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Properties of radio frequency magnetron sputtered silicon dioxide films

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Abstract

The rf sputtering method, using Ar/O_2 mixture, was applied to fabricate silicon oxide films. The compressive internal stresses, resulted from thermal expansion mismatch, of films deposited on polycarbonate are larger than those of films deposited on glass substrates. Addition of oxygen to the sputtering ambient reduces both the film deposition rate and grain size. The adhesion of the SiO_2 film to the glass substrate are measured with pull-off test and/or scratch test. Films sputtered in the presence of oxygen are more wear-resistant than those without oxygen.

1. Introduction

Silicon dioxide (SiO_2) films have found applications in many areas, such as optics [1–3], electronics [4–6], tribology [7,8], etc. In silicon microelectronics, SiO_2 films are generally employed for diffusion masking and passivation or protection of silicon devices [4,5]. Many novel optical coatings utilizes SiO_2 films to obtain the desirable refractive index in multilayer optical devices as well as the tribological resistance of the SiO_2 films for the anti-wear coating [7,8]. The usual methods employed for forming SiO_2 films involve oxidation of silicon at elevated temperatures ($T > 900°C$). However, the high temperature processing results in junction degradation [4]. There are many low temperature methods used in the preparation of SiO_2 films, such as evaporation [2,3], pyrolytic decomposition [9], plasma enhanced chemical vapor deposition [4–7], and reactive sputtering [9,10]. Rao and Mohan utilized SiO_2 as the starting materials for electron-beam evaporation and prepared a highly stoichiometric SiO_2 films [11]. Valletta et al. reported the preparation of SiO_2 films by reactive sputtering in Ar/O_2 mixture. They found that the deposited films were extremely porous and contained large amounts of H_2O when the film deposition rates were above 250 Å/min [10].

In this study, SiO_2 films were prepared by radio-frequency (rf) magnetron sputtering. Magnetron sputtering can deposit films over large areas at rates comparable to electron-beam evaporation without the degree of radiation heating typical of thermal source. It is considered to be one of the best methods for preparing optical films, such as In_2O_3:Sn [12–17]. In this research, the SiO_2 films were sputtered in an $Ar–O_2$ atmosphere. The effect of Ar/O_2 ratio on the deposition rate, the film morphology, the optical properties, as well as the adhesion of SiO_2 films to the glass substrates are evaluated.

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2. Experimental details

SiO_2 films were prepared by using a commercial rf magnetron sputtering system (ION TECH, England). The sputtering target was a 1 inch hot-pressed SiO_2 ceramic (99.9% purity) supplied by Superconductive Components, USA. The substrates employed were Corning 7059 glass, polycarbonate sheets and p-type Si (100) wafers. The substrate was fixed directly above the target and a mechanical shutter was attached to the target. High purity Ar (99.999%) or Ar/O_2 gas mixture was introduced through a mass flow controller after the vacuum chamber was evacuated to about 2×10^{-6} Torr. The rf power (13.56 MHz) was introduced through an rf power supply (Rf Plasma Products, USA) with an automatic matching network which could be tuned for minimum reflected power. Before deposition, the target was usually presputtered for 20–30 min to remove any contaminants and eliminate any differential sputtering effects.

Film thickness was measured with a stylus surface profiler. An X-ray diffractometer (XRD, Rigaku Dmax-B, Japan) was used to identify the crystalline phase of the film. The microstructure of the films was analyzed using a scanning electron microscope (SEM, Hitachi S-4000, Japan). The optical transmittance of the films were measured with an ultra-violet 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, USA) and a scratching adhesion tester (CSEM Revettest, Switzerland). 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 and 10 mm/min, respectively. The coating detachment was observed using acoustic emission detectors to measure high frequency vibrations caused by coating detachment. The 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.

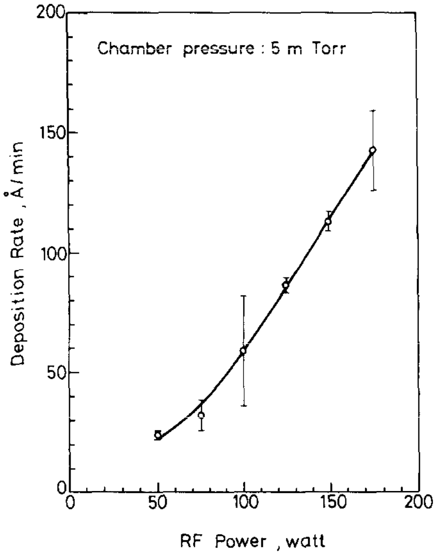

Fig. 1. The deposition rate of SiO_2 films as a function of sputtering power.

3. Results and discussion

Deposition rate is defined as film thickness divided by deposition time, and it is important in film thickness control, especially for precise multilayer coating. Fig. 1 shows the deposition rate of SiO_2 films as a function of sputtering power at a target-to-substrate distance of 5 cm and an argon pressure of 5 mTorr. The deposition rate increases with in-

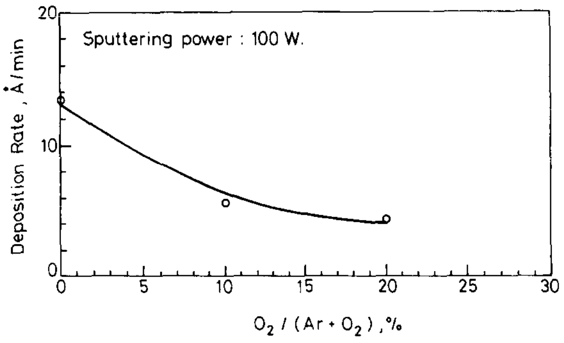

Fig. 2. The deposition rate of SiO_2 films on glass substrate as a function of oxygen percentage.

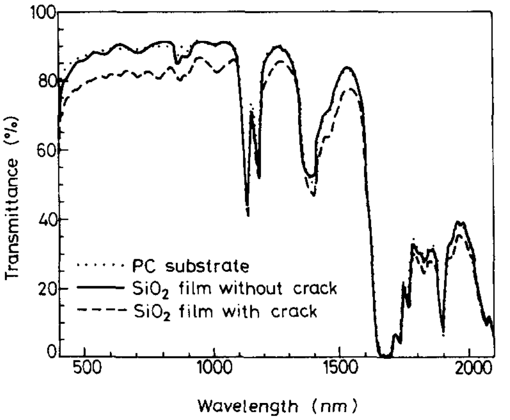

Fig. 3. The spectral characteristics of SiO_2 films on polycarbonate substrates.

creasing sputtering power. The high deposition rate at large sputtering power is attributed to the high energy of the sputtered neutrals. The higher sputtering power causes an increase in the density and average energy of the sputtered neutrals, which must then be subjected to a larger number of collisions before they are thermalized [15].

Fig. 2 gives the deposition rate of SiO_2 films as a function of the oxygen percentage at a sputtering power of 100 W. The deposition rate decreases from ~ 13 Å/min to ~ 4 Å/min as oxygen percentage from 0 to 20%. For SiO_2 films deposited on polycarbonate substrates, cracks are found after specimens stored in the atmospheric environment for several hours or several weeks. It implies a release of residual stress after room temperature storage. The stress S_T accumulated in the film after deposition is

$$S_T = E_f(\alpha_f - \alpha_s)(T_D - T_M), \quad (1)$$

where E_f is the Young's modulus for the film, α_f and α_s are average thermal coefficients of the film and the substrate, respectively, T_D is the film deposition temperature and T_M is the temperature during stress measurements, i.e., room temperature. The residual stress of the film is attributed to thermal expansion mismatch, $\alpha_f - \alpha_s$, and a temperature

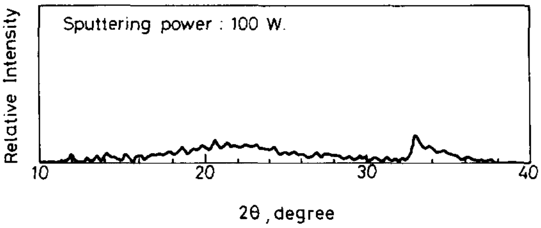

Fig. 4. The typical X-ray diffraction patterns of the as-sputtered SiO_2 film on glass substrate.

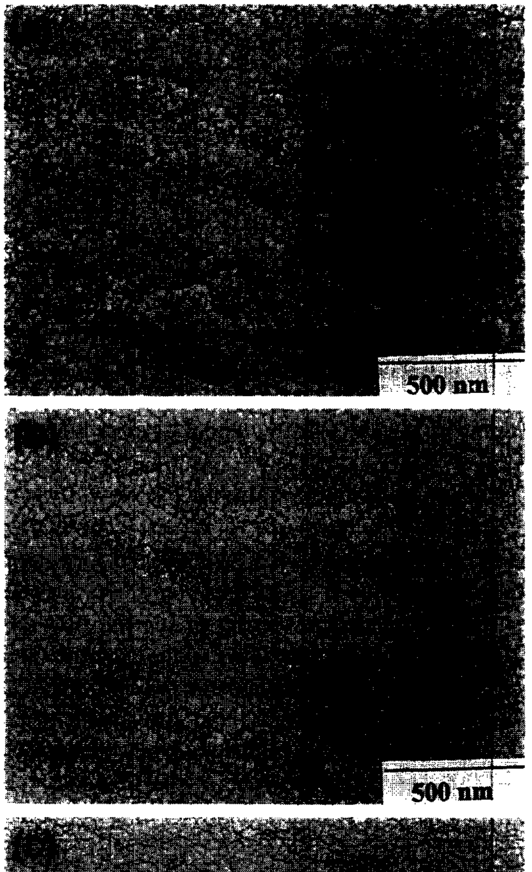

Fig. 5. SEM micrographs of SiO_2 films prepared at various oxygen percentages: (a) 0%, (b) 10%, (c) 20%. The sputtering power is 100 W.

change, $T_D - T_M$. The thermal expansion coefficients of the SiO_2 film, Corning 7059 glass and PC substrate are $2 \times 10^{-6}/°C$ [18], $4.6 \times 10^{-6}/°C$ and $39 \times 10^{-6}/°C$ [19], respectively. The deposition temperature was ~ 90°C. Hence a compressive stress was built-up in the film and strain energy were accumulated. Cracks initiation and propagation would release the residual energy inside the films. Fig. 3 shows the spectral characteristics of the SiO_2 film with and without crack on polycarbonate substrates. An apparent reduction in the transmittance is observed for the cracked film. It is attributed to the increasing light scattering for the cracked film since cracks on the film increase the surface roughness of the film.

The as-deposited films are amorphous, as exhibited in the X-ray diffraction patterns shown in Fig. 4. The surface morphology of films prepared at various oxygen percentages are illustrated in Fig. 5. SiO_2 grains of the films are smaller than 20 nm. Films sputtered at higher oxygen content have smaller grain size.

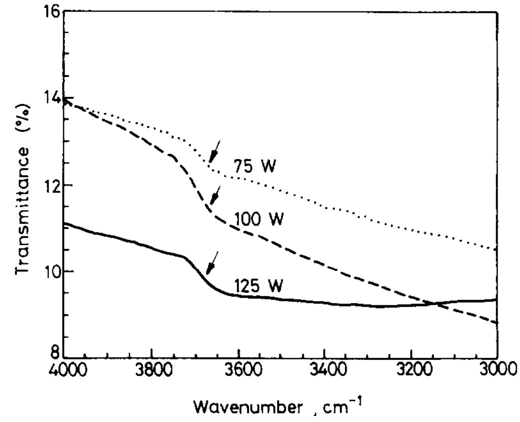

Fig. 7. The infrared spectra for SiO_2 films on silicon wafers prepared at various sputtering powers. Sputtering atmosphere: Ar. Arrows indicate the absorption band due to hydrogen bonded hydroxyl groups and absorbed water.

The Fourier-transform infrared spectroscopy is one of the best techniques for structural evaluation of silicon oxide films. Fig. 6 shows the infrared spectra in the region between 1400 cm^{-1} and 600 cm^{-1} for SiO_2 films prepared at various sputtering powers. 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 [20]. As shown in Fig. 6, 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 positions of SiO_2 reported in the literature [9,10,20]. Fig. 7 shows the infrared spectra in the region between 3000 cm^{-1} and 4000 cm^{-1} for SiO_2 films prepared at various sputtering powers. 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 sputtering power increases, the intensity of the absorption band enhances. It implies the increase in the porosity of

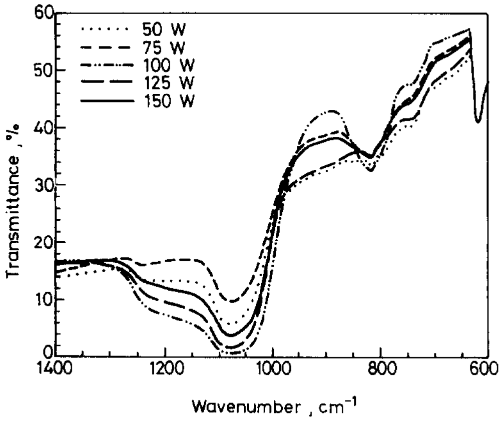

Fig. 6. The infrared spectra for SiO_2 films on silicon wafers prepared at various sputtering powers. Sputtering atmosphere: Ar.

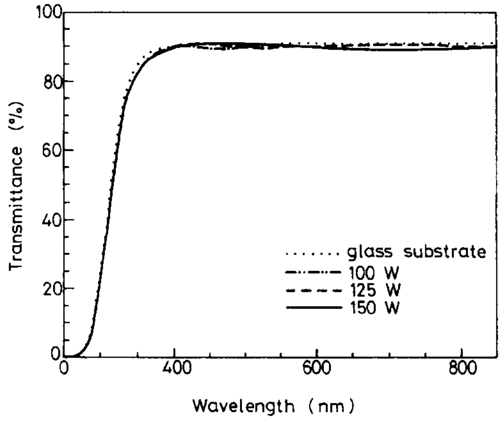

Fig. 8. Transmittance of SiO_2 films on glass substrates prepared at various sputtering powers. Sputtering atmosphere: Ar.

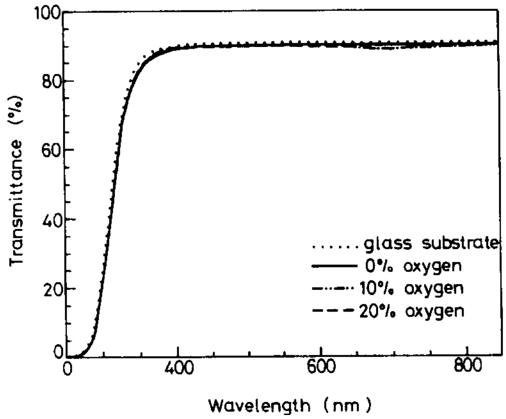

Fig. 9. Transmittance of SiO_2 films on glass substrates prepared at various oxygen percentages. Sputtering power: 100 W.

the film as films is deposited at high sputtering power.

Fig. 8 shows the spectral characteristics of SiO_2 films prepared at various sputtering powers. It can be seen in Fig. 8 that the transmittance of the film is high and all the films are free from absorption except oscillations due to interference effects. Fig. 9 shows the transmittance of SiO_2 films prepared at various oxygen percentages. Transmittance of the film is high and very close to that of the glass substrate. The variation of transmittance with wavelength appears to be similar for all films.

Table 1 summaries the results concerning the adhesion of SiO_2 films to glass substrates. As indicated in Table 1, a high pull-off strength (> 500 kg/cm^2) is obtained for films deposited on glass substrates. Almost all the failures occurred within the glass substrate and did not occur at the interface between the film and the glass substrate. It implies that the bonding between the SiO_2 film and the glass substrate is excellent.

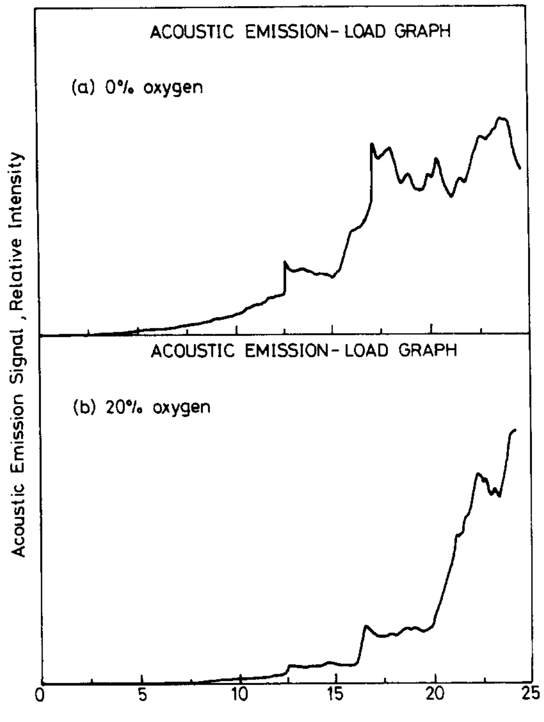

Fig. 10. The acoustic emission curves for SiO_2 films prepared at various oxygen percentages.

The scratch test is also employed to study the adhesion of the film and substrate. 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. Fig. 10 shows the acoustic emission curves for films prepared at various oxygen percentages.

Table 1
Adhesion of SiO_2 films deposited on glass substrates

Sputtering atmosphere [a]	90%Ar + 10%O_2	90%Ar + 10%O_2	90%Ar + 10%O_2	80%Ar + 20%O_2	100%Ar
Sputtering power (W)	150	125	100	100	100
Pull-off strength (kg/cm^2)	501 [b]	266 [b]	416 [b]	396 [b]	305 [b]
Critical load (N)	—	—	—	8.0 ± 2.0	5.9 ± 0.9

[a] Chamber pressure is 6 mTorr.

[b] Failure occurred within glass substrates.

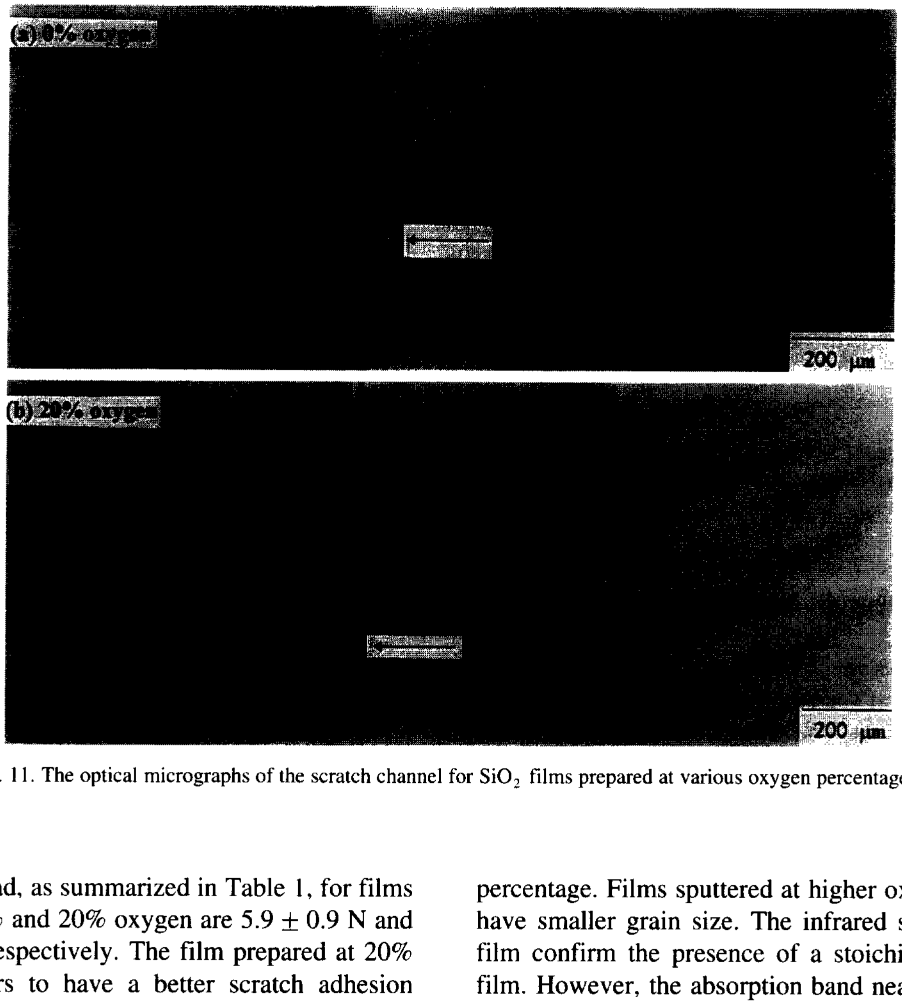

Fig. 11. The optical micrographs of the scratch channel for SiO_2 films prepared at various oxygen percentages.

The critical load, as summarized in Table 1, for films prepared at 0% and 20% oxygen are 5.9 ± 0.9 N and 8.0 ± 2.0 N, respectively. The film prepared at 20% oxygen appears to have a better scratch adhesion property than those prepared at 0% oxygen. Fig. 11 shows the corresponding scratch channel by the optical microscope. The arrow indicates the scratch direction. A serious scratch damage is observed for film prepared at 0% oxygen, as observed in Fig. 11. Roughly semicircular arcs appear in front of the scratch channel, as shown in Fig. 11. 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. Conclusion

Silicon dioxide films were prepared by rf sputtering using Ar/O_2 mixture as sputtering gas. The deposition rate decreases with the increase of oxygen percentage. Films sputtered at higher oxygen content have smaller grain size. The infrared spectra of the film confirm the presence of a stoichiometric SiO_2 film. However, the absorption band near 3650 cm^{-1} suggests the existence of surface hydroxyl groups and porosity. The adhesion strength of SiO_2 film to the glass substrate is larger than the strength of the substrate after pull-off test. Films prepared at 20% oxygen appear to be more wear-resistant than those prepared without oxygen.

Acknowledgements

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