

Mechanisms of reduction of the internal stress in hydrogenated silicon oxide films prepared by Ar-H₂ sputtering

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Abstract

Silicon oxide films deposited by Ar-H₂ sputtering exhibited significantly smaller internal stresses than conventional films deposited by Ar-O₂ sputtering. This phenomenon was found to be caused by the introduction of Si-H bonds into the Si-O-Si network structure. As a result of hydrogenation, the number of planar ring type defects in the network was successfully reduced, and the Si-O bonding force constant seemed to decrease, judging from Raman and IR spectroscopy. These results suggest that the hydrogenation produced a structural relaxation of the Si-O-Si network, leading to the reduction in stress.

keywords: Stress; Silicon oxide; Sputtering

1. Introduction

The large stress induced in deposited films is a serious problem for film based devices, for example optical polarizers consisting of Al/SiO₂ multilayers, etc. [1-3]. In such optical devices, highly stressed layers not only lead to mechanical failure of the devices but also cause light scattering at the film interface which fluctuates with the accumulation of stress. In order to reduce the large compressive stress in thick silicon oxide films for optical applications, we proposed previously hydrogenation of the film via Ar-H₂ sputtering instead of the conventional Ar-O₂ sputtering [4,5]. Generally, Ar atoms introduced into the film from the sputtering gas become a source of internal stress [6,7]. In the hydrogenated film (SiO_{2-x}:H), however, a relaxation of the Si-O-Si network structure due to partial Si-H termination seemed to reduce the effect of the trapped Ar atoms [4]. Here, the mechanism of such a structural relaxation of SiO_{2-x}:H films was investigated by Raman and IR spectroscopy. The results are discussed from the viewpoint of the bonding configuration of Si-O-Si.

2. Experiments

The 1 μm thick SiO_{2-x}:H films were prepared on Si(100) and metallic aluminum substrates by magnetron r.f. sputtering using a fused SiO₂ target and Ar-H₂ mixture as sputtering gas. The gap between the substrate and the target was 125 mm.

The H₂ content was varied between 0 and 30 vol.%, while the total gas flow rate and pressure were fixed at 120 standard cm³ min⁻¹ and 0.2 Pa respectively. The r.f. power was varied from 200 to 600 W. The substrate was not intentionally heated during film deposition.

The internal film stress was derived from deflection of the substrate due to the film deposition which was measured by a stylus method [8]. The refractive index of the film was measured by a prism coupler at light wavelength λ = 633 nm. Raman spectroscopy was performed for the films on aluminum substrates using a 30 mW incident light beam of λ = 514.5 nm from an argon-ion laser. The light backscattered from the film was monochromated and detected by a charge coupled device camera. The films on Si substrates were evaluated by a Fourier transform IR spectrometer. The chemical composition was measured for 0.3 μm thick films deposited onto Si substrates by an elastic recoil detection (ERD) method and Rutherford backscattering spectroscopy (RBS), for which the He²⁺ incident beam energy and dose value were fixed at 2.275 MeV and 50 μC respectively.

3. Results and discussion

3.1. Reduction in internal stress in SiO_{2-x}:H film

Table 1 shows the deposition parameters, measured refractive indices and internal stresses of SiO_{2-x}:H films. A negative sign for the stress indicates that the film stress is compressive.

Table 1
The deposition parameters and film characteristics for the SiO_{2-x}H films

| Number | Deposition parameters | | | Deposition rate (nm s^{-1}) | Refractive index at 633 nm | Internal stress (MPa) |
|--------|-----------------------------|-------------------------|--------------------------------|---|-------------------------------|--------------------------|
| | Sputtering pressure (Pa) | Sputtering power (W) | H_2 flow ratio (%) | | | |
| 1 | 0.20 | 200 | 0 | 0.181 | 1.4750 | -72 |
| 2 | 0.20 | 200 | 10 | 0.160 | 1.5064 | -65 |
| 3 | 0.20 | 200 | 20 | 0.147 | 1.5327 | -54 |
| 4 | 0.20 | 200 | 30 | 0.135 | 1.6095 | -39 |
| 5 | 0.20 | 400 | 0 | 0.404 | 1.4861 | -117 |
| 6 | 0.20 | 400 | 5 | 0.366 | 1.4943 | -106 |
| 7 | 0.20 | 400 | 10 | 0.352 | 1.5017 | -104 |
| 8 | 0.20 | 400 | 20 | 0.329 | 1.5293 | -83 |
| 9 | 0.20 | 400 | 30 | 0.309 | 1.5441 | -69 |
| 10 | 0.20 | 600 | 0 | 0.590 | 1.4852 | -134 |
| 11 | 0.20 | 600 | 10 | 0.521 | 1.4943 | -121 |
| 12 | 0.20 | 600 | 20 | 0.489 | 1.5155 | -96 |
| 13 | 0.20 | 600 | 30 | 0.441 | 1.5273 | -87 |

Table 2
The deposition parameters and film characteristics for the SiO_{2-x} films

| Number | Deposition parameters | | | Deposition rate (nm s^{-1}) | Refractive index at 633 nm | Internal stress (MPa) |
|--------|-----------------------------|-------------------------|--------------------------------|---|-------------------------------|--------------------------|
| | Sputtering pressure (Pa) | Sputtering power (W) | O_2 flow ratio (%) | | | |
| 1 | 0.20 | 400 | 5 | 0.228 | 1.4713 | -169 |
| 2 | 0.20 | 400 | 10 | 0.178 | 1.4685 | -182 |
| 3 | 0.20 | 400 | 15 | 0.159 | 1.4687 | -170 |
| 4 | 0.20 | 400 | 20 | 0.138 | 1.4688 | -179 |
| 5 | 0.20 | 400 | 25 | 0.133 | 1.4684 | -179 |

For comparison, similar measurements were taken for SiO_{2-x} films deposited by conventional Ar- O_2 sputtering, see Table 2. As seen in Table 1 and Table 2, the internal stresses of the SiO_{2-x}H films are smaller than those of the conventional

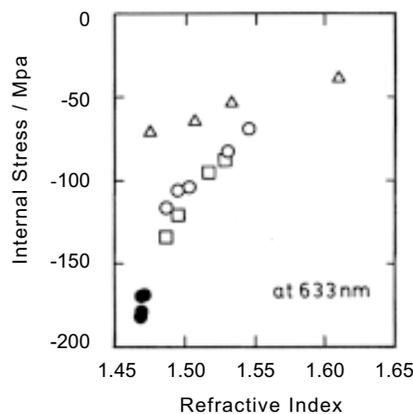


Fig. 1. Relationship between internal film stress and refractive index of the SiO_{2-x}H films prepared under various sputtering gas compositions (see Table 1) with rf powers of 200 W (Δ), 400 W (\circ), 600 W (\square). The closed circles show the results for conventional films deposited at 400 W r.f. power in Ar- O_2 gas environment (see Table 2).

SiO_{2-x} films. The internal stress of SiO_{2-x}H films decreased with decreasing r.f. power and increasing H_2 content in the sputtering gas. However, the content of Si-H bonds was found to be increased in the stress-reduced films using IR spectroscopy on the Si-H bending mode at 880 cm^{-1} . This increase in Si-H bonds in the SiO_{2-x}H films was also observed as an increase in the refractive index, as shown in Fig. 1 in which the relationship between the internal stress and refractive index is plotted for SiO_{2-x}H films deposited at 200 W (triangles), 400 W (circles), 600 W (squares) and conventional SiO_{2-x} films (closed circles). Compared with the constant refractive index of the SiO_{2-x} films, in the SiO_{2-x}H films there is a good correlation between the film stress and the refractive index (i.e. Si-H content).

3.2. Mechanism of stress reduction in SiO_{2-x}H film

Fig. 2 shows Raman spectra of the various SiO_{2-x}H films deposited at 400 W. No Raman peak due to Si-OH bonds (approximately 3650 cm^{-1}) was observed for any of the samples. Two Raman peaks appeared at 490 and 600 cm^{-1} and were assigned as D_1 and D_2 lines caused by planar four-

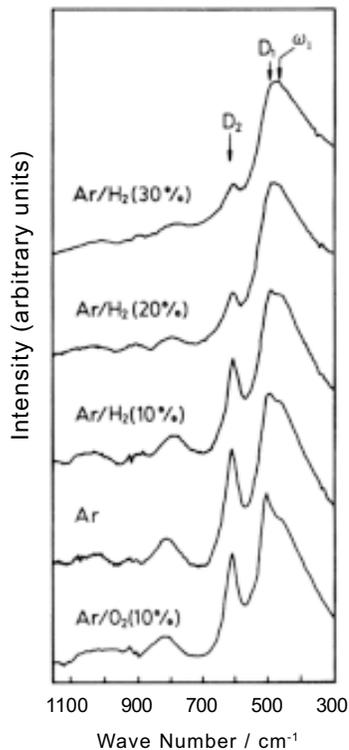


Fig. 2. Raman spectra of the SiO_{2-x}H films deposited at 400 W r.f. power and at H_2 gas ratios of 0 to 30 vol. %. The spectrum of conventional film deposited at 400 W with an Ar- O_2 (10%) mixture is also shown. Peaks at 490 and 600 cm^{-1} correspond to the planar four-fold (D_1) and three-fold (D_2) ring structures in the Si-O-Si network.

fold and three-fold ring type defects in the Si-O-S network respectively [9]. However, the intensity of these D lines decreased in the films deposited under H_2 -rich sputtering gas to show a larger amount of Si-H bonds. The reduction in structural defects in the highly hydrogenated films was probably due to partial breakage of the Si-O-Si network by the formation of Si-H bonds. The significant exclusion of defects from the SiO_{2-x}H films was one of the reasons for the reduction in internal stress.

As an additional reason for the reduction in stress, the fluctuation in elastic parameters of the Si-O-Si bonds due to the introduction of Si-H termination was investigated. Fig. 3 shows values of the IR peak frequency of Si-O stretching (TO_3) and Si-O-Si bending (TO_2) modes as a function of the internal film stress. Both peak frequencies shifted to lower values with decreasing film stresses. According to the generally known molecular model of IR spectra for SiO_2 , a decrease in the TO_3 frequency means a decrease in average bond angle of the Si-O-Si configuration [10,11]. However, this assumption of possible angular distortion in the film was inconsistent with the observed decrease in TO_2 mode frequency. The molecular model also predicted that the TO_2 frequency would increase when the Si-O-Si bond angle became smaller. Therefore, the concurrent decrease in TO_3 and TO_2 mode frequencies shown in Fig. 3 could be attributed to a decrease in the

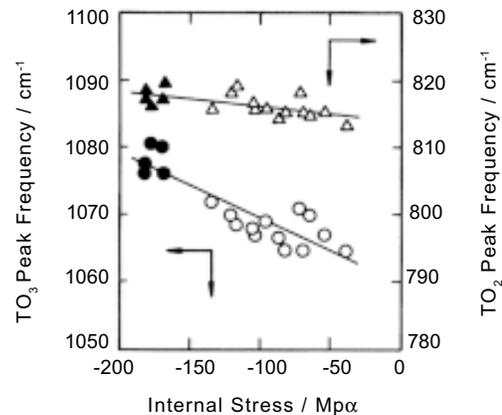


Fig. 3. Relationship between the TO_3 and TO_2 peak frequencies of IR spectra and the internal film stress of SiO_{2-x}H films. Closed symbols show the results for conventional SiO_{2-x} films.

Si-O bonding force constants (α and β); α and β are the central force and non-central force constants in the SiO_4 tetrahedron respectively.

Fig. 4 shows the relationship between the calculated force constants and the internal film stress. The calculation was performed from the measured TO_2 and TO_3 frequencies and an assumed Si-O-Si bond angle of 144° for stoichiometric SiO_2 glass [12], using an equation in Ref. [11]. It was noted that the value of α decreased with a decrease in film stress, while the value of β was almost unchanged, suggesting that the smaller bonding force constant α in the SiO_{2-x}H films was the origin of the stress reduction. This result could be explained as follows. A localized film stress induced by a small longitudinal change ΔL in the Si-O bond was simply expressed by Hook's law. When a similar change ΔL was introduced into SiO_{2-x}H and SiO_{2-x} films by the incorporation of Ar atoms etc., the induced stress was smaller in the hydrogenated film because of its smaller value of α .

As a reason for the smaller value of α in the SiO_{2-x}H films, a decrease in positive charges localized on the Si atom due to the formation of Si-H bonds was considered, because the

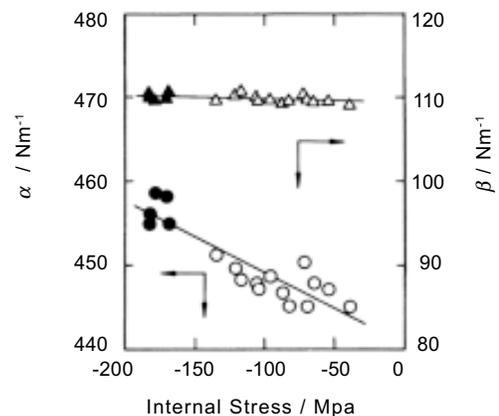


Fig. 4. Dependence of the central α and non-central β force constants on film stress of the SiO_{2-x}H films. Closed symbols show the results for conventional SiO_{2-x} films.

difference in electronegativities between the atoms are small for Si-H (0.3) compared with Si-O (2.0). The weakly charged Si atoms might result in the presence of loose Si-O bonds having smaller α values.

4. Conclusion

The mechanism of stress reduction in SiO_{2-x}H films was investigated from the viewpoint of the local bonding configuration in the Si-O-Si network. Raman spectroscopy of the films revealed that the hydrogenation effected a significant reduction in planar four-fold and three-fold ring type defects in the network, which appeared in the conventional SiO_{2-x} films. A decrease in Si-O bonding force constant α was also found for the highly hydrogenated films by IR spectroscopy. These results could be explain the stress reduction via structural relaxation in the Si-O-Si network.

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