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TECHNICAL PAPER

Reactive and Non-Reactive Deposition

Comparison of PVD Processes

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Physical vapor deposition (PVD) processes are the most commonly used deposition techniques for the widest variety of materials and coating applications. The process for transforming solid materials into vapors of their atoms requires the addition of energy in order to release atoms from their bonds. The energy source can be thermal, such as that supplied by electron-beam or resistance-heated sources. Or alternatively, the source can be non-thermal vaporization, such as that achieved by high kinetic energy impacting species in sputtering techniques. Depending on the material used, (i.e. metals, metal compounds of oxides or fluorides, or alloys and mixtures), and the desired layer composition, vaporization energy will range from < 1eV to 10's of eV. Vaporization energy is a key parameter in PVD as it relates to reactive vs non-reactive processes.

In the case of the deposition of pure metals, a non-reactive vaporization process is required. The vaporization of compounds results in partial decomposition of the starting compound. When depositing optical thin-film layers, incomplete stoichiometric composition such as sub-oxidation produces absorption and refractive index differences. The presence of absorption is more severe in the UV (ultra violet) than in the IR (infrared) and for coatings that are intended for high laser damage threshold applications. When compounds are to be deposited, reactive processes must be involved. A few common exceptions exist: SiO_2, SiO, and Al_2O_3 can be deposited in a non-reactive environment with acceptable optical and mechanical properties.

With the introduction of reactive processes that function to completely oxidize metal-oxide compound layers, the quality of coatings produced by PVD processes is currently state-of-the-art. The resulting improved coating technology incorporates ions in an energetic plasma environment. Also, uses accelerated ions to deliver energy and to influence film layer growth morphology. Previous Coating Materials News issues have discussed these processes in relation to specific materials; the following is an overview of the technology.

Reactive Thermal Deposition

High substrate temperature promotes oxidation or nitridation and densification for many compounds. An alternate to the high-temperature process is ion-assisted deposition (IAD). IAD employs an ion gun to bombard the growing metal-oxide film with a mixture of Ar^+ and reactive O^+ or N^+ ions, thereby supplying energy to complete the reaction as well as compact the layer and increase adhesion. Typical ion energies are 50 to 70eV. In plasma ion-assisted deposition (PIAD), an energetic plasma consisting of electrons, Ar^+ and reactive O^+ or N^+ ions, fills the coating chamber and promotes complete reactivity. Highly reactive ionized species condense on the substrate. PIAD is also used with resistance-heated and E-beam processes to produce dense, transparent, adhesive coatings for severe environments including high laser damage threshold coatings.

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A Comparison

An illustration of the optical properties of reactive vs non-reactive thermal processes is shown in *Figures 1 and 2*. Figure 1 plots the refractive indices of Ta_2O_5 deposited by E-beam alone, E-beam with IAD, and E-beam with PIAD. These represent processes with increasing reactivity. Baking the film layer in air increases oxidation either by providing energy to further reaction with included oxygen, or by stimulating reaction with external oxygen. A high index can be produced without added energy. However, the extinction coefficient is an order of magnitude higher than the other processes where the addition of energy results in lower absorption and lower but consistent indices.

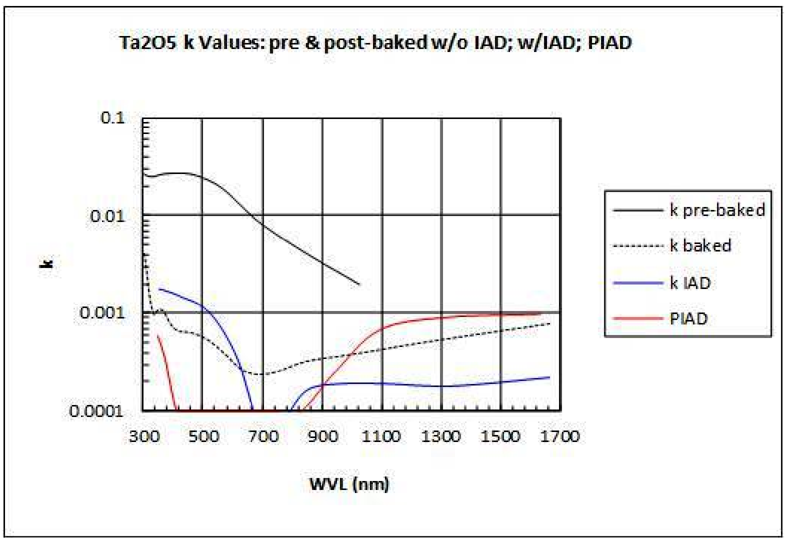


Figure1. Extinction coefficient of Ta_2O_5 layers deposited by E-beam with and without energetic reactive assisting processes.

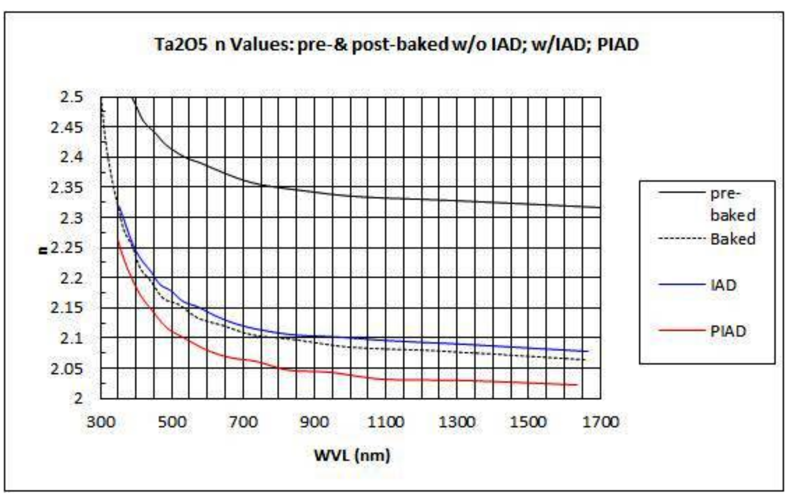
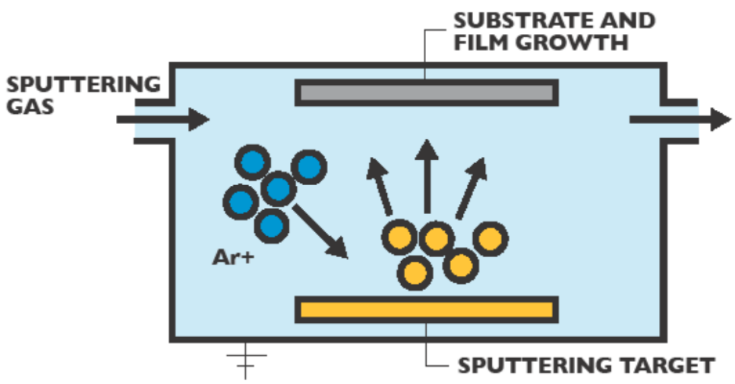


Figure 2. As for Figure 1, indices.

Non-Thermal Reactive Deposition: Sputtering

Deposition of film layers by sputtering enables a greater variety of materials to be used to make coatings for optical as well as tribological and electrical applications. Basically, high energy heavy ions, typically Ar^+ , are generated in a plasma discharge between a cathode (source or target) and the anode where the substrate is located. The sputtered targets are enveloped in a reactive atmosphere consisting of a plasma of electrons and Ar^+ ions. Ions are accelerated toward the substrate with energies greater than 50 eV and knock atoms off the target. The activated and reactive metal and Ar ions then deposit on the substrate where, in the case of metal oxide compound film layer compositions, oxidative reactivity occurs.



The most commonly used sputter techniques, DC magnetron, ion-beam, and RF, rely on high-energy (>50 eV) ions to sputter atoms off solid targets of a metal or from a compound using RF. The highly reactive atmosphere forms dielectric compounds on the target as well as on the substrate and surrounding chamber walls. If the compounds are permitted to build up a film, arcing and slowing of the sputter rate would occur. Pulsed DC magnetron sputtering employs mid-to-high frequency cycled voltages to maintain a consistent and high sputtering rate by frequently removing the dielectric film and returning to a clean metal target surface. A stable process requires strict control of the desired operating point between metal and oxide states of the target surface. That point is a function of gas pressure and discharge voltage. Sophisticated monitoring techniques for the plasma spectral emission intensities of the ionized gases and metal species, or of the gas flow rate, are used to make sputtering a highly repeatable and efficient process.

The rate at which a material is sputtered is dependent on the binding energy of the atom; the sputter yield is the ratio between the number of released atoms and the number of incident ions. The yield is proportional to ion energy and therefore to the applied power (ion energy and ion current flux). Some yield values for common materials used in optical coatings with 500 eV Ar ion energy are: Ag 2.5; Al 0.9; Hf 0.4; Nb 0.6; Si 0.7; Ta 0.5; and Ti 0.5. The deposition rates for pure metals is relatively high, requiring 2 ions to release 1 atom. The generation of metal oxide films is lower because of the operating parameters already described that need to be present to encourage reaction. Sputter yields for compound targets is ~10 times lower, which is the reason metal targets are used in reactive sputtering processes to deposit compounds such as Al_2O_3, HfO_2, Ta_2O_5, Nb_2O_5, and others.

Many other parameters associated with sputter power, such as partial and total pressures of the working gas (Ar), the oxidizing gas(s), incidence angle, and substrate temperature, determine the film's optical, chemical, mechanical and environmental stability properties. Those properties manifest film morphology, adhesive and cohesive strengths, intrinsic stress, hardness, composition (absorption), and uniformity. Tighter parameter control in sputter processes lends the advantage of better production repeatability.

Geometric Consideration: Distribution Uniformity

Coating large areas or rolls is best accomplished by using sputter targets because these sources can be scaled in size without limit. Hence, they will produce a more uniform layer thickness distribution than thermal sources. The latter emit in a modified cosine distribution pattern, usually a cosine exp >1. To distribute a uniform thickness, therefore requires masking of multiple sources and two-axis substrate rotation mounting. In *Figures 3 and 4*, the uniformity distributions are compared for a single point source, as typical for E-beam, and an extended source, as with sputtering. The 25 cm diam planet is undergoing single axis rotation and is placed 50 cm from the two types of single sources. No masks are used to even out the distribution in these examples. The broader source produces a more uniform distribution.

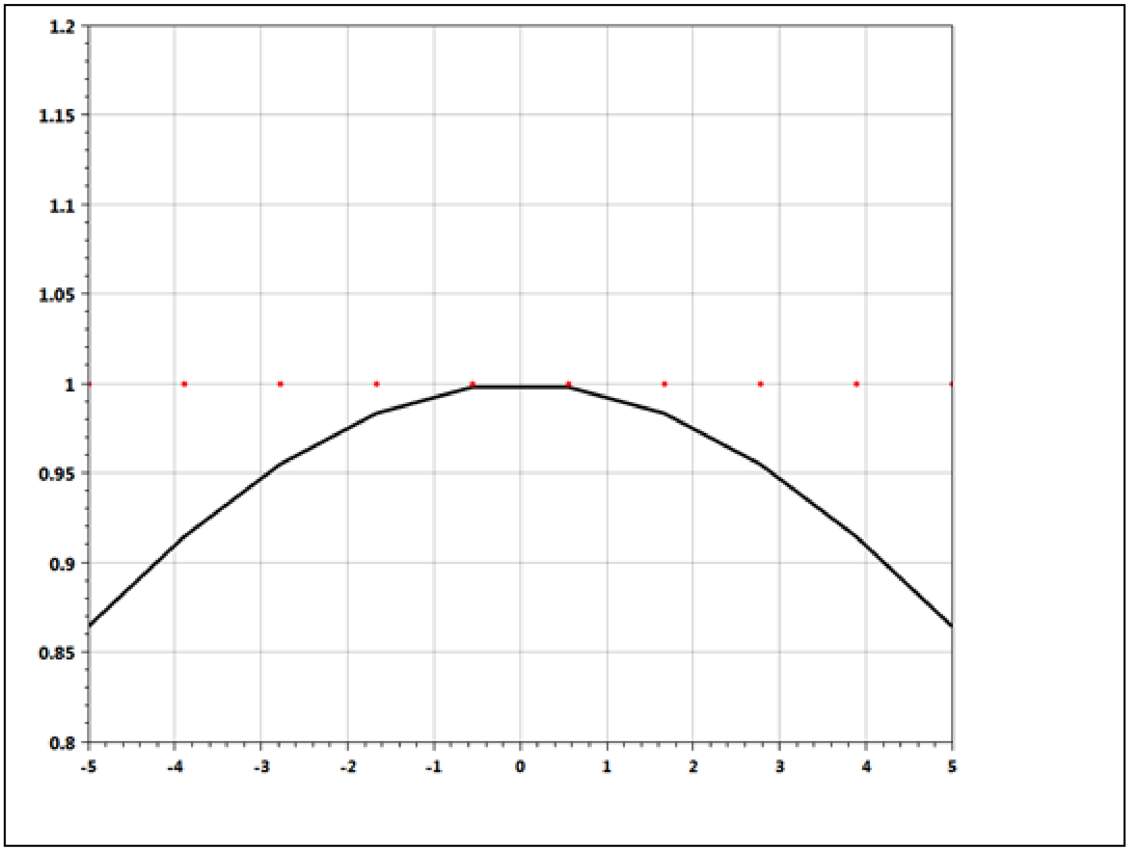


Figure 3. Radial distribution from an E-beam source on a 25 cm (10 inch) rotating planet 51 cm (20 inches) separated. Computed using Dr. Bill Southwell's "UniformityPro 4™" modeling software (www.tablemountainoptics.com).

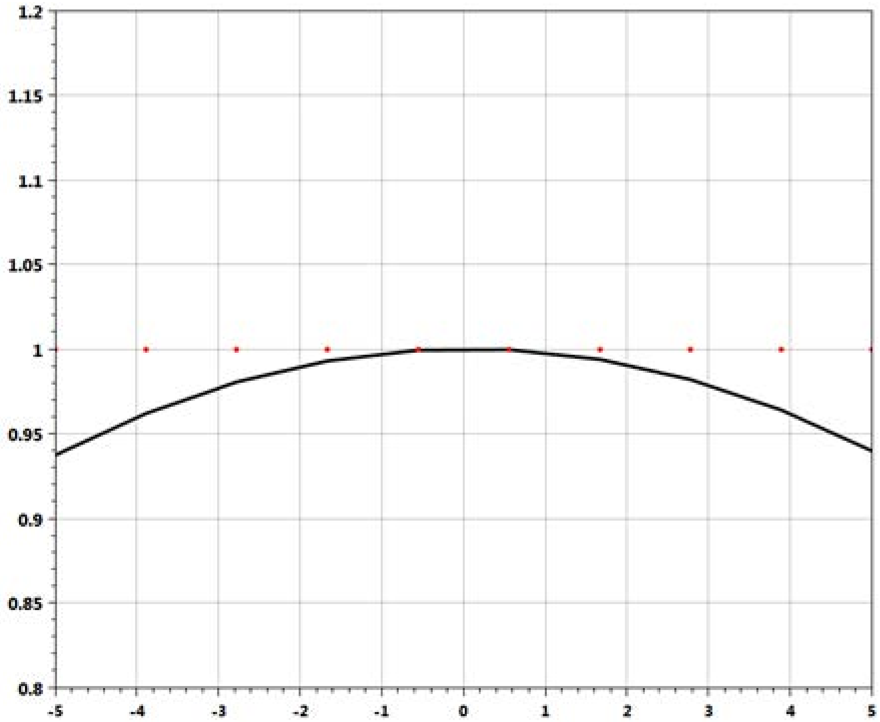


Figure 4. As for Figure 3, but with source dimensions 15.2 cm (6-inches) square representing a sputtering target.

Summary
This brief overview discusses a few of the aspects that distinguish reactive and non-reactive PVD processes, and highlights some of the advantages of reactive sputtering.

If you are interested in more information on PVD processes, contact the experts at Materion, one of the world's premier advanced materials companies. They produce a broad range of precious and non-precious metal sputtering targets in nearly any shape, size or material composition and provide shield kit cleaning services.

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