Deposition of Dense and Hard Coatings By Ion-Assisted and Plasma-Assisted Vacuum Processes

Karl H. Guenther

Vacuum-deposited thin films have suffered because some of their properties are inferior to those of the respective bulk material. The growth process of these films is the fundamental reason for weaker properties, which include density and hardness. It causes a less-than-dense, columnar or dendritic microstructure, that is apt to change electrical, mechanical, and optical properties upon adsorption and resorption of environmental contaminants—predominantly water molecules from humid air. Through ion-assisted deposition (IA D), researchers have attempted to grow thin films with "bulk-like" microstructure and properties, many times utilizing the co-irradiation of the growing film with energetic ion beams. At the University of Central Florida, a major alternative R&D effort is in progress to study and apply reactive low voltage ion plating (RLVIP) techniques for thin film growth, employing a state-of-the-art, high-vacuum deposition system with extensive process diagnostics and thin film characterization.

Process Parameters Affect Complexity

Thin film growth processes are complex phenomena, depending on a number of process parameters, including substrate temperature, deposition rate, and partial pressure of the reactive gas (if present), to name just a few. The complexity can be reduced to a single determining parameter—the surface mobility of the elementary species after their condensation on the surface—which results from the combined influence of those many process parameters.[1,2]

At low surface mobility, condensing species nucleate practically where they arrive and may obstruct the path of subsequently deposited species to still empty nucleation sites.[3] This causes the film to grow rather loosely packed, containing an appreciable fraction of voids. The resulting porous or columnar structure (Figs. la & lb)' is generally undesirable. It causes a lower-than-bulk refractive index which may easily change upon adsorption and desorption of water molecules from a humid environment.'

At higher surface mobility, the species are able to occupy more of the available condensation sites, and the film becomes more densely packed. The now-widely adopted approach to enhance surface mobility is to provide additional energy to the condensing species. The different packing density of thin films obtained with different deposition techniques yields remarkable differences in optical and structural properties.'

Assisted Deposition Processes

The co-irradiation of the growing film with energetic ions is commonly referred to as ion-assisted deposition (IAD). This process typically involves ion energies in excess of 100 eV (up to several hundred eV), at an ion current density anywhere from 20 to 200 μA/cm^2. Its main advantage is the possibility to retrofit existing coating equipment with one or more ion beam guns, now available in various sizes (from 1 cm to 30 cm extraction orifice diameter). Disadvantages are the beam divergence and pointed nonuniform (Gaussian) ion current distribution which limits, to some degree, the useful area for uniform coating density and thickness distribution (Fig. 2a).[8]

Alternatively, ion beams have been used to sputter-deposit thin films. A primary beam of energetic (1-3 keV) Ar^+ ions is neutralized right after leaving the source, to prevent undesirable beam deflection in electric or magnetic fields that may be present in the coating chamber. Impulse transfer from the incident neutralized ions to the target surface ejects species (atoms, molecules) with a relatively

This is an edited version of a paper presented at the AESF Symposium: Surface Finishing for Electronic Applications. January 30. 1991; in Orlando, Florida

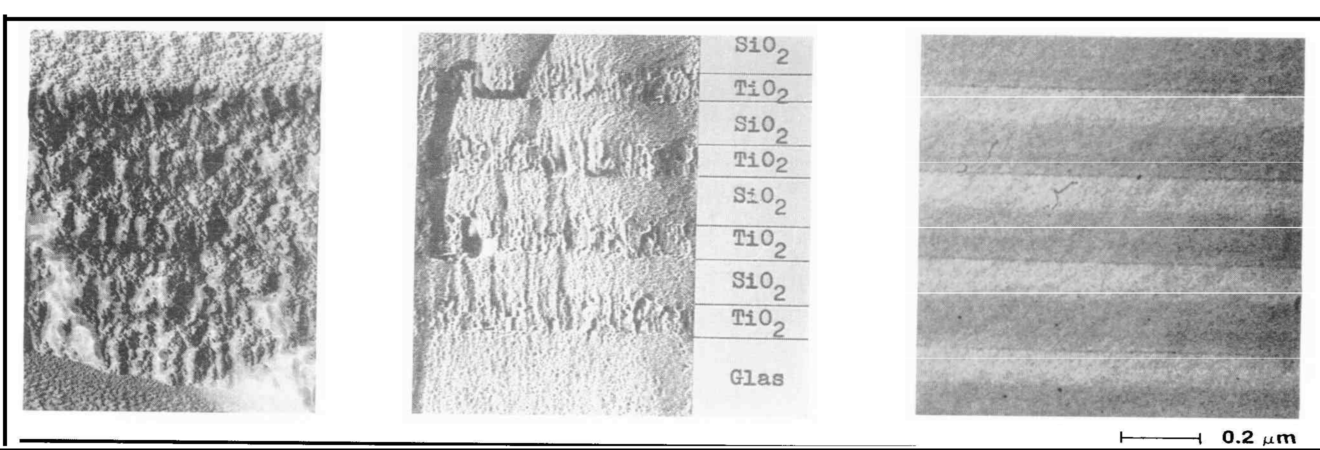
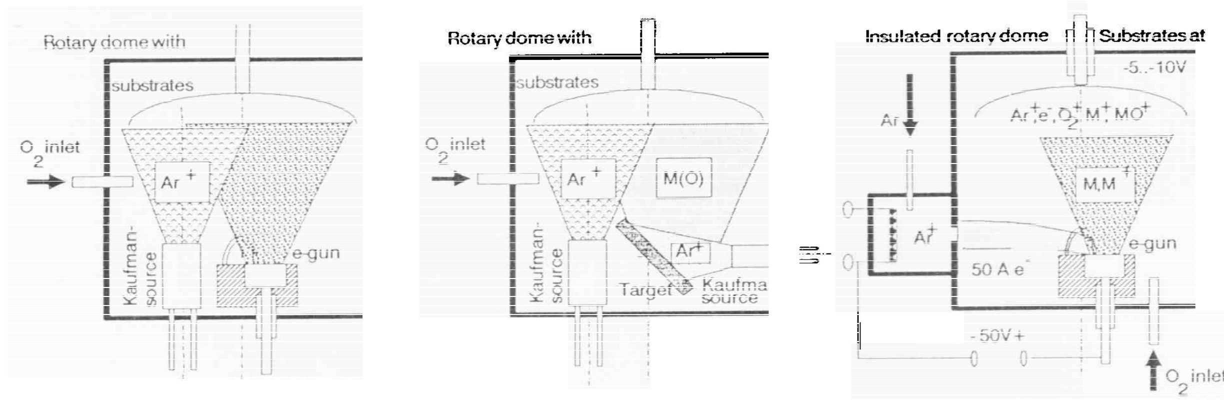


Fig. 1—Electron micrographs of dielectric multilayers (a) electron beam evaporation on glass at approximately room temperature and (b) at a substrate temperature of about 300°C, (c) ion-plated on unheated glass. (Note Because of process heat during me RLVIP process, the actual substrate temperature raises to about 250°C at the end of 2 1/2 hours deposition time for a multilayer stack as shown, without a noticeable change in the microstructure of the thin films from the bottom to the top of the stack).



g. 2—(a) ion-assisted deposition (IAD), (b) ion-beam sputtering (IBSD), (c) reactive, low-voltage ion plating (RLVIP).

high energy of several electron volts, which helps them to form dense films by increasing surface mobility.

For additional improvement, the growing film is sometimes co-irradiated with another ion beam (Fig. 2b), similar to IAD. This kind of (“neutral”) ion-beam sputter deposition (IBSD) is referred to as dual ion-beam sputtering. The beam and target geometry require dedicated equipment and limit the substrates to be coated to essentially flat shapes. While scale-up is possible, it is expensive because the diameters of the ion beams and targets increase linearly with the size of the substrate. In order to maintain a certain ion-to-atom arrival-rate ratio on the substrate surface, ion currents need to increase with the irradiated area (i.e., with the square of the substrate diameter).

The reactive, low-voltage ion plating (RLVIP) process,[9] which is distinctly different from other ion-assisted deposition techniques in that a high flux of low-energy ions of argon, oxygen, and the coating material, irradiates the substrate and growing film surface (Fig. 2c). The vapor sources are melts of metal or sub-oxides produced by a modified electron beam gun. Substrates coated by reactive, low-voltage ion plating are in contact with the plasma sheath and attain a self-bias potential of -5 to -10 V with respect to the plasma. This negative charge accelerates argon, oxygen and metal ions toward the substrate surface. The process is implemented in a state-of-the-art, high-vacuum deposition system of 800 mm (32 in.) chamber size.’

The main advantage of this process is its versatility in terms of size, shape, and number of substrates which can be coated in a batch with excellent uniformity (1 to 3 percent film thickness variation across the 800 mm diameter rotating dome), its scalability (now available also in a 1,100 mm [42 in.] box coater), and the multitude of coating materials which can be used with the RLVIP process (metals, oxides, nitrides).

Improved Film Properties

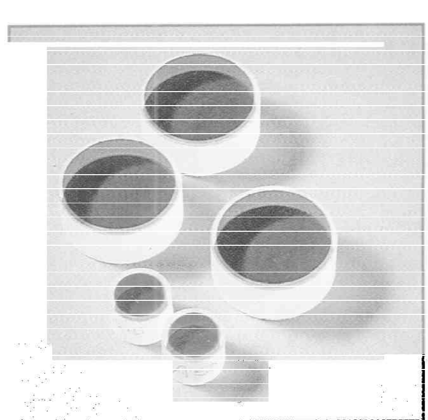
The significantly improved density of ion-plated thin films over those deposited by conventional thermal or electron-beam evaporation (EBD) becomes obvious from a comparison of Figs. 1b and 1c. The electron micrographs of cross sections of multi layer stacks consisting of SiO_2 and TiO_2, deposited by EBD and RLVIP, respectively, show clearly that RLVIP coatings are much denser and smoother than those deposited by conventional processes. The higher density of these thin films is also evident from a higher refractive index. The smoothness of their boundaries as seen in the RLVIP multi layer cross-section (Fig. 1c) has been repeatedly confirmed by surface roughness measurements.[10]

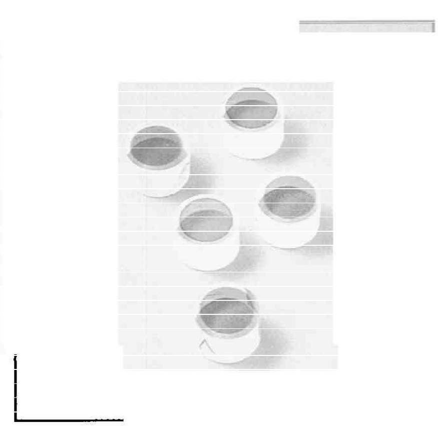
Under certain conditions, the top surface of thick single layers and multi layer stacks, deposited by RLVIP, have a lower root-mean-square (rms) roughness than the substrate surface. We are currently investigating this potential surface smoothing capability for optical applications where the surface smoothness achievable by conventional polishing techniques is limited—SiC mirrors,[11] for example.

Once this smoothing capability becomes routinely reproducible, the RLVIP process will revolutionize optical manufacturing by making obsolete the final super polishing effort which is currently applied to many laser optics surfaces. These experimental studies are backed by the theoretical explanation of the film growth process’ and its numerical simulation with a computer model.[12]

Applications

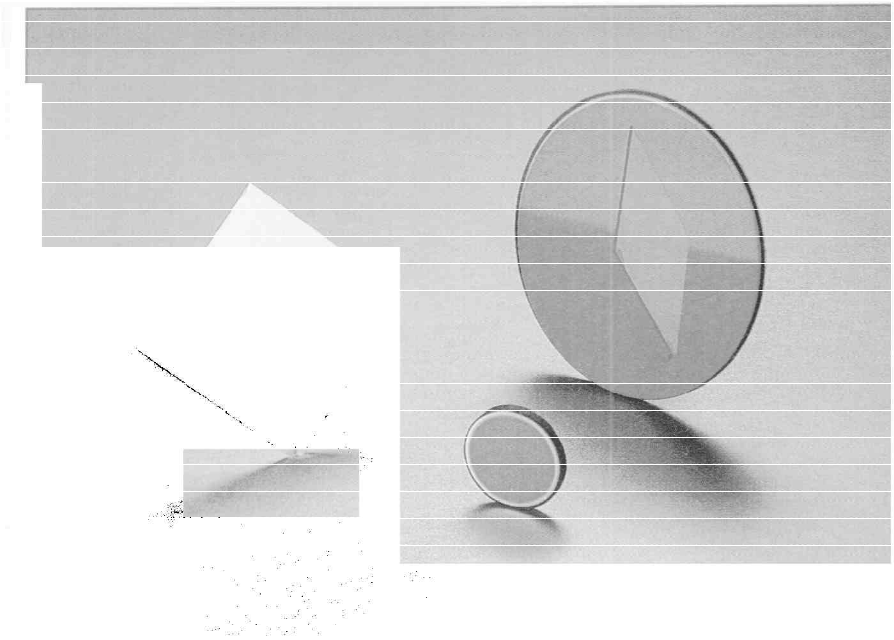
The RLVIP process is used mostly for the deposition of multi layer interference filters, polarizers,[13] and anti-reflection coatings, consisting of various oxides, silicon, and germanium, with the latter two materials used for infrared applications. ” The





Low-loss, ion laser mirrors, coated with a proprietary, modified Q-Plate process. Photos courtesy of Coherent Auburn Group, Auburn, CA.

*BAP 800, Balzers High Vacuum, Hudson. NH

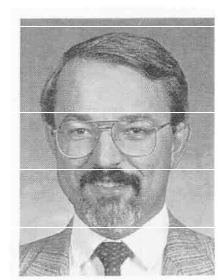


Reactive Low Voltage Ion Plated (RLVIP) Optics: Large Diameter-Optical bandpass interference filter surface coating on an absorbing glass optic. The multi-layer dielectric RLVIP coating allows high-temperature operation of the optic without the degradation that conventional optical bandpass filters would suffer. *Small* Diameter—Red light attenuation coating to provide humidity protection of the environmentally sensitive optic. Square—"Ultraviolet-blue light" color separation coating on a quartz window to provide stabilized color separation in a high-humidity environment. The mechanical fixturing marks in the corners of the production plate make visible the interference coating on the transparent substrate. Photo courtesy of Corion Corporation, Holliston, MA.

process was also applied to the deposition of front surface aluminum mirrors, evaporating the aluminum from an electron beam gun with the assistance of plain argon plasma, and one or more dielectric layers, with reactive, low-voltage ion plating on top of the aluminum for environmental protection. Corrosion tests of these coatings showed up to *20* hours' survival time for immersion in 0.2M NaOH solution—up to a factor of 10 from previous best results obtained with electron beam evaporation. This result demonstrates the high packing density of ion-plated thin films which make them impervious to corrosive agents and to humidity from the ambient atmosphere.[15] The high packing density manifests itself also in microhardness measurements, performed with a Vickers-diamond indenter.[16-18] In fact, it is the extraordinary hardness (and wear resistance) which has the biggest commercial impact on the application of some of these new and improved deposition techniques for thin film coatings. The excellent wear-resistant properties of ion plated TiN lead to a whole new coating technology for cutting tools. " Further improvements were brought about by the development of ion plated titanium carbonitride films.[20] However, ion plating of metallic substrates (tools)[21] allows the application of an external bias and is therefore different to the low-voltage, reactive ion plating of optical (dielectric) elements which attain a self-bias. ❑

References

1. K.H. Guenther, *Proc.* SPIE, 1324, 2 (1990).
2. K.H. Guenther, accepted for publication by Opt.*Eng.* (1990).
3. K.H. Guenther, Appl. *Opt.,* 23, 3806 (1984).
4. K.H. Guenther, *Proc.* SPIE, 346, 9 (1982).
5. K.H. Guenther, R. Menningen, and C.A. Burke, *Proc.* SPIE, 399, 246 (1983).
6. J.M. Bennett, et al., *Appl. Opt., 28, 3303 (1989).*
7. R.A. Roy and D.S. Yee, in: J.J. Cuomo et al., eds., *Handbook of ion Beam Processing Technology, Noyes* Publ., Park Ridge, NJ, 1989.
8. F. Flory, *Proc. SPIE, 1270, 172 (1990).*
9. Balzers Ltd., Liechtenstein; Balzers High Vacuum, U.S. patents 4,448,802 (1985); 4,619,748 (1986).
10. F.J. Boero, R.A. Chipman, and K.H. Guenther, *NIST Spec. Publ.,* U.S. Dept. of Commerce, 775,339 (1989).
11. K.H. Guenther, *Proc. SPIE, 1323, 29 (1990).*
12. J. Cryer, K.H. Guenther, S. Nunez, and S. Zarrabian, to be published.
13. K.H. Guenther and Z. Taubenfeld, *Proc. SPIE, 1125,* 122 (1 989).
14. K.H. Guenther, P. Sachdeva, and Z. Taubenfeld, *Proc. SPIE, 1112, 417 (1989).*
15. K.H. Guenther, 1. Penny, and R. Willey, *Proc. SPIE,* 1125, 114 (1 989).
16. K.H. Guenther, H. Bangert, A. Kaminitschek, and A. Wagendristel, *Conf. Digest, Topical Meeting on Optical interference Coatings,* Opt. Sot. of America, April 1984.
17. H. Bangert, A. Wagendristel, and K.H. Guenther, *Proc. SPIE, 652,* 134(1986).
18. K.H. Guenther, H. Bangert, and A. Wagendristel, submitted for publication in *Appl. Opt.*
19. E. Moll and E. Bergmann, Surf. & Coatings Technol., 37,483 (1989).
20. E. Bergmann, H. Kaufmann, R. Schmid, and J. Vogel, *Surf. & Coatings Technol., 42, 237 (1990).*
21, N.A.G. Ahmed, *Ion Plating Technology—Developments and Applications, Wiley,* Chichester; (1987).



About the Author

Karl H. Guenther, whose PhD in Physics is from the University in Innsbruck (Austria), is an Associate Professor of Engineering Science and Physics at the University of Central Florida, where he conducts his research at the Center for Research in Electro-Optics and Lasers (CREOL), 12424 Research Parkway, Suite 400, Orlando, FL 32826.