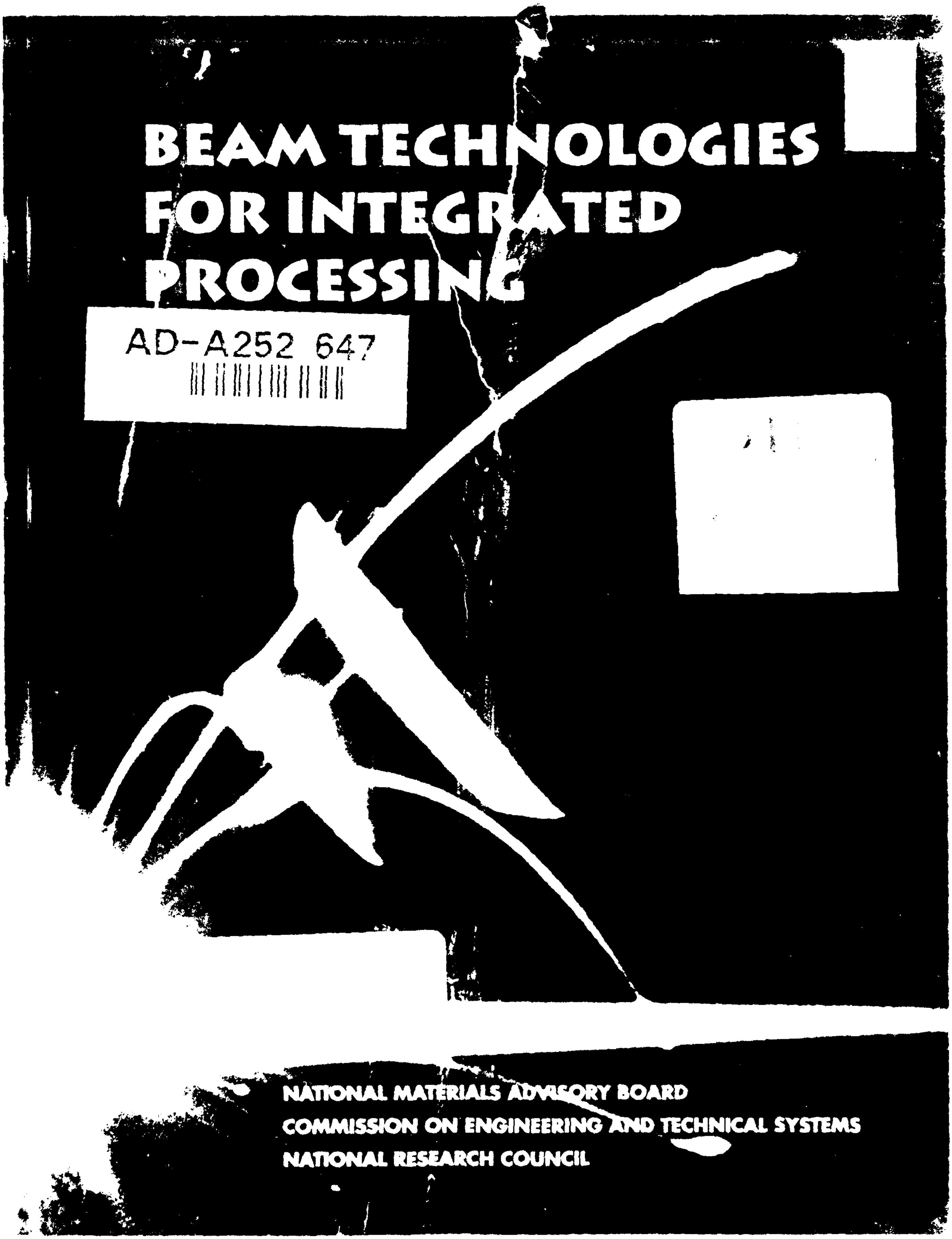

BEAM TECHNOLOGIES FOR INTEGRATED PROCESSING

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Allied-Signal Aerospace Company
19800 South Van Ness Avenue
Torrance, CA 90509

Dr. Dale F. Stein
Dept. of Materials Science & Eng.
Arizona Materials Laboratories
The University of Arizona
4715 E. Fort Lowell Road
Tucson, AZ 85712

Dr. Earl R. Thompson
Assistant Director of Research for
Materials Technology
United Technologies Research Center
Silver Lane
East Hartford, CT 06108

NMAB STAFF

K.M. Zwilsky, Director
Mary Brittain, Adm. Officer
2101 Constitution Ave., NW
Washington, DC 20418

REPORT DOCUMENTATION PAGE	Form Approved OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data solutions, gathering and maintaining the data needed, and correlating and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302; and to the Office of Management and Budget, Paperwork Reduction Projects (0704-0188), Washington, DC 20500.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE March 1992	3. REPORT TYPE AND DATES COVERED One of a series under subject contracts. 1989-1995

4. TITLE AND SUBTITLE Beam Technologies for Integrated Processing	5. FUNDING NUMBERS Contracts MDA903-89-K-0078 and MDA972-92-C-0028
6. AUTHOR(S) Committee on Beam Technologies: Opportunities in Attaining Fully-Integrated Processing Systems	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Materials Advisory Board National Research Council 2101 Constitution Avenue, NW Washington, DC 20418	8. PERFORMING ORGANIZATION REPORT NUMBER NMAB-461
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of Defense/National Aeronautics and Space Administration Washington, DC 20301	10.SPONSORING/ MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES	
12a. DISTRIBUTION/AVAILABILITY Approved for Public Release Unlimited Distribution	12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

Beam technologies offer opportunities for application in many manufacturing schemes. Various beam technologies are reviewed, and applications to electronics and engineered materials are identified. Examples of existing manufacturing processes are described. Recommendations for R&D efforts are developed for enhancing the understanding of the operation and capabilities of beam technologies and their applications.

14. SUBJECT TERMS Energetic Beams, Materials Processing, Beam Technologies, Materials Deposition and Modification	15. NUMBER OF PAGES 95
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	10. LIMITATION OF ABSTRACT None

NSN 7540-01-280-5500

Standard Form 298 (REV. 2-89)
Prescribed by ANSI Std. Z39-18
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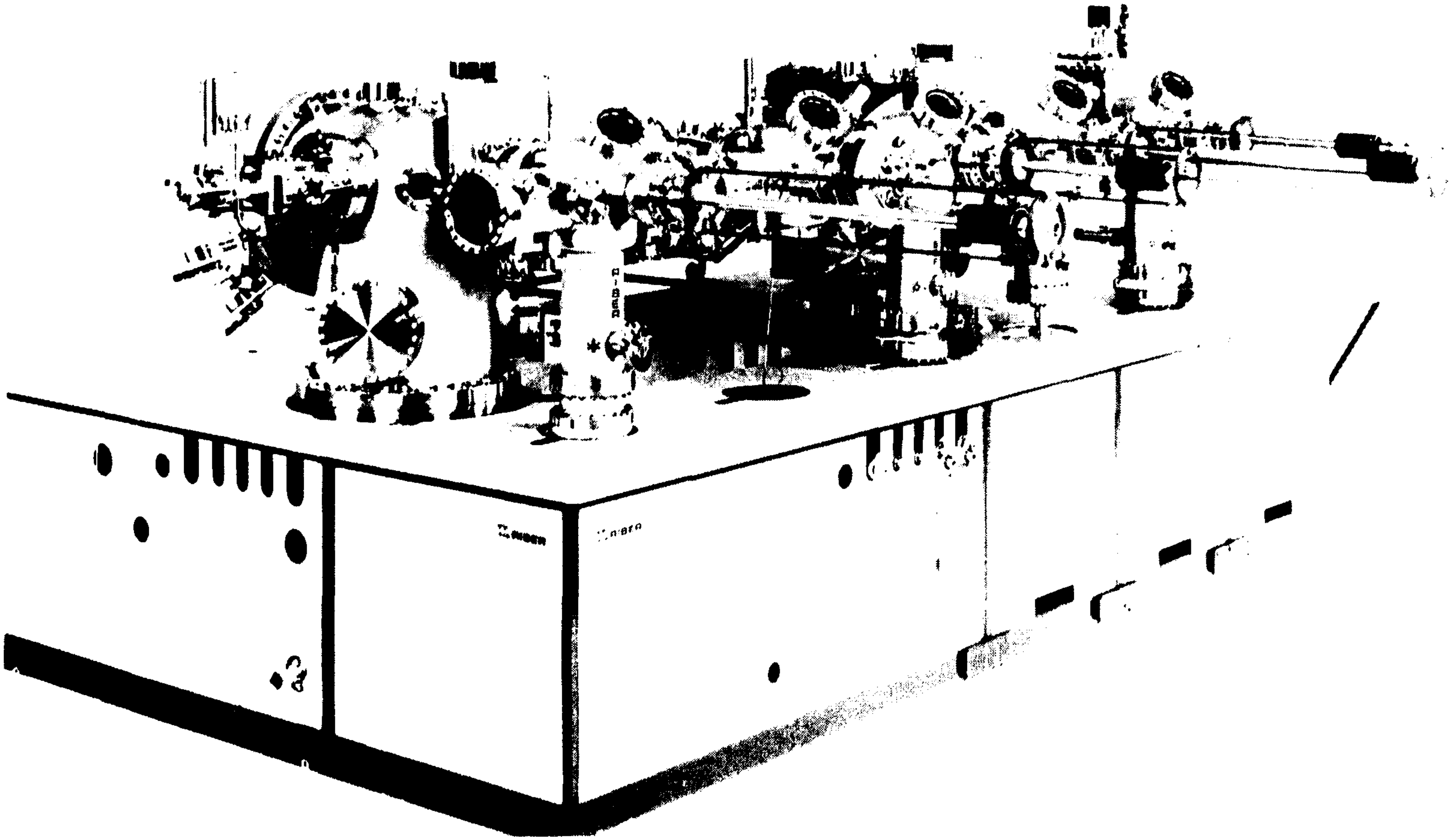

Cover: Laser and Material Interaction During Welding
(Courtesy of E. A. Metzbower, Naval Research Laboratory.)
Frontispiece: Molecular beam epitaxy (MBE) in-situ processing of semiconductor films.
(Courtesy of A. Y. Cho, AT&T Bell Laboratories.)

BEAM TECHNOLOGIES FOR INTEGRATED PROCESSING

Report of the Committee on Beam Technologies:
Opportunities in Attaining Fully-Integrated Processing Systems

NATIONAL MATERIALS ADVISORY BOARD
COMMISSION ON ENGINEERING AND TECHNICAL SYSTEMS
NATIONAL RESEARCH COUNCIL

NMAB-461
National Academy Press
Washington, D.C.
1992

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

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

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This study by the National Materials Advisory Board was conducted under Contracts No. MDA 903-89-K-0078 and MDA972-92-C-0028 with the U.S. Department of Defense and the National Aeronautics and Space Administration.

Library of Congress Catalog Card Number 92-60205.
International Standard Book Number 0-309-04635-1.

This report is available from the Defense Technical Information Center, Cameron Station, Alexandria, VA 22304-6145.

Printed in the United States of America

ABSTRACT

Beam technologies play an important role in microelectronic component fabrication and offer opportunities for application in other manufacturing schemes. Various beam technologies are reviewed, and applications to electronics and engineered materials are identified. Examples of existing manufacturing processes that employ beam technologies are described. Recommendations for research and development efforts are developed for enhancing the understanding of the operation and capabilities of beam technologies and their applications, which could lead to more widespread use in integrated systems in the industrial manufacturing sector.

PREFACE

Recent advances in beam technologies, sensors, control, and information processing have created new opportunities for integrated processing of materials and components. Technologies involving directional transfer of energy for deposition, removal, or modification of atomic and molecular species comprise many of the beam technologies included in this study. Integrated processes are characterized by their wide flexibility–that is, new designs are accommodated by software modifications rather than hardware modifications, continuous flow or transfer station operations, enclosed systems, on-line inspection, and on-line process control. They appear to offer the potential of shorter lead times, higher productivity leading to lower cost, elimination of many batch processing steps, and possible improved quality, reliability, and performance of the final product.

The committee set out to identify individual beam processes (in the broad definition) suitable for integrated processing and determined that the two important factors with respect to the suitability of beam processes are the environmental constraints and the interaction time. A variety of beam technologies are reviewed in the processsing of semiconductor, metallic, ceramic, polymeric, and composite materials along with several examples of existing process integration.

While the original objective of the study was to identify applications where fully integrated beam processing could lead to improvements in productivity, the committee came to realize that fully integrated systems are very product and materials specific, and therefore could not be addressed in a generic way. Detailed cost analyses could likewise not be developed for the same reason. Instead, the committee developed recommendations for research and development programs on common problems and deficiencies related to employing more effective, fully integrated beam processing technologies. The committee believes that an R&D program of this type would overcome current problem areas and result in industrial benefits that will enhance U.S. competitiveness in materials and manufacturing.

David Richman,
Chairman

ACKNOWLEDGMENTS

The committee is grateful to a number of individuals who provided extensive background materials for its use. A number of experts met with the committee to make informal presentations: Bernard H. Kear, of Rutgers University, discussed beam technologies as a fabrication tool; Gary G. Tibbetts, of General Motors Research Laboratories, discussed vapor-grown carbon fibers; Robert R. Doering, of Texas Instruments, and Sherry J. Gillespie, of IBM, discussed activities directed toward silicon integrated processing. Joseph L. Pentecost, of the Georgia Institute of Technology, is thanked for his input on the use of microwave beams for high-efficiency heating of materials.

The government liaison representatives are thanked for their participation in numerous committee discussions and for providing valuable support materials and data for committee use. They were most helpful in assisting the committee in defining the scope of the study and offering technical guidance during development of the committee's report drafts.

The chairman thanks the committee members for their dedication and patience during the numerous iterations and revisions of the report drafts. Committee member Anthony J. Perrotta is thanked for acting as report coordinator to assist the chairman in assembling the report for final review. Particular thanks go to committee members who served as chapter or section coordinators to assemble pertinent facts for various parts of the report and for presenting the data in a timely, open-minded, and professional manner.

On behalf of the committee, the chairman thanks George Economos, NMAB Program Officer, and his secretary, Aida Neel, for their assistance during the committee's deliberations and report writing.

COMMITTEE ON BEAM TECHNOLOGIES: OPPORTUNITIES IN ATTAINING FULLY-INTEGRATED PROCESSING SYSTEMS

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AIDA NEEL, Administrative Secretary

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1

INTRODUCTION

Modern materials applications (e.g., integrated circuits, optoelectronic devices, advanced engines for aerospace and ground transportation, cutting tools, and wear-resistant bearing surfaces) require increasingly precise control of the structure and composition of matter over smaller and smaller dimensions. This has led to the evolution of new, refined synthesis techniques, which allow the requisite control. Many of these techniques utilize the directional transfer of matter or energy through a vacuum or vapor phase. Examples of such techniques are molecular beam epitaxy (MBE), chemical vapor deposition (CVD), evaporation, and sputtering. These and other related technologies, referred to as beam technologies, are the subject of this report.

While some of these techniques go back to the nineteenth century (e.g., evaporation, CVD), others are quite new (e.g., MBE); all are evolving rapidly in response to the demands that applications place on the materials. Utilization of beams in electronic materials that require small complex structures has resulted in further development of beam processing methods. The additional requirements of a continuous fabrication line for a fully integrated process will no doubt lead to further development and sophistication of beam systems that include incorporation of on-line sensing devices that can control the process. In engineered materials, beam technologies have been used extensively for coatings and surface modifications. More recently, beams have been used for the formation of continuous fiber, net shapes, and composites. These applications are the outgrowth of technology demands on beam processing.

Beyond this normal outgrowth, and also of vast importance, is the ability of some of the beam techniques to prepare new structures and compositions of matter that lead to new applications. Examples are the ability to prepare materials monolayer by monolayer, which has led to the development of quantum-well devices for optoelectronic applications, and the ability to prepare diamond films by several different beam technologies, which has led to the availability of diamond in plate and cone shapes, something that was not previously possible. Yet another area in which beam technologies are playing an important role is in the preparation of nanophase materials, an area of increasing interest because of the unique properties of these materials. This latter synthesis of small building-block particles presents a challenge for the development of a high-yield beam process for generating nanosize powders similar to other powder forming processes, which subsequently can be incorporated into a fully integrated process.

A potentially important feature, which all these beam technologies have in common, is that they are all "dry" processes that are carried out in a vacuum or a controlled gaseous ambient. As such, they are closed system operations readily adapted to being joined to other dry processes. This capability makes these technologies candidates for components in the integration of materials processing technologies. The potential for shorter lead times, higher productivity, and improved quality, reliability, and performance makes process integration an attractive opportunity. The rapid advances being made in sensor technology, process control, and information processing have created new opportunities for integrated processing of materials.

A large capital investment, appropriate planning, and education of the work force will be required to implement beam or beam-assisted integrated processing. Inexpensive capital will probably be needed to fund this advancement, as is now done in Japan. Second, equipment manufacturers need to provide standard interfaces between machines (both software and hardware are needed for this) to allow the viability of an acceptable integrated process. Again, the Japanese are doing well in this area of development. A primary thrust of the present study was to evaluate the suitability of beam technologies for process integration and to identify the needs and barriers to their successful incorporation into such systems. This necessarily leads to consideration of the needs (e.g., technical development, computer-integrated manufacturing system) that will be required to allow economical processing.

In the following chapters, a summary and the major recommendations are described first, followed by a review of various beam technologies. This is followed by a review of the applications of some techniques to the processing of various materials. Here elemental and compound semiconductors are separated from other materials because of the already important applications that beam technologies have to microelectronic manufacturing. Additionally, the development of beam technologies for microelectronic manufacturing was originally conceived to be an example of integrated processing that could be applied to the study of engineered materials (metals, ceramics, polymers) and their susceptibility to beam-assisted integrated processing. However, fully integrated processing was found not to be well established in microelectronics. Therefore, a study is required in this area similar to that for the engineered materials. Examples of integrated materials processing using beam processing are reviewed, followed by a discussion of the needs and barriers for further integration.

2

SUMMARY AND RECOMMENDATIONS

SUMMARY

Electronic Materials

Semiconductor device manufacturing utilizes many beam technologies. The emphasis on the need to produce smaller and more complex microelectronic structures has led to the development of sophisticated beam processing techniques. Beam technologies are used extensively in integrated circuit manufacturing for materials deposition, to improve the thickness and compositional uniformity of metals, dielectrics, and semiconducting materials deposited on substrates. Over the past 10 years, in order to obtain product uniformity and quality while achieving size reduction, sputtering has replaced evaporation for metals deposition in integrated circuits, and low-pressure chemical vapor deposition has given significant improvements for dielectric materials, metals, and polysilicon deposits. For the most part, ion implantation has replaced diffusion for almost all semiconductor doping process steps since it gives more uniform control of dopant concentrations and impurity profiles.

Essentially all of the patterning of silicon integrated circuits (ICs) is done by optical lithography, with electron beam lithography used for defining very small features for some circuit designs in some small-volume applications. The apparent successor to optical lithography is x-ray lithography, where features of 0.1 μm have been demonstrated in test devices. Because of this capability, several industrial and university groups are using enhanced synchrotron x-ray sources to develop advanced IC fabrication processes.

Newer device structures, such as heterojunction field effect transistors (HFETs), which require close control of epitaxial structures (e.g., gallium arsenide [GaAs], aluminum gallium arsenide [AlGaAs]), depend heavily on metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) techniques. Similarly, fabrication of optoelectronic components, which in the past were fabricated by liquid-phase epitaxy or chloride-transport vapor-phase epitaxy, also depend on MBE and MOCVD techniques to fabricate higher-performance, yet more complex, devices incorporating superlattices and quantum-well confinement. Complementary beam technologies, involving plasma etching and ion milling for selective materials removal, along with rapid optical annealing to activate the implants of heterostructure devices, are also important in the IC fabrication process.

Engineered Materials

Beam technologies have been used extensively to produce new materials in areas other than microelectronics, such as coatings and surface modifications, formation of net shapes, composites, nanophases, and optical surfaces, including the treatment of polymeric substrates. CVD and physical vapor deposition (PVD) have been used extensively over the past 30 years to apply metal, alloy, and ceramic coatings on metal, ceramic, or polymer substrates of various sizes and shapes. These applications range from wear-resistant coatings on cutting tools and magnetic media on tape to optical coatings on polymeric materials.

The technologies have progressed in the area of PVD to plasma-assisted CVD (PACVD) and reactive evaporation (RE) processes to aid in the deposition of more refractory materials such as nitrides, carbides, and high-temperature oxides. Reactive evaporation and laser ablation, the modern version of flash evaporation, have both been successful for depositing films of high-temperature superconducting oxides such as $YB_2Cu_3O_{7-x}$. Electron impact ionization and excitation of reacting gases has led to development of the activated reactive evaporation (ARE) process. This has allowed the synthesis of refractory silicide and carbide films at much lower substrate temperatures. An interesting variation of the ARE process, in which a low melting compound of the element is used, led to the formation of cubic boron nitride by evaporation of boric acid in an ammonia plasma.

Enhanced CVD processes have taken the form of either thermally assisted CVD or PACVD for thermal and electron excitation deposition, particularly for selective-area deposition. The plasma- or photon-assisted CVD process is quite useful in depositing ceramic coatings (Si_3N_4, SiC, AlN, Al_2O_3, etc.) at lower temperatures than conventional CVD. This feature is important when the substrate is susceptible to temperature-induced irreversible structural or electrical changes. A further process improvement, known as remote PACVD, is used to protect both the substrate and the growing film from ion bombardment.

Recently, considerable interest has been centered on the growth of diamond, diamond-like, and cubic boron nitride coatings. Synthesis of these films, especially diamond, has been performed using a variety of chemical and PACVD techniques as well as PVD techniques. In particular, the PACVD technique (with direct current, radio frequency, or microwave excitation) has been used extensively for the synthesis of diamond and diamond-like coatings. Ion-beam-assisted and low-temperature ARE also have been used to prepare diamond films. In all these beam methods of deposition, it appears that the concentration of atomic hydrogen must be controlled to give good-quality diamond films. Unfortunately, it is still difficult to prepare single-crystal films of diamond; in most cases a polycrystalline film is formed.

The two beam techniques utilized for surface modification of materials are ion implantation and laser treatment. Ion implantation is used in a number of critical-use applications. It has flexibility in that any element can be implanted into a substrate without thermodynamic constraint (e.g., not requiring chemical reaction) at or near room temperature to maintain the dimensional integrity of the part. The main application has been surface treatment of metals. However, in recent years considerable interest has emerged in the treatment of ceramic and polymer substrates.

Laser surface treatment, since it can be employed in atmosphere or nonvacuum ambient environment, offers greater flexibility for modifying a surface. Hardening of metal surfaces, increasing corrosion resistance of materials, and laser welding are typical applications. The ease of implementing lasers, compared to ion beams, makes this approach potentially more suitable for integrated manufacturing, unless other vacuum steps are also required.

In addition, lasers are being applied to materials forming. They are used for both deposition and removal of material in shaping operations. Lasers are used to form shapes through such processes as solidification, sintering, polymerization, and CVD. The advantages of a laser in an integrated processing system for forming shapes are the short interaction times, high flexibility, and ease of on-line inspection and process control. A commercial process already has been developed using lasers for hole drilling and sheet cutting; presently, sheet metal cutting accounts for the largest fraction of CO_2 laser sales. Two other processes worth mentioning are laser-assisted machining, which has been used in turning hard-to-machine metallic alloys, and laser-assisted chemical etching, which is used to shape hard ceramic materials.

Ceramic powders, whiskers, and fibers have been synthesized using beam forming technologies. These have been important developments for production of composites and generation of nanophase materials that exhibit unusual properties. The catalyzed growth of both carbon and silicon carbide whiskers has been achieved using hydrocarbon gases and hydrogen, and silicon carbide and silicon monoxide precursors. When combining these chemical beams with an iron catalyst, in the case of carbon whiskers, growth rates as high as several millimeters per minute have been achieved. Similarly, silicon carbide whiskers have been beam-grown with average tensile strengths of 8.4 GPa, strains of 1.74 percent, and elastic modulus of 578 GPa, properties that are superior to those of the best polymer-derived ceramic fiber yarns.

Continuous monofilaments of boron and silicon carbide are presently being produced on fine-wire substrates using CVD. The CVD-produced SiC fiber has properties superior to poly carbosilane-derived fibers, although, presently, its fiber diameter is too large for weaving processes. These fiber manufacturing developments are good examples of integrated manufacturing using beam technologies.

Lastly, matrices of metals or ceramics have been formed using chemical vapor infiltration (CVI). Prominent examples are SiC fiber/SiC matrix and carbon fiber/SiC matrix. Current commercial CVI processes have the advantages of a near-net-shape process and a relatively low temperature process that involves no high-pressure sintering, thereby minimizing fiber damage.

Nanophase powders, which have properties different from their bulk counterparts because of their high surface area-to-volume ratios, have been synthesized using beam technologies. Applications include ultrafine titania in paints and pigments, catalysts, sintered powder products, magnetic recording media, optical applications, and biomaterials. Argonne National Laboratory and Nanophase Technologies, Inc., an offspring firm, are generating equiaxed nanophase materials by a gas condensation process. It can produce pure metals as well as oxides (e.g., TiO_2, Al_2O_3, MgO) using oxygen in the low-pressure chamber rather than an inert gas. A high-pressure sputtering process (200 mT gas pressure) has been developed at UCLA for the generation of ultra-fine particles (10-20 nm in diameter) of Cu, Au, SnO_2, and Al_2O_3.

New opportunities are emerging for extending flexible machining systems (FMS) to include additional processing and control steps as related to beam technologies. Future processing of materials with microwave energy is an attractive energy-saving approach. Alternative cost-effective manufacturing technologies, such as beam technologies, warrant serious consideration to replace mechanical fabrication of some components. Great opportunity exists for fully integrating gear-making operations using energy beams.

Integrated Processing

The IC manufacturing process flow generally is still batch oriented, as it was before the widespread introduction of beam technologies. Wider process margins are required for batch-processed wafers than would be required for individually processed wafers if adequate control systems existed to repeatedly process individual wafers in a single-wafer system. Information between the process steps is rarely fed forward to modify the subsequent step based on the previous step data; therefore, measurements of results and modification of process steps on a wafer-by-wafer basis are not possible in the batch processing environment. Some systems have automatic control of the process variables, but little exists by way of real-time monitoring of actual process results.

No standardized interface exists for material flow from system to system. Several proposed standards are being developed at this time. High volume is required to justify the large capital expenditure for a continuous fabrication line. A major effort is required to interface the various process equipment that must transfer the material and the process information. Cluster tools that can perform multiple process steps are being introduced into the semiconductor industry. Significant problems must be overcome in throughput, cost, uptime, real-time control, process information flow, and process step development before there can be considerable use of integrated process tools.

Some important considerations for expanding integrated beam processing systems are as follows:

- more studies to better understand the process steps so that the proper experimental variables can be measured and process simulation models developed,
- development of computer algorithms based on simulation models coupled with expert system artificial intelligence techniques to develop smart control programs,
- education of students with cross-disciplinary skills to undertake the above items, and
- foster team building between equipment vendors and materials processors.

RECOMMENDATIONS

The committee concludes that all of the beam technologies treated in this report are capable of incorporation into fully integrated processing systems. The embodiment of each incorporation will be material-specific; however, there are common problems and deficiencies which must be overcome before any fully integrated beam processing system is realized in actual manufacture. Foremost among these in the need to monitor the process in situ and control it in real time. Achieving this ability and addressing other important issues requires the following actions:

- Conduct fundamental mechanism studies: Further studies are needed for the understanding of the fundamental mechanisms by which these techniques work. Understanding of the underlying physics and chemistry is necessary to establish the proper parameters to be monitored or controlled.

- Develop in-line sensors: Direct monitoring of the process requires the development of proper sensors. Having accurate real-time knowledge of each process step will be necessary for both machine control and elimination of inspections.

- Develop process models: An element required in machine control is the availability of accurate process models and simulations. These are essential to properly interpret sensor readings and thereby issue control commands.

- Improve equipment reliability: High equipment uptime is a prerequisite for an economical integrated process. Equally important are ease of maintenance and self-monitoring equipment.

- Develop vendor-user communication: Close communications must exist between the equipment maker and the equipment user to identify and correct weak points in the design and to incorporate modifications that improve machine performance in a timely and efficient manner.

- Adopt standards and interface specifications.

- Properly educate the work force: As process equipment becomes more sophisticated and more complex, highly skilled workers are required to maintain the equipment.

3

BEAM TECHNOLOGIES

For the purpose of this report, beam technologies are defined as those involving directional transfer of matter or energy through a vacuum or the vapor phase. This chapter reviews the various beam technologies and focuses on the important operating principles of each. A summary table of many of these processes is found at the end of this chapter (Table 3-5). Applications to specific materials are reviewed in Chapters 4 and 5.

The sections that follow review various materials beam techniques used for processing. Physical vapor deposition (PVD), which includes both evaporation and sputtering as well as variations on these two fundamental processes, is examined. Molecular beam epitaxy (MBE), which is closely related to evaporation, is discussed next, followed by chemical vapor deposition (CVD). Included in the discussion of CVD are some variations such as plasma-assisted CVD and laser-assisted CVD. The use of microwave electron cyclotron resonance plasmas, a recent technique receiving much attention in semiconductor processing, is also reviewed. Ion beams are considered in a subsequent section. Energy beams, including laser, electron, x-ray, and microwave beams, are discussed in the last section of this chapter.

ATOMIC AND MOLECULAR MATERIAL BEAMS

Beam processes, such as PVD, CVD, electrodeposition, and MBE, are the primary processes considered below. All deposition processes consist of three steps: generation or supply of the depositing species, transport of the species from source to substrate, and film growth on the substrate. In some processes these steps can be controlled individually (e.g., in PVD, plasma spray, and MBE). In other processes the three steps occur simultaneously (e.g., in CVD processes). The versatility of a process depends on the ability to vary each of the three steps independently of the others. Furthermore, in plasma-assisted vapor deposition (PAVD) processes, the plasma parameters (electron density, electron energy, and electron energy distribution function) influence each of the three steps.

Physical Vapor Deposition

PVD processes consist of two fundamental classes of deposition techniques in which one or all constituents of the deposit are generated from a condensed source (solid or liquid) either by heat-induced vaporization (evaporation) or momentum transfer processes (sputtering). These can be either "direct" or "reactive" processes. Reactive processes are those that occur in the presence of a reactive gas so that a compound is formed in the gas phase or on the substrate surface. These processes are extensively covered in various books (Holland, 1966; Bunshah, 1982; Maissel and Glang 1970). Some are described briefly below.

Direct Evaporation Processes

The direct evaporation process is used extensively for metals and elemental semiconductors. In the case of ceramic materials, however, evaporation occurs with dissociation of the compound into fragments. In very few systems, such MgF_2, B_2O_3, CaF_2, SiO and some other group IV divalent oxides, evaporation occurs without dissociation. The stiochiometry of the deposit in a dissociation situation depends on the ratio of various molecular fragments striking the substrate, the sticking coefficient of the fragments striking the substrate (which may be a strong function of the substrate temperature), and the reaction rate of the fragments on the substrate to reconstitute the compound. In the case of ceramic systems, where one of the constituents is a gas in its elemental form, the films generally are deficient in the gaseous constituent (e.g., direct evaporation of Al_2O_3 results in a deposit deficient in oxygen). The imbalance of stoichiometry occurs to a lesser degree in ceramic systems where all the constituents are solids that have nearly the same vapor pressure in their elemental forms. The direct evaporation process, using electron beam or thermal evaporation techniques (see Figure 3-1), has been successfuly used for preparing transition meal carbides, silicides, and borides (Maissel and Glang, 1970; Budhani et al., 1984; Yokotsuka et al., 1987). The slight variation in the stoichiometry of the coatings of such systems deposited by a single-source evaporation can be avoided if a multisource evaporation technique is used. A schematic diagram of a two-source evaporation process is shown in Figure 3-2. This technique is used quite extensively for the deposition of transition metal silicides (Hunter et al., 1978), as well as sulfides and selenides of group II elements (e.g., Zn and Cd).

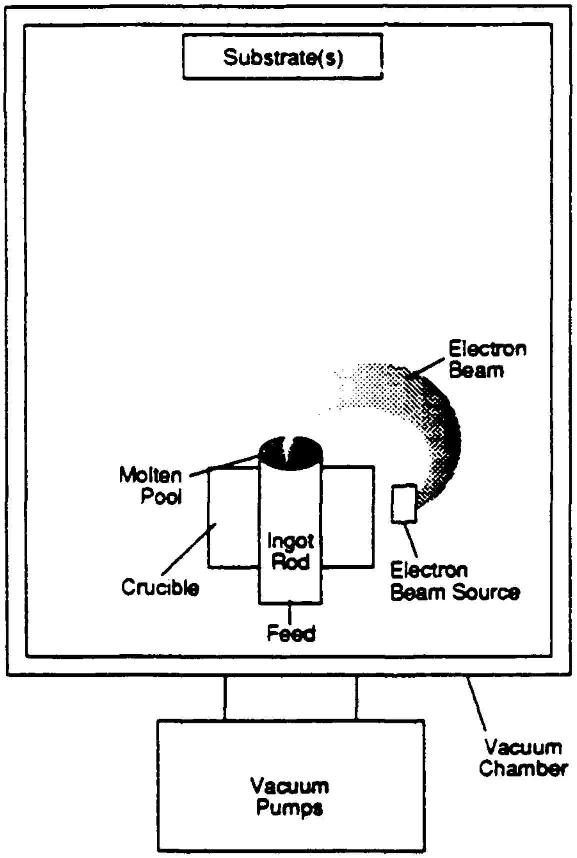

Figure 3-1 Schematic of an evaporation-deposition process using electron beam heating.

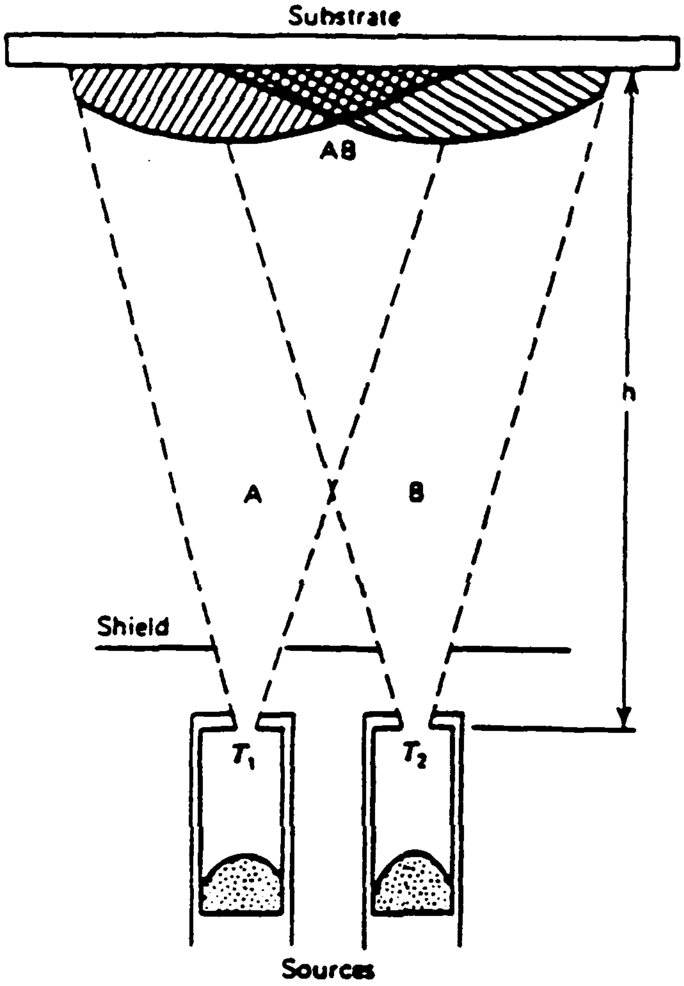

Figure 3-2 Schematic of the two-source evaporation process.

Flash evaporation is a very old method of depositing compounds, such as GaAs, PbTe, etc., whose constituents have a high vapor pressure and where it is important to maintain the stoichrometry of the deposit. In this technique, fine particles of the compound of the correct stoichrometry are sprinkled onto a heated surface (e.g., a tungsten strip at 2000°C). The particles are instantly and completely converted to the vapor phase (Maisel and Glang, 1970).

Laser ablation is a modern version of the flash evaporation process where a pulsed laser beam is used to locally heat a compound target and evaporate small discrete volumes in rapid succession, which preserves the stoichrometry of the deposit. The most important application is the deposition of thin films of high temperature superconducting oxides (e.g., $YBa_2Cu_30_{7-x}$). A major limitation of both of these is the small area of the deposit.

Direct Reactive Evaporation Processes

The reactive evaporation (RE) process is used to compensate for the loss of gaseous constituents of a ceramic during its direct evaporation. Thus, for example, stoichiometric Al_2O_3 films can be deposited by direct evaporation of Al_2O_3 in an atmosphere of oxygen. However, because of the high melting point and the extreme reactivity of ceramic melts, it is generally difficult to evaporate ceramic materials. To avoid these problems, the reactive evaporation process is commonly used in a mode where the metallic constituent of the ceramic is evaporated in a partial pressure of the reactive gas to form a compound in the gas phase, or on the substrate, as a result of a reaction between the metal vapor and the gas atoms (e.g., $4Al + 3O_2 \rightarrow 2Al_2O_3$). The reactive evaporation method has been used to synthesize films of SnO_2, $SnInO_3$, In_2O_3, Al_2O_3, SiO_2, $Cu_xMo_6O_8$, Y_2O_3, and TiO_2, and, more recently, $YBa_2Cu_3O_{7-x}$-type perovskite superconductors.

Since the reactive gas in the RE process is in a molecular state, and thus less likely to react with the vapor species, the formation of a well-crystallized stoichiometric film requires high thermal activation at the substrate. This problem becomes acute in situations where the reactive gas consists of more than one molecule; typical examples are SiH_4 and CH_4 or C_2H_2 for the formation of silicides and carbides. The concept of electron-impact ionization and excitation of the reactive gas in the substrate-source space (Bunshah and Raghuram, 1972) led to the solution of the problem. The ionization and excitation of the gas activates the compound-forming reactions, whereby the compound films can be synthesized at a much lower substrate temperature. This process is known as activated reactive evaporation (ARE) (see Figure 3-3).

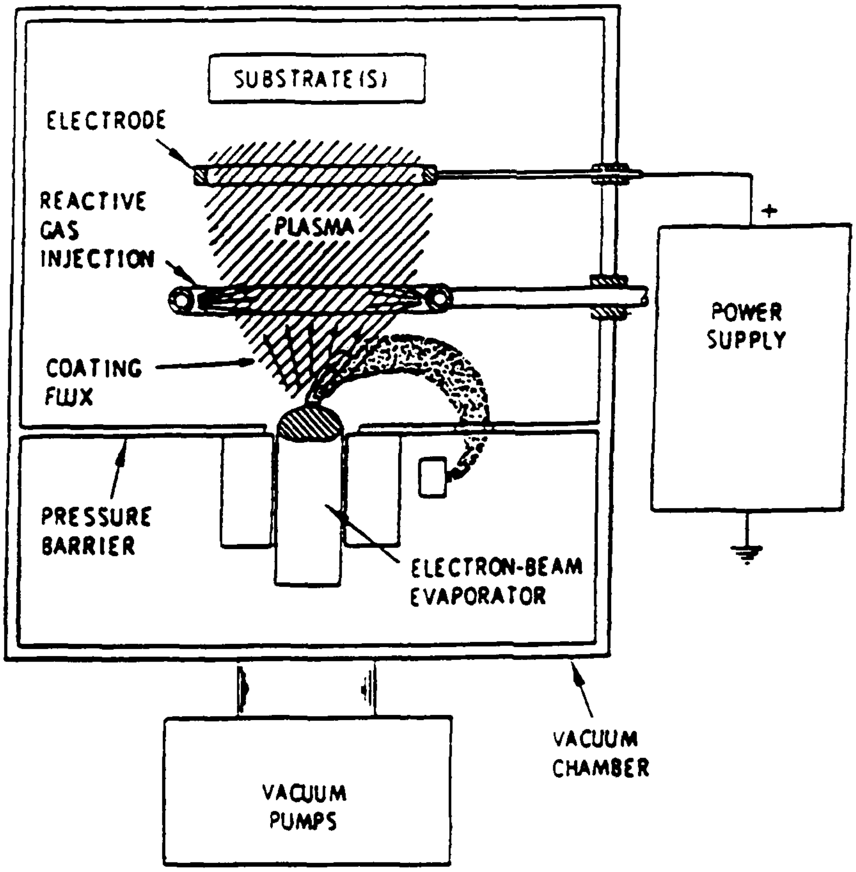

Figure 3-3 Schematic of the activated reactive evaporation process.

Synthesis of TiC by reaction of Ti metal vapor and C_2H_2 gas atoms, using a carbon-to-metal ratio close to unity, was achieved with this process. Moreover, by varying the partial pressure of either reactant, the carbon-to-metal ratio of carbides could be varied at will. The ARE process has also been applied recently to the synthesis of all five different Ti-O oxides. The researchers (Bunshah and Raghuram, 1972) noted that in the ARE process (i.e., with a plasma), as compared to the RE process (i.e., without a plasma), a higher oxide was formed for the same partial pressure of O_2, demonstrating a better utilization of the gas in the presence of a plasma.

A variation of the ARE process using a resistance-heated source instead of the electron-beam-heated source has been developed (Nath and Bunshah, 1980) and is particularly useful for evaporation of low-melting metals, such as indium and tin, where electron beam heating can cause splattering of the molten pool. The plasma is generated by low-energy electrons from a thermionically heated filament and is pulled into the reaction zone by an electrical field perpendicular to the evaporation axis. The ionization probability is further enhanced by a superimposed magnetic field that causes the electrons to go into a spiral path. This process has been used to deposit transparent conducting films of indium oxide and indium-tin oxide. The ARE process has several other variations (Bunshah and Deshpandey, 1987). The process has also been used in a dissociative mode, where instead of using an elemental evaporation source, a low-melting compound of the elements can be used. For example, cubic boron nitride films can be deposited by evaporating boric acid in an ammonia plasma (Bunshah and Deshpandey, 1987).

Direct Sputtering Processes

The basic sputter deposition process involves removal of atoms from the surface of a solid or liquid target by energetic ion bombardment and collection of the sputtered species on an adjacent solid substrate,as illustrated in Figure 3-4. A target, consisting of the material to be deposited, is held at a negative potential, ranging from a few hundred volts to a few kilovolts. For a critical value of the chamber pressure (from 1×10^{-3} to 0.1 Torr), application of the voltage initiates a plasma discharge in the vicinity of the target. The target, because of its negative potential, is bombarded by the ions present in the plasma. The plasma is sustained by stochastic ionization of the gas atoms or molecules by secondary electrons emanating from the target.

In situations where the gas ions are sufficiently heavy, bombardment of the target leads to sputtering of the target surface by a momentum transfer process. Argon, because of its high atomic number and nonreactivity, is the commonly used sputtering gas. Since the sputtering rate is directly dependent on the number of ions striking the target, its magnitude can be increased by increasing the ion density in the vicinity of the target. Higher ion densities can be achieved by application of magnetic fields. This modification of the sputtering process is known as magnetron sputtering. If the target material is electrically conducting, a direct current (dc) voltage can be used for sputtering. In the case of insulating targets, a radio frequency (rf) potential must be applied.

Reactive Sputtering Processes

The dc magnetron sputtering technique has been successfully used to deposit films of transition metal silicides and borides using a composite ceramic target. As in the case of evaporation, however, sputtering leads to dissociation of the target material into atoms and molecular fragments, which results in a deficiency of the gaseous constituents of the material. This off-stoichiometry problem can be eliminated by adding the constituent gas in the plasma along with the argon. This process modification is called reactive sputtering.

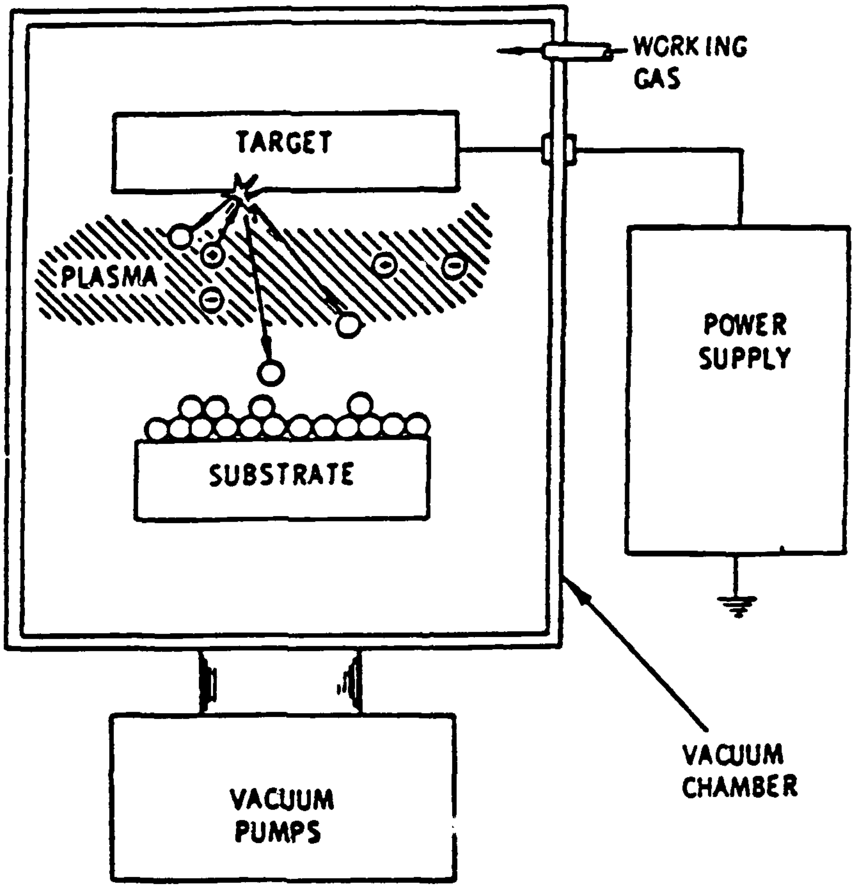

Figure 3-4 Schematic of a sputter-deposition process.

Plasma reactions of the gas with the target during reactive sputtering lead to formation of a compound layer on the target that slows the rate of sputtering. This phenomenon is known as target poisoning. Recently, many different approaches have been proposed to overcome the poisoning problem. They involve maintaining a composition gradient in the gas phase by injecting the reactive gas near the substrate where the film forms and maintaining the working gas for sputtering near the source; using getters to trap the reactive gas to reduce the amount reaching the target; using conductance-limiting baffles between the target and substrate; controlling the gas composition, relative to the metal sputtering rate, with the use of mass spectrometric sensors in a feedback mode; and creating a second plasma near the substrate to activate the compound-forming reactions and combinations.

A major modification of the reactive sputtering process has been introduced for depositing transition metal silicide films. The technique involves dc magnetron sputtering of the metal of interest in a silane-diluted argon plasma. Unlike the sputtering from a composite target, the process allows deposition of the silicides over a wide range of composition. This method differs from conventional reactive sputtering in the sense that one of the products of dissociation of the gas is a solid.

Recently, rf or dc reactive magnetron sputtering, employing a single ceramic target, has been used to deposit films of a large class of ceramic materials. It, nevertheless, suffers from some disadvantages:

- The poor thermal conductivity of ceramics does not allow effective cooling of the target during sputtering, which results in local hot spots, with consequent spitting of the material and deposition of the particulates in the films. The ceramic targets also develop massive cracks after prolonged use.

- In the case of multicomponent targets, such as those used for deposition of high temperature exide superconductors and tungsten bronzes, the preferrential sputtering of one of the components leads to a lack of stoichmetry in the films.

Ion Beam Sputtering Processes

In the basic ion beam sputtering process, an energetically well-characterized beam of inert gas ions, generated from an ion source, bombards the target to be sputtered. In the case of electrically insulating targets, neutral beams are used. The sputtered species are deposited on a substrate situated in a relatively high vacuum. If a metal target is used for the growth of a ceramic film, the reactive gas can be introduced directly in the discharge chamber of the ion gun or a separate gun can be used, as shown in Figure 3-5. Table 3-1 lists some ceramic systems that have been successfully deposited using ion beam and reactive ion beam deposition techniques.

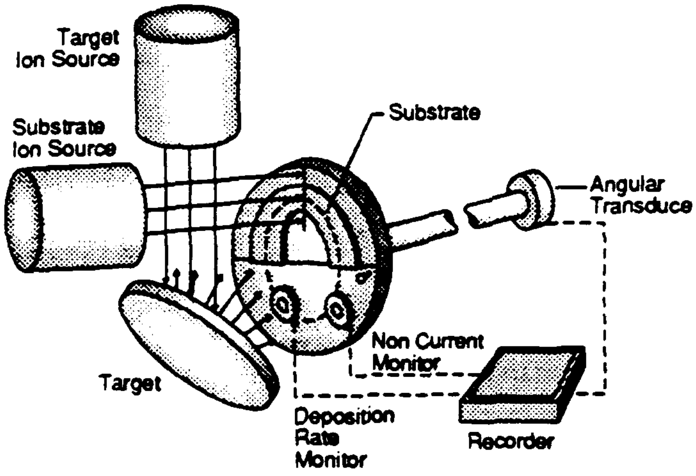

Figure 3-5 Schematic of ion beam sputtering with reactive gas injection.

Table 3-1 Ceramic Films Prepared by Reactive Ion Beam Sputtering

Ceramic Compound	Beam Energy (keV)	Target Material	Gases
AlN	Dual beam Ar+(1.5), N2+(0.8)	Al	Ar and N_2 (separately)
	Single beam (0.8 -2.0)	Al	$N_2 + H_2$
BN	Ion source of $B_3N_3H_6$	No target	$B_3N_3H_6$
Si_3N_4	$Ar^+ + N_2^+$ (1.0 - 0.5)	Si	$Ar + N_2$
α-Si_xN_{1-x}:H	$Ar^+ + N_2^+$ (1.0 - 0.5)	Si	$Ar + N_2 + H_2$
AlO_xN_y	Ar and N_2 neutral beam	Al	$Ar + N_2 + O_2$ leak
SiO_xN_y	Ar and O_2 neutral beam	Si	$Ar + O_2$
$In_2(Sn)O_3$	Ar^+ (0.5)	In/Sn alloy	$Ar + O_2$
SnO_2	Ar^+	Sn	$Ar + O_2$
Al_2O_3	Ar^+ (1.0)	Al	$Ar + O_2$
Refractory Oxides			
Y_2O_3, TiO_2, Ta_2O_5	Ar^+	Refractory Metal	$Ar + O_2$
Refractory Nitrides (e.g., NbN)	$X_e^+ + N_2^+$ (7.5)	Nb	$X_e + N_2$
Other materials			
Lead zirconium titanate (PZT)	Ar^+ (2.0)	Pb,Zr,Ti oxide ceramic	$Ar + O_2$
$YBa_2Cu_3O_7$	Ar^+ (1.8)	$YBa_2Cu_3O_{7-x}$ oxide ceramic	$Ar + O_2$

Molecular Beam Epitaxy

Many materials, ranging from semiconductors to metals and insulators, have been deposited as epitaxial (single-crystal) films by MBE. Molecular beam epitaxy is a term used to denote the epitaxial film deposition process involving the reaction of one or more thermal-molecular beams with a crystalline substrate surface under vacuum conditions (Parker, 1985). The conventional MBE process is related to vacuum evaporation, but in addition it offers very precise control over the incident atomic or molecular fluxes while the substrate is held at a precisely determined temperature (under ultrahigh vacuum conditions) to allow the formation of high-quality, single-crystal films. During the past two decades, multilayered composites that form heterostructures or periodic structures, called superlattices, have provided new degrees of freedom for device physicists and device engineers to obtain electrical or optical properties that could not be obtained from less complex naturally occurring materials.

The conventional MBE fluxes or beam formations are by evaporation of elemental materials from cylindrical effusion cells, as shown in Figure 3-6. In the case of growing gallium arsenide (GaAs), for instance, one effusion cell would be filled with pure gallium and the other with pure arsenic. The growth temperature may range from 550° to 700°C (Cho, 1983). For the growth of

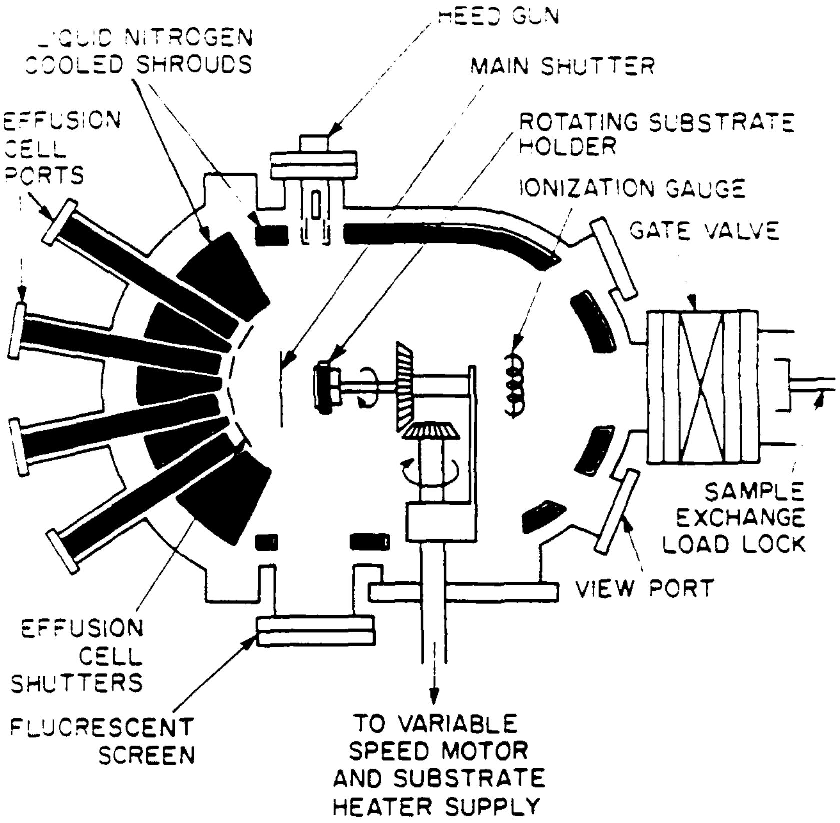

Figure 3-6 Schematic of a conventional MBE system.

silicon, high-temperature evaporation is required. Electron beam evaporation is generally used to achieve the high temperature for the growth of silicon. More recently, the beam flux has been generated by thermal decomposition of gaseous molecules, such as AsH_3 and PH_3 for obtaining arsenic and phosphorous atoms respectively (Panish and Temkin, 1989).

This gas-source MBE (GSMBE) has been most successful for the growth of quaternary materials, such as $Ga_xIn_{1-x}As_yP_{1-y}$, because the control of the phosphorous beam flux from a gas source is much better than that evaporated from solid phosphorus. For the modification of GSMBE using metalorganic gas sources, the names chemical beam epitaxy (CBE) and metalorganic MBE (MOMBE) have been introduced. A list of semiconductors grown with MBE is shown in Figure 3-7.

The typical growth rates of MBE are 1 to 5 μm/h. These growth rates are most suitable for the fabrication of electronic and optical devices, where the structures require precise thicknesses and where the desired total layer thickness is typically less than 1000 nm (1 μm). The capability to grow single-crystal films with atomic-layer dimensional precision and with abrupt interfaces for complex structures makes MBE a unique crystal growth technology for the fabrication of future-generation microwave and optoelectronic devices. Since most semiconductor devices require at most only a few micrometer-thick epitaxial layers, the technique sometimes is commercially practical despite the low throughput. At present, multiwafer systems holding seven 2-in. or three 3-in. wafers are commercially available. The yield and uniformity (thickness variation of 1.5 percent over a 3-in. wafer) are the key factors for using MBE in production. It should be noted that MBE is not suitable for the growth of thick films in the millimeter range because of low deposition rates.

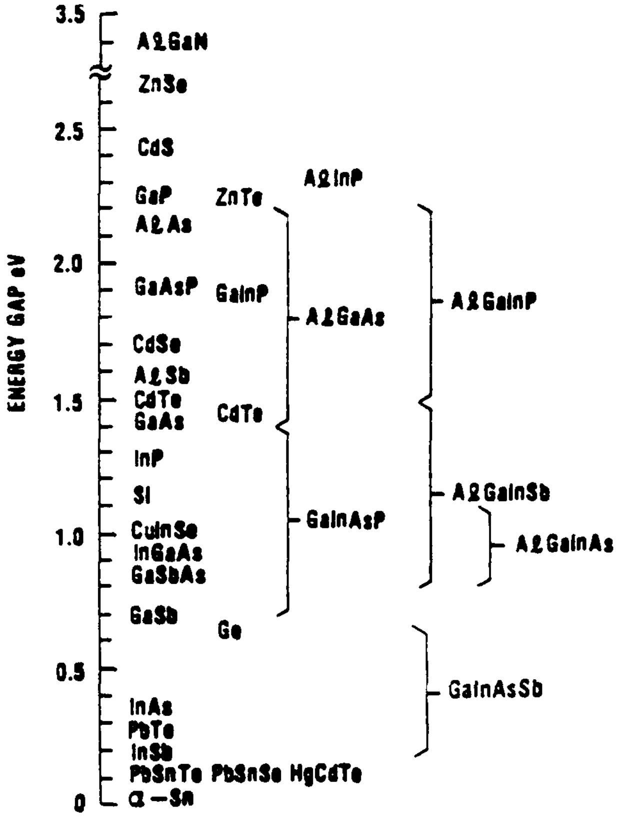

Figure 3-7 Semiconductors grown by MBE.

Chemical Vapor Deposition Processes

The use of volatile chemical intermediates to transport substances has been known since the latter half of the nineteenth century. While work on this technique has been ongoing since that time, only in the past 40 years has the method been extensively developed as a materials processing technique. Early work on crystal growth by CVD was done mostly in sealed ampules, but today the principal use of the technique is in flow systems (Figure 3-8).

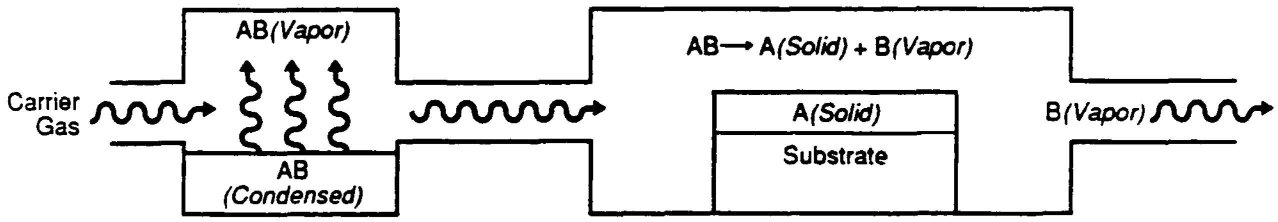

Figure 3-8 Schematic of illustration of conventional CVD.

The transporting species may be presynthesized and transported under its own pressure or with a carrier gas, or it may be synthesized in situ by passing a reactive gas (such as HCl) over the material to be transported (e.g., a group III metal). The reactive gases are then brought together in a deposition zone, which is generally heated, where the reactions give the desired product. Depending on the conditions in the deposition zone (e.g., temperature, concentration, pressure, species, and flow rates), the deposition may vary from epitaxial growth on the substrate to formation of an ultrafine powder.

CVD has been used in the semiconductor industry for both preparation of high-purity, single-crystal layers and deposition of polycrystalline and glassy layers used in devices. Preparation of semiconductor-grade silicon involves production of volatile chlorosilane from impure silicon. The chlorosilane is purified by distillation. Silicon is produced by CVD of the chlorosilane onto a hot filament to yield polycrystalline silicon, which is then remelted and grown into single-crystal boules.

An attractive feature of CVD is that the chemical reactions involved in the process often occur at temperatures much below the melting (or decomposition) temperature of the material being prepared. Thus, it is possible to grow crystals of materials at temperatures below their melting point. This offers a significant advantage in preparing high-purity materials since contamination from the container or the system hardware is reduced at these lower temperatures.

The requirement for thermal dissociation in conventional CVD requires substrate temperatures in excess of 600°C, in most cases, for any significant deposition to occur. The high substrate temperatures have both advantages and adverse effects on the properties of the films. Higher substrate temperatures promote the growth of a dense and well-crystallized structure with a minimum of trapped impurities. Also, since the dissociation reactions occur on the surface of the substrate itself, the conventional CVD process does not have the line-of-sight limitation of the PVD processes. With CVD, all parts of an irregularly shaped substrate are coated uniformly provided the temperature and gas flow conditions are the same everywhere. A wide class of oxides, borides, silicides, nitrides, and carbides has been deposited by the conventional thermal CVD process. Some typical CVD reactions for the deposition of ceramics are listed in Table 3-2.

Table 3-2 Typical CVD Reactions for Depositing Ceramic Materials

$$\begin{aligned}
Si(CH_3)Cl_3(g) &\rightarrow SiC(s) + 3HCl(g) \\
SiCl_4(g) + CH_4 &\rightarrow SiC(s) + 4HCl(g) \\
3SiH_4(g) + 4NH_3(g) &\rightarrow Si_3N_4(s) + 12H_2(g) \\
SiH_4(g) + 2H_2O(g) &\rightarrow SiO_2(s) + 4H_2(g) \\
2AlCl_3(g) + 3CO_2(g) + 3H_2(g) &\rightarrow Al_2O_3(s) + 3CO(g) + 6HCl(g) \\
2Al(CH_3)_3(g) + 9O_2(g) &\rightarrow Al_2O_3(s) + 6CO(g) + 9H_2O(g) \\
Al(CH_3)_3(g) + NH_3(g) &\rightarrow AlN(s) + 3CH_4(g) \\
BCl_3(g) + NH_3(g) &\rightarrow BN(s) + 3HCl(g) \\
SnCl_4(g) + O_2(g) &\rightarrow SnO_2(s) + 2Cl_2(g)
\end{aligned}$$

Spray pyrolysis, a subcategory of thermally assisted CVD, involves the spraying of a solution, usually aqueous, containing soluble salts of the constituent atoms of the desired end compounds onto a heated substrate. A typical example of the spray pyrolysis process is deposition of tin oxide films by thermal dissociation of an alcoholic solution of $SnCl_4$. In addition, preheating (temperatures between 200° and 500°C) of the sprayed droplets can be used to ensure vaporization of the reactants before they undergo a heterogeneous reaction at the substrate. The technique is very simple and is adaptable for mass production of large-area coatings in industrial applications. Various geometries of the spray setups are employed, including an inverted arrangement in which larger droplets and gas-phase precipitates are discouraged from reaching the substrate; the results are films of better quality. This technique has been used extensively to deposit films of ZnO, In_2O_3, SnO_2, CdS, Al_2O_3, and other ceramic systems.

The higher deposition temperatures required in a CVD process have adverse effects in situations where the substrate is susceptible to temperature-induced irreversible structural or electrical changes. This type of problem is encountered when depositing dielectric coatings on previously processed electronic devices or substrates. However, low- temperature CVD of ceramic coatings can be realized by plasma-assisted CVD (PACVD) processes using either rf or dc glow discharge plasmas (see Figure 3-9).

One of the most common examples of PACVD processes is the growth of silicon nitride from a mixture of SiH_4 and NH_3 gases. In this particular case, the electron-impact dissociation of silane and ammonia leads to the following fragments:

$$\begin{aligned}
SiH_4 + e^- &\rightarrow SiH, SiH_2, SiH_3, Si, H, + e^- \\
NH_3 + e^- &\rightarrow NH_2, HN, N, H, + e^-
\end{aligned}$$

The reaction between the nitrogen- and hydrogen-containing species in the plasma results in a solid deposit commonly written as Si_xN_{1-x}:H. The physical properties (e.g., electrical conductivity, optical absorption, refractive index), the Si/N ratio, and the stress state of the plasma CVD-prepared silicon nitride are highly sensitive to the amount of bonded hydrogen in the material and the degree of ion bombardment during film growth (Budhani et al., 1984). Apart from silicon nitride, the PACVD technique has been used to deposit a wide range of other ceramic materials.

To avoid ion bombardment of the growing film in a parallel-plate PACVD process, a process modification has been introduced in which the substrates are placed away from the plasma. The technique is known as remote PACVD.

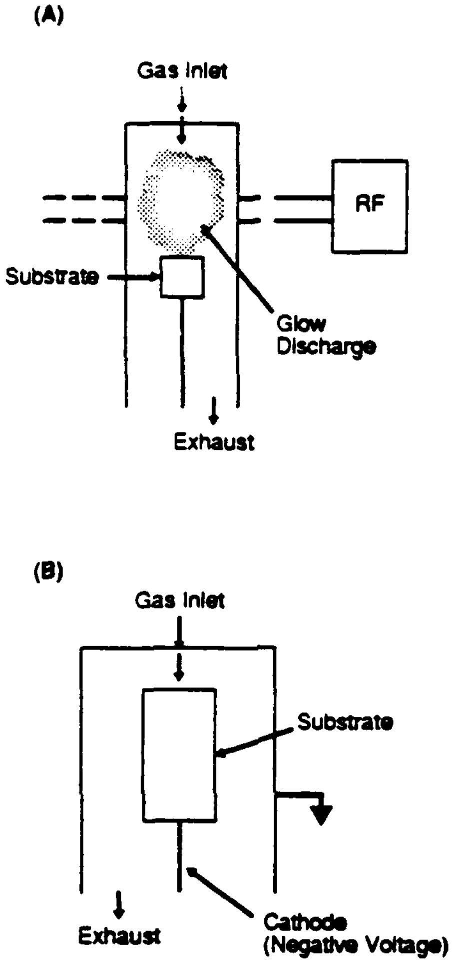

Figure 3-9 Schematic illustration of plasma-assisted CVD: (A) rf glow discharge, (B) dc glow discharge

Another technique now being investigated is laser-assisted CVD (LACVD), which may be carried out in two ways. In one use, the laser heats the substrate locally where deposition is desired, and, by controlling the general substrate temperature to below that where deposition occurs, selective growth of the depositing species can be achieved. Alternatively, the laser may be of a wavelength that excites one of the gaseous species causing reaction of that species; then, by shining the laser through the gas close to the substrate surface, deposition may be induced on the surface. A listing of some ceramic materials produced by CVD (also CCVD), with the deposition temperature and precursor molecules, is given in Table 3-3.

Microwave Electron Cyclotron Resonance Plasmas

In the past several years electron cyclotron resonance (ECR) plasmas have become increasingly attractive for semiconductor processing (Yamada and Torii, 1987). In addition, these plasmas may be used for deposition of SiO_2, Si_3N_4, and SiC (Ohki et al., 1988). Initially, they were used in ion

Table 3-3 Ceramic Materials Produced by CVD

Coating	Chemical Mixture	Deposition Temp. (°C)	Method	Application*
		CARBIDES		
TiC	$TiCl_4$-CH_4-H_2	900-1000	CCVD	wear
	$TiCl_4$-$CH_4(C_2H_2)$-H_2	400-600	PACVD	elec
HfC	$HfCl_x$-CH_4-H_2	900-1000	CCVD	wear, cor,ox
ZrC	$ZrCl_4$-CH_4-H_2	900-1000	CCVD	wear, cor,ox
	$ZrBr_4$-CH_4-H_2	>900	CCVD	wear, cox,ox
SiC	CH_3SiCl_3-H_2	1000-1400	CCVD	wear, cor,ox
	SiH_4-C_xH_y	200-500	PACVD	elec, cor
B_4C	BCl_3-CH_4-H_2	1200-1400	CCVD	wear
B_xC	B_2H_6-CH_4	400	PACVD	wear, elec, cor
W_2C	WF_6-CH_4-H_2	400-700	CCVD	wear
Cr_7C_3	$CrCl_2$-CH_4-H_2	1000-1200	CCVD	wear
Cr_3C_2	$Cr(CO)_6$-CH_4-H_2	1000-1200	CCVD	wear
TaC	$TaCl_5$-CH_4-H_2	1000-1200	CCVD	wear, elec
VC	VCl_2-CH_4-H_2	1000-1200	CCVD	wear
NbC	$NbCl_5$-CCl_4-H_2	1500-1900	CCVD	wear
		NITRIDES		
TiN	$TiCl_4$-N_2-H_2	900-1000	CCVD	wear
	$TiCl_4$-N_2-H_2	250-1000	PACVD	elec
HfN	$HfCl_x$-N_2-H_2	900-1000	CCVD	wear, cor,ox
	HfI_4-NH_4-H_2	>800	CCVD	wear, cor,ox
Si_3N_4	$SiCl_4$-NH_3-H_2	1000-1400	CCVD	wear, cor,ox
	SiH_4-NH_3-H_2	250-500	PACVD	elec, cor,ox
	SiH_4-N_2-H_2	300-400	PACVD	elec
BN	BCl_3-NH_3-H_2	1000-1400	CCVD	wear
	BCl_3-NH_3-H_2	25-1000	PACVD	elec
	$BH_3N(C_2H_5)_3$-Ar	25-1000	PACVD	elec
	$B_3N_3H_6$-Ar	400-700	CCVD	elec, wear
	BF_3-NH_3-H_2	1000-1300	CCVD	wear
	B_2H_6-NH_3-H_2	400-700	PACVD	elec
ZrN	$ZrCl_4$-N_2-H_2	1100-1200	CCVD	wear, cor,ox
	$ZrBr_4$-NH_3-H_2	>800	CCVD	wear, cor,ox
TaN	$TaCl_5$-N_2-H_2	800-1500	CCVD	wear
AlN	$AlCl_3$-NH_3-H_2	800-1200	CCVD	wear
	$AlBr_3$-NH_3-H_2	800-1200	CCVD	wear
	$AlBr_3$-NH_3-H_2	200-800	PACVD	elec, wear
	$Al(CH_3)_3$-NH_3-H_2	900-1100	CCVD	elec, wear
VN	VCl_4-N_2-H_2	900-1200	CCVD	wear
NbN	$NbCl_5$-N_2-H_2	900-1300	CCVD	wear, elec
		OXIDES		
Al_2O_3	$AlCl_3$-Co_2-H_2	900-1100	CCVD	wear, cor,ox
	$Al(CH_3)_3$-O_2	300-500	CCVD	elec, cor
	$Al[OCH(CH_3)_2]_3$-O_2	300-500	CCVD	elec, cor
	$Al(OC_2H_5)_3$-O_2	300-500	CCVD	elec, cor
SiO_2	SiH_4-CO_2-H_2	200-600	PACVD	elec, cor
	SiH_4-N_2O	200-600	PACVD	elec
TiO_2	$TiCl_4$-H_2O	800-1000	CCVD	wear, cor
	$TiCl_4$-O_2	25-700	PACVD	elec
	$Ti[OCH(CH_3)_2]_4$-O_2	25-700	PACVD	elec
ZrO_2	$ZrCl_4$-CO_2-H_2	900-1200	CCVD	wear, cor,ox
Ta_2O_5	$TaCl_5$-O_2-H_2	600-1000	CCVD	wear, cor,ox
Cr_2O_3	$Cr(CO)_6$-O_2	400-600	CCVD	wear
		BORIDES		
TiB_2	$TiCl_4$-BCl_3-H_2	800-1000	CCVD	wear, cor, elec
MoB	$MoCl_5$-BBr_3	1400-1600	CCVD	wear, cor
WB	WCl_6-BBr_3-H_2	1400-1600	CCVD	wear, cor
NbB_2	$NbCl_5$-BCl_3-H_2	900-1200	CCVD	wear, cor
TaB_2	$TaBr_5$-BBr_3	1200-1600	CCVD	wear, cor
ZrB_2	$ZrCl_4$-BCl_3-H_2	1000-1500	CCVD	wear, cor, elec
HfB_2	$HfCl_x$-BCl_3-H_2	1000-1600	CCVD	wear, cor

SOURCE: Stinton et al. (1988).

*elec, electronics; cor, corrosion-resistant coatings; wear, wear-resistant coatings; ox, oxidation-resistant coatings.

sources for nuclear fusion plasmas and particle beam physics, but work in Japan in the early 1980s demonstrated their promise for improved etching and deposition. There is now rapidly expanding research and development work on processing applications using ECR, and a growing number of commercial suppliers of ECR sources and systems can be found in the United States, Japan, and Western Europe.

Microwave ECR occurs when a plasma is excited by 2.45 GHz microwave radiation in a 875 gauss (G) magnetic field. Microwave energy is absorbed efficiently because the electron cyclotron frequency equals the microwave frequency. Electrons are confined by the magnetic field, leading to a high-density plasma (10^{10} to $10^{12}/\text{cm}^3$) and a high degree of dissociation of the molecular gases. This electron confinement enables stable ECR plasmas to be sustained at pressures from 10^{-3} to about 10^{-5} Torr (compared to diode plasmas requiring 0.1 Torr or magnetron plasmas requiring 0.01 Torr).

ECR systems appear to be well suited for the coming generations of single-wafer processing systems. High rates of etching and deposition result from high plasma density, higher than in conventional reactive ion etching (RIE) and plasma deposition systems. Excellent etch anisotropy is provided by low-pressure operation, and low material damage and high etch selectivity are obtainable because ions strike the wafer with low energy. Reactive gases are handled easily since there is no cathode or filament and source gases are utilized efficiently, providing economy and minimizing effluent to the environment. Because ECR works best at low pressures, it is well suited for integration with inherently ultrahigh vacuum processes such as MBE.

Among the disadvantages or complications of ECR processing are the intense UV radiation environment, which may damage devices; the effects of fringing magnetic fields on other equipment; safety concerns about microwave leakage; and the relatively high cost of equipment, including large vacuum pumps to handle high gas throughput at low pressure. Although uniformity over large wafers remains a concern, recent work has demonstrated improved uniformity by controlling the shape of the magnetic field with magnets on both sides of the wafer (e.g., Figure 3-10).

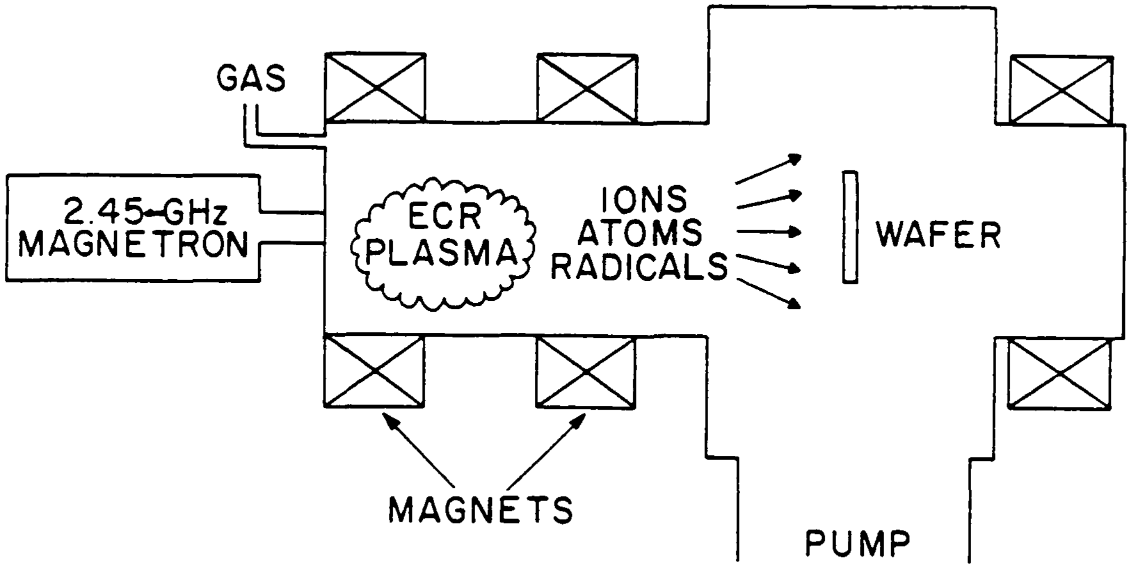

Figure 3-10 Schematic of a diverging-field ECR system.

At least three ECR source designs are now common: (1) diverging magnetic field systems, in which electrons stream from the source along magnetic field lines and low-energy ions are extracted by the resulting electric field. Ion energies from this source have been measured in the range of 50 eV and below. (2) Ion beam systems, in which a set of grids extract a beam of ions from the ECR plasma region. Operation of these systems is similar to that of conventional reactive ion beam etching (RIBE) systems. (3) Distributed ECR (DECR) systems, in which ECR regions are set up around the periphery of a chamber by microwave antennae that are positioned close to a multipolar set of magnets. The resulting ions and radicals diffuse to a wafer placed in the center of the chamber.

Many uses of ECR processing have been demonstrated successfully. Among the most successful are etching of Si and SiO_2 with fluorocarbons and etching of GaAs, AlGaAs, and InP with chlorine (Cl_2) and other chlorine-containing molecules. Radio frequency bias of the substrate was used in some of this work to provide independent control of ion energy. Dielectrics have been deposited at high rates, including, for example, deposition of SiO_2 from gas mixtures such as SiH_4 and O_2 and deposition of silicon nitride from SiH_4 and NH_3. Silicon has been grown epitaxially from SiH_4 below 650°C, after in situ surface cleaning by ion sputtering with ions from the same ECR source or by reaction with active species from a hydrogen (H_2) ECR plasma. Various metals have been deposited by using argon ions from an ECR plasma to sputter metals from targets arranged coaxially or in front of the ECR source.

Ion Beams

Ion beams are of particular interest from the point of view of attaining a fully integrated processing system. They are commonly used for processing semiconductor wafers and in some cases have already been integrated with other processing equipment. In addition, the technology is ideally suited for modifying surface properties of materials in a wide variety of applications, ranging from biomaterials to aerospace applications. For classification purposes, ion beams can be divided into the following three categories:

- Low-energy ion beams (below 1 KeV) are used mostly for modifying the interfaces of materials (e.g., for etching, changing the surface energy, improving the adhesion of a surface) and in many applications are accompanied by deposition or removal processes.

- Medium-energy ion beams (10 KeV to 1 MeV) are used for modifying surfaces and interfaces of metals, ceramics, and polymers. (This energy range also includes ion implantation, diagnostic procedures such as SIMS, and ion beam lithography.)

- High-energy (over 1 MeV) ions are used for the production of radionuclides for nuclear medicine, diagnostic monitoring in industrial applications, and characterization of surfaces (e.g., Rutherford backscattering).

Beams of practically any ion species can be created. The most common species for semiconductor applications are B, P, As, Sb, Ga, BF_3, Si, and Ge. For treatment of nonsemiconductors, the common species are N, C, Ti, Cr, P, Mo, Y, Ar, and Ta. For the production of radionuclides, the most common ions are light species such as H and He.

Energy Beams

Important characteristics and unique features of some beams as energy sources are reviewed briefly in this section, particularly lasers, electron beams, x-rays, electromagnetic induction, and microwaves. These discussions help in understanding how each is being applied or is being developed for manufacturing schemes.

Laser Beams

The features of lasers are sufficiently attractive and unique to merit explanation of their development as processing tools. Consider, for example, the following features: (1) lasers are intense sources of directed energy, (2) laser irradiation can be carried out in a variety of atmospheres, (3) lasers produce effects that are very localized in space and time, and (4) the motion of the laser beam relative to the workpiece can be easily automated. These features, along with the commercial development of reliable lasers suitable for the industrial environment, have led to their widespread use in manufacturing and materials processing (Duley, 1983).

The development of lasers as processing tools has created new opportunities for attaining fully integrated processing systems (Bass, 1983). Owing to the high-intensity characteristic of focused laser beams, their effects often require only short interaction times. Thus, substitution of a laser processing step for the slow processing step in a continuous flow or transfer station system may be an effective strategy for improving productivity. In contrast to electron beam processes, laser beam processes do not require a vacuum environment and can be carried out in a variety of reactive or protective atmospheres. The ease with which the motion of a laser beam can be controlled and automated facilitates its use in flexible manufacturing systems. The noncontacting characteristic of laser beams leaves clearance around the workpiece, where sensors can be placed for on-line inspection and process control.

Three important characteristics of lasers for use as tools in fully integrated processing systems are their spatial distribution of intensity, their temporal distribution of intensity, and their wavelength. The amount of energy deposited in a region per interval of time determines the temperature change and thus the effect on materials. The distribution of intensity in space and time also determines the degree of localization of the effect. The spatial distribution of intensity delivered by the laser depends on the mode of the laser; it can be highly localized with a three-dimensional Gaussian-type distribution (TEM_{00} mode) or more spread out with a "top-hat"-type distribution (TEM_{10} mode). The temporal distribution can be a continuous wave (cw) or pulsed, with a variety of wave shapes and duty cycles possible.

Lasers are monochromatic; the wavelength of a particular type of laser is perhaps the most important factor in selecting it for a particular application. Wavelength determines the extent to which laser energy is absorbed, transmitted, and reflected by a specific material. Since the laser is normally used as a heat source, the beam must be absorbed by the workpiece material. The wavelength also determines the materials used in the optical path and thus affects the ease and efficiency with which the beam can be brought to the workpiece. For a particular focal-length lens, the wavelength also determines the focused spot size of the laser beam and hence the average intensity and degree of resolution possible in a particular process. The lasers used most often in materials and manufacturing processes are the CO_2, Nd-YAG, and excimer lasers. Some of their characteristics are listed in Table 3-4.

Table 3-4 Laser Characteristics

Laser	Wavelength	cw or pulsed
CO_2	10.60 μm	cw or pulsed
Nd-YAG	1.60 μm	cw or pulsed
Excimer		
ArF	193 nm	pulsed
KrF	248 nm	pulsed
XeCl	308 nm	pulsed
XeF	351 nm	pulsed

Electron Beams

High-power electron beam (EB) sources have been used extensively in industry for vacuum melting, evaporation, welding, surface conditioning, and machining since the late 1950s; the initial applications were in welding and melting (Bakish, 1962; Bunshah and Cocca, 1968; Schiller et al., 1976). The electron beam is a very high efficiency energy source as compared to other sources such as lasers, radiation, and electromagnetic induction. The following advantages are identified:

- Heat can be applied to any defined area on the surface of the material to be heated.
- Extremely high power inputs can be concentrated into a very small area.
- Power density requirements vary for different applications, as shown below:

Application	Approximate Power Density Range (W/cm^2)
Annealing	10^2-10^3
Melting	10^3-10^5
Evaporation	10^4-10^7
Welding	10^6-10^8
Machining (metal removal)	up to 10^9

Note: By comparison, power densities of about 10^4 W/cm^2 and 10^5 W/cm^2 are available from the oxyacetylene flame and the electric arc, respectively. It should be noted that in most of the highest-current and high-power-density electron beam machines existing today, the power density is not space charge limited but is limited by the temperature of the cathode and the quality of the electron optics.

- No medium is needed to transfer energy from the source to the material to be treated, as, for example, in gas flames and electric arcs.
- Heating is carried out in high vacuum, thereby almost inherently providing a reasonably clean environment.

- If crucibles are used for containing the material being processed, in many cases they are made from water-cooled copper, thus avoiding contamination from the ceramic crucible material liner. In some cases, crucible liners of other materials are used.

- Conversion of electron energy to heat in the material being bombarded is very efficient.

- Power can be applied and controlled independent of melting rate (in contrast to consumable-electrode arc melting), which allows melting and superheating of the materials at a rate consistent with its impurity content to effect optimum refinement.

- Beam intensity, focus, shape, and position are controllable precisely and almost instantaneously, which makes programming an electron beam process, such as machining, straight forward.

A gun system must consist of at least two elements--a cathode and an anode. Additionally, there are electrostatic or electromagnetic systems to focus and scan the beam. A dual classification system is used for such sources:

- Classification I

  -- Work-accelerated, where the anode is the workpiece.
  -- Self-accelerated, where the anode is part of the gun structure and is located fairly close to the cathode. Electrons emitted by the cathode are accelerated by the potential difference between the cathode and the anode, pass through a hole in the anode and continue onward to strike the grounded workpiece.

- Classification II

  --Electrons are produced from the cathode by:

  - thermionic emission from metal surfaces
  - extraction from a localized or confined plasma.

Any combination of the above classifications is possible--for example, a work-accelerated plasma EB source, or a self-accelerated thermionic gun. Thermionic EB guns are further subdivided into the following types: close cathode, distant cathode, Pierce-type, and transverse linear cathode. Plasma EB guns are further classified into the following two types: cold cathode (Stauffer and Cocca, 1963) and hot hollow cathode (Morley, 1963).

Comparisons between thermionic and plasma EB guns can be made. A thermionic EB gun filament assembly must be kept at pressures less than 10^{-3} Torr to keep discharges to a minimum since very high voltages are used (3 to 200 kV). This requires a differentially pumped chamber with the beam extracted through a hole in the pressure-isolation wall. The beam power can go from very low (a few watts) to very high (up to 1.2 MW) power. Plasma EB guns do not operate at very high power levels but can be used at pressures up to 0.1 Torr, thus eliminating the need for a differentially pumped chamber.

Cathode erosion by sputtering caused by ion bombardment is common to all types of guns, thus becomes the lifetime-limiting factor. All guns, except the cold cathode gun, need or may benefit from beam focusing and deflection.

X-ray Lithography

As optical lithography moves into the 0.35-μm to 0.25 μm pattern size range, the limits of its capability are approached. X-ray lithography offers a high-throughput solution to the submicrometer pattern regime below this value. In addition, better resolution, reduced impact from particulates, and greater depth of focus are x-ray lithography's main features. However, the technology is complicated by a number of unsolved problems, including mask materials, resists, and x-ray sources.

A mask for x-ray lithography is a very thin membrane (less than 5 μm) of a low atomic number material with a high atomic number absorber material defining the pattern. This mask must be transparent to x-rays and flat with minimal distortion. Production-scale fabrication of masks is still more a goal than a reality. The resists for x-ray lithography also present difficulties for good resolution, sensitivity, and contrast, while still retaining resistance to dry etching. Resist development has resulted in significant progress, but considerably more is needed for moving the technology into manufacturing.

X-ray sources themselves have presented the most significant problem; x-ray tubes, lasers, plasma sources, and storage rings have been investigated. In Japan a number of x-ray lithography centers based on synchrotrons are under development. The brightest sources are the synchrotrons, which emit collimated beams--an advantage in minimizing the penumbral blur that occurs when uncollimated beams intersect mask structures and cast wider shadows on the target. These systems are, however, large and very expensive.

Synchrotrons can be integrated readily with the rest of the fabrication process, in that the beam lines connect it into the clean room where the remainder of the manufacturing occurs. Much of the focus today is on the development of more compact x-ray systems. In the United States, IBM stands out among chip manufacturers for aggressively pursuing next-generation x-ray technology. A compact synchrotron ring is being installed at IBM's East Fishkill (N.Y.) facility, which will be open for a fee to other U.S. chip manufacturers. It should be noted that a number of other lithographic techniques (e.g., E-beam, ion-beam, deep-UV) have been and are still being examined for fine-line pattern size applications and offer important alternatives in this area.

Microwave Beams

Microwave beams are not generally feasible power sources for use in normal processing schemes since the typical wavelengths (λ) of 30- to 100-GHz energy (wavelengths of 1 cm to 3 mm, respectively) would require optics with apertures of several feet to collimate a useful high-intensity energy beam. Microwave energy can be concentrated, however, in small waveguides and cavities of various sizes, and processing can be accomplished inside such waveguides and cavities. Typical rectangular waveguide cross-sections are approximately $\lambda/2$ by $\lambda/4$ (e.g., at 10 GHz a waveguide of about 1.3 by 2.5 cm and a cavity of about 5 to 7.5 cm wide and 7.5 cm high).

Microwave generators capable of intermittent high power have been available for about 50 years. Pulse powers of several megawatts can be generated by magnetrons developed for radar applications, but pulse lengths are short and average power is in the kilowatt range. For continuous power, klystrons and gyrotrons, developed for electronic countermeasures, heating, and communications, provide continuous power in the hundred kilowatt range at some frequencies. The major limitation in the development of higher-power devices is in the electron generation area, where hot cathode techniques are limited and the problem of removal of high thermal loads from the normal losses in high-power electron tube devices. High voltages in small geometries also present problems (Sutton, 1988).

Table 3-5 Selected Characteristics of Some Beam Deposition Processes

	Evaporation	Ion Plating	Sputtering	Chemical Vapor Deposition	Thermal Spraying
Mechanism of production of depositing series	Thermal energy	Thermal energy	Momentum transfer	Chemical reaction	From flames or plasmas
Deposition rate	Can be very high (up to 750,000 Å/min)	Can be very high (up to 250,000 Å/min)	Low except for pure metals (e.g. Cu-10,000 Å/min)	Moderate (200-2,500 Å/min)	Very high
Depositing specie	Atoms and ions	Atoms and ions	Atoms and ions	Atoms	Dropless
Throwing power for:					
a: Complex shaped object	Poor line-of-sight coverage except by gas scattering	Good; but non-uniform thickness distribution	Good; but non-uniform thickness distribution	Good	Poor
b: Into small blind holes	Poor	Poor	Poor	Limited	Very limited
Metal deposition	Yes	Yes	Yes	Yes	Yes
Alloy deposition	Yes	Yes	Yes	Yes	Yes
Refractory compound deposition	Yes	Yes	Yes	Yes	Yes
Energy of depositing species	Low ≃0.1 to 0.5 eV	Can be high (1-100 eV)	Can be high (1-100eV)	Can be high with plasma-aided CVD	Can be high
Bombardment of substrate/deposit by inert gas ions	Not normally	Yes	Yes or no depending on geometry	Possible	Yes
Growth Interface perturbation	Not normally	Yes	Yes	Yes (by rubbing)	No
Substrate heating (by external means)	Yes, normally	Yes or no	Not generally	Yes	Not normally

Source: Bunshah and Raghuram, 1972.

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4

BEAM APPLICATIONS IN MICROELECTRONICS

Several beam techniques have been incorporated or show promise of applicability in microelectronics manufacture. As a result, this highly competitive industry is one that is most likely to benefit early from the process integration discussed in this report. This chapter reviews important microelectronics applications of beam technologies and outlines uses of these technologies in semiconductor device manufacturing.

BEAM APPLICATIONS IN SEMICONDUCTOR DEVICE MANUFACTURE

Many of the well-developed and widely used applications of beam technologies are in the manufacture of semiconductor devices. The continuous need to produce smaller and more complex structures with higher quality and yield has provided the major emphasis for much of the development of sophisticated beam processes and beam processing equipment. Some of the applications of beam technologies in the fields of integrated circuit and optoelectronics fabrication are reviewed here to illustrate the capabilities and advantages of these technologies over previous manufacturing techniques.

Silicon Integrated Circuits

Although the manufacture of integrated circuits (ICs) is a very precise and complex process, only a few general types of operations are performed. These operations involve deposition, patterning, etching, cleaning, doping by ion implantation, oxidation, diffusion, and heat treatment. A typical sequence of steps is illustrated in Figure 4-1, a sequence performed many times to fabricate a complete circuit. The beam technologies used for the various operations are listed in Table 4-1. Specific examples of some uses of beam technologies are described in the sections that follow.

Beam Technologies for Materials Deposition

Continuous improvement in the speed and functionality of IC has been achieved by a dramatic reduction in the sizes of transistors and interconnection elements. Key to achieving this reduction has been the ability to improve the thickness and compositional uniformity of the metals, dielectrics, and semiconducting materials deposited on the substrate.

Over the past 10 years, sputtering has replaced evaporation as the technology of choice for depositing thin films of metal on IC. Sputtering offers advantages of better control of alloy composition, such as from an Al-Cu-Si alloy target, as well as in situ sputter etching, good thickness uniformity, and superior adhesion. In addition, deposition of refractory metals is generally achieved much better by sputtering than by evaporation.

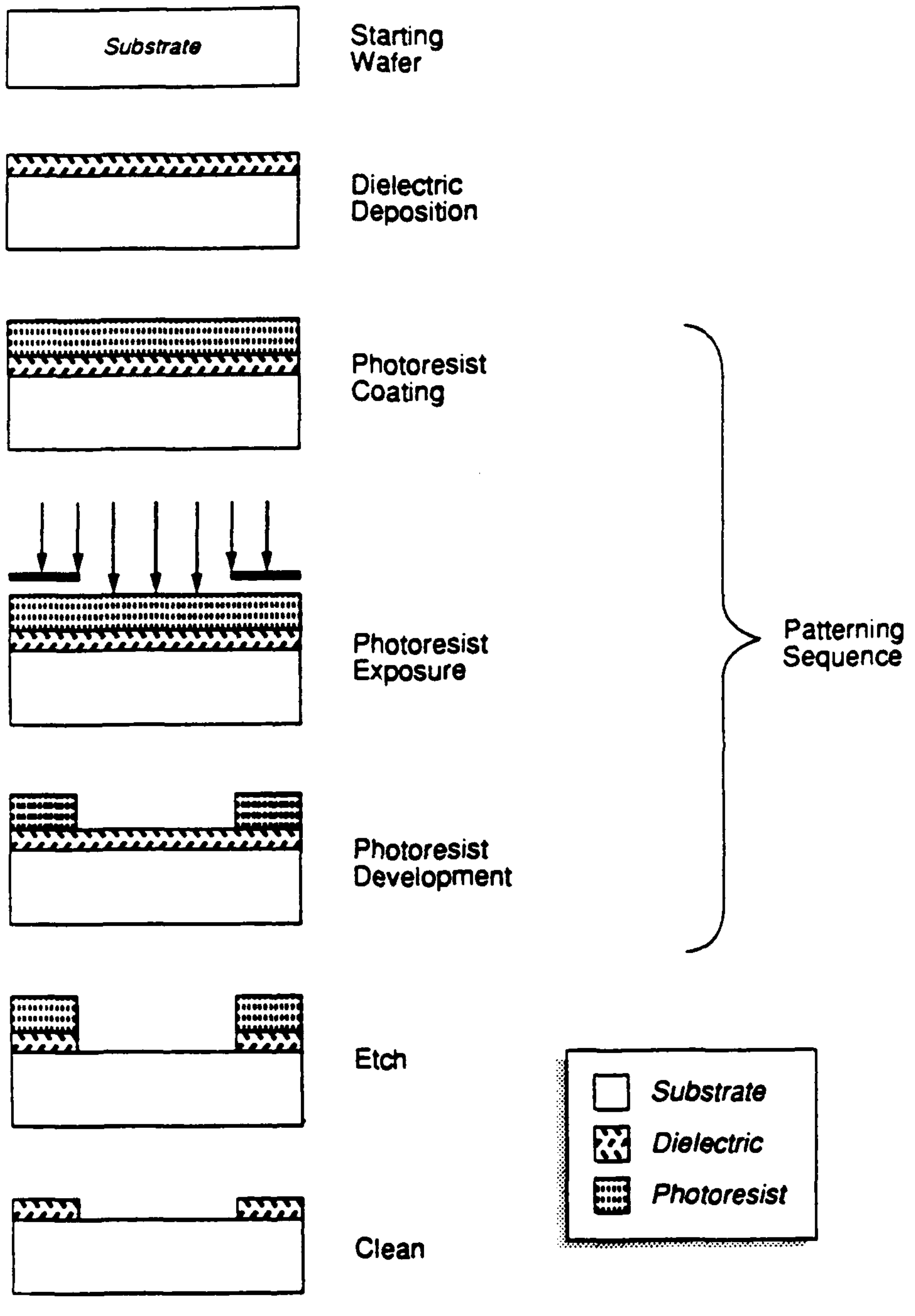


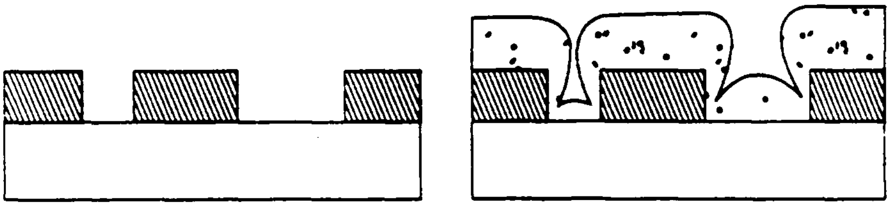
Figure 4-1 Typical IC processing sequence.

Table 4-1 Beam Applications in Silicon IC Manufacture

Deposition Technologies		Material	Uses
CVD		Si Epitaxy	Growing controlled layers of semiconductors
		Polysilicon	Gate electrodes, capacitor plates, interconnects, resistors
		SiO_2	Insulator, diffusion or implant mask
		Si_3N_4	Insulator, oxidation mask
		W	Via plugs, interconnects
PACVD		Silicon	TFTs, resistors, photovoltaics
		SiO_2	Insulator, diffusion or implant mask
		Si_3N_4	Insulator, oxidation mask, passivation
PVD		Al, Au	Interconnects
PAPVD		Al, Ti, W	Interconnects, barriers
		Ni-Cr, SiCrO, TaN	Resistors
		SiO_2	Insulator
		Si_3N_4	Insulator
		Silicon	TFTs, resistors, photovoltaics
Ion beam		B, P, As	Controlled semiconductor doping
Patterning Technologies			Uses (ultimate resolution)
X-ray			Masked resist exposure, feature size of ≤ 0.1 µm
FIB			Direct deposition or etching, feature size of ≤ 0.1 µm
Optical			Masked photoresist exposure, feature size of ≤ 0.25 µm
e-beam			Direct write resist exposure, feature size of ≤ 0.1 µm
Etching Technologies	Etching Gas	Material	Uses
Plasma etching	C_2F_6	SiO_2	Diffusion and implant windows, vias
	CF_4/SF_6	Si_3N_4	Diffusion and oxidation windows
	CF_4/SF_6	Silicon	Trench isolation, polysilicon interconnect
	Cl_2/BCl_3	Aluminum	Metal interconnect
	CF_4/SF_6	Tungsten	Metal interconnect
Plasma etching, unpatterned	C_2F_6	SiO_2	Spacers, planarization
	CF_4	Si_3N_4	Masking layer removal
	CF_4	Polysilicon	Storage capacitors, three-dimensional structures
	CF_4/SF_6	Tungsten	Via plugs
Sputter etching	Ar	Any	Cleaning, surface layer removal
Cleaning Technologies			
Sputtering	Ar	Any	Surface cleaning prior to deposition
O_2	O_2	Photoresist	Photoresist removal and surface cleaning
H_2 plasma	H_2	SiO_2	Surface cleaning prior to epitaxy

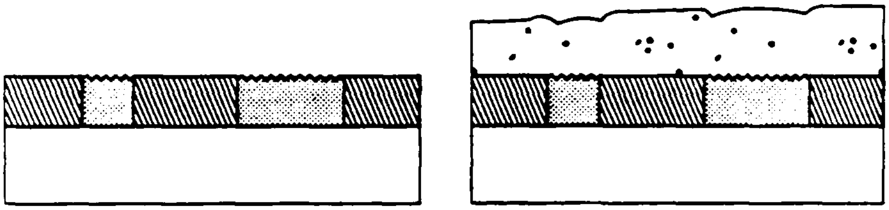
Low-pressure chemical vapor deposition (LPCVD) is another major technological improvement of the past [illegible] years. By reducing the deposition pressure to the 1- to 10-Torr range, significant improvements in film quality, cleanliness, and uniformity have been achieved for dielectric and polysilicon depositions. Thickness uniformities of 2 to 3 percent are routinely achieved by batch LPCVD systems. The ability of LPCVD to uniformly and conformally cover very large aspect ratio features has been a major contributor to the ability to manufacture megabit random access memories (RAMs). Selective LPCVD of tungsten shows great promise for improving the reliability of IC interconnections and for increasing their performance (Bertagnolli et al., 1988; Kaanta et al., 1988). Figure 4-2 illustrates interconnect cross-sections with and without tungsten via plugs. An extension of the via-fill method has been used to form a fully planarized refractory metal interconnect scheme (Thomas et al., 1988).

Ion implantation has replaced diffusion for almost all semiconductor doping process steps. It allows controlled impurity profiles and dopant concentrations to better than ±3 percent. The resulting implant doping profiles are not as dependent on temperature and solid solubility as are diffusion doping profiles. Implantation also allows a major reduction of the thermal budget for temperature-sensitive process steps and permits buried-layer profiles, which cannot be readily accomplished with thermal diffusion.



(a) Via Pattern

(b) Typical Step Coverage



(c) Selectively Filled Vias

(d) Via Fill Step Coverage

Figure 4-2 Metal step coverage improvement by selective via filling using LPCVD.

Beam Technologies for Patterning

Essentially all of the patterning of silicon ICs is performed by optical lithography, with an optical step-and-repeat lithography sequence being the technology of choice for advanced circuit fabrication. As feature sizes are reduced, the limits of optical lithography will be reached. Electron beam (EB) lithography is used currently in some circuit designs for defining small features and also in some small-volume commercial applications. Because of its high resolution, EB pattern generation is the technology of choice for producing complex optical and x-ray photomasks. Improved EB capabilities or perhaps use of ion beam writing systems will be required to produce the x-ray masks of the future. Because serial EB is slow, its application to conventional IC production is very limited.

An apparent successor to optical lithography is x-ray lithography. Present research demonstrates that existing x-ray technology can achieve 0.1-μm lithographic features. Although many technical problems remain, the capabilities and costs of production-type x-ray equipment are well enough understood that several industrial and university groups are building or using synchotron x-ray sources to develop IC fabrication processes (Warlaumont, 1989). Electron and ion beams, both focussed and masked, have merit in overcoming some of these lithography problems.

Beam Technologies for Etching

Fine-geometry circuit elements have been made possible by major advances in dry etching. All present methods for dry etching depend on the use of a plasma to generate chemically active radicals in the low-pressure gas ambient. This provides the unique capability to etch highly anisotropically, which allows preparation of much smaller feature dimensions and gives the ability to create three-dimensional structures. The combination of LPCVD deposition and anisotropic etching has led to recent increases in dynamic RAM (DRAM) density (Ema et al., 1988; Shen et al., 1989). The anisotropic capability of dry etching also allows fabrication of several key features in IC circuits, as shown in Figures 4-3 through Figure 4-5.

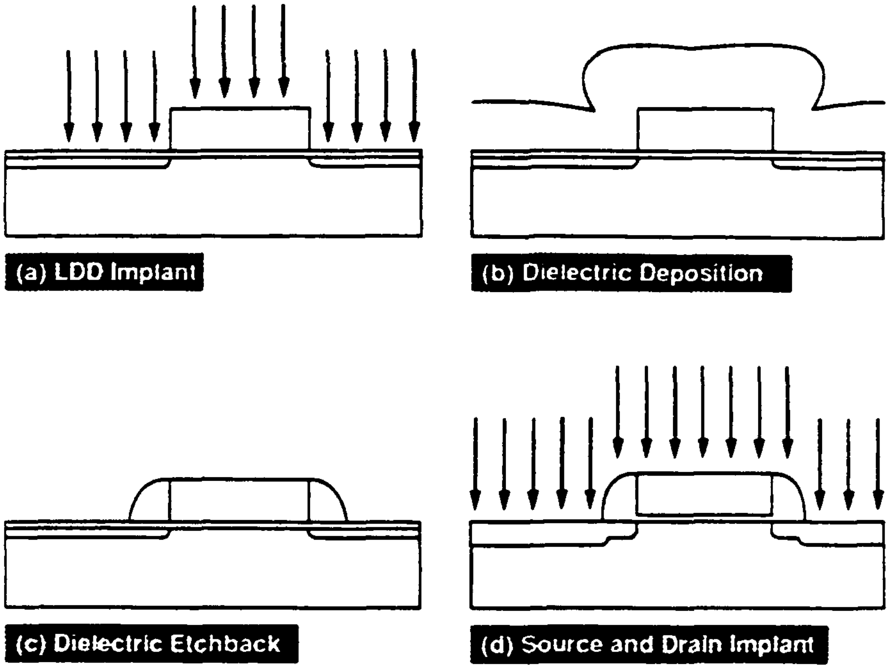
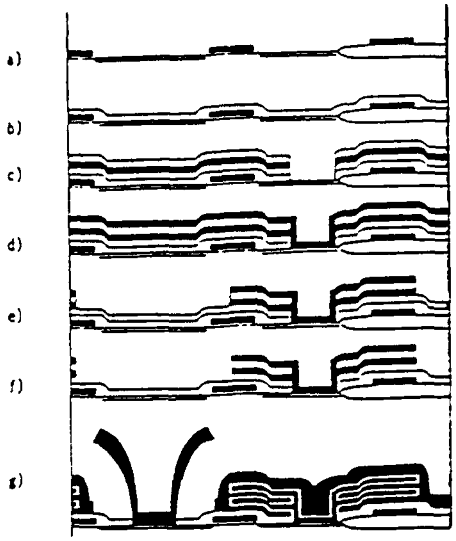


Figure 4-3 Schematic of a spacer-protected metal-oxide semiconductor (MOS) transistor formation.



(a) transister formation; (b) SiN deposition; (c) SiO_2, polysilicon, SiO_2 deposition; and contact hole formation; (d) polysilicon deposition; (e) storage electrode patterning; (f) SiO_2 removal by hydrofluoric acid solution; (g) capacitor film growth, polysilicon deposition, cell plate, and bit line formation. No extra mask process is necessary to form fin structure; the number of fins can be easily changed.

Figure 4-4 Schematic of a stacked "fin" capacitor formation process.

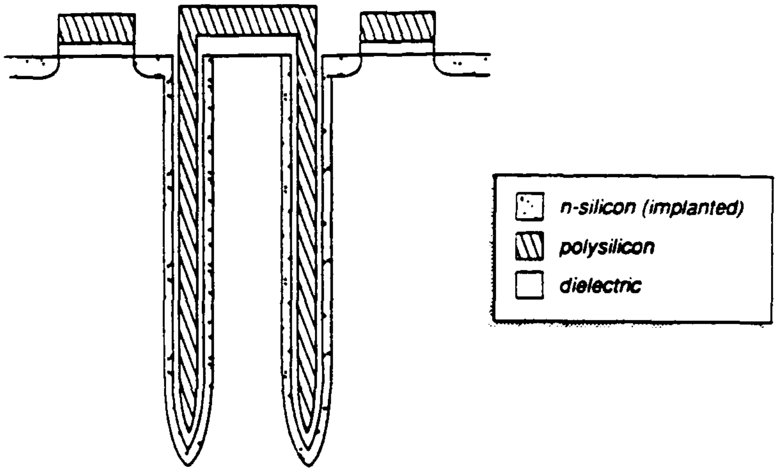


Figure 4-5 Schematic trench-capacitor cell structure.

BEAM TECHNOLOGIES FOR COMPOUND SEMICONDUCTOR ICs

Most of the processing technologies used for compound semiconductor IC fabrication are identical to those used for silicon ICs. Newer device structures, such as heterojunction field effect transistors (HFETs) and heterojunction bipolar transistors (HBTs), depend heavily on metal-organic chemical vapor deposition (MOCVD) and MBE beam technologies to create highly uniform, precisely controlled epitaxial layers of different materials (Asbeck et al., 1987; Ng et al., 1989). Table 4-2 describes additional beam technologies that are applied to the fabrication of compound semiconductor ICs.

Table 4-2 Beam Applications for Compound Semiconductor IC Processing

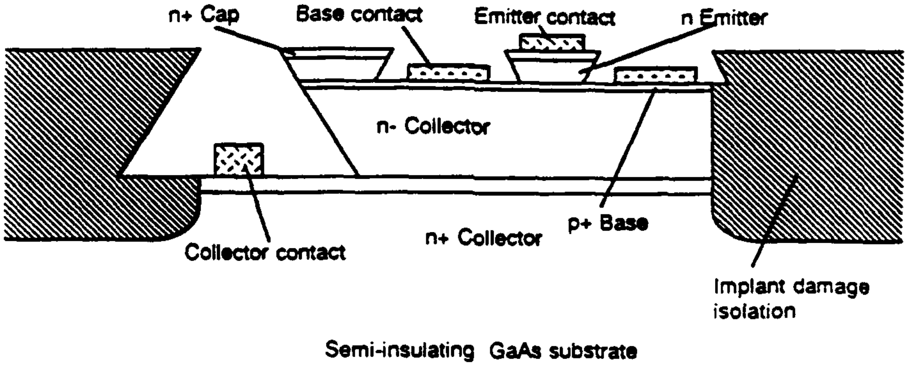
Deposition Technologies		Material	Uses
MOCVD		GaAs	Buffer layers, FET channels
MBE		AlGaAs	Super lattice buffers, heterojunction transistors
		InGaAs	Heterojunction transistors, contacts
		InAlAs	Heterojunction transistors, contacts
Etching Technologies	Etching Gas	Material	Uses
Plasma etching	Cl_2	GaAs	Selective material removal, backside vias
Ion milling	Ar	Gold	Interconnect etching
Heating	Ambient		Uses
Rapid optical anneal	Ar, AsH_3, N_2		Implant activation, contact formation

The two highly precise growth technologies, developed to prepare epitaxial layers of compound semiconductor with the extremely precise control of stoichiometry, doping, and thickness required for high-performance devices, are MBE and MOCVD. Figure 4-6 shows two of these complex structures.

Material	Mole fraction	Car. dens.	Thickness
i InAlAs	.52/.48		4000Å
n InAlAs	.52/.48	3E16	200Å
i InAiAs	.52/.48		100Å
i InGaAs	.65/.35		150Å
i InAlAs	.52/.48		100Å
n InAlAs	.52/.48	3E18	100Å
i InAlAs	.52/.48		3000Å
i InAlAs/InGaAs Superlattice			

Semi-insulating InP Substrate

A. Layering sequence in a InAlAs-GaAs high electron mobility transistor (*HEMT*).



Layering Sequence Component	Material	Car. dens.	Thickness
n+ cap	GaAs	1E19	500Å
n emitter	AlGaAs 25%	5E17	2000Å
p+ base	GaAs	1E19	700Å
n- collector	GaAs	3E16	7000Å
n+ subcollector	GaAs	5E18	6000Å

B. Layering sequence in a GaAs-AlGaAs heterojunction bipolar transistor (HBT).

Figure 4-6 Illustration of complex transistor structures.

Beam Technologies for Heating

The abrupt interfaces and bandgap engineering necessary to produce heterostructure devices must be preserved during device processing. Prolonged high-temperature annealing will cause layer mixing and loss of interface abruptness. To minimize these problems, rapid thermal annealing is often used to activate the implants of heterostructure devices. Heat-up and cool-down times of a few seconds are accomplished by optical heating of the substrate with large banks of high-intensity lamps. The same technique is often applied to form ohmic contacts to GaAs and to Si ICs when the thermal budget is tight.

OPTOELECTRONICS

Processing techniques to fabricate optoelectronic components are similar to those used to fabricate heterojunction compound semiconductor devices. GaAs-AlGaAs heterojunction layers have been in use for over 20 years. In the past most such devices were fabricated by liquid-phase epitaxy or chloride-transport vapor-phase epitaxy. Today, MBE and MOCVD techniques provide the capability to fabricate higher-performance yet more complex devices that use superlattices and quantum-well confinement. These may contain integrated devices employing both GaAs and InP semiconductors.

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5

BEAM APPLICATIONS IN ENGINEERED MATERIALS

The application of beam technologies to produce new materials and components, other than microelectronics, is not a new development. This chapter reviews the function of beams in the development of coatings and surface modification and the formation of net shapes, composites, nanophases, and optical surfaces, including treatment of polymeric substrates. New exotic developments in beam processing of materials and some applications for beam technologies also are examined.

COATINGS

Metal, alloy, and ceramic coatings onto metal, alloy, ceramic, or polymer substrates of various sizes and shapes have been extensively developed and used in the past 30 years. They cover a wide spectrum of applications as summarized in Table 5-1, which lists specific materials and processing methods employed. The techniques used to prepare these materials are classified into two main groups, physical vapor deposition (PVD) and chemical vapor deposition (CVD). These techniques and their applications were discussed previously in Chapter 3.

Diamond, Diamond-like Carbon, and Cubic Boron Nitride Coatings

Considerable interest has been aroused in the synthesis of diamond films because of their potential applications in microelectronics, optics, and tribology (Spear, 1989). Synthesis of diamond films by a variety of CVD, PACVD, and PVD techniques has been reported. Applications of these coatings have been limited by the inability to deposit films with smooth surface morphology and with desired optical and electrical properties at acceptable deposition rates, and at deposition temperatures low enough to be compatible with ultraviolet (UV) and infrared (IR) materials or with other process steps employed in microelectronics.

Some characteristic properties of individual carbon phases are compared in Table 5-2. The type of film deposited depends on the deposition technique. Table 5-3 lists some potential applications of diamond and diamond-like carbon (DLC) films along with the properties required for each application. Single-crystal diamond films have application for microelectronic and optoelectronic devices. Their high thermal conductivity makes them a candidate for heat sinks, and their electronic properties make them a candidate material for high-power microwave- and millimeter-wave devices and as heat sinks for various high-power devices. Moreover, their large bandgap (about 5.45 eV) can be used to make a variety of UV detectors, and their high resistivity makes possible low-noise UV detectors. Finally, because of their high hardness, there is great interest in tribological applications, such as cutting tools, except for the cutting of steel, where solution of the carbon into the steel can occur. In 1991, several companies have put on the market diamond-coated cutting tools for machining aluminum alloys and polymer-based composites.

Table 5-1 Coatings, Depositing Methods, and Applications of Various Beam-Prepared Materials

Applications	Materials	Processes
Decorative:	Al	Evaporation
on textile fibers, watches, bezels, eyeglass	TiN, Ti(C,N), Cr_3C_2, Cr_3N_2	PAPVD PAPVD
Wear-resistant coatings on cutting tools, dies, punches:		
Cement carbide substrates	TiC, TiN, Al_2O_3	CVD
	Multilayers	PACVD (pilot plant)
High-speed steel, die steel substrates	TiN, Ti(C,N), Ti, Al, N, TiC	PAPVD using electron beam, cathodic arc, and sputtering sources
Corrosion-resistant coatings:		PVD
Steel strip	Al, Zn, Sn, Cr_3N_2	High-rate electron beam evaporation
	Zn	Resistance-heated source
Steel fasteners, aircraft parts, etc.	Al	PAPVD using resistance-heated evaporation sources
High-temperature oxidation and corrosion resistance of turbine materials	Ni-Co-Cr-Al-Y, Co-Cr-Al-Y, Ni-Cr-Al-Y,	Electron beam evaporation
	Al	CVD
Magnetic media on tape	Fe, Co, oxides	Evaporation, sputtering, oblique incidence evaporation
Heat barriers and moisture barrier coatings on polymeric films	Al	Electron beam evaporation in a continuous or semicontinuous film
Optical coatings on polymeric film	Various metals, oxides, multilayers	Sputter deposition
Optical coatings on components such as lenses	MgF_2, oxides	Electron beam evaporation, sputter deposition
Optical coatings on glass mirrors, head lamps	Al, Ag	Evaporation, sputter deposition
Photovoltaic solar cells	a-Si:H	PACVD

Table 5-2 Properties of Diamond, Diamond-Like Carbon, and Graphite

	Diamond	DLC	Graphite
Crystal structure	Cubic 3.567	Amorphous with small-crystal regions mixed with sp^2 and sp^3 bonds[a]	Hexagonal a = 2.47 c = 6.79[d]
Density (g/cm^3)	3.51	1.8-2.0	2.26
Chemical stability	Inert, inorganic acids	Inert, inorganic solvents, acids	Inert, organic acids
Hardness (vickers, kg/mm^2)	7,000-10,000+	900-3,000	--
Thermal conductivity (cal-cm/cm^2-sec°C)	20 at 20°C	--	30-40 $(\parallel_c)$,[b] 1-2 $(\perp_c)$[c]
Optical Properties			
Refractive index (n)	2.42	1.8-2.2	2.15 $(\parallel_c)$,[b] 1.8 $(\perp_c)$[c]
Transparency	UV-VIS-IR	VIS-IR	Opaque
Optical gap (eV)	5.5	2.0-3.0	--
Electrical Properties			
Resistivity (Ω-cm)	$>10^{16}$	10^{10}-10^{13}	0.4 $(\parallel_c)$,[b] 0.20 $(\perp_c)$[c]
Dielectric constant (ε′)	5.7	4-9	2.6 $(\parallel_c)$,[b] 3.28 $(\perp_c)$[c]
Dielectric strength (V/cm)	$>10^{12}$	10^6-10^{10}	--

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[a] electronic orbital configuration of the carbon atom

[b] parallel to the "c" axis of the crystal

[c] perpendicular to the "c" axis of the crystal

[d] crystal lattice dimensions in the two axis directions, in Å units

Table 5-3 Applications of Diamond and Diamond-Like Carbon Films

Application	Property Requirement	Type of Coating That Could be Used
Decorative coatings	Hard, transparent in visible range of the spectrum	Diamond-like (DLC), small-grain polycrystalline diamond films or DLC and diamond composite coatings
<u>Tribology</u>		
Wear-resistant coatings for cutting tools	Hard, corrosion resistant, wear resistant and chemically inert	Same as above
Impact-resistant coatings for cutting tools	Very thin films (100 Å) with high hardness, corrosion resistance, and chemical inertness	Same as above
<u>Optics</u>		
Protective coatings for IR optics	Hard, corrosion resistant, chemically inert, transparent in IR region	Same as above
Antireflection	Same as above and refractive index coatings for Ge	DLC coatings of about 2.0
Protective layer for solar cells used in space	Low radiation damage, transparent in visible range of the spectrum	DLC, polydiamond, or composite DLC and diamond
X-ray windows	Self-standing film with high transmission and low damage threshold for x-rays, smooth surface topography	Fine-grained polycrystalline diamond film
<u>Electronic and Optoelectronic</u>		
Protective layer for electronic devices,	Hard, chemically inert, corrosion resistant, insulating high breakdown voltage	DLC, polydiamond, or composite of DLC and diamond
Heat sinks for high-power devices	Same as above and very high thermal conductivity	Polycrystalline diamond
Printed circuit boards	Same as above	Polycrystalline diamond
Lasers, UV sensors, etc.	Same as above and with stringent requirements on optical bandgap, defect states, surface topography, etc.	Large-grain polycrystalline and single crystal-diamond, doped diamond
Transistors, high-power devices, IMPATT devices, etc.	Same as above, together with stringent requirements on resistivity, dielectric constant, coefficient of thermal expansion, mobility, carrier concentration, etc.	Single-crystal diamond (preferably epitaxial diamond) and doped diamond films

Diamond films have been prepared by CVD, PACVD, and ion beam deposition techniques. CVD techniques used for the synthesis of diamond films are the chemical transport method, hot-filament thermal CVD techniques, electron-assisted CVD, and flame torch methods. It appears that independent and accurate control of atomic hydrogen in the process environment is key to the deposition of good-quality diamond films. PACVD techniques (with dc, rf, or microwave excitation) have been widely used for the synthesis of diamond and diamond-like carbon coatings. In addition, ion-beam-assisted and low-temperature ARE have been used to prepare diamond films. Recently, small-area diamond single-crystal films have been prepared on a copper substrate that have potential use for microelectronic applications (Narayan et al., 1991).

Diamond-like carbon produced by sputter deposition is principally used as a wear-resistant coating for magnetic disks. Some varieties of also are used for coating polymeric eyeglass lenses for abrasion resistance.

Cubic boron nitride (CBN), like diamond, is a metastable material at ambient temperatures and pressures. It possesses an attractive combination of properties similar to diamond--high thermal conductivity, high electrical resistivity, very high hardness, chemical inertness, transparency over a wide range of wavelengths, from UV through the visible into the IR, and has a large bandgap.

Synthesis of CBN films can be accomplished by various CVD, PACVD, and PAPVD techniques, at deposition temperatures from ambient to 1000°C, depending on the process used. Almost all the reactant species used in CBN synthesis are either toxic or explosive. To avoid this problem, a unique process has been developed using the reaction between nontoxic boric acid and ammonia in a PAPVD process to deposit CBN films at temperatures as low as 400°C. Unlike diamond films, there is no difficulty in nucleating the material on a variety of substrates. Various applications in tribology, optoelectronics, and microelectronics have been studied. CBN is a very potent competitor to diamond films, and the state of development is considerably advanced. Unfortunately, it lacks the mystique associated with diamond.

SURFACE MODIFICATION

Two beam techniques are predominant in surface modification of materials; ion implantation and laser treatment. Ion implantation is presently used in a limited but demanding number of high-technology, high-precision, and high-value-added, critical-use applications. The main advantages of ion implantation (Sioshansi, 1989) are flexibility in that any element can be introduced into any substance; no thermodynamic constraints exist, such as the requirement of an elevated temperature for diffusion or initiation of a chemical reaction; no refinishing or reheat-treating of the part is required, since the ion implantation can be performed at or near room temperature; no noticeable change occurs in the dimensional integrity of the part, no shape distortion, and no need for final finishing or polishing of the components; and no discrete interface is produced that can fail, since the ions penetrate into the original surface.

The main application of ion implantation to date has been in the treatment of metals. However, in recent years there has been significant interest in the treatment of ceramic and polymer substrates by ion implantation. Table 5-4 shows the variety of materials treated by ion implantation and lists the properties influenced by the process. Many of these have been reviewed recently by Smidt (1990a,b).

Table 5-4 Materials Modified by Ion Implantation

Material	Properties Influenced	Benefits
Metals	Hardness, hard-phase precipitates	Wear resistance
	Compressive stress, amorphization	Low friction, fatigue resistance
	Alloy formation, metastable-phase formation	Corrosion resistance, oxidation resistance
Ceramics	Compressive stress, amorphization	Improved fracture resistance; fatigue resistance
Polymers	Cross-linking, carbon-carbon bonds, densification	Increased wear and scratch resistance, increased electrical conductivity

Source: Sioshansi, 1988.

There are numerous applications in which ion implantation has been tested in fields ranging from aerospace to biomaterials. Table 5-5 lists some successful ion implantation applications. There are many new applications where ion implantation is currently under investigation. These are mainly in areas of changing the optical properties of materials, influencing catalysis of surfaces, creating new magnetic alloys, improving adhesion properties of surfaces, and, finally, improving biocompatibility of materials. These applications are expected to have a significant impact on future trends in surface-engineered components.

Laser treatment, since it can be employed in atmosphere or nonvacuum ambients, offers greater flexibility for modifying large, irregular surfaces. Laser beams are being used to harden metal surfaces, and they provide corrosion resistance. In addition, selective etching using lasers is in fairly widespread use (e.g., as a marking tool). Laser welding also is finding application but on a limited basis. The ease of implementing lasers, compared to ion beams, makes this approach particularly suitable for integrated manufacturing.

APPLICATIONS OF LASERS TO MATERIALS FORMING

The unique features of lasers have led to their use in a variety of shaping operations, including the removal (Copley, 1986) and deposition of materials (Deitz, 1990). They are routinely used for hole drilling and cutting sheets (Steen and Kamalu, 1983) and show promise for use in turning and milling operations (Copley, 1985). Lasers also can be used to build up shapes through processes such as solidification (Breinan et al., 1980), sintering (Deckard and Beaman, 1989), polymerization (Hull, 1986), and in CVD (Osgood et al., 1983). They have been used

Table 5-5 Some Successful Ion Implantation Applications

Ion Species	Material	Problem	Applications	Status
Ti+C	Ferrous alloys	Wear	Bearings, gears	Production valves, dies
Cr	Ferrous alloys	Corrosion	Surgical tools	
Ta+C	Ferrous alloys	Scuffing wear	Gears	Pilot production
P	Stainless steels	Corrosions	Marine products, chemical processing	Research
C, N	Ti alloys	Wear, corrosion	Orthopedic prostheses, aerospace components	Production
N	Al alloys	Wear, mold release	Rubber and polymer molds	Preproduction evaluation
Mo	Al alloys	Corrosion	Aerospace, marine	Research
N	Zirconium alloys	Hardness, wear, corrosion	Nuclear reactor Chemical processing	Production
N	Hard chrome plate	Hardness	Valve seats, godets, travellers	Pilot production
Y, Ce, Al	Superalloys	Oxidation	Turbine blades	Research
Ti+C	Superalloys	Wear	Spinnerettes	Preproduction evaluation
Cr	Cu alloys	Corrosion	Battery technology	Research
B	Be alloys	Wear	Bearings	Pilot production
N	WC+Co	Wear	Tool inserts, PC board drills	Pilot production
N, Al, Ti, etc.	Ceramics	Oxidation, wear, toughness	Adiabatic engines turbine parts	Research
Ar, N, etc.	Polymers	Conductivity	Microelectronics	Research
Ti, Al, etc.	Polymers	Mechanical properties	Aerospace automotive	Research

Source: Sioshansi, 1987

routinely to build up shapes by welding (Mazumder, 1983) and soldering. The advantages in carrying out any of these processes with a laser in an integrated processing system are short interaction times, the atmosphere may be varied, a high degree of flexibility, and ease of on-line inspection and process control.

Shaping and Removal

Important issues with respect to many material removal processes are the roughness and cleanliness of the machined surface, the material removal rate, and the strength and toughness of the laser-machined article. These issues, along with those related to process integration, are discussed in this section.

Hole drilling and sheet cutting with lasers have proven to be commercially viable processes. In fact, on a dollar basis, sheet metal cutting accounts for the largest fraction of CO_2 laser sales. In this application, laser cutting provides an economical alternative to a punch and die for cutting nonstandard shapes in small to moderate size batches. Creating a computerized numerical control program for laser cutting is a much less expensive step than fabricating a punch and die set for press work. Nevertheless, the use of laser cutting in combination with a punch and die to handle standard shapes has proven to be a cost-effective, flexible approach to sheet metal cutting. Both operations are now routinely carried out in series in continuous flow and transfer station systems. Material is removed by melting the substrate and blowing the melt away with an inert gas jet. In some cases a reactive gas jet is used (e.g., oxygen for cutting steel or titanium), where some of the metal burns, and the enthalpy of the oxidation reaction adds to the energy provided by the laser to melt additional material. Excellent edge quality is attained, so that the need for subsequent deburring operations is often eliminated. Because of the speed of the cutting, there is little time for heat transfer to the workpiece, so the heat-affected zone is normally very small.

Advantages of laser hole drilling include the capability of drilling fine holes with high aspect ratios, no machining forces are introduced, applicability to a wide range of materials, and adaptability to numerical control. Laser-drilled holes tend to be tapered, and resolidified material, vapor-deposited residues, and (in polymeric materials) charred regions are often observed. Nevertheless, laser hole drilling has been used successfully in a wide variety of applications, including drilling fine holes in diamond dies (e.g., with a ruby laser), cooling holes in nickel-base superalloy turbine blades, perforation of cigarette paper for use with low-tar and low-nicotine filters, and holes in baby bottle nipples. Truly remarkable results have been attained in machining polymeric and organic materials with excimer lasers. A high degree of spatial resolution and excellent surfaces can be attained, even to such accomplishments as holes drilled in a human hair (Znotins et al., 1987).

Laser-assisted machining, a form of hot machining, has been used in turning hard-to-machine metallic alloys. In this process the laser heats the material in front of the cutting tool, thereby improving its machinability. Under force-limited cutting conditions, for example, a factor of two increase in material removal rate, without increase in cutting force, has been reported for difficult-to-machine turbine materials, such as Inconel 718 and Ti-6Al-4V.

Lasers have also been used to shape hard ceramic materials by ablation. In Si_3N_4, for example, high material removal rates (1 cm^3 in 200 sec) and smooth surfaces (3-μm arithmetic average surface roughness) have been reported for a moderate incident power of 560 W and a scan speed of 240 cm/sec (Wallace and Copley, 1989). Although laser machining causes some loss of strength, it has been shown that this loss can be completely recovered by an inexpensive etching treatment (Tao et al., 1989). In some cases, reactive gases have been used in conjunction with laser ablation to help remove the reaction products, a process called laser-assisted chemical etching.

Desktop Deposition

There has been considerable interest recently in the concept of "desktop" manufacturing, which permits production of a three-dimensional shape in two steps. The first step involves positioning a computer graphics rendering of the shape with respect to coordinate axis and sectioning the shape into thin layers. The second step converts the shape of each layer to a set of instructions that are communicated to a laser that scans a surface so as to reproduce the layer. In one version of this process, the layer is reproduced by selective polymerization by the laser of a layer of liquid resin. In another version the layer is reproduced by selective sintering by the laser of a layer of plastic or wax powder. So far, desktop manufacturing has been mostly applied to plastics and waxes, with considerable success in attaining smooth surfaces and good shape definition (Deitz, 1990). The technique has found application in prototyping and modeling with considerable interest in applying the technique to form waxes for prototype investment castings (ASM International, 1990). There is a possibility that the technique could be extended to structural materials through application of other processes, such as sintering, melting, and laser chemical vapor deposition (LCVD).

Joining

Lasers have been used with considerable success to produce autogeneous weldments and hard facing and for soldering. The laser's characteristic short interaction times have the beneficial effect of limiting undesirable reactions in the joining of dissimilar metals.

POWDER PREPARATION

The increasingly stringent requirements on structural and electronic ceramics often cannot be met using traditional mechanically reduced powders. In addition, the increased prominence of covalently bonded ceramics (e.g., SiC and Si_3N_4) has increased the requirements for nonconventional, highly sinterable powders. The improved powders should include the following characteristics (Bowen, 1980): small particle size, freedom from agglomeration, narrow size range, spherical shape, and highly controlled purity. Such powders can be produced either by liquid (e.g., sol-gel), solid (e.g., decomposition of salts such as carbonates), or vapor-phase techniques. The common theme in all these techniques is that the powders are built up or synthesized rather than broken down or comminuted. The vapor-phase techniques, in general, can be categorized as beam processes and will be considered briefly below.

Vapor-phase techniques for powder processing have been described in a number of recent papers (Kato, 1987; Rice, 1987; Marra and Haggerty, 1987). These techniques have a number of potential advantages for the production of closely controlled powders, such as high purity of the product because of the high-purity gaseous reactants, loosely agglomerated powders because of the highly diluted reaction, ultrafine powders with narrow size distributions, and versatility for producing a wide variety of powders, including metals as well as oxide and nonoxide ceramics. In laser processing the gas is heated directly by coupling the emitted photons with the absorption lines of the reactant gas. In an optimized process the efficiency is essentially equal to that for conversion of electrical energy to laser output. Silane (SiH_4) absorbs strongly at the 10.6-μm wavelength of a CO_2 laser. Thus, silicon, silicon nitride, and silicon carbide are readily synthesized by the following reactions (Cannon et al., 1982):

$$SiH_4(g) \rightarrow Si(s) + 2H_2(g)$$
$$3SiH_4(g) + 4NH_3(g) \rightarrow Si_3N_4(s) + 12H_2(g)$$
$$SiH_4(g) + CH_4(g) \rightarrow SiC(s) + 4H_2(g)$$

The other reactant gases, such as methane and ammonia, where required, are heated indirectly by collisional processes.

Conventional CVD has also been used to produce a wide variety of powders. The key to producing fine powders is the use of a high degree of supersaturation so that homogeneous nucleation occurs. Particle size is determined from the relative nucleation and growth rates, which are controlled by the reaction parameters. Among the powders that have been produced by conventional CVD processes are Si_3N_4, SiC, TiN, ZrN, VN, TiC, Mo_2C, α-Fe_2O_3, TiO, α-Al_2O_3, ZrO_2, and Nb_3Sn (Kato, 1987).

Other vapor-phase processes that have been used for powder processing include inductively coupled and microwave plasma systems, steam hydrolysis, chloride oxidation (Johnson, 1987), and high-pressure sputtering (Suh et al., 1991).

COMPOSITES FABRICATION

Metal-matrix and ceramic-matrix composites, and the ceramic whiskers and fibers on which they are based, are advanced technologies whose applications are just beginning. A variety of innovative processes have been developed for them, many based on beam processing techniques. Vapor deposition techniques, discussed below, have been used to form both the reinforcing whiskers and filaments for metal and ceramic composites, and chemical vapor infiltration of fiber preforms is used for matrix formation in ceramic composites. Recent applications of beam technologies to composites are summarized in Table 5-6.

Table 5-6 Summary of Applicatins of Beam Technologies to Composites

Application	Process	Materials
Whisker growth	Rice hull pyrolysis	ß-SiC
Fiber production	Vapor-liquid-solid (VLS)	ß-SiC, TiC, ZrN, TiN, ZrC
Fiber coating	Chemical vapor deposition	ß-SiC, boron
Metal matrix	Chemical vapor deposition	BN, C, etc.
Ceramic matrix	Electron beam evaporation	Ti-6Al-4V, Ti
	Chemical vapor infiltration	SiC, Si_3N_4, Al_2O_3, B_4C, TiC, BN, Si

Fiber and Whisker Preparation

Chemical vapor processing is widely used to produce ceramic whiskers, platelets, and continuous fibers for reinforcement of composites. The chemistry and properties of the fiber-matrix interface are important in developing ceramic-matrix composites, and each interface must be tailored to give a bond strength that is suitable to provide an appropriate toughening mechanism (e.g., to control fiber pullout). CVD is probably the most common method currently used for coating fibers to thicknesses ranging from nanometers to several micrometers to provide an appropriate interface between fibers and matrix (Cranmer, 1989; Kerans et al., 1989).

Silicon carbide whiskers are grown today on a commercial basis from the pyrolysis of rice hulls, which are composed mostly of cellulose with hydrated amorphous silica (Lee and Cutler, 1975). Heating rice hulls in a coking furnace at 1200° to 1800°C causes a reaction between silicon suboxide and carbon via the gas phase to form silicon carbide whiskers (Nutt, 1988). These whiskers currently are finding commercial application as reinforcements in ceramic cutting tools and are being intensively evaluated in structural composites. Vapor-grown particulates, as well as whiskers, have been used as reinforcements in ceramic cutting tools (Rothman et al., 1986; Lee and Borom, 1988).

In addition to SiC, whiskers of TiC, ZrN, TiN, and ZrC have been formed by CVD. In each case, the source of carbon was methane, with metal tetrachlorides for the metal ion and nitrogen for the nitride ion. Nickel, palladium, and platinum, among others, were effective for catalytic growth of these whiskers on a mullite procelain (Kato et al., 1977; Kato and Tamari, 1980; Wokulski and Wokulska, 1983). The growth temperature, typically 1100° to 1300°C, produced whiskers with diameters ranging from 10 to 300 μm and lengths of a few millimeters. The TiC whiskers appear to grow by a vapor-liquid-solid (VLS) mechanism on Ni at the initial stage and by a vapor-solid (VS) mechanism on mullite after the initial stage (Tamari and Kato, 1979). Whisker technology reviewed by Levitt (1970) provides rather extensive coverage of CVD and other growth methods.

Catalyzed growth of both carbon and silicon carbide whiskers has been reported. Japanese (Koyama and Endo, 1972, 1983), French (Oberlin et al., 1976), and American (Tibbetts, 1989) investigators have reported the growth of carbon whiskers from metal catalyst particles (usually Fe), of a few nanometers in diameter, exposed to a mixture of hydrocarbon gases and hydrogen at a temperature near 1000°C. The growth rate may be as high as several millimeters per minute. The filament length is several centimeters, while the whisker diameter remains about the same as the catalyst particle (Tibbetts, 1989). Baker and coworkers have been actively studying the catalyzed growth of carbon filaments using controlled-atmosphere electron microscopy, in which a gas reaction cell is incorporated within an electron microscope (Baker and Harris, 1978). This permits continuous observation of the gas-solid reactions as they occur. A comprehensive review of the literature on the formation of filamentous carbon was published by Baker and Harris (1978). The whiskers can be made thicker by in situ CVD to diameters of 7 to 10 μm and can be grown to several centimeters in length. Strengths of 2.9 GPa (420 Kpsi) and modulus values of 240 GPa (34 Mpsi) have been measured. The whiskers can be given a very high degree of preferred orientation by high-temperature heat treatment to produce a morphology consisting of graphitic "C" planes wrapped around the whisker axis. This configuration gives many unique properties, including exceptionally high thermal conductivity along the whisker axis. A detailed theoretical analysis of the growth process has been presented by Tibbetts (1989).

In a somewhat analogous development, workers at the Los Alamos National Laboratory (Milewski et al., 1985) have reported the VLS process for producing β-SiC whiskers. Growth of the whisker occurs by precipitation from the supersaturated catalytic liquid at the solid whisker/liquid catalyst interface. A basic requirement is that the molten catalyst take into solution the atomic components of the whiskers to be grown. For silicon carbide growth, transition metals and iron alloys satisfy this requirement (Milewski et al., 1985). The process, operated at 1400°C using 30-μm stainless steel catalyst and methane, hydrogen, and silicon monoxide precursors, produces whiskers of a rounded triangular cross-sectional shape (4 to 6 μm in diameter) with lengths ranging from 10 to 100 mm. Tensile strength values average 8.4 GPa (1,220 Kpsi), with average fracture strain of 1.74 percent and an average elastic moduius of 578 GPa (83 Mpsi). These mechanical properties are superior to those of the best polymer-derived ceramic fiber yarns (Petrovic et al., 1985).

Continuous monofilaments of boron and silicon carbide are being produced on a fine wire substrate by CVD. Boron fibers (Table 5-7) are formed by CVD onto an electrically heated fine tungsten filament. A gas mixture of boron trichloride and hydrogen is used to deposit the boron. The tungsten wire core is about 3 μm in diameter, with the final boron filament being 100 to 200 μm in diameter. The properties of this fiber are quite good, having an elastic modulus of 58 Mpsi, a tensile strength >500 Kpsi, and a density <2.6 g/cm^3. To avoid reactions between the boron filament and metals during high-temperature fabrication of the composites, the surface of the fiber is coated by CVD with a thick diffusion barrier of B_4C. The B_4C coating also increases the tensile strength by about 10 percent and improves composite properties.

Silicon carbide filaments are produced by the decomposition of methyl trichlorosilanes on a carbon core (Suplinskas and Henze, 1982; Marzik, 1984). The CVD-produced SiC fiber has properties superior to polycarbosilane-derived fibers (Yajima, 1980), although its fiber diameter (>100 μm) is too large for weaving or for some fabrication processes. The fibers are available with a final coating of carbon that improves chemical compatibility in certain matrices and also improves fiber strength and handleability.

Table 5-7 Properties of CVD-Produced Boron Fibers

Property	Boron Filament Containing a Tungsten Core	Boron Filament Coated with Boron Carbide
Diameter (μm)	100-200	200
Length	Continuous	Continuous
Elastic modulus (Mpsi)	58	58
Tensile strength (Kpsi)	510	>600
Density (g/cm^3)	2.57-2.46	2.5
Use temperature (°C)	540	600
Approximate cost ($/lb)	350	1,000

Metal-Matrix Composites Fabrication

Metal-matrix composites are of strong interest today for advanced applications where lightweight, high specific stiffness, and good high-temperature strength are required. An example of a successful application of metal-matrix composites is the boron-aluminum composite tubing used as cargo bay stiffeners on the space shuttles.

CVD-derived filaments are of particular interest for high-performance metal-matrix composites, both for their superior properties and because the monofilament form lends itself well to metal-matrix fabrication processes. In addition to the cargo bay stiffeners mentioned above, extensive work is under way on titanium alloys reinforced with CVD-derived SiC fibers (Lancin et al., 1988).

Beam technologies have been employed to produce metal-matrix composites, although squeeze casting or spray techniques (Zanchuk, 1988) are used more commonly. Titanium alloy (Ti-6Al-4V) foil was made some years ago on a pilot plant scale using electron beam evaporation (Hughes, 1974). Even earlier, Bunshah and Juntz (1965) showed that electron beam distillation is an attractive technique for depositing sheets of reactive metals such as titanium.

Ceramic-Matrix Composites Fabrication

Ceramic whiskers can be processed with ceramic powders to give a ceramic-matrix composite having improved fracture toughness (Milewski, 1986). Ceramic cutting tools, formed with SiC whiskers and TiC particulates in an alumina matrix, have met with considerable success (Rothman et al., 1986; Lee and Borom, 1988) and are now available commercially. The matrix is based on SiC whiskers in an oxide matrix (Rhodes, 1985; Tiegs and Becher, 1985). The SiC whisker-reinforced alumina cutting tool produces a twofold increase in toughness relative to monolithic alumina. The aerospace industry considers it to be the state-of-the-art cutting tool material for rough machining of Ni-based superalloys (Baldoni and Buljan, 1988). However, it is chemically unsuitable for machining ferrous alloys (Billman et al., 1988) because of dissolution of the carbon of the matrix into the iron.

Whisker-reinforced ceramic composites also are under development for a variety of structural applications, including automotive turbocharger rotors (Akimune et al., 1989). Continuous ceramic-fiber/ceramic-matrix composites are being produced by a variety of techniques (Prewo, 1989). Prominent among these is chemical vapor infiltration (CVI). The CVI process was first employed for processing carbon-carbon composites (Buckley, 1988) and is the dominant process for producing carbon-carbon composite aircraft brake linings.

CVI has also been used to form a Nicalon-fiber/SiC-matrix and carbon-fiber/SiC-matrix composites. Ceramic-ceramic composites made of alumina fibers embedded in an alumina matrix were obtained from fibrous alumina preforms using a CVI technique based on gaseous alumina precursors ($AlCl_3$-H_2-Cl_2). This process is similar to that used for the SiC matrix mentioned earlier. CVI has also been used for forming B_4C, TiC, and BN matrices (Colmet et al., 1986). Silicon carbide fiber-reinforced silicon composites have been formed by CVD of silicon from a mixture of $SiCl_4$ and H_2 (Hwan et al., 1988). Silicon nitride matrices with both carbon and mullite fibers also have been reported (Gulden et al., 1990a,b). Improvements in fracture toughness have stimulated theoretical analyses of CVI in ceramic-to-ceramic composites, giving models for silicon carbide, alumina, and titanium carbide-matrix deposition within a ceramic-fiber bundle (Tai and Chou, 1988).

CVI has many advantages that have gained it a prominent position as a process for consolidating large, complex, thin-section ceramic- and carbon-matrix composites. Among the key advantages are the following:

- It is a near net-shape process.
- It involves no high-pressure sintering compaction process, so mechanical fiber damage is minimized.
- It is a very pure matrix with no sintering additives that would compromise high-temperature performance.
- It employs processing temperatures that are relatively modest, so thermal damage to the fibers is minimized.

Current commercial CVI processes used for both carbon and ceramic matrices are performed in isothermal reaction chambers (Theis, 1972; Newkirk, 1981; Naslain et al., 1983). In this consolidation process the reactant gases diffuse into the preform and deposit the material on the fiber surfaces to produce a relatively dense composite. The decomposition products diffuse out of the preform and are exhausted from the reaction chamber. The infiltration process is most effective at relatively low temperatures and pressures, where the deposition rates are low. Under these conditions the process is limited by surface reaction rates rather than by mass transport, and deposition occurs uniformly throughout the porous preform. In practice, economics drive the process to higher deposition rates, where localized sealoff can prematurely terminate the infiltration process.

"Directed" CVI processes, involving thermal-gradient, forced flow, or combined thermal-gradient and forced flow systems, have been developed to obviate the limitations of the isothermal approach (Caputo and Lackey, 1984). These approaches minimize the kinetic limitations of the CVI process and reduce the potential for preferential deposition at the external surface of the preform. A new and innovative class of composite materials has been termed microlaminate condensates. Microlaminate condensates are thick coatings or self-supported shapes produced by alternate deposition of the two species from evaporation or sputtering sources. The boundaries between the two laminate layers are noncoherent. The thickness of each laminate varies from 0.1 to 300 μm, and the entire thickness of the deposition can be as high as 1 mm.

Various material systems have been prepared and studied, such as Fe-Cu, Cu-Ni, Cu-Ca, TiC-Ni, and TiC-TiB. The strength of the composite increases with decreasing laminate thickness, particularly below 5 μm. The strength and hardness properties obey the Hall-Petch relationship (Mocvhan and Bunshah, 1982). Thermal conductivity across the thickness of the laminate is markedly reduced. Thus, a metal-ceramic laminate can have the low thermal conductivity of a ceramic without the brittleness. This suggests potential use of thermal barrier coatings (Radhakrishna et al., 1988).

NANOPHASE MATERIALS

Nanophase materials (at least one dimension in the nanometer size range) possess properties that in many cases are considerably different from the bulk material because of their very high surface area-to-volume ratio (A/V). The large A/V values can be achieved with films (one dimension), fibers (two dimensions), and fine particles (three dimensions). Nanophase matter can be incorporated into composites (particulate, fiber, or laminate) or in applications that use the properties of the fine particles themselves. Examples include those concerned with ultrafine particles of TiO_2 in paints and pigments to the more high-technology applications such as catalysts, ultrahigh-modulus composites, sintered powder products, magnetic recording media, optical applications, and biomaterials applications. Some typical application areas are listed in Table 5-8. More recently, ultrafine particles of organic molecules have been prepared by gas-phase condensation techniques for potential use in medicine. Some radical changes in properties have been observed (e. g., organic materials that are hydrophobic in bulk form become hydrophyllic when finely divided).

The preparation methods for ultrafine particles can be divided into two major classifications: (1) chemical methods (e.g., redox reactions, sol-gel techniques, polyol processes, flame pyrolysis, CVD, PACVD, and arc or plasma torches) and (2) physical methods (e.g., gas-phase condensation of vapor species in which the depositing species are produced by evaporation using resistance heating, induction heating, arc or electron beam sources, and sputtering). Metal as well as compound particles (oxides, nitrides, etc.) can be prepared; the latter group (compounds) is often produced by reaction of the metal particle with the corresponding reactive gas (Hayashi, 1987; Kato, 1987; Hayashi et al., 1988; Eastman and Siegel, 1989).

Japanese scientists have placed very high priority on basic studies of ultrafine particles in the size range 1 to 100 nm. Their basic work dates back to the early 1970s. In 1987 a 5-year project, operated by the Research and Development Corporation of Japan (JRDC), was concluded at a cost of 1.5 billion yen. The results are published in research articles referenced below as well as in a book in Japanese published in 1988. Recent issues of the Materials Research Society Bulletin have been dedicated to fine particles (1989-1990). In addition, the National Materials Advisory Board published a comprehensive, broad-based committee report on nanosized particles (NMAB-454, 1989). Only nanosized materials formed by beam technologies are the concern of the present study.

In contrast to vapor-grown nanosized carbon fibers, iron whiskers of 5 to 30 nm were produced by CVD (Schladitz, 1968; Lashmore et al., 1977). These α-iron crystallites (Fe-1.8C) showed an exceptional strength of 8 GPa, indicating a potentially large increase in strength (as with the nanolaminates to be mentioned later) with a decrease in crystal size. Furthermore, a joint effort involving Japan's National Defense Academy (Yokosuka, Japan) and Tohuku University (Sendai, Japan) has shown that dispersions of nanoscale silicon carbide or silicon nitride particles greatly strengthen and toughen alumina, magnesia, and mullite-based ceramics (Tennery, 1989).

Synthesis of fine ceramic powders from chloromethylsilanes using pulsed excimer radiation is presently being worked on in Australia. In this technique the silane is placed in a glass container and heated to approximately 10°C below its boiling point to produce a sufficiently high vapor pressure in the reaction chamber (13.3 KPa). The vapors are photodecomposed by an excimer laser (Ar-F gas mix) operating at 193 nm. The laser energy is absorbed by all of the silane and the decomposition fragments used in the study. The resultant particle sizes of amorphous silicon or β-SiC varied from less than 10 nm to a maximum of 1.5 μm. Earlier work using continuous wave CO_2 infrared laser-induced photodecomposition of silanes produced ultrafine silicon powders for the production of reaction-bonded Si_3N_4 monoliths with superior strength properties (Cannon et al., 1982; Haggerty et al., 1986).

Argonne National Laboratory is generating equiaxed nanophase materials by the gas condensation process reported by Kashu et al. (1974). The gas condensation method consists of evaporating materials inside a vacuum chamber at 1 x 10^{-7} Torr and then backfilling with low-pressure gas, typically a few hundred pascals of an inert gas such as He. If compounds are to be formed in the condensation process, reactive gases are used. Evaporated atoms collide with gas atoms inside the chamber and form small gas-borne particles rather than a continuous film that would form in vacuo. The condensed fine powders collect on a hollow tube (cold finger) filled with liquid nitrogen from outside the chamber. This synthesis method can produce pure

Table 5-8 Applications of Ultrafine Metal Powders

Materials	Field	Application		Merit
Ag Au Ag-Pd Ni - base alloys Fe - base alloys	Electronics	Electric - conductive paste: for capacitor electrode for hydrid circuitry		1) Formation of close-meshed film with ultrafine metal powders 2) Low sintering temperature on the surface of the substrate
		Recording magnetic materials: for credit cards for cash service cards		High coercive force resulting from metal and alloy powders with a ferromagnetic property
Ni	Metallurgy	Sintering	Additional elements: for dispersion strengthen alloy for sintered filter	1) Superior scattering property 2) Small particle size < 1 μm in diameter
		Joining	Filler materials: for vacuum soldering for brazing Insert materials: for diffusion bonding	1) Small particle size 2) Fresh surface condition
Al Ag Ni	Chemistry	Gunpowder	Rocket propellant	More combustible fine Al powders due to larger surface
		Catalyst	Oxidation of ethylene	Complete chemical reaction
Ni - base alloys Fe - base alloys Co - base alloys	Mechanics	Ferromagnetic fluid: for vacuum seal of shaft		1) Ferromagnetic material 2) Superior scattering property
Stainless steel Ni Cu	Textiles	Electric-conductive textiles: for preventing static electricity for an electric blanket		Good scattering ability for synthetic fiber solution
Au	Ceramics	High-grade glaze: for china		1) Scattering ability 2) Superior luster
Metal powder replaceable for $Pb(C_2H_5)_4$	Petroleum	Additive elements: for high-octane gasoline		Nontoxic high-octane gasoline

metals as well as oxides by using oxygen as the gas (e.g., TiO_2, Al_2O_3, and MgO). To produce Al_2O_3, gas-condensed Al-metal particles need to be heated to 1000°C in air to transform the metal particles to α-Al_2O_3; this results in a very small increase in particle size (about 18 nm), since the low-temperature oxidation is incomplete and produces only an oxide film on the metal particles.

In contrast to molecular beam epitaxy, which is not a volume production method, a semicommercial-scale electron beam vapor deposition process for forming multilayer structures has been constructed. This technique produces alternate layers of aluminum (20 to 1600 nm thick) and a second metal (0.1 to 20 nm thick of Cr, Fe, Mg, Mn, Ni, or Ti) (Bickerdike et al., 1984-1985). This material can be deposited at rates of up to 5-cm thickness in an 8-hour period--a yield of layered nanocrystalline material adequate for mechanical property evaluation. Alternatively, annealing of suitable combinations of such multilayer deposits produces amorphous phases at low temperatures, which can be crystallized to give extremely fine grained equiaxed crystallites (Johnson, 1986). Similarly, using electron beam vapor deposition, multilayered nanostructure laminates of Al-Cu and Al-Ag were formed on a substrate. The Al-Cu laminates showed a tensile yield stress of about 650 MPa when the layer thickness was below 70 nm; above that thickness the yield stress rapidly dropped off (e.g., about 250 MPa at 200 nm thickness). These laminates were formed at impractical deposition rates (4 μm/h) for structural fabrication, relative to those formed by Bickerdike and associates (1984-1985) mentioned above (Lechoczsky, 1978).

OPTICAL SURFACES AND DEVICES

Structures synthesized for the modification of optical properties generally rely on interference effects produced by the wave nature of light. Thus, the structure dimensions (number of wavelengths) and refractive index (wavelength in the medium comprising the structure) must be precisely controlled.

Films on surfaces, generally multilayers of insulators or semiconductors, are used to make such items as band-pass filters, dichroic filters, and reflecting or antireflecting surfaces (MacLeod, 1986). These require one-dimensional uniform control of thickness. This control is provided by monitoring, during deposition, optical transmission and reflection of the film with an optical beam. Theoretical analysis of the change in property with thickness is required for interpretation of the monitor, and extensive studies have been undertaken to determine the best method to analyze the light beam for optimal control. This technology is presently highly advanced, achieving thickness control on each of the 20 to 30 layers in the total fiber of between 2 and 10 percent, depending on the application. Physical vapor deposition, often electron beam evaporation, is used. Laser mirror coatings are an important application of such films. Careful use of conventional technology suffices for most optoelectronic devices, and special deposition to avoid absorption is necessary only in large high-power devices. Low absorption requirements also exist for Rugate filters used in laser filters, where high incident power necessitates low absorption and many carefully controlled layers to achieve significant power rejection.

Optically transmitting and electrically conducting films are used in some solar cells, matrix displays, and light shutters. In such applications the films are used for their bulk properties (and only incidentally provide interference effects), although they are often patterned. Optical absorption by the free carriers is a problem that has been solved by the use of large bandgap indium-tin oxide. This material can be applied in many ways, but sputtering is preferred because of cost, and it has become a common commercial process.

Architectural and automotive films are deposited on windows to control energy transfer within some specified aesthetic or visibility constraint (Granquist, 1989). For maximum reduction of air conditioning loads, high reflectance is needed over both the visible and infrared spectra. For colder climates, however, maximum energy conservation requires high transmission of the solar energy in the visible and near infrared, but high reflectance (low emissivity) in the intermediate infrared to return radiation back into the building. A few examples of such practical optical solutions are given in Table 5-9. Some of these films are routinely manufactured, with annual outputs of over 2 million square meters per system, for use in such volume applications as automobiles and buildings.

Table 5-9 Practical Optical Solar Energy Solutions Using Deposited Films

Process	Material	Characteristic
Sputtering	TiO_2:Ag:TiO_2	Good visible transmission, good infrared reflection
Sputtering, pyrolysis	In_2O_3:Sn, SnO_2:F	Fair visible transmission, good infrared reflection
Sputtering	ZnO:Al	Good visible transmission, fair infrared reflection
Sputtering electron beam, evaporation	Noble metals	Good infrared reflection

Dielectric optical waveguides on substrates (Miller and Kaminow, 1984) are used today chiefly in discrete couplers, which may be directional, star, wave-division multiplexing, or polarization retaining. As optoelectronics evolves, applications may be expected in hybrid circuits. Even with fully integrated circuitry available, some applications for discrete and hybrid components are expected to exist. Planar devices, most amenable to beam processing, compete with discrete couplers made by commercially available bulk methods. Most planar devices are used for research and are made by diffusion, plasma-enhanced CVD, or silica soot (fume) deposition. Microlenses (Iga et al., 1984) also may become part of hybrid circuits; they have been made by diffusion or, as Fresnel lenses, by electron beam machining. Presently, commercial lenses are made by bulk processing.

Active dielectric devices in electrooptics include such components as switches, isolators, and spectrum analyzers. Almost all such switches are presently made by diffusing titanium into lithium niobate to make the device structure (Thylen, 1988), but ion implantation has also been used. The titanium provides the refractive index change to create the waveguides within the electrooptic material. These switches have the largest bandwidth from low frequencies of any switch and thus potentially have a broad range of applications. They are presently employed in commercially available equipment for signal processing. Faraday isolators are presently discrete devices, and attempts to make them in a form suitable for integrated optics are still beset with problems.

POLYMERS

The volume of polymeric substances used in industry is constantly growing, and plastics are used as substitutes for metals in a variety of applications. Beam technologies are responsible for formation of a variety of specialty plastic materials. These technologies are used either for treatment of bulk or surfaces of polymers. The main objectives for treatment of polymers are outlined in Table 5-10.

Table 5-10 Objectives for Treatment of Polymers with Beam Technologies

Bulk Treatment (beam species)	Surface Treatment (beam species)
Co-polymerization (electron, gamma)	Metallization (PV, PACVD, LCVD)
Irradiation (electron, gamma)	Surface hardening (ions, PACVD, PVD)
Sterilization (electron, gamma, PVD)	Chemical resistance (PVD, PACVD, ion)
Cutting, shaping, forming (lasers, heat)	Gas permeation (ion)
Densification (lasers, heat, ion)	

MATERIALS FOR ENERGY PRODUCTION

The unique ability to tailor the characteristics and properties of materials produced by CVD has led to the use of these materials in a number of advanced energy applications where conventional materials were inadequate. In this sense, CVD has been an enabling technology.

The coated-particle nuclear fuel concept is based on CVD of carbon and ceramic coatings on a fuel "kernel" in a fluidized bed (Gulden, 1986). One of the most promising concepts for nuclear power in space is in-core thermionics. The heart of this concept is the tungsten emitter produced by CVD. The emitter has a duplex structure with the inner coating, deposited from tungsten hexafluoride, providing strength and creep resistance, and the outer layer, deposited from the chloride, has a (110) texture to provide the maximum electron work function (Yang and Hudson, 1967).

The first wall of magnetic confinement fusion devices will require structures with low neutron activation, high melting temperature, and low physical and chemical sputtering rates. "Armor tiles" coated by CVD processes with carbon and refractory ceramic materials have been developed for this application. A codeposited coating of pyrolytic carbon and silicon carbide has proven particularly effective because of its unusually high resistance to chemical sputtering (Hopkins et al., 1984). In situ boron carbide coatings also have been used (Veprek et al., 1989).

BIOIMPLANT DEVICES

Ion implantation has been shown to be very effective in reducing the wear of titanium-based total joint replacements in the orthopedic field (Sioshansi, 1987). The superior wear resistance results from both increased hardness of the titanium alloy (Ti-6Al-4V) and the lower coefficient of friction from homogenization of the two-phase alloy and formation of nitride, oxide, and carbide precipitates on the surface of titanium components.

The new-generation orthopedic implants are manufactured from Ti-6Al-4V alloy for its ideal biocompatibility. The Ti-6Al-4V alloy has a superior corrosion and fatigue resistance compared to the traditional cobalt-chromium-molybdenum alloy and has a lower modulus of elasticity that provides a better match for the bone. In total joint replacement the titanium component articulates against an ultrahigh molecular weight polyethylene (UHMWPE) surface. Improvements in the wear resistance of Ti-6Al-4V are of significant interest to the orthopedic community.

Ion implantation of species, such as nitrogen and carbon, into the Ti-6Al-4V component has been shown to increase the microhardness of the alloy (Sioshansi, 1987). A threefold increase in microhardness (at loads of 1 to 2 g) can easily be achieved in these alloys. Recent work (Sauer, 1986) at MIT has shown that nitrogen implantation into Ti-6Al-4V changes the two-phase microstructure (the appearance of alpha and beta microplates) of the Ti-6Al-4V plates and renders the material impervious to standard etchant solutions. Earlier work showed that a reduction in the coefficient of friction of the Ti-6Al-4V alloy from 0.48 to 0.15 results from nitrogen-ion implantation at 100 keV to a total dose of 4×10^{17} ions/cm^2 (Oliver et al., 1984).

The increased hardness and lower coefficient of friction in the titanium alloy are believed to be the reason for a lower wear rate of the alloy and a much reduced wear rate of the articulating UHMWPE surface; a 1000-fold reduction has been observed in the corrosive wear of the titanium-polyethylene couple. The significant reduction of the wear of the titanium-UHMWPE system has convinced orthopedic manufacturers to specify this process in treating their products. (IONGUARD is the registered trademark of Spire Corporation, and the 1000 Series is used for processing titanium-based orthopedic implants.) This application has already reached market maturity, and large quantities of titanium-based orthopedic knees and hips and smaller quantities of wrists, shoulders, fingers, and toes are routinely prepared using the ion implantation process.

Pyrolytic carbon has been found to be exceptionally biocompatible (Bokros et al., 1972; Haubold et al., 1981). Addition of a few percent SiC in a CVD codeposition process provides the strength and wear resistance required for artificial heart valves (Kaae and Gulden, 1971; Shim and Schoen, 1974). As a result of these unique characteristics, heart valve components coated with carbon and SiC, codeposited by CVD, have come to dominate the artificial heart valve market in the past decade. These materials are also being evaluated for other applications, such as subcutaneous leads, joint replacements, and dental implants.

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6

INTEGRATED PROCESSING

The combining of two or more process steps into a single piece of equipment, or into a single operating system, under unified control is process integration. A simple example of process integration is the cleaning of a substrate surface by sputtering followed by sputter deposition of material onto the cleaned surface, all done in a single closed system. The operation of an oil refinery to produce gasoline from crude oil is a more complex example of process integration. This chapter presents some examples of integrated materials processing that use beam technology.

INTEGRATED PROCESSING IN MICROELECTRONICS

A number of factors are coming together today to accelerate the push toward integrated materials processing. In the area of integrated circuit and optoelectronic device fabrication, these incentives and needs include:

- increased wafer size,
- reduced feature size,
- need for ultraclean wafer environment,
- prevention of oxidation of work on exposure to air,
- need for reduced inspection time,
- reduced equipment and process expense,
- need for quicker turnaround time,
- need for more rapid changeovers,
- increased process complexity,
- reduced handling, and
- in situ process control.

As illustrated in Chapter 4, beam processing is used extensively in the manufacture of state-of-the-art semiconductor circuits and optoelectronics. Most of these processes have been introduced as replacements for less accurate or more difficult to control process techniques. Integration of process steps and processing equipment is only beginning to occur in this industry, where the traditional processing techniques are batch oriented. Most of the process steps and process controls are centered around individual pieces of equipment in which the particular deposition, etching, patterning, and heating steps occur. Statistical process control techniques have been applied to identify the process capability of each step and to improve the repeatability and yield of the fabrication process.

Integrated Processing for Integrated Circuits

Fabrication of integrated circuits, as described briefly in Chapter 4, consists of a complex sequence of process steps that require high precision, repeatability, and cleanliness. During the past decade, circuit dimensions have decreased by more than a factor of 10 and circuit complexity has increased by more than 10 times, largely because of the improved processing capabilities provided by beam technologies. These beam technologies have displaced previous techniques on a step-by-step basis; however, the general process flow is still batch oriented, as it was before the widespread introduction of beam technologies.

Traditional Integrated Circuit Processing Techniques

The reasons for the existence of a batch process flow relate to the economics of achieving cost-effective equipment utilization and throughput for time-consuming steps such as oxidation and diffusion and the economics of batch processing in wet chemical steps such as cleaning, etching, and photoresist removal. The capital equipment costs and throughput limitations of these steps still heavily favor batch processing whenever they are used. Significant effort has been expended on reducing the variability of the process steps across the batch. Wider process margins are required for batch-processed wafers than would be required for individually processed wafers if adequate control systems existed to repeatedly process individual wafers in a single-wafer system.

Because individual pieces of equipment have vastly different batch sizes and process times, the work-in-process inventory is large, the inventory is stored at many points in the process, and the cycle time is fairly long. Process control is centered on the individual piece of equipment and the process is related to the equipment. Most modern semiconductor process equipment has local microprocessor control of the process input variables, which allows several variations of the same process to be run with minimal operator intervention. Material flow between the process steps is accomplished by removing the wafers from one system, storing them in a cassette and box, manually transferring them to the next station, and then loading them into the next system. Because of the varying exposure times of the wafers between steps, there generally is a cleaning or surface treatment operation between any two major process steps. These cleaning operations add significantly to the processing complexity, time, and cost. They are, nevertheless, necessary because of the exposure of the semiconductor wafers to the ambient atmosphere.

Information flow between the process steps is sometimes computerized, but often measurements are made and recorded by paper documentation, which moves with the wafers. This information is rarely fed forward to modify the subsequent process step based on the results of the previous step. Measurements of results and modification of process steps on a wafer-by-wafer basis are not possible in the batch processing environment.

Advances Toward Integrated Processing

The economics of larger wafers, coupled with the requirements for more stringent cross-wafer uniformity and reduced feature size, have been major driving forces in the development of single-wafer or continuous flow beam processing equipment for the manufacture of integrated circuits.

The lithography process is a single-wafer process because a mask can be used only for printing one wafer at a time. Introduction of the wafer stepper, which has been the main driver for reduced geometries, has accelerated the move to larger wafers, thereby reducing the cost per exposure by amortizing the alignment and wafer handling time over a larger number of exposures. As wafer sizes increased, the uniformity of deposition and etching across a wafer in traditional batch beam processing systems became inadequate. Single-wafer systems have now been developed for high uniformity and repeatability across a single wafer. To prevent throughput problems, deposition and etch rates had to be dramatically increased at the cost of selectivity and substrate damage. New processing techniques had to be developed for other process steps when single-wafer equipment was developed.

Single-wafer or continuous flow process equipment now exists for most of the process steps required for state-of-the-art integrated circuit fabrication. Dielectric and metal deposition systems that remove wafers from a cassette, process them, and reload them into a cassette are available. Likewise, cassette-to-cassette plasma etchers for dielectrics and metals also exist. Most aluminum etching is still done in batch-mode equipment, but automatic wafer handlers are available for loading and unloading. Photoresist and lithography equipment has long been cassette to cassette oriented. Most dry etching systems have some type of endpoint detection, so that the process is somewhat tolerant of etch rate variation and incoming material variations. Other systems have automatic control of the process variables, but little exists by way of real-time monitoring of the actual process results. Except for the 25-wafer cassette, no standardized interface exists for material flow from system to system. Several proposed standards are being developed at this time.

Integrated processing lines for single-product manufacturing (e.g., dynamic random access memories [DRAMs]) can be built to take advantage of continuous work flow when process flexibility is not required. Such a line can be configured by providing a separate piece of equipment for each process step, instead of performing many similar steps in one machine. For a typical metal-oxide semiconductor (MOS) process with 10 masking levels, 10 separate lithography cells would exist, one for each mask level. The material would flow continuously from station to station through the sequence of fabrication steps. High volume is required to justify the large capital expenditure for such a fabrication line, and, without significant improvement in flexibility and process control, such expenses cannot be justified for small-volume or applications-specific products. Even when such a process line is built, a major effort is required to interface the various pieces of process equipment that must transfer the material and information.

Integrated Processing Tools

In the past three years a few beam processing systems have been introduced that can perform multiple process steps. Such systems have become known in the semiconductor industry as cluster tools. The earliest tools were the multichamber etch or deposition systems. These systems allow sequential steps to be performed without cross-contamination, which results from the transfer of wafers from one station to another. Each process station can be configured to "optimize" the conditions for a given step. The systems are flexible, so that chambers also can be run in parallel or in any desired combination of serial and parallel steps. The etching of multilayer films, followed by photoresist strip, is a typical application for such cluster tools.

The development of integrated processing tools to do more complex fabrication sequences is limited by many factors, such as development cost, range of process expertise, unknown market requirements, and lack of equipment interface standards. The Modular Equipment Standards Committee (MESC), of the Semiconductor Equipment and Materials International (SEMI), was formed to develop standards for mechanical, utility, software, and control interfaces for future integrated processing systems. These standards will enable circuit manufacturers to choose the component systems necessary for their fabrication processes and have assurance that the systems can be integrated into a working whole. Nevertheless, it is expected that in the next 3 to 5 years, little will exist in integrated process tools beyond throughput-enhanced single-wafer systems. Significant problems of throughput, cost, uptime, real-time control, information flow, and process step development need to be overcome before significant use of integrated process tools will occur. Extensive development programs could accelerate progress in this vital area (Design Test Manufacture, 1991).

These needs are recognized as important steps toward integrated processing in semiconductor electronics as exemplified by cooperative research efforts at the Semiconductor Research Corporation and SEMATECH for the semiconductor industry (consortia for the advanced development of IC technology, system architecture, and packaging, and for manufacturing processes and materials, and equipment development). In addition, the Engineering Research Center at North Carolina State University, funded by the National Science Foundation, has a focus on IC integrated processing. DARPA and the Air Force also have an active program (MMST) at Texas Instruments, Inc.

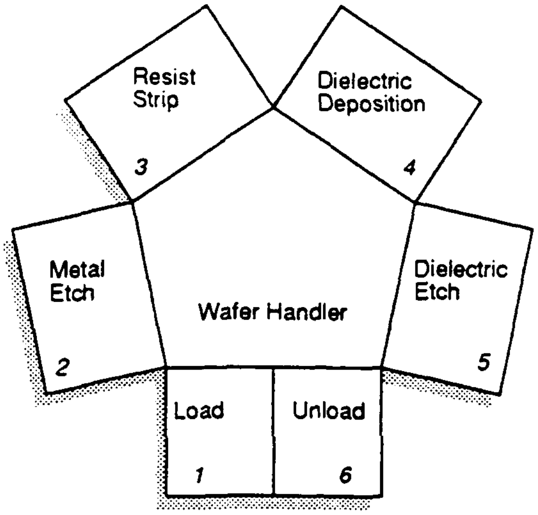
Applications for Integrated Processing Tools

In evaluating potential uses for integrated processing tools, an assumption is made that the photolithographic steps will be done on optical steppers employing photoresist technology and wet chemical development. This means that each masking step will be done outside an enclosed-environment beam processing tool. The steps that could be performed by an integrated processing tool would consist of etching, stripping, cleaning, and deposition. The advantages of such sequences would be cleanliness, prevention of surface contamination from exposure to room atmosphere, reduced cycle time (compared to single-wafer systems), and the opportunity for improved control and quality from the ability to continuously monitor and adjust the process. Some examples of possible integrated processes are shown in Figures 6-1. An experimental system has been developed in Japan for the integrated processing of optoelectronic device structures.

INTEGRATED PROCESSING FOR METALS AND CERAMICS

Integrated processing systems are employed in the manufacture of some metallic and ceramic articles. Increasingly, machining steps are carried out by flexible machining systems (FMSs), which consist of a group of machine tools linked by an automatic materials-handling system and controlled by a computer. A workpiece is loaded onto a carrier or pallet and sent from one machine tool to the next, according to a specific manufacturing plan. Tools are changed automatically, and quality control is performed on-line with automatic measuring tools. Direct labor is kept to a minimum and often is restricted to loading and unloading workpieces from the FMS and periodic maintenance procedures. With the development of beam technologies, new opportunities are emerging for extending FMS to include additional processing steps.

Consider a traditional approach to the manufacture of metallic articles. An alloy is cast into ingot form and then rolled to produce a variety of shapes--blooms, plates, bars, sheets, rods, and wire. These shapes might be used as is or subjected to further shaping processes. Sheet, for example, might be sheared with a punch and die to produce a small batch of flat-shaped parts. A bar might be cut into short lengths, then forged into a more complex shape. Rods might be machined by an automatic lathe. In some cases a joining process such as welding, brazing, or soldering might be required to produce the specified shape. At some point, heat treating might be required to enhance mechanical properties. Finally, the article might be surface treated to improve its wear resistance, corrosion resistance, or appearance. Of course, as an alternate, the amount of preliminary shaping required to produce a part with a complex shape can be greatly reduced by starting with a casting or a preform produced from powder rather than with mill products.

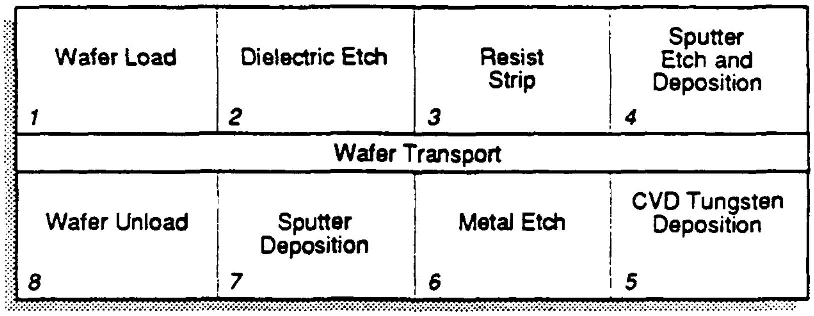


A. Metal Etch and Dielectric Deposition Process Sequence

1 Wafer Load
2 Metal Etch
  Surface Removal
  Aluminum Etch
  Barrier Etch
3 Resist Removal
4 PECVD Oxide Deposition
5 Planarization Etchback
4 PECVD Oxide Deposition
6 Wafer Unload

B. Spacer Formation Process Sequence

1 Wafer Load
4 PECVD Oxide Depositoin
5 Planarization Etchback
6 Wafer unload



Dielectric Etch and Metal Deposition with Via Fill Sequence

1 Wafer Load
2 Plasma Oxide Etch
3 Resist Strip
4 Sputter Clean and Nucleation Layer Deposition
5 CVD W Deposition
6 Tungsten Etchback
7 Aluminum Deposition
8 Wafer Unload

Figure 6-1 Examples of integrated processing sequences.

Ceramic articles have traditionally been manufactured from powders. The initial steps in the manufacturing process, after powder preparation, involve compacting and sintering. Normally the emphasis is to produce a part as close to the desired shape as possible before sintering, because sintered ceramics are very hard and not easily machined.

Beam technologies have already found many applications in the traditional manufacturing environment. Electromagnetic induction, laser beams, and electron beams are used to heat treat metals and alloys. The electron beam and the laser have been used in welding. The laser has been used to machine hard ceramic materials at much higher rates than previously possible. Beam technologies are also used in a variety of coating processes. Beam processes, which were described in Chapter 3, have several characteristics that favor their use in integrated processing systems; these include short interaction times, noncontacting functionality, and, in some cases, environmental flexibility. Two specific examples are presented below where beam technologies play important roles in the integration of processing steps: multilayer architectural glass coatings and single and multilayer coatings for stainless steel sheet. The precision gear (discussed in a later section) is taken as an example of integrated processing in the manufacture of a mechanical component with the use of beam technologies.

Finally, it should be recognized that further development of beam technologies may lead to the development of radically new approaches. Based on some applications described in Chapter 5, it is not difficult to envision an integrated manufacturing system in which the starting materials are vapors. These vapors either react directly at a surface to produce a deposit, or a reaction takes place in the vapor phase to produce nanophase particles that are then deposited on the surface. The deposition is carried out selectively by a beam process similar to that employed in desktop manufacturing to produce a three-dimensional shape. It may be possible, by such an approach, to produce both homogeneous and composite materials that have unique and desirable properties.

Microwave power applications currently are concentrated in processes for rapid heating using the power in cavity-type systems. The most common heating is for uniform water removal in difficult-to-dry materials and for food processing. The high electrical losses (energy absorption) of water at microwave frequencies make this attractive since most foods contain significant amounts of water and drying operations are self-limiting as the water is removed. The present equipment may be either multimode cavities, where little effort is made to match the dimension of the cavity to the wavelength of the energy, or tuned cavities where dimensions efficiently reflect the wavelength of the energy. Future uses will largely depend on the development of practical information on the effective dielectric properties of the materials to be heated and possible use of additives to enhance energy transfer by increasing the dielectric loss of the material without undesirable side effects.

Recent work in the use of microwave energy for heating ceramics and composites to very high temperatures has been most promising. Diffusion appears to be enhanced in high-field, high-frequency (above 25 GHz) energy, and temperatures above 1500°C are easily achieved. Future processing of materials with microwave energy is an attractive energy-saving approach, since the energy is concentrated in the part and no furnace mass is heated and cooled.

Architectural Glass Coatings

Large coated architectural glass panels are a common sight on newer high-rise buildings all over the world. The purpose of these coatings is to control the energy transport through the glass for more efficient heating or air conditioning. The coatings are multilayers of metals and ceramics, whose exact compositions are tailored to specific needs. The coating materials and layer thickness are proprietary to each equipment supplier. The initial coating line at Libby-Owens-Ford (built in 1971) used specially designed electron-beam-heated evaporation sources that had the beam trajectory in a horizontal direction. A company announcement describes a patented coating (tin oxide base) on glass, deposited by chemical vapor deposition (CVD) during the manufacture of clear float glass. It is transparent and has high electrical conductivity, stable up to 1300°F (700°C) for such applications as oven windows, commercial freezers and refrigerator doors, and copy machine platens (OPTONET: Industry Briefs, 1991).

More recent in-line coating systems use the sputtering process with the glass transported horizontally or vertically depending on the individual design. The process is a multistep in-line configuration consisting of glass washing, drying, insertion into an in-line multichamber vacuum coater, and exit from the chamber to various inspection stations. Feedback from the in-line inspection steps, which measure the optical properties, are used to control the process parameters.

Architectural glass is sputter coated with multilayers of metals and ceramics that control the transmission of energy through the glass. Glass sizes range up to about 3 by 6 m and have an annual output that ranges from 18,000 to 2,000,000 m^2 per system. The coatings are applied by sputter deposition in horizontal or vertical configurations in air-to-air systems. A more recent development (1986) is a bent glass coater for shapes 152 cm (61 in.) wide by 274 cm (110 in.) long with a vertical rise of 41 cm (about 16 in.). The system processes three to four windshields per load every 3 min with an annual capacity of 300,000 to 400,000 windshields. As many as 24 sputtering cathodes are used for each system, with a total process time per part of about 2 to 5 min.

In-line Dry Coating Process for Stainless Steel Sheet

Perhaps the most ambitious in-line coatings system comes from the recent development (by Nippon Steel Corp.) of a pilot plant for corrosion-resistant and decorative coatings on stainless steel sheet employing three coating processes in sequence. The three coating processes are ion plating or biased activated-reactive evaporation, magnetron sputtering, and plasma CVD (see Figure 6-2). Development of the differential vacuum chamber permits interconnection of the three different coating processes with different operating pressures for continuous deposition. Single-layer films (e.g., TiN, TiC, SiO_x, Al_2O_3, Cr), as well as multilayer films, can be coated for a variety of applications. SiO_x coatings on a low-cost bright-annealed stainless steel (e.g., type 430) give excellent corrosion resistance against chloride-ion attack, comparable to the more expensive

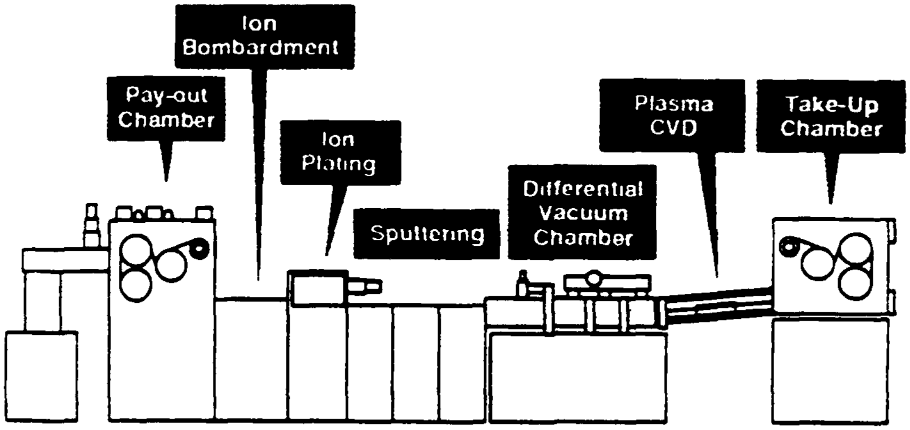


Figure 6-2 In-line dry coating process.

Fe-26/Cr-21 stainless steel. Any desired interference color from blue to pink can be produced by an Al_2O_3 coating on type 304 stainless steel by varying the coating thickness. Stainless steel sheets of 0.1 to 0.5 mm thickness, 370 mm width, and 300 m length move through the chambers at a web speed of 0.01 to 0.4 m per minute (Hashimoto et al., 1988).

Mechanical Fabrication

Precision gear manufacture is used here to illustrate how beam technology can be employed to attain a fully integrated processing system for the manufacture of a mechanical component. Gears are basic and essential components for military, aerospace, and civilian machinery and equipment. The U.S. capacity to produce gears is declining as imports displace domestic components on both the domestic and international fronts, so alternative cost-effective manufacturing technologies warrant serious consideration for further development and exploitation.

Current techniques for producing gears involve a number of steps normally carried out on different machines and often at different locations. A low-carbon steel preform is initially machined into a blank by a turning operation, then annealed to remove residual stresses. The teeth are then cut using processes such as milling, hobbing, or broaching. The part is then selectively carburized (heated in a carbon-active environment) to increase the carbon content in regions where increased hardness and fatigue resistance are desired. Prior to carburizing, the gear is copper plated in those regions where increased carbon content is not desired. Following carburization, the part must be reheated and quenched in oil to develop a fully hardened layer at the surface, called the case. Once fully hard, the gear is ground to eliminate any distortion that resulted during heat treating.

Great opportunity exists for fully integrating gear-making operations. Central to the integration is use of an energy beam, such as magnetic induction, laser, or electron beam, to harden the gear at a station of an FMS that is shaping the gear. Thus, shaping steps and heat-treating steps are integrated, thereby eliminating batching of the gears for copper plating and carburization treatments. In this approach a steel with a carbon content in the range 0.4 to 0.6 percent is used, rather than a low-carbon steel, which in the traditional technique must to be carburized to attain the required surface hardness. Table 6-1 compares the steps required in manufacturing a precision gear by traditional die-quenching and free-quenching operations to those required using a dual-frequency, induction-hardening approach.

It is also interesting to note the similarity of steps involved in gear making to those involved in integrated circuit (IC) chip making. In gear making, the use of masks and copper plating corresponds to the use of masks and photoreist in IC chip making. The purpose in both cases is to produce localized property changes at the surface. In gear making the aim is to locally change the surface hardness, thereby increasing the resistance of the metal to fatigue and pitting failure. In IC chip making the aim is to produce localized changes in electrical properties. Carburization in gear making is analogous to doping in IC chip making. For both gear making and chip making, the masking, plating (photoresist), and carburization (doping) processes are batch processes. In both these situations there is a desire to replace wet processes with dry processes. Both laser heating and electron beam heating could be used in place of dual-frequency induction heating in the sequence of steps shown in Table 6-1. The use of electron beam heating, however, requires a vacuum environment.

Table 6-1 Comparison of Dual-Frequency Induction Gear Hardening and Conventional Hardening Methods

Die-quench operations	Dual-frequency operations
1. Rough machine	1. Rough machine
2. Degrease	2. Core treat
3. Mask	3. Degrease
4. Copper plate	4. Temper
5. Unmask	5. Finish machine
6. Inspect plate	6. Load induction machine
7. Load carburize furnace	7. Unload
8. Slow cool	8. Inspect
9. Clean	
10. Copper strip	
11. Finish machine gear teeth	
12. Load hardening furnace	
13. Die quench	
14. Degrease	
15. Temper	
16. Shot blast (clean)	
17. Inspect	
18. Required finishing operations	

Source: Storm and Chaplin, 1989.

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7

REQUIREMENTS AND PROBLEMS FOR FURTHER INTEGRATION

The committee concludes that integrated processes as a manufacturing scheme are attractive for lowering the overall cost of the final product because of the potential for providing:

- greater flexibility through software modification rather than hardware modifications;
- shorter lead times;
- higher productivity; and
- improved quality, reliability, and performance.

As the critical dimensions in integrated circuits shrink from 0.5 to 0.35 μm or less, present manufacturing practice requires increasingly cleaner environments to keep the defect density low enough to maintain adequate yields. This has required not only development of processing tools with the requisite cleanliness but also increasingly cleaner rooms in which the equipment is housed. Each incremental improvement drives up the cost of a fabrication facility to the point where a new state-of-the-art facility costs in excess of $500 million. If this trend continues and manufacturing technology does not change, the cost of a facility for manufacturing of 64 M-bit random access memory (RAMs) may exceed $1 billion (see Figure 7-1). The application of improved integrated processing has the potential of reducing the steepness of the projected cost curve.

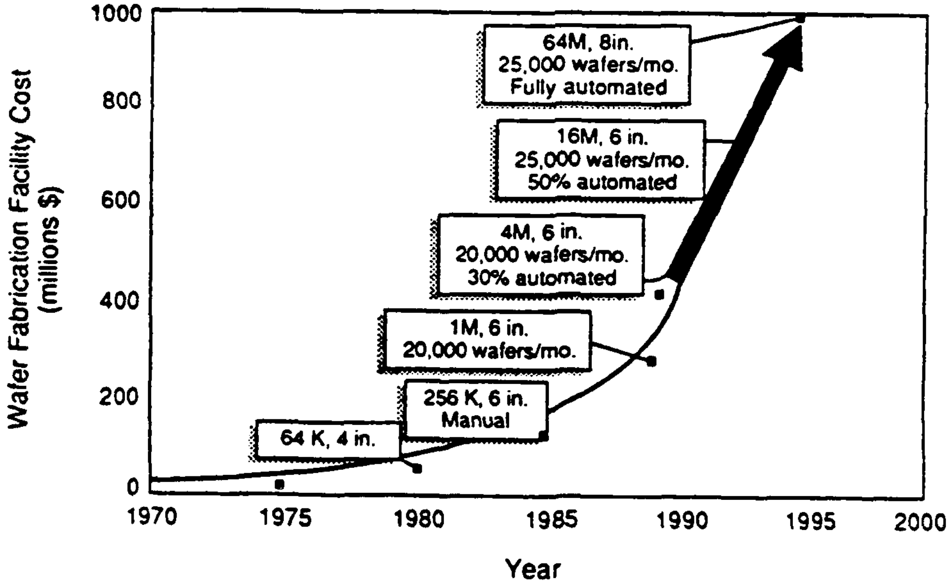

Figure 7-1 Wafer fabrication facility costs--current and future trends.

Source: Based on Semiconductor International (Dec. 1989).

Integration of related processing steps can lower this cost through such factors as the sharing of common functions such as load locks, wafer handlers, and central computers. As discussed in Chapter 6, this is now nearing reality in the microelectronics industry with the increasing use of cluster tools (Figure 6-1). In these, three or four process steps are arranged around a central wafer handling mechanism that is fed through a single load lock, which lends itself to yield improvement thus reducing overall costs. Such configurations also lower the area of clean room floor space required for equipment. A process that isolates the wafer from the factory environment throughout the manufacturing process will alleviate the need for such a large area of expensive clean room facilities as well as the need to isolate workers from the factory environment, all of which are expensive overhead items. A way of achieving this is to more fully integrate the manufacturing process.

Achieving integrated processing requires elimination of the numerous inspections that are now carried out to ensure that only "good" wafers are carried forward in the fabrication process. These inspections are now necessary to minimize the cost of processing unacceptable wafers and assure the proper functioning of the various process steps. Elimination of inspections can be achieved if sufficient in situ monitors can be inserted into the process steps and the output from these monitors can be fed into a real-time process control network. This represents a major advance from the way that most process steps are now carried out. As noted in Chapter 6, most process tools monitor and control the input variables to the machine (e.g., current, voltage, gas flow). At the present time, except for a few cases, such as measurement of ion current in ion implantation and end-point detection in plasma etching (by optical techniques), no direct monitoring is performed for what is happening at the wafer.

Development of real-time process monitors requires, for each process step, establishing the critical parameters to be measured, and then identifying the appropriate noninvasive sensors that must be developed; work on such sensors is important to this technology. To use the output from these sensors for real-time process control, process simulation models must be developed and combined with expert system artificial intelligence technology to develop "smart" real-time process controls.

Another problem to be overcome is maximizing the throughput of an integrated process. Different process steps require different operation times and may be used more than once in the fabrication of a given circuit. Using current technology, a typical fabrication facility for a 16 M-bit dynamic RAM (DRAM) circuit production of 3 million units per month will consist of 50 lithography stations, 35 ion implanters, 60 etchers, 20 sputtering units, etc. Such a multiplicity of tools also allows for redundancy, which permits continued production when a single tool breaks down or is inoperative for any reason. Proper architecture of an integrated system must accommodate these situations. A point to be made here is that each process must have sufficient uptime to ensure long continuous runs of the entire system. Otherwise the amount of redundancy that must be built into the integrated process will increase the cost, the size of real estate occupied by the system, and the complexity of the control processor. These factors could render total integration unachievable. Another feature needed for achieving integrated systems is to have the various vendors' machines capable of being joined to each other or to some common third body. In addition, each machine's microprocessor should be capable of talking to the system computer.

To achieve fully integrated semiconductor processing, any liquid steps, such as spin-on photoresist or dips to clean up etching or deposition steps, most probably will have to be replaced by dry processes. The time to develop new resists and application systems will undoubtedly make this the last operation to be integrated.

Implementation of the above advances will require close cooperation among the process engineers, equipment vendors, and process designers. It is most likely that additional wafer area will be required for process monitoring. Also, equipment will have to be redesigned to accommodate line-of-sight to such areas. These modifications will occur only if the overall economics are favorable. The example of integrated processing of integrated circuits has been discussed in some detail because the same generic problems apply to integrated processing of other materials. Determining what properties to measure, and developing the sensor systems and process simulation models, will still be required, as will development of "smart" control algorithms. One significant difference between silicon and many other materials relates to the size and shape of the material being processed. Whereas the small size of silicon wafers allows development of single-process modules connected serially or in clusters, this may not be the case for other materials. As was shown in Chapter 6, several applications involve large sheets or continuous ribbons of material that must be manufactured by in-line processes.

A more interesting case of integrated beam processing is the use of various energy beams to shape and harden a gear. Here, measurement of significant variables is easier because the workpiece is not in a protected environment. Processes for other materials, requiring as many steps as found in silicon device fabrication, have yet to be developed, but, as application of beam technologies increases, these materials will follow the lead of silicon processing. Nevertheless, it is recognized that modular integrated processes offer the opportunity to achieve process upgrades by changing modules rather than building whole new factories. In addition, for small fabrication runs, software-controlled flexibility would allow fewer tools to do a broader range of processes.

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APPENDIX A

ACRONYMS AND ABBREVIATIONS

ac	alternating current
AI	artificial intelligence
ARE	activated reactive evaporation
A/V	surface area-to-volume ratio
CBE	chemical beam epitaxy
CBN	cubic boron nitride
CCVD	conventional chemical vapor deposition (also CVD)
CVD	chemical vapor deposition (also CCVD)
CVI	chemical vapor infiltration
cw	continuous wave
dc	direct current
DECR	distributed ECR
DLC	diamond-like carbon
DRAM	dynamic RAM
EB	electron beam (also e-beam)
ECR	electron cyclotron resonance
FET	field effect transistor
FIB	focused ion beam
FMS	flexible machining system
GaAs	gallium arsenide
GSMBE	gas-source MBE
HBT	heterojunction bipolar transistor
HEMT	high electron mobility transistor
HFET	heterojunction FET
IC	integrated circuit
IMPATT	impact avalanche and transit time
IR	infrared
LACVD	laser-assisted CVD
LCVD	laser CVD
LDD	low-doped drain
LPCVD	low-pressure CVD
MBE	molecular beam epitaxy
MMST	Microelectronics Manufacturing Science and Technology
MOCVD	metalorganic CVD
MOMBE	metalorganic MBE
MOS	metal-oxide-semiconductor
Nd-YAG	neodymium-yttrium aluminum garnet
PACVD	plasma-assisted CVD (also PECVD)
PAPVD	plasma-assisted PVD
PECVD	plasma-enhanced CVD (also PACVD)
polydiamond	polycrystalline diamond

PVD	physical vapor deposition
PAPVD	plasma-assisted PVD
RAMs	random access memories
RE	reactive evaporation
rf	radio frequency
RIBE	reactive ion beam etching
RIE	reactive ion etching
SEMI	Semiconductor Equipment and Materials Institute
SIMS	secondary ion mass spectroscopy
TACVD	thermally assisted CVD
TFT	thin film transistor
UFMP	ultrafine metal powders
UHMWPE	ultrahigh molecular weight polyethylene
UV	ultraviolet
via	a conducting through-path perpendicular to the plane of the substrate
VLS	vapor-liquid-solid

APPENDIX B

BIOGRAPHICAL SKETCHES OF COMMITTEE MEMBERS

DAVID RICHMAN received his BS degree in 1954 from Yale University and his PhD degree in 1959 from Cornell University, both in physical chemistry. He joined RCA Laboratories as a staff member in 1959, became head of semiconductor materials research in 1970, and was made director of the Materials Processing Research Laboratory of the David Sarnoff Research Center in 1979. In 1991 he was appointed adjunct professor at the Stevens Institute of Technology and director of the Consortia for Surface Processing at David Sarnoff Research Center. He received the David Sarnoff Award in 1967 and the RCA Laboratories Outstanding Achievement Award in 1969. He is a member of Sigma Xi, the American Chemical Society, the Electrochemical Society, the American Association for Crystal Growth, and the AIME Electronic Materials Committee. Dr. Richman is a prime investigator at SEMATECH and is a member of the New Jersey Governor's Round Table on Superconductors. His areas of expertise include crystal growth, polymer processing, thin film technology, materials characterization, vapor-phase growth, and video disc development and manufacture.

ROINTAN F. BUNSHAH received his BSc degree in 1948 from Benares Hindu University and his MS degree in 1951 and DSc degree in 1952 from Carnegie Institute of Technology, all in metallurgy. He worked as research metallurgist and instructor in the Metals Research Laboratory, Carnegie Institute of Technology from 1952 to 1954; as research scientist and adjunct professor at New York University from 1954 to 1960; and as senior metallurgist at the Lawrence Radiation Laboratory from 1960 to 1969. Since 1969 he has been a professor of engineering at the University of California at Los Angeles. He received the Hadfield Medal of the Geological Mining and Metallurgical Institute of India in 1948 and the Graede-Langmuir Award of the American Vacuum Society in 1986. He is a member and fellow of the American Society for Metals International, an honorary life member of the American Vacuum Society (president 1970-1971), and an honorary life member of the Indian Vacuum Society. His areas of expertise include vacuum metallurgy, dispersion strengthening of metals, ultrahigh vacuum techniques, plasma-assisted physical and chemical vapor deposition processes, electronic and optoelectronic materials, and super-hard coatings for wear resistance.

ALFRED Y. CHO received his BSEE degree in 1960, his MS degree in 1961, and his PhD degree in 1968, from the University of Illinois, all in electrical engineering. He worked with the technical staff in research at the Ion Physics Corporation from 1961 to 1962 and at the Science Technology Laboratory of TRW from 1962 to 1965 and as research assistant in electrical engineering at the University of Illinois from 1965 to 1968. He joined AT&T Bell Laboratories as a member of the technical staff in 1968 and became research department head in 1984. He is director of AT&T Bell Laboratories Semiconductor Research Laboratory. Dr. Cho received the International Prize in New Materials of the American Physical Society in 1982, the Morris N. Liebmann Award of the Institute of Electrical and Electronics Engineers in 1982, the Solid State Science and Technology Medal of the Electrochemical Society in 1987, and the Graede-Langmuir Award of the American Vacuum Society in 1988. He was elected to the National Academy of Sciences and the National Academy of Engineering in 1985. He is a member of the Institute of Electrical and Electronics Engineers, the American Physical Society, the American Vacuum Society, the Electrochemical Society, the New York Academy of Sciences, the Materials Research Society, and the American Association for the Advancement of Science. His areas of expertise include thin film technology, molecular beam epitaxy for growth of semiconductors, insulators, and metal film layers for microwave and optoelectronic component fabrication.

STEPHEN M. COPLEY received his AA degree in 1957, his BA degree in 1959 in physics, his MS degree in 1961, and his PhD degree in 1964 in engineering science from the University of California at Berkeley. He joined the Advanced Materials Research and Development Laboratory of Pratt and Whitney Aircraft in 1964 and served as supervisor of the Alloy and Materials Research Section from 1968 to 1970. He was a faculty member of the University of Southern California from 1970 to 1990 and held the Kenneth T. Norris Chair of Metallurgical Engineering. He is professor and chairman of the Metallurgical and Materials Engineering Department at Illinois Institute of Technology and serves as vice provost of the Academic Planning and Budgeting and as director of the Center for Manufacturing and Materials Process Engineering. Dr. Copley is a fellow and trustee of the ASM INTERNATIONAL and is currently president of the society. He is also a member of the Metallurgical Society of the AIME, the American Ceramic Society, the American Society of Mechanical Engineers, the Society of Manufacturing Engineers, the Materials Research Society, and Sigma Xi. He received the Education Achievement Award in 1978 and the Educator of the Year Award in 1976, both from the Society of Manufacturing Engineers. His areas of expertise include laser systems, applications of lasers as a directed heat source for shaping, joining and modifying properties of surfaces, and synthesis of amorphous and crystalline metastable phases by lasers.

TERRY D. GULDEN received his BS degree in 1960 in ceramics from the University of Washington and his MS degree in 1962 and PhD degree in 1965 from Stanford University in materials science. He worked as a ceramist at the United Technologies Center from 1960 to 1961 and as research associate at the Berkeley Nuclear Laboratory from 1965 to 1966. He held numerous staff and management positions since 1966 with the General Atomics Company, where he is director of advanced materials technology. Dr. Gulden is a member of the American Association for the Advancement of Science, the American Ceramic Society, and the Materials Research Society. His areas of expertise include radiation effects in solids, transmission electron microscopy, internal friction, chemical vapor deposition, creep and deformation behavior of ceramics and metals, and nuclear reactor and composite materials development.

CONILEE G. KIRKPATRICK received her BS degree in 1969 and her MS degree in 1970, both from Washington University, and her PhD degree in 1974 from the University of Illinois, all in electrical engineering. She worked at the General Electric Company's Research and Development Center as staff physicist in electrical engineering from 1974 to 1979. She joined the Microelectronics Research and Development Center of Rockwell International in 1979 as principal scientist, and was later director of GaAs Operations, where she directed the construction and operation of a digital and microwave GaAs integrated circuits pilot line and also managed the Defense Advanced Research Projects Agency (DARPA) GaAs Pilot Line Program. In 1988 she became senior scientist at Science Applications International Corporation, focusing on neural network technology. Dr. Kirkpatrick has served as consultant to the Electronics Division of the Electrochemical Society. She is a member of the Institute of Electrical and Electronics Engineers, the Society of Women Engineers, and the American Physical Society. Her areas of expertise include ion implantation; growth of compound semiconductors; radiation effects on solids; semiconductors; and memory, display, and integrated circuit devices.

ROBERT D. MAURER received his BS degree in 1948 from the University of Arkansas and his PhD degree in 1951 in physics from the Massachusetts Institute of Technology. He was given an honorary LLD degree by the University of Arkansas in 1980. He served as a member of the physics staff at the Massachusetts Institute of Technology from 1951 to 1952. Dr. Maurer worked at Corning Glass Works as a physicist from 1952 to 1962, as senior research associate from 1962 to 1963, as manager of applied physics from 1963 to 1978, and was made research fellow from 1978 until his retirement in 1989. He received the George W. Morey Award of the American Ceramic Society in 1976, the Morris N. Liebmann Award of the Institute of Electrical and Electronics Engineers in 1978, the Industrial Applied Physics Prize of the American Institute of Physics in 1978, the Ericsson

International Prize in Telecommunications in 1979, and the IEEE/OSA Tyndall Award in 1989. Dr. Maurer is a member of the National Academy of Engineering, member and fellow of the American Ceramic Society, member and fellow of the Institute of Electrical and Electronics Engineers, and member of the American Physical Society. His major areas of expertise include the physical behavior of glasses and optical communications.

JAMES M. MIKKELSON received his BS, his MS, and his EE degrees in 1972 from the Massachusetts Institute of Technology, all in electrical engineering. He was a member of the technical staff and project manager at Hewlett-Packard Company from 1973 to 1984, where he was responsible for the development of very large scale integration (VLSI) metal-oxide semiconductor (MOS) processes and refractory metal interconnections. In 1984 he was one of the founders of Vitesse Semiconductor Corporation, where he is vice president of technology development. Mr. Mikkelson is a member of Tau Beta Xi, Sigma Pi, Eta Kappa Nu, the Institute of Electrical and Electronics Engineers, the American Vacuum Society and the International Society for Hybrid Microelectronics. He received the Outstanding Paper Award from the 1981 International Solid State Circuits Conference. His areas of expertise include semiconductor device physics and modeling; semiconductor process architecture, design, and development; compound semiconductor processing; beam processing of integrated circuits; integrated circuit process equipment integration; circuit design; and yield improvement.

ANTHONY J. PERROTTA received his BS degree in ceramics in 1960 from Pennsylvania State University and his MS degree in 1962 and PhD degree in 1965 from the University of Chicago in mineralogy-crystallography. He worked as a physical scientist in ceramics, mineralogy, and crystallography at the Union Carbide Corporation Research Institute from 1967 to 1969 and as senior research scientist at Gulf Research & Development Center from 1969 to 1985. Since 1985 he has been an ALCOA fellow at the ALCOA Technical Center. He is a member of the Materials Research Society, the Metallurgical Society of American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME), the American Ceramic Society, and the Sigma Xi. His areas of expertise include crystal structure, phase equilibria, and thermal and catalytic properties of mineralogical and ceramic materials.

NORMAN E. SCHUMAKER received his BS degree in chemistry in 1963 from Wabash College and his MS degree in 1965 and his PhD degree in 1968, both in physical chemistry, from the Massachusetts Institute of Technology. He worked as a member of the technical staff at AT&T Bell Laboratories from 1968 to 1984 and in 1984 founded Emcore Corporation, where he is president and chief executive officer. Dr. Schumaker is a member of the Institute of Electrical and Electronics Engineers, the American Chemical Society, the American Electrochemical Society, and the American Physical Society. He is also a member of Sigma Xi, Phi Beta Kappa, and Delta Phi Delta. His areas of expertise include advanced materials and process technology development, electron beam and molecular beam epitaxy, and MOCVD processing equipment development and manufacture.

PIRAN SIOSHANSI received his BS degree in electrical engineering in 1967, a BS degree in mathematics in 1968, an MS degree in physics in 1969, and a PhD degree in nuclear physics in 1972 from Purdue University. He did postdoctorate work at Straussburg University's Nuclear Research Center from 1972 to 1973; served as director of the Nuclear Research Center in Tehran, Iran, from 1973 to 1978; and was assistant professor at Louisiana State University from 1979 to 1981. Since 1981 Dr. Sioshansi has served as vice president of ion implantation and is vice president of surface engineering at the Spire Corporation. He was given the Employee of the Year Award by the Spire Corporation in 1986. His areas of expertise include ion beam modification of surfaces; materials modification by ion implantation for semiconductors, biological implants, and bearings; wear analysis and measurement; accelerators; trace chemical analysis; and materials implantation in diamond and sapphire.

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ISBN 0-309-04636-1