Thin Film Deposition Processes

Russell Messier, Guest Editor

Thin film materials pervade our everyday life as transparent conductors in LCD watches and computer displays and in defrosters for automobiles... antireflection coatings for camera lenses... optical fibers for communication... architectural glass coatings for both color and energy efficiency... solar cells... decorative coatings on plastics such as for toys and automobiles parts... a whole host of electronic and optoelectronic devices... hard coatings for cutting tools, drill bits, and bearings... even metallic coatings inside potato chip bags to keep the chips crisp!

Without thin films our lifestyles would be drastically different. And this trend toward increased use of thin film technology will only continue.

The varied reasons for using thin films and the specific deposition processes for preparing them are often complex; but usually relate to function, cost, beauty, materials and energy efficiency, and performance. In addition to technological applications, scientists are finding thin films to be an invaluable tool for investigating new physical phenomena, even at the quantum level. For instance, two of the most important new materials—high temperature ceramic superconductors and diamond coatings—are currently being made by several thin film deposition processes in order to explore both their scientific and technological potential.

Just 25 years ago the variety of deposition processes for preparing thin films was quite limited. Thin film scientists and technologists had at their disposal electrodeposition, elementary chemical vapor deposition, evaporation, and dc sputtering. Commercial equipment for electron-beam evaporation, a mainstay in the optical coatings industry, was just being developed. Most of the deposition processes reviewed in this and next month's MRS BULLETIN were either not commercially available or were not even conceived of then.

And since large-scale computers were not available, molecular dynamic studies of film growth were only in the minds of physicists and materials scientists. Only within this decade are computers with sufficient speed and capacity available, and interestingly they are based in significant part on the development of thin film coatings used in microelectronic chips.

The level of sophistication that has been achieved over this time is best seen in the molecular beam epitaxy (MBE) and organometallic vapor phase epitaxy (OMVPE) deposition processes. In both the deposition process concept is simple, but it required developments in vacuum technology, sophisticated electronic controllers, purity of gases, solids and liquids used in the processes, new materials (e.g., high vapor pressure organometallic precursors), etc., before useful thin film materials could be achieved. The degree of crystal perfection and purity in each of these processes is excellent, and because they are layer-by-layer deposition processes, the ability to design new multilayer materials and electronic devices of practical and scientific importance is limited only by our imagination and ingenuity.

And yet MBE and OMVPE take radically different approaches to achieving similar results of controlled epitaxial growth. In MBE, temperature is the primary parameter controlling high adatom mobility, and ultraclean and ultrahigh vacuum conditions allow the atoms sufficient time to do their predictable merry dance on the growing film surface, unimpeded by impurity atoms. OMVPE, on the other hand, substitutes chemistry for temperature and pure gases for ultrahigh vacuum. With OMVPE the ability to produce high purity organometallic precursor gases of sufficient purity, low dissociation temperature, and low cost are limiting factors—but once achieved, OMVPE has the advantages of low capital equipment cost and relatively high material throughput.

Not all thin film applications require, or even desire, crystalline perfection. Chemical vapor deposition (CVD) processes carried out under more "normal" conditions of chemical purity are still widely used despite the high temperatures required to dissociate the input gases because CVD has the potential for a high degree of control, conformal coating, and low cost. And thermal evaporation has been historically the most widely used deposition technique, with substrate temperatures varying from very low to high values, and a resulting wide range of crystallite sizes and properties.

Deposition processes involving plasmas have become more prominent since the mid-1960s—first with rf sputtering, then plasma-assisted CVD, followed by magnetron sputtering, plasma spraying, ion beam deposition, and several variations and combinations (e.g., activated reactive evaporation, ion plating, ion-assisted deposition). We have seen how bombardment processes can augment thermal and chemical processes in achieving specific goals—such as films with controlled characteristics and resulting properties, usually at low substrate temperatures. Unfortunately, measurement and control of the bombardment process is often difficult, due partly to the interrelationship of the various control parameters ("knobs on the front panel"). The fact is, this additional process of bombardment can be both a blessing and a bane to the thin film technologist since it allows a wide latitude in preparation-property relations. The question is whether the technologist can optimize, understand, and control this process.

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And this brings me to the final point—in general, a thin film $\neq$ bulk material! The majority of films prepared commercially or scientifically are not perfect single crystals in their well-defined low free energy state, but can contain voids, grain boundaries, short-, intermediate-, and long-range order and disorder, clustering at the nanometer-level, compositional variations, etc., depending on the preparation conditions. Thin films can be designed to have low to high diffusion, graded or abrupt interfaces, amorphous to single-crystal structures, metastable to stable structures, fine-grained to coarse-grained microstructures, dense and uniform morphology to highly anisotropic, columnar morphology, etc. It is the wide variety of deposition processes that allows this infinite array of thin film materials.

And usually the question arises—which technique is "best"? The answer is never straightforward since there is considerable overlap in the ability to prepare thin film materials with specific properties. Each of the deposition processes has advantages and disadvantages, and the final choice usually depends on the balance of technical, scientific, and economic considerations.

The number of articles in the November and December issues of the MRS BULLETIN reflects this wide diversity and covers the range of materials and applications that thin films present to our scientific and technological society. Each author has attempted to give a broad view of the individual processes by describing the basic process along with variations, overlaps, in addition to resulting film characteristics, properties, and applications of representative materials.

- I.K. Schuller, University of California-San Diego, demonstrates the power of modern supercomputers to perform full molecular dynamics simulations of elementary nucleation and growth processes in metals, semiconductors, and insulators and also in single crystal to amorphous structures. The current good agreement between calculations and experimental observations is encouraging, and Schuller predicts that we will be seeing many more such simulation studies. Initially we should expect simulations to elucidate aspects of epitaxy, bombardment, interface structures, and specific growth process parameters, while film growth involving large numbers of particles, such as columnar growth, will have to await more powerful computers and computation schemes.
- T.D. Moustakas, Boston University, covers the molecular beam epitaxy process by describing some experimental aspects and the importance of *in situ* surface studies—particularly RHEED. He then enumerates the advantages and uses of MBE films for both scientific and technological applications by providing examples from the extensively studied semiconductor area. He expects increased use of MBE for metallic and insulating materials.

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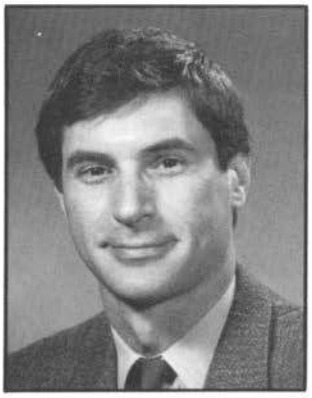
- S.K. Ghandhi and I.B. Bhat, Rensselaer Polytechnic Institute, outline the development of organometallic vapor phase epitaxy to its present status (with MBE) as the semiconductor deposition technique of choice. They cover the relevant chemistries for preparing compound semiconductors and also the importance and design of deposition reactors. Although the growth mechanisms of GaAs have been studied in detail due to its technological importance, more complicated chemical systems are not nearly as well understood. New trends in OMVPE, based on both plasmas and photon enhancement of the processes, are covered.
- Finally, T.M. Besmann, D.P. Stinton, and R.A. Lowden, Oak Ridge National Laboratory, review the oldest of the deposition processes—chemical vapor deposition—and show that it is very much alive. Used extensively by industry, new materials and applications are being developed, ranging from composite, diphasic coatings for increased fracture toughness to a whole range of electronic materials. As for MBE, OMVPE, and the deposition processes to be covered in next month's issue of the MRS BULLETIN, it is enhancements of the basic process which are allowing for even newer applications.

I am certain you will find these articles on "Deposition Processes" informative and exciting, and you will obtain a snapshot of their current status and future directions. Thin films are an important part of the fabric of modern technology and the sophistication of our ability to prepare and understand them is constantly improving. ☐


Russell Messier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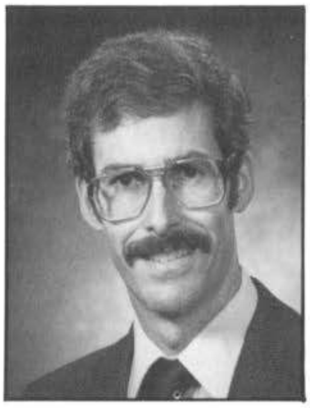
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Russell Messier, Guest Editor for the November and December issues of the MRS BULLETIN, is a staff member at Pennsylvania State University's Materials Research Laboratory and is on the faculty of the university's Department of Engineering Science and Mechanics. His studies have ranged from conventional thin film research, the development of x-ray phosphors, and solar absorbers to theories on the optical behavior of daguerreotypes. During the last decade his research has emphasized the relations among basic sputtering processes, thin film morphology, and resulting film properties. An outcome of that research was the development of a fractal-like void network model which is providing an approach to quantitative preparation-property relations for films prepared under low mobility conditions. He is also involved with a team of scientists in unveiling diamond coating science and technology in the United States. Messier is a member of the Materials Research Society, the American Vacuum Society, IEEE, and SPIE.

Theodore M. Besmann received a BE in chemical engineering from New York University and an MS in nuclear engineering from Iowa State University While completing his PhD at Pennsylvania State University, he established the first chemical vapor deposition system at that institution's Materials Research Laboratory. Since 1975 Besmann has been at Oak Ridge National Laboratory, where he currently heads the Ceramic Surface Systems Group in the new High Temperature Materials Laboratory. A member of the Materials Research Society, Besmann's recent research involves multiphase coatings by CVD, chemical vapor infiltration methods for preparing ceramic composites, and modeling and diagnostics related to CVD.

Richard A. Lowden is a development engineer in the Metals and Ceramics Division at Oak Ridge National Laboratory. He received a BA in chemistry from St. Vincent College and an MS in materials engineering from the University of Tennessee. Presently Lowden is involved in the development and characterization of composites fabricated through the use of chemical vapor infiltration techniques. He is also using chemical vapor deposition to investigate advanced coatings.

David P. Stinton is a lead engineer in the Metals and Ceramics Divisior at Oak Ridge National Laboratory. He earned a BS and an MS, both in ceramic engineering, from Virginia Polytechnic Institute. At Oak Ridge, Stinton's work involves the fabrication of fiber-reinforced ceramic composites by chemical vapor deposition, as well as the utilization of CVD for application of hard, toughened, corrosionresistant, and oxidation-resistant coatings.

Sorab K. Ghandhi obtained a PhD in electrical engineering from the University of Illinois, then worked at General Electric, Philco, and Rensselaer Polytechnic Institute, where he is currently a professor in the Electrical, Computer, and Systems Engineering Department. Ghandhi's research focuses on the growth and characterization of modern electronic materials, with an emphasis on the organometallic epitaxy of III-V and II-VI semiconductors. A member of the Materials Research Society, a Fellow of IEEE, and a recipient of Distinguished Teaching and Faculty Awards at Rensselaer, Ghandhi is author of more than 180 publications and three books, including *VLSI Fabrication Principles: Silicon and Gallium Arsenide*.

Ishwara B. Bhat received a BT in electrical engineering from the Indian Institute of Technology, and MS and PhD degrees from Rensselaer Polytechnic Institute. From 1985 to 1987, he served as a research associate in the Electrical, Computer, and Systems Engineering Department at Rensselaer, where he now works as a research assistant professor. His current research interests include the OMVPE growth of II-VI compounds, and the fabrication and characterization of infrared detectors. Bhat is the co-author of more than 25 technical papers on compound semiconductor materials.

Theodore D. Moustakas is a professor of electrical engineering and physics at Boston University, where he is researching the growth and electronic properties of metastable materials, and artificially modulated structures produced by molecular beam epitaxy. Prior to his current appointment, he received a PhD from Columbia University, conducted postdoctoral research at Harvard University, and was a senior research scientist for Exxon Research and Engineering Company. With 75 publications and 10 patents to his credit, Moustakas is a member of the Materials Research Society and also the American Physical Society, the American Vacuum Society, and the New York Academy of Sciences.

Ivan K. Schuller is a professor of physics at the University of California-San Diego, and a special-term appointee at the Materials Science Division of Argonne National Laboratory. His research interests and numerous published works focus on experimental and theoretical aspects of epitaxial growth, and on the elastic, transport, superconducting, and magnetic properties of thin films. Schuller is a member of the Materials Research Society, and was the co-organizer of the symposium on "Interfaces, Superlattices, and Thin Films" at the 1986 MRS Fall Meeting. ☐