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Study of the Time Dependence of the Internal Stress of SiO_2 Optical Thin Films

by

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Abstract

Recently, the demand of the optical thin films as the optical components is increasing. The internal stress of the film is an important factor which relates to the adhesion of the film. In this report, the time dependence of the internal stress of SiO_2 optical thin film is discussed in terms of the optical measurements in the infrared region. The SiO_2 thin films deposited on the glass substrate showed the compression stress irrespective of the vacuum deposition or the ion-assisted deposition. But the sample by the vacuum deposition released the compression stress very much as the time elapsed. The Si-OH molecular bond at 930 cm^{-1} was observed in the FT-IR spectrum of the vacuum deposited sample. It is considered that the Si-OH molecular bond will contribute to release the compression stress of the film.

Keywords: Thin film, SiO_2, Internal stress, Long term

1. Introduction

Recently, the use of optical thin films as electronic components has increased. Accordingly, the lifetime of the optical components must be at least equal to that of the electronic parts. The durability of a film changes depending on the internal stress in the film. Therefore, when depositing high-quality optical thin films, it is necessary to understand the mechanism of the internal stress. A number of studies have been conducted on the changes in stress of optical thin films occurring within a short period of time (several days) immediately after deposition [3]. However, optical thin films often peel off from the substrate after a longer period of time (several months or years). In this research, we aim to understand the causes of the changes that occur over long periods of time in the internal stress of thin films. To do this, the changes in the internal stress of optical thin films were examined over several months (~10000 h). The investigated thin films were composed of SiO_2, which is the most commonly used material with a low refractive index. The SiO_2 films were deposited by conventional vacuum deposition and ion-assisted deposition (IAD).

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2. Experiments

2.1 *Thin film preparation*

SiO_2 films were prepared by using IAD equipment (SID-1100, Sincron Co., Ltd.). The operating mode of this equipment can be changed from IAD mode to conventional vacuum deposition mode without an ion source. The deposition material was heated by an electron beam (EB) in the vacuum deposition mode. The film samples were prepared under three different sets of conditions, where the ion-assisted conditions were changed as shown in Table 1. A square specimen (40 mm × 40 mm) of BK-7 glass at a thickness of 1 mm was used as the substrate. Granular SiO_2 (Canon Optron Co. and Merck KGaA) was used as the coating material. The deposition rate of the film was 0.8 nm/s. O_2 gas was introduced into the chamber, and the substrates were mounted onto a hemispherical substrate holder (dome), which was rotated at the speed of about 30 rpm around the vertical axis.

2.2 ***Stress measurement***

The values of the internal stress of the films were deduced from the radius of the curvature of the substrates as measured with a Fizeau interferometer (F-601, Fujinon Co.) [4]. The internal stress of the films was calculated using the following equation:

$$\sigma = \frac{\delta E_S d_S^{\,2}}{r^2 3(1-\nu) d_F} \qquad (1)$$

where δ is the displacement of the center of the substrate; d_F and d_s are the thickness of the substrate and film, respectively; E_s and ν are Young's modulus and Poisson's ratio of the substrate; and r is the length of the substrate. A schematic diagram of the parameters required for the calculation is shown in Fig. 1. The thickness of the thin film was measured by using a stylus film thickness meter (Dektak3030, Sloan Co.). The time dependence was measured at regular time intervals after the deposited SiO_2 film was taken out of the coating apparatus. The structure of the SiO_2 optical thin films was observed by FT-IR, XRD, XPS and SEM.

Table 1 Parameters of ion gun for IAD method.

	Accelerating voltage (V)	Ion current (mA)
Condition 1	350	350
Condition 2	750	750
Condition 3	1000	800

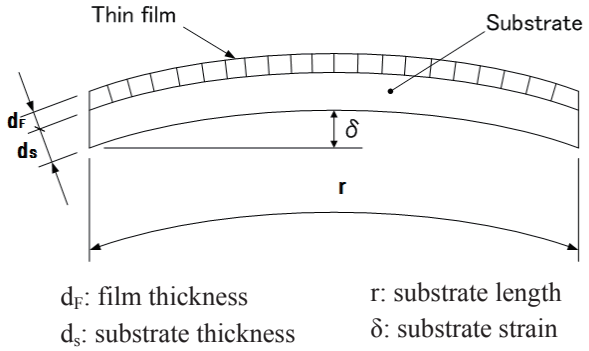


Fig.1 Parameters for calculation of internal stress.

3. Results

3.1 ***Time dependence of internal stress***

The internal stress of each sample was measured as shown in Fig. 2. Compressive stress was observed for SiO_2 thin films prepared under each coating condition. The most notable decrease in internal stress was observed in the film prepared by the vacuum deposition, while the film prepared by the IAD showed a small decrease. Moreover, the stress of the film deposited by IAD increased as the ion beam accelerating voltage and ion beam current were increased. Although the internal stress of the film prepared by vacuum deposition was high soon after the deposition, it decreased rapidly compaired with the film prepared by the IAD.

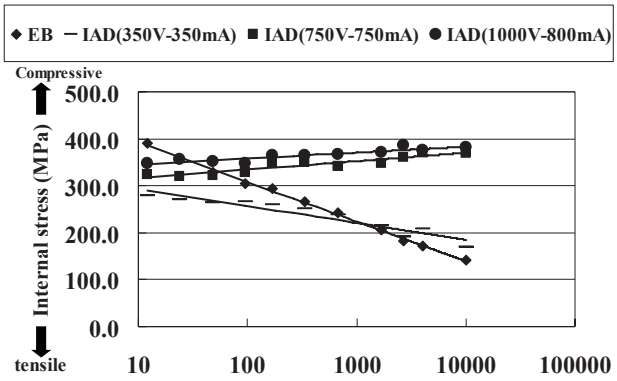


Fig.2 Internal stress of films prepared under various deposition conditions.

3.2 ***Measurement of infrared reflection spectra***

The reflection spectra in the infrared region for each sample are shown in Fig. 3. The shape of the reflection spectra in the infrared region differed depending on the coating processes. The infrared-active SiO_2 bonds are shown in Table 2; the Si-O-Si and Si-OH bonds cause the vibration mode at around 1000~1100 cm^{-1}. Si-OH molecular bonds at around 930 cm^{-1} were observed in the sample with notable changes in internal stress (conventional vacuum deposition sample). However, Si-OH bonds were not observed in the sample for which the changes in internal stress were smaller.

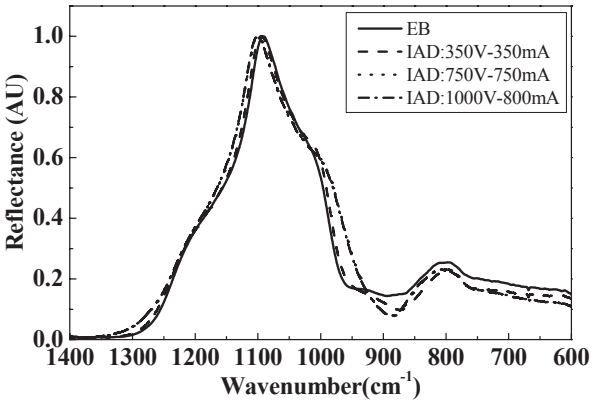


Fig.3 Infrared reflection spectra (12 h later).

The samples prepared by conventional vacuum deposition and low-energy IAD (350V-350mA) exhibited changes in their infrared spectra along with the elapsed time (Fig. 4). However,

the thin films prepared by high-energy IAD (750V-750mA and 1000V-800mA) did not exhibit any changes in their infrared spectra along with the elapsed time.

Table 2 Bonds of silicon molecule [5].

Molecule	Bond	Range (cm^{-1})	Intensity	Note
Si-O-φ	Si-O	970-920	strong	
Si-OH	Si-OH	930-960		broad peak
Si-φ	Si-φ	1435-1425	medium	
	Si-φ	1130-1090	strong	
Si-O-Si	Si-O-Si	800		bending
Si-O-Si	Si-O-Si	1090-1080	very strong	cyclic tetramer
Si-O-Si	Si-O-Si	1080-1050	very strong	cyclic greater than tetramer
Si-O-Si	Si-O-Si	1100-1000	very strong	open chain

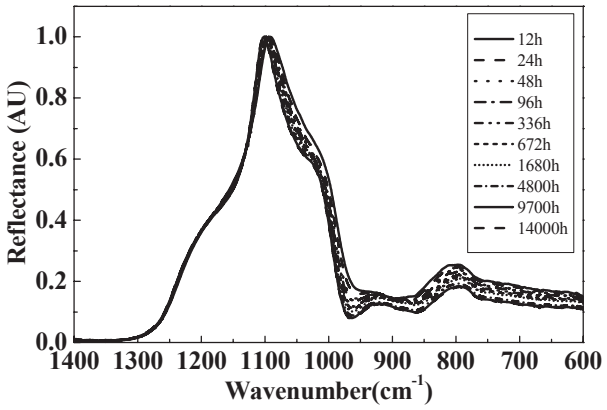


Fig.4 Infrared reflection spectra (EB method).

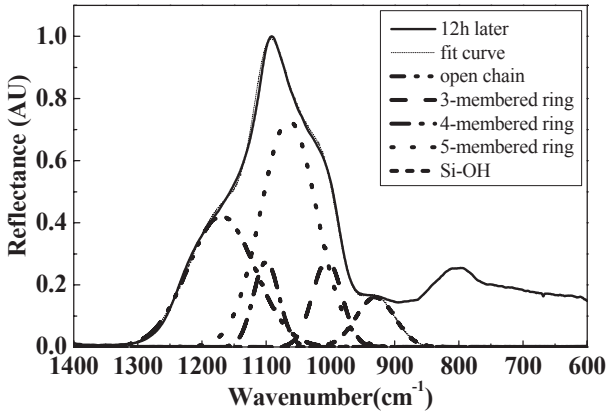
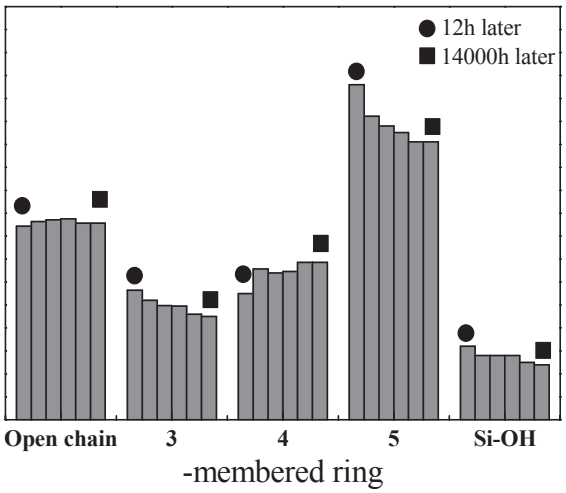
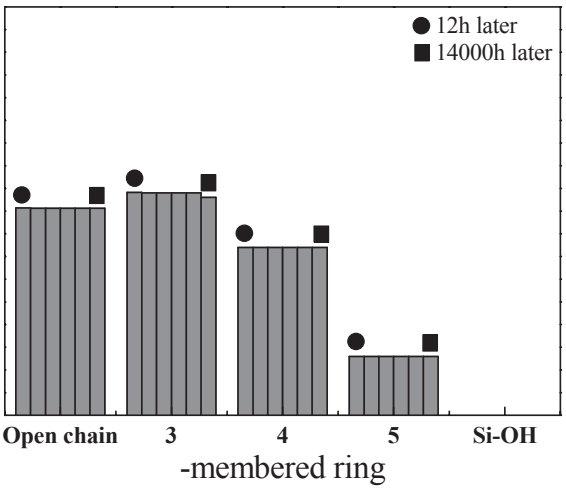


Fig.5 IR reflection peaks for each ring structure and Si-OH (EB method).

SiO_2 film is constructed with tetrahedral structural units. The tetrahedral units form N-membered ring structures. The peaks observed in the infrared reflection spectra are attributable to the various ring sizes (Fig. 5). In the samples that exhibit a large change in internal stress, the number of 3- and 5-membered rings decreased, and the number of 4-membered rings increased (Fig. 6(a)). It has been reported that the 4-membered ring has stable binding energy which is thought to cause the change in N-membered ring [6]. In contrast, the samples with a small change in internal stress did not exhibit a change in ring structure (Fig. 6(b)). Therefore, it is supposed that the molecular structure relates the change in internal stress.



(a) EB method
(sample with large change in internal stress).

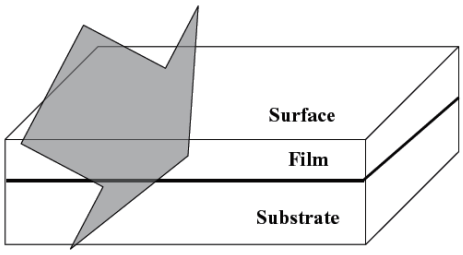


(b) IAD1000V-800mA
(sample with small change in internal stress).

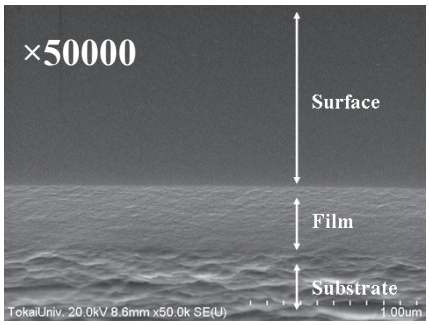
Fig.6 Change in number of N-membered rings.

3.3 *SEM images*

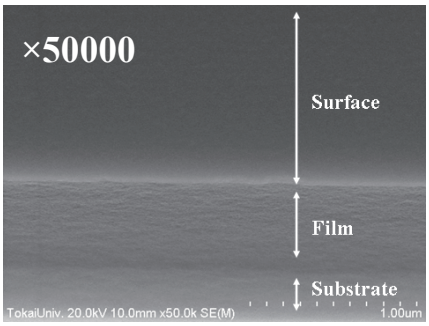
Large magnification FE-SEM measurements were made to examine the macroscopic structure of the films (Fig. 7). Both (b) and (c) show that dense films were formed. Smooth surface, but not voids or columnar structures, were observed in SEM images of the thin films. With IAD at 1000V-800mA (b), a very dense film is formed to the extent that the border with the substrate is almost indistinguishable. Therefore, these results indicate that high-density thin films were deposited over a macroscopic range.



(a) Schematic view of the SEM observation angle



(a) EB method



(b) IAD(1000V-800mA)

Fig.7 SEM images of thin films.

3.4 *X-ray diffraction spectrum*

The X-ray diffraction spectra of the thin films deposited under each condition show only halos (Fig. 8). However, the full width at half-maximum (FWHM) of the peaks differed between each condition. Thus, the structure of Si-O-Si network was thought to depend on the deposition conditions.

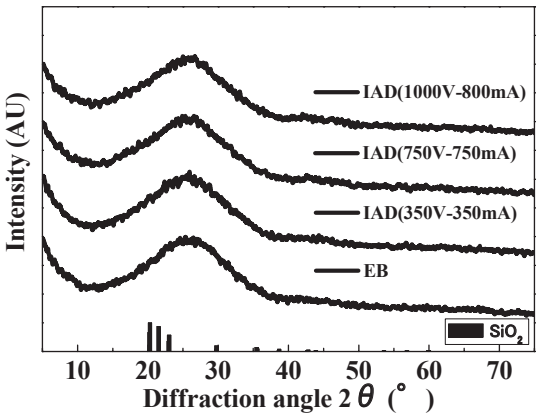
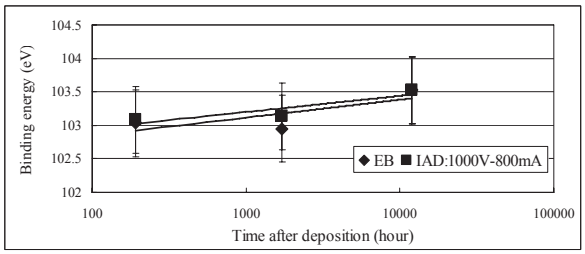


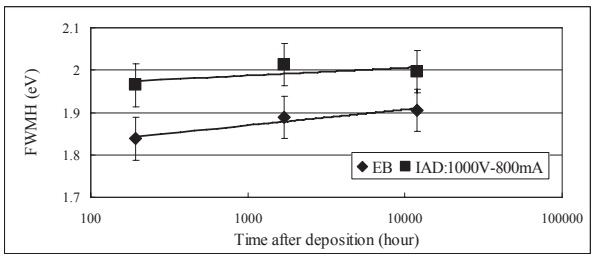
Fig.8 X-ray diffraction spectra.

3.5 *XPS measurement*

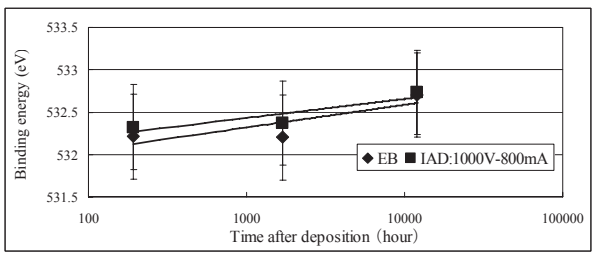
The time dependence of the binding energy and FWHM of the Si-2p and O-1s peaks are shown in Fig. 9. The position of these peaks did not change (Fig. 9(a) and (c)). However, the FWHM of the peaks differed between films prepared by the EB method and IAD at 1000V-800mA (Fig. 9(b) and (d)). Therefore, the bond angles and bond lengths differed. In other words, the structure of the films prepared under each condition is thought to differ.



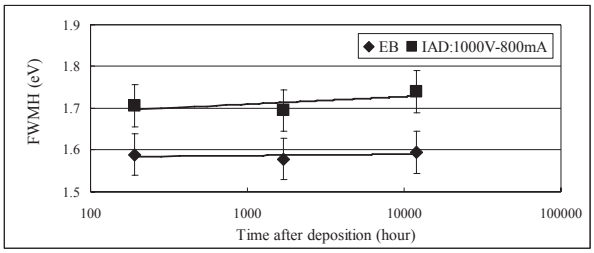
(a) Peak position of Si-2p



(b) FWHM of Si-2p



(c) Peak position of O-1s



(d) FWHM of O-1s

Fig.9 Changes in binding energy and FWHM.

4. Discussion

The change in internal stress along with the elapsed time is greatest for the film deposited by conventional vacuum deposition. The change in the stress of the film deposited by IAD becomes smaller as the power of the ion gun increases. The crystallization of the films was not unequivocally confirmed through SEM and XRD observations. Therefore, it is difficult to consider whether macroscopic factors (e.g., film structure) play a role in the observed changes in film stress. On the other hand, the infrared spectrum showed a satisfactory correlation with the change in stress of the film, which suggests that microscopic factors (molecular bonds) influence the change in stress of the film. In particular, Si-OH molecular bonds at around 930 cm^{-1} were observed in the sample exhibiting a notable change in internal stress (EB method), while Si-OH molecule bonds were not observed in the samples where the change in internal stress was small (IAD: 750V-750mA, 1000V-800mA). In addition, the ring patterns of the tetrahedron structural units that constitute SiO_2 were found to change over time for film prepared by EB method. In contrast, this ring pattern change was not observed in the sample with a small change in internal stress. Therefore, it is thought the change in internal stress is related to the change in molecule structure. Differences in FWHM were observed by XPS analysis; therefore, it is thought that the film structure differed depending on the film deposition conditions.

5. Conclusions

(1) The films prepared by both deposition methods exhibited compressive stress.
(2) The film exhibiting a notable change in internal stress along with the elapsed time showed Si-OH bonding in its infrared reflection spectrum.
(3) It is considered that change in molecular structure along with the elapsed time causes the decrease of the internal stress of the film.

6. Acknowledgements

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