NRL STRATEGIC SERIES

Plasma Processing and Processing Science

Panel on Plasma Processing

Naval Studies Board
Commission on Physical Sciences, Mathematics, and Applications
National Research Council

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PANEL ON PLASMA PROCESSING

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Preface

To assist with its long-term strategic planning, the Naval Research Laboratory (NRL) requested that the Naval Studies Board of the National Research Council (NRC) form a panel on plasma processing science. NRL's request for independent advice acknowledged the importance of this area of science to a broad range of applications. Specifically, the use of plasmas for processing has found utility in numerous techniques for materials preparation and processing. Applications include the preparation of electronic materials (using processes such as chemical vapor deposition, reactive ion etching, and others); plasma spray techniques for coatings; the modification of metal surfaces to improve hardness, surface cleanliness, and so on; corrosion resistance; superconducting and magnetic films; and friction reduction. The subject of plasma processing, including discussion of key science and technology questions, has been addressed in the NRC report *Plasma Processing of Materials: Scientific Opportunities and Technological Challenges* (National Academy Press, Washington, D.C., 1991). That report discusses many scientific opportunities in the field, particularly those having microelectronic application.

In response to NRL's request, the Panel on Plasma Processing was formed and directed to assess, based on both NRL's strengths and opportunities in the area, whether NRL should develop a coordinated and focused research program in plasma processing of materials and, if so, identify potential characteristics and research thrusts. As part of the effort, the panel was requested to identify selected research opportunities in the field as a whole and meet with NRL researchers working in the areas related to plasma processing of materials and receive briefings on existing and planned research efforts. Anticipating that the program would draw on NRL's extensive experience and expertise in the areas of plasma generation and transport, plasma-matter interaction and plasma modeling, and materials processing using plasma processing techniques, NRL also requested that the panel consider NRL's current capabilities in the areas overlapping the proposed program.

In this context, specific questions posed for the panel's consideration were the following:

1. To what extent and in what areas is progress in this multidisciplinary field dependent on the development of a scientific foundation that is not yet present at NRL?

2. What set of new or existing research objectives can lead to tractable experiments or theory with conclusive results that promote (1) scientific advances and (2) technical utility (within a reasonable and finite/appropriate time scale) for potential programs at NRL?

3. What cooperative efforts at NRL can provide the opportunity for synergistic interactions among the various thrust area units working with the subject?

4. What additions and alterations to NRL's current facilities are needed to address new or coordinated research challenges?

5. What collaborations with other research organizations would enhance NRL's ability to contribute to progress in this field?

During the course of the study, the panel met three times—June 28-29, 1993, at NRL, July 29, 1993, at the University of Wisconsin Center for Plasma Processing, and August 21-23, 1993, at NRL.

Contents

Introduction and Summary

Among the research laboratories of the Department of Defense, the Naval Research Laboratory (NRL) has enjoyed a tradition of excellence in basic research, driven by the premise that expertise at the forefront of science and technology should reside within the military branch of the government. In the past, NRL has been strongly represented in the field of plasma physics, especially in pulsed power, particle beams, and laser-plasma interactions, and in the applications of these fields to controlled fusion. The horizons of plasma physics have, however, broadened in the last decade, and the frontiers of this discipline have moved to areas with lower energy content, such as space plasmas and plasma processing.

The fastest growing area within plasma physics is its application to the fabrication of materials and manufacture of devices, particularly of semiconductor devices. As part of its long-term strategic planning, NRL has been considering whether to divert some of its research capability to this new field. At the request of NRL, the Panel on Plasma Processing was formed to provide guidance on the following general questions: (1) What are some of the research opportunities in the field as a whole; (2) Does the existing NRL research capability in plasma physics, chemistry, surface science, and materials processing provide a sufficient base for building a focused research program that can address these opportunities; and, if so, (3) What other issues, such as outside collaborations, would need to be addressed?

The panel finds that many opportunities exist for the research capabilities resident at NRL to have significant impact on the use of plasmas in industrial manufacturing. In Chapters 2 through 8, research opportunities are presented in the specific areas of modeling and simulation of plasma processing, semiconductor processing, plasma deposition and polymerization, ion implantation and surface modification, thermal plasmas, flat panel displays, and low-temperature plasmas. In view of the shifting emphasis in plasma physics away from high-temperature applications toward low-temperature industrial plasmas and based on its identification of selected opportunities in the field and its evaluation of NRL's research capabilities in chemistry, materials science, surface science, and plasma physics, the panel recommends the following.

The Naval Research Laboratory should develop a coordinated and focused program in plasma processing and processing science. The program should have the following features:

1. The program should focus on a few emerging technologies, such as those drawn from the suggestions in Chapters 2 through 8, on which NRL efforts could have a strong impact and for which NRL could strive to become a nationally recognized center. Each chapter includes a section entitled "A Role for NRL" that identifies research directions.

2. In redirecting some of its resources to plasma processing and processing science, NRL should capitalize on its tradition of excellence in basic research by focusing the program on areas where it can be a national leader, without directly competing with industry or other established national programs on near-term objectives. NRL's emphasis on fundamental science should be maintained.

3. By nature, plasma processing and plasma science are highly interdisciplinary fields. Therefore, collaboration among the existing groups at NRL in a focused research program is a prerequisite for success. The program should have a formalized structure, with its own

director to ensure coordination among the groups, and include an ongoing seminar series with external speakers designed to facilitate cooperation, communication, and interest among the participants.

4. The research program should be well balanced in terms of experimental and modeling efforts. It should strive toward establishing the knowledge base as well as the technology base for the chosen emerging technologies.

5. To establish and maintain contact with the mainstream of processing science, NRL should form collaborations with industry, universities, and other laboratories. NRL has had experience with setting up Cooperative Research and Development Agreements (CRADAs) and could use these as mechanisms for accomplishing the goal of increased collaboration. (Chapters 2 through 8 identify current academic, industrial, and federal laboratory efforts in the field.)

It is the judgment of the panel that NRL has sufficient facilities in place to enable it to play a key role in many important issues pertaining to the plasma processing of semiconductors in ultralarge-scale integrated (ULSI) manufacturing. It is also the panel's judgment that the first priority for NRL should be to intensify interactions with the outside world to understand the current issues and to gain insight on where to focus its efforts. NRL personnel should increase their involvement with the materials processing community by attending relevant conferences, presenting contributed papers, and seeking invitations to give invited papers. As NRL implements the recommendations of this panel and redirects its research thrusts in the area of plasma processing of materials, the Laboratory management and research team should be prepared for the period of learning, retraining, and reorganization that will be required for it to become a significant and respected element in the field. Chapter 9 offers specific conclusions on how NRL's capabilities in plasma physics, chemistry, surface science, and materials processing can be used to support the research program that is recommended in this report.

Modeling and Simulation of Plasma Processing

RESEARCH OPPORTUNITIES

Requirements of the Microelectronics Fabrication Industry

The microelectronics fabrication industry must reduce the cost and time required to produce new plasma equipment and new processes in order to remain competitive with Japanese and other offshore suppliers. The industry is looking primarily toward modeling and simulation (M&S) to aid in this endeavor. It is generally acknowledged that M&S will not, in the foreseeable future, be reliable and accurate enough to produce "machine drawings" for plasma equipment that "works" with no further experimental development. Rather, the industry is looking toward M&S to reduce the number of hardware iterations required to develop new plasma tools, thereby producing great savings in cost and time.

The two spatial scales of interest to M&S are reactor scale and feature scale. The goal of reactor scale modeling is to optimize the uniformity of reactive fluxes (ions and radicals) to the wafer being processed. The goal of feature scale modeling is to predict etching profiles and rates as functions of the magnitude and composition of the reactive flux and as functions of the aspect ratio of the trench. The requirements for relevant reactor scale models are discussed briefly below.

Multidimensional Models

The phenomena of interest in plasma tools for microelectronics fabrication are inherently multidimensional, and so models must be at least two-dimensional to significantly affect the design of plasma equipment. One might argue that three-dimensional models will ultimately be required. It is doubtful that in the next few years our limited knowledge of the plasma chemistry (see below) will warrant this additional effort.

Plasma Chemistry

Although the uniformity of volumetric plasma generation is largely a plasma physics problem, virtually all other characteristics of interest (e.g., etch rate, lag in reactive ion etching [RIE], anisotropy, selectivity) are driven by the details of the plasma chemistry. Very subtle aspects of plasma chemistry can have a large influence on the final product. For example, the sputtering of oxygen atoms from quartz liners in electron-cyclotron resonance (ECR) reactors can be responsible for producing desirable passivation layers on the sidewalls of trenches. Relevant plasma equipment models must therefore have the capability of including complex plasma chemistry. This presupposes, of course, the availability of fundamental cross-section and rate coefficient data.

Surface Chemistry

In low-pressure, high-plasma-density tools, the flux of reactants from the wafer is a nonnegligible fraction of the total mass flux through the reactor. Many plasma equipment design issues may ultimately depend on the disposition of the reactant flux returning to the plasma. At gas pressures of less than tens of mTorr, the collision frequency of radicals or ions with the walls is greater than with the gas molecules. One could argue that, under these conditions, the "plasma" chemistry is indeed dominated by reactions occurring on the surfaces of the chamber and the wafer.

Electromagnetics

It is generally accepted by industry that the traditional RIE plasma tool will not be adequate for feature sizes of < 0.5 μm and wafer sizes > 200 mm. ECR plasma tools have been investigated in recent years as a low-gas-pressure, high-plasma-density alternative to RIE. Issues related to uniformity over large wafers and to cost of ownership have motivated the investigation of other plasma sources, particularly inductively coupled plasmas (ICPs) and helicon sources. Since all of these advanced reactors are electromagnetically driven devices, plasma equipment models must have the capability to couple wave propagation with plasma chemistry self-consistently.

Current Status of Modeling and Simulation

Modeling and simulation (M&S) of plasma processing reactors and plasma-assisted materials processing (PAMP) have progressed significantly during the past 5 years. This rapid progress has resulted from the maturity of new modeling techniques and the availability of high-performance computers, in the form of both remote mainframes and desktop workstations. At a minimum, plasma equipment models must solve the continuity equations for charged and neutral species and Poisson's equation for the electric potential. At best, plasma equipment models include a full kinetic description for all charged particles and neutrals (hot atoms having energies exceeding 100 eV have been observed in RIE tools). Four classes of models for PAMP are being developed for advanced plasma equipment—particle-in-cell simulations, kinetic models, fluid or hydrodynamic models, and hybrid models.

Particle-in-Cell Simulations

Particle-in-cell (PIC) simulations coupled with electromagnetics are, in principle, exact representations of plasma equipment subject to limitations in our knowledge of the details of the plasma chemistry. PIC simulations have the advantage of easily addressing complex geometries. They suffer from being extremely computer intensive, particularly in multiple dimensions, and being poor at resolving large dynamic ranges in the densities of reactants. For example, one can easily have a dynamic range of 10^4 in important reactants, making it difficult to have a statistically meaningful number of pseudoparticles for all species.

Kinetic Models

Kinetic models are, in principle, direct solutions of Boltzmann's equation for all pertinent species. An example of a kinetic model is the "convective scheme," which uses a Green's function propagator to advance fluid-like elements in a velocity-position phase space. Kinetic models have advantages (exact solutions of the problem) and disadvantages (computer-intensive applications) similar to those of PIC simulations. They have the additional advantage that they are not statistical and therefore do not suffer from noise in the solution of Poisson's equation. They are also able to address large dynamic ranges in densities.

Fluid or Hydrodynamic Models

Fluid models solve the hydrodynamic equations of motion (continuity, momentum, energy) for charged and neutral species coupled with Poisson's and Maxwell's equations. Fluid models have the advantage of being relatively mature and often borrow numerical techniques from similar models developed for fusion and combustion. They suffer from the inability to produce kinetic information, such as energy distributions of ions. They also suffer from having questionable applicability at gas pressures less than tens of mTorr.

Hybrid Models

Hybrid models combine kinetic and fluid simulations in an iterative fashion. Typically, a kinetic simulation is used to generate energy or velocity distributions, which, in turn, are used to generate source functions and transport coefficients. A fluid model uses those values to produce densities and electric fields. The fields and densities are cycled back to the kinetic model and the process iterated to convergence. Most advanced equipment models use hybrid techniques of one sort or another.

Two-dimensional models of ECR, RIE, and ICP reactors have been developed by a number of groups in the United States and abroad. These groups include Sandia National Laboratories, Lawrence Livermore National Laboratory, IBM T.J. Watson Research Center, Auburn University, University of California at Berkeley, University of Houston, University of Illinois, University of Wisconsin, Eindhoven University (Netherlands), Paul Sabatier University (France), and the Australian National University (Australia). The general weaknesses of these models are that they lack detailed plasma chemistry, plasma surface interactions, full electromagnetic capabilities, and geometrical flexibility. However, in at least three instances, these models are being used by plasma equipment manufacturers to iterate new designs and to hone existing designs of a low-pressure ICP system. These equipment-design-capable models are hybrid models that have separate electromagnetic, kinetic, and fluid modules and have the capability to rapidly vary geometry and materials.

A ROLE FOR NRL

NRL has embarked on a modeling program for ECR reactors. The intent of this effort appears, initially, to be to provide a learning platform for the NRL M&S team and to complement the experimental diagnostics program. The personnel and techniques employed in this effort are excellent, and in general the work is progressing toward an equipment-design-capable model. The program has had a good start.

The NRL effort must, however, address the same weaknesses that are inherent in many of the other plasma equipment modeling activities: lack of robust plasma chemistry, lack of plasma surface interactions, and lack of relevance to the needs of the microelectronics fabrication industry. The NRL M&S team could also greatly leverage their code development efforts by adapting simulation techniques for plasma equipment that have been previously developed by others. This is particularly true with respect to plasma chemistry and plasma surface interactions. It is ultimately the flux of radicals and ions onto the wafer that determines the etch or deposition rate; therefore, determining their properties should occupy a significant portion of the effort. The existing computational effort on molecular dynamics should be an integral part of this program.

Many physics issues should be addressed with respect to the use of ECR tools in microelectronics fabrication, and in this regard the NRL effort is on track, even though the microelectronics industry is disenchanted with this technology. In spite of the promise and unresolved issues of ECR plasma tools, the U.S. semiconductor industry is moving away from ECR for microelectronics fabrication and moving toward other technologies such as ICP and helicon sources for 200-mm wafers. This situation is largely dictated by issues related to the cost of ownership of ECR equipment and the fact that Hitachi (a Japanese plasma equipment manufacturer) currently dominates the world market for ECR plasma tools and owns the majority of the patents. Attempts by U.S. equipment vendors to penetrate the ECR market for very large scale integrated (VLSI) circuit fabrication have had limited economic impact. As a result, investigations are being conducted on "nontraditional" configurations of ECR, such as distributed sources, that do not conflict with current patents and may offer advantages with respect to plasma uniformity.

The lack of U.S. vendors offering ECR products does not imply that development of models for ECR microelectronics fabrication has no relevance to the U.S. semiconductor industry, since the use of ECR is still being considered as an alternative technology. This situation does imply, however, that development of models for ECR will not likely gain mainstream attention with either the tool coefficients. A fluid model uses those values to produce densities and electric fields. The fields and densities are cycled back to the kinetic model and the process iterated to convergence. Most advanced equipment models use hybrid techniques of one sort or another.

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The NRL M&S team would profit from interaction and visits with Sematech, Semiconductor Research Corporation, plasma equipment vendors (e.g., Lam Research, Applied Materials, PMT), and end-users to become familiar with the problems facing the microelectronics industry and to learn what is expected of M&S. For example, understanding and remediating the RIE lag (the phenomenon that features having different aspect ratios etch at different rates) have a high priority with almost all equipment vendors. There is an expectation by the vendors and end-users that any plasma equipment model "worth its salt" should be able to shed some light on these topics. There is also great concern about the effects of specific types of construction materials on the uniformity of the plasma and generation of particles. The details of these latter issues may be specific to particular equipment vendors or end-users. One should also appreciate the extremely short time scales of interest to the industry. For example, Sematech Equipment Improvement Programs, in which specific plasma equipment tools are "improved," have durations of less than 1 year.

There are currently two, and soon to be a third, major modeling efforts for plasma equipment for microelectronics fabrication at other national laboratories. Sandia National Laboratories has a CRADA with Sematech to develop plasma equipment models for low-gas-pressure, high-plasma-density tools with emphasis on ICPs. Lawrence Livermore National Laboratory has a CRADA with AT&T Bell Laboratories and IBM T.J. Watson Research Center, as well as many "side agreements" with individual vendors, for plasma equipment modeling with emphasis on ICPs, helicons, and alternate configurations. Los Alamos National Laboratory is currently negotiating a CRADA with Semiconductor Research Corporation to perform similar modeling with emphasis on feature scale issues and may team with one of the other national laboratories. The greatest contribution that the NRL M&S effort can make to the micro-electronics industry will most likely come as a contributing member to this growing team of national laboratories, a task that will require significant coordination on both the scientific and managerial levels. The panel strongly urges the NRL M&S team to leverage and coordinate its efforts with those of the other national labora-tories and universities engaged in plasma equipment modeling.

Semiconductor Processing

RESEARCH OPPORTUNITIES

In ultralarge-scale integrated (ULSI) semiconductor fabrication, plasma processing plays a vital role in (1) plasma etching, (2) plasma-assisted chemical vapor deposition (PECVD), and (3) physical vapor deposition (PVD). In the plasma etching area, there is a very active development of high-density plasma (HDP) sources. This work is driven primarily by the need to operate at lower pressure to reduce the feature size dependence of the etch rate, improve profile control, reduce particulate formation, reduce residues and sidewall passivation layers, and reduce surface damage by controlling the ion and electron energies. Each of these needs engenders a large array of interesting problems suitable for basic studies. The optimization and characterization of plasma sources themselves are currently under intense study and will probably continue to be subjects of interest for several years.

Although all the U.S. tool vendors are actively engaged in HDP tool development, none of the vendors is pursuing electron-cyclotron resonance (ECR) technology for etching applications. At this time this is basically a business decision, since in stringent tests Japanese ECR etching technology has been performing very well. ECR technology is viewed as a Japanese technology, with Hitachi commanding an insurmountable lead in the Japanese market. Since the Japanese semiconductor tool market is essential for U.S. tool vendors, technologies are pursued in the United States that, in their judgment, offer the potential of being superior to ECR technology, for example, the transformer-coupled plasma technology of Lam Research and Applied Materials and the helicon technology of PMT and Lucas Laboratories. Given this situation, it is unlikely that a major effort in ECR technology aimed at manufacturing would greatly benefit any of the U.S. tool vendors.

For semiconductor manufacturing technology, the feature size dependence of the etch rate and the difficulty of decoupling profile control from the pattern density are probably the most important concerns at this time. Directional etching is achieved by sidewall passivation. The amount of sidewall passivation depends on the amount of etch product and mask area, and it changes dramatically as one moves from isolated features to densely populated portions of the integrated circuit. The amount of sidewall passivation material determines the profile of the structure and thus important device parameters like the channel length of a field-effect transistor. Controlling this pattern sensitivity has become a major manufacturing issue and a challenge to plasma processing scientists.

The formation of particulates from the reactant gases is a serious problem in plasma processing because the sheath fields of the plasma trap the particles and release them onto the wafer as contaminants when the plasma is turned off. The problem of dusty plasmas, which also is of concern in space research, is already under intense study by groups at IBM and the Universities of Arizona and Iowa, but there is still a need for innovative ideas. Another key problem that has often been noted in HDP technology is charging-induced damage in these high-current devices. Although several possible mechanisms have been identified, a model that explains all the experimental observations is lacking at this time.

Numerous applications and challenges exist in the plasma-assisted growth area. Important applications that are just starting to be explored are plasma-assisted chemical vapor deposition of metals (e.g., Al), PECVD of insulators, and PECVD of photoresist materials. An immense potential exists for the all-dry processing of photoresist materials. In PECVD there is still support for ECR technology in the United States; for instance, Lam Research offers ECR technology for the deposition of silicon dioxide.

Plasma-based surface cleaning may also become an enabling technology for cluster processing in the semiconductor industry. At this time most of the surface cleaning steps are still being performed using traditional wet methods. These methods are incompatible with the goal of complete vacuum cluster processing and with environmental considerations. A satisfactory dry-cleaning method will probably, more than any other unit-process step, change the way semiconductors are being processed.

The greatest research opportunities, however, are to be found in the field of optical diagnostics. There are three general stages in the production of microelectronic circuits in which diagnostics are important. These stages, listed without priority, are (1) development and characterization of precompetitive materials and processes, (2) comparative analysis and characterization of tools and processes in development, and (3) sensor development for process control and fingerprinting of manufacturing processes. Diagnostic techniques are central to research on semiconductor processing, and significant advances can be made in these areas.

A ROLE FOR NRL

NRL has demonstrated the necessary expertise and equipment for state-of-the art analytical measurement of chemically reactive species in plasma processes. This capability may be used to augment industrial-support programs and federally funded initiatives and for internal NRL and Department of Defense (DOD) missions. Application of this resource to the Dual Use concept is practical and of considerable benefit to NRL and U.S. industry. This section presents an outline of several avenues by which NRL can benefit U.S. competitiveness by partnering with the domestic microelectronics industry and outside programs. In formulating this discussion, the panel adopted a broad-minded, university and industrial perspective based on its members' experience, current topics in the scientific literature and professional conferences, and the announced initiatives of federally funded agencies. These suggestions do not address current defense needs; NRL can provide the best insight into this important aspect of the program. Instead, the panel hopes that NRL can mesh DOD applications and programs with the programs suggested below to provide maximum synergy and vitality for NRL and the U.S. technology base.

The capabilities and facilities provided by NRL are well aligned with the three areas listed above and provide opportunities for NRL to have an impact on U.S. industry. Activities in these technology areas also provide opportunities for NRL and outside researchers to interact and exchange ideas. A robust program of this kind will jumpstart NRL's initiative in the industrial sector by rapidly providing first-hand knowledge of and a perspective on industrial needs and problems. In addition to the technical applications detailed below, personnel programs are also needed to obtain maximum benefit for DOD and industry. One such personnel exchange program is suggested in Chapter 9.

Development and Characterization of Precompetitive Materials and Processes

The continuing trend toward smaller and faster devices and modular packaging of devices drives a need for devices with ever-smaller critical dimensions and for producing films with low or high dielectric constants and materials with special properties, such as boron nitride and diamond films, optoelectronic components, and Si/III-V alloys. Existing instrumentation and personnel at NRL are well suited for these tasks. NRL researchers could greatly assist industry and outside consortia by providing expertise in materials characterization and in situ diagnostic measurements, especially in ventures directed toward developing new materials and evaluating material properties for electronic technologies. Current NRL capabilities of interest include the following:

- Micro-Raman scattering;
- Optical emission and absorption spectroscopy (vacuum ultraviolet [VUV], ultraviolet, visible, infrared);
- Attenuated total internal reflection;
- Fourier transform infrared absorption spectroscopy;
- Infrared diode laser absorption;
- Laser-induced fluorescence (LIF) and multiphoton variations of LIF;
- Resonance-enhanced multiphoton ionization spectroscopy;
- High-resolution electron energy loss spectroscopy;
- Mass spectrometry;
- Low-energy electron diffraction spectroscopy;
- Film interference measurements;
- X-ray photoelectron spectroscopy;
- Auger electron spectroscopy; and
- Coherent anti-Stokes Raman scattering.

This extensive diagnostic capability places NRL in a unique position for partnership with industry and technology consortia. It also distinguishes NRL from university programs that may be more limited in equipment availability and interdisciplinary collaboration.

Programs in this arena could include analysis of film properties for microelectronic technologies and the effects of ion bombardment and radiation damage thereon, development of surface structures and novel materials, and scientific issues such as reaction mechanisms and avoidance of process problems during plasma processing. Some topics in this arena are issues relating to the following:

- The mechanism of diamond film deposition;
- Organometallic vapor phase epitaxy;
- Stress-free dielectric films;
- Influence on etch and deposition uniformity in large-area plasma processes;
- Particle formation and transport during plasma processing;
- Reactive ion etching and VUV damage;
- Generation and consequences of ionizing radiation in plasma processing; and
- Electrical defects caused by plasma processing.

A number of federally funded initiatives have been implemented recently to encourage research along these lines. Some of these programs are directed toward semiconductor technology and some involve computer display technology. In both areas, improvements in plasma processing are often cited as a national technological need. Often, these initiatives require or encourage collaboration between diverse partners. NRL should continue to compete in these programs and can further its competitive stance by partnering with industry and consortia involving university and federally funded laboratories.

The precompetitive posture of programs in this arena provides an uncomplicated opportunity for association with university groups, other national laboratories, and industrial partners. Publication of results should be unencumbered by proprietary concerns. The success of programs in this area will ensure future collaborations with other outside partners as the capabilities of NRL become more widely known through publications and presentations to workers in the microelectronics field. NRL should continue to be represented at semiconductor conferences and increase its dialog with that community. NRL could serve the national interest by offering its facilities and expertise in areas for which much of industry would be reluctant to expend resources because of the lack of direct (short-term) competitive benefit of research.

Nanolithography and plasma process techniques are also needed to fabricate advanced technology components. However, the high cost of developing and optimizing fabrication technology and the proprietary concerns typical for this aspect of technology development suggest that NRL's role is best suited for exploratory and characterization programs rather than for dedicated or "stand-alone" process development. In-house processing facilities at NRL are convenient and timely for building one-of-a-kind test structures. These facilities should be maintained for this purpose.

Comparative Analysis and Characterization of Tools and Processes in Development

Industrial research and development workers are often faced with a selection of competing tools and processes needed to fabricate a product in a planned program. Proper selection of the best fabrication equipment is needed for cost-effective manufacturing and to compete in the global marketplace. All too often, selection of tools and processes is driven by scheduling deadlines long before any reasonable understanding of the various technologies is available. In addition, as industry strives to reduce product costs, research and development investment invariably suffers, thereby creating vulnerability to errors in tool and process strategy with possible long-lasting effects.

An alternate approach to the current one involving redundant evaluations of the various technologies by each company is to rely on a centralized facility or program for objective, side-by-side comparison. This offers clear advantages in cost-efficiency and thoroughness. Industry partners will still require some independent evaluation for their proprietary concerns; even at a fundamental level of study, however, centralized evaluation of new tools and processes benefits all parties. Results of these studies should also be published and presented at conferences. By highlighting concerns in the open literature about newly developed tools and processes, such a program would serve to accelerate optimization and debugging of new technologies. Often, industrial laboratories capable of this type of work are restrained in their interaction with tool suppliers because of proprietary interests and concern about possible inference of future plans by their competitors.

An opportunity exists for NRL to contribute to the nation's technology base by providing domestic industry with an informed evaluation of the global advantages and disadvantages of various tools and processes. This evaluation should be maintained at a scientific level, rather than advocating certain technologies. This stance is also needed to maintain objectivity and credibility with domestic industry. NRL can serve as an *industry-neutral resource* for evaluating technologies and tools under consideration for near-term manufacturing. The diagnostic capabilities outlined above also serve well in this program arena. A role of this kind would take several years to develop, as NRL researchers become more attuned to industry and technology needs and as their customers come to trust NRL's contribution and objectivity.

One example of this comprehensive program would be comparative evaluation of several high-density-plasma tools currently being considered for 0.35-mm (and beyond) generation technology (64-MB DRAM). A host of enhanced plasma tools and processes is now in development, including helical wave and helicon resonance reactors, magnetically enhanced reactive ion etchers, ECR plasmas, and inductively coupled plasmas. Yet, to date there has been no side-by-side comparison of all of these tools and only limited side-by-side evaluation of some tools for some process applications.

Serious questions still persist regarding fundamental aspects of these high-density-plasma tools, with important implications for the domestic microelectronics industry. Which tool offers the lowest ion temperatures? The answer affects the ultimate directionality of ion-enhanced etching. Which high-density tools can be scaled up for 200-mm and even 300-mm wafers with acceptable uniformity? Does mode formation dominate in some tools with a consequent influence on center-to-edge uniformity? How serious is ion damage for circuit components in the various tools? How do particles form and move in the different high-density-plasma tools? Since each tool has an independent plasma source and a radio-frequency-biased wafer holder, can in situ cleaning processes be developed to strip unwanted film deposits from tool walls, including those films requiring ion bombardment for removal? Which tool is most prone to film deposits and thus will require greater maintenance activities? What is the influence of cross-chamber chemical contamination on clustered wafer processing? Does plasma generation of VUV light or x-rays cause defects or alter the photoresist in partially developed wafers? These questions are best answered by comparative evaluation of the competing tools. Answers to these fundamental issues would offer significant advantage to the U.S. microelectronics industry. NRL's objective and professional evaluation of some of these issues would be greatly valued by industry and would also attract resources from outside funding agencies.

The obvious drawback to this program is the need for multiple, advanced processing tools. These tools generally cost more than $1 million and final design tools are more suited for manufacturing applications than for research studies. These problems pose serious obstacles to the proposed program. However, it must be recognized that general scientific issues are addressed in this program arena, rather than a dedicated process development effort. Because of this, laboratory prototype tools are preferred over the manufacturing versions. In addition, laboratory prototype designs are genuinely practical simulations of the commercial tools. Repeatedly, it has been shown that generic problems identified in laboratory-type reactors are also observed in final product, commercial reactors. The use of laboratory-type mock-up reactors for the various high-density-plasma tools provides a cost-effective and acceptable alternative to the purchase of multiple commercial reactors. This approach has the endorsement of several tool vendors and would open opportunities for cooperative efforts with NRL researchers in designing lower-cost mock-up tools.

Sensor Development for Control and Fingerprinting of Manufacturing Processes

It is rapidly becoming evident that robust manufacturing processes for advanced technologies require real-time process control for cost-containment and product assurance. Properly used, sensors maintain process windows and correct for natural variances, minor impurities, and aging effects in tools. Sensors may even be used to highlight and correct for deficiencies of *previous* process steps and human errors. By maintaining an extensive database of sensor input, one can use archival analysis of product results to infer second-order processing effects and to optimize for imprecise fabrication line concerns such as tool maintenance and long-term drift.

NRL's experience in sensor development and in diagnostic techniques is well suited for working with outside partners and industry to develop suitable sensors for semiconductor manufacturing. Sensors are required not only for detection of gas-phase reactive species and to measure surface conditions, but also for tool inputs, such as feed gas, impurities, and radio frequency power—including arcing and spikes. Modeling may be used to help evaluate the sensitivity of processes to variations in sensor measurements of the process, thereby providing a first-order estimate of tolerances and required sensitivity of the sensor.

Sensor development can become a commercial enterprise, and some small companies dedicated to this product line have been started. However, these small operations often lack the equipment and expertise to develop the sophisticated sensors needed for reliable process control. Larger companies would probably use commercially available sensors but, in most cases, will not devote the personnel and resources to developing sensors if they are not likely to be company products. Thus, a void is formed between the entrepreneurial small companies interested in manufacturing sensors (but lacking resources to develop them) and their customers who wish to purchase rather than develop sensors. Researchers at NRL should be encouraged to work with small companies interested in manufacturing sensors and with larger companies likely to use sensors. In this way, NRL would again provide a centralized resource to domestic industry and would be furthering its mission toward Dual Use.

One example of note, useful for future planning of activities in this arena, is the recently completed and highly successful Microelectronics Manufacturing Science and Technology (MMST) program funded by the Advanced Research Projects Agency (ARPA) and cooperatively executed between Wright-Patterson Air Force Base and Texas Instruments. This program resulted in the development and testing of a wide range of process control sensors, many of which involved optical diagnostic measurements in plasma processes. Ellipsometry, a conventional technique sensitive to thin film structures, but previously considered too slow for real-time monitoring, was greatly expanded and improved on in the MMST program, eventually developing into a real-time sensor for manufacturing tools. Follow-on programs are now being proposed by ARPA. The sensors developed in the MMST have already been licensed by other companies, thereby completing the technology infusion mechanism proposed by the MMST program planners and endorsed by ARPA.

NRL can participate in or initiate similar programs, using its expertise in sensors, optical diagnostic techniques, and in-house tools. Interservice programs involving cooperative efforts with Air Force and Army laboratories are also encouraged and would offer additional expertise and insight into sensor development.

Plasma Deposition and Polymerization

RESEARCH OPPORTUNITIES

Semiconductor Fabrication

In addition to being essential to the etching process, high-density plasmas at somewhat higher pressures are also needed for deposition of insulating layers and metal contacts in the processing of semiconductors. In the deposition of SiO_2 and Si_3N_4 dielectric layers, the same problems of oxide damage, high-aspect-ratio trenches, and RIE lag (the influence of neighboring structures) are likely to be encountered as in the etching process. A new problem is the formation of dielectrics of desirably low permittivity ($\varepsilon < 2.5$); no suitable material has yet been found. This presents an opportunity for advanced research, perhaps yielding a new dielectric material that can be formed only in a plasma environment.

Barrier Coatings

The formation of barrier coatings, for instance, in automobiles, food packaging, or pharmaceutical capsules, has great potential as a widespread plasma application. In food containers, such as potato chip bags or plastic soft drink bottles, the problem is to prevent leakage of O_2 into the container or CO_2 out of it. This can usually be done by fluorinating the surface using CF_4 plasma. Treatment is also required to improve the adhesion of paint so that printing can be done on plastic containers. Reliability and aging are also improved. Examples from the automobile industry include gas tanks and bumpers. Plasma treatment of the inside of a plastic gas tank with CF_4 can slow the permeation of gasoline through the walls. However, methanol cannot be contained as easily, and, should there be a trend toward the use of methanol mixtures, a new material or process would have to be developed. Problems that could lead to fruitful lines of research include (1) efficient creation of suitable plasmas, including line sources that could process continuous webs of material; (2) plasma production in complicated geometries, such as the inside of a plastic bottle; and (3) the development of new materials that would make plastics more easily recyclable.

Fibrous Materials

Plasmas are commonly used to treat textiles and lignocellulosics (paper and wood) to improve their wettability, dyeability, adhesion, or optical properties, such as ultraviolet transparency. For instance, paper towels or diapers can be treated to improve their water absorption, filter paper to decrease water absorption, and synthetic or wool fabrics to improve the adhesion of dyes. The process involved is not one of coating but of actual chemical surface modification; for instance, the addition of a hydroxyl (OH) group will usually improve wettability. Plasmas of hexymethyldisulfoxide (HMSDO) or tetramethyl tin (TMT) are commonly used for this purpose. The physical and chemical processes occurring on the fiber surfaces are not well known, and there are opportunities for research on the composition of the precursor radicals formed in the plasma using such standard diagnostics as electron spectroscopy for chemical analysis. Once the mechanism is better known, the industrial tools for treating such materials can be optimized for speed, economy, and rate of degradation. The scalability of the process to handle large volumes needs to be shown, as well as the advantage of plasma processing over wet chemistry in terms of the volume of liquid waste generated.

Optical Coatings and Photonics

Plasmas have been used for some time to deposit coatings on optical elements such as lenses and filters, as well as for more mundane applications such as reflectors on automobile bumpers or highway signs. A newer use under development is the manufacture of multilayer optical fibers. Furthermore, a more glamorous and potentially more important application looming on the horizon is the fabrication of integrated circuits containing photonic elements—a necessary step in the move toward optical computing. To handle photons on a chip, a polymer such as polymethylmethacrylate (PMAA) can be spin-coated onto a patterned silicon wafer, and plasma deposition can be used to create a graded-index structure that can then be patterned and etched. This is obviously a new research direction with many problems to be overcome but with a large payoff.

Plasma Polymerization

One of the most commonly used plastics is methyl methacrylate (MMA), commonly known as Plexiglas or Lucite. In this material, the long polymer chains are arranged in a linear (not cross-linked) manner, resulting in a comparatively weak material. On the other hand, plasma polymerized methyl methacrylate (PPMMA) has a dense, highly cross-linked structure and can be used to strengthen the surfaces of plastic containers, textiles, or even metal automobile parts. This can be done by exposing the surface to an MMA or HMDSO plasma. Another advantage of the plasma polymerization process is the retention of the original monomer structure, whereas other processes tend to change it. It is not understood how the cross-linked structure is formed, what the precursors are, and what plasma parameters will optimize the process. Though there is not yet any commercial application of this process, it is clear that further research may lead to the improvement of many manufactured products.

A ROLE FOR NRL

Deposition of new materials is a suitable use for the excellent laboratory ECR equipment in NRL's ion/plasma processing group. As mentioned above, the development of a low-permittivity dielectric for integrated circuits is a challenge—such a development would be a significant contribution to ULSI technology. Formation of III-V compounds such as GaN, using ECR as a deposition source, may well be a rich field of investigation. Materials developed here could then be incorporated into unique circuits made in the fabrication line of the Surface and Interface Sciences Branch in the Electronics Division. Production of such one-of-a-kind devices could justify the maintenance, though not the upgrading, of a fabrication facility at NRL.

The extensive diagnostics capabilities at NRL in the Chemical Vapor Processing Group and the Surface and Interface Sciences Branch laboratories could be applied to the problem of understanding the precursor radicals in the deposition and polymerization processes. Though it has great potential, plasma polymerization is not well understood, and NRL's personnel are capable of making significant progress in this direction also.

Ion Implantation and Surface Modification

RESEARCH OPPORTUNITIES

Introduction

Ion implantation is a major application of plasma processing in a variety of applications in which the surfaces of materials are to be treated. The implantation process requires a source of ions and a means to accelerate them toward the surface. Two general methods are in use today: *ion beam* implantation, in which a beam of ions is directed toward a substrate, and *plasma* implantation, in which the ions produced in a plasma discharge surrounding or near the object to be implanted are extracted from the plasma and accelerated into the object.

Ion implantation is designed to modify the surface properties of materials without changing their bulk properties. The implantation process may offer improvements in their properties or may actually be used to degrade the surface, depending on the application. It is becoming economically attractive in Japan, Europe, and the United States and can be done on metals and alloys, as well as on semiconductors, ceramics, insulators, and polymers. Some of the surface properties that can be modified by this process are hardness, fatigue, toughness, adhesion, wear, friction, corrosion oxidation, dielectric properties, magnetic properties, superconductivity, resistivity, and catalysis.

In general, both the substrate material and the implanted species, if it can be ionized, can cover a wide range of substances. As a result, a vast array of ions can be implanted into an equally wide range of substrates. Furthermore, both implantation processes tend to operate at low pressure so that (1) a vacuum chamber is required for the workpiece and (2) collisions between charged particles and other species present in the vacuum chamber, for example, neutral particles, free radicals, electrons, and so on, tend to be minimized. The result is that the implantation process is physical, rather than chemical, in nature. However, significant numbers of chemical reactions may often occur within the substrate, since the particle density in the substrate is very high and the ions travel a comparatively short distance, thus making their concentration high near the surface.

Plasma and Ion Beam Implantation Technology

As an ion enters the surface of a material, it collides with atoms and interacts with electrons. Each nuclear or electronic interaction reduces the energy of the ion until it finally comes to rest within the target. Typically, interactions follow a statistical process, and the implanted profile is often approximated by a Gaussian distribution as follows:

$$N(x) = N_p \exp[-(x - R_p)^2 / 2\Delta R_p]$$

where the average distance an ion travels before it stops is called the projected range R_p. The peak concentration N_p occurs at a range of R_p. Because of the statistical nature of the process, some ions will obviously penetrate beyond the projected range R_p and some will not travel as far as R_p. The spread of the distribution of the implanted ions is characterized by the standard deviation ΔR_p and is called the straggle. The area under the Gaussian distribution curve is the implanted dose Q,

$$Q = \int_0^\infty N(x)dx .$$

If the implant is contained entirely within the target, and the distribution is Gaussian,

$$Q = \int_0^\infty N(x)dx \quad \text{ions/cm}^2 .$$

The implanted dose can often be controlled to within a few percent. In addition, doses in the range of 10^{10} to 10^{18} cm^2 are needed for many applications and are almost impossible to achieve by a thermal diffusion process in many applications. Range and straggle are roughly proportional to ion energy.

Ion Beam Implantation

In conventional ion implantation devices, an ion beam is extracted from a plasma source, accelerated to the desired energy, and then transported to the target. Typical beam currents are very small (in the microampere range) and the beam "footprint" area is less than 1 cm^2. To process large-scale targets, and to avoid shadowing if the target is nonplanar, a combination of beam rastering and target manipulation during the process is required.

Plasma Source Ion Implantation

In the plasma source ion implantation (PSII) process, the object is immersed in a plasma in which the Debye length is much smaller than the dimensions of the object. The strongest electric field is then in the cathode sheath, which accelerates positive ions to the negatively biased object, which serves as a cathode. If the pressure is kept low enough to prevent an arc discharge, positive ions can be accelerated to energies of 100 kV or more and can be implanted into the cathode surface.

To control the process, the implantation voltage is pulsed. The process begins with the application of a high negative potential to the object relative to the vacuum chamber wall. As the potential of the surface becomes more and more negative, the sheath, or the region surrounding the surface from which the electrons have been expelled, expands into the plasma, reflecting the electrons ahead of it. Being more massive, the ions do not have time to move as the boundary sweeps through them. When the ions find themselves on the other side of the boundary, they are in a region of a strong inward electric field, which accelerates them to the cathode.

Currently, the factors and their interactions that influence this process are poorly understood from the standpoint of the behavior of the material that is implanted. To further advance this field, an understanding of how the bombarding particles interact with the base material and how to apply this knowledge to manufacturing techniques is required for industry to further exploit this technology. Three aspects of this technique, surface hardening and wear resistance, corrosion and oxidation resistance, and semiconductor applications, are ideally suited for the use of statistical methods for experimental design and, in particular, of response-surface methods for exploring interaction effects. These are crucial tools for further developments in this area.

Applications

To be applied successfully in industry, many of the applications of ion implantation must be demonstrated to be cost-effective. Here two classes of implantation applications—metals and dielectrics—are discussed. The inherent differences in metallic, as compared with dielectric, implantation need to be considered. In both cases, the substrate requires an applied bias voltage for ion acceleration, but dielectrics will undergo charging and therefore inherently degrade the ion acceleration sheath, thus modifying the implantation. Accordingly, the acceleration voltage will be applied either to a backing conductor or to a conducting metallic, graphitic, or diamond-like carbon film deposited on the substate, which will also act to inhibit its charging.

Implantation of Metals

Recent work using this process has shown remarkable improvement in properties of nitrogen-implanted alloy die steel and of nitrogen-implanted aluminum tools for machining high-temperature alloys. The effects of implanting nitrogen into a surface previously enriched, for instance with carbon and/or boron by vapor deposition, are now being examined.

This process is called ion beam enhanced deposition (IBED), and either ion beam or plasma implantation can be used. Ultimately, this work will be extended to cover the effect of incident nitrogen ion energy (on depth of hardening), concomitant fatigue properties, characterization of the microstructure by transmission electron microscopy or atomic force microscopy, and mechanical properties versus depth by nano-hardness measurements. Such studies are a prerequisite to control of the manufacturing process and require statistical experimental design techniques for their implementation.

It has been conclusively demonstrated that ion implantation can beneficially modify the surface-sensitive mechanical properties of steels. Fatigue life has been extended by as much as a factor of 2, the coefficient of sliding resistance reduced by as much as a factor of 100, and the wear resistance increased by a significant amount. Most studies have concentrated on the use of nitrogen ions, but the use of C, B, Ti, and Mo ions has also shown promising results. When PSII is used in large-scale manufacturing, such as of automobile parts, practical problems arise that may have scientific solutions. For instance, secondary emission from the highly negative object can constitute a dominant fraction of the power that the circuit must supply. This not only increases the cost but also creates a heat problem. Control of secondaries and of unipolar arcs is a familiar problem to plasma physicists.

A very useful application of this process is in the implantation of medical prostheses. For instance, artificial hip joints with complicated shapes have been implanted with nitrogen ions for wear and hardness improvement to increase the lifetime of such devices.

Implantation of Nonmetals

Four major classes of nonmetallic materials are amenable to treatment by PSII: glasses, ceramics, polymers, and semiconductors. Extensive examination of the effectiveness of PSII for substrate modification is envisaged: magnetic domain formation in glasses, erbium doping of polymer waveguides, lattice structure modification of mica, dopant implantation into semiconductors, and surface property modification of plastics and polymers for thin film deposition and for wear improvement of gears and drive units.

The deposition of thin metallic coatings on polymeric surfaces has many important industrial and research applications, for example, in flexible electronic circuits, sensors, electromagnetic shielding, and flexible reflecting surfaces. Historically, however, adhesion of metallic coatings on polymers has suffered from unreliable bonding and delamination. One theory for this frustrating situation is that, in the vacuum environment used for metal-coating deposition, water trapped within the polymer is released, oxidizing the surface of the metal at the metal/polymer interface, thus leading to delamination. Recent research experience indicates that significant adhesion improvement for metallic coatings on polymer surfaces can be realized through the use of IBED. In this process, the metal coating deposition is performed simultaneously with low-energy (< 1 keV) ion beam irradiation. High-energy beams appear to yield results inferior to those of lower-energy beams in this application, presumably because of excessive polymer chain scission and surface nitriding.

Ion implantation of dielectrics, especially polymers, has led to dramatic improvements in their hardness. For example, after implantation, the surfaces of some polymers may become harder than stainless steel, although the process may actually be a result of carbonization of the polymer rather than by the formation of new compounds by implantation itself.

In semiconductor applications, ion implantation is a major component in microfabrication. Typically, beam implantation is used; this often imposes a lower limit on the available ion energies, making it difficult, for example, to produce the shallow-depth implants needed for the next generation of microelectronics. Plasma implantation, however, has been shown to produce shallow implants. In addition, the potential of silicon-on-insulator (SOI) technology using separation by oxygen, separation by implantation of nitrogen, or separation by implantation of oxygen and nitrogen will permit the manufacture of semiconductor devices on a thin silicon film mechanically supported by a thin insulating substrate. Present technologies limit the thickness of the silicon wafer used for microchip manufacturing to more than 500 μm to avoid unwanted electrical coupling, but only the first few micrometers at the top of the wafer is used for most transistor fabrication. With the use of SOI technology, this limit can be dramatically reduced.

A ROLE FOR NRL

Implantation in industry can take many forms ranging from individual "job shops" to tool and component manufacturers to users with on-site implantation machines. As a result, it is important for NRL to consider how implantation technology can impact all three of these aspects.

NRL can use its expertise in high-energy beams and can build on its existing strengths in this area. It is important to consider how this expertise can be used to expand the applications; these should include IBED, which itself can be used for a much wider range of applications. The energy ranges of the NRL implantation systems should be extended to lower and higher energies. Optimization of the implantation process is extremely important for economic viability, that is, for the shortest possible processing time.

Current research on ion implantation has revealed a number of scientific and technical problems that can serve as examples of areas in which NRL can make a contribution. These areas include design of efficient pulse modulators for high power delivery, control of secondary emission, processes in plasma and sheath formation, computation of ion trajectories near complex boundaries, electric fields in implantation of dielectric materials, implantation of mixtures of ions, numerical simulation of surface kinetics, and implantation and doping of semiconductors.

It is of course not sufficient to understand the physical processes and demonstrate that the implantation can take place; an economic assessment is also required to show feasibility. It is important to concentrate on industrial applications that have a potential for commercialization. NRL should facilitate collaborative activities with ongoing implantation groups that are specifically oriented toward industrial applications.

Thermal Plasmas

RESEARCH OPPORTUNITIES

Introduction

Thermal plasma processing is carried out near atmospheric pressure, so that it involves different regimes of density, power, and heat flow from those in the preceding technologies. It must be viewed in the context of much broader trends that exert a strong influence on the development of this technology. Materials and materials processing are attracting increasing attention, a trend that will continue into the next century. This trend will not be restricted to the development of new materials but will also include the refining of materials, the conservation of materials (by hard facing, coating, and so on), and the development of new processing routes that are more energy efficient, more productive, and less damaging to our environment. Thermal plasma processing will play an important role in these developments. Its potential for developing new materials-related technologies is increasingly recognized, and many research laboratories all over the world are engaged in advancing the frontiers of knowledge in this field. An interesting example of the use of plasma processing has been demonstrated recently in connection with a breakthrough in the field of diamond film deposition. Thermal plasmas provide the highest deposition rates among all known diamond film deposition techniques.

In spite of great strides over the past 25 years, the number of successful industrial applications on a broad base has been relatively small. The primary reason for the relatively slow growth of this technology has been the lack of a solid engineering base. Industrial efforts have not been sufficiently paralleled by basic studies at universities and national research laboratories, and, as a consequence, the required engineering base for many processes is still poorly developed. This problem is directly linked with the nature of thermal plasma processing as a highly interdisciplinary field that cannot succeed without extensive interdisciplinary endeavors. Knowledge of plasma physics, gaseous electronics, fluid dynamics, and heat transfer has to be combined with experience in surface chemistry, electrochemistry, and materials science.

The following sections outline research opportunities associated with various thermal plasma applications.

Plasma Spraying

Plasma spraying is considered to be one of the prime candidates for producing high-temperature-resistant coatings (ceramics) for turbine blades and antiwear and anticorrosion coatings for high-temperature applications. Although plasma spraying is a well-established commercial process, its science base is still in the development stage. Arc-flow interactions within the plasma torch and the fluid dynamics of the plasma jet are still poorly understood. In spite of this drawback, extensive efforts are in progress to develop completely automated plasma spray systems using robotics for substrate/torch motion and feedback control for the plasma spray jet.

Wire-arc spraying is an inexpensive thermal plasma coating process in which the material to be deposited is introduced as wires that serve as consumable arc electrodes. A cold or heated gas jet across the arc drives the molten droplets from the electrode tips toward a substrate, forming a coating on the substrate. Eliminating the need for water cooling of its electrodes allows miniaturization of the spray system, making it suitable for many applications, including bore hole coating. In spite of its economic advantages, this technology has found only limited use in the manufacturing industry because of the lack of a well-developed engineering base for this process. Only in recent years have basic studies of the arc-wire spray process been initiated for improving both our knowledge and technology base.

Plasma Chemical Vapor Deposition

One of the most promising new developments in thermal plasma processing is the plasma chemical vapor deposition (PCVD) process. As a relatively new film deposition technique, it can deposit high-quality, even epitaxial, films at deposition rates considerably higher than those obtained by competing low-pressure methods. One of the most visible developments of this technology is the deposition of diamond and ceramic films, which is expected to have a strong impact on manufacturing processes. In contrast to the previously discussed coating technologies, PCVD is still in the laboratory stage; that is, present research efforts concentrate on the establishment of the knowledge base for this emerging technology.

In the process of PCVD, a high-energy-density plasma produces high-density vapor-phase precursors for the deposition of relatively thick films. A direct current plasma torch, for example, generates a high-temperature, high-velocity plasma jet that impinges on a cooled substrate. With temperatures close to the torch nozzle exit exceeding 10^4 K, the precursor material that is injected into the plasma is rapidly vaporized and dissociated and, because of the high velocities of the plasma jet (of the order of 100 m/s), accelerated toward the substrate. In front of the cooled substrate, a boundary layer with steep gradients forms. Such boundary layers in chemically reacting gases attracted strong interest in spaceflight and reentry simulation and have been extensively analyzed in these connections.

As the temperature across the thermal boundary layer drops from the plasma temperature to the substrate temperature, the chemically active species will be rapidly driven across the boundary layer by the extremely steep gradients there. Because of the rapid traverse of the species across the boundary layer, chemical reactions appear to be more or less "frozen," resulting in a strong chemical nonequilibrium situation in the boundary layer, where the species concentration is determined mainly by diffusion rather than by chemical reactions. Maintaining a high concentration of chemically active precursors across the boundary layer is crucial for achieving high deposition rates.

In spite of impressive progress over the past years, the chemistry in the boundary layer and at the substrate surface during the PCVD process is still poorly understood. Efforts are continuing to establish realistic models for this situation and demonstrate by corresponding experiments their validity.

Plasma Waste Destruction

Destruction of waste, especially of toxic waste, has grown into an increasingly pressing problem. Among various waste destruction processes, thermal plasma waste destruction is considered to be a viable option for certain types of waste.

Thermal plasma reactors offer unique advantages for the destruction of hazardous wastes: (1) the high energy density and temperatures associated with thermal plasmas and the corresponding fast reaction times offer the potential of large throughputs in a small reactor; (2) the high temperatures can also be used to obtain very high quench rates, allowing the attainment of metastable states and nonequilibrium compositions; (3) the high heat fluxes at the reactor boundaries lead to fast attainment of steady-state conditions, allowing rapid start-up and shutdown times compared with other thermal treatment devices such as incinerators; (4) use of electric energy reduces gas flow needs and off-gas treatment requirements and offers control over the chemistry, including the possibility of generating marketable coproducts; and (5) all the characteristics combined allow easy integration into a manufacturing process that generates hazardous waste, thus permitting the destruction of the waste at the source. The major disadvantage of the plasma process lies in the use of electricity as an energy source, which unfavorably influences the process economics. A further consideration is that plasma processes have more parameters to control than do traditional processes and require, therefore, a higher degree of automation in the process control, which translates into interesting research opportunities.

It also should be emphasized that waste destruction as a new technology is to a large extent driven by government regulations.

Plasma Metallurgy

Thermal plasma metallurgy comprises melting and remelting technologies as well as extractive metallurgy. The key advantages of thermal plasma approaches, as specifically applied to melting/remelting technologies, include:

- The ability to achieve a steady-state, uniform flow of partially ionized gas with bulk gas temperatures well above those obtainable with chemical (combustion) flames or resistance heater systems;
- Operation in an inert or reactive environment, thus providing complete control of the atmosphere; and
- The possibility of a compact system that can process material in a variety of forms at high throughput rates and with relatively high electrical and thermal efficiency.

Today, a wide variety of arc plasma torches are in use or projected for scrap melting, alloying, iron melting in cupolas, and remelting technologies. These plasma torches operate with direct or alternating current in either the nontransferred or transferred mode and at power levels up to almost 10 MW. In the case of nontransferred arcs, the plasma torch is essentially an arc gas heater producing extremely hot gases, which emanate from the torch in the form of a plasma jet. The more common approach, however, makes use of transferred arcs where the molten pool serves as one of the electrodes and the major energy input is at the arc root of the molten bath surface.

The considerable interest in extractive metallurgy is evidenced by the numerous laboratory and pilot-plant-scale studies reported in the literature (extraction of iron, titanium, molybdenum, and ferroalloys). Two different types of furnaces have been used for plasma extractive metallurgy: transferred arc reactors for ferroalloy production (similar to those used for melting), and reactors in which a reducing gas is preheated and upgraded by using plasma torches. The reduction of the ores to be treated is performed in a furnace filled with coke, which is mainly used as a refractory material for providing a sufficiently long residence time for the injected ore particles to be reduced.

Newer thermal plasma developments concern the extraction of heavy metals from baghouse dust and the recycling of catalytic converters for recapturing platinum. Since thermal plasma metallurgy consumes large amounts of electric energy, economic considerations have been a primary criterion for the development of such technologies. In addition, technical problems associated with electrode lifetime of high-power plasma torches have played a major role.

Thermal Plasma Synthesis

Over the past years, thermal plasma synthesis of ultrafine and ultrapure powders has been attracting increasing interest, especially in connection with the synthesis of ceramic materials. High-intensity arcs, plasma jets, and high-power radio frequency discharges are the primary sources for producing thermal plasmas required for this emerging technology.

Because of the high temperatures ($>10^4$ K) that are typical for thermal plasmas, chemical reactions are much faster than those encountered in conventional processing. Also, quench rates of the product powders are necessarily very rapid to avoid decomposition of the products. Fast reaction and quench rates result in very short overall processing times—as short as milliseconds. This translates into small reactors with relatively high throughput rates. In spite of this attractive feature, the relatively higher processing costs of using plasma processing must be offset by some superior material properties.

A number of ultrafine oxide powders have been produced in thermal plasmas. Ultrafine oxides have a wide range of uses in surface coatings, high-density ceramics ("high-tech" ceramics), pigments, catalysts, and dispersion strengthening of metals. Three arc-related plasma techniques have been explored: reaction of volatile metal chlorides with oxygen, evaporation and subsequent condensation of oxide powders, and evaporation of bulk oxides. Industrially, TiO_2 and high-purity SiO_2 are produced by the chloride process. Mixed oxides of chromia and titania or chromia and alumina have been produced by introducing mixed chlorides into the plasma reactor.

In recent developments, the synthesis of nanometer-size particles in thermal plasmas has been demonstrated. Such small particles are considered to be the key for a new generation of engineered materials with unusual properties.

Plasma Consolidation

Plasma consolidation includes the processes of spheroidization, densification, and sintering. The first two of these processes are already commercially developed, whereas plasma sintering is still in the laboratory stage.

Frequently, spheroidization and densification occur simultaneously as porous, irregularly shaped agglomerates are injected into a thermal plasma. Equipment similar to that used for plasma spraying is employed for these processes, but the particle size of the agglomerates may be substantially (» 100 mm) larger than that used for plasma spraying. As the particles sinter and/or melt in the plasma, they assume a nearly spherical shape and densify at the same time. Commercially, fine particles are spheroidized in a plasma for a variety of applications, including materials with a controlled porosity, catalysts, abrasives, and materials used for powder metallurgy. A wide range of different materials have been spheroidized, including oxides and carbides.

Plasma densification of presintered agglomerates of metals (e.g., W, Mo) and of carbide-metal mixtures (e.g., WC-Co) has been used to produce spherical, densified powders. Such powders possess excellent flowability, which is beneficial to subsequent thermal coating operations.

Sintering of high-tech ceramics in thermal plasmas has the potential of drastically reducing the time period required for this process, compared with conventional technology. In addition, plasma sintering offers the opportunity for restrained grain growth and for tailoring heat transfer during the sintering process, which may result in desirable structures and properties of the sintered materials. The essential characteristics of plasma sintering and of any other sintering process are an increase in density and strength of a powder compact on heating.

Plasma sintering is a process that may cover a pressure range from 760 to a few Torr. For pressures below 75 Torr, the plasma may no longer be classified as a thermal plasma because of substantial deviations from local thermodynamic equilibrium.

A ROLE FOR NRL

At this time the NRL does not have any research project directly associated with thermal plasma processing. There is, however, a new project, in the planning stage, in which destruction of waste by a thermal plasma process is considered for applications on naval vessels.

The following suggestions take waste destruction into account in addition to recommendations in the field of PCVD. Although no previous experience exists in the thermal plasma area at NRL, the expertise residing at the laboratory is sufficient to branch out into thermal PCVD.

Thermal Plasma Waste Destruction

The NRL has initiated a new research project on thermal plasma waste destruction, geared toward applications on naval vessels. This seems to be a research project that is high on the priority list of the Navy.

Since there is no direct expertise available at NRL, the Laboratory should take advantage of the already existing knowledge in this particular field within the United States. The available literature on plasma waste destruction is at best "spotty," and therefore it seems advisable to establish contacts with active research groups at universities and national laboratories to prevent "reinventing of the wheel." An internship at one of the pertinent research institutes, for example, could be of great benefit in bringing this project up to speed.

Plasma Chemical Vapor Deposition

Diamond Films

Over the past several years there have been an increasing number of efforts directed toward producing diamond under thermodynamically metastable conditions, driven by the tremendous application potential because of diamond's unrivaled combination of unusual properties. Numerous processes have been suggested and developed over the past decade.

NRL has become internationally renowned for its pioneering work in the deposition of diamond films in the chemical vapor processing group. Modeling of diamond deposition processes at NRL has been combined with sophisticated diagnostics, and the quality of this work has found worldwide acclaim. As pointed out during the NRL site visit, an expanded laboratory facility is being set up combining all experiments presently located in different rooms. The ion/plasma processing group is also involved in diamond film deposition using ECR plasmas. In addition, there is another group at the NRL that is primarily concerned with diamond deposition using flames, and this group seems to be more interested in the application aspects of diamond films.

Considering the expertise and infrastructure at the NRL, it is believed that all the prerequisites are available for addressing both the knowledge and the technology base of this emerging technology. Since NRL's knowledge base is already in an advanced stage, the Laboratory should devote at least some of its resources to developing the technology base. In this context, the highly interdisciplinary nature of this technology should be stressed, making collaboration of all related groups at the NRL, as well as with industry, desirable.

Another aspect relates to the deposition technologies. The chemical vapor processing group should be able to incorporate and evaluate the potential of other deposition techniques such as, for example, thermal plasma deposition, which is currently not used in its laboratory. It is conceivable that broad-based activities of this group may grow into a national center for diamond science and technology.

Cubic Boron Nitride Films

Cubic boron nitride (cBN) is a superhard material, with properties similar to those of diamond—that is, it is chemically inert, optically transparent, thermally conducting, and electrically insulating. Only diamond exceeds the hardness of cBN, but the latter's inertness against ferrous materials is superior even to that of diamond. As an electronic material, its bandgap is even larger than that of diamond. Cubic boron nitride is considered to be an excellent tool material for machining of hard steels, bimetallics, and other exotic materials; for instance, cBN coatings would be of primary interest for cutting tools.

Besides the previously mentioned similarities to diamond, which is a metastable phase of carbon, cBN is also a metastable phase, in this case of boron nitride, with the hexagonal structure as the stable form. The synthesis of cBN films, however, has proven to be much more difficult than that of diamond films.

Although cBN deposition of thin films is a more challenging task, the similarity of the two materials and the wealth of knowledge and experience with diamond deposition residing at

NRL suggest that the Laboratory should embark on this emerging technology. The potential payback would certainly justify the risk involved.

Carbon Nitride

Another exotic material that made the headlines a few months ago is carbon nitride (C_3N_4). According to predictions, the hardness of β-C_3N_4 should exceed that of diamond and other properties should be similar to those of diamond. Recently, scientists at Harvard University succeeded in synthesizing CN films and demonstrated structural evidence for the formation of β-C_3N_4. There is no question that this material offers exciting prospects for both basic research and engineering applications.

NRL should be in a unique position to pursue work along this line. This may not be feasible immediately, but it should be considered in connection with a long-range plan.

Flat Panel Displays

RESEARCH OPPORTUNITIES

Introduction

Vision is one of man's most highly developed senses. Thus it is no surprise that display technology is playing an ever-increasing role as we move deeper into the information age. Performance requirements for displays depend on the application; critical attributes include:

- Resolution;
- Color;
- Fidelity;
- Cost;
- Energy consumption;
- Efficiency;
- Brightness;
- Ruggedness, reliability, lifetime, and mean time between failure;
- Weight;
- Volume;
- Ease of interface;
- Size; and
- Availability/sourcing.

Of particular interest are the flat display technologies that lend themselves to portability and low included volume. These are the display technologies that will drive the ubiquitous spread of display technology. The impact of these displays will span consumer, commercial, industrial, and military applications.

Today the cathode ray tube (CRT) display is the benchmark against which all other displays are measured. CRTs are manufactured globally, and although the technology is quite mature, they continue to dominate in unit volume, revenue, and breadth of applications. The newer technologies are driving into niche markets—personal television sets, portable computers, rugged industrial equipment markets, and military applications. Table 1 lists these newer display technologies. The dominant new display technology is the liquid crystal display (LCD). Production of these displays is not global but is concentrated in Japan.

That the dominant center of LCD technology and its concomitant technological infrastructure lie outside the United States is of concern industrially, politically, and militarily. Indeed, the Executive Branch has taken a strong stand on the urgent need for the United States to become competitive in the world market in flat panel displays. The nation is growing more aware that its security depends on its industrial technology strength. In peacetime, military applications alone cannot support a major technology and certainly cannot compete when a civilian application is driving a technology. Herein lies both the opportunity and the difficulty for NRL's plasma processing research. The opportunity is to provide a U.S. competitive technological advantage; the difficulty is that the issues are more than technological, and entrenched positions will be hard to overcome. However, the promise of a large commitment of funds for this field opens the way for new participants in this arena.

The technological research and development opportunities for plasma processing in display technology are generally of two types: (1) precision processing of the type that also impacts the semiconductor industry (VLSI, submicrometer processing); and (2) large-area processing.

Projection displays are expected to play major roles in applications for very large displays (high-definition television [HDTV], conference, and group displays) and for very small personal displays (virtual reality and head-mounted displays). Here the critical issue is high performance in small sizes. Precision of production is more important than cost per unit area. The expectation is that display (die) sizes can be made smaller to reduce cost while still increasing performance functionality, as in VLSI experience.

Table 1. New Display Technologies

Technology	Size
• Passive matrix LCD Simple multiplex Active addressing	Large/small
• Active matrix LCD Amorphous silicon Polycrystalline silicon Transfer silicon	Large/small
• Thin film electro-luminescent displays	
Passive matrix	Large
Active matrix	Small
• Digital micromirror devices	Small
• Plasma displays	Large
• Field emission displays	Large

Most of the interest in flat displays is for direct view displays. Thus cost per unit of display area is critical for a practicable process. Typical display sizes are about 10 inches diagonally for video graphics array (VGA) displays with 480 × 640 resolution. The market desires larger, 15-inch diagonal, and higher-resolution, 768 × 1024 and 1024 × 1280, displays but as yet few applications can afford them because of high manufacturing costs.

The remainder of this section identifies, for each of the display technologies listed in Table 1, the current and potential future roles of plasma processing.

Passive Matrix Liquid Crystal Display

There are two basic types of LCD configurations: passive matrix and active matrix. Low-cost large and small LCDs are typically of the passive matrix type. Passive matrix LCDs consist simply of two transparent substrates having transparent electrodes. The substrates are separated by a gap of about 10 μm filled with the liquid crystal material. One substrate contains column electrodes, and the other contains the row electrodes. Picture elements (pixels) are defined by the intersection of these orthogonal electrodes. Today such LCDs are produced *without* any plasma processing. Potentially, plasma dry etching could replace the wet etching techniques currently used to define the electrode structures, but this is not currently pursued because of the higher cost of plasma processes. However, the environmental impact of liquid waste may eventually change the cost balance.

Active Matrix Liquid Crystal Display

The active matrix liquid crystal display (AMLCD) is the flat display technology of choice for high-performance applications—both large-area, direct-view displays and small-area, projection displays. In active matrix LCDs, one substrate contains the active matrix and the other acts as a ground plane and is electrically featureless. The active matrix consists of an array of isolated pixels connected to a matrix addressing structure via thin film, field-effect transistors. Gates of these thin film transistors (TFTs) are organized as the matrix rows, and the sources are organized as the matrix columns.

Although the geometry of these TFTs is large compared with current VLSI chips, these 2- to 10-mm geometries do warrant precision processing. Plasma dry etching techniques similar to those used in the semiconductor industry are commonly used where wet chemical etching does not suffice. An R&D opportunity exists for increasing the etch rates and uniformity of large-area etching processes.

Silicon is the material from which these TFTs are fabricated. Two silicon forms are typically used: hydrogenated amorphous silicon (aSi) and high-temperature polycrystalline silicon (pSi). For special applications, transfer crystalline silicon (xSi) is also being developed.

Amorphous Silicon

Hydrogenated amorphous silicon is used for large-area, direct-view displays. These displays are formed on glass substrates that cannot tolerate very high temperatures. A plasma-enhanced chemical vapor deposition (PECVD) process is used to deposit the aSi on the glass substrates at temperatures of about 300° C.

Current PECVD techniques are relatively slow and therefore costly. Deposition rates have to be low in order to form electrically high-quality material and to avoid gas phase nucleation and particulates that substantially reduce the active matrix yields. An additional problem is that the equipment requires frequent, time-wasting cleaning in order to maintain the high yields needed for operating displays. A clear opportunity exists for an R&D contribution if better understanding can result in high deposition rates and reduced equipment downtime required for cleaning.

Polycrystalline Silicon

High-temperature polysilicon is currently deposited on quartz substrates by chemical vapor deposition at temperatures of about 600° C. Lower-temperature PECVD processes could offer improved economics by reducing the heat-cooling cycle times while increasing the deposition rate of high-quality silicon. Hydrogen passivation of the polysilicon is typically part of the active matrix process in order to reduce the leakage currents in the pSi TFTs to a useful level. This passivation is achieved by plasma processing of the polysilicon TFT. Here, too, there is an opportunity to increase the passivation efficacy and overall processing rates.

Many experts are convinced that *large-area* pSi active matrix LCDs on *glass* substrates will be the next-generation AMLCD technology. It is anticipated that plasma processes will play a major role in this development by enabling the large-area, *low-temperature* processing that will be required for fabrication on glass substrates. Specific processes that need to be developed include PECVD of silicon, anisotropic plasma etching, hydrogen plasma passivation, and perhaps large-area ion doping.

Transfer Silicon

Kopin, a small U.S. company, is currently commercializing another type of silicon active matrix LCD. In the Kopin technology, the active matrix is formed in a thin silicon layer on top of a thickly oxidized silicon substrate. After processing, this thin silicon layer is transferred to a glass substrate. At this point it can be handled in much the same way as an aSi active matrix substrate to fabricate a complete active matrix LCD. The exciting aspect of the Kopin technology is that it results in excellent display performance because the thin silicon layer is of crystalline quality, and furthermore the active matrix is processed exactly like it is for fabricating VLSI circuits. Here the role of plasma processing is identical to that used in VLSI technology.

Thin Film Electroluminescent Displays

Currently commercial thin film electroluminescent (TFEL) displays are only of the passive matrix type. They consist of (1) a glass substrate on which is deposited a transparent conducting film that is patterned to form vertical stripe electrodes, (2) an insulating dielectric layer, (3) a thin film electroluminescent phosphor, (4) another insulating dielectric layer, and (5) a deposited film of aluminum that is patterned to form horizontal stripes. The first and last layers constitute the electrodes of the passive matrix. At this time no plasma processes are used in the fabrication.

Under development but not yet commercialized is an active matrix TFEL display technology. These displays are fabricated by depositing the TFEL material onto a silicon-active matrix fabricated on a dielectrically isolated silicon wafer. Plasma processing is used for etching and deposition as with other VLSI silicon devices.

Digital Micromirror Devices

Digital micromirror devices (DMDs) are currently being commercialized by Texas Instruments. The DMD consists of an array of mirrors, each about 15 × 15 μm, fabricated on a silicon wafer. Each mirror is capable of a torsional deflection caused by an electrostatic drive circuit built below the mirror on the silicon wafer. The array of mirrors forms an image-generating light valve. By means of a Schlieren optical system, a very efficient, high-resolution projection display system can be built. The DMD itself is fabricated using "standard" silicon VLSI processes. Accordingly, any plasma processing enhancements that serve the semiconductor industry will have a synergistic impact on DMD displays. As with other displays, cost reductions are particularly important.

Plasma Displays

Plasma displays are receiving an increased amount of attention because they seem to be particularly suited to consumer on-the-wall HDTV applications. These are relatively low-resolution displays—one or two pixels per millimeter—but they need to be of high reliability and performance and cost-competitive with CRTs. Basically, the display consists of an array of gaseous glow discharge cells. To achieve color, each cell also contains a phosphor that is excited by ultraviolet emission from the glow discharge. Fabrication of these displays is achieved primarily by means of various thick film processes. These processes are adequate for the resolutions required for HDTV and enable application and patterning of the relatively large volumes of materials needed to form the individual pixel discharge cells. At this time no plasma processes are used in the fabrication.

Field Emission Displays

Significant R&D effort is being applied to the field emission display (FED) technologies. These devices are basically low-voltage cathodoluminescent displays formed by a matrix of field emitters separated by a narrow gap from a phosphor-coated faceplate. They are vacuum devices like CRTs. The field emitters are organized as an x-y matrix and use row-at-a-time addressing similar to electroluminescent and LCD displays. Major anticipated advantages of the FED devices are high brightness, self-emissivity, low cost, low factory startup cost, and scalability to large areas. Several approaches are being developed for the field emission cathodes. These include amorphic diamond films and metal microtips. At this time no plasma processes are used in the fabrication of either type of FED. Although currently experimental devices are fabricated using shadowmask depositions, plasma etching of the amorphic diamond films into the individual pixel areas may be advantageous in the future. Additionally, growth of amorphic diamond films with the appropriate properties by plasma-enhanced chemical vapor deposition may be more cost-effective than the current technology of laser ablation.

A ROLE FOR NRL

The challenge for introducing plasma processing into display applications is to *maintain* process performance while *increasing* process areas and rates and *decreasing* process equipment capital costs and operation and maintenance costs. To achieve this, an improved understanding of plasmas and plasma processes will be necessary. Particular emphasis should be placed on "linear" plasma processing geometries (line sources), that is, systems that scale easily in one dimension and achieve scaling in the other direction by substrate motion on a continuous moving belt.

There is a growing trend for the semiconductor industry to migrate toward larger and larger silicon wafer sizes. Wafer diameters of 12 to 16 inches are likely to be in use by the year 2000. An ancillary benefit of developing improved plasma deposition, etching, and passivation processing techniques for silicon-based AMLCDs is that these processes are likely to be applicable in VLSI fabrication as the industry migrates to larger and larger wafer sizes.

As with VLSI processes, one can expect that, in the various display industries, there will be a growing concern with the environmentally benign disposal of wet etchant wastes. Gaseous processes, such as plasma etching, generally result in fewer waste disposal problems and effluent volumes than, say, wet etching. Accordingly, although the required break-throughs are challenging, so are the opportunities for large-area, low-cost plasma processes.

There are more similarities than differences among the technology requirements for VLSI and silicon-active matrix LCDs, although VLSI geometries are almost an order of magnitude smaller. Thus, as an example, anisotropic plasma etching is required to maintain critical dimensions in small etching geometries for VLSI, whereas in displays, anisotropic etching is required to maintain process tolerance over larger areas with minimum dimensions. Overetching in depth can be tolerated, whereas lateral etch nonuniformities cannot.

A second example can be drawn from the need for faster processing. Single wafer processing in VLSI needs faster process rates to achieve competitive economics. Displays also need faster process rates because display areas are large, yet their marketable costs per unit area are low. Other problems encountered in VLSI fabrication will also become important in dry processing of displays: cleaning of substrates, control of particulates, and charge-induced damage in the etching process.

To have an impact in display applications, NRL needs to proactively form teaming relationships and cooperative joint R&D programs and sponsor programs with display producers and would-be producers, researchers, and infrastructure suppliers. Specific contacts should be made with the MCC FED Consortium, the newly formed U.S. Display Consortium (USDC), and the North American Flat Panel Division of SEMI, as well as key U.S. display manufacturers. The corporate members of the USDC would be a good start: AT&T, Electro-Plasma, Magnascreen, Optical Imaging Systems, Photonics Imaging, Planar Systems, Plasmaco, Standish Industries, Tektronix, and Xerox, plus Micron Display, Sarnoff, SI Diamond Technology, MRS, Applied Materials, and so on. NRL expertise in FEDs is an internal resource that could be leveraged to acquire visibility in the display community.

Low-Temperature Plasma Physics

RESEARCH OPPORTUNITIES

Because of its undisputed advantages in a large variety of applications, plasma processing will undoubtedly play an ever larger role in manufacturing, especially in the semiconductor and display industries. The science of low-temperature, partially ionized plasmas, on which this technology depends, has roots in the field of gaseous electronics-arcs and glow discharges, switches, and diodes. The immense interest in high-temperature plasma physics since the 1950s has spawned the development of experimental and theoretical techniques undreamed of in the days of Townsend and Faraday. Only rarely, as in the case of electron-cyclotron resonance (ECR) sources, have these developments been applied to low-temperature plasmas. The advances in analysis and computational techniques, and in the knowledge of waves and instabilities resulting from fusion and space physics research, can now be brought to bear on the problem of partially ionized, multispecies plasmas. These studies would differ from the modeling work discussed in Chapter 2 in that they concern isolated problems rather than the whole final product. The discovery of new physical phenomena and evaluation of the importance of previous known effects would serve as inputs to the modeling studies. Given below are several examples of interesting topics of this nature that are suitable for both theoretical and experimental research.

Diffusion in weak magnetic fields. In gas discharges with a magnetic field between 10 and 1000 gauss (G), the thermal electrons are the magnetic field, but the ions and primary electrons are not. Ambipolar diffusion of the plasma across the magnetic field in that case does not follow standard formulas. When the ion and primary electron Larmor radii are of the order of the discharge radius, the problem is particularly difficult. What is needed is a simple treatment, even an approximate one, which does not require a full-blown computation for each set of parameters.

Contours of electric potential in a finite cylinder. When a magnetized plasma is bounded both radially and axially, the equipotential contours are expected to be saddle-shaped, having a potential minimum across a diameter and a potential maximum along the axis. In practice, however, measurements usually show a potential hill in both directions, indicating that some other mechanism is operative. This mechanism could be high-frequency waves or low-frequency drift waves, which can redistribute the electrons differently from classical collisions.

Stochastic heating in rf sheaths. In rf plasmas, the potential drop across the wall sheaths can have large oscillations at the rf frequency. Electrons entering and reflecting from the sheath can gain or lose energy, depending on the rf phase at the time they entered. This effect leads to a broadening of the electron energy distribution, thus affecting the formation of various molecular species in the plasma.

Ion temperature in low-pressure discharges. The spread of ion energies is important for anisotropic etching of semiconductors. Normally, the ion temperature is determined by energy gain from collisions with electrons and energy loss from collisions with neutral atoms. In low-pressure discharges of a few mTorr or below, however, the ion distribution is usually broader. This energy gain could be from ambipolar electric fields, sheath fields, plasma instabilities, or some mechanism yet to be discovered.

Ionization processes. In classical gas discharge theory, the electron-ion pairs forming the plasma are imagined to be produced by electron impact on neutral atoms. These could be fast electrons in the "primary" electron distribution, or they could be electrons so far in the tail of the thermal distribution that their energies exceed the ionization potential. In the dense plasmas of today, however, particularly the high-pressure discharges used in deposition, multistep ionization via metastables can occur. In fact, in high-pressure discharges such as used in the lighting industry, the propagation of ionization energy occurs via transport of resonant photons rather than electrons. This subject requires both theoretical and experimental study, and the results for etchant gases should yield information on the cross-section data that need to be obtained.

Electron runaway in high-pressure rf discharges. In direct current discharges between a cathode and an anode, applying too large an electric field will cause the discharge to break into an arc. In electrodeless rf discharges, however, extremely large electric fields can be applied without arcing. In that case, some electrons can "run away" into a velocity region of decreasing cross section and therefore reach ionizing energies even when the mean free path for a thermal electron is extremely short. This phenomenon would be expected to occur preferentially in gases, such as hydrogen, that do not have a large peak in the cross-section curve.

Landau and cyclotron damping in rf discharges. Production of primary electrons by Landau damping has been postulated for helicon discharges, but there has been no prediction or measurement of the number of electrons accelerated in this manner. More recently, cyclotron damping has been proposed as an additional mechanism that can be important in low magnetic fields. These kinetic absorption mechanisms may be important in low-pressure plasmas used for materials processing.

Particle confinement by multidipole magnetic fields. Large uniform plasmas can be produced by letting plasma stream from a source into a "magnetic bucket" with permanent magnets lining the walls. Previous studies of confinement by such surface fields were concerned with the overall confinement time of the plasma. In etching tools, however, it is the confinement of each velocity class of electrons that matters, since the electron distribution has a large effect on the production of the various molecular species and on the damage incurred on thin oxide layers. This problem should be reexamined in the light of the new requirements.

Expansion of plasma in rapidly diverging magnetic fields. In "remote" plasma sources, the substrate to be processed is exposed to plasma that has come from the ionization source along magnetic field lines that are sharply curved. The usual adiabatic invariants are not preserved in such an environment, but there may be other invariants if the system is axisymmetric. The manner in which the electrons and ions of various energies move will determine the potential and density gradients in the downstream plasma, as well as the ionization occurring there. Though numerical modeling may ultimately be needed to treat this complicated problem, insight into the physics can be gained by considering general principles such as the invariants mentioned above.

Plasma instabilities. All plasmas, particularly magnetized ones, are subject to instabilities. In industrial devices, there can be drift instabilities due to gradients in density or temperature; gravitational instabilities due to curving magnetic field lines; or streaming instabilities due to non-Maxwellian distributions, such as in ECR. No devastating instabilities have yet been seen, but they will no doubt be found someday. In that case, stabilizing measures, such as minimum-B fields, are well in hand because of what has been learned in magnetic fusion.

A ROLE FOR NRL

The theoretical and experimental study of basic plasma phenomena in industrially relevant plasmas will benefit from the experience of personnel with extensive knowledge of plasma physics as well as considerable insight and experience in finding and solving simple, tractable problems within a complicated system. NRL has such expertise. An opportunity exists for NRL to draw on this expertise and focus its basic research on understanding the intrinsic behavior of low-temperature plasmas.

Conclusions and Recommendations

RECOMMENDATION FOR A PROGRAM IN PLASMA PROCESSING AND PROCESSING SCIENCE

As part of its long-term strategic planning process, the Naval Research Laboratory (NRL) has been considering establishing research programs in a number of areas with broad technological applications that address the needs of the nation, the missions of the Department of Defense, and those of the Navy. Plasma processing of materials is one such technology. At the request of NRL, the panel has addressed and in this report provided guidance on the following general questions: (1) What are some of the research opportunities in the field as a whole; (2) Does the existing NRL research capability in plasma physics, chemistry, surface science, and materials processing provide a sufficient base for building a focused research program that can address these opportunities; and, if so, (3) What other issues, such as outside collaborations, would need to be addressed?

The panel finds that many opportunities exist for NRL to have significant impact on the use of plasmas in industrial manufacturing. In Chapters 2 through 8, research opportunities are presented in the specific areas of modeling and simulation of plasma processing, semiconductor processing, plasma deposition and polymerization, ion implantation and surface modification, thermal plasmas, flat panel displays, and low-temperature plasmas. In view of the shifting emphasis in plasma physics away from high-temperature applications and toward low-temperature, industrial plasmas and based on its identification of selected opportunities in the field and its evaluation of NRL's research capabilities in plasma physics, chemistry, surface science, and materials processing, the panel recommends the following:

The Naval Research Laboratory should develop a coordinated and focused program in plasma processing and processing science. The program should have the following features:

1. The program should focus on a few emerging technologies, such as those drawn from the suggestions in Chapters 2 through 8, on which NRL efforts could have a strong impact and for which NRL could strive to become a nationally recognized center. Each chapter includes a section entitled "A Role for NRL" that identifies research directions.

2. In redirecting some of its resources to plasma processing and processing science, NRL should capitalize on its tradition of excellence in basic research by focusing the program on areas where it can be a national leader, without directly competing with industry or other established national programs on near-term objectives. NRL's emphasis on fundamental science should be maintained.

3. By nature, plasma processing and plasma science are highly interdisciplinary fields. Therefore, collaboration among the existing groups at NRL in a focused research program is a prerequisite for success. The program should have a formalized structure, with its own director to ensure coordination among the groups, and include an ongoing seminar series with external speakers designed to facilitate cooperation, communication, and interest among the participants.

4. The research program should be well balanced in terms of experimental and modeling efforts. It should strive toward establishing the knowledge base as well as the technology base for the chosen emerging technologies.

5. To establish and maintain contact with the mainstream of processing science, NRL should form collaborations with industry, universities, and other laboratories. NRL has had experience with setting up Cooperative Research and Development Agreements and could use these as mechanisms for accomplishing the goal of increased collaboration. (Chapters 2 through 8 identify current academic, industrial, and federal laboratory efforts in the field.)

It is the judgment of the panel that NRL has sufficient facilities in place to enable it to play a key role in many important issues pertaining to the plasma processing of semiconductors in ultralarge-scale integrated manufacturing. It is also the panel's judgment that the first priority for NRL should be to intensify interactions with the outside world to understand the current issues and to gain insight on where to focus its efforts. NRL personnel should increase their involvement with the materials processing community by attending relevant conferences, presenting contributed papers, and seeking invitations to give invited papers.

CONCLUSIONS BASED ON NRL'S PRESENT RESEARCH CAPABILITIES

The panel has the following specific conclusions on how NRL's capabilities could support the research program recommended above.

1. The chemical vapor processing group is currently the best known and most active one in this field. Although it would be tempting to build the NRL materials processing effort around this group, a diversified program should not be dominated by any one group. This group should be one of several strong and active groups.

2. This same group can provide in-depth treatment of surface chemical and gas-phase chemical issues. For example, selectivity is a key issue in gate conductor etching, and the group may be able to provide novel insights.

3. A sophisticated diagnostics laboratory set up as a user facility will probably not attract interest from industry. Equipment manufacturers tend to do their testing in-house, partly to protect proprietary information.

4. The NRL microfabrication facility can be used to process special devices such as measurement structures needed for sidewall passivation studies. NRL should not try to upgrade this facility, since it is highly unlikely that it can ever become a state-of-the-art fabrication line.

5. The current emphasis on electron-cyclotron resonance (ECR) should be continued as an initial phase of NRL's entry into plasma processing. To complement the NRL diamond deposition work, it may make sense to focus on plasma-enhanced chemical vapor deposition for the present. NRL's effort is not big enough to be spread over many different applications. Its strongest asset seems to be its high degree of complementarity. This could be leveraged best by focusing on one key problem to make a significant impact.

6. The ECR work of the ion/plasma processing group on diamond deposition is an ideal complement to the diamond work in the chemical vapor processing group. The ECR tool can be easily adapted to other materials and should be able to make significant contributions rapidly. At a later time, the use of alternate high-density plasma tools may be studied for diamond film deposition.

7. The real-time diagnostics used in the Electronics Division could be important for the understanding of dry etch damage issues. Dry etch damage is clearly an important issue in gate conductor etching. This effort would benefit enormously by becoming part of a well-aimed overall effort on optical diagnostics, working together with the chemical vapor processing group.

8. The plasma modelers indicated that they would be able to treat the power absorption in ECR plasmas. This is an interesting issue, particularly with respect to the role the microwave coupling device plays (e.g., linear versus circularly polarized microwaves, and so on) and how the plasma nonuniformity affects wafer etch nonuniformity. After having established a degree of recognition and visibility, the modeling group can begin to compete on important current issues.

9. In view of the anticipated increase in flat panel display production, NRL can take advantage of the opportunity to initiate research on the plasma problems in the fabrication of large-area displays. This industry is practically unaware of the benefits of improved plasma processing, and almost no work on this subject yet exists. NRL currently has at least one expert on display technology, and his experience can be utilized for this task.

10. Waste destruction and conversion by plasma methods is a new field in which advances would benefit not only the Navy but also the general public. Within the context of NRL's scientific mission, however, one must try to find intellectually challenging problems in the chemical or plasma processes involved, rather than treat this as a brute-force engineering exercise. Diagnostics and sensors are also important in this industry.

11. Though NRL has personnel with expertise in pulsed ion beams who can contribute to the field of ion or plasma implantation, the existing pulsed power equipment probably cannot be used effectively in plasma manufacturing. A new approach is needed here.

12. Technical problems require technical solutions, and the microelectronics industry is no exception to this rule; however, even the best technical solutions can fail through human shortcomings in communication, planning, and program evaluation. To this end, it is further concluded that a companion personnel exchange program, under which NRL researchers could spend blocks of time at partner locations in industry and universities, and vice versa, would be invaluable in furthering NRL's contributions to the field. Activities such as this are generally necessary for effective communication, not only among industry, government, and universities, but even between different branches or divisions of the same company or armed service. In the successful Microelectronics Manufacturing Science and Technology program, cited elsewhere in this report, workers from Wright-Patterson Air Force Base conducted some work at their Dayton, Ohio, facility and also collaborated with Texas Instruments workers in Dallas, Texas. Despite the inevitable complications caused by temporarily relocating employees, the panel believes the benefits of long-term collaboration through these programs far outweigh the short-term difficulties of setting up relocation programs and shuttling employees. Additionally, the Office of Naval Research and NRL could together consider this important aspect of the Dual Use concept and its far-reaching benefits of one-on-one communication between government and industry.