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双离子束溅射中红外 SiO_2 薄膜热稳定性研究

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摘　要:通过双离子束溅射方法在蓝宝石、硅衬底上制备了单层 SiO_2 薄膜,分析了 SiO_2 薄膜残余应力、表面形貌、微观结构以及光学性能(可见-近红外 0.4～1.2 μm 和中红外 3～5 μm 波段)在 400 ℃～1 000 ℃温度范围内的演化规律.研究结果表明:在 400 ℃附近,SiO_2 薄膜残余应力存在局部极小值;SiO_2 薄膜光学性能的演化与膜层表面质量、内部残余应力及微观结构变化密切相关;经 1 000 ℃高温处理后,蓝宝石窗口表面 SiO_2 薄膜红外透射性能仍能保持很好的稳定性,且膜层表面没有出现显著的气泡、开裂等损伤形貌.该研究结果可为恶劣环境下光学窗口头罩表面薄膜系统的设计提供指导.

关键词:薄膜;红外窗口;离子溅射;热稳定性
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Thermal Stability of Mid-infrared SiO_2 Thin Films Deposited by Dual Ion Beam Sputtering Method

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Abstract: SiO_2 films are deposited on Si and sapphire (α-Al_2O_3) substrates by Dual Ion beam sputtering method. The microstructure, surface morphology, residual stress and optical stability of SiO_2 coating in the wavelength of 0.4～1.2 μm and 3～5 μm are investigated, systematically. The results indicate that the residual stress goes through a local minimum value at ～400 ℃. There is a close relationship between the optical constant and the surface conditions, residual stress, microstructure of SiO_2 film. As the temperature increases up to 1 000 ℃, SiO_2 film can keep well thermal stability without notable damage morphology. The result can give some guidance for designing the optical coatings used in harsh environments.

Key words: Thin film; Infrared window; Ion beam sputtering; Thermal stability
OCIS Codes: 160.4670; 310.6860; 310.6870; 240.0310; 260.3060

0 Introduction

Single-crystal aluminum oxide (Sapphire) is current the material of choice for infrared windows that must

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survive the harsh environment. It possesses excellent thermal stability, extraordinary mechanical property, low scattering, and superior high-temperature infrared property[1-3]. For those reasons, sapphire has been widely used as lens, optical window in real applications. For optical and mechanical characteristics, however, it has relatively high surface reflectivity and the thermal shock resistance is limited by the loss of mechanical strength at high temperatures[4]. To improve the properties of sapphire, some literatures revealed that AR coating (such as amorphous SiO_2 layer) can be used to enhance the window transmittance by reducing reflection and increase the crystal strength arising from the pre-compression[5].

Currently, SiO_2 film can be deposited by many techniques such as Chemical Vapor Deposition (CVD), RF magnetron sputtering, ion beam assisted deposition (IAD) and sol-gel method[5-15]. In recent years these methods have developed rapidly[16-19]. For example, Linda F. Johnson pointed that SiO_2 and SiO_2/Si_3N_4 thin films can improved the strength and infrared transmittance of sapphire substrate at high temperature[20]; FENG Li-ping[21-22] prepared the SiO_2 thin film on sapphire substrate by RF magnetron reactive sputtering method. The deposition rate, composition, structure and optical properties of films had been investigated. Wang Ying-jian[23] prepared SiO_2 thin films on sapphire substrates by evaporation coating method; Li Yun-gang[24] and Wu Zhi-xiong[25] designed and prepared the SiO_2/Y_2O_3 films on sapphire by RF- reactive magnetron sputtering. The high temperature transmittance of both coated and uncoated sapphire was measured. However, there are few reports about the preparation of SiO_2 thin films on sapphire substrate by Double Ion Beam Sputtering method. In addition, because of the development of optical coatings which are deployed in more extreme environment, even minor degradation of the coating structure can impact the stability of optical properties and limit the life of the optical system[7]. It is very meaningful to investigate the thermal stability of SiO_2 film after heat treatment. In this experiment, we deposited single-layer SiO_2 film on sapphire and Si substrates using Veeco Ion Tech SPECTOR system. And the influences of thermal exposure on film composition, microstructure, surface morphology, optical constant, root mean square values of surface roughness and residual stress are also characterized systematically.

1 Experimental

In this paper, the samples were deposited on silicon and sapphire substrates ($\phi 50 \times 5$ mm) using Veeco Ion Tech SPECTOR system, which has two ion sources, one is a 16 cm ion source for sputtering and the other is a 12 cm ion source for assistance. The sputtering chamber was evacuated to a base pressure of 4.0×10^{-4} Pa before deposition. The targets was SiO_2 (>99.99% purity). High purity argon (99.999%) and oxygen (99.999%) were introduced to RF ion beam source and target surface in the deposition process. The discharge voltage was 1 250 V with a 0.6 A current. The deposition rate of SiO_2 film was ~0.35 nm/s. All the substrates used in our experiments came from the same batch. Before the substrates were placed in the chamber, they were subjected to a series of chemical cleaning. The SiO_2 film thickness on silicon and sapphire substrates are ~500 nm and ~632.8 nm, respectively. Additionally, Fig. 1 presents the flow chart of thermal treatment. Concretely, it was performed by heating the specimens of silicon substrates to the desired temperatures (200 ℃, 400 ℃, 600 ℃, 800 ℃ and 1 000 ℃) using a furnace with air environment and the increasing rate was about 7 ℃/min. The composition, the surface morphology, the RMS roughness, the optical constants and the crystalline structure of SiO_2 single layer were investigated by X-ray Photoelectron Spectroscopy (XPS), Scanning Electron Microscope (SEM), Atomic Force Microscopy (AFM), Spectroscopic Ellipsometry (SE) and X-Ray Diffraction (XRD), respectively[26]. In the experiment, root mean square surface roughness (RMS) was evaluated at Engineering Research Center in biomaterials,

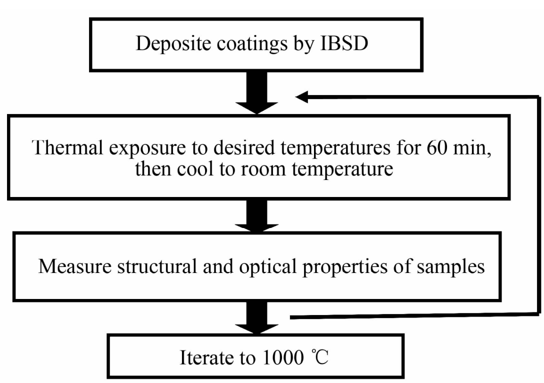

Fig. 1 Flow chart of experimental procedure

Sichuan University. The Atomic Force Microscopy (AFM) is made by OLYMPUSOPTICAL CO., LTD. The Instrument type is BX60. The interfacial morphology of the film was observed by HITACHI/S-4800 Scanning Electron Microscope (SEM). The accelerating voltage is 0.5～30 kV. The XPS patterns were recorded using $MgK\alpha$ radiation at 12 kV and 10 mA. Combining the XPS peak area together with their relative sensitivity factors, the ratio could be estimated. The crystalline structure was characterized by XRD measurement with $CuK\alpha$ as the incident radiation in the θ-2θ mode. The total residual stress, σ_f, was deduced from the Stoney's formula[27]. In addition, the transmittance of sapphire sample was also studied after 27 ℃ (room temperature), 500 ℃ and 1 000 ℃ heat treatment using a Fourier transform infrared (FTIR) spectrometer.

2 Result and discussion

2.1 Structure characterization

The X-ray Photoelectron Spectroscopy (XPS) is used to determine the composition of film and the typical XPS spectrums of (a) Si2p and (b) O1s for the as-deposited film are presented in Fig. 2. The peaks at 103.7 eV and 532.65 eV correspond to Si2p and O1s, respectively, which are related to Si-O bonding in the SiO_2 film. Deduced from the results of XPS spectra, the surface O/Si ratio for the as-deposited SiO_x film is 2.1∶1. The result indicates that the chemical composition of the as-deposited SiO_2 film is close to the standard stoichiometry ratio. Fig. 3 shows the XRD patterns of SiO_2 thin film measured at different temperature. It can be seen that in the as-deposited SiO_2 film has an amorphous structure. As the temperature increases, there is a typical halo pattern of SiO_2 glass around 22°[28-29].

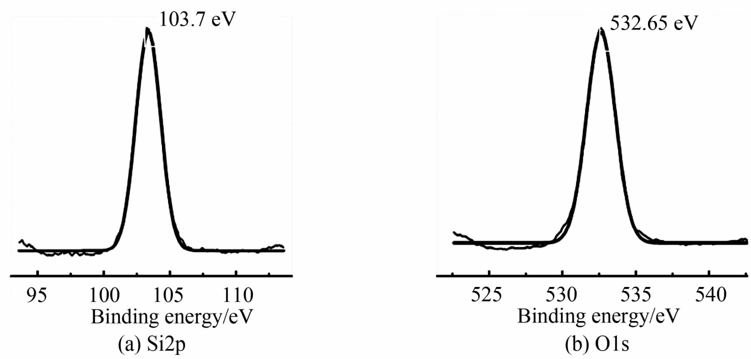

Fig. 2 XPS spectra of SiO_2 coating

2.2 RMS and surface morphology characterization

For the single layer SiO_2 film, the RMS roughness at different temperatures are also investigated by AFM. From Fig. 4, it can be seen that the surface roughness are about 0.135 nm, 0.1531 nm, 0.153 5 nm and 0.157 3 nm at the temperatures of 27 ℃ (as-deposited), 400 ℃, 800 ℃ and 1 000 ℃, respectively. The RMS increases firstly and then remains almost a constant of ～0.153 nm between 400 ℃ and 600 ℃. There is neither visible crack nor blisters for single layer SiO_2 film at 1 000 ℃ (as shown in Fig. 5). SiO_2 coating shows significantly higher temperature stability. The thermal robustness of SiO_2 coating is closely related to the amorphous structure, the internal stress and mechanical property.

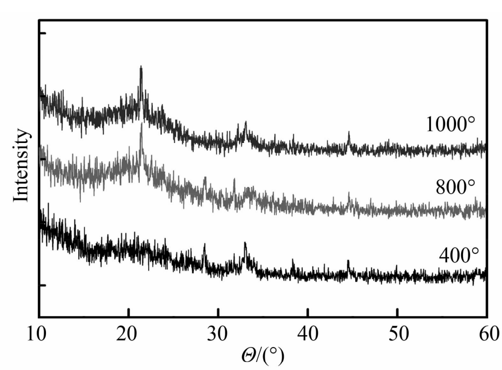

Fig. 3 The X-ray diffraction of SiO_2 thin film after different thermal treatment

2.3 Residual stress characterization

Fig. 6 presents the variation of residual stress in the single layerSiO_2 film on Si substrate before and after heat treatment. As shown in Fig. 6, the as-deposited SiO_2 film has a compress stress in the range of 376 MPa which illustrates that SiO_2 films deposited by DIBS is compact and have relatively higher packing

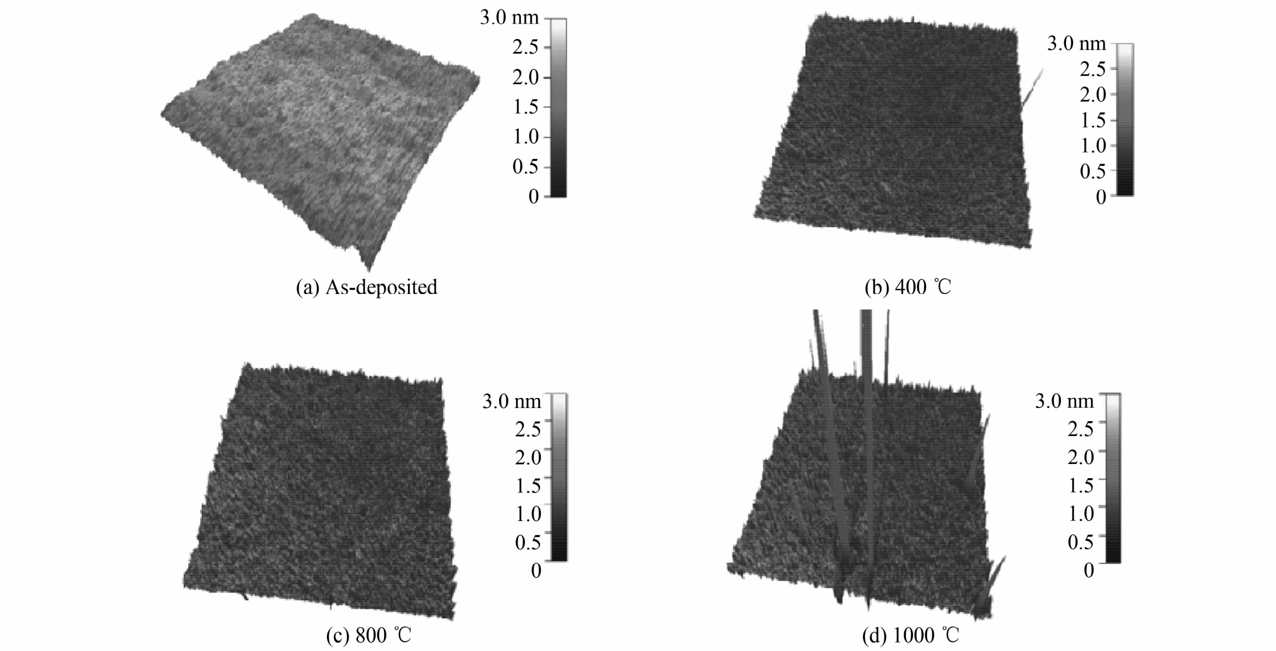

Fig. 4 AFM pictures of SiO_2 thin film after different thermal treatment

density. Such structure is benefit to improve the thermal stability, reduce the absorption and enhance the optical constants of film. As the temperature increases from 27 ℃ to 400 ℃, the compressive stress releases and decreases gradually. The regular change of the stress is due to the increase of atomic activity in the annealing process. With the increase of atomic motion, the high internal stress generated by the defects and structural mismatch in the film is released. Especially, when the temperature increases up to thetemperatures of 600～800 ℃, the compressive stress occurs again due to the crystallite grain growing up, grain boundary area decreasing, oxidation and water absorbed in pits driven away[30-31].

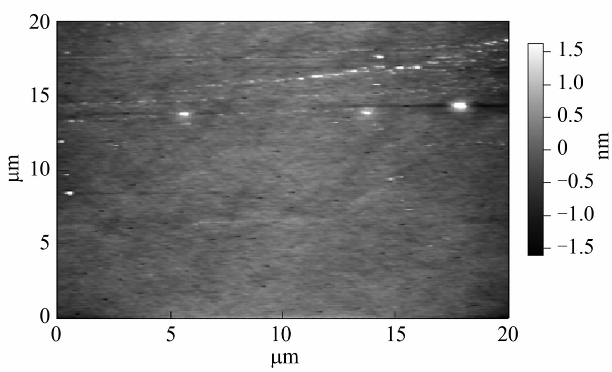

Fig. 5 The surface topography of single-layer SiO_2 thin film at 1 000 ℃

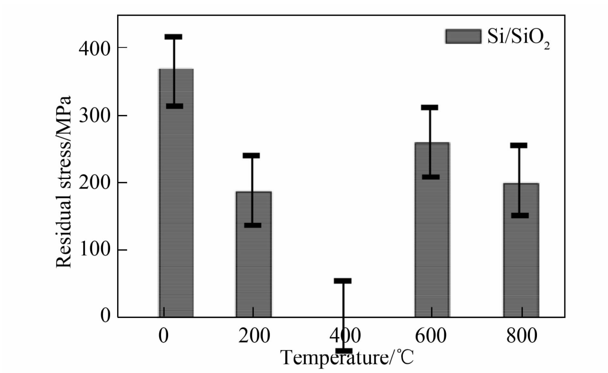

Fig. 6 Variation of the residual stressfor single-layer SiO_2 films after different thermal treatment

2.4 Optical characterization

In this study, the optical constants of SiO_2 thin film in the range of visible light are obtained via Spectroscopic Ellipsometry (SE). Fig. 7 present the dispersion curves of the refractive index, n and extinction coefficient, k for SiO_2 film at different temperatures. In the calculation, once the extinction coefficient, k is lower than 1.0×10^{-3} in the measured wavelength range, the film is regarded as non-absorbing material and the impact on the transmission is neglected.

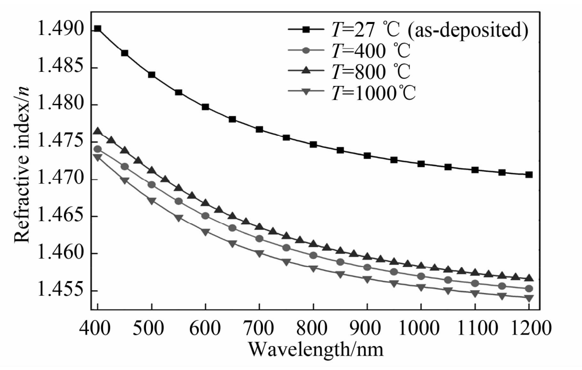

Fig. 7 Dispersion curves of the refractive index, n for SiO_2 films after different thermal treatment

Based on the measured results, it can be believed that there is a close relationship between the optical constant and the surface condition, residual stress, micro-structure for SiO_2 films. Concretely, the refractive index, n of the as-deposited SiO_2 film is about 1.48 at the wavelength of 550 nm. It decreases significantly after 60 min thermal exposure to the high temperature. The largest change of refractive index for SiO_2 amounts to more than 1%. For the SiO_2 film, the sharp changes of n are obviously correlated with the changing of residual stress and structure in film and they are in turn strongly affected by the special treatment temperature. As indicated in Fig. 3, the SiO_2 film maintains amorphous structure during the thermal treatment. The compressive stress is ~370 MPa for the as-deposited SiO_2 film (see in Fig. 6). When the temperature increases up to 400 ℃, the internal stress is released leading to the decrease of packing density. So the refractive index (n) of SiO_2 thin films decreases. Additionally, the increasing of compressive stress can be observed at ~800 ℃. Such compression stress can lead to contraction of Si substrate parallel to the plane of film and make the structure compact.

Fig. 8 presents spectral transmittance (2~5 μm) of sapphire substrate and the substrate coated with SiO_2 films after thermal treatment. The exposure time for the sample was 60 min. From Fig. 8(a), it can be seen that the uncoated substrate has an average transmittance of ~86.2% over 3~4.5 μm. The average transmittance of the sample was still about 86.2% with increasing temperatures. Fig. 8(b) presents the optical transmittance of the coated sample. As seen clearly, sapphire coated with SiO_2 film has a higher transmittance than uncoated sample before and after annealing. The sapphire coated with SiO_2 film on one side has an average transmittance of ~88.2% in the wavelength of 3~4.5 μm at room temperature. A broad absorption peak is seen at 3 000~3 800 cm^{-1} in the FTIR spectra, which is assigned to the stretching modes of O-H bands and related to free water (capillary pore water and surface absorbed water). Fig. 8(b) presents that the average transmittance of sapphire coated with SiO_2 film on one side has been improved from 88.2% to ~90.6% in 3~4.5 μm with increasing temperatures. The average transmittance of the coated sapphire after 600 ℃ and 1 000 ℃ was 90.6% and 90.8%, respectively. The little change in transmission of coated sapphire makes it possible to be operated accurately in such a service environment.

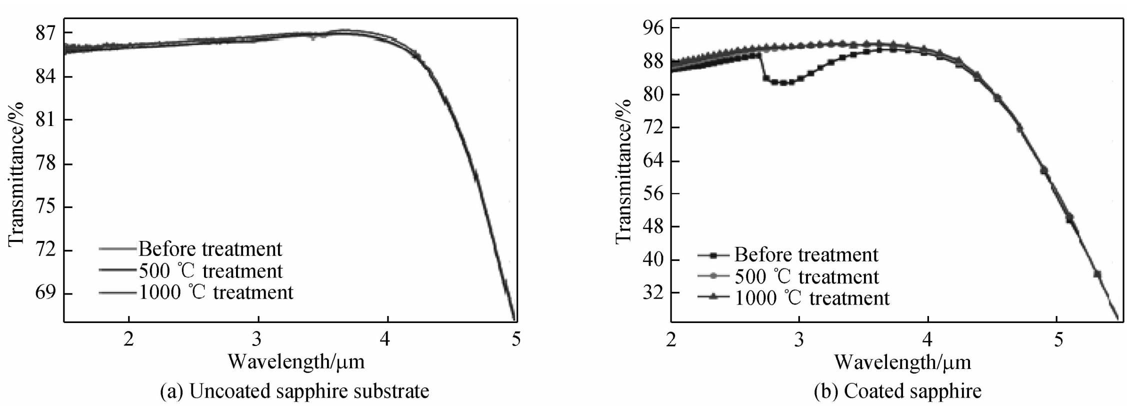

Fig. 8 Spectral transmittance of sapphire uncoated and the sapphire coated with SiO_2 films before and after thermal treatment

3 Conclusion

In this study, SiO_2 films with amorphous structural have been obtained by double ion beam sputtering method. The chemical composition of the as-deposited SiO_2 film is close to the standard stoichiometry ratio and it exhibits compressive stress (~376 MPa). With the temperature increases, the residual stress goes through a local minimum value at about 400 ℃ and then increases monotonically while the RMS increases firstly and remains almost constant between 400 ℃ and 600 ℃. The average transmittance of sapphire coated with SiO_2 film on one side has been improved from 88.2% to ~90.6% in 3~4.5 μm with increasing temperatures and there are neither visible cracks nor blisters for the film. Therefore, the SiO_2 film deposited by double ion beam sputtering exhibits excellent optical and thermal stability at high temperatures of 800 ℃ and 1 000 ℃.

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