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Nanostructuring HfO_2 Thin Films as Antireflection Coatings

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Hafnium dioxide (HfO_2) films deposited on silicon substrates can be nanostructured by the glancing angle deposition technique into various porous morphologies, leading to a variation of the refractive index in a range of 1.94–1.16. This makes HfO_2 thin films effective antireflection coatings on many substrates. For example, a 160-nm-thick HfO_2 film of an appropriate refractive index can cut more than half the reflection of visible light off the surface of SiC or Al_2O_3 substrates. This study provides an easy way to design, prepare, and optimize the performance of antireflection coatings on different substrates.

LIGHT reflection off the surface limits the performance of optical devices in case high transmittance is required (e.g., the window of solar cells and a high-power laser device). Efforts have thus been focused on finding ways to minimize the light reflection and enhance the transmittance, where antireflection (AR) coating is a good choice. The reflection can be largely suppressed when AR coatings meet the following requirements: (1) the coating material is highly transparent; (2) $n_e^2 = n_0 n_s$, where n_e, n_0, and n_s are the effective refractive indices of the coating, air, and substrate, respectively; and (3) the coating thickness is an odd multiple of 1/4 of the light wavelength.[1] Condition (3) can be met by controlling the thickness. However, as highly transparent materials are limited, ways to tune their refractive index are very much required to optimize the performance and broaden the application of AR coatings.

Glancing angle deposition (GLAD) is a powerful method to nanostructure films due to the shadowing effect,[2–4] by which porous films of different morphologies such as column, helix, and spring can be fabricated.[5–7] As the refractive index is related to the porosity, the GLAD method could be a good technique to tune the refractive index of films of any material.[8–10] Hafnium dioxide (HfO_2) is a known optical material due to its high laser-induced damage threshold (LIDT), high refractive index ($n = 2$), high transparency from infrared (IR) to ultraviolet (UV) as well as its low reflectivity in the visible and near-IR region.[11,12] It is one of the most frequently used high-n optical coating materials, especially when a high LIDT is needed, and is expected to be a good AR coating for a number of substrates once its refractive index can be tuned.[13]

In this letter, we report that by morphologically engineering HfO_2 films using the GLAD method, its refractive index can be varied in a wide range of 1.94–1.16; thus HfO_2 films can be good AR coatings on any substrate if their refractive index is within 3.76–1.35. The performance of HfO_2 films on SiC and Al_2O_3 substrates confirmed that GLAD is a powerful technique to prepare nanostructured AR coatings.

HfO_2 films were deposited by the GLAD technique using an e-beam deposition system with a background vacuum level better than 3×10^{-5} Pa. In order to obtain the relationship between the oblique angle α (defined as the angle between the trajectory of the incident vapor flux and the surface normal of the substrate) and the refractive index, HfO_2 films were deposited on Si (001) substrates at $\alpha = 0°$, 60°, 70°, 76°, 80°, 84°, and 88°, respectively, at a deposition rate of 4 nm/min and a substrate rotation speed of 0.11 rpm. By measuring the refractive index of the films with an ellipsometer, the α–n curve was constructed for HfO_2 thin films. From this curve, the oblique angles for depositing an HfO_2 AR coating on SiC and Al_2O_3 substrates were obtained. To check its validity, HfO_2 coatings were also deposited at two other different oblique angles on both substrates. The morphology of all samples was examined by a scanning electron microscope (SEM), with their structure identified by X-ray diffraction (XRD) analysis. The performance of the HfO_2 coatings on both substrates was evaluated by measuring the transmittance and reflectivity off the surface with a spectrophotometer.

Figure 1 shows a typical growth morphology of the HfO_2 films deposited on silicon substrates at various incident angles. The SEM images were taken by an FEI QUANTA 200 SEM working at 15 kV. These images show clearly that the morphology of the film is highly dependent on the oblique angle. For example, at an angle of $\alpha = 0°$, i.e. vertical deposition, the film is dense and flat. When the film was deposited at angles $\geq 70°$, the film became rough and porous as self-standing nanostructures were formed (see Figs. 1(b)–(f)). One may also notice that the film became more porous when the film was deposited at higher angles, such as 80°, 84°, and 88°. XRD patterns of these films (not shown) taken by a Rigaku XRD using the Cu$K\alpha$ radiation indicated that they are all amorphous in structure.

The refractive index of the amorphous HfO_2 films deposited at various oblique angles was measured by an SOPRA GES-5 ellipsometer (SOPRA Company, Courbevoie, France) at wavelengths from 200 to 900 nm. Figure 2(a) plots the refractive index of the HfO_2 films as a function of the wavelength. One can see that the refractive index of the film declined when it was deposited at higher incident angles. For example, n_e of the film at 600 nm decreased from 1.94 to 1.16 when deposited at 0° and 88°, respectively. This is caused by the formation of nanostructures by the GLAD technique.[14] Figure 2(b) shows n_e at 600 nm versus the angle. It is known that n_e of a porous film is given by an average of air and material when the pore size is much smaller than the wavelength. Using the n_e at 600 nm, the porosity of the above HfO_2 films was calculated under the Bruggemann approximation,[15] and was also included in Fig. 2(b).

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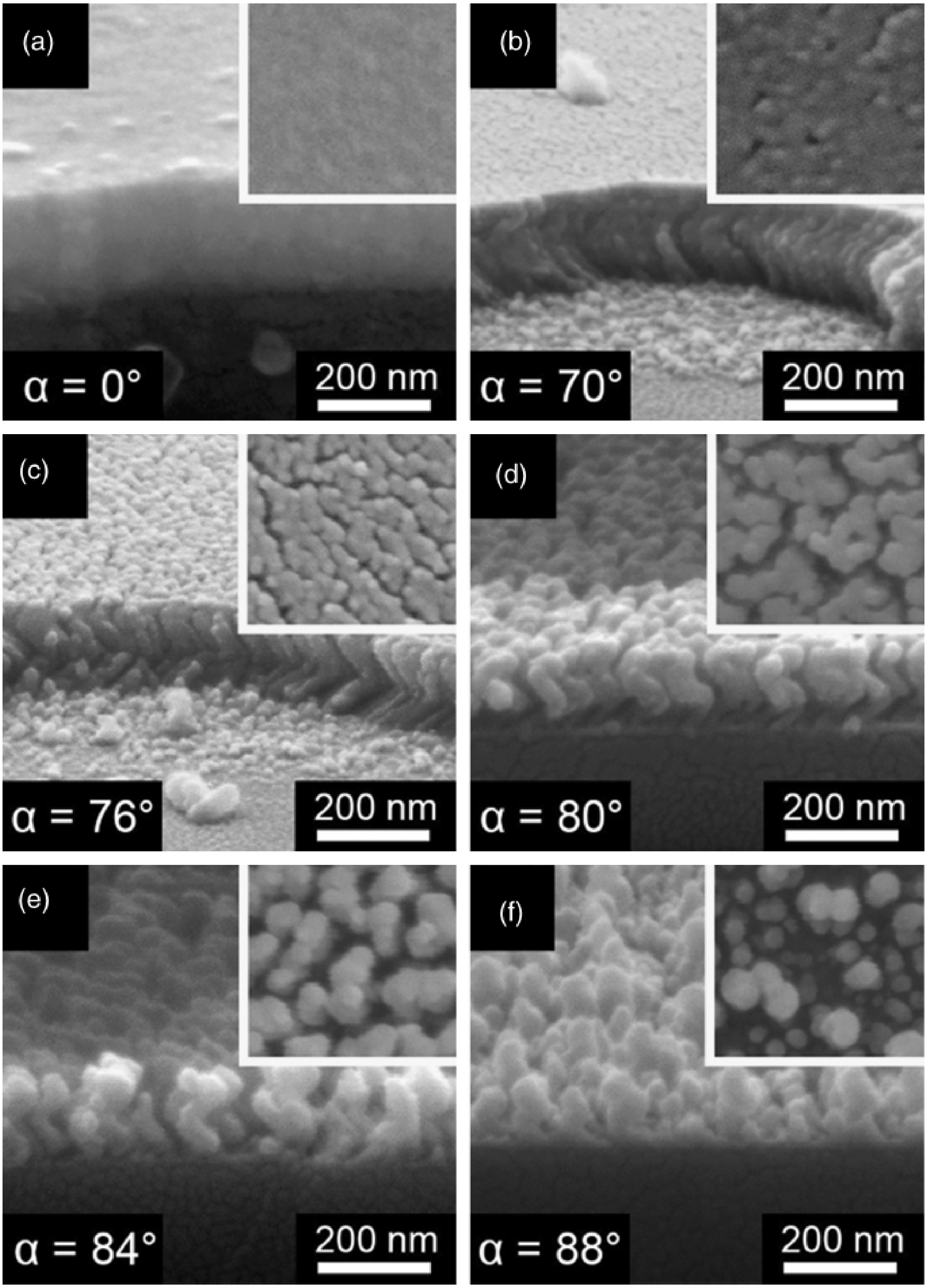

Fig. 1. Side-view scanning electron microscope (SEM) micrographs of HfO_2 films deposited on silicon substrates at various oblique angles. Insets of the figures show top view SEM micrographs.

The α–n curve indicates that the GLAD technique is a powerful means to adjust the porosity and refractive index of thin films.

The α–n curve indicates that nanostructure engineering the thin films can broaden the application of a material as AR coatings. In case of HfO_2, as its refractive index can now be tuned from 1.94 to 1.16, it might be used as AR coatings on substrates with a refractive index in a wide range of 3.76–1.35. In addition, the α–n curve offers a useful tool to prepare HfO_2 AR coatings on different substrates, i.e., simply selecting an oblique angle. Take SiC as an example; its refractive index is 2.4. Using HfO_2 as the AR coating, the refractive index of the HfO_2 film should be ~1.55, where an angle of 74° is suggested by the α–n curve. If preparing HfO_2 AR coatings on Al_2O_3, whose refractive index is 1.8, the ideal refractive index of the coating is 1.34, corresponding to an angle of 78°. For comparison, another two films with the same thickness were also deposited on the substrates at angles of 0° and 84°, corresponding to a refractive index of 1.94 and 1.19, respectively.

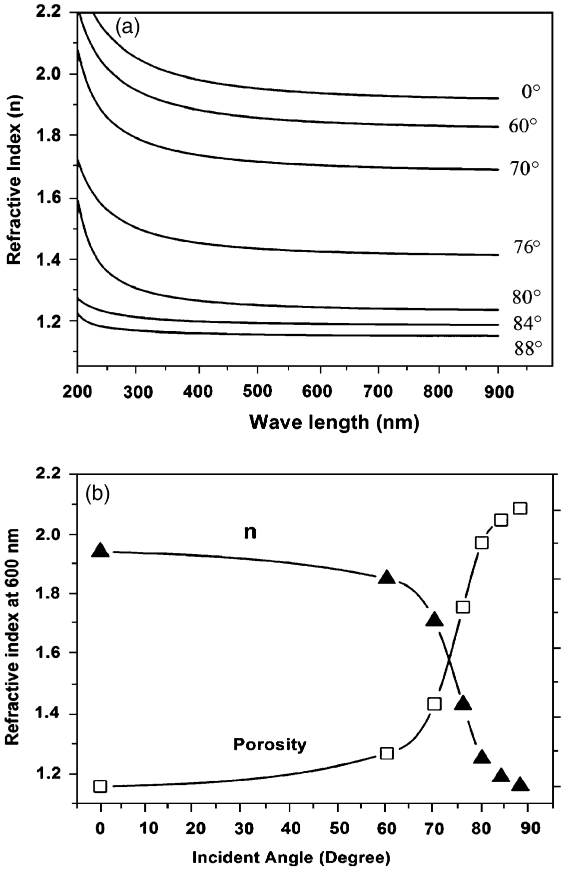

Fig. 2. (a) The refractive index spectra of the above HfO_2 films in the wavelength range of 200–900 nm; and (b) the refractive index at a wavelength of 600 nm and the calculated porosity of the films, as a function of the oblique angle.

Figure 3(a) shows SEM images of HfO_2 coatings deposited at three angles on a 750-nm-thick SiC film (magnetron sputtered on BK7 glass substrates). One can see that the SiC film is dense, flat, and continuous, and that the morphology of HfO_2 coatings ($\sim$160 nm thick) is similar to that shown by Fig. 1. The transmittance was measured by a UNICAM UV500 spectrometer in the range of 400–850 nm and is shown in Fig. 3(b). The incident angle of the light was parallel to the surface normal of the samples. Using the sample without coating as a reference, the relative transmittance of all samples was plotted in Fig. 3(c). One can see that among the three HfO_2 coatings, the one deposited at 74° showed the best performance, i.e. it enhanced the transmittance up to 20%, in agreement with the prediction by the α–n curve. To further confirm this, the reflectivity of all samples is measured by a U-3400 spectrometer and is shown in Fig. 3(d). The incident angle of the light was 45° off the surface normal of the samples. It can be seen once again that the HfO_2 coating deposited at 74° is the best one. It cut more than half the reflectivity in comparison with that of the reference.

When coated on Al_2O_3 substrates, the HfO_2 films behaved similarly. Figures 4(a) and (b) show the relative transmittance and reflectivity of the samples not coated and coated by HfO_2 films deposited at an oblique angle of 0°, 78°, and 84°, respectively. Here, the bare Al_2O_3 substrate was used as a reference. Clearly, one can see that the coating deposited at an oblique angle of 78° (i.e., $n = 1.34$) shows the best performance. In the wavelength range measured, it enhanced the transmittance by $>$10% and cut the reflectivity by more than 50%. This indicates that the GLAD technique is really a powerful means to prepare AR coatings.

In summary, we demonstrated a way to broaden the application of a material as an AR coating and optimize its performance by nanostructure engineering films by GLAD to tune its refractive index, and constructed the α–n curve for the preparation of HfO_2 AR coatings on different substrates with a wide refractive index range from 1.35 to 3.76.

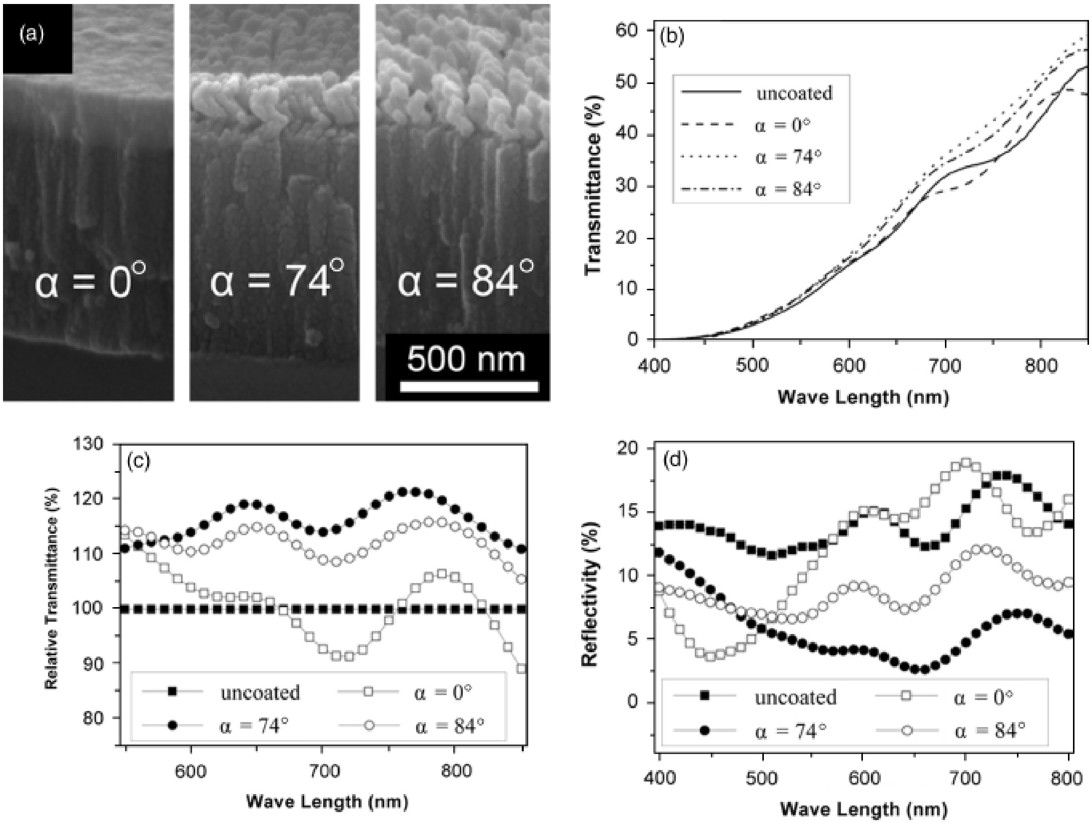

Fig. 3. (a) A typical side-view scanning electron microscope image of SiC films on BK7 glass substrates and coated by HfO_2 thin films deposited at angles of 0°, 74°, and 84°, respectively; (b) the transmittance spectra of the four samples; (c) the transmittance spectra of the samples relative to the SiC sample; and (d) the reflectivity spectra of the four samples.

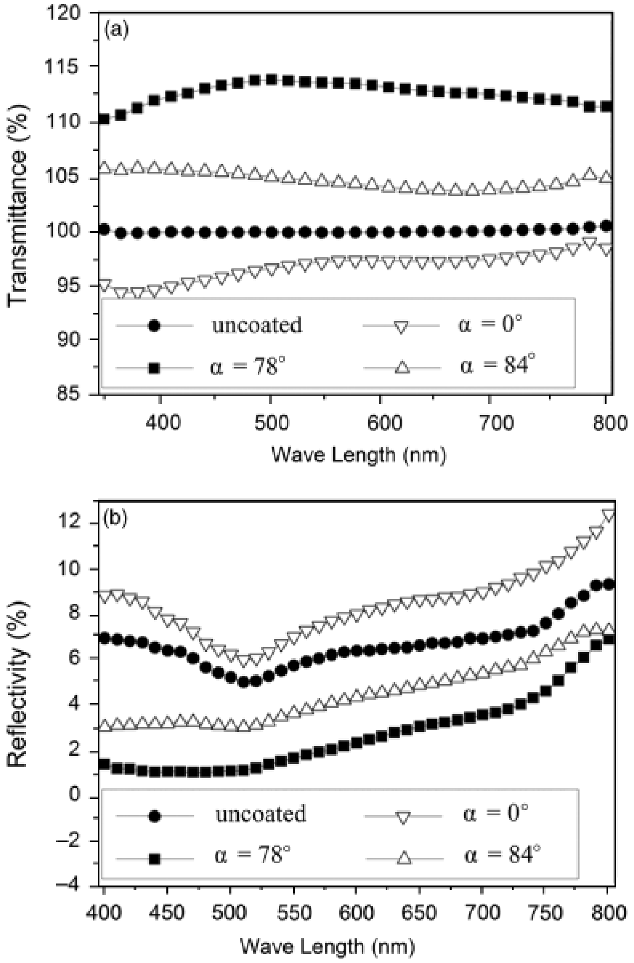

Fig. 4. (a) The enhancement of light transmittance by coating the Al_2O_3 substrate with HfO_2 films deposited at angles of 0°, 78°, and 84°, respectively; and (b) the light reflectivity of the samples uncoated and coated with HfO_2 films.

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