Comparative study on the effects of suspension way of sample holder on the large-aperture uniformity of refractive index of HfO$_2$ films

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Abstract. For large-aperture dielectric film optics, the uniformity of film refractive index across the aperture is crucial to the uniformity of reflectance and transmittance. Herein, a comparative research has been performed on the refractive index uniformity of HfO$_2$ films across the Φ560 mm-aperture sample holder for inclined suspension and horizontal suspension. It’s revealed that the refractive index of HfO$_2$ film at edge position of sample holder increased about 1.52% compared to that of HfO$_2$ film at center position for inclined suspension, while the refractive index varied only about 0.25% for horizontal suspension. The further analysis performed on film crystallization, morphology and microstructure show that the large variation of refractive index between the films at center and edge positions of inclined suspension sample holder was attributed to the different growth properties. The film at the edge crystallized more slightly and was denser, thus being of higher refractive index. And the different growth properties of the two films at center and edge positions can be explained in the light of the co-effects of atomic shadowing, reemission and diffusion of ad-atoms during film growth.

1. Introduction

The large-aperture dielectric film optics are indispensable to laser fusion facility [1], to which the spectrum performance of optics are especially important. The spectrum uniformity, as an assessment...
of spectrum performance of a large-aperture dielectric film optic, depends on the uniformity of thickness and refractive index \((n)\) of dielectric films. And optimizing the large-aperture uniformity of film thickness is always a research focus for various film deposition techniques, because thickness inhomogeneity can result in the spectrum drifting significantly along the radial direction of a large-aperture optic. Although it’s challenging to improve thickness uniformity of the large-aperture films, many strategies have been tried by researchers, for example, optimizing position of the evaporation source \([2]\) and way of the substrate movement \([3-6]\) in coating chamber, inserting a mask between substrate and evaporation source \([6]\), and so on.

By contrast, the large-aperture uniformity of film refractive index attracts less attention from researchers, because it’s generally better than that of film thickness and has slighter influence on the spectrum uniformity for common optics. However, it becomes vital to those special optics requiring constant transmittance or reflectance at specified light wavelength, thus should be carefully studied as well as film thickness uniformity. Herein, hafnia \((HfO_2)\) films, which are widely used as high refractive index material in the field of high power laser due to their high damage threshold \([7-9]\), had been deposited by reactive e-beam evaporation. And the effects of substrate suspension on the large-aperture uniformity of \(n\) of HfO\(_2\) films had been investigated.

2. Experimental

HfO\(_2\) films were deposited on fused silica substrates \((\Phi 50 \text{ mm} \times 5 \text{ mm})\) through the reaction of oxygen and hafnium gas evaporated by e-beam evaporation. The substrates were fixed into substrate holes of the sample holder in figure 1a. The substrate holes are equally spaced with interval of 70 mm along the radius of sample holder, covering a deposition area of \(\Phi 560 \text{ mm}\) aperture. And half of the substrate holes are noted and named as 2-0#, 2-1#, 2-2#, 2-3# and 2-4#, respectively, which are also the sample names of deposited HfO\(_2\) films in the following description. As the sample holder rotates in a planetary way during film deposition, the properties of HfO\(_2\) films deposited on these noted positions are adequate to represent the film properties across the whole deposition area of \(\Phi 560 \text{ mm}\) aperture in consideration of the symmetry of planetary rotation. To maximize effects of the suspension way of sample holder on the \(n\) of HfO\(_2\) films, 60°-inclined suspension (figure 1b) and horizontal suspension (figure 1c) had been adopted. It should be noted that HfO\(_2\) films for 60°-inclined suspension and horizontal suspension had to be deposited in the coating machine of APS1504 and ZZS1350, respectively, due to the mechanical configuration of the coating machine. Nevertheless, it remains feasible to compare the effects of suspension way on HfO\(_2\) films because the two coating machines (APS1504 and ZZS1350) are extremely similar with each other in the key aspects. For example, the location of the heater, e-gun, evaporating source, quartz crystal controller and evacuating outlet, as well as the configuration of evacuation system, are similar with each other for the two coating machines. As for 60°-inclined suspension, substrate positions of 2-1# and 2-4# had been selected to deposit HfO\(_2\) films, while positions of 2-0# and 2-3# had been selected for horizontal suspension. The background pressure was controlled below \(2.0 \times 10^{-4} \text{ Pa}\) prior to film deposition, and the deposition process was controlled automatically by quartz crystal controller. Detailed process conditions can be found in table 1.

The spectra of fabricated HfO\(_2\) film samples had been measured by spectrophotometer
(PerkinElmer, Lambda 950). The $n$ of samples had been derived from the spectra by the OptiLayer software [10]. The crystalline structure of samples had been analyzed by X-ray diffractometer (PANalytical, EMPYREAN). The surface morphology of samples had been measured by atomic force microscope (Park System, XE-150) with the non-contact mode. And the microstructure of samples had been characterized by field-emission scanning electron microscope (FEI, Helios NanoLab 650).

### Figure 1. Schematic diagrams of sample holder (a) and its suspension ways (b, c).

### Table 1. Detailed process conditions of HfO$_2$ film deposition for 60°-inclined suspension and horizontal suspension.

| Suspension way of sample holder | Monitoring rate (nm/s) | Temperature (°C) | Oxygen pressure ($\times 10^{-2}$ Pa) | Monitoring thickness (nm) |
|--------------------------------|-------------------------|------------------|---------------------------------------|--------------------------|
| 60°-inclined                    | 0.1                     | 210              | 1.8                                   | 50                       |
| horizontal                     | 0.5                     | 250              | 1.5                                   | 200                      |

### 3. Results and discussion

Figure 2 shows the transmission spectra of deposited HfO$_2$ film samples for 60°-inclined suspension and horizontal suspension of sample holder. In the figure the spectra of sample 2-1# and 2-4# for 60°-inclined suspension differ obviously with each other. For example, the minimum transmittance of sample 2-1# around $\lambda=600$nm varies about 1.18% with respect to sample 2-4#, indicating that there is notable difference on $n$ between the two samples. On the contrary, the spectra of sample 2-0# and sample 2-3# for horizontal suspension almost overlap with each other, suggesting that the two samples are of similar thickness and $n$. It’s worth noting that some transmission maximums of samples have exceeded the transmittance of blank fused substrate, especially for sample 2-1#, indicating that the $n$ of the HfO$_2$ films are somewhat inhomogeneous and gradually decrease from the substrate to the film surface [11]. This $n$ variation is opposite to that of HfO$_2$ films deposited by ion beam sputtering [12]. Moreover, the more the maximum exceeds, the more inhomogeneous the $n$ is. Thus it can be concluded that $n$ of sample 2-1# is more inhomogeneous than that of sample 2-4# for 60°-inclined suspension. Likewise, $n$ of HfO$_2$ films for 60°-inclined suspension are more inhomogeneous than those for horizontal suspension.
Figure 2. The transmission spectra of HfO$_2$ film samples for 60°-inclined suspension and horizontal suspension.

Figure 3. The $n$ of HfO$_2$ film samples for 60°-inclined suspension and horizontal suspension.

Figure 3 depicts the dependence of $n$ on light wavelength derived by the OptiLayer software, showing that the $n$ of HfO$_2$ films at the edge of sample holder are larger than those of HfO$_2$ films at the center regardless of suspension way of sample holder. Moreover, $n$ varies a lot between the two samples (sample 2-1# and sample 2-4#) of inclined suspension, while the $n$ is almost same for samples (sample 2-0# and sample 2-3#) of horizontal suspension, coinciding with above analysis on the sample spectra. The obvious difference on $n$ of sample 2-1# and sample 2-4# reveals that the $n$ of HfO$_2$ film is also relatively inhomogeneous along the radial direction of sample holder for inclined suspension.

Table 2 lists some results calculated by the OptiLayer software from the spectra and gives a quantitative analysis on the variation of $n$. With regard to inclined suspension, the $n$ at $\lambda=1053$ nm of sample 2-4# increases about 0.028 compared to sample 2-1#, and the variation amplitude is as large as 1.52%. However, the $n$ at $\lambda=1053$nm of sample 2-0# increases slightly compared to sample 2-3#, about 0.005, corresponding to a variation amplitude of only 0.25%. Moreover, the $n$ inhomogeneity of sample 2-1# and sample 2-4# is +4.2% and -1.5%, respectively, where the negative sign means $n$ decreases from substrate to film surface. Whereas, the $n$ inhomogeneity of sample 2-0# and sample 2-3# are same with each other, only -0.3%. The larger $n$ inhomogeneity of inclined samples than those of horizontal samples are attributed to the severer crystallization and more columnar growth for films deposited on inclined substrate [13]. Thus, it could be concluded that sample 2-1# is of severer crystallization and more columnar structure. The more columnar structure the film has, the more pores the film has, subsequently resulting in the decrease of $n$. Thus, the $n$ of sample 2-1# is smaller than that of sample 2-4#. Regarding to horizontal suspension, the $n$ inhomogeneity of sample2-0# and 2-3# are almost same, suggesting that they are of similar structure, thus possessing similar $n$.

A simulation had been performed by the OptiLayer software to quantitatively analyze the effects of $n$ variation on a sampling mirror, of which the reflectance was supposed to be required to 0.2%±0.025% at $\lambda=1053$nm. The structure of the mirror during simulation was designed to be “fused silica\HfO$_2$\SiO$_2$”, in which the thickness of HfO$_2$ film and SiO$_2$ film were kept constant, and n values (in table 2) for HfO$_2$ films and n=1.4 for SiO$_2$ films were adopted without consideration of the dispersion of $n$. The simulation results were plotted in figure 4. Figure 4a shows that the variation of
reflectance of sampling mirror is about 0.1% with \( n \) variation of 0.028 (in table 2) for inclined suspension, far beyond the required limit of 0.025%. By contrast, the reflectance varies only about 0.015% with \( n \) variation of 0.005 (in table 2) for horizontal suspension. In other words, the reflectance inhomogeneity along the radial direction of \( \Phi 560 \) mm-aperture sample holder is as large as \( \sim 50\% \) for inclined suspension, while it is only \( \sim 7.5\% \) for horizontal suspension. From this point of view, horizontal suspension is superior to inclined suspension for fabricating larger aperture optics that require highly accurate transmittance or reflectance with the existing process conditions.

**Table 2.** Results calculated from the spectra by the OptiLayer software.

| Suspension way of sample holder | Sample | Film thickness (nm) | \( n \) (\( \lambda = 1053 \) nm) | Inhomogeneity of \( n \) along the film thickness | Variation of \( n \) (\( \lambda = 1053 \) nm) | Variation of the inhomogeneity of \( n \) |
|--------------------------------|--------|---------------------|-------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 60\(^{\circ}\)-inclined         | 2-1\#  | 87.18               | 1.8298                        | -4.2\%                         | 0.028                          | 2.66\%                        |
|                                 | 2-4\#  | 84.56               | 1.8576                        | -1.5\%                         |                                  |                                |
| horizontal                      | 2-0\#  | 244.80              | 1.8231                        | -0.3\%                         | 0.005                          | ~0                             |
|                                 | 2-3\#  | 243.88              | 1.8276                        | -0.3\%                         |                                  |                                |

**Figure 4.** Simulations by the OptiLayer software on the effects of \( n \) variation on the reflectance of a sampling mirror for 60\(^{\circ}\)-inclined suspension (a) and horizontal suspension (b)

**Figure 5.** Plots the X-ray diffraction (XRD) spectra of HfO\(_2\) film samples. All the curves in figure 5 have been normalized for comparative analysis. It’s clear that all the spectra present several strong peaks, demonstrating that all HfO\(_2\) films have crystallized. And the crystalline phase has been proved to be monoclinic by comparing with the powder diffraction file (PDF\#06-0318)\(^{[13, 14]}\). Although the film thickness (in table 2) of horizontal samples are almost three times those of inclined samples, the peak intensity of horizontal samples are nearly equal to those of inclined samples, indicating that the horizontal samples have crystallized much more slightly than the inclined samples. Similarly, the peak intensity of sample 2-4\# is weaker than that of sample 2-1\# for inclined suspension, suggesting that sample 2-4\# has crystallized more slightly than sample 2-1\#. And these conclusions from XRD spectra further demonstrate the rationality of above analysis on film growth and \( n \) inhomogeneity of samples.
Figure 5. Spectra of X-ray diffraction on the HfO$_2$ film samples

Figure 6 presents surface morphology graphs of sample 2-1# and sample 2-4# for inclined suspension by atomic force microscope (AFM). It’s clear that the surface are smooth and full of sphere grains with uniform size, suggesting that both of sample 2-1# and sample 2-4# have crystallized. The root-mean-square roughness ($R_q$) for $5 \mu m \times 5 \mu m$ is 1.23 nm and 1.41 nm for sample 2-1# and sample 2-4#, respectively. Moreover, the sphere grain size of sample 2-4# is smaller than that of sample 2-1#, indicating the weaker crystallization of sample 2-4#, which is consistent with above XRD analysis. Regarding to horizontal samples (sample 2-0# and sample 2-3#), AFM graphs in figure 7 show that the sphere grain size are similar with each other, but smaller than those of inclined samples, indicating that the two horizontal samples are of similar growth properties and have crystallized much more slightly than inclined samples. And the $R_q$ is 1.54 nm and 1.36 nm for sample 2-0# and sample 2-3#, respectively.

Figure 6. AFM graphs of sample 2-1# (a) and sample 2-4# (b) for 60°-inclined suspension
Figure 7. AFM graphs of sample 2-0# (a) and sample 2-3# (b) for horizontal suspension

Figure 8 and figure 9 exhibit scanning electron microscope (SEM) photos of the samples. Lots of micro gaps arise due to the aggregation of grains for sample 2-1# in figure 8a, while no visible aggregation as well as gaps can be found for sample 2-4# in figure 8b. Thus the emerging of the gaps would be a reason for the smaller \( n \) of sample 2-1# than sample 2-4#. The optical absorption at \( \lambda=355 \) nm (measured by laser calorimetry and not shown here) is 793.4 ppm and 577.4 ppm for sample 2-1# and sample 2-4#, respectively. And the higher absorption for sample 2-1# would result from the multiple reflections of light among the gaps of columnar in the film\[15, 16\]. On the contrary to inclined samples, the microstructure of horizontal samples in figure 9 present almost no difference, thus leading to small variation of \( n \) between sample 2-0# and sample 2-3#.

The above-mentioned differences on crystallization, surface morphology and microstructure among the samples can be discussed in the light of atomic shadowing, reemission and diffusion of ad-atoms\[17, 18\]. With regard to horizontal suspension, the incidence angle \( \theta_e \) and \( \theta_i \) (shown in figure 1b and figure 1c), which are the angles between the evaporating source and the normal of the substrates at the center and edge of sample holder, respectively, are both small, thus the atomic shadowing is depressed, resulting in the smaller grains and dense microstructure. Moreover, the sample holder is far away from the evaporating source and rotates in a planetary way, thus the difference between \( \theta_e \) and \( \theta_i \) is small. The small difference of incidence angles leads to the similar co-effects of atomic shadowing, reemission and diffusion of ad-atoms on the film deposition of sample 2-0# and sample 2-3#. Therefore, sample 2-0# and sample 2-3# exhibit similar film properties and \( n \).

As for 60°-inclined suspension, the incidence angles are relatively larger, thus atomic shadowing is enhanced, resulting in larger grains and more gaps of sample 2-1# and sample 2-4# than those of horizontal samples. Moreover, the incidence angle \( \theta_e \) of sample 2-4# varies in a much wider range than \( \theta_e \) of sample 2-1# during planetary rotation of sample holder. The wider variation range of incidence angle can depress the atomic shadowing, eventually leading to smaller grains, denser microstructure and larger \( n \) of sample 2-4# compared to sample 2-1#.
4. Conclusions

HfO$_2$ films have been deposited by reactive e-beam evaporation and the effects of suspension way of substrates on the large-aperture uniformity of refractive index of HfO$_2$ films have been comparatively studied. The optical transmittance and OptiLayer software analysis reveal that the refractive index of deposited HfO$_2$ films for 60°-inclined substrate suspension present inhomogeneity along the normal as well as the radial direction of sample holder, while the refractive index are homogeneous in both directions for horizontal substrate suspension. From this point of view, the horizontal suspension is superior to inclined suspension to fabricate large-aperture optics that require highly accurate transmittance or reflectance under the existing experimental conditions. Regarding to inclined suspension, the film at the edge of sample holder crystallized more slightly and was denser, thus possessed larger refractive index than the film at the center of sample holder. And the inhomogeneity of refractive index for inclined suspension results from the different combined effects of atomic shadowing, reemission and diffusion of ad-atoms during the film deposition.
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