XPS Study of Surface Properties in the Superionic Conducting Glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$ Bombarded by Ion and Electron Beams

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ABSTRACT

XPS analysis has been used for characterizing the effects of Ar ion and electron beam bombardment on the surface properties of superionic conducting glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$. Cations in this particular glass were significantly reduced by Ar ion bombardment. This is attributed to the imbalance between cations and anions induced by preferential sputtering of anions. The O 1s peak is shifted to higher binding energy by Ar ion bombardment. This is mainly attributed to the sputtering of silver in preference to molybdenum. The electron beam bombardment increases the surface concentration of silver and induces a change in the chemical state of silver from Ag^+ to Ag^0. The isothermal enrichment process of silver at surface can be described by the Johnson-Mehl-Avrami equation; $W = 1 - \exp[-(3.74 \times 10^{-4} t)^{1.1}]$.

1. INTRODUCTION

A group of glasses containing silver halides are well known as "superionic conducting glasses" /1,2/ because of their high ionic conductivity at room temperature. The conductivity of these glasses is of the order of 10^{-2} $\Omega^{-1}cm^{-1}$, comparable to those of the aqueous electrolytes containing NaCl and $AgNO_3$ /1/. The glass belonging to the system AgI-Ag_2O-MoO_3 is one of the typical superionic conducting glasses. This glass system has been studied by different techniques to delineate the relationship between structure and properties, particularly with reference to their high ionic conductivity /3,4,5/. A recent structural study using an advanced X-ray diffraction method /5/ indicates that the glass system can be visualized as a network structure consisting of MoO_4 tetrahedral units along with Ag^+ and I^- ions.

The chemical state of species in a glass has a strong influence on its transport and dielectric properties /6,7/. Thus, information about the chemical state would be useful for the understanding of Ag^+ conduction mechanism in the glass. X-ray photoelectron spectroscopy (XPS) is one of the powerful techniques for characterizing the chemical state and concentration on the solid surface. In XPS measurements, ion bombardment is frequently applied for the purpose of inducing changes in the chemical state and concentration, as exemplified by studies for the CuI-Cu_2O-MoO_3 system /8/. Besides, electron beam bombardment is expected to induce change of the surface state of glass due to the fast ion migration. However, so far, no attempt has been made to characterize the chemical binding state in AgI-Ag_2O-MoO_3 glass. This consideration has prompted an XPS study of the chemical state of species and concentration of elements on the surface of the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$.

2. EXPERIMENTAL PROCEDURE

The glass sample having the composition of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$ was prepared from high-grade chemical reagents AgI, Ag_2O and MoO_3 (Wako Chemical Co. Ltd.). Calculated amounts of the materials were weighed, dried in the oven and then heated in a silica glass tube. After melting at 770 K, the melt was quenched in a pure copper mold. Samples were fabricated with dimensions of $1\times2\times5mm^3$. The samples for XPS measurements were cleaved in air. 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 on the surface is considered to be insignificant in this work.

XPS measurements were carried out using Ulvac Φ-5600 in which the incident X-ray beam was monochromated Al K_α(1486.6 eV). Mainly Ag 3d, I 3d, Mo 3d and O Is 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 (XAES) for silver were also recorded to investigate the chemical state of silver, since the chemical shift in Ag 3d XPS spectra is very small between Ag^0 and Ag^+. The Ar ion bombardment of glass sample by irradiated Ar ions was carried out for 300 s using attached ion gun with acceleration voltage 3 keV. Electron beam bombardment with beam characteristics of 20 mA - 30 eV was carried out for maximum 2 hours by using the attached electron gun.

3. RESULTS AND DISCUSSION

3-1. The effect of Ar ion bombardment on XPS spectra.

Figures 1 (a) and (b) show Ag 3d XPS spectra of the $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$ glass as cleaved and bombarded by Ar ions for 300s which generates a steady state sputtering profile. While the Ag $3d_{5/2}$ peak and $3d_{3/2}$ peak of the as cleaved sample are located at the 368.1 eV and 374.1 eV, respectively, those of the Ar ion bombarded sample are located at 368.4 eV and 374.0 eV. Since the difference of binding energies between Ag^+ and Ag^0 is small, it is not easy to discern how significantly the chemical state is changed by Ar ion bombardment. A better diagnosis of the reduced state of silver /9/ was obtained in Ag M_4VV XAES spectra. Ag M_4VV XAES spectra of the as-cleaved and Ar ion bombarded samples are shown in Fig. 2 (a) and

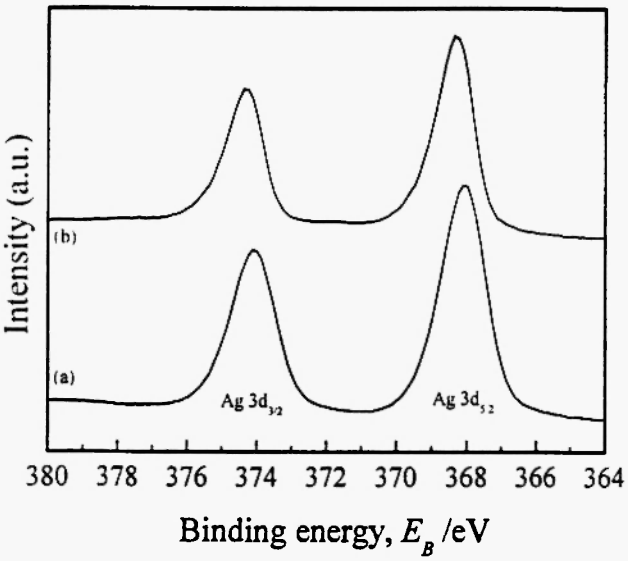

Fig. 1: Ag 3d XPS spectra of the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$; (a) cleaved in air, and (b) bombarded by Ar ions.

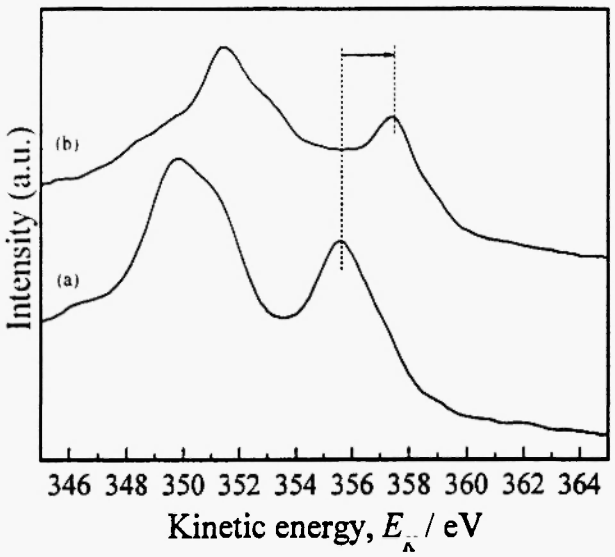

Fig. 2: Ag M_4VV XAES spectra of the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$; (a) cleaved in air, and (b) bombarded by Ar ions.

(b), respectively. The peak position of as-cleaved sample (a) is 355.5 eV and that of Ar ion bombarded sample (b) is 357.5 eV. The former corresponds to the signal from Ag^+ (e.g. 355.6 eV for AgI) /9/, whereas the latter corresponds to that from metallic Ag^0 (e.g. 357.6 eV for metallic Ag) /9/. This indicates that Ag^+ on the glass surface can be reduced to metallic Ag^0 by Ar ion bombardment.

Figure 3 shows I 3d XPS spectra from the samples as-cleaved and bombarded by Ar ions. I $3d_{5/2}$ and $3d_{3/2}$ peaks are located at 619.6 eV and 631.2 eV for as-cleaved sample, and 619.5 eV and 631.1 eV for Ar ion bombarded sample, respectively. Although the peak height is altered by Ar ion bombardment, the peak positions are almost unchanged.

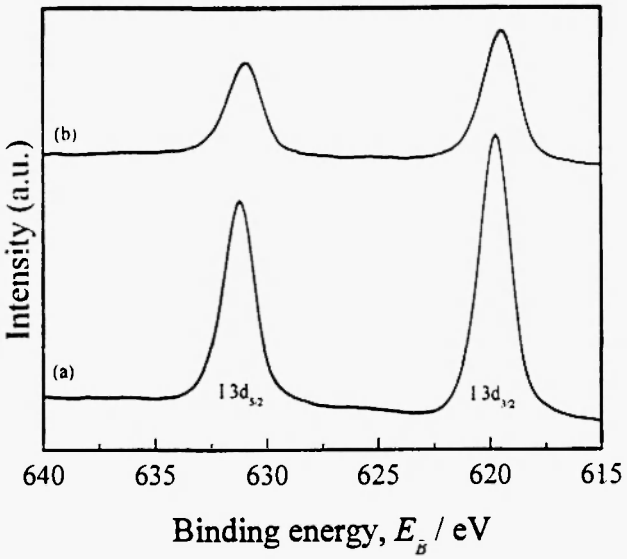

Fig. 3: I 3d XPS spectra of the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$; (a) cleaved in air, and (b) bombarded by Ar ions

The Mo 3d XPS spectra from the glasses as-cleaved and bombarded by Ar ions are shown in Fig. 4. The peak positions of Mo 3d's for MoO_2 and MoO_3 are also shown in the figure for comparison. Electronegativities of O, Mo and Ag are 3.44, 2.16 and 1.93, respectively. Since the electronegativity difference between silver and oxygen is greater than that between molybdenum and oxygen, the electron density of molybdenum in Mo-O-Ag bonding is higher than that in the Mo-O-Mo case. Hence, the replacement of Mo-O-Mo by Mo-O-Ag

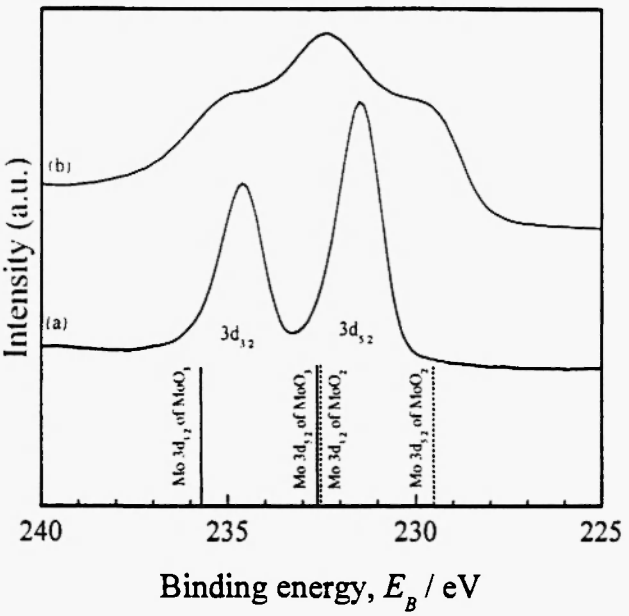

Fig. 4: Mo 3d XPS spectra of the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$; (a) cleaved in air, and (b) bombarded by Ar ions.

bonding enhances the electron density of molybdenum, and this will induce the peak shift of molybdenum toward the lower energy side. The Mo $3d_{5/2}$ and $3d_{3/2}$ peaks of the as-cleaved sample are located at 231.5 eV and 234.6 eV, respectively. They are lower than 232.6 eV and 235.7 eV of MoO_3 /9/. From the electronegativity point of view, it would appear that a part of Mo-O-Mo bonds are replaced by Mo-O-Ag bonds when silver is added to the oxide glass matrix. However, Mo $3d_{5/2}$ and $3d_{3/2}$ peaks are found to be shifted to 230.0 eV and 232.4 eV by Ar ion bombardment. The latter correspond to those of Mo^{4+} in MoO_2 /9/ (229.5 eV for Mo $3d_{5/2}$ and 232.5 eV for Mo $3d_{3/2}$). This result indicates that a significant amount of Mo^{4+} ions are formed on the surface of this glass by Ar ion bombardment.

O 1s XPS spectra from the as cleaved and Ar ion bombarded samples are given in Fig. 5 together with the positions of O 1s peaks in Ag_2O and MoO_3 for comparison. The O 1s peak of the as-cleaved sample is located at 529.9 eV which is the middle of the values for MoO_3 /9/ (530.9 eV) and Ag_2O /9/ (529.2 eV). This result also suggests the existence of Mo-O-Ag bonding in the glass. The O 1s peak of the glass is shifted from

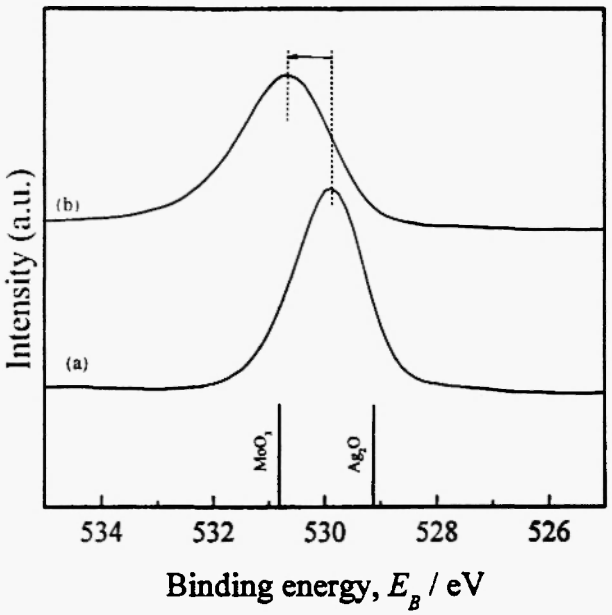

Fig. 5: O 1s spectra of the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$; (a) cleaved in air, and (b) bombarded by Ar ions.

529.9 eV to 530.6 eV by Ar ion bombardment.

The peak shift by Ar ion bombardment may be explained by considering the balance of constituent elements. Figure 6 shows a change in relative mole ratio of two elements by Ar ion bombardment. The relative mole ratio [%I]/[%Ag] decreases from 0.43 to 0.29, [%Ag]/[%O] from 1.21 to 0.29, and [%O]/[%Mo] from 3.40 to 2.15, respectively. These results indicate that the order of preferential sputtering is I > Ag > O > Mo. The ratio [%anions]/[%cations] also decreases from 0.99 to 0.83. This suggests that the reduction of cations is attributed to imbalance between anions and cations arising from preferential sputtering of anions. The ratio [%Ag]/[%Mo] decreases from 4.0 to 1.1. The preferential sputtering of silver to molybdenum observed in this glass should be an origin for the shift of O 1s peak to higher energy as shown in Fig. 5.

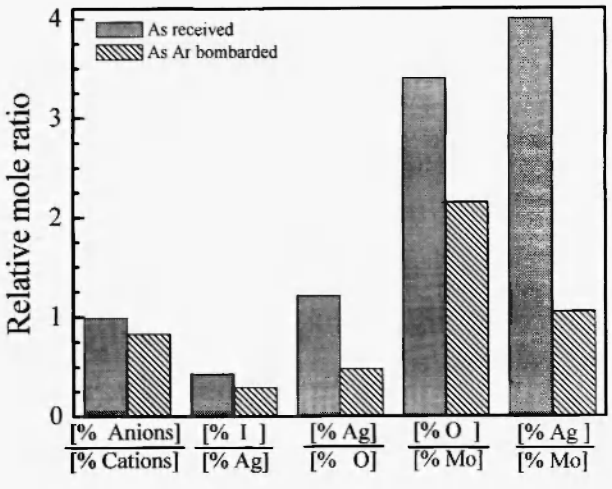

Fig. 6: Change in relative mole ratio of two element by Ar ion bombardment in the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$.

3-2. The effect of electron beam bombardment on XPS spectra.

Figure 7 shows wide XPS spectra for the $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$ glasses cleaved in air and bombarded by electron beam for 7200 s. The spectrum for the sample aged at 323 K for 7200 s is also shown for comparison. The peaks associated with silver including Ag 3d peak are found to be enhanced conspicuously by electron beam bombardment, whereas it is insensitive to aging at 323 K. This indicates that silver is enriched on the surface of the sample by electron bombardment. Changes in surface concen-

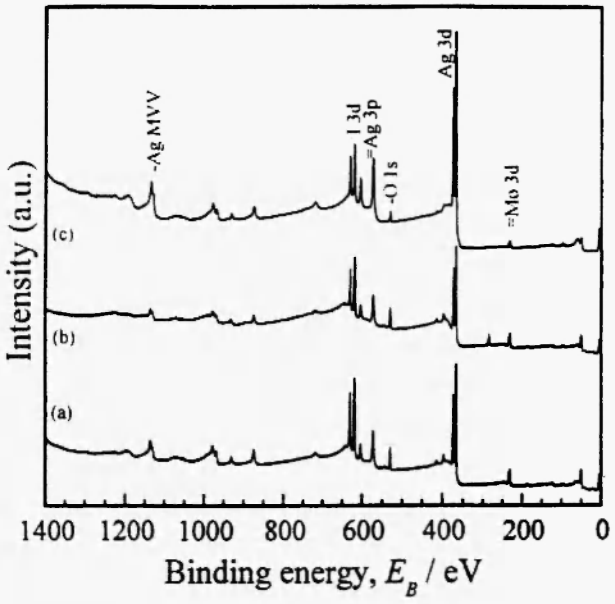

Fig. 7: Wide spectra of the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$; (a) cleaved in air, (b) aged at 323K for 7200 s, and (c) bombarded by electron beam.

tration of Ag, I, Mo and O are shown in Fig. 8 as a function of electron beam bombardment time at 293 K. It shows more clearly the effect of electron beam bombardment on the surface concentration. It is apparent that concentration of silver increases with increasing electron beam bombardment time.

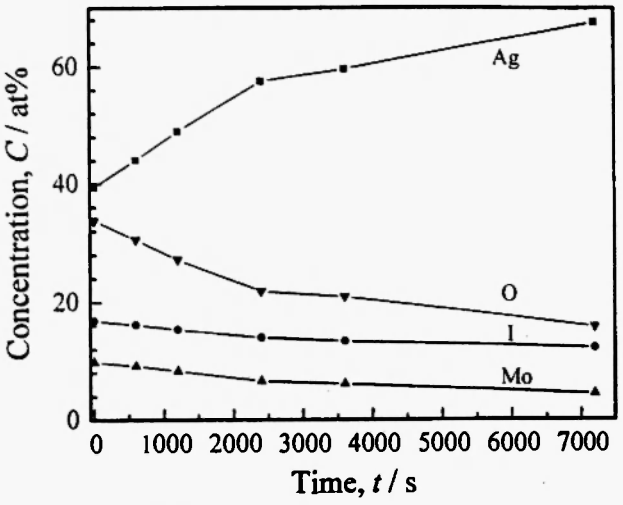

Fig. 8: Changes in the surface concentration of Ag, Mo, I and O with time during electron beam bombardment at 293 K.

The Ag M_4VV XAES spectra from the glasses as-cleaved, bombarded by argon ions and aged at 323 K are illustrated in Fig. 9. The peak of glass bombarded by argon ions is found to be located at 357.4 eV, whereas the peaks of the as-cleaved and aged samples are found be located at 355.7 eV. The peak shift from 355.7 eV to 357.4 eV manifests that metallic silver, Ag^0 was formed on the surface of glass by the electron beam bombardment.

Since the chemical state of silver on the electron beam bombarded glass surface is found to be similar to that in metallic silver Ag^0, the silver enrichment process shown in Fig. 8 may be considered as a surface precipitation of silver. The process of precipitation of the second phase at the surface of the glass can be described by the Johnson-Mehl-Avrami equation /10,11,12/.

$$W = 1 - \exp[-(kt)^n] \quad (1)$$

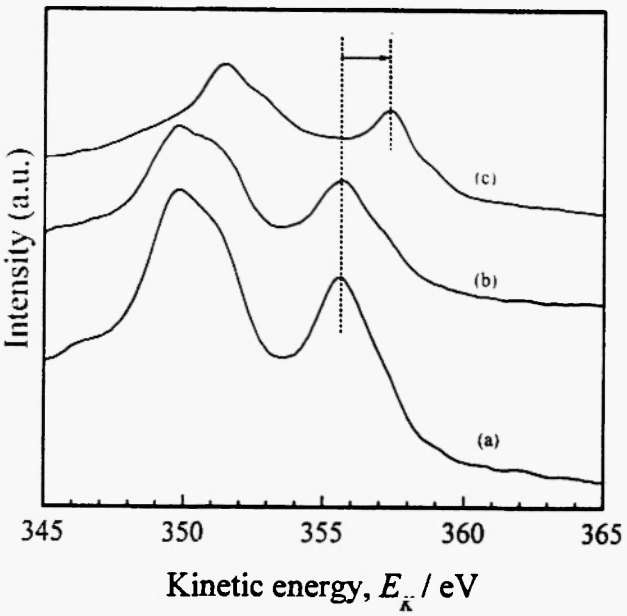

Fig. 9: The Ag M_4VV XAES spectra of the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$; (a) cleaved in air, (b) aged at 323 K, and (c) bombarded by electron beam.

where W is the fraction of total precipitation at time t, n Avrami's exponent and k effective apparent reaction rate constant. Taking the logarithm of eq. (1) twice and rearranging, one obtains,

$$\ln[-\ln(1-W)] = n \ln k + n \ln t \quad (2)$$

Avrami's exponent n is directly obtained by plotting $\ln(1-W))$ versus $\ln t$ as shown in Fig. 10. The evaluated value of n from the slope of the straight line obtained by least squares fitting is 1.1; the deduced value of k is 3.74×10^{-4}. The value of Avrami exponent n may be correlated to the crystallization mechanism involving nucleation and growth, which is classified with increasing, constant, decreasing and zero nucleation rate for a surface controlled process and diffusion controlled one as summarized in ref. /13,14/. The model for the Avrami kinetics proposed by Ilschner /15/ is known to be useful in interpreting the n value for crystallization of secondary phase in a matrix. According to such refined model, Avrami's exponent of $1 < n < 1.2$ implies the condition of diffusion controlled growth with zero nucleation as cited by Collins *et al.* /16/. Then, the

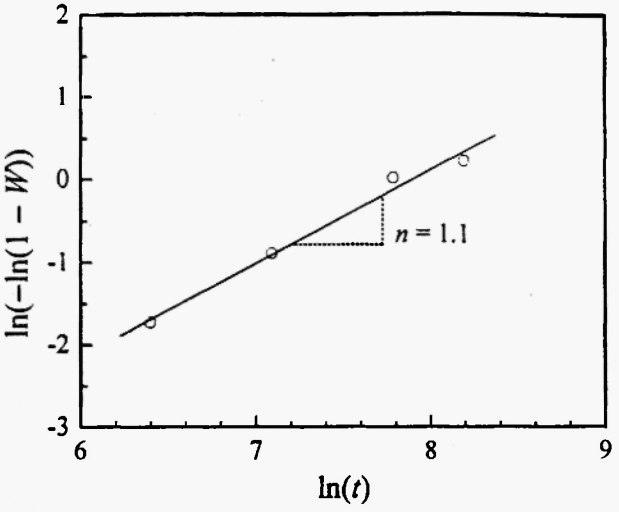

Fig. 10: Avrami plot for determination of the Avrami exponent n for the silver precipitation process in the glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$.

present result of Avrami's exponent, $n = 1.1$ implies that the Ag enrichment process in $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$ glass by electron beam bombardment is quite likely to be a diffusion-controlled growth of metallic silver with zero nucleation rate.

4. CONCLUDING REMARKS

The effects of Ar ion and electron bombardment on the surface chemical binding state and composition of superionic conducting glass of $(AgI)_{0.4}(Ag_2O)_{0.3}(MoO_3)_{0.3}$ have been investigated by using XPS. The obtained results can be summarized as follows;

(1) The ratio of cations to anions in this particular glass is significantly reduced by Ar ion bombardment. This is attributed to the imbalance between cations and anions induced by preferential sputtering of anions.

(2) The peak of O 1s is shifted to higher binding energy by Ar ion bombardment. This is mainly attributed to the sputtering of silver in preference to molybdenum.

(3) The electron beam bombardment increases the surface concentration of silver and induces a change in the chemical state of silver from Ag^+ to Ag^0.

(4) The isothermal enrichment process of silver at surface can be described as $W = 1-\exp[-(3.74 \times 10^{-4}t)^{11}]$ following the Johnson-Mehl-Avrami equation.

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