Title	Secondary Ion Characteristics of Glasses Sputtered by Ar Ion
Author(s)	Iwamoto, Nobuya; Tsunawaki, Yoshiaki
Citation	Transactions of JWRI. 1976, 5(2), p. 247-249
Version Type	VoR
URL	https://doi.org/10.18910/8754
rights	
Note	

Secondary Ion Characteristics of Glasses Sputtered by Ar Ion †

Nobuya IWAMOTO* and Yoshiaki TSUNAWAKI**

It is well known that metal ions such Al^{3+} and Ti^{4+} behave as amphoteric ions in slags.[1] In order to know the basicity of slags, it is important to clarify the coordinate state of these ions in connection with the behaviours as network former or modifier.

Al^{3+} ions in slags have been studied widely with the measurements of density[2], refractivity[2], viscosity[3], ultra-violet absorption edge[4], infrared absorption[2,5] and so on. The result obtained is as follows:
For M_2O–SiO_2–Al_2O_3 glasses having an Al/M ratio smaller than unity, aluminum ion can substitute to the position of silicon in the glass network. When Al_2O_3 content is greater than that of M_2O, the excess Al^{3+} ions in glasses are unable to participate in the glass network but take an average coordination number of six.

On the other hand, the state of Ti^{4+} ions in slag remains unclearer. Rao[6] have measured softening temperature, thermal expantion, durability to water, tensile strength, density, refractive index, dielectric constant and the degree of oxygen packing in the K_2O–SiO_2–TiO_2 glasses. He suggests that Ti^{4+} ions becomes a network-former in its own right and is capable of taking part in the network in tetrahedral or octahedral coordination, depending on the composition of glass. We[7] have speculated from the Raman spectra that K_2O–SiO_2–TiO_2 glasses show peculiar bands at about 770 and 980 cm^{-1} which might be caused by TiO_6 and TiO_4 groups according to Rao's proposal, respectively.

Turnbull and Lawrence[8], however, denied that Ti^{4+} ions becomes a network former in itself because the dependence of TiO_2 content on total molar refractivity of Na_2O–SiO_2–TiO_2 glasses shows the monotonical change.

Morinaga, Itoh, Suginohara and Yanagase[9] regarded also from their infrared measurements of CaO–SiO_2–TiO_2 glasses that Ti^{4+} ions took tetrahedral and octahedral sites depending on the CaO/SiO_2 mole ratio but only diluted the slag network.

As above mentioned, it is difficult sufficiently to understand the behaviours of amphoteric metal ions in glasses. It will be, therefore, necessary to study moreover on various glasses containing amphoteric ions by helps of other methods.

This note reports the secondary ion characteristics of Na_2O–SiO_2–Al_2O_3, Na_2O–SiO_2–TiO_2 and K_2O–SiO_2–TiO_2 glasses sputtered by Ar ion using an ion micro probe mass analyzer (Hitachi IMA-SS).

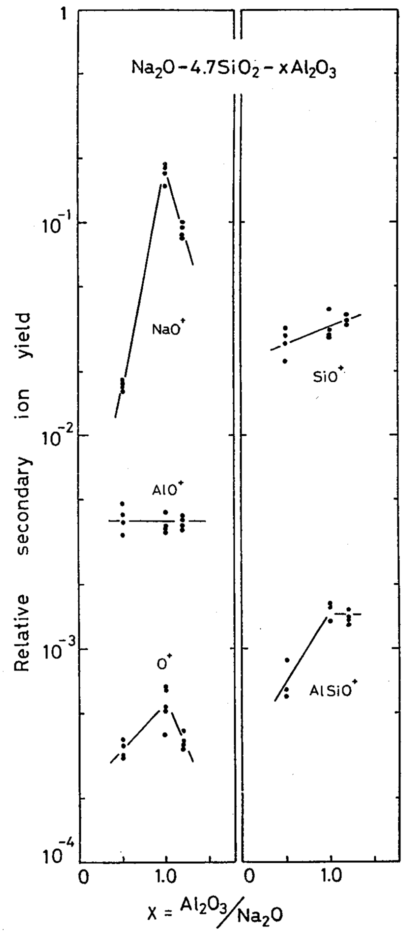

Fig. 1 O^+ ion and various molecular ions yield of Na_2O–SiO_2–Al_2O_3 glasses sputtered by Ar ion.

† Received on Sep. 16, 1976
* Professor
** Research Instructor

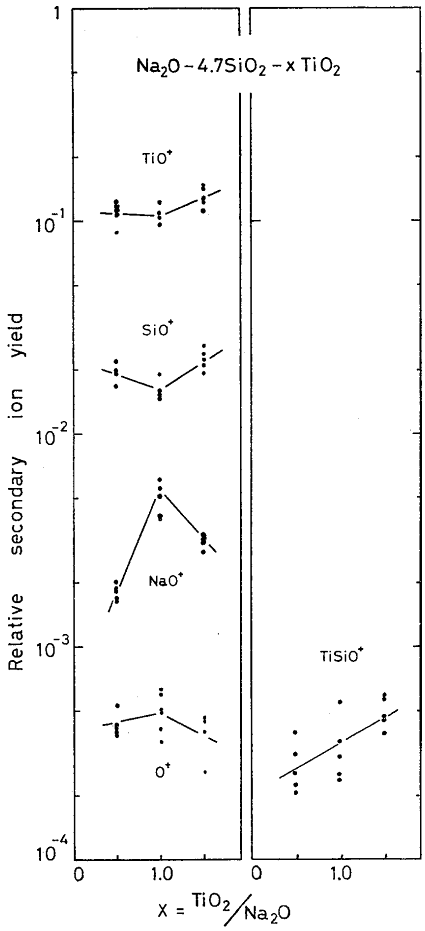

Fig. 2 O^+ ion and vaious molecular ions yield of $Na_2O-SiO_2-TiO_2$ glasses sputtered by Ar ion.

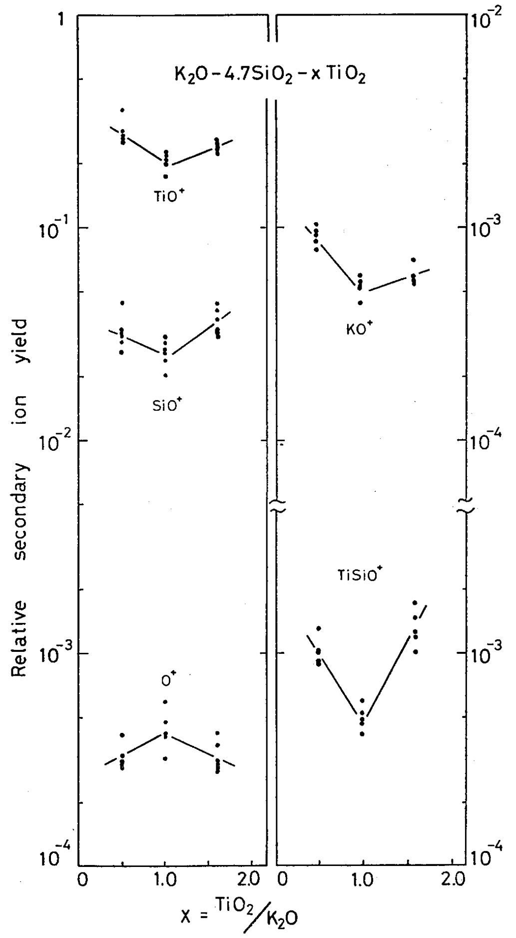

Fig. 3 O^+ ion and various molecular ions yield of $K_2O-SiO_2-TiO_2$ glasses sputtered by Ar ion.

IMA has the ability to sputter and ionize the atoms of molecular species composed of a solid surface when the atoms in the specimen accept the larger energy from the primary ion than the bonding force.[10] It is, therefore, expected that the quantity of secondary ion (i.e. ionized atom from the solid surface) will give an information about the bonding structure of materials to be studied. Especially, it is considered from our measurements of some oxides[11] and intermetallic compounds [12] that matrix molecular ions or multiply charged matrix ion will be ramarkably affected by the state of atoms in a solid.

Each relative molecular and oxygen ion yield of $Na_2O-4.7SiO_2-xAl_2O_3$, $Na_2O-4.7SiO_2-xTiO_2$ and $K_2O-4.7SiO_2-xTiO_2$ glasses versus to x value is shown in Figs. 1, 2 and 3, respectively. Each yield of molecular ions is normalized by the intensity of each single charged metallic ion. The change at x=1 of most ions might mean the change of Al^{3+} or Ti^{4+} ion state in glasses as mentiond above.

In Figs. 1 and 2, O^+ ion yield becomes maximum at x=1. It was expected that SiO^+ ion yield depended strongly on the x value. However, for the glasses containing TiO_2, SiO^+ ion yield has slightly a minimum at x=1, on the other hand, it becomes slightly larger with the increasing of Al_2O_3 content for the glasses containing Al_2O_3. The yields of AlO^+ and TiO^+ ions did not show so large change that can be expected. It must be considered that NaO^+ ion yield changes extremely at x=1 for both glasses containing Al_2O_3 and TiO_2. However, the value of the former is about ten times larger than that of the latter glasses. This fact might be because the bonding strength between Na and O dependes strongly on the contribution of Al_2O_3 or TiO_2 to the network.

In Fig. 3, KO^+ ion yield show a minimum at x=1 contrary to that of NaO^+ ion in $Na_2O-SiO_2-TiO_2$ glasses. It will be difficult to interpret the results with only the difference between the polarizabilities of Na^+ and K^+ ions. Perhaps, their alkaline ions will give different contributions as modifier to glass networks.

In Figs. 1, 2 and 3, the ion yields of $AlSiO^+$ and

$TiSiO^+$ show the dissimilar tendencies which will be due to the differences of behaviours of Na^+, K^+, Al^{3+} and Ti^{4+} ions in glasses.

In conclusion, it is very difficult to interpret successfully all the phenomena of various secondary ions and, furthermore, to find out some reasonable structures of glasses. However, it will be recognized that in the regions of x smaller and larger than unity, both glasses containing Al_2O_3 and TiO_2 might change the state in any way but the change are not necessarily equivalent. Moreover it seems that Na^+ and K^+ ions will behave differently in glasses as network modifier.

References

1) N. Iwamoto: Trans. JWRI., 5 (1976), p.87.
2) D. E. Day and G. E. Rindone: J. Amer. Ceram. Soc., 45 (1962), p.489.
3) E. F. Riebling: J. Chem. Phys., 44 (1966), p.2857.
4) G. H. Sigel, Jr.: J. Phys. Chem. Solids, 32 (1971), p.2373.
5) Y. Suginohara and T. Yanagase: J. Japan Inst. Metals, 31 (1967), p.1229.
6) Bh. r. Rao: Phys. Chem. Glasses, 4 (1963), p.22.
7) N. Iwamoto, Y. Tsunawaki, M. Fuji and T. Hattori: J. Non-Crystalline Solids, 18 (1975), p.303.
8) R. C. Turnbull and W. G. Lawrence: J. Amer. Ceram. Soc., 35 (1952), p.48.
9) K. Morinaga, T. Ito, Y. Suginohara and T. Yanagase: J. Japan Inst. Metals, 38 (1974), p.1065.
10) M. Kaminsky: "Atomic and Ionic Impact Phenomena on Metal Surfaces" Springer-Verlag, New York (1965)
11) N. Iwamoto, Y. Tsunawaki and S. Matsuda: Trans. JWRI., 4 (1975), p.101.
12) N. Iwamoto, Y. Tsunawaki and T. Takeuchi: ibid., 5 (1976), p.93.