TECHNICAL PAPER

Notes on Deposition Processes and Applications

Authors: Samuel Pellicori and David Sanchez
Materion Coatings Material News

Introduction

Deposition process technology continually evolves and adapts to address specific optical coating applications and production volumes. The deposition of thin solid films of desired composition, morphology, optical or electrical and mechanical properties involves complex physio-chemical processes. Film layers condensed and grown from the vapor state, while having the same chemical composition as the source material, often possess physical properties that differ from their source material. Their nano-structural morphology and electronic states differ from the bulk due to disorder such as poly-crystalline, single crystal and amorphous states and impurity or vacant states. Multiple deposition processes have been developed with the goal of reproducing the desirable bulk properties in film layers having thicknesses as small as a few nanometers.

While the same ultimate thin film compound can be fabricated by multiple deposition processes, no single technique serves all compounds optimally. All processes share the common goals of high reproducibility with high production yield and high throughput rate consistent with efficient and economical materials usage. As technology advances, more processes are incorporating multiple techniques beyond the conventional isolated metal mirror, window, filter and reflector production capabilities of optics houses, and have begun to resemble cluster tools more typical of Integrated Circuit platforms. To best address new wafer level support, we present a basic overview of deposition processes and applications, and perhaps suggest an approach to best align resources to meet the challenges of tomorrow. As we have discussed in previous articles, there may be important differences in the metal or compound supply chain which are crucial in the most extreme usage cases. The reader is encouraged to refer to previous CMNs where these topics, materials and deposition technologies, are discussed in greater detail [1].

Film Growth Deposition

Before discussing techniques for depositing thin optical film layers, we'll present a brief outline of the growth process itself. Materials transformed to the vapor state during evaporation or sputtering of atoms of the source material condense on other surfaces. Rapid solidification leads to non-equilibrium and disordered semi-amorphous nano-structures. Consequently, the growing film exhibits optical and physical properties that differ significantly from the bulk source material. To counter the disordered growth associated with the low-energy processes, thermal evaporation (EB and resistance-heated), additional momentum is supplied to mobilize the arriving atoms. This promotes more ordered and denser nano-structure. Dense amorphous nano-structure is required to achieve environmental stability of optical, mechanical, and laser-resistant properties [2].

Deposition Processes

Physical vapor deposition (PVD) processes are the most common for production optics such as consumer products. Typical examples are eyewear, mirrors, display panels, personal cell devices, instrument windows, etc. Special applications for laser optics and optics intended for harsh environments also rely on PVD with specific process modifications designed to enhance performance. Applications include scientific, space and military optics and many more.

Among the common thermal techniques are resistance-heated evaporation for material with evaporation temperatures <~1000⁰ C for metals and some IR materials, and electron beam evaporation for materials requiring ~2000⁰ C temperature such as oxide compounds. During these relatively low energy thermal techniques a concurrent flux of high-energy ions from various sources can be directed to the growing films to increase film density (compactness) and assure complete chemical reactions. These assisted techniques include ion-assisted PVD (IBAD), Plasma Ion assisted (PIAD) deposition, and Plasma-enhanced PVD (PEPVD). Ions can be thermionically generated from the following: a hot cathode, End Hall gridded, cold cathode ion sources, or from a rf oscillator. A plasma created by the ion density can either fill the chamber using the walls as an anode or directed to the growing film by ion optics as for PIAD.

The alternate PEPVD process depends on the chamber walls acting as an electrode to fill the entire vacuum space with an energetic plasma of ions, where the energetic plasma enables conformal coverage instead of the line-of-sight deposition characteristic of convention EB, resistance-heated and their ion-assisted modifications. High energy enhancements improve the film qualities: density and hardness, environmental stability, bulk-like index with low absorption, strong adhesion, and high LIDT. The higher energy of the ions in IBS and other high-power sputtering processes can damage the compound targets, and growing film can create high compressive stress and high heat loading that can cause issues with bonding.

Where higher ion energy and density are required, magnetron and ion-beam sputter (MS, IBS) deposition techniques are used. Typical examples include optical and tribological films from pure metals, alloys or nitride and oxide compounds. Several configurations exist and are powered by either a R.F. power supply for sputtering insulating compounds, or a D.C. power supply for reactive deposition of conductive metals. When pulsed D.C. power is provided in PDCMS, high deposition rates are available, and composition can be consistently maintained because the target (anode) surface is prevented from oxidizing.

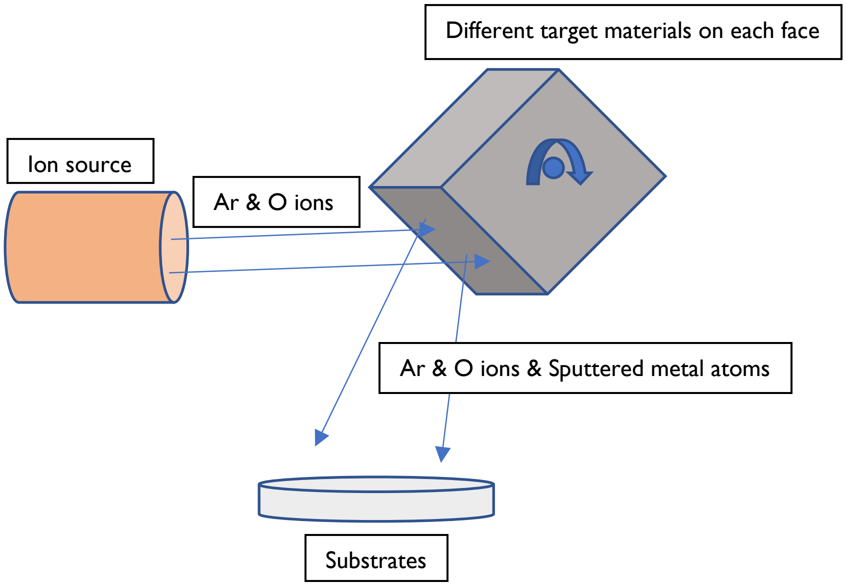

Figure 1. Illustration of the components of an ion beam sputtering (IBS) system. Up to four materials can be selected by rotation of the target cube. The substrate holder is rotating during deposition for the best uniform coverage.

PVD thickness uniformity is adequate for planar geometry surface coverage. Chemical vapor deposition (CVD), alternatively, is useful for surfaces that have curvature or small topographical features because the reaction for solid film growth occurs on the surface. The list of materials that can be deposited is dependent only on the availability of a suitable chemical precursor (liquid, gas or salt). Uniform coverage is not restricted to line-of-sight geometry as it is for PVD. The addition of a plasma as in PECVD permits the reactions to proceed at low surface temperatures, even as low as the service temperature of polycarbonate and acrylic, ~100^{0} C. Interior surfaces can also be coated, which makes the deposition unique.

In atomic layer deposition (ALD), film growth proceeds atom-by-atom from appropriate chemical precursors. Nearly all optically relevant coating materials have been deposited by ALD. ALD can precisely grow very thin layers and is also applicable to non-planar geometries. Work continues to develop ideal precursors for ALD for critical metal layers like Au, Mo, Pt and W, as well as less dangerous precursors for Al, Hf, and Zr oxide dielectric deposition.

Both PVD and CVD processes can be scaled to produce large-area coatings in in-line, roll-coating and cluster tool systems.

Substrate composition and the preparation of their surfaces play an important role in the selection of the deposition process as related to application and intended operating environment. High polish with limited surface defects that include residual polish contamination, scratches and pits are required qualities for coatings exposed to the environment. Substrate surface quality is especially critical for high-energy laser applications. Polymer substrates for commercial and consumer applications such as eyewear and display panels are more difficult to achieve a high polish. They also require low deposition temperature processes such as sputter deposition, although procedures are in place that limit time of exposure to heat sources in e-beam evaporation.

A brief summary of applications and processes for optical coatings is presented in Table 1 (inspired by N. Kaiser's recent talk) [3]. Many articles by P. M. Martin discuss deposition processes in greater detail [4].

Application	**Materials**	**Deposition Process**
Glass (polarizers, smart phones)	SiO_2, Ta_2O_5, TiO_2, Nb_2O_5	EB (IAD), MS
Polymers	SiO_2, Ta_2O_5, TiO_2	EBIAD, PDCMS, PECVD
VNIR: AR, HR, Bandpass, Edge Filters	SiO_2, Ta_2O_5, TiO_2, Nb_2O_5	EBIAD, PDCMS
UV to 225 nm	SiO_2, HfO_2, Al_2O_3	EB
UV <225 nm, Excimer	MgF2, LaF_3, AlF_3, LiF, GdF_3	EB, IBS
SW & MWIR (2-5µm & 3-5 µm)	SiO_2, Ta_2O_5, Al_2O_3	PDCMS
LWIR (8 -13 µm)	YF_3, YbF_3 + mixtures, ZnSe, Ge	EB
High-energy Laser (AR, HR)	Oxides & Fluorides as above	EB
Tribological- optical	HfO_2, Y_2O_3, Ta_2O_5, ZrO_2, Si_3N_4, and mixtures, DLC	EBIAD, PECVD
Transparent Conductive Oxides	ITO, AZO, etc	MS, ALD, PECVD
Solar cells, OLED, ophthalmic,		PECVD

D.C. reactive magnetron sputtering uses metal targets and a plasma containing Ar as the sputtering gas, and oxygen or nitrogen as the reactive gas, depending on the final composition. Ions: Ar+, O+, and N+ compose the energetic plasma. MS of fluorides will require the presence of fluorine as the reactive gas. The danger associated with fluorine gas or gaseous pre-cursor compounds precludes MS as a deposition process for fluoride films. Recent developments successfully apply IBS for depositing fluoride compound film layers. In some cases, annealing in nitrogen can improve the quality of films deposited by MS or IBS. Further care must be taken for full oxides and fluoride targets themselves to prevent heating-induced stresses due to their brittle nature. To produce coatings with high LIDT, the deposition process must provide complete oxidation and an amorphous microstructure with low defects. High-energy techniques cause non-stoichiometric composition and defected morphology. Therefore, EB and low-energy sputter processes are the preferred techniques for high LIDT at wavelengths shorter than ~400 nm.

Concluding Remarks

In this brief overview, we discussed the current state of the technology relative to industrial production coating processes. Process and materials modifications will continue to be developed. While there is no optimum all-encompassing deposition process, each application requires its own specialized process. A future adjunct discussion concerning the limits and expectations that a particular approach may offer could include key factors such as higher power consumption, hazardous precursors or rare metals/compounds. Understanding factors that allow the tools to fulfill their potential include raw materials, substrates and ion sources are important for advancing the technology.

References

1. Coating Materials News. https://materion.com/resource-center/newsletters/coating-materials-news. For example: V27 Issues 1, 2, 3; V28 Issue 2.

2. S. F. Pellicori, "Fundamentals of Thin-film Growth and Influences on Mechanical & Environmental Durability Properties." CMN

3. Norbert Kaiser, "New Trends and Developments in the field of Optical Interference Coatings", OSA Optical Interference Coatings conference, 2 June 2019, Santa Ana Pueblo, New Mexico.

4. Peter M. Martin, Vacuum Technology & Coating, www.vtcmag@snet.net

Authors

Samuel Pellicori, Consultant
Pellicori Optical Consulting, Santa Barbara, CA
Phone: 805.682.1922
Email: pellopt@cox.net

David Sanchez, Sr. Materials/Applications Scientist
Materion Advanced Materials, Milwaukee, WI
Email: David.Sanchez@Materion.com