Chemical States of Fluorine Atoms and Laser-Induced Crystallization in rf-Sputtered Thin Films of Amorphous Lead Fluorosilicate

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SYNOPSIS

Amorphous films of lead oxyfluorosilicate were prepared with a rf-sputtering technique, and the distribution profiles of the component elements and chemical states of the fluoride ions were analyzed with an X-ray photoelectron spectrometer. Si atoms with an expanded coordination, O_4Si-F, were present near the surface, and O_3Si-F units were present in the deeper part of the films. Electrical resistance indicated transition to a conduction state for the films containing fluoride ions, while the films were crystallized to precipitate low quartz by the irradiation of He-Ne laser of 3 mW up to 1 sec.

1. INTRODUCTION

In the processes of preparing thin films such as plasma CVD and rf-sputtering gas phase particles of high kinetic energy states lose drastically their energy to be quenched to a solid state. The resulted films therefore may exhibit structures and properties different from those of corresponding bulk solids. The films are also capable of a phase transition between amorphous state and crystalline state induced by laser irradiation and thus capable of giving a new

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microscopic composite structure. A laser beam irradiation of strong intensity may draw series of pits or lines on the films. Therefore, promising materials are such thin films of oxyhalide glasses[1] that have lower melting temperatures and higher halide ion conductivity since (a) they are applicable to photomemories taking advantage of the photoinduced phase transitions between an amorphous state and a crystalline one, (b) they may exhibit increased ionic conductivity due to interaction between ion-conductive matrix and precipitated insulator particles[2], and since (c) such fast-ion conductive channels may even be formed though they are impossible under ordinary conditions. It is thus interesting to investigate laser interaction of such oxyhalide thin films and to discuss suitability for optoelectronic materials.

In the present experiment, we prepared thin films of the F-O-Pb-Si system with an rf-sputtering technique and examined film compositions, chemical states of fluorine atoms, and fluoride ion conductivity as well as we observed laser induced a phase transition of the films.

2. EXPERIMENTAL

Reagent grade SiO_2, PbO, and PbF_2 were weighed so as to give 100g mixtures of a molar ratio 30:40:30. A few drops of 2-butanol were added to the batches before they were mixed well and pressed into a disc of 10cm in diameter. The discs were served as the target material for the rf-sputtering (Shinku Riko SBR-11) after being dried in an air bath for 12 h at 100°C. Slide glasses were used as the substrate. The sputtering conditions are summarized in Table 1. Film compositions were determined X-ray photoelectron spectra (XPS) and F, O and Si depth profiles were measured (Shimadzu ESCA-750). The binding energy for F 1s and O 1s core electrons was calibrated with assuming Si 2p=110.0 eV. Electrical resistance was measured with a two-electrode method and was converted to conductivity with measured film thickness. The phase transition of the films were observed under a scanning electron microscope after irradiating 3 mW He-Ne laser beam (0.2 mm in diameter, and the wave length=632.8nm) for 1/500, 1/60, 1/8, and 1/1sec.

Table 1. Sputtering conditions

rf power	100W
Sputtering gas	Ar
Pressure	0.006 Torr
Sputtering time	45 min
Substrate	Na-Ca slide glass

3.   RESULTS AND DISCUSSION

3.1 XPS depth profiles and chemical states of fluoride ions

The thin films contained black precipitation that was supposed to be colloid particles of metallic lead when the films were sputtered with newly prepared targets or under a high rf power. However, all the sputtered films were X-ray amorphous, irrelevant to the sputtering conditions. A preliminary experiment had shown that fluoride ion content in the films decreased when sputtering was conducted in a longer period on a target. Thus it was suggested that the fluoride ion content was controllable. Figs. 1 and 2 show the depth profiles of the elements composing films F1 and F5, respectively, where the former film had a larger fluoride ion content than the latter. 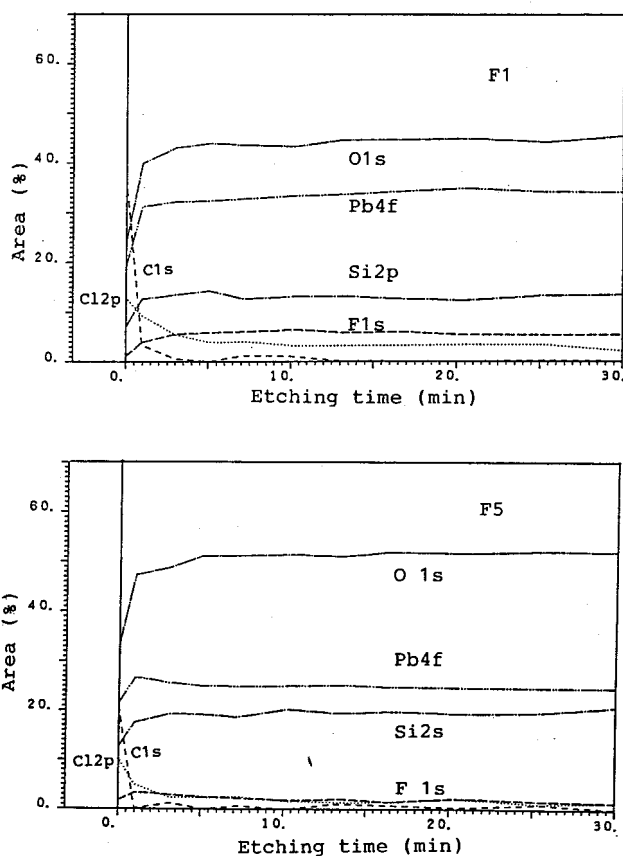It is evident that each element in both films is uniformly distributed in the bulk range deeper than the outermost surface layer (<2 min in Ar ion etching time). It should be mentioned that chloride ions were detected for all the samples. Those ions supposedly were introduced as an impurity from hydrochloric acid solutions employed for cleaning the slide glass substrates. Presence of sodium ions and protons were accordingly expected but they were not detected by XPS. Figure 3 shows the XPS of F 1s core electrons for film F1 at various etching times. Two peaks were observed: the stronger one at 692 eV and the weaker one at 695 eV. According to Osaka et al. [1], the former peak is assigned to
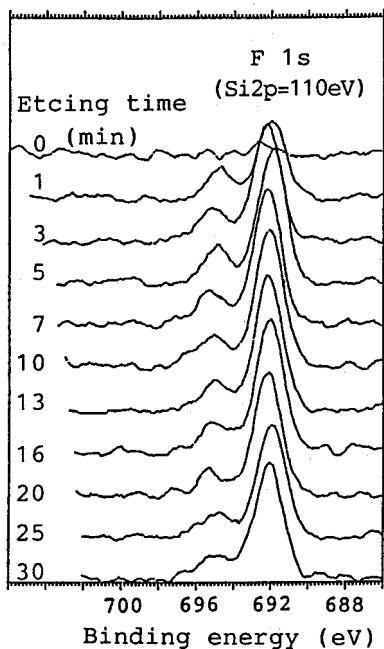
Fig. 1 (top) and Fig. 2(bottom) Depth profiles of component elements for films F1(top) and F5(bottom).

Fig. 3. F1s sprectra for film F1 at various etching times.

the fluoride ions of high ionicity, surrounded by lead ions, and the latter to those of high covalency, bonded to Si atoms. The chemical states of the fluoride ions in film F5 could not referred to because the peaks were so weak due to small fluoride ion contents.

3.2 Oxygen 1s spectra

XPS of O 1s electrons for films F1 and F5 at each etching time were exhibited in Figs. 4 and 5, respectively. The spectra consist of a main peak near 538 eV and a shoulder near 540 eV. Those peaks can be assigned to a non-bridging oxygen atom (NBO) and bridging one (BO), respectively, on the basis of the XPS study on bulk silicate glasses [3-5]. In both series of the spectra, peak position seemed to shift with etching time. However, when the peaks were deconvoluted into
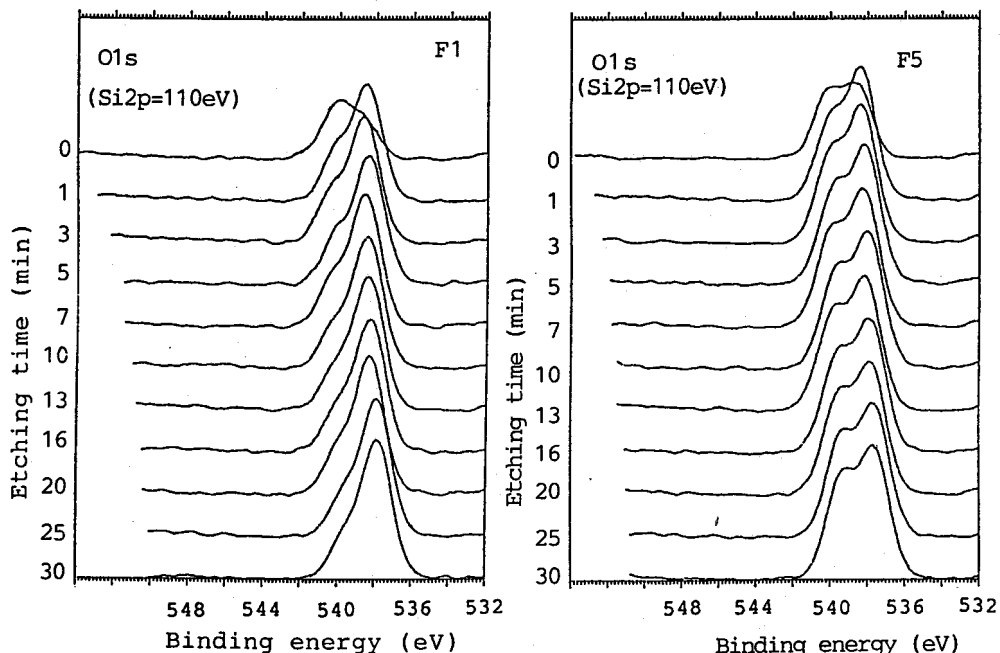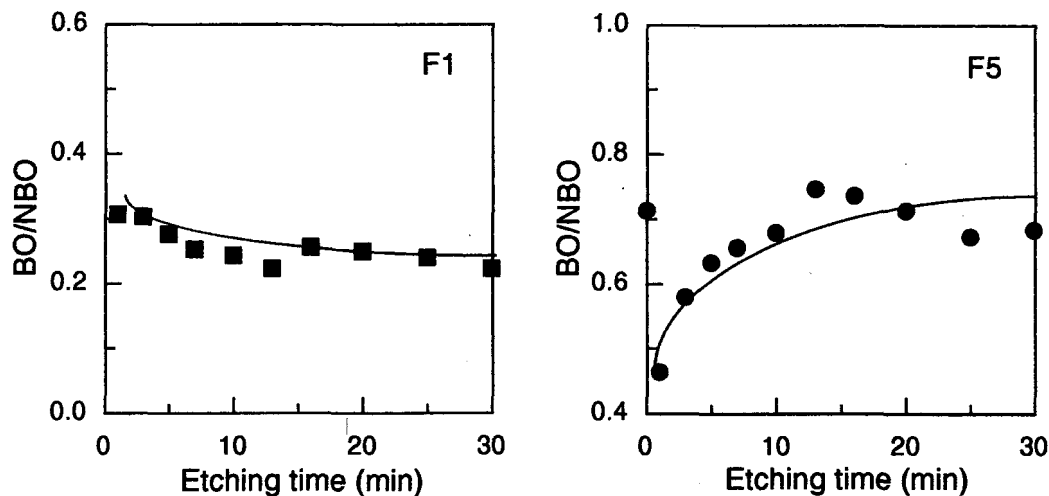

Fig. 4 (left) and 5 (right). O 1s spectra for films F1(left) and F5(right) at various etching times.

two Gaussian peaks, the position of each component peak remained unchanged. Thus the apparent shift in the position was accounted for by varied relative intensity of the two component peaks.

Figs. 6(a)(left) and (b)(right)   The ratio of the fractions of bridging oxygen (BO) and non-bridging oxygen (NBO) as a function of etching time.

3.3 Constitutions of the films

The ratio BO/NBO in the total amount of oxygen atoms can be represented by the peak area ratio of the both O 1s components, and the ratio (F-Si)/(F-Pb) can be evaluated in a similar way based on the F 1s XPS peak area. The ratio BO/NBO was plotted in Figs. 6(a) and (b) for films F1 and F5, respectively, as a function of etching time. It is reasonable that F1 shows a larger ratio BO/NBO at each depth than F5, because F1 has a greater content of fluoride ions as discussed later. In the bulk range of the films deeper than 2 min etching, the ratio BO/NBO slightly decreased in F1 from 0.3 to 0.2, while it showed a slight increase in F5 from 0.5 to 0.7. On the other hand, the ratio of the fluoride ions (F-Si)/(F-Pb) plotted in Fig. 7 increased with a distance from the surface, indicating that the fraction of the covalent fluoride ions increased at the expense of the ionic fluoride ions.

With the results indicated above, continuity of an Si-O network in the films can be correlated with the changed ratio (F-Si)/(F-Pb). We should first reconfirm that (a) the content ratios of the component atoms like F/Si or O/Si are constant as shown in Figs. 1 and 2 and (b) the binding energies of O 1s electrons remain unchanged in Figs. 4 and 5. However, the ratio BO/NBO decreases in the inner
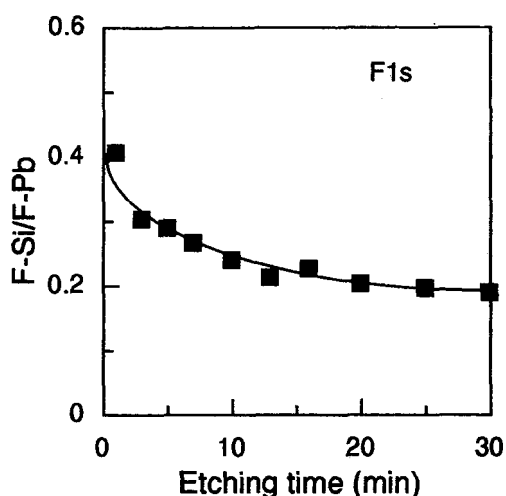
Fig. 7 The ratio of the fractions of fluride ions covalently bonded to Si (F-Si) and those sorrounded by lead (F-Pb).

part of film F1, indicating the increase in the fraction of NBO. That is, average size of the network is greater near the surface whereas worse continuity happens in the deeper part of the films. Then a problem arises whether the change in the network size has been brought by the introduced fluoride ions or not.

Two kinds of Si-F bonds are illustrated in Fig. 8: (a) is the case of Si atoms of four-fold coordination, and (b) is for those with an expanded coordination of 5. The fraction of NBO inc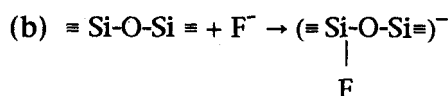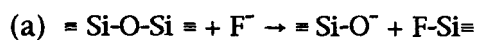reases with formation of Si atoms of type (a), whereas it remains unchanged with formation of type (b). It is evident that the fraction of covalent fluoride ions decreased as the ratio BO/NBO increased. Consequently, the present results can be interpreted as showing (1) Si atoms of type (b) are predominant near the surface; (2) the fraction of type (a) increases in deeper range of the films and the network is gradually broken, accompanying increase in the fraction of the fluoride ions with more ionicity.

3.3 Electrical conductivity and laser induced phase changes

Electrical conductivity σ of film F1 is plotted in Fig. 10 as a function of temperature where the film thickness was 0.9μm. The conductivity of film F5 exceeded the lower limit of the measuring system. σ for film F1 followed an Arrhenius type equation (1)

(a) $\equiv$ Si-O-Si $\equiv$ + F$^-$ → $\equiv$ Si-O$^-$ + F-Si$\equiv$

(b) $\equiv$ Si-O-Si $\equiv$ + F$^-$ → ($\equiv$ Si-O-Si$\equiv$)$^-$
$\qquad\qquad\qquad\qquad\qquad\quad$ |
$\qquad\qquad\qquad\qquad\qquad\quad$ F

Fig. 8 Two types of Si-F bonds are possible. Coordination of Si in (a) remeains 4 but is expanded to 5 in (b).

$$\sigma = \sigma_0 \exp (\Delta E/kT) \qquad\qquad (1)$$

where ΔE is an apparent activation energy of conduction, k and T bear universal meaning. F1 had ΔE= 106.5kJ/mol, 1.2 times as large as ΔE for a bulk glass of
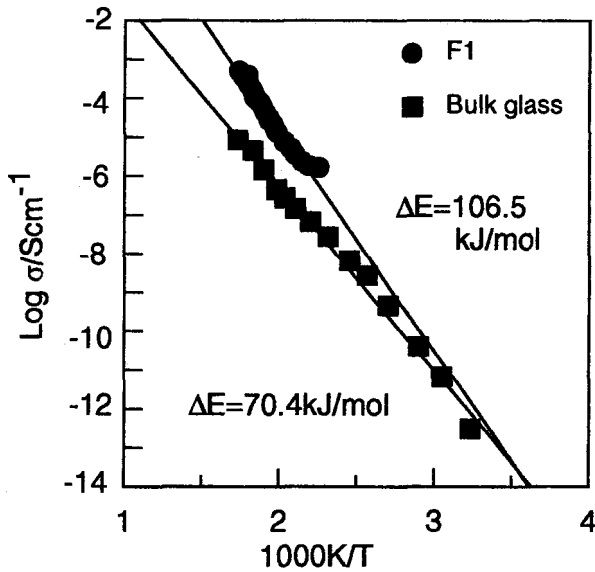
Fig. 9 Electrical conductivity of film F1 shows an Arrhenius type dependence on temperature. that of a bulk glass of composition $3.2PbF_2 \bullet 68.7PbO \bullet 28.1SiO_2$ [6] is also shown.

composition $3.2PbF_2 \bullet 68.7PbO \bullet 28.1SiO_2$ (ΔE= 91.4kJ/mol) [6] and 3 times for a fast ion conductive PbF_2 crystal (ΔE=35.8kJ/mol) [6].

Schematically illustrated in Fig. 11 is a phase transitioned region of films induced by irradiation of 3 mW He-Ne laser for 1/500, 1/60, 1/8, and 1 sec. A 1/500 sec irradiation induced a high phase transition in the area of about 11 µm in diameter as well as an area of 18 µm for weaker degree of transition. That phase transition was known to be crystallization of α-quartz with the XRD patterns of the irradiated films, as shown later. Both area grew from 11 to 17 µm and 18 to 30 µm after 1/60 sec irradiation. After 1/8 sec, the size of the both area grew little though it seemed the degree of crystallization increased slightly. After 1 sec irradiation the size of the center region grew to 19 µm and the surrounding area of a weaker crystallization degree grew to diameter of about 34 µm. The reason for the apparent difference of the two area in the degree of crystallization is not understood yet, but it may be related to intensity distribution of the employed laser beam. Fig. 11 shows X-ray diffraction profiles for film Fl after
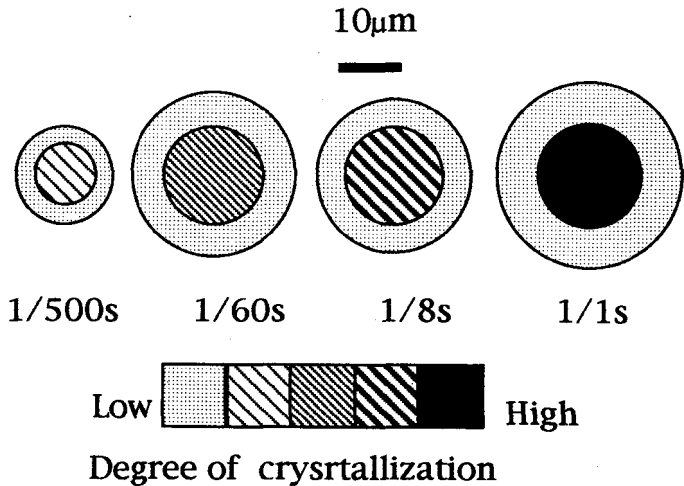

Fig. 10. Schematical illustration of laser induced phase transition region. Laser beam: He-Ne, 3mW, 0.2mm.

being irradiation up to 1 sec. Only a diffraction was observed near 26.2° from low-quartz. It seems strange that a spot with area of only 30 μm in diameter gives a diffraction peak of over 1 kcps. Film F5 showed similar phase transitions, precipitated phase, and diffraction pattern or intensity.
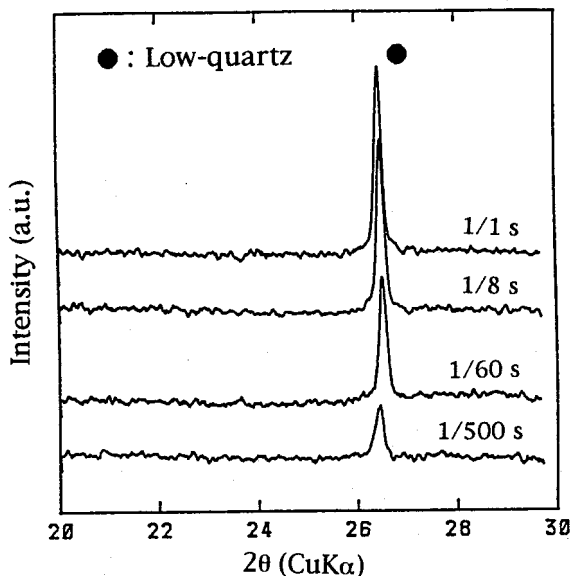

Fig. 11 X-ray diffraction profiles of film F1after being irradiated by the laser for 1/500, 1/60, 1/8, and 1/1s.

Acknowledgment

REFERENCES

1]   A. Osaka, Y-H. Wang, Y. Miura, and T. Tsugaru, J. Mat. Sci., 26 (1991) 2778-82.
2]   K. Shahi and J.B. Wagner, Jr., J. Electrochem. Soc., 128 (1981) 6.
3]   R. Brückner, H-U. Chun, and H. Goretzki, Glastechn. Ber., 51 (1978) 1-7.
4]   B.M.J. Smets and T.P.A. Lommen, J. Non-Cryst. Solids, 46 (1981) 21-32.
5]   B.M.J. Smets and D.M. Krol, Phys. Chem. Glasses, 25 (1984) 113-18.
6]   Y-H. Wang, K. Kobayashi, A. Osaka, Y. Miura, and K. Takahashi, J. Am. Ceram. Soc., 71 (1988) 564-68.