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# Secondary Ion Characteristics of PbO-SiO<sub>2</sub> Glasses Sputtered by Argon Ion †

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## Abstract

*This study describes the secondary ion characteristics of fused quartz and silicate glasses containing various amounts of PbO using an ion micro mass analyser (IMA). Observed multi-charged secondary ions were only Si<sup>2+</sup> and Si<sup>4+</sup>. Si<sup>3+</sup> and higher multi-charged ions were not observed clearly. The prominent cluster secondary ions were O<sub>2</sub><sup>+</sup>, SiO<sup>+</sup>, Si<sub>2</sub><sup>+</sup>, SiO<sub>2</sub><sup>+</sup>, Si<sub>2</sub>O<sup>+</sup>, Si<sub>2</sub>O<sub>2</sub><sup>+</sup>, PbO<sup>+</sup>, SiPb<sup>+</sup> and SiOPb<sup>+</sup>. The intensities of PbO<sup>+</sup> and SiO<sup>+</sup> showed the opposite variation depending on the content of PbO in silicate glasses. This phenomenon seems to reflect the bonding character of glasses that lead ion in silicate glasses breaks the Si-O linkage and then weakens the bond strength between silicon and oxygen.*

**KEY WORDS:** (Slag) (PbO-SiO<sub>2</sub> Glasses) (IMA) (Secondary Ion Characteristics)

## 1. Introduction

When the ion beam (primary ion) bombards the surface of a solid material, the atoms in it accept some energy from the ion beam and are ejected from the lattice site. These ejected atoms repeat collisions each other. If the atoms get larger energy than the lattice bonding force from the primary ions, they are sputtered from the solid surface<sup>1)</sup>. Some of the sputtered atoms are ionized (secondary ion) and are able to be analysed by means of a mass spectrometer. In fact, various kinds of secondary ions such as single-charged, multi-charged and cluster ion were observed<sup>2-4)</sup>. It seems that the investigation of these various secondary ions suggests the reflection of solid structure of the specimen. We have been, therefore, studying the secondary ion, especially cluster ion, characteristics<sup>4-6)</sup>. This paper describes the secondary ion characteristics of fused quartz and silicate glasses containing various amounts of PbO sputtered by argon ions using an IMA (HITACHI IMA-SS). Lead silicate glasses will be convenient materials to investigate the secondary ions relating to the structure of glasses because of the wide spread compositional region of vitreous state.

## 2. Experimental Procedure

A fused quartz on the market was used in this study. On the other hand, lead silicate glasses were produced from analytical grade reagents as starting materials. Com-

positions of the glasses were PbO·2SiO<sub>2</sub>, 2PbO·3SiO<sub>2</sub>, PbO·SiO<sub>2</sub>, 3PbO·2SiO<sub>2</sub> and 2PbO·SiO<sub>2</sub>. A batch of 5 g placed in a platinum crucible was melted at 1000°C for 2 hr. The glass melt was taken out from the furnace and cooled in air. After the fragment of glass sample was polished with alumina powder, it was washed in ethylalcohol with an ultrasonic cleaner.

The measurements of secondary ion emission were performed under the following conditions; primary ion energy 5-12 KeV, probe size about 500 μm diameter, the vacuum in sample chamber 8 × 10<sup>-7</sup> - 4 × 10<sup>-5</sup> torr. In order to avoid the charging because of the insulated property of glasses, electrons from a tungsten filament were showered on to the specimen. The electric current was controlled by getting maximum signal of each secondary ion.

## 3. Results and Discussion

Each relative secondary ion intensity of, for example, PbO·2SiO<sub>2</sub> is shown in Fig. 1. Similar result was obtained for fused quartz except for the secondary ions containing Pb. Multi-charged secondary ions of Si<sup>2+</sup> and Si<sup>4+</sup> were observed but Si<sup>3+</sup> and higher multi-charged ions were not observed clearly. This phenomenon might indicate that Si<sup>2+</sup> and Si<sup>4+</sup> will be favored in silicate glasses. The observed cluster secondary ions were O<sub>2</sub><sup>+</sup>, SiO<sup>+</sup>, Si<sub>2</sub><sup>+</sup>, SiO<sub>2</sub><sup>+</sup>, Si<sub>2</sub>O<sup>+</sup>, Si<sub>2</sub>O<sub>2</sub><sup>+</sup>, PbO<sup>+</sup>, SiPb<sup>+</sup> and SiOPb<sup>+</sup>. It is

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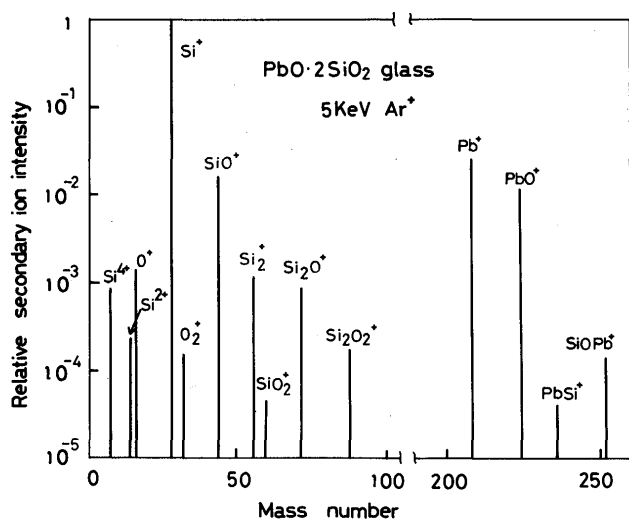


Fig. 1 Relative secondary ion intensity of PbO·2SiO<sub>2</sub>.

interesting that the intensities of Si<sub>2</sub>O<sup>+</sup> and Si<sub>2</sub>O<sub>2</sub><sup>+</sup> are larger than that of SiO<sub>2</sub><sup>+</sup> as in the case of alkali halides<sup>7)</sup>.

Figure 2 shows the relative secondary ion intensity to that of Si<sup>+</sup> except for PbO<sup>+</sup>/Pb<sup>+</sup> for various compositional glasses. Open circles of Pb<sup>+</sup> show the results measured for the powdered specimen. They are larger than

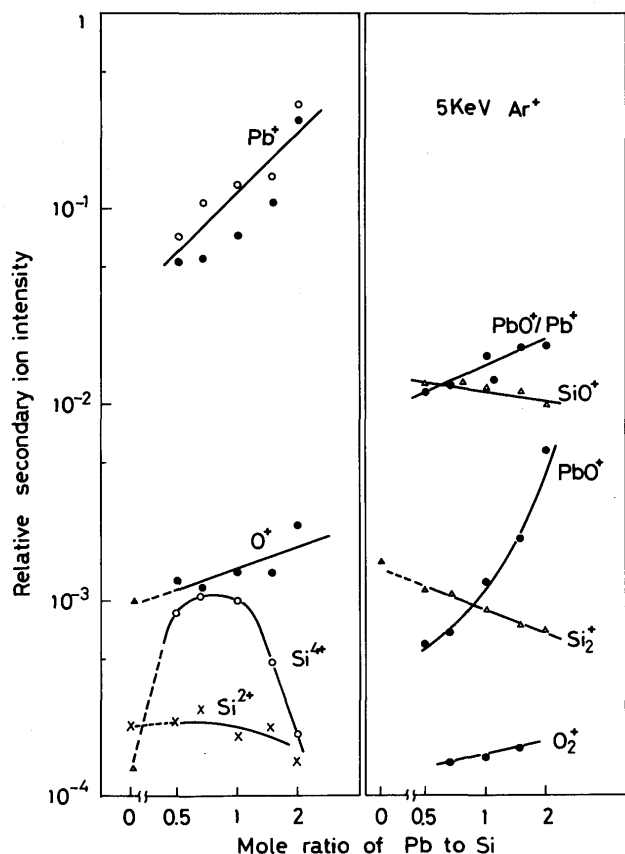


Fig. 2 Dependence of relative secondary ion intensity on the composition of PbO·SiO<sub>2</sub> glass.

those obtained for bulk glasses. This phenomenon may be due to the yield enhancement in the presence of absorbed oxygen. The solid lines of Pb<sup>+</sup> and O<sup>+</sup> are ones calculated from the nominal mole ratio of the glasses. In multi-charged secondary ions, the intensity of Si<sup>4+</sup> showed the maximum for a certain compositional glass while the intensity of Si<sup>2+</sup> did not have evident variation according to the PbO content. In cluster secondary ions, the variation of Si<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>+</sup> intensities will be interpreted in term of content of silicon and oxygen in glasses. It is most interesting in cluster secondary ions that the intensity of PbO<sup>+</sup> increased with PbO content in glass, while that of SiO<sup>+</sup> decreased. The opposite variation of PbO<sup>+</sup> and SiO<sup>+</sup> seem to reflect the bonding character of glasses that lead ion in silicate glasses break the Si-O linkage and then weakens the bond strength between silicon and oxygen<sup>8,9)</sup>. The larger cluster ions such as Si<sub>2</sub>O<sup>+</sup> and Si<sub>2</sub>O<sub>2</sub><sup>+</sup> seemed to decrease in intensity with increasing of PbO

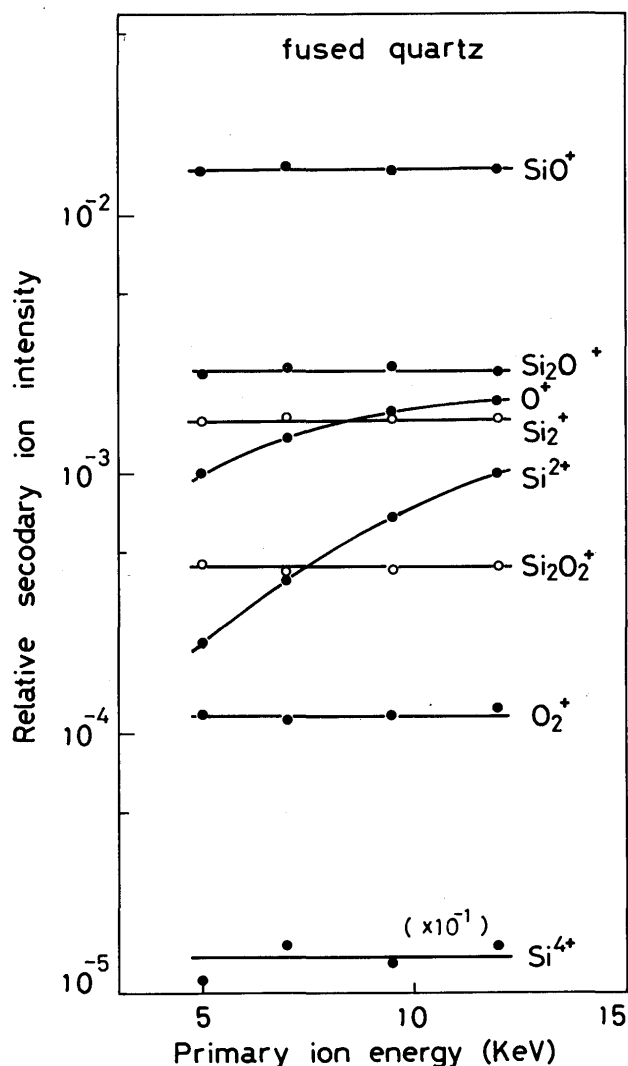


Fig. 3 Dependence of relative secondary ion intensity on primary ion energy for fused quartz.

content in glass in spite of the large experimental error.

Figures 3 and 4 show the dependence of the secondary ion intensity for fused quartz and 2PbO·3SiO<sub>2</sub> glass on the primary ion energy, respectively. Their intensities are normalized by that of silicon ion. The secondary ion intensities of the other glasses have also similar features. Although the variations of PbO<sup>+</sup> and SiO<sup>+</sup> were expected, only the prominent increasings of O<sup>+</sup> and Si<sup>2+</sup> were observed. The variation of Si<sup>2+</sup> may be interpreted with kinetic secondary ion emission. However, this phenomenon may be partially due to adsorbed nitrogen. Perhaps, the further studies with Auger spectroscopy will make it clear.

The dependence of secondary ion intensity on the atmospheric pressure in the sample chamber is shown in Fig. 5. Their intensities are normalized by that of silicon ion. The pronounced variations were not observed for fused quartz. In Fig. 5, it is seen that many secondary ions changed in intensity depending on the oxygen partial pressure. Especially the opposite dependence of SiO<sup>+</sup> (and Si<sub>2</sub>O<sup>+</sup>) to PbO<sup>+</sup> in larger oxygen partial pressure

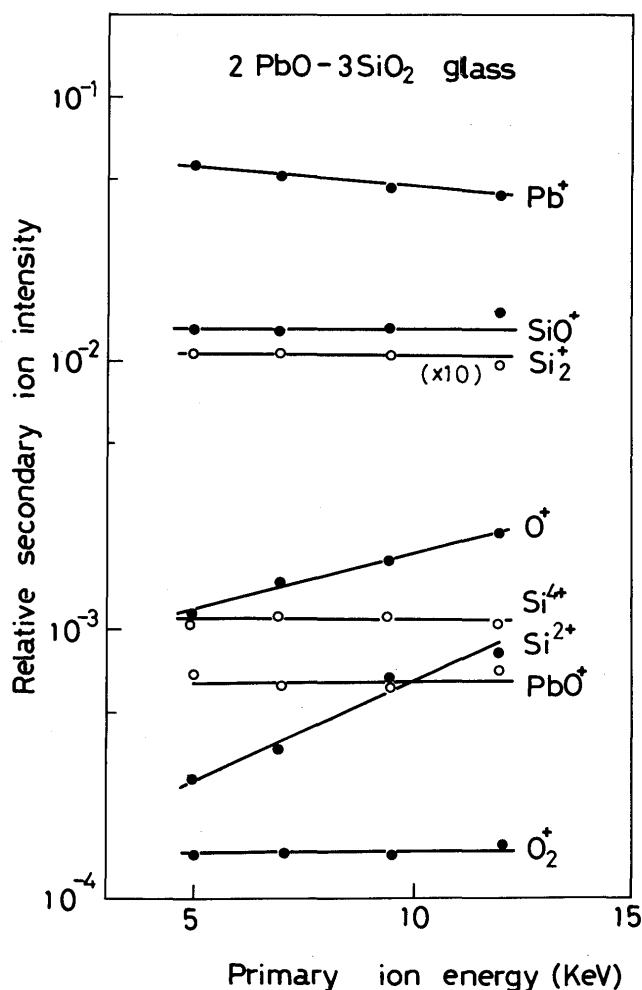


Fig. 4 Dependence of relative secondary ion intensity on primary ion energy for 2PbO·3SiO<sub>2</sub> glass.

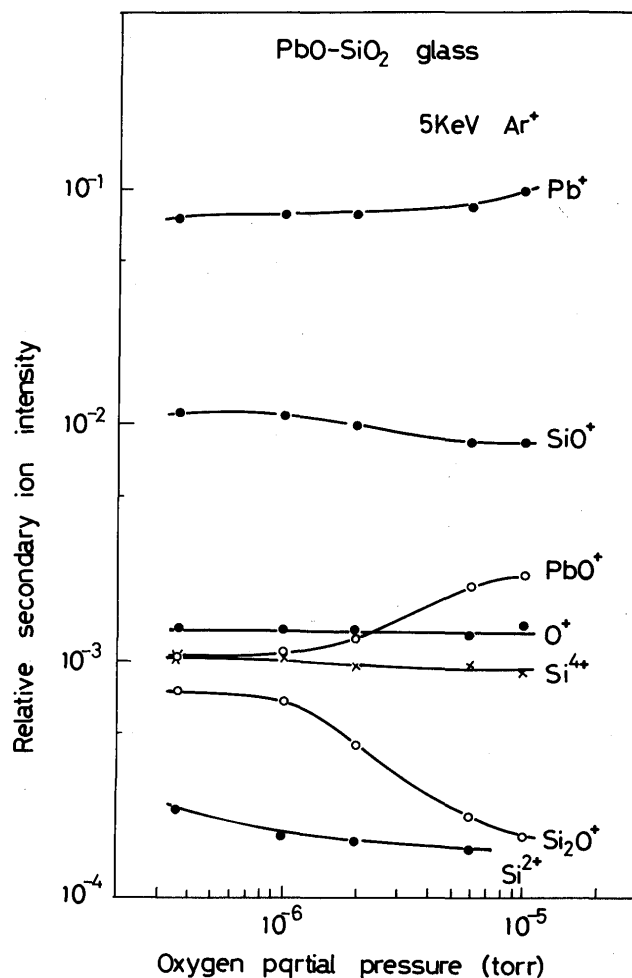


Fig. 5 Dependence of relative secondary ion intensity on the atmospheric pressure in the sample chamber for PbO-SiO<sub>2</sub> glass.

than 10<sup>-6</sup> torr seems to be significant. If it is so, a bold hypothesis may suggest that adsorbed oxygen might weaken the bonding between silicon and oxygen interacting with primary ion because of the similar tendency of PbO<sup>+</sup> and SiO<sup>+</sup> as Fig. 2.

In this study, various secondary ions ejected from fused quartz and PbO-SiO<sub>2</sub> glasses were measured. It seems that many ions appear as result of bond breaking. Considering the structure of PbO-SiO<sub>2</sub> glasses investigated by some workers<sup>9-11</sup>), especially PbO<sup>+</sup> and SiO<sup>+</sup> seem to reflect the bonding character of the vitreous state. Further studies such as the negative secondary ion, secondary ion energy and Auger analyses will make clearer the relation between the cluster secondary ions and the bond strength in glasses.

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