of gas inlet and pumping ports,the design of the vacuum pumping layout,the electrode and electromagnetic power coupling configurations,and the wafer clamping mechanism,among other equipment components,before constructing a prototype chamber (that is,before “cutting metal”).Process design involves the selection of process chemistries and operating conditions (e.g.pressure,power,gas flow rate) that will provide the desired processing characteristics (e.g.uniformity,rate,anisotropy in etching,film properties in deposition).Real-time process control involves the ability to make appropriate measurements of the important processing variables (or to infer these quantifies from other,more convenient measurements)and to adjust operating conditions to remain within

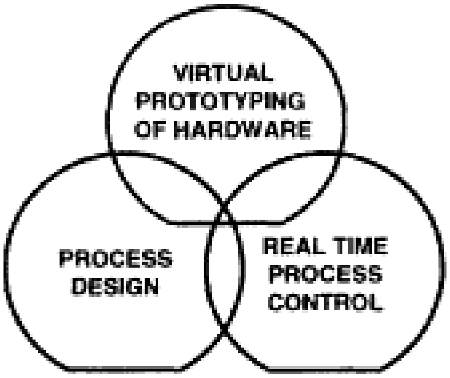


Figure 1.1
Overlapping functions of modeling:the “modeling design engine.”(Courtesy of A.Voshchenkov,Lam Research Corporation.)

combinations) will be most effective in controlling the process. The current approach involves the use of empirical correlation techniques such as response surface methodology, but these have limited validity outside the conditions under which the data were obtained. Also, model-based process control offers the opportunity to incorporate what is known about the process dynamics into the process control scheme.

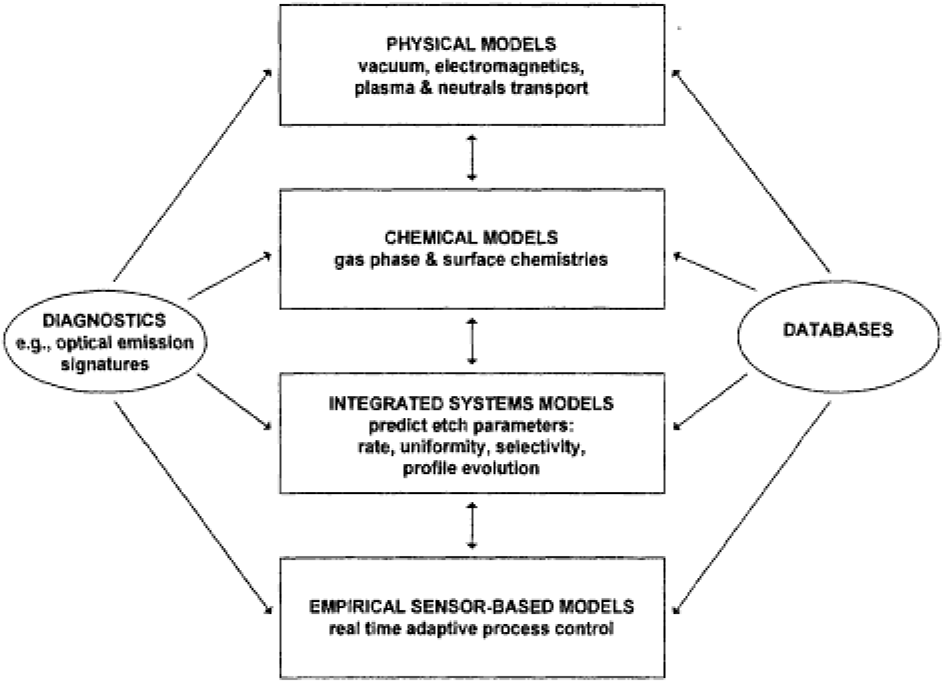


Figure 1.2
Coupled, comprehensive models. Databases and diagnostics are important at all levels. (Courtesy of A. Voshchenkov, Lam Research Corporation.)

A set of integrated comprehensive models that are envisioned by plasma tool suppliers[7] is shown in Figure 1.2. This set includes physical models to predict transport and electromagnetic phenomena; chemical models for both gas phase and surface chemistry; integrated system models to enable predicting what is happening at the wafer surface in terms of macroscopic phenomena at the tool scale; and finally empirical sensor-based models for real-time, adaptive process control. Process diagnostics play a key role in all of these models, from validation of the physical and chemical models to helping to identify and develop the appropriate sensors for process control applications. The models envisioned in Figure 1.2 are termed "comprehensive," but it is recognized that hardware and chemistry process models need not capture every detail in order to be useful. Convenient user interfaces, and the development of compatible modeling modules that can be integrated into evolving simulation codes, are the keys to exploiting current advances without limiting future developments as they become available. Databases are the subject of other chapters in this report, and as illustrated in Figure 1.2, they play an important role in all of the subsets of the comprehensive model.

CHIP MANUFACTURER PERSPECTIVES

The semiconductor industry has established the necessity of plasma processing for both deposition and etching of materials. These applications include highly anisotropic etching of deep trenches in silicon, highly selective etching of polysilicon gates on very thin gate oxides, and blanket photoresist removal. Plasma deposition has been applied to metals, to barrier layers between films that might otherwise interdiffuse and/or react, and to insulators such as silicon dioxide and silicon nitride. In addition, plasmas are often used to clean surfaces of debris and other unwanted materials. From the point of view of the chip manufacturer, the development of plasma processes has been chiefly an experiment-driven procedure, and this has carried the industry to working with submicron features.

Advances in very large scale integration (VLSI) have brought the industry to the point that small differences in process precision can have a large economic impact. An example is apparent in the area of microprocessor manufacturing. After fabrication, microprocessors today are sorted based on the maximum speed at which they will operate. This sorting is determined primarily by the precision in etching the gate and metal wiring levels. Relatively small losses in the precision of these etching steps result in slower devices. (It should be noted that it can be difficult to separate the roles of lithography and etching in this loss of precision. Sometimes it is possible to compensate for problems in lithography with alterations in the etching step.) The sales price of a single chip can differ by hundreds of dollars between the fastest speed category and a slower one. Control of processes on the feature length scale, across the entire wafer, must be maintained over time scales that can range from seconds to many hours. During etching of a single wafer, short transients that might last on the order of seconds during the start or end-point of an etch can influence processing characteristics. In addition, variations on time scales of tens of minutes due to, for example, relatively slow changes in tool wall temperature, can be important. On even longer time scales, wall surface deposits slowly build up and must eventually be removed in a cleaning step. These are some of the major forces driving the industry to better understand and control plasma processes. The industry is looking to modeling and simulation to help gain this understanding.

Another area of concern for chip manufacturers is in the so-called back end of the line (BEOL) where the metal interconnects are formed. As noted in Table 1.1, the number of these interconnect levels is increasing. At the same time, the defect density must be reduced. However, the danger of introducing device-threatening contamination and/or damage during these steps increases as the number of processing steps increases with the number of levels of metalization. Problems such as this have prompted interest in contamination-free manufacturing (CFM). Plasmas are acknowledged generators of particles, both from chamber walls and from processes occurring within the plasma. Particles become charged in the plasma and are often trapped above the wafer. An important opportunity exists for plasma modeling and simulation to contribute to better understanding and eventual control of particles in plasma process equipment. Improvements in plasma tool design and operation are needed to minimize particle nucleation, growth, and eventual deposition on the wafer.

Models for plasma processes today exist largely at two levels, based on the two major length scales in the technology: the microfeature level (~ 0.1-10 μm) and the tool level (~ 1-100 cm). However, between the microfeature level and the tool level is a mid-scale level that involves patterns of features on wafers, the edge region of the wafer, and so on. This mid-scale level is on the order of 0.1 mm to 1 cm, and to date it has received less attention from the modeling and simulation community. However, issues associated with a dependence of etching characteristics on the local pattern (such as the density of lines) are of considerable practical importance to the chip manufacturer. Connections between the mid-level scale and the tool scale must be developed in order to address these concerns. In addition, many important phenomena occur on the molecular scale (~ 1-100 Å).

Modeling and simulation are needed for developing processes that produce the desired uniform results. There is a clear need to minimize the time it takes to develop a process for a new pattern, minimizing the feature size and "adjacency" problems noted above. Cost is increasingly important. Tool productivity in terms of cost per operation is key to competitiveness. Reduction of the number and complexity of experiments through simulation is increasingly attractive since engineering experiments have become very costly. Achieving these efficiencies requires valid models, access to model data, and calibration techniques.

In order to involve plasma process engineers in the use of plasma equipment models, it is important that such models be relatively fast and easy to use. Multidimensional simulations tend to be relatively time-consuming (a few to several tens of hours), even on fast workstations. This is probably too slow for the process engineer. In addition, user interfaces are now relatively crude. One option, therefore, is to develop less comprehensive but faster running models that are coupled to an etch profile simulator. With a convenient user interface, this combination of relatively simple models might be a useful aid to the plasma process engineer. Acceptance of such a simulation package would set the stage for the use of more complex models by industrial engineers.

RECOMMENDED PRIORITIES FOR DEVELOPMENT OF AN IMPROVED DATABASE

Although there are many applications of plasmas to a wide variety of processes as noted above, it is appropriate to attempt to establish several applications that, from an industrial point of view, seem especially promising for modeling. These applications are listed in Table 1.2. The first application is polysilicon gate etching in chlorine- and bromine-containing gases. The second is SiO_2 etching in hydrofluorocarbon-containing gases (i.e. $C_xF_yH_z$), with various other gases added such as O_2 and N_2. The third is a common plasma-enhanced chemical vapor deposition (PECVD) application, SiO_2 deposition. The primary gases for this application include SiH_4, O_2, N_2O; SiH_4, O_2, Ar; and tetraethoxysilane (TEOS). Note that this list is not all-inclusive in that in some cases other gases are used in addition to the major gases listed in Table 1.2.

TABLE 1.2 Recommended Priorities for Developing an Improved Database

Application	Gases
Poly-Si etching	Cls_2, Br_2, HBr, O_2, N_2
SiO_2 etching	CF_4, CHF_3, C_2F_6, O_2, N_2, CO, Ar
SiO_2 deposition	SiH_4, O_2, N_2O; SiH_4, O_2, Ar; TEOS

The rationale for these choices is that all three are major applications with widespread interest in the industry, and they all appear to be applications that will persist for at least the next 3 to 5 years. Gate electrode etching is a key in controlling the effective channel length for complementary metal oxide semiconductor (CMOS) devices, and therefore plays a major role in the sorting of microprocessor speeds described above. This has a direct impact on chip profitability, and is in need of close attention as a result. Dielectric etching (mainly contacts and vias) is crucial because of the increasing aspect ratios (3-4 and above), coupled with a high degree of selectivity between the oxide and the silicon (50:1 is desired but difficult to achieve). Dielectric etching is also the largest segment of the plasma etching market. For PECVD, simultaneous deposition and etching offers the opportunity to fill gaps between metal interconnect lines. As the number of metalization levels increases, this application will become more important. Other PECVD oxide deposition applications include planarization layers.

The list of recommended chemical systems and associated applications in Table 1.2 does not in itself constitute a "database." For each of these systems, the database consists of a choice of chemical species to include in the overall mechanism, the key reactive pathways by which the selected set of chemical species are created and destroyed, and, in addition, rate expressions and parameters describing the nature of the interactions between these selected species and with surfaces. These needs are discussed in greater detail in subsequent chapters. In this chapter, the emphasis is on identifying the general chemical systems that are related to a selected set of common industrial processes (i.e. those listed in Table 1.2), rather than on prioritizing individual collisional and/or reactive processes.

It should be noted that, in addition to the recommended high-priority chemical systems listed in Table 1.2, there are many other chemical systems that are of interest in various applications of plasma processing in integrated circuit manufacture. These include physical vapor deposition techniques such as sputtering and reactive sputtering; conventional metal etching (Al/Cu alloys); photoresist stripping/ashing; plasma-enhanced chemical vapor deposition of a variety of materials; compound semiconductor etching; and emerging applications involving etching of ferroelectric materials and noble metals. These are all important applications of plasma processes, and it is likely that new applications will emerge in the future. Plasma modeling and simulation have the potential to significantly improve these applications as well as the ones listed as recommended priorities. Although the systems listed in Table 1.2 were judged to be the prime candidates for database development support, it is certainly true that other applications are important and deserve support as well.

FINDINGS

1. The integrated circuit manufacturing industry remains in its historical pattern of rapid technological change, coupled with impressive rates of growth. This pattern has begun to seriously challenge plasma equipment suppliers to continue the trend toward ever higher performance/cost ratios. Rapidly changing plasma process requirements, increasingly stringent process control requirements, and pressure to decrease the time to market for both new semiconductor products and new plasma equipment all contribute to the demand for a more effective approach to plasma process engineering. Meeting these more stringent requirements will make the U.S. semiconductor manufacturing industry more competitive and responsive to both civilian and defense markets.
2. Plasma processing tools are, in most cases, designed and optimized empirically. Real-time control of plasma processes is limited to individual subsystem loops for variables such as flow or pressure. Feedback control of important process parameters such as etching rate, uniformity, and selectivity has not been adopted by the industry. Further improvements in performance by means of empirical adjustments will soon reach a point of diminishing returns, if they have not already.
3. Control of processes in plasma reactors must occur on length scales that range from tens of angstroms to tens of centimeters and time scales that range from seconds to tens of hours. Loss of control at any point in this spectrum of length and time scales can result in reduced yields of components and therefore significant economic losses. For example, precise control of transistor gate and metal wiring levels across the entire chip is necessary to manufacture microprocessors at the highest speeds. Loss of this control over etching precision produces slower microprocessors and a loss of hundreds of dollars per chip. Obviously, across-wafer control is equally important to maintain high yields and therefore high profitability.

CONCLUSIONS

1. Plasma modeling and simulation can develop into a powerful scientific and engineering tool, but a number of obstacles are limiting the pace of progress. It is generally agreed that the primary obstacle is a lack of a suitable database for the many physical and chemical processes that make up a plasma process. This includes not only data characterizing individual collisional processes, but also the selection of the key chemical species, and the reaction pathways for these species.
2. The most promising applications on which to focus for developing or improving the database are poly-Si etching, SiO_2 etching, and SiO_2 deposition. These applications are currently important and appear likely to remain important for the next 3 to 5 years at least.

The remainder of this report is intended to sharpen the focus on the existing state of the art in plasma modeling and simulation, and the database that supports it. While the treatment is not exhaustive, each subsequent chapter aims to summarize the most important current issues and to point the way to the most fruitful directions for improvement.

REFERENCES

1. *Semiconductor International*, May 1996, p. 83.
2. A. Ghanbari, Workshop on Database Needs in Plasma Processing, Washington, D.C., April 1-2, 1995.
3. *Ibid.*
4. Semiconductor Industry Association, *The National Technology Roadmap for Semiconductors* (SEMATECH, Austin, Tex., 1994).
5. P Singer, "New Frontiers in Plasma Etching," *Semiconductor International* 19(8):152 (July 1996).
6. *Ibid.*
7. A. Voshchenkov, Workshop on Database Needs in Plasma Processing, Washington, D.C., April 1-2, 1995.

2

Tool Scale and Feature Scale Models

INTRODUCTION

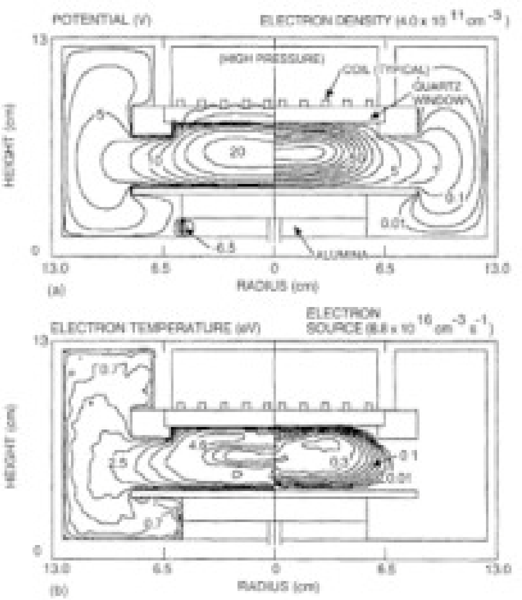
Chapter 1, "Industrial Perspectives," outlines the most promising ways to apply plasma modeling and simulation to attack problems that most directly affect plasma tool suppliers and chip manufacturers. The purpose of this chapter is to summarize the current state of plasma modeling and simulation and to identify the most pressing issues that could limit the pace of progress in solving industrially relevant problems.

The major industrial problems on which modeling may have an impact involve decreasing the time and cost of developing new plasma tools (shortening the time to market), improving the efficiency of optimizing tool performance to meet changing process objectives, and helping to implement real-time process control into operating tools. Each of these goals implies a somewhat different type of plasma modeling approach. In addition, some plasma models can be developed relatively quickly, while others will take more time. They all share the need to be systematically tested against experimental measurements (validated), and they need to be in a form that can be used conveniently by engineers involved in design, optimization, and control of plasma tools in industry. However, the greatest need for any plasma model is in the area of an improved database for the multitude of elementary processes that collectively determine the physical and chemical dynamics of the system.

TOOL SCALE MODELS

Over the past decade, modeling and simulation of plasma reactors at the tool scale, meaning the scale of the entire reactor (including the entire wafer), have attracted much attention.[1] This is due in large part to the recognition that the problems in the effective application of plasma processes, outlined in Chapter 1, might be fruitfully attacked using modeling and simulation. However, glow discharge plasma simulation is a challenging task, primarily because of (1) the nonequilibrium nature of the plasma, (2) the disparate time scales (< 1 ns to several seconds), and (3) the complexity of the gas phase chemistry and especially the surface chemistry.

In an electrical glow discharge, external electromagnetic energy is applied to the system, heating electrons and ions. Since the gases rarely are more than a few percent ionized (at most), electrons experience collisions mostly with much heavier neutral species. The very small mass ratio of the collision partners (electrons/neutral molecules) results in a low efficiency of energy transfer in elastic collisions between electrons and neutral species. Electrons continue to gain energy from the electric fields until their mean energy is sufficiently high to excite inelastic collisions with neutrals. Electron mean energies are typically several electron volts (eV), and the resulting ionization of neutral molecules is the primary sustaining mechanism in a glow discharge. (Note that 1 eV is approximately equivalent in temperature to 11,000 K or 20,000 °F). Because of the ambipolar electric fields in the plasma, positive ions are usually accelerated to the boundaries of the plasma and then accelerated further across the sheath potential to impact the surface. Electrons typically diffuse against the confining ambipolar fields to the walls and recombine there with positive ions. In electronegative gases, negative ions form through electron attachment, and are usually lost through gas phase processes such as positive ion-negative ion recombination or electron detachment. Electrons with several eV mean energy can not only ionize molecules, but also can easily dissociate most molecules into fragments. These fragments are the main chemical precursors for both film deposition and etching. Chemisorbed neutral molecular fragments at surfaces, especially when impacted by energetic positive ions from the discharge, are responsible for the chemical reactions that lead to etching. These processes are taking place in chambers with (often) fully


POTENTIAL (V)
ELECTRON DENSITY (4.0 x 10 11 cm -3)
(HIGH PRESSURE)
COIL (TYPICAL)
QUARTZ WINDOW
ALUMINA
HEIGHT (cm)
RADIUS (cm)
13
0
13.0
6.5
0
6.5
13.0
5
20
10
5
1
0.1
0.01
-6.5
(a)
ELECTRON TEMPERATURE (eV)
ELECTRON SOURCE (6.6 x 10 16 cm -3 s -1)
HEIGHT (cm)
RADIUS (cm)
0.7
2.5
4.5
0.7
0.3
0.1
0.01
(b)

addition, there must be extensive sets of comparisons between experimental measurements and model predictions in order to validate the models that are proposed.

An important feature alluded to in Chapter 1 is the role of the mid-level, between the tool scale (tens to hundreds of centimeters) and the microfeature level (~ 1 μm). This mid-level involves effects near the edge of the wafer, the effects of pattern area loading on the wafer, and similar phenomena. The length scale is typically less than 1 cm (on the order of the size of a single chip) but greater than 10 μm. This is an awkward intermediate scale, since resolving tool scale simulations on a scale of ~ 0.1 cm or less becomes very expensive computationally. Further work is needed to develop strategies to couple models of various length scales.

Capabilities Needed for Tool Scale Models

Tool scale models need to be capable of predicting the behavior and uniformity of the plasma sufficiently well that the following effects can be modeled:

1. Alternative chemistries,
2. Pressure,
3. Power,
4. Gas flow and composition,
5. Changing geometrical configuration (tool shape, wafer edges, clamps),
6. Chamber wall effects: seasoning and cleaning, and
7. Applied magnetic field.

In order that the models be useful, the minimum requirement is that the models capture the qualitative trends. In addition, they must be set up in such a way that they can be coupled conveniently to the feature scale models, discussed below.

Barriers to Using Tool Scale Models

Some of the barriers to the use of current-generation tool scale models are listed below:[2]

1. There is a lack of mature models that include physical accuracy, computational accuracy, and robustness. Physical accuracy refers to the accuracy of the underlying equations and assumptions in the model. Computational accuracy refers to possible problems with actually solving the equations in the model. For example, finite difference or finite element methods' solutions to discretized equations do not always correspond to the solution of the original differential equation. Robustness refers to loss of convergence, "touchy" solutions, and similar problems. Robustness is a nontrivial issue to overcome when highly coupled, nonlinear equations are being solved, as in the case of glow discharge plasmas.
2. There is a lack of integration among different parts of the simulation codes. This means that models of the tool geometry, the grid generators, the visualization tools, the graphical interfaces, and other design tools are not linked together in convenient ways.
3. There is a lack of commercial software suppliers. Commercial software suppliers provide documentation, consistent support, model updates, and continuous development. Generally, these features are lacking in university and national laboratory codes (although exceptions exist).
4. There is a lack of a database. All simulations require information about various processes occurring within the system being modeled. In the case of plasma models, this requirement includes information regarding electron-impact phenomena, ion-neutral collisions (e.g. ion-molecule reactions), neutral-neutral reactions, and the various processes occurring at surfaces bounding the plasma.

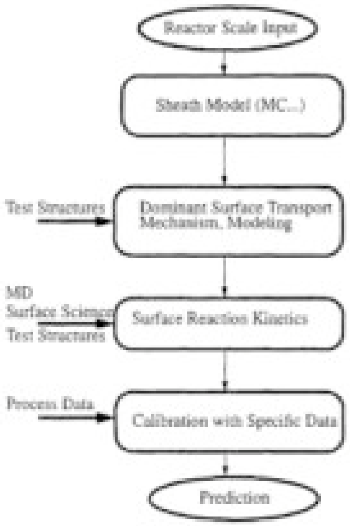


Figure 2.2
Strategy for feature-scale modeling and characterization.(Courtesy of V.Singh,Intel Corporation.)

that would have occurred if the sputtering step had not been used. The simulation both allows an understanding of the causes of the void formation and provides a methodology to optimize conditions in such a way as to avoid the problem in practice.

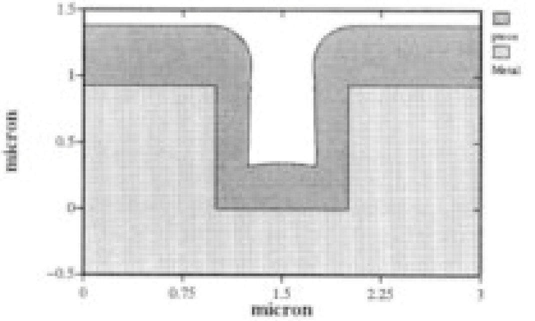
GENERAL ASSESSMENT OF MODELING STATE OF THE ART AND VISION OF FUTURE CAPABILITY AND IMPLIED NEEDS

In summary, the current state of modeling can be described as well established in some regards, but immature in others. For tool scale models, the treatments of neutral gas mass transfer, fluid flow, and heat transfer, while complicated by relatively low pressures and associated problems with transition-regime and sometimes free molecular flow, are well developed fields. Treatments of electric discharge physics, including electron and ion kinetics, and electromagnetic phenomena in gas discharges, are less well developed, but the general strategies for attacking these problems axe fairly well established. If one were interested in modeling rare-gas discharges, one might conclude that most of the major complications had been identified and solution strategies developed, although of course not all problems have been solved. Similarly for feature scale models, profile surface advancement algorithms have been well developed, especially for two-dimensional or axisymmetric features. Progress is being made to extend these techniques to three-dimensional features.

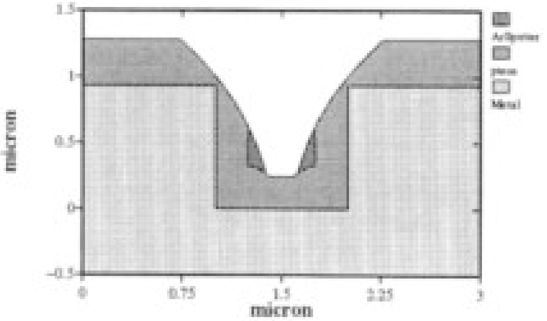
Two major issues challenge current capabilities in modeling low-pressure gas discharge plasmas for semiconductor manufacturing. The first is chemical complexity. This issue arises from the use of complex mixtures of halogen-containing gases, as well as other gases that are relatively little studied. The chemical scheme includes reaction products from chamber walls, photoresist reaction products, etching products, and slowly changing wall reactivities as films form on walls. Including these effects increases the difficulty of modeling by orders of magnitude. The second issue has to do with length scale disparities. The tool or wafer scale is tens of centimeters, but the microfeatures that one must control are on the order of fractions of microns. It is very difficult to measure (while the wafer is in the plasma tool) the quantities that one is most interested in controlling, such as the feature linewidth, the sidewall angle, the composition of trace species on the surface, or the introduction of chemical or mechanical imperfections that lead to electrical device failure or reliability problems. There is, in addition the difficult problem of the mid-scale between the feature scale and the tool scale. Little progress has been made to resolve mid-scale model formulation or solution.

The need to deal with the first problem, chemical complexity, is the major motivation for the present report, because the way chemical complexity manifests itself in modeling is through the need for parameters to characterize the way the various species in the plasma interact with each other and with walls. This is true for models at all length and time scales.

Any vision of future capabilities revolves around the central question of how one represents the chemical species in the plasma. In the immediate future, perhaps the next 5 years, it is not likely that models of industrial plasma processes will be developed that will seriously attempt to include *all* chemical species present, including *all* kinetic information (i.e. velocity and internal energy distributions). Furthermore, the proper characterization of the state of surfaces exposed to plasmas is sufficiently far from being fully understood that models of surface processes will necessarily be approximate. Fortunately, it is generally *not necessary* to make models so comprehensive. In order to make the problem tractable, one must choose some subset of all chemical species present and some approximate treatment of the interactions these species have with bounding surfaces. These choices, along with choices concerning dimensionality, how much of the surrounding environment and materials to include in the model, and how one treats the kinetics of the charged species and electromagnetic phenomena, all constitute the "model." It is axiomatic in modeling that what should be included in a model can properly be judged only by what one wishes to do with the model. There is a wide range of possibilities, from well-mixed reactors that seek to


1.5
1
0.5
0
−0.5
micron
0
0.75
1.5
2.25
3
micron
pecvd
Metal

(a)


1.5
1
0.5
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−0.5
micron
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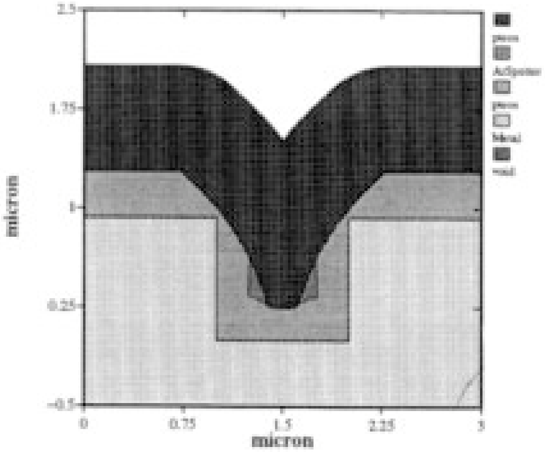
0.75
1.5
2.25
3
micron
ArSputter
pecvd
Metal

(b)


2.5
1.75
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0.25
−0.5
micron
0
0.75
1.5
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3
micron
pecvd
ArSputter
pecvd
Metal
void

(c)

created and destroyed through a set of chosen reactions. The tens of chemical species present interact through perhaps hundreds of elementary gas phase and surface reactions. Parameters characterizing the rates of creation and loss of the chemical species in the model must be measured, computed, or estimated. It is likely that interactions between many species are synergistic: no single species is responsible for selectivity, for example. Interactions will depend on temperature, competing physical and chemical processes, and probably other factors that are unknown at present. Species present in low concentration may play a key role in the overall chemical balances and cannot be ignored simply because they are not one of the major species. In addition, surface chemical processes can be affected by small concentrations of species in the gas phase, because there are relatively few surface-active sites in comparison to typical fluxes from the gas phase.

An important point in modeling is that in many cases a reduced set of chemical species and reactions will serve as a good approximation to the complete set. The goal is then to identify what this reduced set should comprise and how to determine the kinetic parameters that govern their interactions. The most promising way to develop the set of chemical species, their interacting mechanisms, and the parameters in the rate expressions (the "database") is to propose a model, and then critically compare model predictions to measurements. Iteration on the original mechanism will then improve the chosen set. Sensitivity analyses will help identify, within a given model, which of the processes are the most important. In some cases, critical comparisons between model predictions and diagnostics can help to determine the database. Other modelers, starting with a different initial guess of species and mechanisms, may iterate to a different final set.

It might be helpful to provide a specific example of how this interaction might work in practice. Let us consider the case of fluorocarbon plasma etching of dielectric films, for example silicon dioxide. This is the largest single etching application in the microelectronics industry, but it is poorly understood and difficult to control. It has proven necessary to use a chemistry that results in polymeric film deposition in order to maintain a high selectivity between silicon dioxide and silicon. The fluorocarbon molecules tend to reduce the etching rate of silicon because the carbon remains involatile in the absence of oxygen at the surface. For a SiO_2 surface, this problem does not exist and the fluorocarbon molecules are volatilized along with the silicon and oxygen, resulting in etching. It is thought that this polymeric film forms and is etched by a complex combination of neutral and ionic species interacting at surfaces. This mechanism suggests that developing a model for the system will be challenging, since it is likely that many fluorocarbon radicals and ions participate in the plasma-assisted polymer etching and deposition kinetics.

It is important to understand that relatively little progress has been made in developing and testing mechanistic models of plasma chemistry under typical industrial conditions. In a typical high-density plasma oxide etching tool, there will be, in addition to the exposed oxide to be etched, photoresist, various wall materials such as anodized aluminum, other ceramic-like materials, and the deposited polymeric film mentioned above. The inlet gases might include C_2F_6, O_2, and Ar, for example. Consider first the neutral species that might be involved in this plasma: all of the inlet gases, and all combinations of their dissociation products (e.g. C_xF_y, COF_x, CO, CO_2, O, Ar, C, F); all products of reactions between these species and the materials to be etched (e.g. SiF_x, SiO_xF_y); all products of reactions between these species and the photoresist (hydrocarbon-based, with other species added for lithographic or other purposes); and, finally, products resulting from reactions between the chemically active species in the plasma and the reactor wall materials and/or the deposited fluorocarbon film. In addition to these neutral species (several tens), there will be many and various positive and negative ions formed from neutral species.

Collision cross sections between the neutral species and electrons must be obtained. Ion-molecule rate coefficients are necessary to predict ion composition. Some species will no doubt be in excited states (vibrational and/or electronic). Ultraviolet photons released in the plasma could conceivably play a role in both gas phase and surface chemistry. Each of the proposed species has no doubt many individual reactions, both in the gas phase and especially at surfaces. Surface chemical reactions are difficult to model in the presence of the plasma because of the complicating role of energetic ions in modifying surface composition and structure. Wall temperatures in the chamber often heat sufficiently to significantly affect reaction rates there.

Even if we knew the 10 major chemical species in the plasma (in general we do not), it would be a major task to assemble the data necessary to model even the most important of the chemical reaction rate processes in the gas phase and at the surface. It seems premature at this stage to attempt to identify individual collisional processes (e.g., the cross section for electron impact dissociative excitation of CF_2 into CF and excited F) as being especially important and worthy of attention above all the many other similar processes.

In order to develop a database to model this system, it will be necessary initially to identify the key chemical species that participate in the main gas phase and surface reactions. One way to begin this process is to make spectroscopic measurements of as many of the radicals and stable species in a fluorocarbon plasma as possible. This might include sampling for a mass spectrometer, optical emission spectroscopy, laser-reduced fluorescence, ultraviolet absorption, and infrared (IR) absorption (with a Fourier transform infrared (FTIR) spectrometer or a diode laser) for the gas phase species. Surface species might be identified with reflectance-absorbance IR measurements, or with total internal reflection methods, or possibly some form of spectroscopic ellipsometry. Laser-induced desorption of surface species followed by one of the gas phase techniques can be a powerful surface diagnostic. Each of these measurement techniques could contribute information about plasma and surface composition, and changes in these compositions under varying conditions could give hints about possible mechanisms for interspecies conversions. Pulsing the plasma and observing the decay or growth of various species could provide further information about kinetics. Ideally, these measurements would be made in a plasma configuration that is easily modeled, and the identified species could be included in the model, along with electrons and the relevant positive and negative ions.

Estimates of electron-neutral and ion-neutral collision cross sections, coupled with preliminary values for kinetic rate coefficients for gas phase and surface reactions, would be included in the model. The model would predict spatial profiles of various chemical species, and these profiles would be tested by direct comparison with measurements. The inevitable initial disagreements between model and measurements provide the basis for iterative improvement of the "first cut" database. As key species and processes are identified, this information would be made available to specialists in measuring specific collision cross sections (between, for example, electrons and radical intermediates) through specialized experimental techniques such as crossed electron-radical beam or electron swarm methods. Ion drift tubes have been used for many years to study the kinetics of selected ion-molecule reactions. Special vacuum chambers designed to measure radical-surface and ion-surface interactions can be used for plasma-surface interaction studies. In some cases, ultrahigh-vacuum beam-surface studies might be useful. These techniques are described in greater detail in subsequent chapters of the report.

This vision of plasma model development implies several types of interactions within the plasma processing research community. Modelers will work directly with plasma diagnostic experimentalists to test their mechanisms and kinetic databases. Teams of modelers and plasma diagnosticians will also work directly with database experts: researchers measuring or computing electron-neutral cross sections, ion-molecule rate coefficients, radical-molecule reactions, radical-wall reactions, and ion-wall reactions. Since it is difficult and time-consuming to make accurate measurements or accurate computations of data, empirical methods to estimate or extend existing database parameters will be developed. In some cases, model results can be made consistent with measurements if collisional data have values in restricted ranges. In this way, models can be used to help determine parts of an improved database.

Researchers will interact through the normal scientific channels of collaborative interactions, reporting through the scientific and technical literature and at scientific meetings, conferences, and workshops. Industrial research and development teams will participate in this process by playing important roles in helping to direct and influence academic and government laboratory researchers through feedback about what processes, chemistries, and problems are most important. Companies that are best able to utilize the flow of information in the research community will be able to gain the most commercial advantage. Individual companies will no doubt develop proprietary databases and proprietary models of their tools and processes. However, this practice should not restrict the public flow of information to and from research teams. Toward this end, it seems desirable to establish at least one data center, in which database information, including collisional process characterization data and mechanism data, would be archived, evaluated, and disseminated.

FINDINGS

Models of low-temperature, nonequilibrium plasmas, especially for the description of physical phenomena, have developed rapidly in the last 5 years. Computing power per unit cost continues to increase rapidly. However, few of the currently available plasma models can be used easily by process engineers. Although attempts have been made to model plasmas with realistic chemistries, the parameter space that can be addressed is limited. Only a handful of studies have been made that attempt to validate models of plasma processes with industrially relevant chemistries. Models that attempt to link the relevant length scales (from tool scale to feature scale to atomic scale) are just now emerging. Simulations can be no more accurate than the data and assumptions on which they are based. The lack of fundamental data for the most important chemical species is the single largest factor limiting the successful application of models to problems of industrial interest.

CONCLUSIONS

1. The main roadblock to development of plasma models that will have industrially important uses is the lack of fundamental data on collisional, reactive processes occurring in the plasma and on walls bounding the plasma. Among the most important missing data are the identities of key chemical species and the dominant kinetic pathways that determine the concentrations and reactivities of these key species.
2. The lack of a central location to collect, analyze, and disseminate the data that are currently available, or that will be available in the future, is limiting progress in the field.

REFERENCES

1. See, for example, "Special Issue on Modeling Collisional Low-Temperature Plasmas," eds. M.J. Kushner and D.B. Graves, *IEEE Trans. Plasma Sci* . 19(2):61 (1991), and "Special Issue on Modeling Collisional Low-Temperature Plasmas," eds. J. Wu, M. Meyyappan, and D. Economou, *IEEE Trans. Plasma Sci*. (August 1995).
2. A. Krishnan, Workshop on Database Needs in Plasma Processing, Washington, D.C., April 1-2, 1995.
3. M.E. Barone and D.B. Graves, *J. Appl. Phys*. 77:12-65 (1995).

3

Radiative Processes and Diagnostics

INTRODUCTION

This chapter discusses gas phase and surface spectroscopic diagnostic techniques that can be used in plasma processing tools. As noted previously, techniques for measuring gas phase and surface quantities (species and energies) are essential for identifying the key chemical species in the plasma and for characterizing the chemical mechanisms that link these key species. Diagnostics are often best used in a complementary fashion with modeling: measurements help to test and validate models, and in turn, validated models help to augment the limited information provided by individual diagnostic techniques. For proper understanding and quantification, each diagnostic technique requires data on one or more physical quantities. Examples are discussed of sources of information on the physical principles of the various techniques, of sources on applications to specific systems, and of critically reviewed compilations of data on physical properties. It is shown that much can be done even when these sources do not provide all the information needed to plan or interpret a diagnostic experiment.

TECHNIQUES FOR MEASUREMENTS OF GAS PHASE SPECIES

There are various well-established optical techniques for the measurement of gas phase species in plasmas. Table 3.1 is a list derived from several recent review articles.[1] These techniques are usually easier to apply at low pressure since lines and bands overlap less and so are easier to identify and analyze. Species identities are provided by spectral signatures (positions and shapes of spectral features), while absolute intensities of the spectral features can provide absolute concentrations. Often, linewidths (for atoms and small molecules) or band structure (for molecular species) can be related to translational and rotational energies or temperatures.

TABLE 3.1 Optical Diagnostic Techniques for Plasma Processing Systems

Gas Phase	Surface
Infrared absorption	Reflection/absorption
Ultraviolet/visible absorption	Multiple internal reflection
Electronic emission	Emission
Actinometry	Ellipsometry
Laser-induced fluorescence	Reflectance difference
Multiphoton ionization	Photoluminescence
Optogalvanic spectroscopy	Optogalvanic spectroscopy
Raman scattering	Surface electromagnetic waves
Stimulated Raman scattering	Second harmonic generation
Stimulated emission	Photoacoustic absorption
Laser-induced photofragment emission	Photothermal displacement
Third harmonic generation	Photothermal deflection
Particle scattering	Laser desorption

Mass spectrometry is also important, though not included in this chapter's discussion of optical spectroscopic techniques. The database needs for this diagnostic are associated primarily with interpretation of mass-resolved ion spectra that result from electron-impact dissociative ionization. The need for data regarding cross sections for electron-impact dissociative ionization, and especially the sensitivity of those cross sections to molecular internal energy near threshold, is addressed in Chapter 5, "Electron Collision Processes."

Information Resources

The spectroscopic database for the properties and interactions of many of the gases used in plasma processing is quite extensive. Ultraviolet or infrared absorption strengths and fluorescence quenching or pressure broadening cross sections are the parameters needed to predict or interpret the results of absorption, emission, and fluorescence diagnostic experiments, and while not every parameter is available for every molecule, information on related species can often provide a basis for estimation. Data may be sparser for more specialized techniques, but the coverage for systems of the greatest interest may be adequate. On the other hand, much of this information is dispersed in many journals. Although some reviews have been written, as diagnostic fields mature there is less interest in continuing to produce comprehensive review articles. In addition, it is rare that either reviews or molecular property measurements are focused on the needs of plasma processing diagnostics. Areas receiving focused attention, such as combustion or atmospheric chemistry, sometimes produce results that also serve the plasma processing community. However, rapidly growing areas involving, for example, heavy metal halogens and metal-organics must be supported entirely within the community. Typically, this means that the research group developing the diagnostic application must also carry out any basic property measurements, the result being that those data may not even appear as the subject of that group's own publication in the primary literature, let alone in one of the centralized repositories briefly reviewed below.

Workers at the National Institute of Standards and Technology (NIST) have produced a number of compilations of atomic line positions and strengths,[2] some of which are now available as electronic databases.[3] However, as was pointed out recently, this is still an active area.[4] The compilation of Huber and Herzberg[5] occupies a similar position for diatomic molecules, and has also been compiled into a NIST database.[6] In general the classic volumes of Herzberg[7] still provide an excellent entry point to the older spectroscopic literature, while some newer spectroscopy texts provide some useful examples.[8] Books edited by Suchard[9] and Boyko,[10] the book by Pearse and Gaydon,[11] two reviews in the 1992 Royal Society annual reports volume[12] and one in the 1990 *Annual Review of Physical Chemistry*,[13] several reviews in the book series edited by Rao,[14] [15] and the ongoing compilation of Jacox, again available in both print[16] and electronic[17] versions, are other useful sources. The review article by Smith and co-workers[18] deserves special mention as a source of collision broadening parameters as well as of infrared band intensities.

The HITRAN absorption line listing[19] and an associated table of unresolved band absorption coefficients,[20] together with software allowing prediction of spectra, form a valuable resource for the set of atmospheric molecules. A NIST electronic database[21] provides moderate-resolution infrared spectra for a selection of 5244 molecules, while a number of commercial databases[22] provide higher resolution and additional species, in both print and electronic forms. One drawback of almost all these infrared spectral compilations, however, is that they are not quantified (path length or concentration are unavailable, or were initially unknown). For this reason, much earlier compilations of quantitative infrared spectra[23] are still useful.

A number of sources provide compiled data or useful keys to the primary literature even though their focus is not on plasma processing. The book by Okabe[24] lists a variety of ultraviolet absorption cross section spectra. Several review articles by Hirota and co-workers[25] provide good introductions to the work of this prolific group and supplement early comprehensive review articles on high-resolution infrared spectroscopy.[26] Volumes whose purpose is to list infrared band positions[27] also provide primary literature references, often leading to full, quantitative spectra. Finally, the JANAF thermochemical tables[28] can perform the same function as part of their documentation of entropy calculations, thus centralizing references to infrared spectra for a large number of molecular species.

Examples of what is involved in the collection and application of primary data to estimate the feasibility of particular diagnostic experiments are given in a 1983 SPIE paper by Wormhoudt, Stanton, and Silver.[29] Focusing on the techniques of laser-induced fluorescence and infrared absorption, it attempted to tabulate the parameters needed to estimate minimum detectable densities of a wide variety of stable and radical species then of interest in the electronic materials area. The fact that most of the 144 references in the paper are to sources of these molecular parameters reinforces the above remarks on the lack of centralized data sources. When molecular parameters were unknown, they were estimated. More than 10 years later, a number of these parameters have been measured, but no systematic review has been performed to assess the reliability of such estimation attempts. The minimum detectability estimates for absorption include a 100 cm path length. In a practical reactor, this path length would require a multipass geometry, a potential barrier to implementation. An alternative approach to achieving the same predicted sensitivity would be to assume smaller minimum detectable absorbances than the 10-3 assumed in the paper. Lower values are routinely achieved in the laboratory but would have to be demonstrated for a particular reactor.

Roles of the Database In Motivating Diagnostic Experiments

The SPIE paper discussed above was intended to promote work in two areas: diagnostics of semiconductor processing systems and laboratory measurements of supporting data. It is of interest to examine a few of the experiments of both types carried out following publication of the paper, the idea being to exemplify some general thoughts about the relationship between diagnostics and their supporting databases. The general points are as follows:

1. Quantitative diagnostic measurements, and comparison with the predictions of quantitative models, are necessary for the quantitative understanding of any phenomenon.
2. The level of quantitative accuracy required for a measurement to be useful is determined by the uncertainty limits expected from current or projected predictive models. This in turn determines the uncertainty levels that are acceptable in the supporting database.
3. Data that are enabling, in the sense that diagnostic experiments will not be attempted in their absence, are often different from the accurately quantified molecular parameters that allow derivation of absolute molecular concentrations and other system quantities.
4. It is important to realize that although at least one molecular parameter must be known accurately for a diagnostic experiment to yield quantitative results, typically at least one system parameter must also be known, and its uncertainties may determine the overall accuracy.
5. To summarize, database needs should be evaluated using at least three criteria: (a) What unknowns prevent first diagnostic experiments from being attempted? (b) What unknowns prevent meaningful comparisons with theoretical predictions? (c) Would reduction in database uncertainties for either reason have no effect because of continuing difficulties in quantifying system parameters?

Examples of the interaction between the fundamental database and the work of diagnostics developers can be obtained from an extensive series of studies using tunable infrared diode laser spectroscopy.[30]

Another method that has great promise in studies of processing plasmas is the two-photon allowed laser-induced fluorescence (TALIF) method. This method measures atomic species' densities using the high peak power of a commercially available 10 ns pulsed laser. Since the atomic species are very reactive, it is relatively easy to devise titration reactions that allow absolute calibration of the atom densities. TALIF has been applied mostly to hydrogen dissociation studies. A listing of other candidates for the TALIF approach and their titration reactions is given in Table 3.2. The work required to ensure linearity of the detector response over a wide dynamic range is quite demanding.

The point to be made here in the context of database needs is that the titration calibration, necessary to quantify the fluorescence collection efficiency, also has the effect of removing the TALIF determination of absolute concentrations from any dependence on atomic or molecular parameters. This independence of the spectroscopic and kinetic database would not apply, however, in cases in which the quenching environment of the experiment was very different from that in which the titration was done. Some data useful in plasma applications can be extrapolated from flame studies, but apart from the data of Piper and co-workers31 on nitrogen-silane reactions, the database for quenching excited species in other etching and deposition environments is sparse.

TABLE 3.2 Candidate Species for Application of TALIF

	Excitation		Fluorescence		
Species	λ (nm)	Transition	λ (nm)	Transition	Titration Reaction
H	205	$1s\,^2S$ - $3d\,^2D$	656	$3d\,^2D$ - $2p\,^2P$	$H + NO_2 \rightarrow OH + NO$
C	280	$2p^2\,^3P$ - $2p3p\,^3P$	910	$3p^3\,P$ - $3p^3\,P^0$	$N + NO \rightarrow N_2 + O$
N	207	$2p^3\,^4S^0$ - $2p^23p\,S^0$	747	$3p\,^4S^0$ - $3p\,^4P$	$C + O_2 \rightarrow CO + O$
O	225	$2p^4\,^3P$ - $2p^33p\,^3P$	844	$3p\,^3P$ - $3s\,^3S$	$O + NO_2 \rightarrow NO + O_2$
Cl	210	$3p^5\,^2P$ - $3p^44p\,^2F$	904	$4p\,^2F$ - $4s\,^2D$	$Cl + ClNO \rightarrow Cl_2 + NO$
Cl	233	$3p\,^2P^0$ - $4p\,^4S^0$	725-775	$4p\,^4S^0$ - $4s\,^4P$	$Cl + ClNO \rightarrow Cl_2 + NO$

SOURCE: Data from A.D. Tserepi, J.R. Dunlop, B.L. Preppernau, and T.A. Miller, *J. Appl. Phys.* 72:2638 (1992); Alden et al., *Optics Communications* 71(5):263 (1989); Das et al., *J. Chem. Phys.* 79:725 (1983).

Another technique reported in a number of very encouraging recent studies[32] is degenerate four-wave mixing (DFWM). This technique has several advantages: first, only two ports are needed, and they can be in line, as opposed to one large-aperture port at right angles to the entrance probe beam port; second, because of the fully resonant nature of DFWM, it is significantly more sensitive than other four-wave mixing techniques such as coherent anti-Stokes Raman scattering (CARS). Examples of the sensitivity include OH in a flame, about 4×10^{11} cm^{-3}; and NO, about 8×10^{11} cm^{-3}. The molecules C_3 and SiC_2 have been measured using DFWM and stimulated emission pumping (SEP) at sensitivities of 10^{12} cm^{-3} per rotational state. The main advantage of DFWM in the present context, however, is an insensitivity to quenching, allowing measurements with laser-induced fluorescence (LIF) levels of sensitivity without the corrections for molecular interactions required for LIF quantification.

SURFACE REACTION DATABASE AND DIAGNOSTICS

Surface reactions are often paramount in controlling the concentrations of atoms and other reactive radicals produced in etching and deposition plasmas. Many measurements have been made of surface reactions, generally using ex situ techniques. Some progress is being made with in situ sensors and ellipsometry (including infrared ellipsometry). Other recent studies have either used measurements of the steady-state (time-averaged) species concentration profiles adjacent to surfaces to extract reaction rates with surfaces, or made time-gated measurements of species decay after switch-off. The first method is more applicable at higher pressures in the reactor. The dynamic range of this approach depends on the accuracy and spatial resolution of the probing method. Generally the limited depth resolution will make extraction of data from finely structured surfaces quite difficult. Recent measurements on defined large areas of different materials adjacent to each other have revealed that surface reactivity is very sensitive to very small concentrations of sputtered material. An alternative diagnostic method is to make time-resolved measurements of the concentration decay, after the radio-frequency supply has been turned off or reduced to a significantly lower power level. Modulated plasma experiments can be used also to determine the gas phase kinetics, the negative ion formation rates, and the formation of clusters. At lower pressures, surface recombination and reaction often dominate the losses, and coefficients can be extracted from the species decay constants and time-dependent profiles adjacent to the surface. There are many indications that the surface reactivity often depends not only on the material and its history, but also on the fluxes and synergisms of other species (ions and neutrals) arriving at the surface. Except for a few cases, relatively little is known about these synergisms.

Information Resources

The database for surface reactions relevant to plasma processing of silicon is also highly dispersed. Useful information is included in several well-known texts,[33] refereed journals, symposia proceedings, trade journals, and course notes. The complete characterization of a modem process is often proprietary to the manufacturer or to the equipment vendor.

Many surface reactions have been studied using clean surfaces under ultrahigh-vacuum (UHV) conditions, and the different types of reactions and possibilities are reasonably well characterized. The difficulty arises when the surface is not that of a freshly cleaned crystal. The coefficients of the present database are not expected to be applicable to the surfaces found in low-pressure plasma reactors. Further, these surfaces are usually exposed simultaneously to fluxes of radicals, ions, and photons. Research is therefore required to bridge the gap between the clean surface science techniques that lead to fundamental understanding, and the etching/deposition/plasma-induced synergisms and the effective etching/deposition rates and selectivities that are important to the process engineer.

It is by now well documented[34] that infrared spectroscopy is one of the most powerful and broadly applicable of surface-sensitive diagnostic techniques. A key factor in its emergence has been the development of generations of capable, reliable, and relatively inexpensive FTIR spectrometers. Experimental configurations include reflection-absorption at grazing or oblique angles, transmission (through a thin film at the Brewster angle), emission, and multiple internal reflection using specially prepared substrates. Some of these techniques are suitable not only for laboratory experiments but also for monitoring and process control applications. In addition to identifying chemical species and their environments, infrared spectroscopy can be the method of choice for measuring surface temperature.

Although many features in surface spectra are readily identifiable based on gas phase band positions, a great deal of the information contained in these spectra is in the properties of these bands (such as details of their shape), or in new bands, which result from environments specific to the surface. Unfortunately, there is a lack of controlled laboratory experiments to conclude that a band assignment is correct beyond all doubt. However, most of the experimental and theoretical techniques exist to create the needed database for infrared surface spectroscopy. For example, isotopic substitution can often supply key evidence for both molecular identities and orientations. Coupling of infrared studies with other surface spectroscopies that do not have in situ potential but that can be applied in UHV systems has already formed the basis for some very fruitful studies, but much remains to be done. A particularly important avenue of investigation, now that atomic force microscopy is becoming a widely available technique, is the correlation of surface roughness with the results of optical techniques such as reflection-absorption.

New Diagnostic Techniques

Other new methods that are assisting the understanding of surface processes include the following:

1. Imaging of radicals interacting with surfaces (IRIS) combines a molecular beam source of radicals in a vacuum chamber with laser-induced fluorescence detection of both incident and reflected species.[35] This technique is described in Chapter 4, "Heterogeneous Processes."
2. Photoluminescence can be used to monitor process-induced damage. Calibration is needed to allow for the effects of temperature, surface condition, and other variables.
3. There is widespread agreement that future ultralarge-scale integration (ULSI) and other applications such as diamond films will be strongly influenced by initial surface properties and nucleation phenomena on surfaces. Recent studies have used not only transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM), but also synchrotron radiation x-ray photoelectron spectroscopy to determine actual surface bonding and oxidation mechanisms. Calibration of the signals from these surfaces and from the much more complex photoresist surface is a formidable

BOX 3.1 RADIATIVE SURFACE DIAGNOSTIC METHODS

Reflection/absorption
Multiple internal reflection
Emission
Ellipsometry
Reflectance difference
Photoluminescence
Optogalvanic spectroscopy
Surface electromagnetic waves
Second harmonic generation
Photoacoustic absorption
Photothermal deflection
Photothermal displacement
Laser desorption and product analysis by mass spectrometry or spectroscopy

4. Database development and review provide common reference points and save individual researchers the task of reviewing the primary literature. In addition, substantial benefits will accrue from new, electronic database technologies: searchability and compatibility with plotting and analysis software, not to mention compact storage of previously unwieldy amounts of data. There is little doubt that the electronic availability of a wide range of spectral data would stimulate the development of new diagnostic techniques and the wider application of existing methods.

REFERENCES

1. G. Hancock, L. Lanyi, J.P. Sucksmith, and B.K. Woodcock, "Atoms, Radicals and Ions Observed in Plasmas— Their Gas Phase and Surface Chemistry," *Pure Appl. Chem.* 66:1207 (1994); P.B. Davies and P.M. Martineau, "Diagnostics and Modeling of Silane and Methane Plasma CVD Processes," *Adv. Mater*. 4:729 (1992); M. Konuma, "Plasma Diagnostics," ch. 4 of *Film Deposition by Plasma Techniques* (Springer-Verlag, New York, 1992); B.L. Preppernau and T.A. Miller, "Laser-Based Diagnostics of Reactive Plasmas," in *Glow Discharge Spectroscopies*, ed. R.K. Marcus (Plenum Press, New York, 1993), pp. 483-508; O. Auciello and D.L. Flamm, eds., *Plasma Diagnostics* (Academic Press, Boston, 1989); R.W. Dreyfus, J.M. Jasinski, R.E. Walkup, and G.S. Selwyn, "Optical Diagnostics of Low Pressure Plasmas," *Pure Appl. Chem.* 57:1265 (1985); R.F. Karlicek, Jr., V.M. Donnelly, and W.D. Johnston, Jr., "Laser Spectroscopic Investigation of Gas-Phase Processes Relevant to Semiconductor Device Fabrication," *Mat. Res. Soc. Symp. Proc*. 17:151 (1983); I.P. Herman, *Optical Diagnostics of Thin Film Processing* (Academic Press, Boston, 1996).
2. J.R. Fuhr, G.A. Martin, and W.L. Wiese, "Atomic Transition Probabilities," *J. Phys. Chem. Ref. Data* 17, suppl. 4 (1988); R.L. Kelly, "Atomic and Ionic Spectrum Lines Below 2000 Angstroms," *J. Phys. Chem. Ref. Data* 16, suppl. 1 (1987); J. Reader, C.H. Corliss, W.L. Wiese, and G.A. Martin, *Wavelengths and Transition Probabilities for Atoms and Atomic Ions*, NSRDS-NBS 66 (U.S. Department of Commerce, December 1980).
3. J. Fuhr, *National Institute of Standards and Technology Atomic and Molecular Physics Database 24, NIST Atomic Transition Probabilities Data Files (Scandium Through Nickel)*, available from Standard Reference Data, NIST, Bldg. 221/Room A320, Gaithersburg, MD 20899 (1994); J.W. Gallagher, *National Institute of Standards and Technology Atomic and Molecular Physics Database 38, NIST Spectroscopic Properties of Atoms and Atomic Ions Database*, available from Standard Reference Data, NIST, Bldg. 22 I/Room A320, Gaithersburg, MD 20899 (1995).
4. P.S. Doidge, "A Compendium and Critical Review of Neutral Atom Resonance Line Oscillator Strengths for Atomic Absorption Analysis," *Spectrochim. Acta B* 50:156 (1995).
5. K.-P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
6. J.W. Gallagher, *National Institute of Standards and Technology Atomic and Molecular Physics Database 48, NIST Spectroscopic Properties of Diatomic Molecules Database*, available from Standard Reference Data, NIST, Bldg. 221/Room A320, Gaithersburg, MD 20899 (1995).
7. G. Herzberg, *Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950, reprinted by Krigger, Malabar, Fla., 1985); G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945); G. Herzberg, *Electronic Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1966).
8. J.M. Hollas, *Modern Spectroscopy* (Wiley, New York, 1986); J.I. Steinfeld, *Molecules and Radiation: An Introduction to Modern Molecular Spectroscopy* (MIT Press, Cambridge, Mass., 1981).
9. S.N. Suchard, ed., *Spectroscopic Data* (IFI/Plenum, New York, 1975).
10. V.A. Boyko, *Spectroscopic Constants of Atoms and Ions* (CRC Press, Boca Raton, Fla., 1994).
11. R.W.B. Pearse and A.G. Gaydon, *The Identification of Molecular Spectra*, 4th edn. (John Wiley and Sons, New York, 1976).
12. R.F. Barrow and P. Crozet, "Gas Phase Molecular Spectroscopy," *Annu. Rep. Prog. Chem. Roy. Soc. Chem.* 89C:353 471 (1992); P.B. Davies, "High Resolution Tunable Infrared Laser Spectroscopy of Transient Molecules," *Annu. Rep. Prog. Chem. Roy. Soc. Chem.* 89C:89-110 (1992).
13. P.F. Bernath, "High Resolution Infrared Spectroscopy of Transient Molecules," *Ann. Rev. Phys. Chem.* 41:91-122 (1990).
14. M.A.H. Smith, C.P. Rinsland, B. Fridovich, and K.N. Rao, "Intensities and Collision Broadening Parameters from Infrared Spectra," in *Molecular Spectroscopy: Modern Research*, vol. III, ed. K.N. Rao (Academic Press, New York, 1985), pp. 112-248.

15. J.M. Brown and M.R. Purnell, "Spectroscopic Parameters for Triatomic Free Radicals and Ions," in *Molecular Spectroscopy: Modern Research*, vol. III, ed. K.N. Rao (Academic Press, New York, 1985), pp. 249-296.
16. M.E. Jacox, "Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules," *J. Phys. Chem. Ref. Data*, monograph 3 (1994).
17. M.E. Jacox, *National Institute of Standards and Technology Atomic and Molecular Physics Database 26, NIST Vibrational and Electronic Energy Levels of Small Polyatomic Transient Molecules* (VEEL version 4.0), available from Standard Reference Data, NIST, Bldg. 221/Room A320, Gaithersburg, MD 20899 (1995).
18. M.A.H. Smith, C.P. Rinsland, B. Fridovich, and K.N. Rao, "Intensities and Collision Broadening Parameters from Infrared Spectra," in *Molecular Spectroscopy: Modern Research*, vol. III, ed. K.N. Rao (Academic Press, New York, 1985), pp. 112-248.
19. L.S. Rothman, R.R. Gainache, R.H. Tipping, C.P. Rinsland, M.A.H. Smith, D.C. Benner, V. Malathy Devi, J.-M. Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S.T. Massie, L.R. Brown, and R.A. Toth, "The HITRAN Molecular Database: Editions of 1991 and 1992," *J. Quant. Spectrosc. Radiat. Transf.* 48:469 (1992).
20. S.T. Massie and A. Goldman, "Absorption Parameters of Very Dense Molecular Spectra for the HITRAN Compilation," *J. Quant. Spectrosc. Radiat. Transf.* 48:713 (1992).
21. S.E. Stein, *National Institute of Standards and Technology Atomic and Molecular Physics Database 35, NIST/EPA Gas Phase Infrared Database* , available from Standard Reference Data, NIST, Bldg. 22 I/Room A320, Gaithersburg, MD 20899 (April 1992).
22. C.J. Pouchert, ed., *The Aldrich Library of FT-IR Spectra*, edn. I, vol. 3, "Vapor Phase" (Aldrich Chemical Company, Inc., Milwaukee, Wisc., 1989); W.A Warr, "Spectral Databases," *Chemometrics and Intelligent Laboratory Systems* 10:279 (1991).
23. D.S. Early and B.H. Blake, *Infrared Spectra of Gases and Vapors* (The Dow Chemical Company, Midland, Mich., March 1965); R.H. Pierson, A.N. Fletcher, and E.S. Gantz, "Catalog of Infrared Spectra for Qualitative Analysis of Gases," *Anal. Chem.* 28:1218 (1956).
24. H. Okabe, *Photochemistry of Small Molecules* (Wiley, New York, 1978).
25. H. Kanamori, Y. Endo, and E. Hirota, "Infrared Diode Laser and Microwave Kinetic Spectroscopy," in *Dynamics of Excited Molecules*, ed. K. Kuchitsu (Elsevier, New York, 1994); E. Hirota, *High-Resolution Spectroscopy of Transient Molecules* (Springer-Verlag, New York, 1985); E. Hirota and K. Kawaguchi, "High Resolution Infrared Studies of Molecular Dynamics," *Ann. Rev. Phys. Chem.* 36:53-76 (1985).
26. R.S. McDowell, "Infrared Laser Spectroscopy, 1980-1983," *Proc. SPIE* 380:494 (1983); R.S. Eng and R.T. Ku, "High Resolution Linear Laser Absorption Spectroscopy—Review," *Spec. Lett.* 15:803 (1982).
27. T. Shimanouchi, *Tables of Molecular Vibrational Frequencies*, NSRDS-NBS monograph 39 (Washington, D.C., 1972); T. Shimanouchi, "Tables of Molecular Vibrational Frequencies. Consolidated Volume II," *J. Phys. Chem. Ref. Data* 6:993 (1977); L.M. Sverdlov, M.A. Kovner, and E.P. Krainov, *Vibrational Spectra of Polyatomic Molecules* (Halstead Press, New York, 1974).
28. M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald, and A.N. Syverud, *JANAF Thermochemical Tables*, 3rd edn., *J. Phys. Chem. Ref. Data*, suppl. 1 (1985).
29. J. Wormhoudt, A.C. Stanton, and J. Silver, "Spectroscopic Techniques for Characterization of Gas Phase Species in Plasma Etching and Vapor Deposition Processes," *Proc. SPIE* 452:88 (1983).
30. H. Schlossberg, "Fluorine-Atom Probe Techniques for Chemical Lasers," *J. Appl. Phys.* 47:2044 (1976); A.C. Stanton and C.E. Kolb, "Direct Absorption Measurement of the Spin-Orbit Splitting and 2p1/2 Radiative Lifetime in Atomic Fluorine ($2p^5$)," *J. Chem. Phys.* 72:6637 (1980); A.C. Stanton, "A Measurement of the Radiative Lifetime of Cl ($3p^5$ 2p1/2)," *Chem. Phys. Lett.* 122:385 (1985); J. Wormhoudt, A.C. Stanton, A.D. Richards, and H.H. Sawin, "Atomic Chlorine Concentration and Gas Temperature Measurements in a Plasma Etching Reactor," *J. Appl. Phys.* 61:142 (1987); J. Wormhoudt, "Radical and Molecular Product Concentration Measurements in CF_4 and CH_4 Radio Frequency Plasmas by Infrared Diode Laser Absorption," *J. Vac. Sci. Technol. A* 8:1722 (1990); J. Wormhoudt, K.E. McCurdy, and J.B. Burkholder, "Measurements of the Strengths of Infrared Bands of CF_2," *Chem. Phys. Lett.* 158:480 (1989); J.J. Orlando and D.R. Smith, "Time-Resolved Tunable Diode Laser Detection of Products of the Infrared Multiphoton Dissociation of Hexafluoroacetone: A Line-Strength and Band-Strength Measurement for CF_3," *J. Phys. Chem.* 92:5147 (1988); P.B. Davies, W. Lewis-Bevan, and D.K. Russell, "Infrared Diode Laser Spectrum of the v_1 Band of CF_2," *J. Chem. Phys.* 75:5602 (1981); C. Yamada and E. Hirota, "Infrared Diode Laser Spectroscopy of the CF_3 v_3 Band," *J. Chem. Phys.*

78:1703 (1983); K. Takahashi, M. Hori, K. Maruyama, S. Kishimoto, and T. Goto, "Measurements of the CF, CF_2 and CF_3 Radicals in a CHF_3 Electron Cyclotron Resonance Plasma," *Jpn. J. Appl. Phys*. 32, L394 (1993); K. Maruyama, A. Sakai, and T. Goto, "Measurements of the CF_3 Radical Using Infrared Diode Laser Absorption Spectroscopy," *J. Phys. D: Appl. Phys*. 26:199 (1993); K. Maruyama and T. Goto, "Variation of CF_3, CF_2 and CF Radical Densities with RF CHF_3 Discharge Duration," *J. Phys. D: Appl. Phys*. 28:884 (1995).

31. L.G. Piper and G.E. Caledonia, "Kinetics of Silane Decomposition by Atomic and Molecular Nitrogen Metastables," *J. Phys. Chem*. 95:698 (1991).
32. R.L. Farrow and D.J. Rakestraw, "Detection of Trace Molecular Species Using Degenerate Four-Wave Mixing," *Science* 257:1894 (1992); S. Williams, D.S. Green, S. Sethuraman, and R.N. Zare, "Detection of Trace Species in Hostile Environments Using Degenerate Four-Wave Mixing: CH in an Atmospheric-Pressure Flame," *J. Am. Chem. Soc*. 114:9122 (1992); G.J. Germann, A. McIlroy, T. Dreier, R.L. Farrow, and D.J. Rakestraw, "Detection of Polyatomic Molecules Using Infrared Degenerate Four-Wave Mixing," *Ber. Bunsenges. Phys. Chem*. 97:1630 (1993); T.J. Butenhoff and E.A. Rohlfing, "Resonant Four-Wave Mixing Spectroscopy of Transient Molecules in Free Jets," *J. Chem. Phys*. 97:1595 (1992).
33. S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood, eds., *Handbook of Plasma Processing Fundamentals, Etching, Deposition, and Surface Interactions* (Noyes Publications, Park Ridge, N.J., 1990); D.M. Manos and D.L. Flamm, eds., *Plasma Etching: An Introduction* (Academic Press, Boston, 1989); G.E. McGuire, ed., *Semiconductor Materials and Process Technology Handbook* (Noyes Publications, Park Ridge, N.J., 1988); T. Vicsek, *Fractal Growth Phenomena* (World Scientific, River Edge, New Jersey, 1992); C.R.M. Grovenor, *Microelectronic Materials* (A. Hilger, Philadelphia, 1989); A. Zangwill, *Physics at Surfaces* (Cambridge University Press, Cambridge, 1988).
34. Y.J. Chabal, "Surface Infrared Spectroscopy," *Surface Science Reports* 8:211 (1988); E.S. Aydil, R.A. Gottscho, and Y.J. Chabal, "Real-Time Monitoring of Surface Chemistry During Plasma Processing," *Pure Appl. Chem*. 66:1381 (1994); G.M.W. Kroesen and F.J. de Hoog, "In-Situ Diagnostics for Plasma Surface Processing," *Appl. Phys. A* 56:479 (1993); P. Hollins, "Surface Infrared Spectroscopy," *Vacuum* 45:705 (1994); P. Jakob and Y.J. Chabal, "Chemical Etching of Vicinal Si(111): Dependence of the Surface Structure and the Hydrogen Termination on the pH of the Etching Solutions," *J. Chem. Phys*. 95:2897 (1991); P. Jakob, Y.J. Chabal, K. Raghavachari, P. Dumas, and S.B. Christman, "Imperfections on the Chemically Prepared, Ideally H-Terminated Si(111)-(l×l) Surfaces," *Surface Science* 285:251 (1993); Z.-H. Zhou, E.S. Aydil, R.A. Gottscho, Y.J. Chabal, and R. Reif, "Real-Time, In Situ Monitoring of Room-Temperature Silicon Surface Cleaning Using Hydrogen and Ammonia Plasmas," *J. Electrochem. Soc*. 140:3316 (1993); K.B. Koller, W.A. Schmidt, and J.E. Butler, "In Situ Infrared Reflection Absorption Spectroscopic Characterization of Plasma Enhanced Chemical Vapor Deposited SiO_2 Films," *J. Appl. Phys*. 64:4704 (1988); M. McGonigal, V.M. Bermudez, and J.E. Butler, "Infrared Reflection Absorption Spectroscopy Study of the Chemisorption of Small Molecules (H_2, O_2 and H_2O) on Silicon," *J. Electron Spectrosc. Relat. Phenom*. 54/55:1033 (1990); P. Spiberg, R.L. Woodin, J.E. Butler, and L. Dhar, "In Situ Fourier Transform IR Emission Spectroscopy of Diamond Chemical Vapor Deposition," *Diamond and Related Materials* 2:708 (1993).
35. p. Ho, W.G. Breiland, and R.J. Buss, "Laser Studies of the Reactivity of SiH with the Surface of a Depositing Film," *J. Chem. Phys*. 91:2627 (1989).
36. K. Tachibana, T. Shirafuji, Y. Hiyashi, and S. Maekawa, "In-Situ Ellipsometric Monitoring of the Growth of Polycrystalline Si Thin Films by RF Plasma Chemical Vapor Deposition," *Jpn. J. Appl. Phys*. 33:4191 (1994).
37. C.C. Cheng, K.V. Guinn, V.M. Donnelly, and I.P. Herman, "In-Situ Pulsed, Laser-Induced Thermal Desorption Studies of the Silicon Chloride Layer During Silicon Etching in High Density Plasmas of Cl2 and Cl2/O2 Mixtures," *J. Vac. Sci. Technol. A* 12:2630 (1994).

4

Heterogeneous Processes

INTRODUCTION

In plasma processing, the term "heterogeneous processes" includes all chemical and physical reactions that occur when a flux (or fluxes) of species is (are) incident on a surface and the interaction of the incident species with the species residing on the surface results in either the gasification of the material or the formation of a new material. It has been pointed out in earlier chapters of this report that surface processes are of central importance in plasma processing. The entire purpose of the technology is to modify a surface, to etch or deposit material, or perhaps to clean or treat the surface in some way. A low-pressure plasma turns out to be an extraordinarily powerful medium within which to effect surface chemical and physical modifications with little impact on bulk material, at low cost, and over large areas. However, plasma-surface interactions are among the most complex and least well understood aspects of plasma processing technology. This chapter presents an introduction to the key issues and the current level of understanding of plasma-surface interactions. Several techniques, experimental and computational, are suggested as most promising in order to advance the state of the database and to improve treatments of plasma-surface interactions in tool scale and feature scale models.

Heterogeneous processes that are of interest to plasma processing include the following:

1. Adsorption of radicals at specific surfaces;
2. Reactions to form certain intermediate or stable products;
3. Desorption (etching) or incorporation into a growing film (deposition) of the products formed under 2 above;
4. Ion enhancement (or suppression) of the above processes;
5. Sputtering;
6. Particle and energy reflection;
7. Ion implantation and production of defects;
8. Diffusion effects (on the surface, through the reaction layer, and ion-enhanced diffusion effects);
9. Redeposition of desorbed products on the sidewalls of structures, the walls of the reactor, and elsewhere;
10. The mutual interaction of etching and deposition processes that occur in parallel, e.g. in fluorocarbon-based silicon dioxide etching;
11. Surface roughening;
12. Electron-reduced desorption; and
13. Electron emission.

The data necessary to characterize or simulate these processes should be available as a function of the relevant parameters, e.g., temperature, crystallinity and coverage of the substrate, kinetic or internal energy, and angle of incidence of the incident species. In many cases, the functional form relating these relevant parameters and the processes listed above are not known. Synergistic effects between ions and neutrals that strike the surface simultaneously are often essential and also need to be characterized.

STATE OF THE DATABASE

Very little exists in terms of organized compilations of heterogeneous process data. This may be explained by the fact that the heterogeneous processes relevant to a plasma process are intimately related to the actual application of the plasma process and thus are highly specific. The actual surfaces that are present in the plasma environment are a result of the response of the initial surface to the incident species profile. It is likely that certain specific surfaces may be produced only in the plasma environment. Because of this characteristic it is not possible to draw on databases that were developed for other technological fields, as is possible in the area of electron impact processes, for example. If information is available, e.g. thermochemical data for solids in the 1985 JANAF thermochemical tables,[1] its use may be questionable, at least for direct ion-surface interactions, because of departures from thermodynamic equilibrium due to ion bombardment.

An important review of the fluorine-silicon system and to a lesser extent of other systems has been published by Winters and Coburn.[2] They present their survey as a summary of "the status of this virtually unexplored field of surface chemistry." The fluorine-silicon model system can serve as a prototype of the complexities encountered in plasma-surface chemistry.

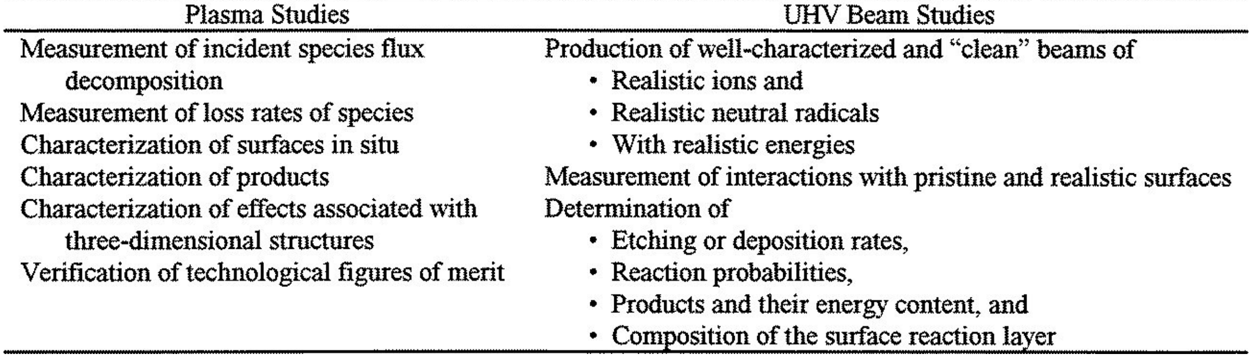
Not all information available on the important key applications has been reviewed in a similar fashion. Surface processes related to poly-Si etching have at least been studied by several investigators using $C1_2$ and HBr gases.[3] For SiO_2 etching in high-density fluorocarbon plasmas many studies exist, but little surface chemistry work has been performed.[4] The surface processes related to silicon dioxide PECVD have been studied by attenuated-total reflectance IR.[5]

TECHNIQUES FOR IMPROVING THE DATABASE

Approach

A two-fold experimental approach appears most promising in improving the database in this field. First, detailed measurements on actual plasma processing systems need to be made. Second, controlled investigations of the different surface science aspects of the plasma etching or deposition process need to be made in an ultrahigh-vacuum (UHV) apparatus using well-controlled and well-characterized beams of different plasma species at the relevant energies. These can interact with the substrate one at a time, two at a time, and so on. The measurements performed under each approach are listed in Table 4.1.

TABLE 4.1 Goals of a Two-Fold Experimental Approach Including Measurements in Actual Plasma Processing Systems and in Ultrahigh-Vacuum (UHV) Reactive Beams

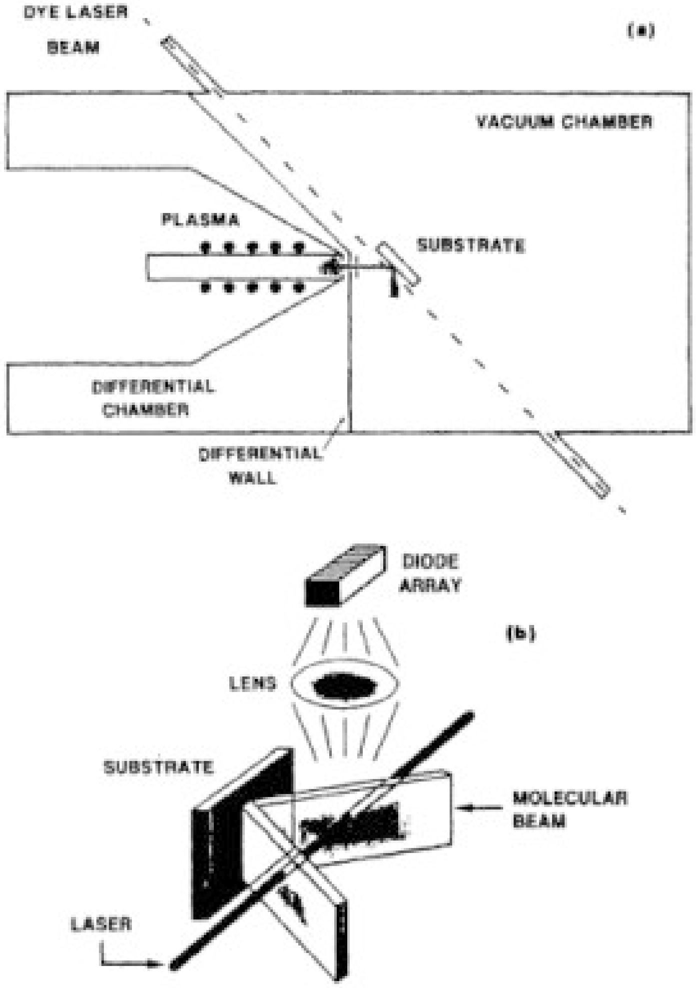


Plasma Studies	UHV Beam Studies
Measurement of incident species flux decomposition Measurement of loss rates of species Characterization of surfaces in situ Characterization of products Characterization of effects associated with three-dimensional structures Verification of technological figures of merit	Production of well-characterized and "clean" beams of • Realistic ions and • Realistic neutral radicals • With realistic energies Measurement of interactions with pristine and realistic surfaces Determination of • Etching or deposition rates, • Reaction probabilities, • Products and their energy content, and • Composition of the surface reaction layer

Measurements On Realistic Plasma Reactors

Incident Flux and Desorbing Flux Analysis

Regarding the incident flux, we would like to know the identities and energies of species incident on the surface; how these species interact with the surface and with each other; the importance of angular effects; scaling with process parameters; and reaction probabilities.


DYE LASER
BEAM
(a)
VACUUM CHAMBER
PLASMA
SUBSTRATE
DIFFERENTIAL
CHAMBER
DIFFERENTIAL
WALL
DIODE
ARRAY
(b)
LENS
SUBSTRATE
MOLECULAR
BEAM
LASER

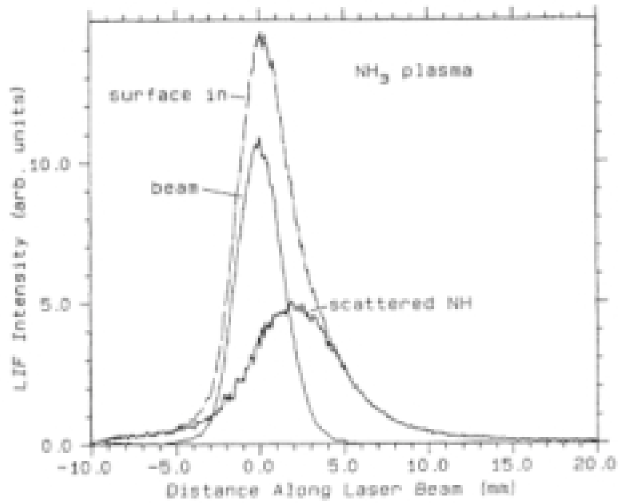


Figure 4.2
Spatial profile of measured fluorescence from an IRIS apparatus using NH radicals impacting and reflecting from a substrate. The scattered NH profile is the difference between the signal with the substrate in place (surface in) and the signal with no substrate (beam). (Reprinted, by permission, from E.R. Fisher, P. Ho, W.G. Breiland, and R.J. Buss, *J. Phys. Chem* 96:9855 (1992). Copyright © 1992 by the American Chemical Society..)

studies that indicate that reaction probabilities on the surface can be a function of the flux. This may be the case if, for example, the flux is so high that the surface does not get a chance to relax to an equilibrium state. Most UHV experiments are done under low-flux conditions where this effect may not be seen often.

Sticking Coefficients

The "sticking coefficient" S (or more precisely, the "loss coefficient") is a lumped parameter that describes the loss rate of a certain species on the surface. The sticking coefficient does not say anything about how that species is lost at the surface. There may be many reaction pathways that result in the loss of the incident species. The most important parameter affecting S is probably the coverage, and, in particular, this involves the determination of the coverage that would be encountered in a plasma processing system. However, the effective surface coverage probably depends on the composition and structure of the surface reaction layer. For example, a Si surface may be covered with F atoms alone, or the fluorine may be present as part of a fluorocarbon film layer. The total F coverage (in atoms/cm^2) may be the same in the two cases, but it is probable that effective sticking coefficients would differ.

Sticking coefficient dependence on temperature is in general unknown, although evidence suggests that in high density plasma reactors etching silicon dioxide, surface temperature can play a key role in polymer deposition.

Sticking coefficients also probably depend on the species incident energy. Energetic species may impact surfaces either due to ion bombardment or through the formation of fast neutrals via charge exchange near the surface. For energetic impacting species, additional unknown factors include the angle of impact and the number and composition of atoms in molecular species. In addition, surface roughness (corrugation) effects may enhance trapping of the incident reactive species.

The underlying mechanisms can be very complex and are in general not known. For instance, F_2 can stick at a crystalline Si surface via either dissociative or abstractive chemisorption. These processes have been shown to depend on incident angle, flux, translational energy, and (for molecular species) rovibrational energy. Pure beams, both atomic and molecular, must be studied as a function of these parameters before the mixed beam effect can be understood. A distinction between thermal and nonthermal reaction pathways must be made here. Surface temperature affects Langmuir-Hinshelwood channels whereas nonthermal channels may not exhibit a temperature dependence.[9] Most studies have focused on thermal channels.

Synergistic Effects

Understanding of synergistic effects, e.g. the ion/neutral synergism or the enhancement of polymer removal by O atoms in the presence of F atoms (a few percent), relates to the essence of "reactive ion etching." The effects of non-ground state species, in particular metastables or electronically excited species, need to be evaluated. For instance, O(^{1}D) atoms appear to be much more reactive than O(^{3}P) atoms (possibly by one or two orders of magnitude). The role of site occupation by other species is unknown. We would like to know if the ions are both reagent and energy source and how that affects the process. Ultraviolet (UV) photons may play a role in promoting surface reactions, either directly by photolytic processes or indirectly by molecular excitation. The nature of the internal excitation in promoting a reaction is not known.

Substrate Temperature Dependence

Tachi's data on cryogenic etching[10] are a good survey of several materials of interest to the microelectronics industry, e.g. Si, SiO_2, Si_3N_4, photoresist, tungsten, tungsten silicide, and aluminum. In these data all effects are convoluted, but they can be used as a basis against which to compare other work. It is not clear whether low-temperature etching results in better feature profile anisotropy because of the reduction of surface reaction rate coefficients or because ions scatter less from cold feature sidewalls, including possibly frozen sidewall layers. The work of Szabo and Engel on the etching of Si in $C1_2$ environments is noteworthy. These authors report surprising phenomena at 77 K and just above that.[11]

Angle Dependence

Winters and Coburn's work[12] showed that the angular dependence of the etching rate in plasma etching environments is very small and does not show the characteristic angular peak at about 60° from normal that is observed for physical sputtering. Often, the angular distributions encountered in practical systems are distributed narrowly about the normal. The dependence of etching rate on angle may be secondary compared to other effects. On the other hand, anisotropy requirements are becoming so stringent that even small effects should be considered. Surface corrugation or roughness can mask angular dependencies. The reaction mechanism, especially for nonthermal pathways, may depend strongly on the angle of incidence. On the other hand, Barklund and Blom showed a very pronounced angular dependence of the nitride etching rate in CHF_3/O_2.[13] This was not seen for SiO_2. They explained it by the angular dependence of the fluorocarbon passivation layer produced by the CHF_3/O_2 plasma.

Computer Simulations

A methodology is required to link the fundamental studies of carefully prepared surfaces to real conditions found in reactors in terms of etching rates, selectivities, anisotropies, etc. This can be done by (a) molecular dynamics (MD) simulations, (b) Monte Carlo simulations, and (c) statistical analysis (multivariate analysis) that relates input or intermediate process conditions to etching rates and other variables. For (c) to be of use the correlation need not be made to the input conditions but to intermediate conditions, such as densities of neutrals and ions, bias voltages that develop, and so on. This would permit sensitivity analysis of different conditions.

Molecular dynamics calculations appear useful.[14] Currently, they are applicable primarily to the silicon halides because of the availability of relatively good interatomic potential energy surfaces. Application to other systems such as SiO_2 and photoresist requires determining realistic potentials for those systems. A large barrier to the use of these techniques may also be the disparity between the time scales used in molecular dynamics (picoseconds) and the time scales associated with neutral and ion fluxes (microseconds to seconds) or product desorption rates. These techniques should be used in conjunction with other techniques borrowed from the vast literature on statistical mechanics (e.g. Metropolis Monte Carlo, lattice gas models, and so on). In principle, combinations of these techniques could be used together with surface diagnostic experiments to shed light on surface reaction pathways and rates. Ultimately, information from the MD calculations could be combined with Monte Carlo or continuum methods for predicting profile evolution.

FINDINGS

1. Processes occurring at surfaces exposed to plasmas are, in general, poorly understood. Even the proper variables characterizing the state of the surface (the state variables) are not fully known. Knowledge of the dependence on the state variables of the rates of chemical and physical processes is correspondingly sketchy.
2. Experimental diagnostics and modeling of plasma-surface processes based on first principles are rudimentary and require much development. Surfaces exposed to plasmas are often strongly modified by the intense bombardment by ions, photons, and radicals. Therefore, not only are the chemical and physical processes themselves strongly perturbed by plasma exposure, but in addition, the surfaces on which the processes take place axe unconventional in their structure and composition.

REFERENCES

1. M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald, and A.N. Syverud, *JANAF Thermochemical Tables*, 3rd edn., *J. Phys. Chem. Ref. Data*, suppl. 1 (1985).
2. H.F. Winters and J.W. Coburn, "Surface Science Aspects of Etching Reactions," *Surf. Sci. Rep*. 14:161 (1992).
3. K. Ono, T. *Oomori*, M. Tuda, and K. Namba, *J. Vac. Sci. Technol. A* 10:1071 (1992); C.C. Cheng, K.V. Guinn, V.M. Donnelly, and I.P. Herman, "In Situ Pulsed Laser-Induced Desorption Studies of the Silicon Chloride Layer During Silicon Etching in High Density Plasmas of $C1_2/O_2$," *J. Vac. Sci. Technol. A* 12:2630 (1994); M. Hayerlag, G.S. Oehrlein, and D. Vender, "Sidewall Passivation During the Etching of poly-Si in an Electron-Cyclotron-Resonance-Plasma of HBr," *J. Vac. Sci. Technol. B* 12:96 (1994).
4. H.F. Winters and J.W. Coburn, "Surface Science Aspects of Etching Reactions," *Surf. Sci. Rep*. 14:161 (1992); J.W. Butterbaugh, D.C. Gray, and H.H. Sawin, *J. Vac. Sci. Technol. B* 9:1461 (1991); G.S. Oehrlein, Y. Zhang, D. Vender, and O. Joubert, "Fluorocarbon High Density Plasmas II: Silicon Dioxide and Silicon Etching Using CF_4 and CHF_3," *J. Vac. Sci. Technol. A* 12:333 (1994); S. Samukawa and K. Terada, *J. Vac. Sci. Technol. B* 12:3300 (1994); M.J. Goeckner, M.A. Henderson, J.A. Meyer, and R.A. Breun, *J. Vac. Sci. Technol. A* 12:3120 (1994).
5. S.M. Hart and E.S. Aydil, "Study of Surface Reactions During Plasma Enhanced Chemical Vapor Deposition of SiO_2 from SiH_4, O_2, and Ar Plasma," *J. Vac. Sci. Technol. A* 14:2062 (1996).
6. E.R. Fisher, P. Ho, W.G. Breiland, and R.J. Buss, *J. Phys. Chem* . 96:9855 (1992).
7. G.S. Oehrlein, J.F. Rembetski, and E.H. Payne, *J. Vac. Sci. Technol. B* 8:1199 (1990).
8. H.F. Winters and J.W. Coburn, "Surface Science Aspects of Etching Reactions," *Surf. Sci. Rep*. 14:161 (1992).
9. K.P. Giapis, T.A. Moore, and T.K. Minton, "Hyperthermal Neutral Beam Etching," *J. Vac. Sci. Technol. A* 13:959 (1995).
10. S. Tachi, K. Tsujimoto, and S. Okudaira, "Low-Temperature Reactive Ion Etching and Microwave Plasma Etching of Silicon," *Appl. Phys. Lett*. 52:616 (1988).
11. A. Szabo and T. Engel, *J. Vac. Sci. Technol. A* 12:648 (1994).
12. H.F. Winters and J.W. Coburn, "Surface Science Aspects of Etching Reactions," *Surf. Sci. Rep*. 14:161 (1992).
13. A.M. Barklund and H.O. Blom, *J. Vac. Sci. Technol. A* 11:1226 (1993).
14. B.J. Garrison, "Molecular Dynamics Simulation of Surface Reactions," *Chemical Society Reviews* 21:155 (1992); H. Feil, J. Dieleman, and B.J. Garrison, *J. Appl. Phys*. 74:1303 (1993); M.E. Barone and D.B. Graves, *J. Appl. Phys*. 77:1263 (1995).

5

Electron Collision Processes

INTRODUCTION

In modeling and simulation of plasma processing applications, quantitative data are needed on the many reactions involving neutral species and positive and negative ions under practical industrial conditions, especially for those substances that are used directly in plasma deposition and etching. For each chemistry to be considered, ideally, electron collision processes involving all possible reactants, products, and intermediates must be investigated. Cross sections or probabilities for the various reaction channels (ionization, excitation, dissociation, attachment, and recombination) will depend on plasma conditions of temperature and on the energy state of the target species.

In this chapter, the general availability of electron-impact cross section data is discussed for each reaction channel. Potential sources of new data, both experimental and theoretical, are described. A set of typical plasma processing substances serve as examples in the discussion of electron-collision cross section availability. These include deposition compounds SiH_4 and SiO_2; etching gases C1, Br, $C1_2$, HCl, F_2, HBr, BCl_3, and CF_4, and decomposition and etching products $SiCl_x$ and $SiBr_x$.

IONIZATION

Atoms

For constituent atoms present in plasma etching and deposition (F, C1, Br, C, N, S, H, O), ionization cross sections have been measured to within ±20%.[1] The situation is similar, if not better, for rare gases used as buffers and dilutants. Single ionization cross sections for all rare gases are known to better than ±8%, for instance. Little ionization data is available for atoms in excited or metastable states,with the exception of laser-excited alkali atoms and metastable rare gases, H, N, and O.

Molecules

For plasmas with complex molecules present in the feed gas, detailed understanding requires identification of the specific ions formed by electron collisions. Thus, cross sections are needed for production of parent molecular ions and dissociative ionization products. These are distinct from total ionization cross sections (the sum for all channels), which are measured in some cases but do not provide adequate information on the specific ionic species produced.

Channel-specific ionization cross sections are available for a variety of plasma processing compounds, including SiH_4, CF_4, SF_6, CCl_2F_2, and O_2, as well as the common purge gas N_2. Total ionization cross sections have been reported for $C1_2$ and F_2. Changes in these cross sections may occur when the target molecules are vibrationally or electronically excited. Experimental techniques are not well developed to study these effects quantitatively.

Experimental and theoretical results for the ionization of vibrationally excited molecules show qualitatively a shift of the ionization threshold to lower energies and a significant enhancement of the cross section in the lower energy region near threshold,[2] two effects that can drastically affect the ionization balance in a low-temperature plasma.

Many dissociative-ionization cross section measurements made prior to 1990 are suspect because many experiments did not properly account for the fact that fragment ions can be produced with excess kinetic energies that are far greater than thermal energies. Ion losses and other discrimination effects involving energetic fragment ions have seriously compromised many dissociative ionization cross section measurements prior to 1990. For the complex molecules used in plasma processing there are only a few examples of reliable data for dissociative ionization, such as CH_4, SiH_4, CF_4, and SF_6; generally the data are lacking. As noted in Chapter 3, "Radiative Processes and Diagnostics," this lack of data for dissociative ionization, especially near threshold, can significantly limit the ability to quantitatively interpret mass spectrometric measurements. This is the case because a common tactic for measurement of radical concentrations with mass spectrometry is to reduce the electron impact energy to near threshold. Generally, this approach allows discrimination between a signal from a parent molecule ionizing dissociatively and the radical of interest. However, if the parent molecule is vibrationally excited (for example), its dissociative ionization cross section may increase near threshold (see discussion above). This results in a significant drop in confidence in the technique, and may invalidate it completely.

Very recently, there have been efforts to measure ionization and dissociative ionization cross sections for complex metal-organic and silicon-organic molecules used in deposition plasmas.[3]

When considering ion formation by dissociation in discharges, polar dissociation must also be taken into account. Although this is usually a minor process for positive-ion formation, it can make a significant contribution to negative-ion formation.

Radicals are a class of highly reactive molecular species that are frequent products in plasma processing. Electron-impact ionization cross sections have been measured to ±20% for SiF_x and CF_x ($x = 1$-3), NF_2, NF, and SO. These studies apply to ground state targets only.

Only a few research groups are actively studying electron-impact ionization, and in even fewer cases have the research programs focused on substances pertinent to plasma processing.

Theoretical Methods and Advances

For molecules and radicals, the state of the art has until recently consisted of empirical and semiempirical methods and simplistic additivity rules. Recently there have been several new developments: (1) two modified additivity rules that attempt to account for molecular bonding; (2) the Deutsch-Mark formalism, which combines a Gryzinsky-type energy dependence with quantum mechanically calculated molecular structure information (also applicable to atoms); and (3) a new binary-encounter dipole theory.

Neutral Dissociation

In cases where electron-impact dissociation produces electronically excited fragments that decay radiatively, studies use the optical excitation function technique. Emissions have been measured over a wide spectral range. Several molecules relevant to plasma processing have been studied, providing dissociation cross sections for CF_4, SF_6, NF_3, BCl_3,[4] and several freons and halogenated methane compounds.

Using traditional beam techniques to measure cross sections for electron-impact dissociation of molecules into neutral products is extremely difficult, especially when the dissociation fragments are in the ground state or do not radiate. This difficulty is caused by the lack of sensitive methods for detecting neutral fragments.

One beam technique that has been used successfully for measurement of dissociation cross sections involves fast neutral beams formed by charge transfer in conjunction with coincident product detection techniques. In these configurations there can be significant uncertainty in the excited state distribution of the neutral target molecules formed in the charge-transfer process. This method has been applied to the relatively simple molecules N_2, O_2, CO, and, most relevant to plasma processing, $C1_2$. The technique can be extended to other simple molecules that are dominated by two-fragment break-up channels. A serious limitation will arise when the method is applied to more complex polyatomic molecules for which many break-up channels with different numbers of fragments compete. This is at present the only suitable method for studying the dissociation of free radicals into neutral ground-state fragments.

Another beam technique is the so-called two-electron-beam technique, in which the first electron beam is used to dissociate the target molecules and a second electron beam "downstream" is used to probe the dissociation fragments. In the most recent variant of this technique, Sugai and collaborators[5] measured absolute and relative dissociation cross sections for various molecules relevant to plasma technology (SiH_4, CF_4, CH_4) using threshold ionization mass spectrometry. With this technique, absolute cross sections can be obtained only for those radical species whose ionization cross sections are known in the near-threshold region.

Another method, the "chemical getter" method, which traps the dissociation products, has been used to determine the total dissociation cross sections for CF_4 and CH_4. This technique has very limited applicability to other targets.

A method with high potential for detection of neutral dissociation fragments in the ground state is laser-induced fluorescence. This method has not, so far, been applied to molecules of interest to plasma processing. Although many fragments can be detected by this method, a limitation is that tunable lasers are available over a limited wavelength range (roughly 250 to 800 nm) that does not include absorption wavelengths of some prominent dissociation fragments in processing plasmas.

The dissociation cross section has been calculated theoretically for a few molecules of interest to plasma processing, most notably Cl_2 and NF_3, for which the calculated cross section agrees reasonably well with experimental data.[6] This calculation is based on the application of the complex Kohn variation method, which, in principle, could be used to calculate cross sections for other targets. Calculations have also been performed for BCl_3 and SiC_2 (V. McKoy, California Institute of Technology, private communication, 1995).

ELECTRON-IMPACT EXCITATION

For atoms, an extensive database of electron-impact excitation cross sections exists. However, due to their corrosive and reactive nature, some atoms relevant to plasma processing (e.g. F, C1, Br) have not been studied. In principle, there is no reason that these atoms could not be studied.

Vibrational excitation data are available for many molecules, but only a few that are used in plasma processing, again due to the corrosive nature of many plasma processing molecules. Exceptions are CF_4, SF_6, and some freons.

There is also a shortage of measured data for electronic excitation (particularly to stable states) of complex molecules. Theoretical methods for calculating the electronic excitation of molecules are maturing and, when properly benchmarked by measurements, can provide cross sections with adequate accuracy.

ATTACHMENT

Cross sections for dissociative attachment range from values (for electronegative gases) that are several orders of magnitude larger than cross sections for positive ion formation, to values (for SiF_4 and CF_4) that are several orders of magnitude smaller than cross sections for positive ion formation. Even when the dissociative attachment cross sections are small, these processes are important for full characterization of the plasma. The negative ions formed may influence the free-electron density and may also participate in nucleation of parasitic dust. Although there have been few measurements, recent exceptions used Fourier transform mass spectrometry techniques and beam techniques to determine dissociative attachment cross sections for SiF_4 and CF_4[7] and SiH_4.[8] Some experimental effort has been devoted to the study of attachment to vibrationally excited molecules.[9]

There exist virtually no data on electron attachment to radicals, although such species are produced in large numbers in plasmas. Only a few research groups are engaged in these types of measurements.

MOMENTUM TRANSFER, SWARM, AND DISCHARGE MEASUREMENTS

For purposes of modeling electrical discharges in gases, it may not be possible or even necessary to use complete, detailed information about the dynamics of electron-molecule collision processes that produce dissociation. It may be sufficient to consider only total or averaged "effective" cross sections that apply to a particular discharge condition specified, for example, by electric field to gas density ratio (*E/N*) or local temperature. Relatively reliable total electron collision cross sections can often be derived from analysis of dam from drift-tube or simple discharge experiments. The approach used requires that there be a reasonably well understood self-consistent model for the transport of electrons that can account for observations of such parameters as the electron drift velocity, ionization growth, the longitudinal and transverse diffusion coefficients, the relative intensity of observable atomic or molecular emissions, and so on. The model must be capable of predicting the kinetic energy distribution of the electrons, e.g., from numerical solution of the Boltzmann transport equation or from a Monte Carlo simulation, and must also be consistent with independently determined cross sections (such as ionization cross sections) that are known to be reliable. This method is most often used to derive momentum transfer cross sections, and inelastic cross sections for low threshold processes such as rotation and vibration. There are numerous compendia of momentum transfer cross sections derived in this fashion.[10] This approach has also been used successfully to generate fairly complete collision cross section data sets for several atomic and molecular species. However, except for a few cases such as SF_6, it has generally been difficult to distinguish dissociation processes from other types of molecular excitation processes. With the advent of more sophisticated diagnostics such as two-photon laser-induced fluorescence, it is possible to measure the densities of neutral dissociation fragments, from which dissociation rates can possibly be extracted. Information about reactive fragment densities can also sometimes be determined indirectly from examining the products of subsequent neutral chemistry in which these species are involved, e.g., fast reactions of H with NO_2 to form NO and of F with H_{20} to form HF.

GENERAL COMMENTS

Of the major system constituents selected as examples, consider SiH_4. Silane has been the object of intense study, especially during the last 5 years.[11] Fundamental studies have provided cross sections for dissociative ionization, neutral attachment, and dissociative attachment. Cross sections are not available for excited-state targets.

Carbon tetrafluoride can be described as a success story, in that it has been the subject of intense study and pertinent data are well known.[12] Accurate cross sections have been measured for dissociative ionization (the parent ion CF_4+ is unstable). A report of recent measurements on neutral dissociation has been published recently.[13]

Cross section measurements have been reported for parent ionization of the radicals CF_x ($_x$ = 1-3) and dissociative ionization of CF_3. Measurements have also been made for dissociative attachment (negative ion formation).

The picture is less complete for the other species in the example set. For the atoms of interest, ionization and excitation cross sections are known. For $C1_2$ and F_2, only total ionization and excitation cross sections are known. Vibrational excitation and momentum transfer cross sections have been calculated. No data were found on dissociative ionization or neutral dissociation. For Br_2, no data have been reported for.

For HCl, cross section sets have been derived from swarm data. Dissociative attachment cross sections have been measured. For HF, vibrational excitation cross sections have been measured and dissociative attachment cross sections derived. No additional data are available, and no complete data set has been proposed. No data were found for HBr and only limited data exist for BCl_3.[14]

By applying existing techniques, one could in principle obtain full data sets for many compounds.

The existing database is most complete for those processes that are least relevant for the modeling and diagnostics of processing plasmas, whereas there is a serious lack of reliable experimental data for the most important processes (dissociation into neutral ground-state fragments, data for free radicals, data for vibrationally excited molecules and radicals, and data for excited target species).

It is entirely feasible to construct an electronic database including sources of data for compounds used in plasma processing and files of the corresponding numerical data. Maintained as an ongoing effort and distributed using modem technologies, such a database would improve the efficiency of efforts to model and simulate plasma reactors.

FINDINGS

Data for electron-neutral collisions are sketchy at best for most species of interest in plasma processing, although some species, such as SiH_4 and CF_4, have received considerable attention. However, little information is available for dissociation products or for species in excited states. Recent progress in computational methods based on quantum scattering offers the possibility that the costly and time-consuming experiments may be augmented or even replaced by large-scale computation.

REFERENCES

1. T.R. Hayes, R.D. Wetzel, and R.S. Freund, *Phys. Rev. A* 35:578 (1987); R.S. Freund, R.C. Wetzel, R.J. Shul, and T.R. Hayes, *Phys. Rev. A* 41:3575 (1990).
2. V. Tarnovsky, A. Levin, H. Deutsch, and K. Becker, *J. Phys. B* 29:135-49 (1996); R. Celiberto and T.N. Rescigno, *Phys. Rev. A* 47:1939 (1993).
3. R. Basher, M. Schmidt, and H. Deutsch, *Contrib. Plasma Phys*. 35:375-94 (1995); S. McGinnis, K. Riehl, and P.D. Haaland, *Chem. Phys. Lett*. 232:99 (1995); R. Basner, R. Foest, M. Schmidt, F. Sigeneger, P. Kurunczi, K. Becker, and H. Deutsch, *Int. J. Mass Spectrom. Ion Processes* 153(1):65 (1996).
4. A. Blanks, A.E. Tabor, and K. Becker, *J. Chem. Phys*. 86:4871 (1987). P.G. Gilbert, R.B. Siegel, and K. Becker, *Phys. Rev. A* 41:5594 (1990).
5. T. Nakano, H. Toyoda, and H. Sugai, *Jpn. J. Appl. Phys*. 30:2908 (1991); T. Nakano, H. Toyoda, and H. Sugai, *Jpn. J. Appl. Phys*. 30:2912 (1991); M. Ito, M. Goto, H. Toyoda, and H. Sugai, *Contrib. Plasma Phys*. 35:405 (1995); H. Sugai, H. Toyoda, T. Nakano, and M. Goto, *Contrib. Plasma Phys*. 35:415 (1995).
6. T.N. Rescigno, *Phys. Rev. A* 50:1382 (1994); T.N. Rescigno, *Phys. Rev. A* 51:329 (1995).
7. I. Iga, M.V.V.S. Rao, S.K. Srivastava, and J.C. Nogueira, Z. *Phys. D* 24:111 (1992).
8. P. Haaland, *J. Chem. Phys*. 93:4066 (1990).
9. L.G. Christophorou, in *Nonequilibrium Processes in Partially Ionized Gases*, ed. M. Capitelli and J.N. Bardsley (Plenum Press, New York, 1990).
10. See, for example, E. Beaty, J. Dutton, and L.C. Pitchford, A *Bibliography of Electron Swarm Data*, JILA Information Center Report No. 20 (December 1979).
11. R. Nagpal and A. Garscadden, "Low-Energy Collision Cross Sections for SiH_4," *J. Applied Phys*. 75:703 (1994).
12. R.A. Bonham, "Electron Impact Cross Section Data for CF_4," *Jpn. J. Applied Phys. 1* 33:4157 (1994).
13. H. Sugai, H. Toyoda, T. Nakano, and M. Goto, *Contrib. Plasma Phys*. 35:415 (1995).
14. R. Nagpal and A. Garscadden, "Electron Collision Cross Section of Boron Trichloride," *Applied Phys. Lett*. 64(13):1626 (1994).

6

Ion Processes, Neutral Chemistry, And Thermochemical Data

INTRODUCTION

In this chapter, the panel assesses the needs and status of cross sections and rate coefficients for ion processes and neutral chemistry in plasma processing reactors. It also assesses the availability of thermochemical data. Requirements for ion transport and cross section data are particularly stringent, because low-pressure plasma etching reactors typically operate at high plasma densities, producing ionization fractions of 10^{-4} to 10^{-2}. Therefore ion collision processes (ion-ion neutralization and scattering, ion-molecule reactions, electron-ion recombination) are proportionally more important compared with neutral chemistry. The range of ion energies for which these cross sections and rate coefficients are required is large. Conventional reactive ion etching (RIE) reactors use capacitively coupled power for ion generation and acceleration and have applied potentials of hundreds of volts. This results in ions having directed energies of tens to hundreds of eV in the sheaths, while their random thermal temperatures in the bulk plasma tend to be small (<< 0.05 eV). Inductively coupled plasma (ICP) and microwave-excited electron cyclotron resonance (ECR) reactors differ from conventional RIE reactors in that they typically **operate** at lower pressures (<< 10 mTorr), higher power deposition, and larger ionization fraction. These conditions allow bulk ion temperatures to climb significantly above the gas temperature (0.1-0.5 eV).

The Knudsen number (*Kn* = mean free path / characteristic dimension) of ICP and ECR reactors may exceed 0.01 to 0.1. These long mean free paths complicate modeling in that noncontinuum algorithms must be employed as transport approaches the molecular flow regime. Large Knudsen numbers also imply that hot atom transport is more prevalent. Hot atoms have translational energies that significantly exceed their random thermal temperature. (The term "hot atom transport" is used here to refer to all hot neutral species: atoms, molecules, and radicals.) Hot atoms are generated by reactions of energetic ions with neutrals (charge exchange) or other ions (ion-ion neutralization); by energetic ions reflecting from surfaces and returning to the plasma as neutrals; and by dissociative electron collisions of molecules. The latter category includes electron impact dissociation of neutral molecules and dissociative recombination of molecular ions. Hot atoms are important for at least two reasons. First, they may impact on the wafer, thereby modifying the etching or deposition. Second, by virtue of their large translational energy, they may participate in reactions having activation energies that are otherwise energetically disallowed.

The availability of neutral chemistry cross sections and rate coefficients varies greatly depending on the specific reaction chemistry being used. Depending on the specific chemistry, rate coefficients may be available from the literature on combustion, upper atmospheric chemistry, or chemical vapor deposition (CVD). An important difference between the database needs in neutral chemistry for plasma etching reactors, as opposed to CVD, is the contributions of excited states. Significant fractions of the neutral species in a plasma processing reactor will have stored internal energy (vibrational or electronic) resulting from collisions with electrons or ions. Reactions that have activation energy barriers for reactants in their ground states may be energetically allowed (or accelerated) if the reactants are either vibrationally or electronically excited, or they may have different branching ratios.

CROSS SECTIONS AND RATE COEFFICIENTS

Ion Processes

The needs for fundamental data on ion processes can be subdivided by energy range as indicated in Table 6.1. The division in energy range is based on two premises. First, the ion distribution in the bulk plasma for the majority of plasma processing reactors can be well described by a Maxwellian or moderately drifting Maxwellian. The temperatures are usually less than 0.1 eV. Transport coefficients and cross sections for processes in this range of energies are usually measured using a swarm or drift tube technique, and characterized by a "random" temperature. Ion energies greater than 0.1 eV are usually found only in the presheath or sheath regions of the plasma. Cross sections for collisional processes in the higher energy range are measured by beam techniques, and usually characterized by a directed energy.

TABLE 6.1 Categorization of Data Needs for Ion Processes

Process	Thermal	Superthermal
	(e < 0.1 eV)	(0.1 < e < 1 keV)
Momentum transfer	•	•
Ion-molecule and charge exchange	•	•
Ion-ion neutralization	•	
Electron-ion recombination	•	
Ion-neutral and neutral-neutral excitation		•

Momentum Transfer

Momentum transfer collisions are elastic and/or inelastic processes resulting in a change in momentum and in which the identity of the ion does not change.

Example: $Ar^+ + Cl_2 \rightarrow Ar^+ + Cl_2$

Beam-measured cross sections should be resolved in energy and angle. Swarm-measured cross sections or rate coefficients should be temperature dependent.

The availability of ion swarm parameters (usually mobilities, diffusion coefficients, and characteristic energies vs. E/N) is good for ions of interest in atmospheric or combustion applications, and poor for ions of interest to plasma processing. These data are typically scattered in the literature. A compendium of ion transport coefficients dating to 1984 is available from Ellis et al.[1]

Ion-Molecule and Charge Exchange Reactions

Collisions resulting in transfer of positive or negative charge from the incident ion are ion-molecule or charge exchange reactions.

Example: $He^+ + Cl_2 \rightarrow He + Cl^+ + Cl$

If the identity of the ion does not change, this process is known as a symmetric charge exchange and is sometimes difficult to distinguish from a momentum transfer collision. Beam-measured cross sections should be resolved in energy and angle. Swarm-measured cross sections or rate coefficients should be temperature dependent. Distribution of products from the target molecule should also be identified.

The availability of data for thermal ion-molecule and charge exchange reactions for molecules of atmospheric or combustion interest is relatively good. Many compendia are available, such as those of Sieck and Lias,[2] Albritton,[3] and Ikezoe et al.[4]

There are isolated instances of measurements of cross sections for these reactions in gases of interest to plasma processing. For example, Morris et al.[5] have measured reaction rate coefficients for

$$\begin{aligned}&C_nF_m^+ + C_2F_4\,,\\&H_2O^+ + C_2F_4,\ C_2F_6,\ CF_3X\ (X = F, Cl, Br, I)\,,\ \text{and}\\&CF_n^+\ (n = 1, 3) + CF_3X\ \ (X = F, Cl, Br, I),\ C_2F_6\,.\end{aligned}$$

Tsuji et al.[6] have made measurements of charge exchange of rare gases with etching gases. For example,

$$\begin{aligned}&Ar^+ + CH_nCl_{4-n}\ \text{and}\\&Ar^+ + (HBr, DBr)\,.\end{aligned}$$

Bohme has measured and assembled a database for ion-molecule reactions for silicon-bearing ions.[7] Mandich and Reents[8] have performed measurements of ion-molecule cross sections in silane systems using Fourier transform mass spectrometry,

$$Si_nH_m^+ + SiH_4 \rightarrow \text{Products}\,.$$

The latter work has shown that there are bottlenecks for silane ion association reactions that may be breached by the internal energy of the reactants or by the presence of impurities such as water. (See Figure 6.1.)

A subset of ion-molecule reactions are ion association reactions $(e.g.\ A^+ + B\ [+M] \rightarrow AB^+\ [+ M])$. The rate coefficients for these processest end to be system specific even for rare gases. Scaling laws for their temperature dependence, however, have been developed by Johnsen9

Superthermal ion-molecule and charge-exchange collisions usually occur in the sheaths. These are processes that are not allowed at thermal energies in the bulk plasma but nevertheless should be addressed in the database for use in higher pressure systems where sheaths may be collisional.

$$\textbf{Example:}\qquad H^+ + He \rightarrow H + He^+$$

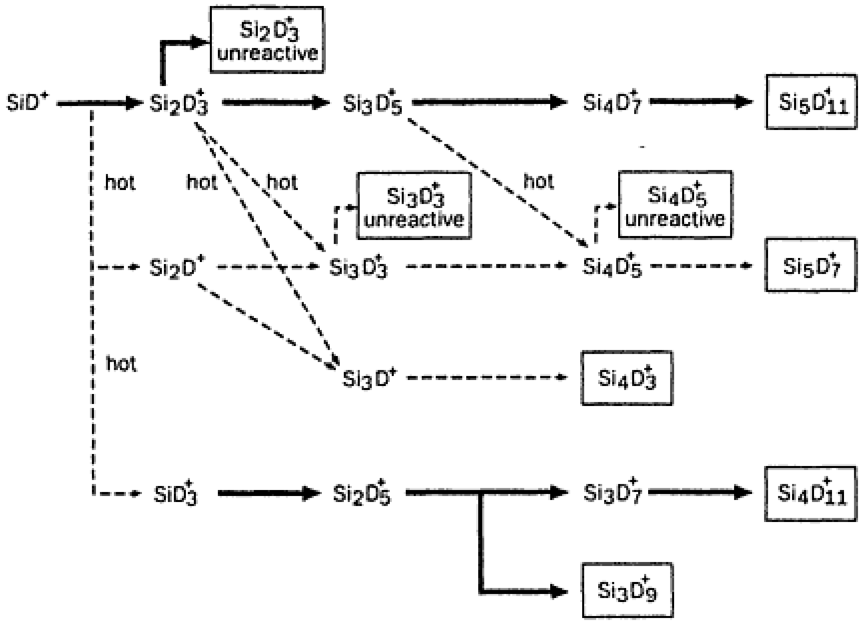


Figure 6.1
Reaction sequence for ion chemistry initiated by SiD^+ in SiD_4. (Reprinted, by permission, from M.L. Mandich and W.D. Reents, *J Chem. Phys*. 95:7360 (1991). Copyright © 1991 by the American Institute of Physics.)

The energy dependence and product channels of cross sections for these reactions are required. Measurements of these cross sections for systems of interest to plasma processing are in general sparse; however, definitive experiments for a subset of the gases of interest have been performed by Armentrout et al.[10] for energies of 0 to 80 eV. (See Figure 6.2.) These systems include

$$\mathrm{Si^+ + (SiH_4, SiD_4, CH_4, SiCl_4, H_2)}\,,$$
$$\mathrm{SiH^+ + H_2}\,,$$
$$\mathrm{(Ar^+, Ne^+, He^+, O^+, O_2^+) + CF_4}\,,$$
$$\mathrm{(Ar^+, Ne^+, He^+, O^+, O_2^+) + SiF_4}\,,$$
$$\mathrm{(Ar^+, Ne^+, He^+, O_2^+) + SiCl_4}\,, \text{ and}$$
$$\mathrm{(O^+, O_2^+) + C_2F_6}\,.$$

The large variety of ion-molecule systems and possible reaction channels puts a large premium on developing scaling laws for these interactions. In this regard Armentrout et al.[11] have proposed scaling laws for cross sections of endothermic ion molecule collisions.

Ion-Ion Neutralization

Ion-ion neutralization processes are collisions between positive and negative ions that result in the neutralization of both reactants.

Examples: $\mathrm{Cl_2^+ + Cl^- \rightarrow Cl_2 + Cl}$

$\mathrm{Ar^+ + BCl_2^- \rightarrow Ar + BCl + Cl}$

The rates of these reactions scale with the square of the plasma density, while the magnitude of Coulomb cross sections scales inversely with energy. Therefore ion-ion neutralization cross sections are required for thermal energies, but are not particularly important for superthermal energies. The total rate of ion-ion neutralization reactions will usually be ignorably small in the sheaths where positive ion energies are large and negative ion densities are small. The distribution of products should be identified.

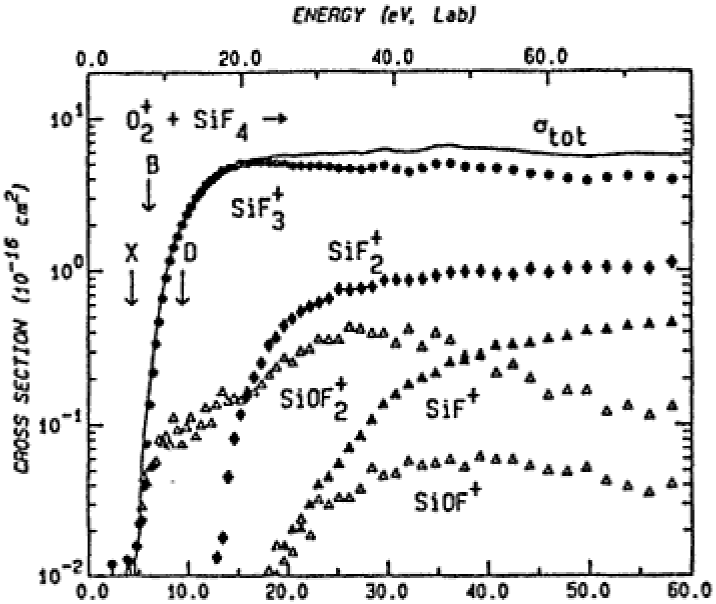


Figure 6.2
Cross section set for impact of O_2^+ on SiF_4. (Reprinted, by permission, from E.R. Fisher and P.B. Armentrout, *Chem. Phys. Lett*. 179:435 (1991). Copyright © 1991 by Elsevier Science - NL.)

Cross sections for these long-range Coulomb collisions are not particularly sensitive to the internal structure of the reactants, and therefore they are amenable to scaling laws based on the electron affinity and ionization potential of the reactants. For example, semiempirical cross sections for ion-ion neutralization at low pressure have been proposed by Moseley et al.[12]

Electron-Ion Recombination

Collisions between electrons and positive ions resulting in neutralization of the ion constitute electron-ion recombination.

Example: $e^- + BCl_2^+ \rightarrow BCl + Cl$

The rates of these reactions scale with the square of the plasma density. Since electron-ion recombination results from a long-range Coulomb force, the cross section often scales inversely with energy. The total rate of electron-ion recombination reactions will therefore usually be ignorably small in the sheaths, and their cross sections (or rate coefficients) are required only in the thermal energy range. At the plasma densities and temperatures of interest for plasma processing, radiative and collisional radiative recombination are not important. Dissociative recombination of molecular ions is the only significant volumetric recombination process. The distribution of neutral products should be identified, as well as their translational energies.

Cross sections for these processes are widely scattered in the literature, with few examples for systems of interest to plasma processing. Recent compendia and reviews of cross sections and rate coefficients can be found in Mitchell[13] and Adams.[14] The temperature dependencies of these processes are also important.[15]

Ion-Neutral and Neutral-Neutral Excitation

Inelastic collisions between ions and neutral species that result in excitation, dissociation, or ionization of the neutral target without transfer of charge are classified as ion-neutral excitation collisions. Hot atom collisions on neutrals can similarly instigate excitation, ionization, or dissociation.

Examples: $Ar^+ + Cl_2 \rightarrow Cl + Cl + Ar^+$
$Ar + Cl_2 \rightarrow Cl + Cl + Ar$

Since there is a threshold energy associated with these collisions, they are important only for superthermal ions and usually only in the sheath regions. Similar reactions involving hot atoms may occur throughout the bulk plasma.

There is fragmentary data scattered through the literature for energetic ion-neutral and neutral-neutral excitation collisions. Phelps[16] has compiled and assessed complete cross section sets (see Figure 6.3) for ion and high-energy neutral impact reaction mechanisms for

N^+, N_2^+, N, N_2	impact on N_2 ,
Ar^+, Ar	impact on Ar , and
H^+, H_2^+, H_3^+, ArH^+, H^-, H, H_2	impact on Ar .

Neutral Chemistry

Many neutral chemistry databases have been developed for combustion and atmospheric chemistry?[17] Processes for evaluation of those databases are well established, and so evaluation is not addressed here. Instead, the panel assesses the status of the availability of rate coefficients and proposes methods to address unmet needs. It is important to emphasize that these needs are better stated in terms of mechanisms, as opposed to a collection of rate coefficients.

Status of the Database

The database requirements for neutral chemistry are both more lenient and more stringent than those for combustion and upper atmospheric chemistry. The gas temperatures of plasma processing systems are typically low, rarely exceeding a few hundred degrees above ambient temperature. Therefore gas phase chemical reactions that have significant activation energy barriers are not important. Plasma processing systems with high gas temperatures typically operate at low gas pressures, where the rates of gas phase chemical reactions are small compared to wall-activated chemistry. At the same time, there are large densities of molecules and atoms in plasmas that have internal energy (vibrational or electronic) or that are translationally “hot”, and that therefore breach activation energy barriers.

The low gas pressures used in tools with high plasma densities (ICP, ECR)may further restrict the number of reactions that one must address. Association reactions typically operate through a transition state that must be stabilized by colliding with a third body to complete the reaction. For example, the association reaction $Cl + Cl \rightarrow Cl_2$ proceeds as

$$Cl + Cl \underset{\tau}{\overset{k_1}{\leftrightarrow}} Cl_2{}^* \overset{k_2}{\rightarrow} Cl_2 .$$

The effective 2-body rate coefficient is

$$k = \frac{k_1}{1 + \frac{1}{M k_2 \tau}}$$

If the operating pressure is sufficiently low so that the back reaction of Cl_2* to 2Cl is fast compared to the rate of stabilizing collisions, then the effective rate of association is small and the reaction may be ignored. The weakness in the existing databases for neutral combustion and atmospheric chemistry is that they were intended to be used at high pressure, and therefore lack rate coefficients for the low pressure fail-off regime.

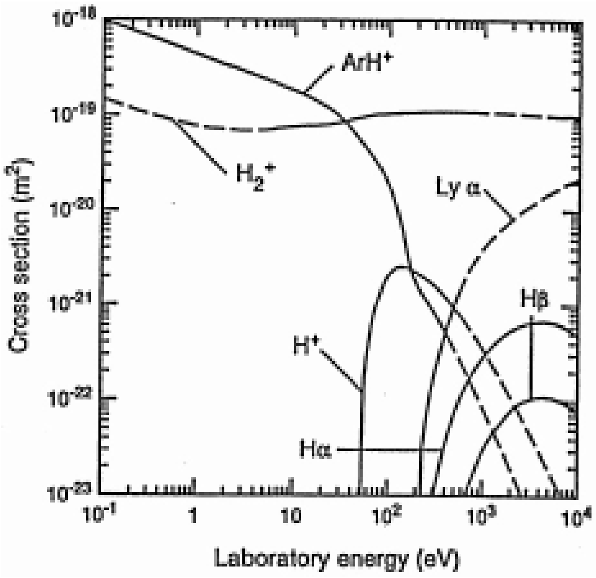


Figure 6.3
Cross sections for excitation and ionization of H_2 resulting from impact of Ar + on H_2 , and by impact of H_2 on Ar. (Reprinted, by permission, from A.Phelps, *J.Phys. Chem. Ref. Data* 21:883 (1992). Copyright © 1992 by the American Institute of Physics and the American Chemical Society.)

The important reactions may also depend on the operating conditions of the reactor, such as power deposition and gas residence time. For purposes of discussion, it is useful to define three classes of species:feedstock (F), secondary (S), and primary (P). The feedstock species are those gases that flow into the reactor from the outside. Primary species, usually radicals, axe atoms or molecules that result from direct dissociation of the feedstock gases, by either electron impact or ion-molecule reactions. Secondary species are produced by reactions between primary species or of primary species with feedstock gases. The degree to which F-P, P-P, P-S, or S-S reactions dominate is largely a function of the degree of dissociation of the gas. A convenient measure of the degree of dissociation is

$$\eta = \frac{P \tau}{N_0 \ \Delta\varepsilon} ,$$

where P is the specific power deposition, N_o is the ambient gas density, τ is the gas replenishment time (either by gas flow or surface reactions), and $\Delta\varepsilon$ is the energy deposition required for molecular dissociation. If $\eta \ll 1$, then the gas is lightly dissociated and F-P reactions are likely the most important. If $\eta \geq 1$, then P-P reactions are likely the most important. Finally, if $\eta \gg 1$, then S-S reactions most likely dominate.

The availability of reaction rate coefficients for thermal neutral chemistry for plasma deposition systems is in some instances very good. For example, the $SiH_4/Si_2H_6/H_2$ system has been studied extensively in the context of plasma enhanced and thermal chemical vapor deposition, and compendia of rate coefficients have been assembled for use in models.[18] The major uncertainties in these databases are in the formation and reaction of higher silanes $(Si_nH_m, n \geq 2)$. These reactions are particularly important with respect to particle formation.

The situation is similar for databases for plasma enhanced chemical vapor deposition (PECVD) of SiO_2 using $SiH_4/O_2/N_2O$ mixtures. The gas phase chemistry of this system has recently been addressed in the context of modeling remote PECVD of SiO_2[19] and thermal CVD.[20] In this system, the mechanisms for the deposition pathways are still uncertain, largely due to the uncertainties in surface reaction rate coefficients. This uncertainty reflects back on the "goodness" of the gas phase database. For example, it has been proposed that Si-O bonds are formed on the growing film[21] and that precursors are dominantly fragments of SiH_4 and the oxygen donor. If this is the case, the gas phase database is in moderately good shape. A competing school of thought proposes that Si-O bonds are formed in the gas phase and that silanols (SiH_nO_m) are the deposition precursors. If this is the case, the gas phase database is not adequate since the major uncertainty in the database results from uncertainties in the formation and reactions of silanols.

The status of the database for Si_3N_4 deposition using $SiH_4/N_2/NH_3$ mixtures is similar to that for SiO_2 and is in fairly good shape.[22] The deposition precursors for this system, however, are uncertain, and that situation again affects the "goodness" of the database. It has been proposed that the Si-N bonds form on the surface of the growing film for SH_4/N_2 mixtures, whereas they form in the gas phase for SiH_4/NH_3 mixtures.[23] In the former case, the present status of the database is fairly good. In the latter case, rate coefficients for formation and reactions of the proposed deposition precursors, amino-silanes ($SiH_n(NH2)_m$), are largely unknown.

Databases for deposition of dielectrics using gases other than SiH_4 are currently inadequate. For example, deposition of SiO_2 at low temperatures is often performed using TEOS ($Si(C_2H_5O)_4$); however, the gas phase chemistry is virtually unknown. In all cases, the experimentally derived databases for reactions of vibrationally and electronically excited species range from very poor to nonexistent.

Databases for etching chemistries are less complete than those for deposition, largely because of the lack of experimentally derived rate coefficients. The situation is improving based largely on rapid advances in computational chemistry, which have enabled accurate calculation of rate coefficients in ground and vibrationally excited states. A compendium of experimental and computed rate coefficients for the $CF_4/CHF_3/H_2/O_2$ system has recently been assembled for use at high pressure.[24]

An assessment of neutral chemistry databases for selected chemistries is given in Table 6.2.

Excited State Chemistry and Penning Ionization

Internal energy (either electronic or vibrational) of reactants increases the amount of energy available and therefore may bridge or reduce activation energy barriers. In plasmas, significant fractions of the atoms and molecules can have internal activation energy. To first order, one might simply reduce the activation energy barrier of the process by the amount of the internal energy. This, however, is a questionable practice, according to Armentrout.[25] Electronic energy may not couple directly into the reaction coordinate, and the reaction efficiencies of ground and excited states are often very different even after the effect of total energy has been accounted for.

TABLE 6.2 The Status of Neutral Chemistry Databases for Selected Chemistries

System	Status	Comments
SiH_4 / Si_2H_6 / H_2 (Deposition of a-Si:H, p-Si)	Good	Database was initially compiled for silane combustion, CVD of p-Si, and PECVD of a-Si:H for photovoltaics.
Si_nH_m / O_2 / N_2O (Deposition of SiO_2 oxynitrides)	Fair to good	Database was initially compiled for CVD of SiO_2, silane combustion, and atmospheric chemistry
Si_nH_m / NH_3 / N_2 (Deposition of Si_3N_4	Fair to good	Database was initially compiled for CVD of Si_3N_4 and atmospheric chemistry
C_nH_m / H_2 (Deposition of diamond, diamond-like carbon)	Very good	Database was initially compiled for combustion.
C_nF_m / H_2 / O_2 (Etching of SiO2, Si)	Fair to good	The Plumb and Ryan[a] mechanisms are "standard" but applicable to a limited parameter space. A new reaction mechanism and database developed by M. Zachariah[b] are now available
SF_6 (Etching of p-Si, W)	Fair to poor	Interest in modeling circuit breakers and spark gaps at high pressure Database with questionable application to low pressure
CCl_4 (Etching of p-Si)	Fair	Need for this database is minimal due to phaseout of the use of CCl_4.
BCl_3 / HBr / $C1_2$ / NF_3 (Etching of p-Si, metals)	Poor	These are examples of databases that are currently poor but are amenable to being addressed by calculations

a I. Plumb and K. Ryan, *Plasma Chern. Plasma Proc*. 6:11 (1986);—6:205 (1986);—6:231 (1986).

b D.R.F. Burgess, M.R. Zachariah, W. Tsang, and P.R. Westmoreland, NIST Technical Note 1412 (U.S. Department of Commerce, Technology Administration, July 1995).

A subset of excited state chemistry is electronic quenching and Penning ionization. These reactions are collisions involving excited states of atoms or molecules and resulting in the deactivation of the excited state (quenching) and the transfer of energy to the collision partner. When the collision partner is ionized, the process is termed a "Penning ionization."

Examples:

Quenching: $Ar^* + SF_6 \rightarrow SF_{6-n} + nF + Ar$

Penning Ionization: $He^* + H_2 \rightarrow H_2^+ + He + e^-$

Quenching reactions are important because they can transfer energy to the collision partner producing dissociation, and they may remove intermediates for multistep ionization. Interest in the development of excimer and metal ion lasers in the 1970s and 1980s resulted in a large database for rare-gas metastable quenching. (See, for example, Velasco et al.[26]) In the 1980s and 1990s, interest in PECVD of a-Si:H and its alloys for photovoltaics has supplemented that database with reactions involving SiH_4, Si_2H_6, CH_4, C_2H_6, and GeH_4.[27] In many cases, these rate coefficients and cross sections are for quenching of the excited state on a particular gas, and little information is given on the identity and branching ratios of the products.

Summary

It is clear that a large resource for cross sections and rate coefficients is currently available in the literature. Unfortunately, this resource was developed largely for use in fields other than plasma processing, and therefore is scattered and difficult to assemble. A first and necessary task is to assemble, evaluate, and disseminate the existing data.

As a consequence of past activities in generating databases for combustion, lasers, and atmospheric chemistry, techniques are now available for measuring or calculating many of the missing ion and neutral chemistry rate coefficients and cross sections. It is important to leverage that existing capability to address the database needs discussed here.

A task equal in importance to the generation of rate coefficients and cross sections is the construction of "reaction mechanisms." In many cases these mechanisms may consist of reduced reaction sets that address the conditions of interest but may not be applicable to, for example, higher pressures. In constructing them, sensitivity analyses will identify key reaction sets or sequences that are particularly important and for which data may be lacking.

In all cases, the choice of the systems of interest must be aligned with the current planning of the semiconductor industry, as indicated in the Semiconductor Industry Association's roadmap.[28]

Ion Processes

The ion-molecule database is fragmentary for most of the chemistries of interest. The majority of ion-molecule reaction rate coefficients that are now available were not produced specifically for the semiconductor manufacturing industry, but rather for upper atmospheric chemistry, high-energy radiation chemistry, and gas-discharge or e-beam excited lasers. The techniques developed for generating those databases may be applied to the systems of interest with little new invention. Data for ion-molecule reactions in which either reactant is a radical are generally missing from existing databases and are of crucial importance to plasma processing. In principle, existing techniques can be applied to producing these data; however, new invention may be required to produce pure radical sources. In all cases, rate coefficients for the distribution of and branching ratios for products, and for reactions with radical species, are the least well known and therefore deserve particular attention.

Electron-ion (dissociative) recombination and ion-ion neutralization are also classes of reactions for which experimental techniques exist to measure rate coefficients in the systems of interest. The major gap in the database is the identity of the products. New techniques may be necessary to resolve the identity and branching ratios of the products.

Neutral Chemistry

The database for neutral chemistry is fairly complete for select deposition systems, and significantly less complete for most etching systems. Incomplete data on rate coefficients for those systems are found predominantly among reactions of electronically, vibrationally, or translationally hot species, and among reactions in the fall-off pressure regime. Given thermodynamic properties, vibrational frequencies, and so on, computational methods are available to generate many of these rate coefficients, particularly for translationally and vibrationally hot species, and for the fall-off pressure regime. There is much greater uncertainty in calculations for reactions of electronically excited species. Applying and improving computational methods to fill the gaps in the neutral chemistry database are to be encouraged. These activities should be coordinated with a less exhaustive experimental program that provides high confidence and well-characterized rate coefficients for validating and benchmarking the computationally derived values.

THERMOCHEMICAL DATA

Thermochemical data describe the initial and final states of a chemical reaction in equilibrium with a thermal bath. Such data are essential for benchmarking (testing) models of chemical reactions, e.g., testing the validity of theoretical potential energy surfaces used in reaction models. These data are also[29] used to reduce the complexity of possible reaction schemes used in chemical kinetics models by screening out energetically unfavorable reactions. In addition, in some cases it is possible to estimate reaction rate coefficients using thermochemical kinetics and transition state theory.

Thermochemical data of interest for plasma processing include homogeneous reaction energies, entropies, and energy levels for chemical reactions; molecular dissociation, chemi-ionization, and negative ion formation for ground and excited states of neutral and ionic species; heterogeneous reaction energies, such as heats of desorption; and solid state and thin film quantities related to annealing and transport of impurities and defects. In plasma processing discharges, significant deviations from local thermal equilibrium can exist even for neutral species, and this complicates the use of thermochemical information. Thermochemical properties are often of direct use in the modeling of thermal chemical processing systems, where the kinetic and internal energies of the reacting species are more properly described by a local temperature.

Most of the currently available thermochemical databases have been developed to serve other fields, such as rocket fuel combustion, upper atmosphere chemistry, and pollution abatement. These databases do not include many of the more reactive gas-phase species of interest for plasma processing. One of the best known sources of thermochemical data, the *JANAF Thermochemical Tables*,[30] provides data on molecular geometries, vibrational frequencies, heat capacities, entropies, enthalpies, and equilibrium constants. The extensive polynomial fits to the temperature-dependent thermochemical data are not usually applicable to models of plasma processing systems.

The only relevant compiled sources of thermochemical data found for solids or gas-solid interfaces of interest in plasma processing are represented by the listings of thermochemical properties for solid silicon, carbon, and boron in the JANAF tables. Particularly needed are data on heats of desorption for various adsorbed and absorbed species. Understanding of surface thermochemistry, although not well enough developed to provide an exhaustive compilation, would benefit from data compilations and evaluations to establish the state and availability of the database. Although the first step in this process is to assemble and disseminate the currently available data, the value of evaluated databases must be emphasized. Data and data gathering techniques in original journal articles generally need to be evaluated further by critical comparison with other data and other techniques.

Thermochemical data for gas phase etching-related compounds, such as Si_nCl_m, C_nCl_m, B_nCl_m, and their derivatives, are generally available. One concern is that there are significant differences (10 kcal/mol or 0.5 eV) among heats of formation of some of the $SiCl_x$ molecules and ions (P.B. Armentrout, University of Utah, private communication, 1995). Thermochemical data for gas phase compounds related to amorphous hydrogenated silicon, such as Si_nH_m, and their derivatives are also generally available. No reviews or compilations of data are known to the panel, however, regarding the thermochemistry of these species on semiconductor surfaces.

Theoretical calculations of thermochemical data have become very useful for certain *classes* of compounds, such as organic molecules and small inorganic molecules with atoms from the first and second rows of the periodic table.[31] In addition, recent work has suggested that the reactions of fluorinated hydrocarbons with oxygen, for example, can be fruitfully analyzed using ab initio techniques coupled with transition state theory.[32]

One possibility to improve the database is to develop multiple-species discharge systems for reaction measurements, such as the flowing afterglow technique. This apparatus was successfully applied to determining the energetics and kinetics of ion-molecule and radical reactions of interest to upper atmosphere and pollution chemistry. The principal effort here would have to be placed on surface reactions and properties using plasma-generated species. Currently, experiments on surface reactions are based largely on thermal processes, which generally address incident species at energies below about 700 K.

The calculation of thermochemical properties of ground state species using quantum chemistry and empirical approaches has reached the point of considerable utility for estimation of unknown values. In some cases, however, discrepancies with experimental data emphasize the need for additional refinements to the techniques.

Although the overlap with thermochemistry data requirements is limited, it is desirable to maintain a collaboration with the proposed data generation efforts for chemical vapor deposition (CVD).[33]

Some currently available sources of relevant thermochemical data are listed in the references.[34]

FINDINGS

1. The database for ion-molecule and neutral-neutral chemistry varies considerably. For some species and reactions, the data are good. This is especially true for cases in which there is overlap with processes occurring in the upper atmosphere or in some cases in chemical vapor deposition processes. In other cases, however, most notably for etching processes, few data are available.
2. Thermochemical data are sketchy for many species of interest in plasma processing. These data are important in helping to establish boundaries for reaction pathways and in estimating reaction rate coefficients. Techniques, both experimental and computational, are generally available to obtain these quantities, but few efforts are under way at present to meet these needs.

REFERENCES

1. H.W. Ellis et al., *Atomic Data and Nuclear Data Tables* 7:177 (1976); — 22:179 (1978); — 31:113 (1984).
2. L.W. Sieck and S.G. Lias, "Rate Coefficients for Ion-Molecule Reactions. I. Ions Containing C and H," *J. Phys. Chem. Ref. Data* 5:1123 (1976).
3. D.L. Albritton, "Ion-Neutral Reaction-Rate Constants Measured in Flow Reactors Through 1977," *Atomic Data and Nuclear Data Tables* 22:1 (1978).
4. Y. Ikezoe, S. Matsuoka, M. Takebe, and A. Viggiano, *Gas Phase Ion-Molecule Reactions Rate Constants Through 1986* (Ion Reaction Research Group of the Mass Spectroscopy Society of Japan).
5. R. Morris, A.J. Viggiano, and J.F. Paulson, *J. Phys. Chem*. 97:6208 (1993); R. Morris, A.J. Viggiano, J.M. Van Doren, and J.F. Paulson, *J. Phys. Chem*. 96:3051 (1992).
6. M. Tsuji, T. Fumatsu, H. Kouno, and Y. Nishimura, *Chem. Phys. Lett*. 192:362 (1992); H. Obase, M. Tsuji, and Y. Nishimura, *J. Chem. Phys*. 99:111 (1985).
7. D.K. Bohme, "Chemistry Initiated by Atomic Silicon Ions in the Gas Phase: Formation of Silicon Bearing Ions and Molecules," *Int. or. Mass Spectrom. Ion Processes* 100:719 (1990).
8. M. Mandich and R. Reents, *J. Chem. Phys*. 95:7360 (1991).
9. R. Johnsen, *J. Chem. Phys*. 85:3869 (1986).
10. M.E. Weber and P. Armentrout, *J. Phys. Chem*. 93:1596 (1989); E.R. Fisher and P.B. Armentrout, *Int. J. Mass Spectrom. Ion Processes* 101:R1 (1990); E.R. Fisher, B.L. Kickel, and P.B. Armentrout, *J. Phys. Chem*. 97:10204 (1993).
11. B.H. Boo, J.L. Elkind, and P.R. Armentrout, *J. Am. Chem. Soc*. 112:2803 (1990).
12. J. Moseley, R.E. Olson, and J.R. Peterson, *Case Stud. At. Phys* . 5:1 (1975).
13. J.B.A. Mitchell, *Phys. Rep*. 186:215 (1990).
14. J.G. Adams, *Int. or. Mass Spectrom. Ion Processes* 132:1 (1994).
15. J.S. Chang, R.M. Hobson, Y. Ichikawa, T. Kaneda, N. Maruyama, and S. Teii, *J. Phys. B* 22:L665 (1989).
16. A. Phelps, *J. Phys. Chem. Ref. Data* 20:557 (1991); — 21:883 (1992).
17. See, for example, W. Tsang and R.F. Hampson, *J. Phys. Chem. Ref. Data* 15:1087 (1986); R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson, J.A. Kerr, and J. Troe, *J. Phys. Chem. Ref. Data* 18:881 (1989); F. Westley, J.T. Herron, R.J. Cventanovic, R.F. Hampson, and W.G. Mallard, *NIST Chemical Kinetics Database* (1994).
18. M.J. Kushner, *J. Appl. Phys*. 63:2532 (1988); M.E. Coltrin, R.J. Kee, and G.H. Evans, *J. Electrochem. Soc*. 136:819 (1989).
19. M.J. Kushner, *J. Appl. Phys*. 74:6538 (1993).
20. C.J. Guinta, J.D. Chapple-Sokol, and R.G. Gordon, *J. Electrochem. Soc*. 137:3237 (1990).
21. G. Lucovksy, D. Tsu, and R. Markunas, ch. 16 in *Handbook of Plasma Processing Technology*, eds. S.M. Rossnagel, J.J. Cuomo, and W.D. Westwood (Noyes Publications, Park Ridge, N.J., 1990).
22. M.J. Kushner, *J. Appl. Phys*. 71:4173 (1992).
23. D.L. Smith, A.S. Alimonda, and F.J. von Pressig, *J. Vac. Sci. Technol. B* 8:551 (1990).
24. D.R.F. Burgess, M.R. Zachariah, W. Tsang, and P.R. Westmoreland, NIST Technical Note 1412 (U.S. Department of Commerce, Technology Administration, July 1995).
25. p. Armentrout, *Science* 251:175 (1991).
26. J.E. Velasco, J.H. Kolts, and D.W. Setset, *J. Chem. Phys*. 69:4357 (1978).

27. H. Chatham, D. Robertson, and A. Gallagher, *J. Chem. Phys*. 79:1301 (1983).
28. Semiconductor Industry Association, *The National Technology Roadmap for Semiconductors* (SEMATECH, Austin, Tex., 1994).
29. Y.F. Wang and R. Pollard, *J. Electrochem. Soc*. 142:1712 (1995).
30. M.W. Chase, Jr., C.A. Davies, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald, and A.N. Syverud, *JANAF Thermochemical Tables*, 3rd edn., *J. Phys. Chem. Ref. Data*, suppl. 1 (1985).
31. See, for example, P. Ho and C.F. Melius, *J. Phys. Chem*. 94:5120 (1990).
32. D.R.F. Burgess, M.R. Zachariah, W. Tsang, and P.R. Westmoreland, NIST Technical Note 1412 (U.S. Department of Commerce, Technology Administration, July 1995); M.R. Zachariah, W. Tsang, P.R. Westmoreland, and D.R.F. Burgess, *J. Phys. Chem*. 99:12512-12519 (1995).
33. See, for example, J.R. Whetstone et al, *White Paper for a Chemical Kinetics Database to Support Integrated Circuit (IC) Manufacture*, SEMATECH Technology Transfer #94072443A.XFR (September 1994).
34. M.W. Chase, Jr., C.A. Davis, J.R. Downey, Jr., D.J. Frurip, R.A. McDonald, and A.N. Syverud, *JANAF Thermochemical Tables*, 3rd edn., *J. Phys. Chem. Ref Data 14*, suppl. 1 (1985) [see NIST/SRD Products Catalogue SP 782 for hard-copy, floppy disk, and on-line versions of this and other databases]; L.V. Gurvich et al., *Thermodynamic Properties of Individual Substances*, 3rd edn. (English) (Nauka, Moscow, 1978) [similar to *JANAF*, this reference summarizes rules for estimating thermochemical data from structure]; S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, and W.G. Mallard, "Gas-Phase Ion and Neutral Thermochemistry," *J. Phys. Chem. Ref. Data 17*, suppl. 1 (1988) [see NIST/SRD SP 782 for an updated version on floppy disk]; R.J. Kee, F.M. Rupley, and J.A. Miller, The *Chemkin Thermodynamic Data Base*, Sandia National Laboratories Report SAND87-8215B (1990) [specific heats, standard state enthalpies, and entropies of species and reactions related to combustion and to CVD of silicon from silane; part of the *Chemkin* chemical kinetics code; available from the authors; also see Report SAND89-8009B (1993)]; M.E. Jacox, "Vibrational and Electronic Energy Levels of Polyatomic Transient Molecules," *J. Phys. Chem. Ref. Data* monograph 3 (American Chemical Society, Washington, D.C., 1994); K.P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).

Appendix A: Acronyms and Abbreviations

AFM	atomic force microscopy
BEOL	back end of the line
CARS	coherent anti-Stokes Raman scattering
CD	critical dimension
CFM	contamination-free manufacturing
CMOS	complementary metal oxide semiconductor
CVD	chemical vapor deposition
DFWM	degenerate four-wave mixing
DRAM	dynamic random access memory
ECR	electron cyclotron resonance
E/N	ratio of electric field to gas density
FOM	Fundamenteel Onderzoek der Materie (a research institute in the Netherlands)
FTIR	Fourier transform infrared
FTMS	Fourier transform mass spectroscopy
IC	integrated circuit
ICP	inductively coupled plasma
IR	infrared
IRIS	imaging of radicals interacting with surfaces
JANAF	Joint Army-Navy-Air Force
Kn	Knudsen number
LIF	laser-induced fluorescence
MD	molecular dynamics
MOSFET	metal oxide semiconductor field effect transistor
MPU	microprocessor unit
NIST	National Institute of Standards and Technology
PECVD	plasma-enhanced chemical vapor deposition
PVD	physical vapor deposition
rf	radio frequency
RIE	reactive ion etching
SEM	scanning electron microscopy
SEP	stimulated emission pumping
SIA	Semiconductor Industry Association
SPIE	The International Society for Optical Engineering
TALIF	two-photon allowed laser-induced fluorescence
TEM	transmission electron microscopy
TEOS	tetraethoxysilane
UHV	ultrahigh vacuum
ULSI	ultralarge-scale integration
UV	ultraviolet
VLSI	very large scale integration