Effects of aging treatment on properties of SiO_2 thin films with different deposition technology

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Abstract: SiO_2 thin films is one of the most important low refractive index materials in the field of optical thin film. SiO_2 thin films were deposited on Si substrates by different deposition technique. The optical stability of SiO_2 thin films were investigated as a function of time placed in the air. Optical constants of SiO_2 thin films were calculated using the ellipsometry spectra at different aging times. With the increase of the placed time, the physical thickness and optical thickness of EB–SiO_2 thin films and IAD–SiO_2 thin films increase, but IBS–SiO_2 thin film decreases. The change of optical thickness of SiO_2 thin films are separately 1.0%, 2.3% and –0.2%. When the placed time reaches 120 days, the physical thickness and optical thickness of IBS–SiO_2 thin films, EB–SiO_2 thin films, and IAD–SiO_2 thin films tend to be stable. The results indicate that the optical stability of IBS–SiO_2 thin film is better than other SiO_2 thin films, and in the design of protective coating, SiO_2 thin films should be deposited with ion beam sputtering technique.

Key words: IBS–SiO_2 thin film; EB–SiO_2 thin film; IAD–SiO_2 thin film; optical stability; optical constants

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不同沉积方式 SiO_2 薄膜的自然时效特性

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摘　要: SiO_2 薄膜是光学薄膜领域内常用的重要低折射率材料之一。文中采用不同沉积技术在 Si 基底上制备了 SiO_2 薄膜,并研究了它们光学特性的自然时效特性。采用不同贮存时间的椭偏光谱表征 SiO_2 薄膜的光学特性, 随着时间的增加,EB–SiO_2 薄膜和 IAD–SiO_2 薄膜的物理厚度和光学厚度随着

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增加，但 IBS-SiO_2 薄膜随着减小，变化率分别为 1.0%，2.3%和-0.2%。当贮存时间达到 120 天时，IBS-SiO_2 薄膜、EB-SiO_2 薄膜和 IAD-SiO_2 薄膜的物理厚度和光学厚度趋于稳定。实验结果表明，IBS-SiO_2 薄膜的光学特性稳定性最好，在最外层保护薄膜选择中，应尽可能选择离子束溅射技术沉积 SiO_2 薄膜。

关键词： IBS-SiO_2 薄膜； EB-SiO_2 薄膜； IAD-SiO_2 薄膜； 光学稳定性； 光学常数

0 Introduction

SiO_2 is a low-index and low absorption material, which can operate in the UV to near IR regions combined with high-index oxide layer coatings. In the typical applications of SiO_2 including high-reflection coatings, antireflection coatings, all-dielectric mirrors, beam-dividers, band-pass filters, and polarizers [1-4], optical properties of SiO_2 thin films, such as refractive index, physical thickness and optical thickness are important. Several deposition methods have been tried to prepare SiO_2 thin films including ion beam sputtering (IBS)[5], ion beam assisted deposition (IAD) [6], electron beam evaporation (EB) [7], molecular beam epitaxy (MBE)[8], R.F. Magnetron Sputtering[9], plasma enhanced chemical vapor deposition (PECVD)[10], and reactive pulsed laser deposition (RPLD)[11].

The aging effect of SiO_2 thin films can be a serious problem, especially in protective coating, high-reflection coatings or anti-reflection coatings of high precision laser gyroscope system and gravitational waves detection system[12-15]. The change of physical thickness or refractive index directly impact optical properties of SiO_2 thin films and then affects the system work. So, in the practical application, it should minimize the change of the refractive index and physical thickness of SiO_2 thin films after deposition, and a dense film is also needed. At present, the IBS, EB, and IAD methods are the main deposition technique for film preparation.

In this paper, SiO_2 thin films were deposited on Si substrates by three different deposition technologies. SiO_2 thin films were placed in the thousand-grade purification room. The effects of aging on refractive index, physical thickness, and optical thickness of SiO_2 thin films were investigated.

1 Experiment

Silicon was chosen as the materials of substrates and its size is 41 mm in diameter and 0.3 mm in thickness. SiO_2 thin films were deposited on the silicon substrate by IBS, EB, and IAD technology, and the corresponding samples were defined as IBS-SiO_2 thin films, EB-SiO_2 thin films, and IAD-SiO_2 thin films. The physical thickness of IBS-SiO_2 thin films, EB-SiO_2 thin films, IAD-SiO_2 thin films are about 900 nm, 1 000 nm and 1 000 nm. SiO_2 target with the purity of more than 99.995% was used as IBS-SiO_2 thin films forming materials. Fused silica with the purity of more than 99.99% were used as EB-SiO_2 and IAD-SiO_2 thin films forming materials. When IBS deposition technology was used, the substrate temperature was chosen at room temperature. When EB and IAD deposition technology were used, the substrate temperature was chosen at 200 ℃.

After being coated, IBS-SiO_2 thin films, EB-SiO_2 thin films, and IAD-SiO_2 thin films were placed in the thousand-grade purification room and spectroscopic ellipsometry were measured at different aging times.

Spectroscopic ellipsometry is in general more accurate in determining optical constant because of the sensitivity of the phase difference for small varieties in the optical thickness. In order to study optical stability of SiO_2 thin films with three deposition technique, we have measured the ellipsometry spectra of these samples at different aging times. Spectroscopic ellipsometry measurements were made with a two-channel spectroscopic polarization modulation ellipsometer in the spectral range from 300 nm to 1 000 nm with an interval of 5 nm at an angle of incidence 65° by J. A. Woollam spectroscopic ellipsometry. The complex refractive index of SiO_2 thin films were calculated by using Cauchy model.

2 Results and discussion

2.1 Cauchy model

Over part of the spectra for many materials (dielectrics and semiconductors, not metals), the refractive index n can be represented by a slowly varying function of wavelength. The Cauchy formula is as follows[16]:

$$n=A_n+\frac{B_n}{\lambda^2}+\frac{C_n}{\lambda^4} \tag{1}$$

In the Cauchy formula, the A_n term describes the long-wavelength asymptotic index value, while B_n and C_n are the dispersion terms that add upward slope to the index curve as wavelengths become shorter (B_n and $C_n \geqslant 0$). The Cauchy formula can describe dispersion for a material that is essentially non-absorbing over the measured wavelength range. The parameters A_n, B_n, C_n and the thickness d of the film were considered as fitting parameters in the calculation of Ψ and Δ values. This procedure allows both thickness and refractive index to be determined simultaneously.

It is important to define some quantity (called a maximum likelihood estimator) which represents the quality of the match between the data calculated from the model and the experimental data. The maximum likelihood estimator must be positive and should go to zero (or at least an absolute minimum) when the calculated data matches the experimental data exactly. The mean-squared error (MSE) is as follows[16]:

$$MSE=\sqrt{\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\Psi_i^{\mathrm{mod}}-\Psi_i^{\mathrm{exp}}}{\sigma_{\Psi,i}^{\mathrm{exp}}}\right)^2+\left(\frac{\Delta_i^{\mathrm{mod}}-\Delta_i^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}}\right)^2\right]}=\sqrt{\frac{1}{2N-M}\chi^2} \tag{2}$$

Where N is the number of (Ψ, Δ) pairs, M is the number of variable parameters in the model, and σ is the standard deviations on the experimental data points. Another common maximum likelihood estimator, the chi-square (χ^2) is defined in above equation for comparison.

2.2 Measured data

In order to analyze the Ψ and Δ experimental data, a model consisting of a Si substrate, the effective medium approximation (EMA) with 50% Si and 50% film bulk, the Cauchy layer, and a top surface roughness layer with 50% voids and 50% film bulk were employed. The refractive index and the thickness of SiO_2 thin films were simultaneously determined from analysis of the ellipsometric parameters psi and delta data using a Cauchy dispersion law.

The measured psi and delta data of IBS-SiO_2 thin films, EB-SiO_2 thin films, and IAD-SiO_2 thin films on Si substrate are shown in Fig.1, Fig.2, and Fig.3 respectively.

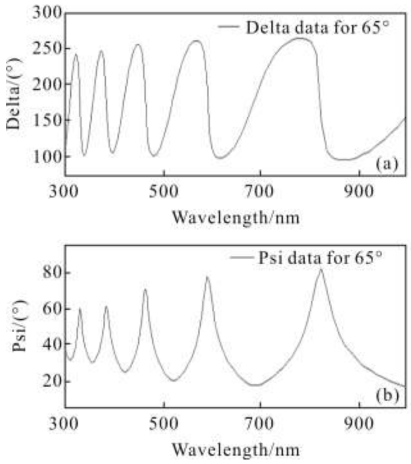

Fig.1 Measured psi and delta data of IBS-SiO_2 thin films on Si substrate

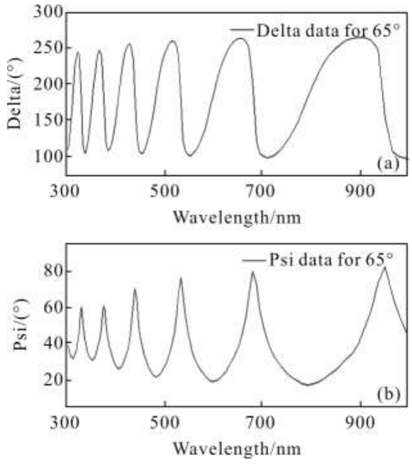

Fig.2 Measured psi and delta data of EB–SiO_2 thin films on Si substrate

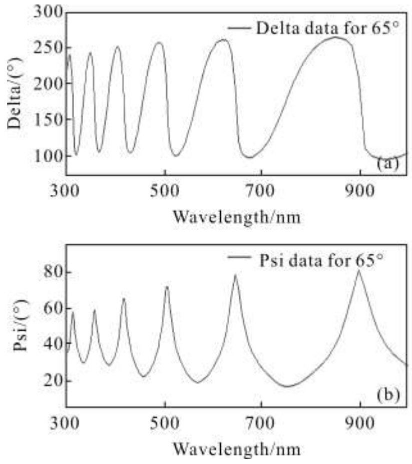

Fig.3 Measured psi and delta data of IAD–SiO_2 thin films on Si substrate

2.3 Optical properties

The calculated dispersive refractive index curves of SiO_2 thin films from 400 nm to 1 000 nm with different deposition technique are shown in Fig.4. It can be seen that the refractive index of IBS–SiO_2 thin films and EB–SiO_2 thin films are almost the same, and the refractive index of IAD–SiO_2 thin films is a little lower than the others. The dispersive curves of IBS–SiO_2 thin films, EB–SiO_2 thin films, and IAD–SiO_2 thin films are almost the same.

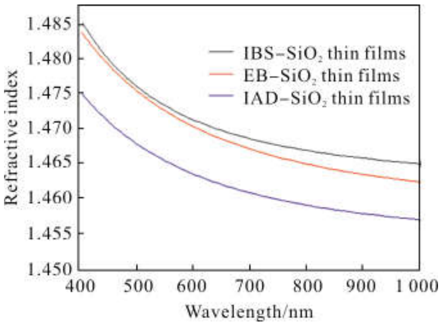

Fig.4 Calculated refractive index curves of IBS–SiO_2 thin films, EB–SiO_2 thin films and IAD–SiO_2 thin films

Because SiO_2 has good optical and mechanical characteristics, it is usually used as low refractive index material to manufacture ultra-low loss optical coating. So the stability of optical thickness needs to be researched. In order to research the specific variety of optical thickness of IBS–SiO_2 thin films, EB–SiO_2 thin films, and IAD–SiO_2 thin films, we chose the wavelength of 632.8 nm for the studied objects. The change of physical thickness and optical thickness of IBS–SiO_2 thin films, EB–SiO_2 thin films, and IAD–SiO_2 thin films on Si substrates at 632.8 nm as a function of time placed in the air are shown in Fig.5, Fig.6 and Fig.7 respectively.

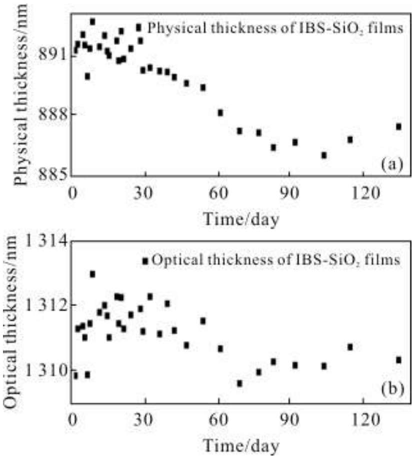

Fig.5 Change of physical thickness and optical thickness of IBS–SiO_2 film on Si substrate at 632.8 nm as a function of time placed in the air

From Fig.5, it can be seen that the physical thickness of IBS–SiO_2 thin films change irregularly after coating, when the placed time reached more than 30 days, the physical thickness began to decrease. When the placed time reached more than 70 days, the physical thickness tended to be stable.

The optical thickness of IBS-SiO_2 thin films is all stable, and the rate of change is less than 0.2%.

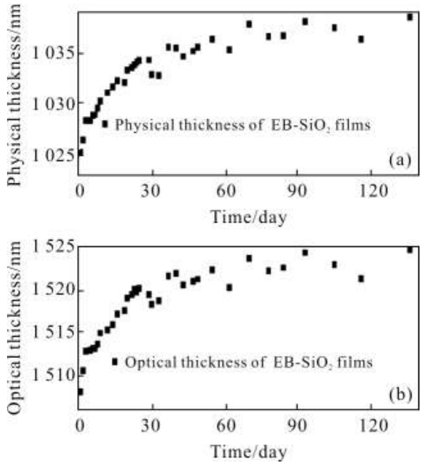

Fig.6 Change of physical thickness and optical thickness of EB-SiO_2 film on Si substrate at 632.8 nm as a function of time placed in the air

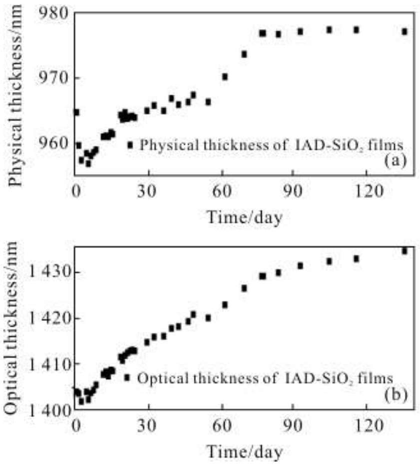

Fig.7 Change of physical thickness and optical thickness of IAD-SiO_2 film on Si substrate at 632.8 nm as a function of time placed in the air

From Fig.6, it can be seen that the physical thickness of EB-SiO_2 thin films change sharply after coating, when the placed time reached more than 60 days, the physical thickness tended to be stable. The variety tendencies of optical thickness are almost the same as the physical thickness, and the rate of change is about 1.0%.

From Fig.7, it can be seen that the physical thickness of IAD-SiO_2 thin films change sharply after coating, when the placed time reached more than 70 days, the physical thickness tended to be stable. The optical thickness of IBS-SiO_2 thin films increases with the increase of the placed time, when the placed time reached more than 135 days, the rate of change is about 2.3%.

Change of optical properties for IBS-SiO_2 thin films, EB-SiO_2 thin films, and IAD-SiO_2 thin films are listed in Tab.1. From Tab.1, it can be seen that the change of refractive index of EB-SiO_2 thin films is the smallest, and the change of refractive index of IAD-SiO_2 thin films is the largest. The change of physical thickness of IBS-SiO_2 thin films is the smallest, and the change of physical thickness of IAD-SiO_2 thin films is the largest. The change of optical thickness of IBS-SiO_2 thin films is the smallest, and the change of optical thickness of IAD-SiO_2 thin films is the largest. The obtained results show that the density of IBS-SiO_2 thin films is the largest so that optical stability of IBS-SiO_2 thin films is the best.

Tab.1 Change of optical properties for IBS-SiO_2 thin films, EB-SiO_2 thin films, and IAD-SiO_2 thin films

	IBS-SiO_2	EB-SiO_2	IAD-SiO_2
Change of refractive index (632.8 nm)	0.6%	-0.3%	1.0%
Change of physical thickness	-0.7%	1.0%	2.0%
Change of optical thickness (632.8 nm)	-0.2%	1.0%	2.3%

3 Conclusion

In conclusion, the optical stability of IBS-SiO_2 thin films, EB-SiO_2 thin films, and IAD-SiO_2 thin films were investigated as a function of time placed in the air by calculating optical constant using ellipsometry spectra. With the increase of the placed time, the physical thickness and optical thickness of EB-SiO_2 thin films and IAD-SiO_2 thin films increase, but IBS-SiO_2 thin film decreases. The change of physical thickness and optical thickness of IBS-SiO_2 thin films is the smallest, and the change of refractive index of EB-SiO_2 thin films is the smallest. We think that the release of the stress is the main cause of physical thickness and optical thickness change. The obtained results show that the density of IBS-SiO_2 thin films is the largest so that optical stability of IBS-SiO_2 thin films is the best. In the design of protective coating, SiO_2 should be deposited by IBS technique.

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