Structural relaxation and stress reduction in hydrogenated silicon oxide films

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(Received 20 July 1995; accepted for publication 14 November 1995)

Ar/H_2 sputtering of a SiO_2 a target can produce thick silicon oxide films with significantly reduced internal stresses compared with those of conventional films prepared by an Ar/O_2 sputtering method. As an origin of the stress reduction, we proposed previously the structural relaxation model of the Si-O-Si network via partial Si-H termination. This model is experimentally supported here by the Raman spectroscopy measurements which show a large decrease of planar three- and four-fold ring-type defects in the hydrogenated Si-O-Si network structure. © *1996 American Institute of Physics.* [S0021-8979(96)05504-8]

The problem of internal film stresses has been investigated to improve the mechanical stability of multilayered devices. In some optical devices, this problem is severe because films and multilayers with thicknesses greater than the light wavelength ($\lambda = 1.55$ μm) are generally required. The authors previously reported the use of an Ar/H_2 sputtering gas mixture as a means to obtain stress-reduced silicon oxide films from a conventional SiO_2 target material.[1] These Ar/H_2 films exhibited less than half the compressive stress of films prepared by Ar/O_2 sputtering, and were successfully applied to the 250-μm-thick multilayered optical polarizers.[2] As a reason for the stress reduction, the authors proposed the structual relaxation model for the Si-O-Si networks of the films via partial introduction of hydrogenated silicon (Si-H). This idea was based on the fact that stress reduction of the Ar/H_2 films cannot be explained by the generally known phenomenon of Ar trapping in films, and that the Fourier-transform infrared (FTIR) spectroscopy measurements detected clear Si-H peaks in the Ar/H_2 films. However, the relation between the hydrogenation and the structural relaxation of the films has not yet been confirmed by experiments. In the present study, the results of Raman spectroscopy measurements for the Ar/H_2 films are presented to support our assumption of the structural relaxation of the films by the hydrogenation. In such films, specific peaks due to three- and four-fold ring-type defects on the Si-O-Si network structure decreased significantly compared with those of the conventional Ar/O_2 sputter-deposited films.

The 1-μm-thick film samples were prepared on 3 in. Si{100} substrates for the present experiment and for confirmation of the repeatability of the previous results: i.e., the internal film stress reduction. Fused SiO_2 was used as the target material for a rf magnetron sputtering method with a sputtering gas of an Ar/H_2 gas mixture (total flow rate: 120 sccm). The H_2 content and supplied rf power were changed from 0 to 30 vol % and from 200 to 600 W. The sputtering pressure was kept at 0.2 Pa, and the substrates were not heated during the deposition process. The internal film stresses measured, according to the method reported by Mack and Reisman,[3] are shown in Fig.1 as functions of the rf power and the H_2 gas ratio. The internal film stresses decreased with both the decreasing rf power and the increasing H_2 gas flow ratio. In the IR measurements of the Ar/H_2 films, a peak at 880 cm^{-1} attributed to the Si-H bending motion was observed. The relative intensity ratios of Si-H: bending/Si-O: bending at 820 cm^{-1} in the IR spectra of Ar/H_2 films increased with the increasing H_2 raio in the sputtering gas: 0.21 for the film deposited at rf of 400 W with Ar/H_2 (10%) gas, 0.26 for Ar/H_2 (20%), and 0.36 for Ar/H_2 (30%), indicating that the internal film stresses were smaller with the increasing Si-H content in the film. On the other hand, the internal stresses of the films prepared by Ar/O_2 sputtering were larger than those of Ar/H_2 films and did not depend on Ar/H_2 ratios. These results are consistent with the previous ones, indicating repeatability of the process.

Figure 2 is a plot of the variation of the refractive index at 633 nm determinded by prism coupler measurements for the films indicated in Fig.1. The refractive index of the films prepared with only Ar gas tended to increase with increasing rf power of the deposition. This was probably due to densification of the films by the higher rf power: A high rf power provides an environment assisting byproduct removal leading to the formation of denser films.[4] It is well known that a film with less density exhibits smaller stress.[5] Therefore, the power applied during sputtering is one of the important parameters for the stress reduction of films as well as the H_2 content in the sputtering gas. On the other hand, it was apparent that the refractive indices of the Ar/H_2 films increased with both the decreasing rf power and the increasing H_2 content in the sputtering gas. The increase in the refractive index of the Ar/H_2 films was related to the amount of Si-H bonds, as confirmed by the previous IR measurements. The authors inferred that the increase in the refractive index of the Ar/H_2 film was mainly caused by the replacement of Si-O bonds with Si-H bonds. From the results of Figs. 1 and 2, it seems that the decrease in the internal film stresses corresponded to the increase in the refractive indices of the films. Such a result sup-

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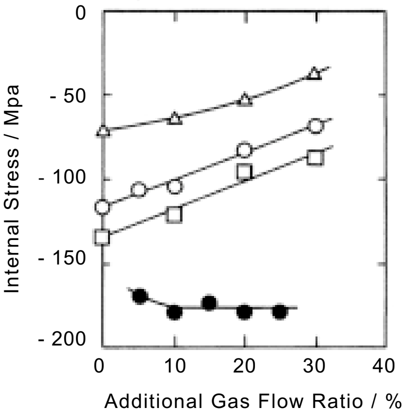

FIG. 1. The dependence of internal film stress on the both rf powers and H_2 gas flow ratios. The films were deposited at 0.2 Pa and ambient temperature with rf of (△) 200 W, (○) 400 W, and (□) 600 W. Solid circles show the results of the Ar/O_2 films deposited at 0.2 Pa and ambient temperature with rf power of 400 W.

ported the belief that both behaviors, the stress and the index of the Ar/H_2 films, depended on the Si-H content in the films.

The film compositions and mass densities of the films were measured by an elastic recoil detection method (ERD) and by Rutherford backscattering spectroscopy (RBS) accompanied with the HIPRA simulation program.[6] The energy and dose of the He^{++} incident beam in both measurements were 2.275 MeV and 50 μC. The details of the measurements were reported elsewhere.[7] Figure 3 shows the ERD depth profiles of the hydrogen contents in the 0.3-μm-thick films deposited on Si wafers with rf 400 W under (a) Ar/H_2 (20%) and (b) Ar/O_2 (10%) sputtering. The corresponding spectrum for a Si wafer is also shown in Fig. 3 to estimated hydrogen amounts due to surface contamination. The hydrogen content of the films was calculated under the assumption that surface hydrogen contents of the samples were equivalent to that of the Si wafer surface. The compositions obtained at a depth of 0.25 μm and the mass densities of these films are listed in Table I. Ar contents of both films were almost the same, while the Ar/H_2 film (a) was denser, suggesting that the amounts of incorporated Ar and the film density were not dominant origins of the internal stress reduction of the Ar/H_2 film (a). As the stress reduction mechanism, the Si-O-Si network of the Ar/H_2 films was partially broken and relaxed by the formation of the Si-H bonds, which was proposed in our previous article.[1] In order to confirm this consideration, a structural change of the films was investigated by Raman spectroscopy measurements.

Figure 4 shows Raman spectra of the 1-μm-thick films deposited at rf of 400 W under various sputtering gas compositions. An aluminum substrate was used here, instead of the silicon wafer, in order to detect only the species combining with the Si atoms of the film. No Raman peak due to (Si)-OH bonding (~3650 cm^{-1}) was detected in any of the samples. In Fig. 4, it was noted that two Raman peak intensities at 490 and 600 cm^{-1} changed systematically depending on the sputtering gas composition: i.e., these peak intensities decreased with an increase in the Si-H content of the films. Such peaks were the D lines due to the planar four-fold ring structure (D_1 at 490 cm^{-1}) and the planar three-fold ring structure (D_2 at 600 cm^{-1}), which were reported by Galeenar,[8] suggesting the existence of ring-type defects in the Si-O-Si network. It was anticipated that the reduction of film density was generated by the planar ring type defects, as shown in the present study. As seen in Fig. 4, the D-line intensities were significantly reduced in the higher hydrogenated films. This can result from the partial break up of the Si-O-Si network by the formation of the Si-H bond in the films: Structures of the Ar/H_2

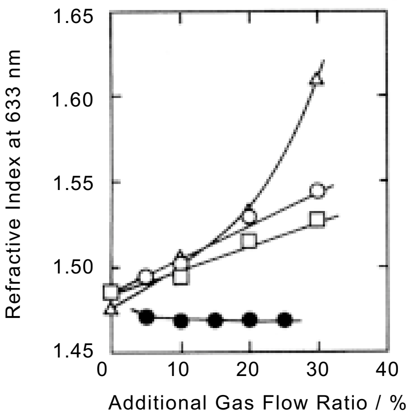

FIG. 2. The optical index of refraction at 633 nm determined by prism coupler measurements for the films indeicated in Fig. 1. Solid circles show the results of Ar/O_2 films.

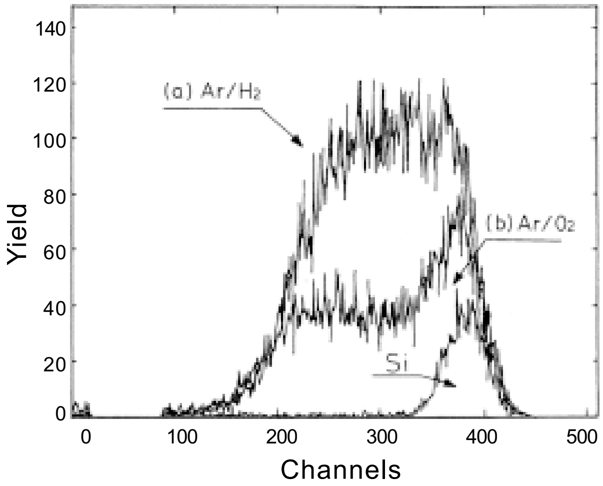

FIG. 3. The ERD depth profiles of hydrogen content in the films deposited at 400 W under (a) Ar/H_2 (20%) gas mixture and (b) Ar/O_2 (10%) gas mixture. The spectrum of the Si wafer is also shown in order to estimate hydrogen amounts due to surface contamination and to calculate hydrogen content of the films.

TABLE I. The composition and mass densities of the films.

Samples	RBS at.%				Film density (g/cm^3)
	H	O	Si	Ar	
Ar/O_2(10%) film	1.5	64.7	32.4	1.4	2.14
Ar/O_2(10%) film	2.3	61.4	35.0	1.3	2.28

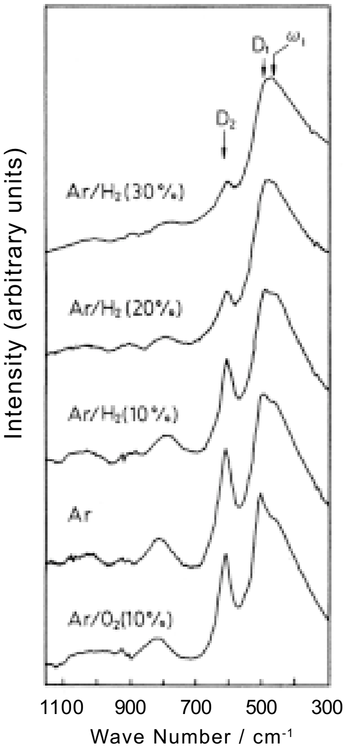

FIG. 4. Raman spectra of the films deposited at rf of 400 W under the H_2 gas flow ratio of 0 to 30 vol %. The spectrum of Ar/O_2 (10%) film deposited at rf of 400 W is also shown. Peaks around 450, 800, and 1050 cm^{-1} are identified quantitatively in terms of the continuous random network (CRN) model (Ref. 8). Additional peaks at 490 (D_1) and 600 (D_2) cm^{-1} correspond to the planar four- and three-fold ring structures in the Si-O-Si network (Ref. 9).

films are considered to be loose compared with those of conventional SiO_2 films. Such structures provide low film stresses, even incorporated Ar in the films applies some distortion (stress) to the sputtered films.

In the present study, it was verified experimentally that our model is adequate for the mechanism of stress reduction of the Ar/H_2 films. The mechanism responsible for the decrease in defects is also to be clarified from the viewpoint of film growth. An improved surface migration of hydrogenated silicon species is thought to be one of the reasons that undesirable silicon oxide clusters, which form the defects, are avoided on a growing film surface. The chemical and physical stability of each bonding species (Si-H, Si-O-Si network, ring, etc.) must be considered. In addition, the estimation of bonding angles around the Si atoms in the hydrogenated films is in progress.

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