Influence of Ar impurities on optical refractive index of sputter deposited a-Si films

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(Received 18 March 1996; accepted 2 January 1997)

Amorphous Si (a–Si) films, sputter deposited under lower Ar pressure conditions, include numerous Ar atoms and exhibit high refractive indices, higher even than that of crystalline Si (c–Si), notwithstanding their lower Si densities. Such behavior in the refractive indices of the films was inconsistent with the conventional explanation considering only the density term in the Clausius–Mossotti relation. In the present study, the contribution of the polarizability changes of the films is proposed in order to account for the result in the refractive index. The molecular orbital (MO) calculations and experiments reveal that the polarizability of the a–Si film is sensitive to change in the angular distortion of the Si–Si bonds brought on by changing deposition conditions. The incorporated Ar atoms are found to cause the distortion in the Si network, leading to higher refractive indices for the less densified films.

I. INTRODUCTION

Optical measurements of amorphous Si (a–Si) films have been carried out in order to investigate their electrical band structure because the a–Si is a suitable material for study of a disordered system.[1] Further, the high refractive indices in the infrared region of the a–Si films have also been noticed, and consequently, the films are being used in infrared optical devices, such as interference filters,[2] laminated polarization splitters,[3,4] etc . The infrared optical refractive indices of the a–Si films were known experimentally to depend on the film deposition conditions and to be greater than that of a crystalline Si (c–Si).[5-7] In general, the densities of the a–Si films are observed to be less than that of c–Si. Therefore, the result, the refractive indices of the a–Si films being higher than that of c–Si, is a very interesting phenomenon because this is an unexpected behavior differing from the conventional explanation considering only the density term in the Clausius–Mossotti relation.[8] In this regards, Brodsky *et al.* reported for a sputter deposited a–Si film that the refractive index at 2 μm in wavelength was reduced from 3.7 to 3.4 after the thermal crystallization process of the film.[9] A decrease in the refractive index was similarly shown by Muro *et al.* for añSi films sputtered at elevated temperatures.[4]

In our opinion, however, the reason for the high refractive indices of a–Si films with low densities has not been clarified enough, yet. As a first step to clarify this phenomenon, we investigated the origin of the refractive index changes in a–Si films deposited under various sputtering conditions. The refractive indices of the films were higher than that of c–Si, despite the lower Si densities of the films, as previously reported. Furthermore, it was found here that the añSi film, which were less densified due to numerous incorporated Ar atoms from the sputtering gas, exhibited higher refractive indices than those of densified a–Si films. As a possible reason for such an inconsistency, we proposed the influence of the polarizability changes of the films on the refractive indices, in addition to the effects from the Si density. The proposal was discussed from both calculations and experiments in terms of the Si–Si bonding configuration of the film.

II. EXPERIMENTS

The amorphous Si (a–Si) films were prepared by magnetron rf-sputtering of a non-doped crystalline Si target. The distance between the target and the substrate was fixed to be 120 mm. Ar was introduced into the sputtering chamber as the sputtering gas at a flow rate of 120 sccm. The substrates were not intentionally heated during film deposition, while the pressure and the supplied rf power were changed, as shown in Table I. The refractive index of the film was calculated from the interference pattern of the reflection spectrum for 1 μm-thick film deposited on the fused SiO_2 Substrate.[9] The Si density and the Ar content were measured by a Rutherford

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TABLE I. Sputtering conditions for a-Si films and their characteristic ties.

Sputtering Parameters			RBS analysis		Raman analysis	
rf power (W)	Ar pressure (Pa)	Deposition rate (nm/s)	Density (g/cm^3)	Composition Si:Ar	TO frequency (cm^{-1})	Γ/2 value (cm^{-1})
375	0.20	0.189	2.05	1:0.07	469	44
560	0.20	0.404	2.14	1:0.07	...	...
750	0.20	0.615	2.17	1:0.06	474	38
375	0.67	0.255	2.16	1:0.04	475	38
560	0.67	0.488	2.23	1:0.03	. . .	. . .
750	0.67	0.715	2.25	1:0.025	474	38

backscattering spectroscopy for the 0.3 μm-thick films on carbon substrates. The films were further investigated by a Raman spectrometer and an x-ray photoemission spectrometer (XPS) to determine the Si–Si bonding configuration.

III. RESULTS

Figure 1 shows the dispersion of the refractive indices on wavelength for the a–Si films prepared under various deposition conditions. As is seen, the refractive indices of the films become larger with an increase of the rf power and with a decrease in the Ar pressure.

Figure 2 exhibits the relationship between the Si density and the sputtering rf power for films deposited at 0.20 and 0.67 Pa. The broken line in the figure indicates the density for a crystalline Si (c–Si). The a–Si films were found to be densified with an increase of the rf power and the Ar pressure. However, the Si densities of the añSi films were lower than that of c–Si (2.33 g/cm^3). The lowest density in the present films was only 88% of the c–Si. Because the Si density of the films was considered to be influenced by the amount of incorporated Ar, the film composition, i.e., the Si : Ar ratio, was measured and listed in Table I. The incorporated Ar amounts tended to be larger in the films deposited under lower Ar pressures. Consequently, the a–Si films prepared under lower Ar pressures exhibited lower film densities due to distorted film structures, as indicated in the next section. We have demonstrated previously similar results concerned with the relation between Ar pressures and film densities for amor-

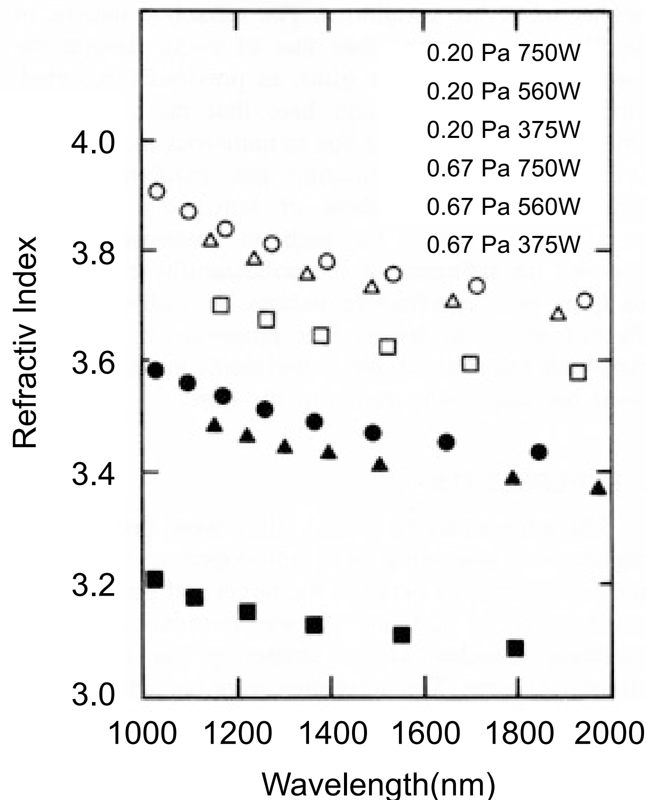

FIG. 1 . Wavelength dependence dispersion of the refractive indices of the films prepared under various deposition conditions.

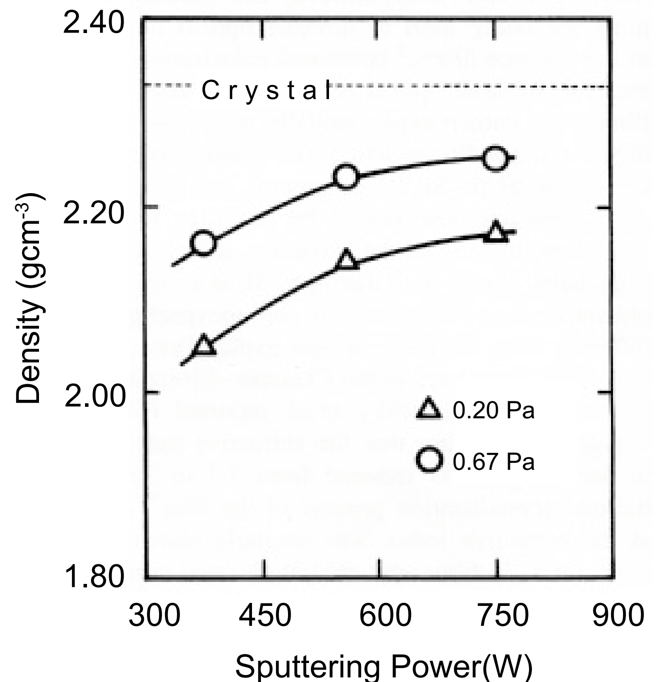

FIG. 2. Relation between the Si densities of the films and the sputtering rf power for two Ar pressures.

phous Ge films.[10] Further, as is shown in Table I, it was observed that the lower Ar pressure, allowing the greater mean free path and energy of the Ar atom, resulted in the low deposition rate for the films. This was probably due to the resputtering of the film surface.

Concerning the influence of the Ar on the a–Si film characteristics, the internal film stress was previously reported to be induced by the distortion of the Si network structure due to the incorporated Ar atoms.[11] Furthermore, the stress was shown to increase with the increase of the Ar amount in the films. [11,12] In the present study, as discussed below, the Ar was also found to cause the above-mentioned change of the refractive index in the a–Si films.

IV. DISCUSSION

The refractive index is known to increase with the density and depends upon the polarizability of materials according to the Clausius–Mossotti relation.[8] In support of this, the a–Si films with the larger refractive indices, which were prepared using higher rf powers, were consistently accompanied by a higher density. When the effect of the Ar sputtering pressures was investigated, however, the refractive indices of the films unexpectedly increased with the decrease of the Si density. These results suggest that, in addition to Si density, the effect of the polarizability of the a–Si films has to be considered to explain the observed variation in the refractive index.

c–Si has a well regulated Si network structure with a constant angle between neighboring Si–Si bonding resulting in a constant polarizability. For the a–Si films, on the other hand, the magnitude of their polarizability seemed to depend on the bonding configuration of the Si. Here, the effect of the variation of the Si–Si bond angle on the film polarizability as the origin of the refractive index change was studied using both calculations and experiments. Figure 3 shows the dependence of bond angle on the polarizability estimated for a $H_3Si–SiH_2–SiH_3$ cluster model, which is the simplest one having a bond angle, by a Modified Neglect of Diatomic Overlap (MNDO) method[13] using the MOPAC ver. 6.[14] In Fig. 3, the magnitude of polarizability of the cluster model was found to change when the bond angle shifted from 120° which is the most stabilized value in bond angle (109° for the c–Si). The calculations supported our presumption that the refractive index of the añSi films was affected by the magnitude of polarizability of the film, provided that the SiñSi bond angle in the a–Si films changed from the bond angle of 109° for the c–Si depending on the film deposition conditions.

In order to verify that the deposition conditions affected the SiñSi bond angles in the films and consequently the refractive index, the present a–Si films were investigated by Raman spectroscopy. The results are listed in Table I, in which the TO band frequency and the half-width of the TO band (Γ/2) are shown. The TO band frequency (main peak) for the c–Si was reported to be about 520 cm^{-1},[15] while it shifted to about 470 cm^{-1} for the present films because of the disorder (i.e., amorphous nature) in the Si network structure.[16] Further, the variation of the Γ/2 values, depending on the film, suggests the existence of a larger distribution in the Si–Si bond angles of the films.[17] It is noted that the film with the lowest density, names "A" hereafter, exhibited the broadest Γ/2, indicating that the Si–Si bond angles were greatly distorted.

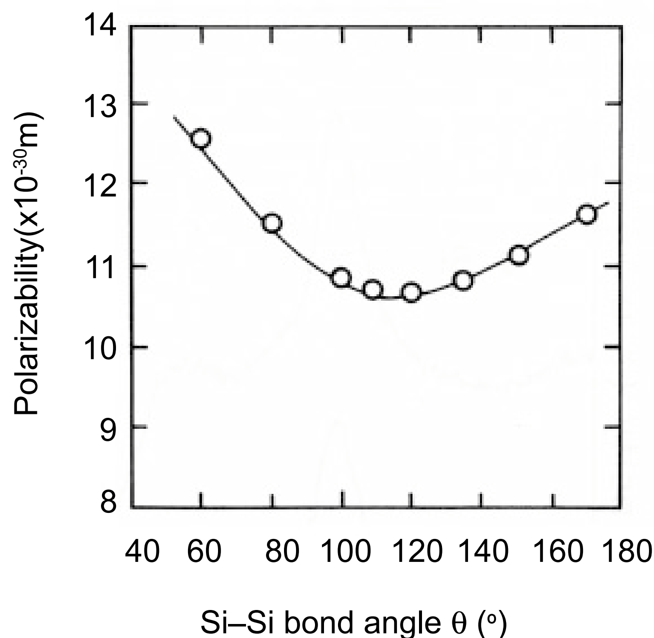

FIG. 3. Dependence of the Si-Si bond angle change on the polarizability estimated for a $H_3Si–SiH_2–SiH_3$ cluster model by the MNDO method[13] with the program of MOPAC ver. 6.[14]

Such distortion in the bond angles was expected to also change the valence band structure of the film. Figure 4 reveals the XPS valence band spectrum for the a–Si film A and the c–Si. As expected, it was indicated that the peak at about 2.5 eV became smaller and shifted slightly toward higher binding energy for film A compared with the c–Si. Further, the peak at about 8 eV also shifted to lower energy and was sharper for film A. Such changes in the valence band spectra for film A could be attributed to a dihedral disorder in the Si–Si bonds, as pointed out by Hayes *et al.*[18] In other words, the electron distribution in the Si valence band of the film was distorted by the dihedral disorder and probably caused the change in the polarizability of the films.

At last, the origin of the angular disorder in the Si–Si bonds was described. With respect to the origin of internal film stresses, we have shown previously that the Ar atoms in the a–Si film induce greater compressive film stress via a volume expansion of the Si network structure.[11] This means

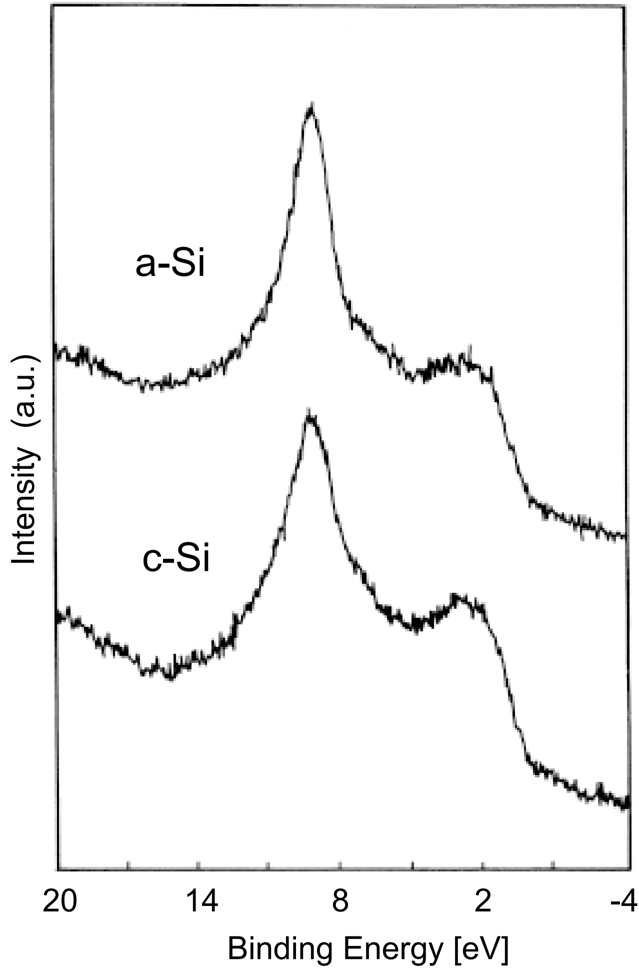

FIG. 4. XPS valence band spectrum for the a–Si film A, exhibited a large rl2 value in the TO-Raman peak, and for the c–Si.

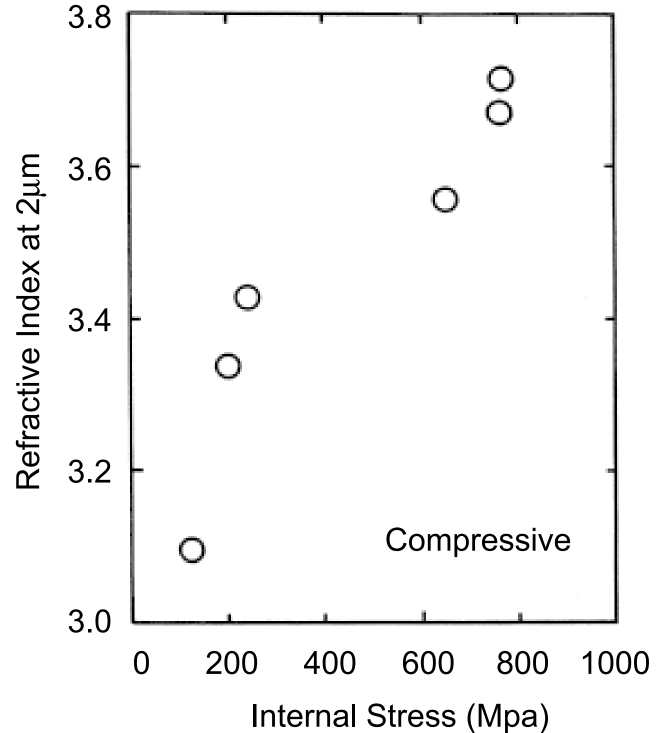

FIG. 5. Relation between refractive indices at 2 μm in wavelength of the films and their internal film stresses. The refractive indices were derived from the results indicated in Fig. 1. The film stresses were measured for 1 μm thick samples deposited on 3 inch Si (100) wafers, according to a method reported previously.[19] All films exhibited compressive stresses.

that the Ar impurities in the film caused the angular distortion of the Si film network. Therefore, a film with greater stress, containing a relatively high concentration of Ar atoms, was expected to exhibit the larger bonding distortion, resulting in the higher refractive index. As shown in Fig. 5, such a relationship between the refractive indices and film stresses was experimentally confirmed for the present a–Si films.

V. CONCLUSION

The a–Si films, sputter deposited under lower Ar pressures, exhibited higher refractive indices despite the fact that they were less densified compared with that of c–Si and with those of the films deposited under higher pressures. It was also observed that the Si network of these less densified films was distorted due to the large amount of Ar atoms trapped in them. Such a structural disorder was found to cause a significant change in the film polarizability from the MO calculations and from both Raman and XPS measurements. As a consequence, the incorporated Ar atoms provided the increase in the refractive index, even though such films were less densified.

ACKNOWLEDGMENTS

The authors are sincerely grateful to Dr. Hirota of Sumitomo Osaka Cement Co., Ltd . and N. Ohta of Hitachi Kasei Co., Ltd. for the advice with the MO calculations. They also wish to thank K. Kubo of Jasco for Raman measurements.

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