Getting Better Optical Coatings That Use Silica and Hafnia

It has been observed[1] that it is beneficial to the design optical coatings to have as large a difference as practical between the high and low index materials used. Most dielectric coating designs can be achieved with just two materials in any given spectral region. It is often practical to have many types of coatings produced in a given facility using only two materials that have well developed processes. Physical, environmental, and application considerations will temper this choice of materials. In the visible spectrum, MgF_2 and TiO_2 offer the greatest index difference (1.38 to 2.4) for materials that are reasonably robust when deposited. However, due to some of the physical, process, and environmental factors, many workers in the field have chosen silica (SiO_2) and hafnia (HfO_2) for their coating materials (1.46-2.0).

SiO_2 and HfO_2 have been found to be desirable optical coating materials for applications from the ultraviolet (UV) to the near infrared (NIR). SiO_2 is a low index material at about 1.46 in the visible spectrum, and HfO_2 has a moderately high index up to about 2.0 (depending on deposition conditions). These materials can be deposited to be quite durable environmentally. However, there have been various difficulties in obtaining totally satisfactory results due to the weaknesses of the processes that have been used. Developments and refinements of the past decade have overcome these limitations. It is now practical to use just these two materials for a large number of the coatings used for applications in the visible, UV, and NIR spectrum.

Silica Deposition Process

Silicon dioxide, silica, SiO_2, or "quartz" is one of the preferred low index materials for a variety of reasons. Although silica is of somewhat higher index than MgF_2 at 1.38 in the visible spectrum, it can often be deposited with less porosity and scattering at lower substrate temperatures. It is relatively durable and can have a good laser damage threshold[2]. With the advent of electron beam evaporation sources (E-guns) several decades ago, it became practical to evaporate fused silica. There are many papers written on its use; a few more recent ones are cited here. Scherer, et al.[3] reported that all their films were compressive and showed extensive analyses of how these stresses reduced with time. They found this "to be driven by a hydrolysis of SiO_2 strained bonds, probably followed by a network rearrangement responsible for stress relaxation." Chow and Tsujimoto[2], and Harris[4] discuss using improved E-beam control to obtain more reproducible results with SiO_2. This study worked to optimize the sweep and other parameters to avoid "carve-in" (which most call "tunneling") and gain other desirable properties of the depositions.

We found that the deposition of critical optical thin film stacks with silicon dioxide from an E-gun was severely limited by the stability of the evaporation pattern or angular distribution of the material, which is also a motivation of the works reported above[2-4]. We had not obtained satisfactory results in some of the more demanding applications with either solid discs or granular SiO_2 starting material. The amount of material deposited on a central monitor chip or control crystal in a box coater did not have a reproducible ratio to that received at other positions in the chamber. **Figure 1** illustrates the variable distribution of silicon dioxide evaporant from an E-gun as is commonly experienced in physical vapor deposition. The

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R.D. Mathis[6] Company's SO-36 resistive source to be satisfactory for our work, which required relatively large amounts of material. To evaporate at about 1 nm/second at the center of a Balzers BAK760, we applied about 600 amps at 1.7 to 2.1 volts (depending on how well the electrical contacts had been made). Our goal was to obtain good silicon dioxide at a rate of 1 nm/second. This cannot normally be achieved by simply evaporating silicon monoxide in an oxygen background, even at elevated temperatures. If the pressure were high, the films would be porous and weak. If the pressure were low, the films would be absorbing and of high index. Without any additional oxygen, SiO films are of about 1.9 index and yellow to brown in color. However, in the NIR at or beyond 1,000 nm, SiO has little or no absorption and has been successfully used with silicon as the high index material for NIR coatings. An adequate supply of energetic ions or neutrals of oxygen are needed to obtain SiO2 at the rates and properties desired. Kaufman-type ion sources can be used to a certain extent at lower rates by combinations of oxygen and argon, but the nature of the Kaufman gun's filament and grids makes its use with oxygen in a high-power mode unfavorable. Some gridless ion guns (such as the DynaVac PS1500[7]), on the other hand, work quite well using oxygen as the ionized gas.

It turned out, although we were not aware of it at the time, that McNeil et al.[8] had done a nice piece of work in this area of SiO_2 from SiO in the 1983 time frame. The general configuration of the chamber used is shown in **Figure 3**. The ion source was aimed at the calotte for best uniformity. The aim point was approximately midway between the points in the calotte, which were directly over the silicon monoxide and titania sources. These sources had uniformity masks at about 3 cm below the calotte and directly over the sources. The titania used as the high index material in this particular application was evaporated from an E-gun diagonally opposite the silicon monoxide source.

We have used this deposition arrangement and technique extensively for the production of stacks ranging from 40 to

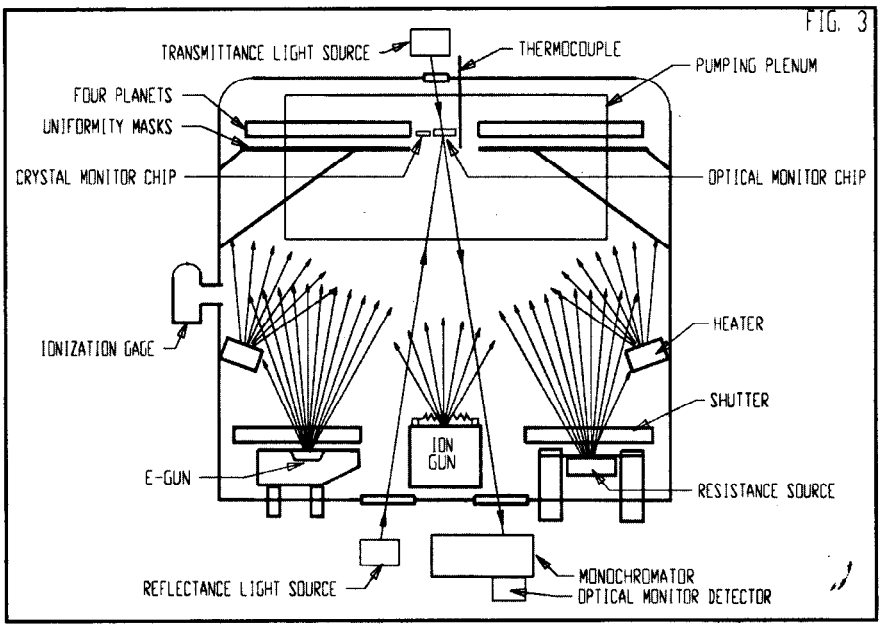
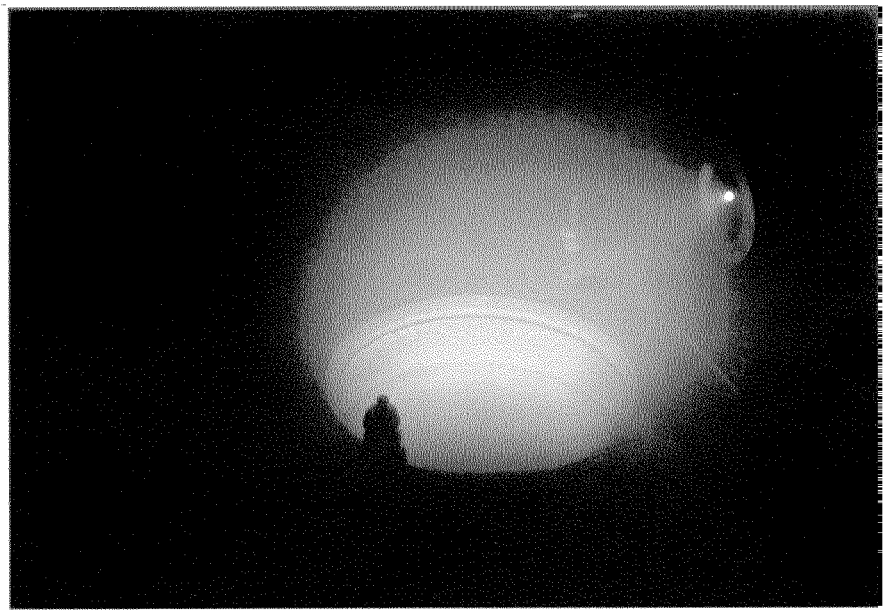


Figure 3. The general configuration of the chamber used for the silica and hafnia processes

90 layers of silicon dioxide and titania. For E-beam evaporation of silica from granules or discs without ion-assisted deposition (IAD), we typically might see a 15- to 20-nm spectral shift with change of water content (humidity) from wet to dry. With IAD from SiO, shifts of less than 1 nm and even zero have been achieved. The deposition conditions of such a run were: 225°C, 1 nm/second for both materials, 30 SCCM of oxygen through the ion gun, 300 drive volts, 5 drive amps, 17 amps for neutralizer, and the chamber pressure was mostly in the range of 1.0×10^{-4} Torr. The choice of temperature was based on the fact that the coatings showed cracking due, presumably, to differential thermal expansion when deposited on substrates at higher temperatures. These films also passed the adhesion and severe abrasion tests of MIL-C-675. The resulting index of the silica could be made anything from 1.45 to values higher than 1.50, depending on the deposition conditions. We found that the conditions that gave little or no humidity shift with this type of coating were not necessarily compatible with some laser damage requirements. However, we think that this might be overcome with further process optimiza-



tion. Additional oxygen background pressure was required to reduce the laser damage and give an index of about 1.46, but the humidity shift partially returned. More ion current is probably required to get a combination of high laser damage threshold and low humidity shift. The ion current available limits the rate at which material can be deposited and properly oxidized and densified. Therefore, the highest ion currents available are usually the most desirable.

We have been able to achieve generally good and repeatable uniformity over a full chamber diameter calotte (1.2 m) by the use of masks. However, the ion gun parameters must be stable, or the uniformity can be seen to have some changes. A change in chamber pressure will change the mean free path of the ions and neutrals and thereby change the effects of the uniformity masks. The ion beam has a distribution that is more concentrated on the axis of the beam. It appears that if an adequate amount of ions reach the less bombarded areas, the excess ions in the central areas are not detrimental. We have had some indication that this is less true when the drive volts are in the higher (500 V) regions. The hypothesis is that some ion sputtering or etching may be occurring at the higher drive volts, and thereby the thicknesses of the layers are slightly reduced at the center of the beam impingement area.

We found the oxygen ion assisted deposition of silicon monoxide to be a solution to the reproducibility problems of silicon dioxide films. We are able to deposit films at acceptably high rates in production environments.

Hafnia Deposition Process

Hafnia has some deposition problems related to those of silica. There apparently was little done with it until the availability of electron beam sources. Ritter[9] shows data that imply its usefulness down to about 220 nm in the UV, and Baumeister and Arnon[10] state that its high transparency extends down to 235 nm. The latter work reports indices at about 500 nm, which vary around 2.0 for deposition on 250°C substrates, depending on the deposition conditions. This work was

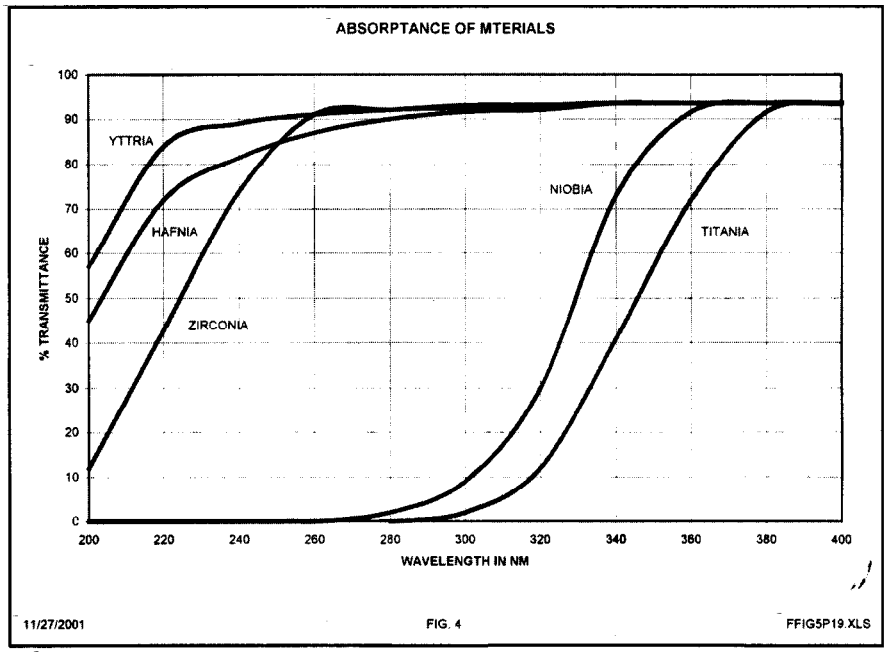


Figure 4. The transmittance of hafnia, yttria, zirconia, niobia, and titania films in the UV.

before the widespread use of IAD, and shows potential for improvement to a stable index between 2.05 and 2.1 with oxygen IAD. Cox and Hass[11] show the benefit of HfO_2 instead of SiO_2 as a protective overcoat on aluminum for the 8 to 12 μm region. Smith and Baumeister[12] reported some later work with hafnia and other materials that showed similar results. Kruschwicz and Pawlewicz[13] gave the optical and durability properties of hafnia and other materials. Our own experience showed it to be a preferred high index material in the UV as compared to zirconia. **Figure 4** shows the transmittance of hafnia, yttria, zirconia, niobia, and titania films in the UV. The yttria transmits a bit further into the UV, but it has an index of 1.72 in the visible as compared to hafnia's 1.93 to 2.1.

There have been several articles pointing to the tunneling effects and other problems such as spitting of HfO_2 and attempts to overcome these problems. Two such papers were by Chow and Tsujimoto[2] and Harris[4]. We found a more satisfactory approach, when an ion source is available. The deposition was treated somewhat like that of converting SiO to SiO_2 as mentioned above. The hafnium metal was evaporated from a vitreous carbon crucible liner in the e-gun pocket. The metal was totally molten and therefore evaporated evenly without any tunneling or spitting. A tungsten liner was tried first, but it was attacked by the molten metal. The liner provides some thermal barrier so that the metal can remain liquid. The oxygen to form HfO_2 was provided by a high power plasma/ion source[7] at 1 kW of drive power (about 10 A at 100 V). This supported a 1 nm/sec rate in a 1.4-m box coater. The films were clear at 350 nm with an index of 2.08+i0, and had the following values at shorter wavelengths: 300 nm, 2.11+i.001; 260 nm, 2.2+i.01; 240 nm, 2.27+i.025; and 2.25 nm, 2.17+i.039.

We also have used hafnia as an adhesion-promoting layer of 5 to 10 nm thick between Ge and ThF_4, and as a stress reduction means. The properties of the bulk material have been reported by Wood, et al.[14] along with yttria-stabilized cubic hafnia and cubic zirconia.

Conclusion

The depositions of both silica and hafnia from the dioxides as starting materials have had significant reproducibility problems due to tunneling and other defects. Processes have been described that use silicon monoxide and metallic hafnium as the evaporation material and complete the oxidation with oxygen ions. These processes have been found to be significantly more stable and reproducible. The combination of these two materials can be a good choice for coatings in the spectral region from about 250 nm well into the near infrared.

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