Advances in thin-film coating technology during the past decades have focused on improving the quality of deposited layers through refinements in materials and deposition processes. Material improvements have included lowering impurity content, controlling chemical composition, and preparing physical forms that increase source utilization efficiency. Chemical processing has eliminated impurity-related detrimental contamination; reduction of the concentration of multiple oxidation states, that can introduce a variety of evaporation or sputtering efficiencies, has resulted in better repeatability of film composition and morphology.

Deposition processes have evolved in conjunction with greater demands on optical and mechanical film quality, durability requirements, and expanded applications. The introduction of new materials, especially relevant to mechanical properties, has also driven deposition process development. It has been known for some time that the energetics of the deposition process play the dominant role in not only film morphology and density, and therefore strength, but also composition as it influences transmission losses and high-energy laser damage thresholds. +

The original Structure-Zone Model (SZM) proposed by Movchan and Demchishin related growth microstructure to substrate temperature, T, which was the source of morphological energy [1]. The microstructure progresses from one that is characterized by low packing densities at low temperatures and large void volume, to one that is more densely packed in columnar structures at higher temperatures. Even at high temperatures, the packing densities deviated from bulk-like and exhibit stress. Later researchers included the influence of process pressure and ion energy in ion-assisted and sputter deposition.

The SZM in Figure 1 (following page) summarizes the progression of deposition techniques from zones of low-energy thermal evaporation to zones of high-energy ion-beam and plasma-assisted processes.

The revised Structure-Zone Model in Figure 1 relates morphology to the normalized deposition energy, E, and has been expanded to include high-power impulse magnetron sputtering and cathodic arc deposition. The latter two processes produce high densities of highly-energetic ions. The energy axis is proportional to ion kinetic energy expressed in eV. Typical energies for thermal evaporation are a few 10ths of an eV; for IAD, 50 – 70 eV; and for magnetron sputtering >10 eV.
Other parameters specific to the process play interdependent roles in determining film growth characteristics. From the diagram, we see that the microstructure progresses to compact smaller grain sizes as substrate temperature or energy is increased, even approaching amorphous. Higher kinetic energy promotes greater mobility on the substrate surface that in turn enables tighter nucleation and denser growth coverage of the surface. Ion kinetic energy substitutes for high substrate temperature in forming fine-grained compact layers, thus permitting deposition on temperature-sensitive substrates through high energy, low-temperature, processes. The excess energy also participates chemical reaction, for example in promoting oxidation and adherence to the substrate. Anders emphasizes that a multi-dimensional diagram is required to truly describe the complex growth dynamics and reactivity of thin layers [2]. For example, while compaction increases with energy, the sputtering effect dominates over growth at energies above certain values.
What Are Advantages of Certain Deposition Processes?
Commonly used deposition processes for optical thin films are reactive magnetron sputtering in various forms and ion-beam sputtering (IBS) [3]. The advantages over thermal (resistance-heated and E-beam) are improved process stability and reproducibility, directly resulting in more accurate production [3, 4, 5]. The trade-off is to abide lower deposition speed compared with the thermal processes. Cathodic arc and high-power impulse sputtering are used to coat large thicknesses (μm) tribologically on tool and wear surfaces at high rates.

Deposition processes have been developed to increase the mechanical strength, wear resistance (hardness), and thermal and chemical durability of thin-film coatings. Improvements are achieved by producing thin-film coating layers with dense low-stress microstructures that are ideally amorphous. It can be seen that a high density of highly energetic ions is the primary parameter in the process that produces dense stable coatings. Large grains that result from low energy conditions have big surface areas and empty spaces between that make them susceptible to volatile water vapor uptake. Exchange of the water accompanying atmospheric humidity fluctuations causes changes in optical and mechanical properties in these low-energy structures. Coatings produced by high-energy magnetron and ion-beam sputtering exhibit nearly zero wavelength shift between ambient humid and vacuum environments and have higher laser-induced damage thresholds (LIDT).

A second technique for densifying coatings is to specially prepare the deposition materials. The objective is to discourage the growth of large grains and columns and force amorphous microstructure. The technique consists of doping the base material with a chemically similar material whose atoms are larger and /or reactive. The theory is that unsatisfied bonds between growing grains interact to reduce the internal energy that has prevented a more homogeneous dense growth. The technique has been used with fluoride compounds such as CeF₃, BaF₂, MgF₂ and others. An interesting benefit is that the LIDT of these modified coatings is higher than that of pure fluoride compound coatings. This suggests that “controlled impurities” impose a smaller effect on LIDT than physical defects such as grains and boundaries.

How Does the Semi-Theoretical Structure Zone Model Relate to Everyday Coating Applications?
Commercial applications of coatings include eyewear, car windows, instrument panels, lighting, display and monitor screens, portable personal electronics screens, and many more. Past issues of Coating Materials News have discussed ophthalmic coatings and display screen anti-reflective (AR) coatings and their wear and environmental requirements. Large-area sputter deposition has replaced thermal evaporation as the more efficient and durable production process for AR coatings in the above applications. Sputtering is a low-temperature process that achieves the required density on polymer materials, thus providing the advantage of lighter weight and flexible plastic components than is possible with glass substrates.

Polycarbonate substrates are also used as protective eyewear for military applications such as goggles and helmets. Durability to abrasive, chemical, and thermal environments is provided by the high-energy deposition processes. Extremely abrasive environments such as wind-blown sand or hypersonic flight
encounters with dust and sand require visible and infra-red (IR) coatings with extraordinary hardness and strength. Because impact pitting, abrasive wear, and erosion are inevitable, even with diamond-like carbon coatings, a few percent transmission loss is accepted within the permitted degradation tolerance of instrument and visual performance. Production of these coatings has been discussed in previous issues of Coating Materials News [see 3, 4, 5]. The solutions involve the proper selection of materials and techniques for their deposition. The SZM provides the process side of the solution. Another challenge is exposure to the marine environment, where durability to salt fog and water is required for visual and IR windows. In this case, the selection of materials plays an equally important role as to that of deposition energy because a tolerated amount of corrosion is expected to occur.

A practical example of the influence of packing density changes that occur with an underdense layer such as MgF₂ is illustrated in Figure 2. It shows the computed reflectance of a wide-band ARC design consisting of oxide layers except for the outermost layer of MgF₂. The packing density of the MgF₂ was varied after the design was optimized for that layer exhibiting a packing density of 0.85. As the MgF₂ absorbs water upon venting the coating chamber and exposure to humid ambient air, its packing density increases as water diffuses into the void volume of the microstructure. This increases the refractive index of that layer. As the packing density increases from 0.85 (n = 1.327) to 0.90 (n = 1.347) to 0.95 (n = 1.366), the reflectance increases.

The effectiveness of the ARC is lost between vacuum and the ambient atmosphere. Because a portion of the absorbed water is not bound, it can escape upon evacuation. The coating is therefore unstable between arid and humid environments. All fluoride compounds exhibit this behavior. Reduction of the shift can be realized through three approaches: using ‘doped” starting materials; very high substrate temperatures (~300°C); or gentle IAD bombardment during growth. The results are directly related to the micro-structure / energy regions in the SZM.

Figure 2. Computed illustration of the loss of AR efficiency as water is absorbed in the outer MgF₂ layer of a wide-band ARC. The index of the MgF₂ layer increases, effectively increasing its packing density.
What Does the Future Portend for Producing More Durable Coatings?

Optical coating technology is a marriage of two technologies: materials science and deposition process development. Each imposes demands on the other.

Reflecting on the continuing progression of deposition technology, it would be premature to state that the optimum production processes have been developed and that little future progress is probable. One can contemplate two directions for future development. One is directed to volume production to satisfy commercial and industrial volumes; the other is special or custom applications and R&D. The latter category would include scientific applications (astronomy, space exploration missions, energy generation, high-energy lab physics, etc.) that are more demanding but low volume. Often progress is advanced as the offspring of the latter category of disciplines using thin-film technology development that eventually filters down to military, commercial and industrial applications. Materion Advanced Materials knows that the quality of every thin film deposition coating is highly dependent on the source material.

Current trends favor sputtering, therefore it is important to tune proper target preparation with optimal coating material processes. These two areas will continue to develop, as driven by increasingly greater demands for deposition efficiency, production economics, environmental challenges, commercial needs, and decorative applications.

REFERENCES


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