Ion-assisted deposition of moisture stable HfO_2 thin-films

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Abstract: This paper reports the process parameters used to make moisture stable HfO_2, the optical properties of HfO_2 in the UV-visible spectral region and gives an example of a moisture stable thin-film coating of a HfO_2/SiO_2 LWP filter.

OCIS codes: (160.4760) Optical properties; (310.3840) Materials and process characterization

Introduction: HfO_2 (hafnium oxide) is a common material used for manufacture of UV filters due to being transparent down to about 250 nm. Also, it exhibits less sensitivity to moisture instability than many other thin-film materials. It is possible to make fully dense, moisture stable films using IAD (ion-assisted deposition). However, unlike many other oxides, it is necessary to use a mixture of argon and oxygen.

Most thin-films deposited without ion-assist are porous and sensitive to moisture going in and out of the voids causing an apparent shift in refractive index depending on the relative humidity (amount of H_2O filling the voids). In previous publications [1,2,3] we have reported wet/dry refractive index changes (Δ_n) as high as -0.05 for TiO_2 and -0.035 for Ta_2O_5 films deposited without IAD. IAD densifies the films, increasing the refractive index of TiO_2 by as much as 0.35 and of Ta_2O_5 by as much as 0.15 while reducing the refractive index change of wet/dry films to zero. Hafnium oxide is an intermediate high index material ($n \approx 1.9$-2.0 in the visible) and exhibits a small change in wet/dry refractive index ($\Delta_n \approx -0.003$) for films deposited without IAD at lower substrate temperatures (<100 °C). One would expect that it would be relatively easy to use IAD during HfO_2 depositions to increase the densities of the films and make them moisture stable.

Parameters similar to those used for other oxides were employed in three different coating machines to prepare IAD films of HfO_2. The results were fairly discouraging. Not only did the IAD films not appear to be denser (higher refractive index) but the wet/dry Δ_n increased to about -0.02 in most cases and even as high as -0.04 to -0.05 for processes with higher pressures. In fact, the moisture stability seemed to be inversely proportional to the deposition pressure and to be unrelated to the ion current density.

Fortunately, in the time frame of conducting this study, Traci Jensen of Omega Optical [4] reported on a design of experiments study conducted on IAD HfO_2 thin-films at the Annual OSA Conference in Providence, Rhode Island. In this report she varied 5 factors (pressure, deposition rate, ion gun current, argon flow and oxygen flow) to determine the best parameters for making moisture stable HfO_2 films. The result of this study was that a lower pressure, lower deposition rate, lower ion current and equal gas flow for argon and oxygen produced the best results. The work at Omega Optical was conducted in a 1 meter box chamber but the area of the parts being coated was relatively small and the ion gun was mounted 9 inches below and off to the edge of a single rotation substrate carrier [5]. Since energy from the E-gun and the ion source would heat the parts during deposition, they used a 130 °C substrate temperature to minimize temperature shift during deposition.

Experimental Set-up: The final part of this study was done in our Application Laboratory using a Denton Vacuum Integrity®-36 coating chamber equipped with a 6-pocket Telemark ST6 E-gun, Denton Vacuum CC-105 ion source, XTC/2 quartz crystal rate/thickness monitors, heaters and 5-11.75 inch planets. Preliminary depositions were done on microscope slides and final characterization was done using silica substrates. Spectral data from clear and frosted samples were used as reported previously [1, 3] to determine optical properties and moisture stability. Having the benefit of the Omega Optical results, a series of tests were conducted at ambient (starting at 40 °C) and slightly higher substrate temperatures (starting at 100 °C) using various combinations of gas flow rates for argon and oxygen. All depositions were done using 2 Å/sec deposition rate and 3 amp drive current. A selected summary of deposition parameters and results are recorded in Table I. The flow rates are nominal based on nitrogen equivalent conversion factors and the pressure values are nominal based on nitrogen ionization efficiency. The refractive index for the IAD and non-IAD films are shown in Figure 1.

A series of 8 layer stacks of HfO_2/SiO_2 were then deposited to refine the conditions for making the best moisture stable film stacks of these materials. It was obvious that the best parameters for making good stacks was to duplicate the conditions of the last run (#39) for HfO_2 and to use 20 sccm of oxygen, 3 amp drive current and 5 Å/sec for the SiO_2 (established in previous work). During these depositions it was noted that out-gassing from the evaporation of the HfO_2 would result in deposition pressures well above the $2.5x10^{-4}$ Torr established for good HfO_2 films. Therefore the HfO_2 material was preconditioned to minimize out-gassing the material while depositing stacks. Also it was determined that the pressure should not be allowed to go above $2.5x10^{-4}$ Torr while depositing HfO_2. Therefore we changed the gas flow conditions through the ion source to 12 sccm of argon (resulting in $2x10^{-4}$ Torr pressure and set the oxygen flow for PID control to make up the balance of the allowed $2.5x10^{-4}$ Torr pressure. This resulted in an oxygen flow rate varying between 3-6 sccm depending on the out-gassing level from the HfO_2. The ion current density while depositing HfO_2 varied over about 130 $\mu A/cm^2$ to 146 $\mu A/cm^2$ depending on location in the planet.

Table I – Selected Process Parameters and Data for HfO_2 Films

Run #	Temp (°C)	Argon/Oxygen Flow (sccm)	Pressure (Torr)	Drive Voltage (V)	n @ 560 nm	n @ 250 nm	k @ 250 nm	D_n
U-18	50-115	0/10	$9x10^{-5}$	n/a	2.04	?	?	-0.003
9	50-115	0/25	$1.9x10^{-4}$	219	2.046	2.208	?	-.016
32	109-141	10/10	$2.5x10^{-4}$	143	2.063	2.39	?	0
27	60-105	10/15	$2.8x10^{-4}$	142	2.051	2.268	?	-0.077
33	107-127	10/18	$2.9x10^{-4}$	128	1.988	2.19	?	-0.02
34	109-135	8/10	$2.1x10^{-4}$	186	2.043	2.227	?	0
39	110-129	12/6	$2.5x10^{-4}$	139	2.05	2.45	.037	0

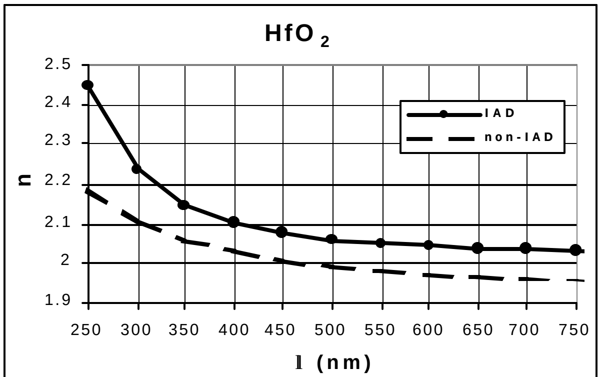

Figure 1. HfO2 refractive index [non-IAD run U-18, IAD run #39.

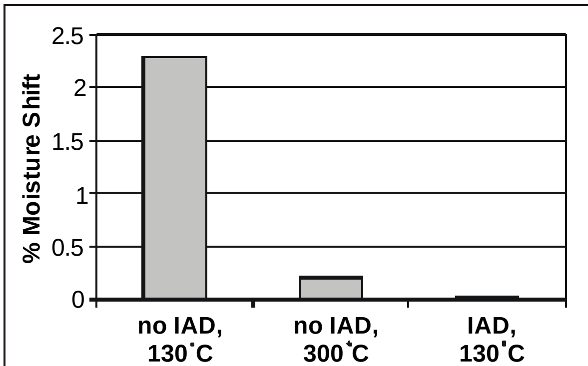

Figure 2. Effect of IAD and deposition temperature on moisture shift of HfO_2 films.

At Omega Optical, a systematic study was performed in which HfO_2 films approximately 500 nm in thickness (16 optical quarter waves measured at 250 nm) were deposited under various conditions in order to determine the optimum ion gun operating parameters. The following process parameters were found to be optimal in our study for minimizing moisture shift and maximizing UV transmission: temperature = 130º C, pressure = $3 x 10^{-4}$ torr, argon/oxygen flow = 23/23 sccm, drive current = 0.5A, and drive voltage = 220V. The effect of ion assist and temperature on the moisture stability of the films is shown in Figure 2. Moisture stability was determined by soaking the sample in water, scanning transmittance, then purging the spectrometer chamber with dry nitrogen and rescanning after 10 minutes or until no further spectral shift is observed. Percent moisture shift is simply (ë$_{wet}$-ë$_{dry}$)/ ë$_{wet}$ x 100%. We find that deposition temperature has a large impact on the moisture stability of films deposited without IAD. The incorporation of IAD, even at a lower deposition temperature, produces films with no measurable moisture shift (<0.02%).

A proprietary design 91 layer HfO_2/SiO_2 longpass edge filter was deposited on a fused silica substrate using the IAD parameters found to be optimal for HfO_2. The ion gun was operated with the same parameters during the SiO_2 layers as during the HfO_2 layers- no attempt was made to adjust the ion gun for optimal SiO_2 coatings. Hafnia layers were deposited at a rate of 3 Å/s, and silica layers at 7 Å/s. The transmission spectrum of the edge filter is shown in Figure 3. The optical density of the filter is between 5 and 6 from 200 nm to 262 nm (data not shown). High optical density is due to the combined effects of absorption, reflection, and scatter by the filter. The wet-dry spectral shift of the filter is shown in Figure 4. Any moisture shift is concealed in the noise of the spectrophotometer, i.e., the wet-dry spectral shift of the edge is less than 0.05 nm, or 0.02%.

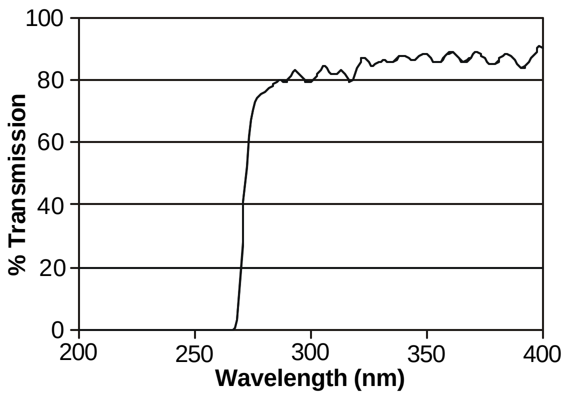

Figure 3. High phase thickness HfO_2/SiO_2 stack edge filter deposited with IAD.

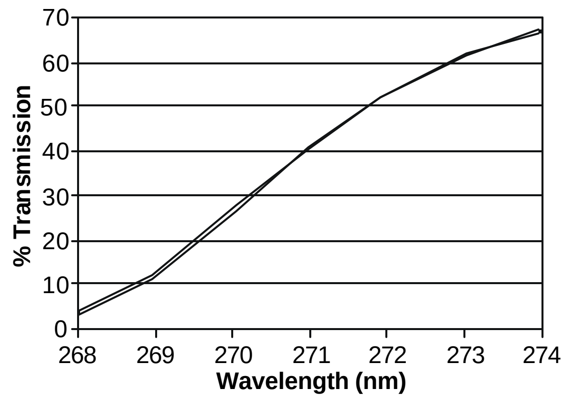

Figure 4. Magnified view of wet-dry shift of edge filter shown in Figure 3.

Conclusion: In this paper we have shown that moisture stable HfO_2 films and stacks containing HfO_2 and SiO_2 can be deposited at lower substrate temperatures (100 °C – 130 °C) using an argon oxygen gas mixture IAD process. It was necessary to use an argon/oxygen mixture (with a minimum level of oxygen) since we were unable to produce good films using oxygen only.

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