Magnetron sputtered oxidation resistant and antireflection protective coatings for freestanding diamond film IR windows


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A R T I C L E   I N F O
Available online 9 September 2008

Keywords:
Protective coatings
Optical quality diamond films
Oxidation resistance
IR transmission enhancement

A B S T R A C T

It is well known that the CVD diamond films start to oxidize at temperatures above 700 °C, which may restrict their use in high temperature oxidation environment, such as for IR windows and cutting tools. Due to its high refractive index, the maximum transmission of diamond film is limited to approximately 71%. In the present investigation, HfO2 and Y2O3 coatings were prepared by reactive magnetron sputtering of pure Hf and Y metal target in Ar+O2 atmosphere. Adherent HfO2 and Y2O3 coatings on high optical quality diamond film samples with optimum thickness for IR transmission enhancement in 8–12 μm and 3–5 μm were obtained. More than 20% increase in transmission was observed for both HfO2/Diamond/HfO2 and Y2O3/Diamond/Y2O3 coating systems. Excellent oxidation resistance for HfO2/Diamond/HfO2 and Y2O3/Diamond/Y2O3 coatings were demonstrated at temperatures up to 950 °C in oxidation environment.

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1. Introduction

Diamond is an ultra-durable optical material with perfect mechanical property, high thermal conductivity and good transmission in near-infrared and far-infrared wavebands except intrinsic absorption peaks in 3–5 μm. Recent progress in CVD diamond technology has resulted in the commercial availability of large area (≥200 cm²) components with the required optical and mechanical properties for application. But the transmittance of diamond is only 71% in theory as the refractive index of diamond is 2.38 and it is well known that the oxidation rate of diamond films becomes appreciable higher than 600 °C [1], which may restrict their use for IR windows in high temperature oxidation environment. Therefore it is desirable to find a suitable protective coating for diamond films which may provide better oxidation resistance and at the same time to increase the transparency by reducing the reflectivity. Transition metal oxides may be the desirable candidate for oxidation resistant and antireflection protective coatings [2].

Hafnium oxide and yttrium oxide are ideal materials as protective coatings of diamond for improving the antireflection and oxidation resistant properties. Hafnium dioxide (HfO2) presents a wide transparent range from the IR to the ultraviolet [3,4], a relatively high refractive index 1.88 and wide band gap [5] and theoretically can increase the transmission of diamond to 93.2% by applying a quarter wavelength coatings. Yttrium oxide presents a lower refractive index 1.80 and can increase the transmission of diamond to 95.5%. Furthermore, HfO2 and Y2O3 can be used as protective coatings because of its thermal stability [6,7]. Yttrium oxide single layer film by reactive ion beam sputtering was shown by Klemm et al. to be a potential protective anti-reflective and oxidation resistant coating for CVD diamond film. Nevertheless the diamond film substrate used was deposited by MWCVD on single crystal silicon wafer with a thickness of only 6 μm [8].

In this paper HfO2 and Y2O3 thin films were deposited on high optical quality freestanding CVD diamond substrates (about 0.6 mm thickness) by direct current reactive magnetron sputtering. The composition, surface morphology, structure and optical property of the HfO2 or Y2O3 coated diamond films are investigated by XPS, AFM, XRD and FTIR. The oxidation behavior and the effect on the IR transmission of the HfO2 or Y2O3 thin film coated diamond films are compared with the as-growth diamond films and as-prepared HfO2 or Y2O3 thin film coated diamond films.

2. Experimental

The HfO2 and Y2O3 thin films were prepared by a DC sputtering system (Beijing Technol. Co., Ltd.) with a cylindrical chamber connected to a turbo molecular pump. Hf (99.99% purity) and Y (99.99% purity) plate with a diameter of 50 mm was used as the target. The discharge mode of the dc sputtering system was power-constant mode and the dc power was 400 W for the experiment. The chamber was initially evacuated to 5 × 10⁻⁴ Pa, and high-purity Ar (99.999%) and O₂ (99.999%) were introduced during deposition. The working pressure was 0.6 Pa. Prior to HfO2 or Y2O3 thin films deposition, the target was pre-sputtered in an argon atmosphere for 5 min in order to remove the surface oxide on the target. The substrate temperature was controlled at room temperature during the sputtering. The target
substrate distance was kept at 80 mm. HfO₂ films were deposited in O₂ + Ar ambient and the flow rate of oxygen and argon was 0.7 sccm and 8.0 sccm during the sputtering. Y₂O₃ films were deposited when the flow rate of oxygen and argon was 1.2 sccm and 7.8 sccm during the sputtering.

Si substrates were used to investigate the effect of experimental parameters on the properties of HfO₂ and Y₂O₃ thin films. The optimized parameters were directly applied to deposit HfO₂ and Y₂O₃ on the diamond substrate. The diamond substrates in the experiment were CVD freestanding polycrystalline diamond films prepared by dc arc jet plasma method. The thickness of the diamond films was...
approximately 0.6 mm. The surface had been polished mechanically and the polished surface roughness (Ra=5 nm) was measured by profilometer (TR200, Time Group INC, China).

The composition of the HfO2 and Y2O3 thin films was determined by the X-ray photoelectron spectroscopy (XPS) (VG, ESCALAB). The surface morphology was observed by atomic force microscopy (AFM) (AJ-IIIa). Crystal structures of the films were characterized by grazing incidence X-ray diffractometry (GI-XRD) (Japan, Rigaku D/max-2500) using Cu Kα radiation at 40 kV and 300 mA, and the X-ray incidence angle was 2°. The infrared analysis was performed using Fourier transformed infrared spectroscopy (FTIR) (FT-IR System Spectrum GX-2000, Perkin Elmer). All transmission spectra were recorded at 4 cm⁻¹ resolution.

3. Results and discussions

3.1. Preparation of the HfO2 thin films

Fig. 1 shows a typical XPS spectrum of the Hf4f and O1s for the as-grown HfO2 films, respectively, which is calibrated from the C1s peak at 284.5 eV. The peak at 16.2 eV and 17.7 eV are corresponding to Hf4f7/2 and Hf4f5/2, which are related to Hf–O bonding in the HfO2 films. The origins of the binding energy shift (ΔBE) are suggested as a number of factors, such as the charge transfer effect, the presence of electric fields, the environmental charge density, and the hybridization. Among these, charge transfer is regarded as a dominant mechanism to cause binding energy shift. According to the charge transfer mechanism, removing an electron from the valence orbital generates an increase in the core electron’s potential and finally leads a chemical binding energy shift [9]. Therefore, it is considered that the Hf4f5/2 and Hf4f7/2 peaks shift in Fig. 1(a) originated from Hf bound to oxygen; indicating that a certain portion of Hf atoms has been fully oxidized. The O1s core level peaks at 530.2 eV is also attributing to O in HfO2 in Fig. 1(b). Deduced from the results of XPS spectra of HfO2 films, the chemical composition of this sample is apparently close to the stoichiometry. The Hf atoms in this sample are almost oxidized due to its chemical reactivity.

Fig. 2 shows typical AFM image for HfO2 thin films with the thickness of 1 µm deposited on the Si substrate. From Fig. 2, it can be observed that the HfO2 film is uniform and compact. Obviously, AFM in Fig. 2 shows nanostructure characteristic in the crystal sizes of the coatings. The roughness of the sample is only 3 nm.

Fig. 3 shows the GI-XRD patterns of the HfO2 thin films prepared on the Si substrates before and after annealing at 900 °C in an oxidizing environment (laboratory air). It can be seen from Fig. 3 that...
the as-grown HfO₂ film is essentially in amorphous state with part of crystalline phase belonging to the monoclinic structure. No other crystalline phase, such as orthorhombic and tetragonal ones [10,11] has been detected. After annealing the HfO₂ films were fully crystal-lized as indicated by the sharp and well-de fined diffraction peaks shown in Fig. 3. A tendency of [−111] texture is evident.

3.2. Preparation of the Y₂O₃ thin films

Fig. 4 shows a typical XPS spectrum of the Y3d and O1s for the as-grown Y₂O₃ films, which is calibrated from C1s peak at 284.5 eV. The peak at 156.8 eV and 158.8 eV are corresponding to Y3d5/2 and Y3d3/2, which are related to Y–O bonding in the Y₂O₃ films. It is considered that the Y3d5/2 and Y3d3/2 peaks shift in Fig. 1(a) originated from Y bound to oxygen, a certain portion of Y atoms has been fully oxidized. The O1s core level peaks at 529.8 eV and 532.3 eV is attributing to O in Y₂O₃ and SiO₂ in Fig. 2(b), because the thickness of Y₂O₃ films on Si substrate is too thin (approximate 100 nm) and so the information of SiO₂ is detected by the XPS. Deduced from the results of XPS of Y₂O₃ films, the chemical composition of this sample is also close to the stoichiometry. The Y atoms in this sample are almost fully oxidized.

Fig. 5 shows typical AFM image for Y₂O₃ thin films with the thickness of 1 µm deposited on the Si substrate. From Fig. 5, it can be seen that the Y₂O₃ film is very uniform and compact. Obviously, AFM in Fig. 5 shows nanostructure characteristic in the crystal sizes of the coatings. The roughness of the sample is only 4 nm.

3.3. IR properties and oxidation resistance of the HfO₂ and the Y₂O₃ coated diamond films

HfO₂ and Y₂O₃ thin film coatings were deposited on high optical quality freestanding diamond films using the optimized deposition parameters and the estimated quarter wavelength thickness for maximum transmission enhancement. There were no major difference in the morphology and structure with that deposited on the Si substrate.

The transmission spectra of HfO₂/Diamond/HfO₂, Y₂O₃/Diamond/ Y₂O₃ coating system and the bare freestanding diamond film are presented in Fig. 7 in the long wave IR range. The IR transmittance of the freestanding diamond film sample was increased from 67% to 88% and 88.2% at the most after depositing HfO₂ thin films and Y₂O₃ thin films in the 8–12 µm long IR wavelength range. It can be seen from Fig. 7 that the antireflection wavelength range for the Y₂O₃ thin film expands to 12 µm, which is wider than the HfO₂ thin films.
Fig. 8 shows the transmission spectrum of the hafnium and yttrium coatings with the quarter wavelength thickness for the mid-wave IR range on the two sides of CVD diamond as compared with the spectrum of the uncoated diamond substrate. From Fig. 8, it can be seen that the average IR transmittance of the diamond film sample with HfO2 and Y2O3 thin films rise from 54% to 66.8% and 64.9% in the 3–5 µm mid-IR wavelength range. However, the maximum increase in transmission is located about 6 µm, indicating the thickness of either HfO2 or Y2O3 coatings may possibly deviate from the desirable quarter wavelength for ideal transmission enhancement in the 3–5 µm mid-IR wavelength range. Nevertheless, a 12–18% increase in IR transmission is good enough for reconsideration for the use of diamond films in the 3–5 µm mid-IR wavelength range. We think this of technical importance.

Fig. 9 shows the effect of high temperature oxidation on the IR transmission of the HfO2/Diamond/HfO2 coating system. It can be seen that the there is essentially no changes in the transmission in the 8–12 µm long wave IR range after 30 s exposure at 900 °C, whilst there is only a slight decrease of less than 8% in IR transmission after 30 s exposure at 950 °C. The HfO2 film still remained attached to the diamond film substrate after the high temperature exposure.

Fig. 10 shows the IR spectra of the Y2O3/Diamond/Y2O3 coating system. It can be seen that the IR transmission is increased after 30 s exposure at 900 °C, whilst there is only a little decrease in IR transmission of less 7% after 30 s exposure at 950 °C. There is no delamination after high temperature oxidation between the Y2O3 coating and the diamond substrate. The reason for the observed increase in IR transmission after 30 s exposure at 900 °C may be due to the complete crystallization of the Y2O3 film, which was not fully crystallized after the post deposition annealing as mentioned previously.

Our results have demonstrated that both the HfO2 and the Y2O3 films are excellent materials for high temperature oxidation protection, and at the same time, for transmission enhancement in the 8–12 µm and 3–5 µm IR range.

4. Conclusions

HfO2 and Y2O3 thin films with smooth surfaces were prepared on high optical quality freestanding diamond films using the reactive dc magnetron sputtering method. The IR transmittance of the freestanding diamond film sample was increased to 88% and 88.2% at the most after depositing HfO2 and Y2O3 films in the 8–12 µm long IR wavelength range; whilst the average IR transmittance of the diamond film sample rose from 54% to 66.8% and 64.9% in the 3–5 µm mid-IR wavelength range. High quality optical diamond films can be protected effectively from oxidation for 30 s exposure in air at temperatures up to 950 °C.

Acknowledgement

The authors wish to thank the NSFC (Natural Science Foundation of China) for financial support under the contract of 50572007.

References