XPS Study of the Effect of Ar-Ion Bombardment and Aging on Surface Properties of Superionic Conducting Glass $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$

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XPS analysis has been used for characterizing the effects of argon-ion bombardment and aging at room temperature on the surface properties of the superionic conducting glass having the composition $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$. Copper and molybdenum ions in this particular glass are found to be significantly reduced by argon-ion bombardment, Cu^{2+} to Cu^0 and Mo^{6+} to Mo^{4+} . The chemical change is attributed to preferential sputtering of iodine and oxygen from the surface of the glass. The concentration of copper on the surface increases and that of molybdenum decreases with aging at room temperature. From aging curves, the diffusion coefficient of copper is estimated to be of the order of $10^{-23} \text{ m}^2 \cdot \text{s}^{-1}$.

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I. Introduction

A number of glasses exhibiting superionic conductivity, especially glasses based on silver halides, have been discovered and their properties have been investigated by a variety of methods⁽¹⁾⁻⁽³⁾. Recently, Cu^+ ion conducting glasses have interest because of their higher electrical conductivity in comparison with systems containing Ag^+ . Transport and structural properties of the glasses containing Cu^+ have measured⁽⁴⁾⁻⁽⁶⁾. The $\text{CuI}-\text{Cu}_2\text{O}-\text{MoO}_3$ glass, which was first synthesized by Machida *et al.*⁽⁷⁾⁽⁸⁾, is one of the typical superionic conducting glasses showing high ionic conductivity at room temperature. The local structures in the $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$ glass have been analyzed using anomalous X-ray scattering⁽⁹⁾. The results provide information on the coordination of ions around Cu^+ and Mo^+ . Local ordering in the glassy oxide matrix produces an environment for copper ions which is similar to that in molten CuI .

In addition to the structural aspects of the superionic conducting glasses, the chemical state and concentration of constituent elements in these materials may be of importance. X-ray photoelectron spectroscopy (XPS) is one of the analytical methods for characterizing the chemical state and concentration on the solid surfaces. However, it should be noted that ion bombardment frequently

applied in XPS measurements may induce changes in the chemical state and concentration of unstable compounds, as exemplified by the system $\text{K}-\text{Cr}-\text{O}^{(10)}$. Since the $\text{CuI}-\text{Cu}_2\text{O}-\text{MoO}_3$ glass also has complex composition, it is useful to investigate the chemical state of ions present on the surface of the glass. According to preliminary results, the surface concentration of the superionic conducting $\text{CuI}-\text{Cu}_2\text{O}-\text{MoO}_3$ glass is considerably different from the bulk concentration, suggesting that the surface concentration of a cleaved surface may change with time. This may be related to the fast migration of ions to the surface from the bulk in the glass. These factors prompted a study of the influence of argon-ion bombardment and aging at room temperature on the chemical state and concentration of species on the surface of the $\text{CuI}-\text{Cu}_2\text{O}-\text{MoO}_3$ glass. XPS was used for characterizing the behavior of the glass having the composition $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$.

II. Experimental

The $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$ glass was prepared using a method reported previously⁽⁷⁾. High-grade chemical reagents CuI , Cu_2O and MoO_3 were weighed, thoroughly mixed and then heated in a silica tube under nitrogen gas. After melting at 970 K, the glass was obtained by quenching into ice water. They were cut into small blocks of about 2 mm diameter and 4 mm length, which were inserted in a sample holder and cleaved in air just before XPS measurements. Although a sample cleaved under ultra high vacuum was also investigated, the XPS results were fundamentally similar to those of samples cleaved in air. Therefore, the influence of adsorption of gases from air

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on the surface may be insignificant.

XPS measurements were carried out using PHI-5600, in which the incident X-ray beam was Mg K α . Mainly, Cu 2p, I 3d, Mo 3d and O 1s XPS spectra were recorded. The energy positions of the spectra were calibrated using Au 4f at 84.0 eV. X-ray excited Auger electron spectra for copper were also recorded to study the chemical state of copper⁽¹¹⁾⁽¹²⁾, since the chemical shift of Cu 2p XPS spectra is very small between Cu⁰ and Cu⁺. The effect of aging after cleavage on the surface concentration was investigated by keeping the samples in air at room temperature. Ion bombardment of glass sample by irradiated argon ions of 3 keV was carried out using an attached ion gun.

III. Results and Discussion

1. Changes in XPS spectra of the glass (CuI)_{0.3}-(Cu₂O)_{0.35}(MoO₃)_{0.35} caused by argon-ion bombardment

Figure 1(a) shows a Cu 2p XPS spectrum from the glass (CuI)_{0.3}(Cu₂O)_{0.35}(MoO₃)_{0.35} bombarded by argon ions for 600 s, which correspond to a steady-state stage in sputtering profiles. A Cu XPS spectrum from this glass as cleaved is shown in Fig. 1(b). The Cu 2p_{3/2} peak is located at 932.8 $\pm$ 0.3 eV in the both cases, in agreement with the peak energy in several Cu⁺ compounds reported⁽¹³⁾. Thus, the argon ion bombardment does not appear to affect the peak significantly. A small satellite peak corresponding to Cu²⁺ is observed in both cases at about 954 eV, which suggests the presence of a small amount of Cu²⁺ ions. The difference in the peak positions of oxide (Cu⁺(Cu 2p_{3/2}: 932.6 eV)) and metallic copper (Cu⁰(Cu 2p_{3/2}: 932.7 eV)) is very small. Cu LMM AES spectra are

more diagnostic of the reduced state of copper⁽¹¹⁾⁻⁽¹³⁾. Cu L₃M₄₅M₄₅ XAES (X-ray excited Auger Electron Spectroscopy) spectra or the sputtered and cleaved samples were measured. The results are displayed in Fig. 2. The spectrum of Cu L₃M₄₅M₄₅ XAES for the cleaved sample correlate with the signals from an oxide (Cu⁺(Cu 2p_{3/2}: 916.2 eV)), whereas the spectrum for the sputtered sample show the presence of metallic copper (Cu⁰(Cu 2p_{3/2}: 918.6 eV))⁽¹³⁾. These results suggest that most of copper ions in this glass are reduced to the metallic state by argon-ion bombardment.

Mo 3d XPS spectra from the glasses bombarded by ions and cleaved in air, are given in Figs. 3(a) and (b), respectively. The Mo 3d_{5/2} and Mo 3d_{3/2} peaks are located at 232.3 $\pm$ 0.3 and 235.1 $\pm$ 0.3 eV in the cleaved sample, respectively, almost consistent with the binding energies of Mo⁶⁺ in MoO₃. Thus, most of the molybdenum in this glass is present as Mo⁶⁺. Additional Mo 3d_{5/2} peak at 229.3 eV and Mo 3d_{3/2} peak at 232.5 eV, comparable to the binding energies of Mo⁴⁺ in MoO₂, appears after bombardment. This suggests that a significant amount of Mo⁴⁺ ions are formed on the surface of this glass by argon-ion bombardment, and the degree of reduction of molybdenum ions is comparable with the case of copper ion.

Figures 4(a) and (b) show I 3d XPS spectra from the sample bombarded by argon ions and cleaved in air, respectively. The I 3d_{5/2} and I 3d_{3/2} peaks are located at 619.7 $\pm$ 0.3 and 631.9 $\pm$ 0.3 eV, respectively, in both cases. O 1s XPS spectra from the ion-bombarded and cleaved glass are given in Figs. 5(a) and (b), respectively. Again, the main peak position located at 530.3 $\pm$ 0.3 eV is not affected by the ion bombardment, although the shape of the peak is somewhat affected by ion bombardment. Thus, although the chemical state of these anions

Fig. 1 Cu 2p XPS spectra of the (CuI)_{0.3}(Cu₂O)_{0.35}(MoO₃)_{0.35} glass (a) bombarded by argon ions, and (b) cleaved in air.

Fig. 2 Cu L₃M₄₅M₄₅ XAES spectra of the (CuI)_{0.3}(Cu₂O)_{0.35}(MoO₃)_{0.35} glass (a) bombarded by argon ions, and (b) cleaved in air.

Fig. 3 Mo 3d XPS spectra of the $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$ glass (a) bombarded by argon ions, and (b) cleaved in air.

Fig. 5 O 1s XPS spectra of the $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$ glass (a) bombarded by argon ions, and (b) cleaved in air.

Fig. 4 I 3d XPS spectra of the $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$ glass (a) bombarded by argon ions, and (b) cleaved in air.

in the surface are unchanged by the argon-ion bombardment, other effects such as change in composition need to be considered.

The surface composition of the samples was estimated from the spectra using sensitivity factors of elements. The surface concentration of the cleaved sample was 34% Cu, 46% O, 8% Mo and 12% I, which is nearly the bulk composition, while the surface concentration of a bombarded sample was 39% Cu, 19% Mo, 39% O and 3% I. These results indicate that significant preferential sputtering of oxygen and iodine takes place during ion bombardment. The imbalance between cations and an-

ions induced by the preferential sputtering may be responsible for reduction of copper and molybdenum on the surface of this glass, as shown in Figs. 2 and 3, respectively.

2. Effect of aging on surface concentration

Figures 6(a) and (b) show wide 2p XPS spectra from the glass $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$ just after cleavage in air, and after aging in air for 6000 s, respectively. These spectra clearly show significant changes in the surface concentration with aging. The Mo 3d and I 3d XPS peaks and the others related to Mo and I decrease considerably on aging, whereas the peaks associated with copper show a relative increase. These facts indicate that copper is enriched on the surface during aging at room temperature. The driving force for the copper enrichment is probably associated with changes in surface energy by composition of the surface layer⁽¹⁴⁾, since an increase in the oxygen concentration suggesting oxidation and a significant change in the state of copper (*e.g.* Cu^+ to Cu^{2+}) by aging was not observed in XPS spectra.

In order to analyze the kinetics of the aging process, changes in the surface concentration of copper, molybdenum, iodine and oxygen have been measured as a function of time. The results are plotted as a function of a square root of aging time after cleavage of the sample in Fig. 7. The concentration is calculated simply using sensitivity factors for elements to follow the relative changes in the surface concentration of the constituent elements. In spite of the simple assumptions used for quantitative estimation, systematic increases in the copper concentration and decreases in the molybdenum and iodine concentration with aging time are observed. Although the oxygen concentration shows a slight decrease with increasing time, the decrement is too small to warrant discussion. The aging behavior is assisted by the fast ion

Fig. 6 Wide XPS spectra of the $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$ glass (a) cleaved in air, and (b) aged at room temperature for 6000 s.

Fig. 7 Changes in the surface concentration of Cu, Mo, I and O with aging time at 295 K.

transport in the glass⁽⁵⁾. The isothermal enhancement of surface concentration of copper in the glass shown in Fig. 7 can be analyzed by a method, analogous to that used for aging processes. If this process is considered as the surface segregation, the segregation kinetics can be described mathematically⁽¹⁵⁾. The equation for the surface concentration C_s in the early stage is given by,

$$C_s = C_0 [1 + (2/a)(Dt/\pi)^{1/2}] \quad (1)$$

where C_0 is the bulk concentration, a the segregated layer thickness, D the diffusion coefficient and t time⁽¹⁶⁾. If the segregated layer is assumed to be 0.2 nm, being nearly the diameter of copper ion, one can obtain a value of $0.8 \times 10^{-23} \text{ m}^2 \cdot \text{s}^{-1}$ for the diffusion coefficient at 293 K and $1.2 \times 10^{-23} \text{ m}^2 \cdot \text{s}^{-1}$ at 295 K, using eq. (1). These values are much higher than the diffusivity of copper in

Fig. 8 Arrhenius plot of diffusion coefficient of copper in the glass $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$, together with interdiffusion coefficients in the previous work⁽⁵⁾.

pure copper at room temperature, which is estimated to be of the order of $10^{-43} \text{ m}^2 \cdot \text{s}^{-1}$ by extrapolation of high temperature data⁽¹⁷⁾. Therefore, the high diffusivity of copper in the glass is related to the characteristic structure of the glass. The local environment of part of the Cu^+ ions in the $\text{CuI-Cu}_2\text{O-MoO}_3$ glass is similar to that in molten $\text{CuI}^{(9)}$. In addition, interdiffusion coefficients obtained at about 600 K in high conductivity system $\text{AgI-CuI}^{(5)}$ may be compared with this present results. The temperature dependence of their values is shown in Fig. 8. The both sets of data were measured by different methods, in different temperature ranges. Nevertheless, the correspondence between two sets of data is reasonable, since the fast diffusion of copper ions is involved in both the cases.

IV. Concluding Remarks

XPS spectra were used for characterizing the influence of argon-ion bombardment and aging at room temperature on the surface concentration of different species in the glass with the composition $(\text{CuI})_{0.3}(\text{Cu}_2\text{O})_{0.35}(\text{MoO}_3)_{0.35}$. It is found that:

(1) Argon-ion bombardment induces reduction of copper and molybdenum ions at the surface of the glass, Cu^{2+} to Cu^0 and Mo^{6+} to Mo^{4+} . The chemical state of iodine and oxygen is not significantly altered. The chemical changes associated with copper and molybdenum may be explained by the imbalance between cations and anions induced by preferential sputtering of iodine and oxygen.

(2) With aging time at room temperature, the concentration of copper at the surface increases, whereas the concentrations of molybdenum and iodine decrease. This may result from the fast diffusion of copper ions in the glass. From the study of the enrichment process of copper to the surface as a function of time, the diffusion coefficient of copper at room temperature was estimated to be of the order of $10^{-23} \text{ m}^2 \cdot \text{s}^{-1}$.

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