

Hafnium Dioxide for Coatings

Production, Deposition, and Properties

Authors: Samuel Pellicori and David Sanchez
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Introduction

Hafnium (Hf) metal is found in small quantities associated with Zirconium (Zr) ores. Its low abundance, complex extraction and purification technology, and specific uses render it an expensive metal. The larger energy and defense market for Zr produces relatively pure Hf metal and oxide as classified by the residual Zr content. While similarly durable, in contrast to the neutron transparent Zr cladding on fuel pellets that power a nuclear reactor, Hf is used to absorb and thus moderate the density of neutrons in an operating nuclear reactor. It forms very hard tribologic, high-temperature (~3900 C) compounds including HfC and HfN, in addition to alloys with Nb, Ta and Ti for critical rocket components exposed to high-temperature exhaust gasses.

Hafnium dioxide (HfO₂) is also used in semiconductor applications and thin-film capacitors because of its high dielectric constant. Hafnium oxide is important in the performance of ultraviolet and Near InfraRed (NIR) spectroscopy lasers, both of which are integral to the growing demand for lasers in manufacturing. Applications for UV lasers include marking (e.g. area barcodes) of ceramics, glass and plastics; patterning and micro-machining of semi-conductors; corneal ablation in ophthalmology, and more. In thin-film optical applications, HfO₂ is used at wavelengths below ~300 nm and ~350 nm, respectively, at which more common materials like Ta₂O₅ and TiO₂ become absorbing. The most important materials for optical coatings applications in UV to IR wavelengths are HfF₄ and HfO₂.

Hafnium Dioxide Deposition Properties

HfO₂ is grouped with similar metal-oxide compounds containing Ta, Nb, Zr, Y, or La that compose the high-index materials commonly used in coating designs for the near-UV to MWIR spectral ranges. Their high vaporization temperatures of greater than or equal to 2000° C require E-Beam evaporation or reactive sputter deposition. In contrast to other oxides, HfO₂ has an affinity for oxygen and produces less (by occurrence) stable sub-phases, a property that leads it to a variety of deposition technologies and approaches. The high melting point of the metal and the oxide are central considerations related to the shape, size and density of the starting material. Depending on the coating design, required laser resilience or dielectric properties, there can be complex source material form preparation and pre-conditioning requirements for the oxide. Preconditioning of the pellet or granular form of the source oxide material can be optimized, and application-specific pellets or starter charges can be furnished.

Product mix and demand from the energy industry, especially because of the Zr content difference between the oxide and the metal, can be of critical importance for optical coatings operating near the UV absorption edges of the material, depending on the wavelength and power densities pertinent to the application.

During deposition, it is typical to find the growth profile of high-temperature refractory oxide compound layers to be inhomogeneous. Crystalline structure and density vary with depth, thus exhibiting a growth morphology that changes from wide columnar features near the substrate to narrower column width near the top. Consequently, refractive index is stratified because the film density is different between top and bottom regions. The inhomogeneity can be caused by pressure, rate or temperature changes during growth. Spectroscopic ellipsometry analysis models the index profile as a “bottom” index and a “top” index of lower value. This inhomogeneity introduces some uncertainty in translating designs to physical coatings and is of concern relative to producing coatings with high laser-induced damage thresholds (LIDT).

Figure 1 shows the inhomogeneous refractive indices and Figure 2 shows the extinction coefficients, k , for HfO_2 deposited using Plasma Ion Assisted Deposition (PIAD) [1]. Stratification of the index is derived by the spectroscopic ellipsometry model; however, the k values are constant. The sharp increase in k at ~ 225 nm indicates the lower wavelength limit of useful high transmission.

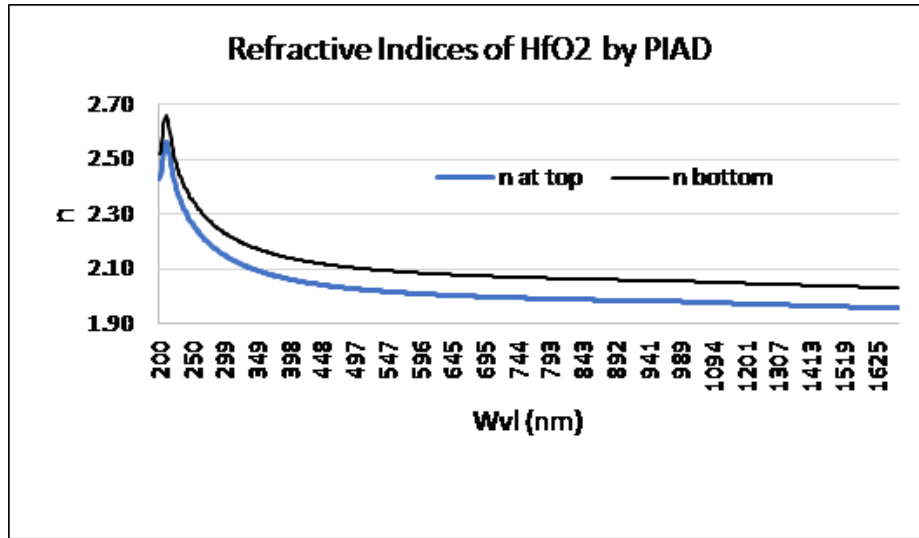


Figure 1. Measured refractive indices of PIAD HfO_2

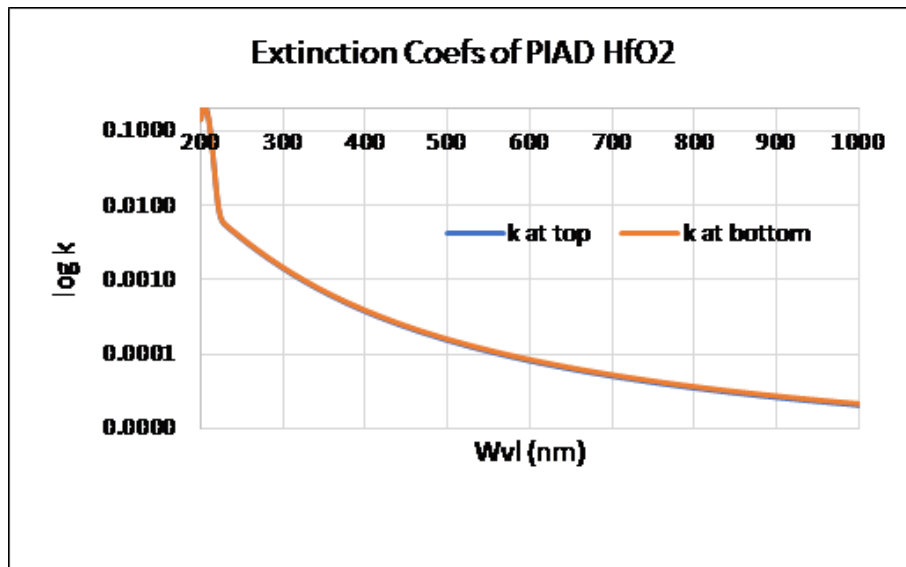


Figure 2. Extinction coefs for PIAD HfO_2

Deposition processes that employ high-energies, such as Ion Assist (IAD) or magnetron sputtering, disrupt the tendency for crystalline growth and lead to layers with better property homogeneity. The negative aspect of high-energy processes

is that a small amount of compound dissociation and electronic defects can be created, adding absorption and resulting in lower LIDT. Studies of films with reduced oxygen content revealed the cause for low LIDT at UV wavelengths was due to the presence of oxygen vacancies [2]. Deposition processes for HfO_2 are reactive E-beam, reactive low voltage ion plating (RLVIP), dual ion beam sputtering (DIBS).

A comparative study of LIDT produced those deposition processes illustrates the importance of the process. It was determined that for nano-second 355 nm coating exposure, the E-beam ion deposition (IAD) process produces coatings with higher LIDT compared with the higher-energy processes [3]. The disadvantage is that the film surface exhibits more roughness than the RLVIP and DIBS films.

The chemical compatibility of HfO_2 films enables good adherence to a variety of substrate materials including silicates (glasses), metals (Al, Au, and Ag), and some non-oxide materials. Sputtered or IAD deposited films form dense water-impermeable protective layers. This is especially applicable to Ag, which is vulnerable to corrosion by reactive atmospheric gasses. A stable reactive deposition can reduce the density of pinhole voids left by dislodged particles compared to other protective coatings. In cases where the highest quality dielectric thin film is required, new ALD techniques are used to make pinhole free, high dielectric constant “k” thin films. While the precursors to this method can be created with the same oxides and metals, high demand from the microelectronics world continues to drive specialty chemical research.

Material process techniques such as mixed oxide compositions are sometimes used to achieve improved physical properties including smoother layers of denser film morphology. Mixtures with SiO_2 and Y_2O_3 lower the final index, whereas mixtures with TiO_2 increase the index but move the absorption edge to longer wavelengths into the visible region [4]. Reproducible mixing is achieved by operating two sputter targets simultaneously.

Optical Coatings for UV Lasers

Optical coatings for the UV region at wavelengths less than 400 nm are compelled to resort to a small number of high-index ($n \sim 2$) layer materials to use in combination with SiO_2 , ZrO_2 , Y_2O_3 , and HfO_2 thin film layers are transparent to <250 nm. Sc_2O_3 is also transparent but is expensive due to scarcity and purification complications including radioactive impurities or geopolitical disruption. In contrast, HfO_2 is useable to ~ 225 nm wavelength and forms stable hard coatings. These properties enable UV laser energy to be generated for multiple UV harmonics of Nd:YAG and Nd:YVO₄. The 3rd harmonic of the 1064 line of Nd:YAG is at 355 nm, the 4th harmonic is at 266 nm, and the 5th harmonic is at 213 nm. High energy densities of the third harmonic of the 1053 nm line of Nd:YLF at 351 nm are used in the high-power coating functional high-reflector and AR coatings for laser fusion energy generation facilities [2]. The National Ignition Facility (NIF) Laser Inertial Fusion energy (LIFE) project is an example where mega-joules of laser energy are expected to produce mega-watts of power (Figure 3).

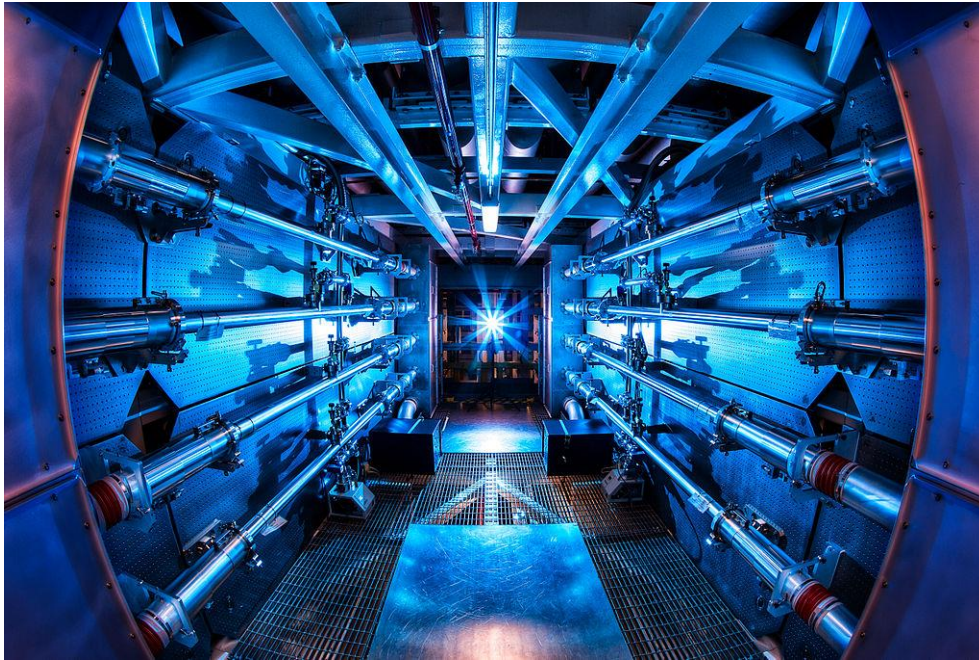


Figure 3. The preamplifiers of the National Ignition Facility are the first step in increasing the energy of laser beams as they make their way toward the target chamber. In 2012, NIF achieved a 500 terawatt shot—1,000 times more power than the [United States uses at any instant in time](#). (Source: [Wikipedia](#)).

The UV lines and the Excimer wavelength at 248 nm and the diode-pumped solid state (DPSS) line at 308 nm all rely upon HfO_2 coatings (only marginally at 213 nm). The Hafnium Oxide layers on the crystals and optics used to generate frequency doubled, and tripled photons are often a co-deposition mix of e-beam, IAD, reactive magnetron and ion beam sputtering processes. Large targets of the oxide and the metal can be expensive, heavy and even fragile (the oxide) but steps can be taken to mitigate risks and optimize utilization – balancing out the cost for the different techniques.

Optical coating applications are not as sensitive as semiconductor applications to the role of Zr and other oxide impurities. This is because full oxidation and stress inherent to the application technology can be more important. Below the metal-oxide absorption edge, fluoride compounds are used and dominate laser wavelengths near and less than ~ 200 nm.

Short pulses (femto-second) of high energy are used in these applications to avoid local heating damage that would be caused by CW and long pulses of visible-range lasers. Material composition is preserved, and higher resolution is provided by the short wavelengths. At short pulse duration and high energy density the thin film coating requires a high LIDT to resist damage caused by vaporization and plasma generation that can limit useable lifetime or even result in catastrophic failure. The HfO_2 formulation and deposition process are optimized for specific laser irradiance.

The established history of using HfO_2 and mixtures of alternative materials with host HfO_2 for high-energy UV laser applications sets the goal for future refinement of coating materials and deposition techniques as required to satisfy future more demanding applications.

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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