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Optical and mechanical properties of reactively sputtered silicon dioxide films

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Abstract. The reactive sputtering method, using an Ar/O₂ mixture, was applied to deposit silicon dioxide film. Both x-ray photoemission spectroscopy (XPS) and infrared absorption spectroscopy were employed to evaluate the structure of SiO₂ films sputtered at various oxygen percentages. The optical and mechanical properties of SiO₂ films on glass substrates were investigated. Films prepared at a higher oxygen content have a higher density and a higher refractive index.

1. Introduction

Silicon dioxide films are extensively used as low-index films in multilayer optical devices [1,2], passivated and/or protective layers of silicon devices [3], scratch resistant coatings for plastic ophthalmic lenses [4,5] and so on. Stoichiometry and stability of the films are important during applications. The usual methods employed for forming SiO₂ films involve oxidation of silicon at elevated temperatures ($T > 900^\circ\text{C}$). However, the high-temperature processing results in junction degradation [3]. There are many low-temperature methods used in the preparation of SiO₂ films, such as evaporation [1,2], pyrolytic decomposition [6], plasma enhanced chemical vapor deposition [3,4,7], reactive sputtering [6,8] and radio frequency (rf) magnetron sputtering [9]. Film composition as well as deposition and post-deposition processing conditions strongly affect film microstructure, and, consequently, many of its macroscopic properties. Rao and Mohan [10] found that the stoichiometry of the electron-beam evaporated silicon dioxide film was improved after post-deposition annealing at 250°C. Valletta *et al* [8] reported that low substrate temperature, high oxygen pressure, and/or large deposition rate ($> 250 \text{ \AA min}^{-1}$) resulted in increased porosity of reactively sputtered SiO₂ films, and, the films contained large amounts of H₂O. Sankur and Gunning [11] studied water sorption and intrinsic stress in composite TiO₂–SiO₂ films and found that annealing reduced the water content of the films. Takahashi *et al* [12] revealed that the compressive internal stresses of sputtered silicon dioxide films were reduced by use of an Ar/H₂ gas mixture instead of the conventional Ar/O₂ ones. However, they reported a deficiency of oxygen which led to optical absorption loss at short wavelengths ($< 700 \text{ nm}$). The

process conditions, microstructure and ambient effects are interrelated. However, a global optimization of the film properties and deposition conditions is necessary in preparing SiO₂ films for applications in a specific field.

In the present study, SiO₂ films were prepared by reactive rf magnetron sputtering. The sputtering deposition method is suitable for fabrication of SiO₂ films because strong film adhesion onto the substrate is achievable. Previous work by Wu and Chiou [9] indicates that the adhesion strength of SiO₂ film to the glass substrate is greater than the strength of the substrate. In this research, the SiO₂ films were prepared by reactively sputtering an Si target in an Ar/O₂ atmosphere. X-ray photoemission spectroscopy (XPS) was employed to study the chemical bonding states of SiO₂ films. Structural evaluation of silicon dioxide films was carried out by Fourier transform infrared spectroscopy. The optical properties, the pull-off strength and scratch adhesion of SiO₂ films to the glass substrates are also explored.

2. Experimental details

Silicon dioxide films were prepared by using a commercial rf magnetron sputtering system (Ion Tech, UK). The sputtering target was a 1" hot-pressed Si ceramic (99.999% purity) supplied by Cerac, Inc., USA. The substrates employed were Corning 7059 glass and p-type Si (100) wafers. Substrates were placed on a holder above the target with a target-to-holder distance of 50 mm and the holder was rotated at $\sim 10 \text{ revs/min}$ by a motor to provide good uniformity. However, the film deposition rate is reduced because the substrate was rotated off the plasma region periodically. The vacuum chamber was pumped by a diffusion pump. High-purity Ar (99.999%) and O₂

(99.5%) was introduced through a mass flow controller after the vacuum chamber was evacuated to about 2.66×10^{-4} Pa (2×10^{-6} Torr). The gas pressure was kept at 0.7998 Pa (6×10^{-3} Torr) and the sputtering power employed was 100 W during deposition.

Film thickness was measured with a stylus surface profiler. An ellipsometer was used to measure refractive indices for films deposited on Si wafers. Chemical binding energy and compositional analyses of the film was performed using an x-ray photoemission spectroscopy (XPS, Perkin PHI-590AM SAM/1905 Esca, Massachusetts, USA) with an Mg K_{α} x-ray source. The microstructure of the film was analysed using a scanning electron microscope (SEM, Hitachi S-4000, Japan). The optical transmittance of the film was measured with an ultraviolet–visible–near-infrared spectrophotometer (Hitachi U-3410, Japan) and a Fourier transform infrared spectrophotometer (Bomen DA 3.002 FTS and MB 100 FT-IR, Canada).

The adhesion strength of the coating was measured by an adhesion pull tester (Sebastian Five Pull Tester, Quad Group, Inc., USA). After the sample surface was cleaned, an epoxy coated stud was attached to the sample surface by a spring mounting clip designed for the stud and the assembly was heated for 60 min at 150°C to ensure that the stud was bound with the sample. In the tests 0.141" diameter studs were used and the epoxy binding strength was about 700 kg cm^{-2} . Scratching adhesion testing was performed using commercially available scratch testing equipment (CSEM Revetest, Switzerland) fitted with an acoustic emission detector. In the scratching test a stylus is drawn over the sample surface under a continuously increasing normal force until the coating is detached. The normal force on the indenter causing coating detachment is called the critical load and it represents a comparative value of the coating adhesion. In the study, the loading speed and sample table speed are 100 N min^{-1} and 10 mm min^{-1} , respectively. The coating detachment was observed using acoustic emission detectors to measure high-frequency vibrations caused by coating detachment. Critical loads indicated were obtained by averaging the values of three to five different scratches. Detailed morphologies of scratch channels were viewed with an optical microscope.

3. Results and discussion

The deposition rate of SiO_2 films prepared by reactively sputtering Si target in Ar/ O_2 ambient is $\sim 44 \text{ \AA min}^{-1}$ for an oxygen percentage ranging from 10% to 20%. This deposition rate is about one order of magnitude larger than those for SiO_2 film sputtered with SiO_2 target [9]. The hardness of the SiO_2 ceramic target results in a low sputtering yield and consequently a small deposition rate. All the as-sputtered films are amorphous. The film thickness for all specimens in this study was 9000 \AA . The Si 2p and O 1s XPS spectra of the as-deposited SiO_2 films are shown in figures 1 and 2 respectively. The position of the C 1s peak is taken as standard (binding energy = 284.6 eV) to compensate for any charge-induced shifts. The observed binding energies of Si 2p and O 1s levels are $\sim 103 \text{ eV}$ and $\sim 523.7 \text{ eV}$ respectively. They

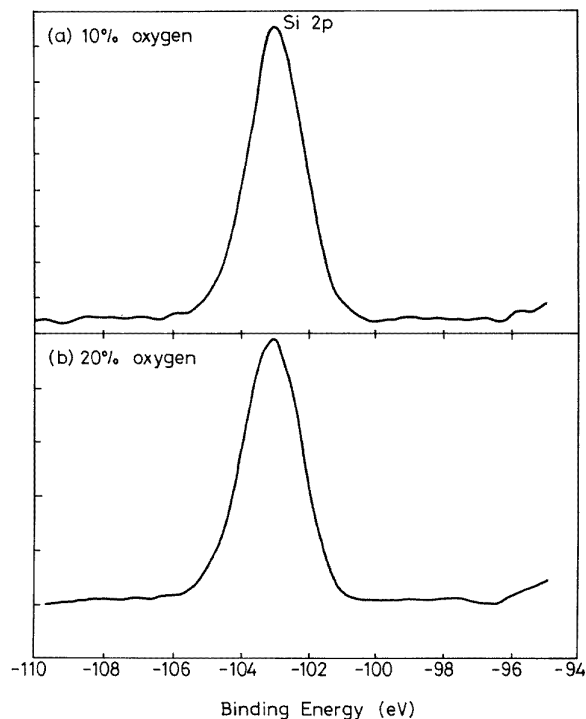


Figure 1. The Si 2p XPS spectra of the as-deposited SiO_2 films prepared at (a) 10% O_2 and (b) 20% O_2 .

Table 1. XPS compositional analyses of SiO_2 films prepared at 10% and 20% oxygen.

$\text{O}_2/\text{O}_2 + \text{Ar}$ (%)	Atomic concentration (%)		
	X_{O}	X_{Si}	$X_{\text{O}}/X_{\text{Si}}$
10	65.68	34.32	1.914
20	69.70	30.30	2.3

agree well with the binding energies of SiO_2 reported in the literature [13]. Table 1 presents the corresponding XPS compositional analyses of SiO_2 films. Here compositional analyses are accomplished by dividing the peak areas by their respective atomic sensitivity factors thus obtaining atomic per cent concentrations. The O/Si atomic ratio of the film is close to that of the nominal composition. Nevertheless, the O/Si atomic ratio of the SiO_2 film prepared at 20% oxygen is larger than that of the SiO_2 film prepared at 10% oxygen. Figure 3 illustrates SEM micrographs of SiO_2 films prepared at 10% and 20% oxygen.

The structures of silicon dioxide films were evaluated using Fourier transform infrared spectroscopy. Figure 4 shows the infrared spectra measured over the wave number range from 1400 to 600 cm^{-1} for SiO_2 films prepared at various oxygen percentages. It has been reported that the wave numbers corresponding to the Si–O vibrational band are 968 , 1035 and 1078 cm^{-1} for SiO , Si_2O_3 and SiO_2 respectively [10]. As shown in figure 4, the positions of the Si–O vibrational band of rf sputtered SiO_2 films are 1080 ± 5 and 840 cm^{-1} . They agree well with the band

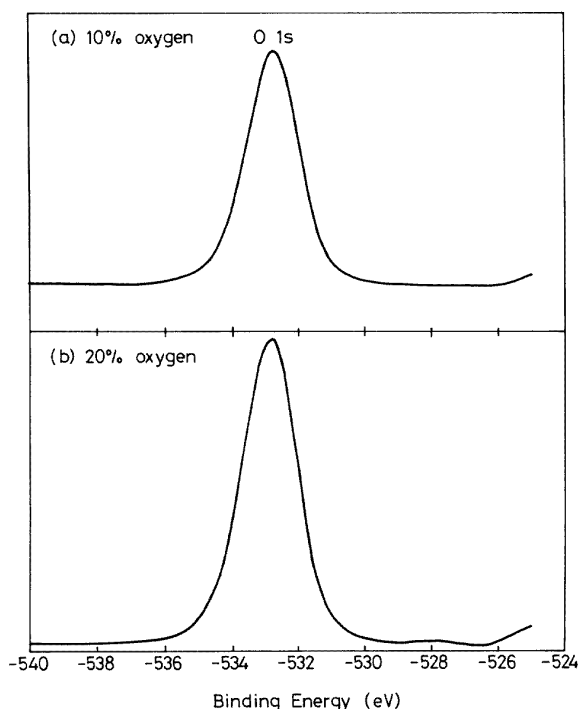


Figure 2. The O 1s XPS spectra of the as-deposited SiO₂ films prepared at (a) 10% O₂ and (b) 20% O₂.

positions of SiO₂ reported in the literature [6, 8, 10]. Pliskin and Lehman [6] have shown that the positions and half-widths of the Si–O vibrational bands near 1090 cm⁻¹ are strongly influenced by the bonding character, stoichiometry, density and porosity of the films. For example, they show that the position of the 1090 cm⁻¹ band shifts to larger wave number and the corresponding band width decreases as pyrolytic SiO₂ films are densified. As shown in figure 4, the band width of the Si–O vibrational band near 1080 cm⁻¹ is broader for SiO₂ film prepared at 10% oxygen than that of SiO₂ film prepared at 20% oxygen. This implies that the film prepared at 10% oxygen is more porous than the film prepared at 20% oxygen.

The corresponding spectra of SiO₂ films in the spectral region where adsorbed water could be found are shown in figure 5. The intensity of the absorption band near 3650 cm⁻¹ due to hydrogen bonded hydroxyl groups and adsorbed water is indicative of the quantity of surface hydroxyl groups and porosity of the oxides. As exhibited in figure 5, the intensity of the infrared absorption near 3650 cm⁻¹ decreases as the oxygen percentage increases. It agrees well with the result in figure 4. As shown in table 2, ellipsometry measurements of the refractive index give values of 1.453 ± 0.003 and 1.460 ± 0.004 for SiO₂ films prepared at 10% and 20% oxygen respectively. The refractive index of the film is influenced by both its density and stoichiometry. Films deposited with less oxygen but the same density will have a higher refractive index due to the larger index of Si-rich films. The effects of density and stoichiometry can compete to some extent in their effect on refractive index. However, films in this study are close to stoichiometric and the major effect will be due to density.

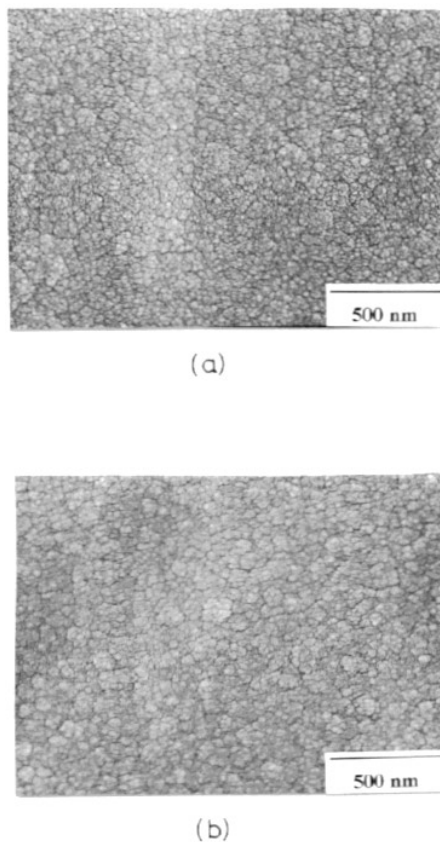


Figure 3. SEM micrographs of SiO₂ films prepared at (a) 10% O₂ and (b) 20% O₂.

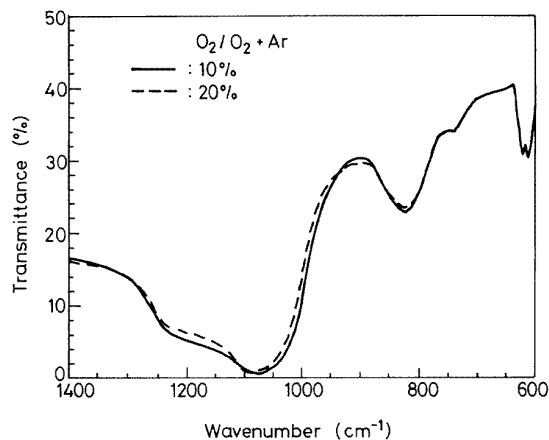


Figure 4. Infrared spectra for SiO₂ films prepared at various oxygen percentages.

The greater the density, the larger is the refractive index.

Figure 6 shows the transmittance of SiO₂ films prepared at various oxygen percentages. As indicated in figure 6, the transmittance of the film prepared at 20% oxygen is marginally larger than that of the film prepared at 10% oxygen. The transmittance of film prepared at 20% oxygen is larger than that of the glass substrate. The spectral characteristics of the film prepared at 10% oxygen are more oscillatory than those of the film prepared at 20%

Table 2. Properties of SiO₂ films deposited on glass substrates at a sputtering pressure of 6×10^{-3} Torr.

Gas ambient	Refractive index	Pull-off strength (kg cm ⁻¹)	Critical load (N)
90% Ar + 10% O ₂	1.453 ± 0.003	531	11.0 ± 2.0
80% Ar + 20% O ₂	1.460 ± 0.004	486†	13.8 ± 3.7

† Failure occurred within glass substrates.

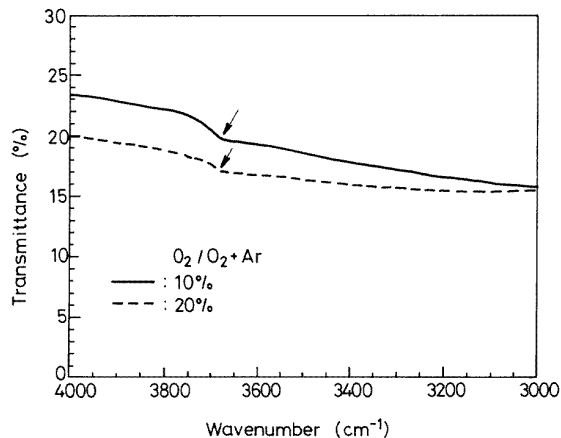


Figure 5. Infrared spectra for SiO₂ films prepared at various oxygen percentages. Arrows indicate the absorption band due to hydrogen bonded hydroxyl groups and adsorbed water.

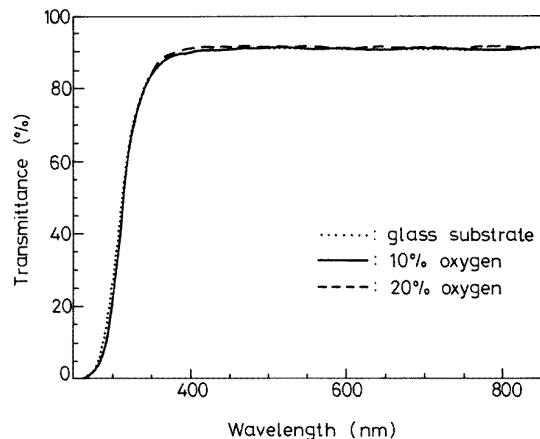


Figure 6. Transmittance of SiO₂ films prepared at various oxygen percentages.

oxygen, although this is not shown clearly in figure 6 on the transmission versus wavelength plot. This is attributed to the smaller refractive index of the film prepared at a lower oxygen percentage (10%). The refractive indices of the Corning 7059 glass substrate, the 10% O₂ sputtered film and the 20% O₂ sputtered film are 1.523, 1.453 and 1.460 respectively. The 10% O₂ sputtered film on glass has a larger refractive index mismatch than the 20% O₂ sputtered one and would contribute to more oscillatory transmission spectra.

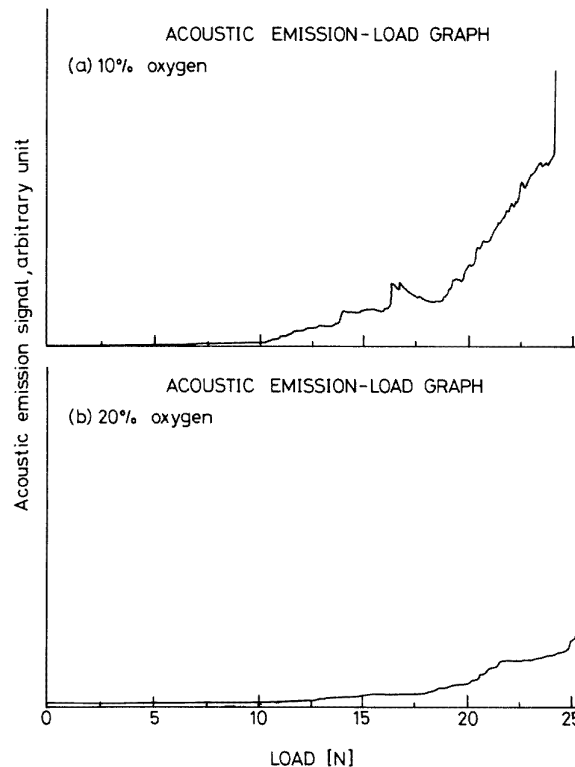


Figure 7. Acoustic emission curves for SiO₂ films prepared at (a) 10% O₂ and (b) 20% O₂.

Table 2 summarizes the results concerning the adhesion properties of SiO₂ films on glass substrates. As indicated in table 2, a high pull-off strength ($> 486 \text{ kg cm}^{-2}$) is obtained for films deposited on glass substrates. For the 20% O₂ sputtered film, failure occurred within the glass substrate and did not occur at the interface between the film and the glass substrate. This implies that the bonding between the SiO₂ film and the glass substrate is excellent.

Figure 7 shows acoustic emission curves for films prepared at 10% and 20% oxygen. The critical loads are $11.0 \pm 2.0 \text{ N}$ and $13.8 \pm 3.7 \text{ N}$ for the 10% O₂ and 20% O₂ sputtered films, respectively. No apparent difference is observed between the 10% O₂ and 20% O₂ sputtered film. The critical load measured by a scratch test technique can be thought of as the adhesion strength of the film on the substrate when films are subjected to wearing and/or abrasion. The reactively sputtered SiO₂ film with an Si target is more scratch resistant than those sputtered with

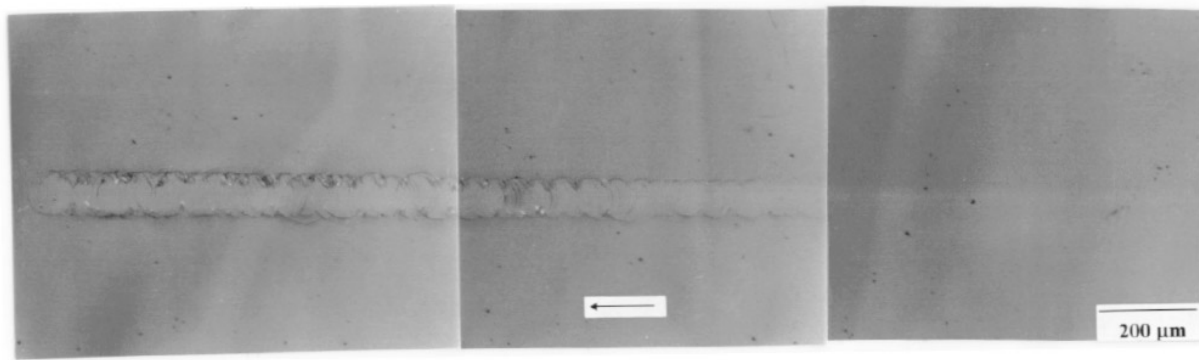


Figure 8. A typical optical micrograph of the scratch channel for the SiO₂ film.

an SiO₂ target. The critical loads are 13.8 ± 3.7 N and 8.0 ± 2.0 N for films prepared with Si and SiO₂ targets respectively [9].

Figure 8 shows a typical optical micrograph of the scratch channel. The arrow indicates the scratch direction. Roughly semicircular arcs appear in front of the scratch channel. The cracking is more intense and is coupled with a loss of adhesion at higher loads. However, the film is not removed as its coherence is high.

4. Conclusions

Silicon dioxide films were prepared by reactively sputtering an Si target in an oxygen-containing ambient. The deposition rate is $\sim 44 \text{ \AA min}^{-1}$ for an oxygen percentage ranging from 10% to 20%. Both the XPS and infrared spectra confirm the formation of SiO₂ compound. However, compositional analyses indicate an increase in O/Si atomic ratio with the increase of oxygen percentage in the sputtering gas. In addition, the absorption band near 3650 cm^{-1} suggests the existence of surface hydroxyl groups and porosity. Films prepared at a higher oxygen content have a higher density and a greater refractive index. In addition, reactively sputtered SiO₂ films with an Si target are more scratch resistant than films sputtered with an SiO₂ target.

Acknowledgment

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