TECHNICAL PAPER

Reactive Deposition – Enabling Enhanced Thin Film Performance

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In most papers outside of sputtering thin film deposition where a full compound is coated, engineers strive to optimize the thin film properties. In comparison to sputtered metal thin films, dielectric compounds degrade during evaporation or seriously challenge sputtering processes due to limited conductivity, mechanical toughness, particles and damaging arcs. Manufacturing, process and post deposition techniques are used to compensate for decomposing evaporation material or to create the highest quality full compound thin films via reactive deposition for high quality performance coatings. Using the classic high index oxides, examples will be given on factors that influence process control from passively reactive e-beam processes and how reactive sputtering targets, techniques and platforms work in concert to reach the highest quality "as-deposited" thin films for precision films. Navigating the challenges of reactive processes, we will examine how the manufacture of substrates, coating materials and the targets themselves are related and exploited to the benefit of process control and adaptability of sputtering systems to provide consistent and valuable options for photonics. Success in the seemingly divergent and certainly complex communication, mobile electronics, remote sensing and medical device segments requires synergy between materials, thin film tool suppliers and researchers like yourselves in order to guarantee proper foundation, new products and application innovations.

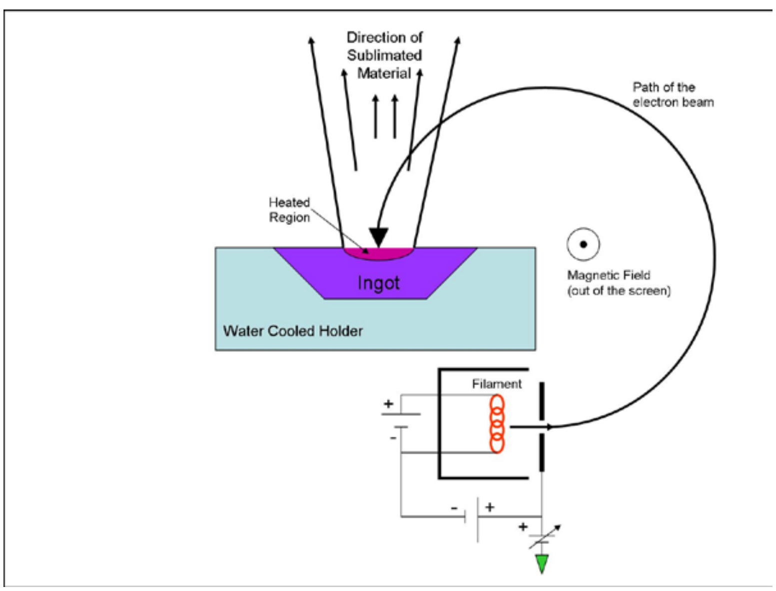

Figure 1 - Classical E-beam Deposition Diagram

In the first and perhaps lowest energy and lowest film density case, the material of interest is an oxide compound. In the classical e-beam deposition (Figure 1), the high-energy beam is directed onto the evaporation material held inside a water-cooled crucible. While often used for easier clean up, liners also moderate the heat flow from the starter charge or granules. This can contribute to rather exotic competing cooling challenges during the iterative heating and cooling of a typical high and low index optical design. For example, the most prolific high index material in the Visible and Near Infrared (VIS-NIR) region is Titanium Dioxide (TIO_2). Figure 2 shows the complexity presented by TIO_2 competing for dominance during evaporation and cool-down in the pocket.

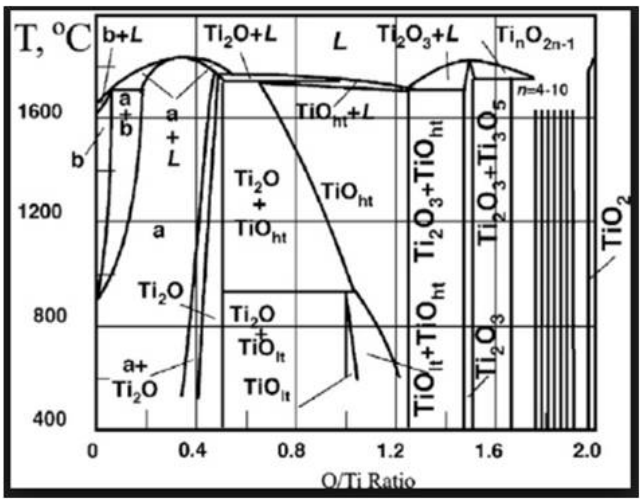

Figure 1 - Ti - TiO_2 Binary Phase Diagram (Huilian Cao)

The diagram shows that during and after typical evaporation, the process must compensate for an increasingly complex stew of sub-oxides based on proximity to evaporation and heat sink. Figure 3 shows an example of characteristics of the most stable sub-oxides, which form and compete in the pocket. They are also examples of individually engineered coating materials which are meant to enable a stable and repeatable deposition process with variable success.

Compound	Appearance	Melting Pt	Bulk Density
TiO	Dark	1750 C	4950 kg/m3
TiO_2	White	1800 C	4230 kg/m3
Ti_2O_3	Violet	1842 C	4490 kg/m3
Ti_3O_5	Black	1777 C	4240 kh/m3

Figure 2 - Table of Basic Titanium Oxides

During evaporation, temperatures exceed 2500 C – the boiling point of the most volatile stable sub-phase. Because any missing oxygen site in the growing film will contribute to absorption, a background pressure of oxygen is added at some point between the substrate and the source. This is optimized with some external energy, such as substrate heaters and/or some type of ion assistance. The latter can also densify the film and maximize the index of refraction of the growing film.

As one can imagine, the process becomes exceedingly challenging for very long and complex optical designs. Changes in density, conductivity and shifting melting points all contribute to "spit" and require strong process engineering. While Ti_XO_Y is the most challenging example, similar practices are necessary for the other oxides HfO_2, Nb_2O_5, Ta_2O_5, Al_2O_3 and even SiO_2. While the materials industry has made strides in creating stable sub-phases over the years that certainly help, such as c-Ti_3O_5 and fused SiO_2, there remain gaps in stability, rate and performance that only higher order reactive processes can address.

There is a more sophisticated reactive process that is completely dependent on ion assistance. It uses chargers, pellets, shavings or granules of the pure metal in the pocket of the e-beam gun. In this case, heat transfer (to crucible and to substrate), carbon from principle melting and gas injection remain key process considerations. Engineers can maximize film properties, realize higher rates and offer repeatability through a fully reactive non-sputtering approach.

For UV optical thin films, any unreacted metal centers or missing oxygen sites are breakdown points for high performance protected mirrors, antireflection coatings and filters. Similar to TiO_2, - but to a lesser extent- HfO_2 reduces to a similarly complex sub-oxide state. Various studies (like that in Figure 4) show that HfO_2 films improved with increased substrate temperature and post-deposition recrystallization. This does imply that for different applications different degrees of reactive deposition can balance or optimize mix of substrate temperature, post deposition annealing and have a direct influence on long-term stability of the coating.

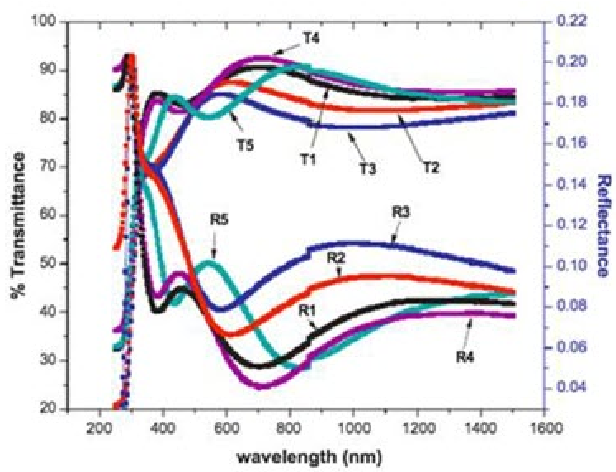

Figure 3 - HfO_2 Thin Films at Increasing Substrate Temperature with Annealing (M. Ramzan)

Coupled with UV-grade fused SiO_2 with makeup oxygen, the metal reactive HfO_2 process currently challenges some sputtered reactive processes. It reflects a cost point less than that of using the full compound due to its high level of required pocket maintenance. Perhaps more importantly, for semiconductor gate dielectrics than for optics, Hafnium Oxide has four standard crystalline phases (monoclinic, tetragonal, cubic and orthorhombic), each having different dielectric constants. For optical applications, the ability to control the amorphous-to-crystalline character can lead to increasingly sophisticated choices for specific coating platform applications.

On one extreme end of reactive deposition, there are several sputtering approaches that use metal or metal-oxide targets. In the first case, metal targets deposit a high rate pure metal flux, which is subsequently oxidized by a special plasma process on a rotating carousel. This Plasma Assisted Reactive Magnetron Sputtering (PARMS) – as in Figure 5 - is highly stable and provides high performance, high layer count for low stress coatings (Figure 6).

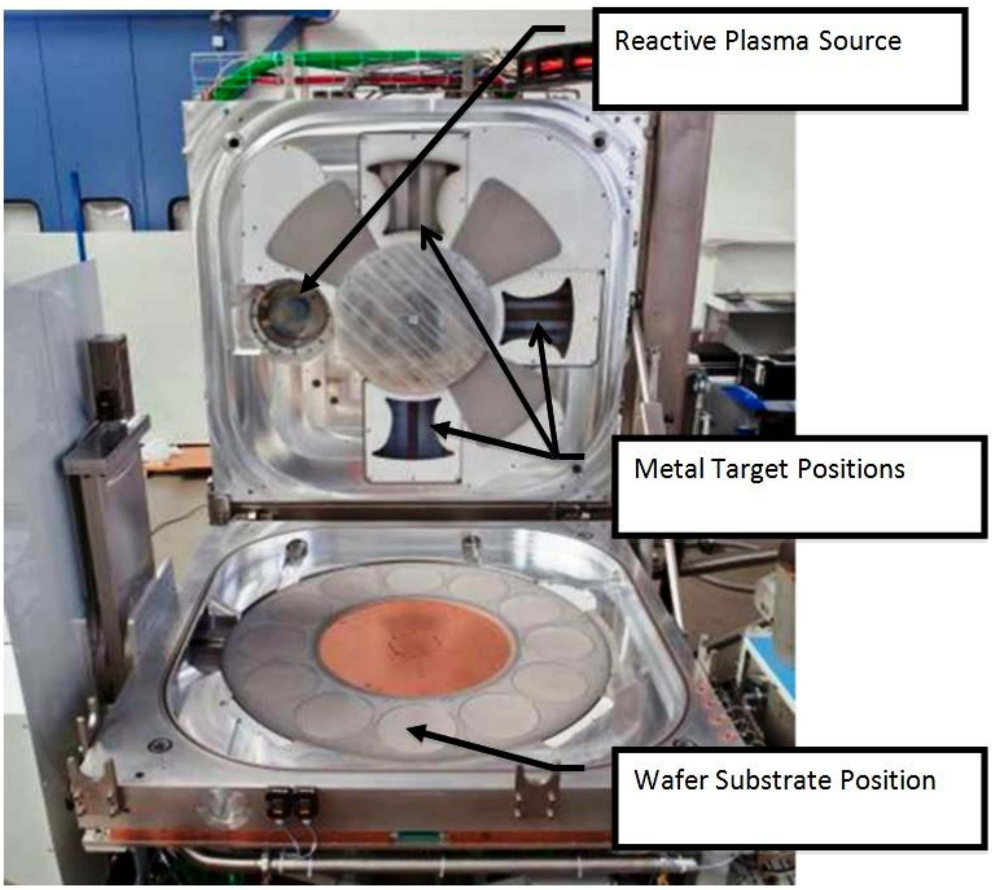

Figure 5 – Sputter Down Buhler Helios 400/800 PARMS Tool (A. Zöller, H. Hagedorn, W. Lehnert, J. Pistner, & M. Scherer/Buhler Leybold Optics)

Material	Ref. index n @550nm	Film Stress [MPa]	Deposition Rate [nm/s]
SiO_2	1,48	-100	0,33
SiO_2	1,48	-300	0,45
Al_2O_3	1,67	-115	0,4
Nb_2O_5	2,365	-150	0,55
Ta_2O_5	2,166	-90	0,6
ZrO_2	2,13	-70	0,5
HfO_2	2,075	-180	0,5

Figure 6 - Claimed Film Characteristics from Helios Showing Index, Stress and Rate

In this case of extreme reactive deposition, high rate metal deposition translates into high quality dielectric layers as result of the plasma oxidizing the metal from the surface up. The energetic oxygen plasma source relieves stress as the film grows and maximizes diffusion.

In a more moderate conventional reactive magnetron sputtering case, oxidation occurs in transit and/or in close enough proximity to the arrival point so that diffusive oxidation is limited. The risk of premature oxidation (particles or Brownian diffusion) is closely tied to the power supply and gas injection parameters. Processes like that depicted in Figure 7 are examples of an approach designed to direct-deposit fully oxidized thin films. Further enhancements on this approach use pulse DC to keep the metal mode targets clean and making efficient use of the reactive gas to minimize unreacted sites and other film deficiencies.

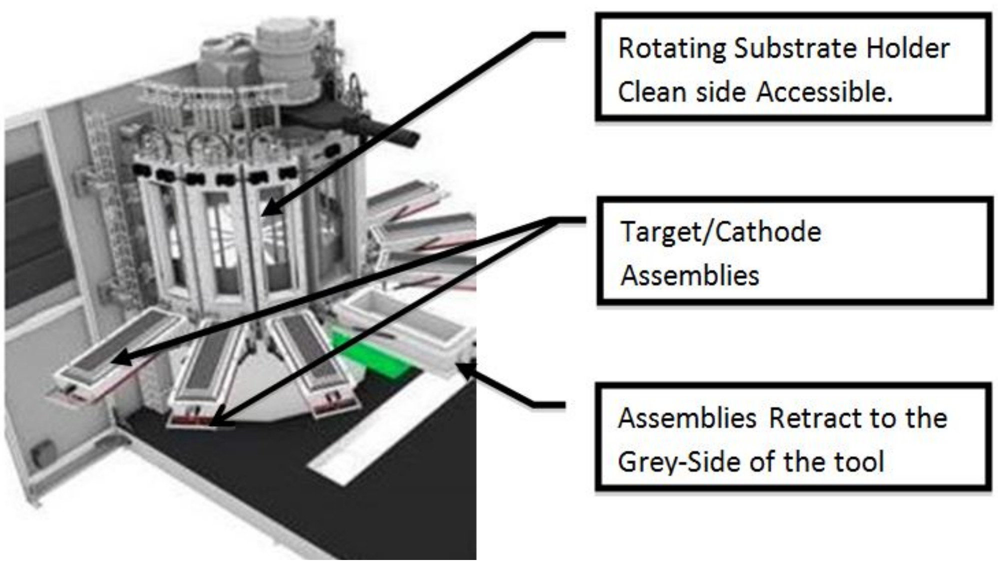

Figure 7 -Evatec MSP Reactive Sputtering System Target Access Side

Pure DC reactive processes may have higher rates, but target poisoning (arcs), target debonding /cracking and elevated process temperatures must be considered in the balance. In all direct reactive sputtering processes, efforts should be made to limit secondary ion damage to the growing film as well as protect against arcs due to counter ion poisoning or particle formation.

The other extreme energy case is Dual Ion Beam Sputtering (DIBS). Figure 8 shows a typical DIBS tool.

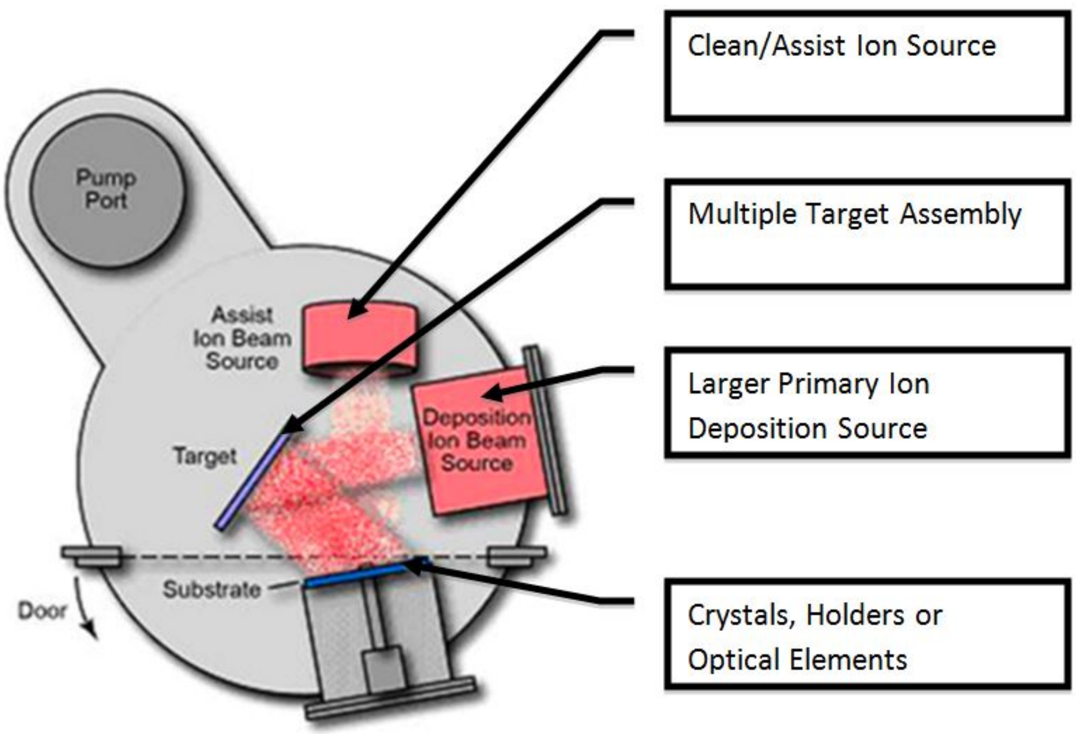

Figure 8 - Typical DIBS System for Optical Coating (N. Anderson, L. Wang & T. Erdogan / Semrock)

In the IBS process, reactions occur on the substrate (assist beam), in transit (primary beam) and by diffusion (at the growing film). In recent years, this process has greatly advanced in managing stress in growing films and increasing rates in line with other PVD processes. A major advantage with an IBS approach is that the process is not as sensitive to less refined rolled metal targets where grain size and orientation would challenge a conventional magnetron approach. Because IBS is more reactive than RF sputtering, it can also be used to deposit high quality dielectric coatings from insulating targets - essentially sacrificing rate in favor of high film density.

Up to this point, we have embraced the fact that high quality metal oxide thin films can be deposited in a range of energy and oxygen delivery regimes. While flammable, the use of oxygen is mature and safe, largely due to the dedication to best practices and diligence of Original Equipment Manufacturers (OEMs). Oxygen-rich plasmas are deployed in physical vapor deposition for critical applications in the Ultraviolet (UV) to the Near IR (NIR) regions. In the Deep UV and Mid & Long Wave (M/LWIR) oxides absorb, thus more exotic materials are required for an ever-expanding technical marketplace. In the Deep UV (DUV) Fluoride compounds dominate as both the high and low index materials. In the Mid and Long Wave IR (M/LWIR) regions, Fluorides are required and joined by Sulfides, Selenides, IR transparent Silicon and Germanium materials.

Simply stated, DUV and M/LWIR evaporation materials and processes have no generally favorable and mature compensation gas as an option. Furthermore, targets may be fragile or have deleterious decomposition products placing even higher demands on materials engineering. Current thermal and electron beam processes for materials like AlF_3, MgF_2, ZnS and ZnSe are subtle if not underappreciated reactive processes. For these processes, the materials are prepared to minimize oxygen and water content that compete – thus influencing growing film properties. As the evaporation material is deposited, there is a local partial pressure of the decomposition products. This includes the free Fluorine, Selenium or Sulfide atoms/ions. These processes can run for a long time and show no immediate clues of an issue in the VIS. At least not until a critical depletion level is reached which is capable of producing only absorbing films. A number of factors can strongly influence the convergence at this point: inter-granular cracking, particle surface area, granular density and packing density. These contribute a key contrast between different reaction and consolidation pathways taken by materials suppliers such as Materion that can influence the deposition process.

There is still valiant and perhaps controversial work to be done, but the stellar efforts on APS and IBS Fluoride compounds continue to fuel the occasional request for Fluoride targets and melted starter charges. Similarly, great strides in solar energy and memory have seen the maturation of Selenium and Sulfur compound thin films. However, these are a bit outside the normal safety and process parameters sought by the larger optics community. Thermal or electron beam processes can be enhanced with ion assistance and need to be carefully monitored, if not artfully crafted, if they are to meet increasing challenges related to film density and imperfections.

By taking a closer look at Reactive Deposition Processes, this article underscores the reason to refine evaporation materials and targets for applications spanning the DUV to LWIR wavelengths. The technical experts at Materion keep abreast of the latest deposition technologies and offer a broad range of thin film deposition materials.

References

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Figure 5 and 6 – Helios 400/800 PARMS Tool, Buhler Leybold Optics, Presentation by A. Zöller, H. Hagedorn, W. Lehnert, J. Pistner, M. Scherer. Company http://www.buhlergroup.com/global/en/products/helios-series.htm#.V5esdSwlupo

Figure 7 – MSP Reactive Sputtering System image, View Evatech company products, http://www.evatecnet.com/media/file/download/id/12/eva_msp_1225-1232_8p_web.pdf

Figure 8 – Anderson, N., L. Wang and T. Erdogan, IBS Coatings for Ultrafast lasers & Applications, DIBS Diagram, Semrock company white paper, with permission. https://www.semrock.com/ibs-coatings-for-ultrafast-lasers-and-applications.aspx