Surface Compositional Studies of Microchannel Plates During Hydrogen Reduction by XPS

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Abstract. Lead silicate glasses are currently the most employed glasses for micro-channel plates (MCP) and other applications. X-ray photoelectron spectroscopy was used to determine the distribution and variation of surface composition of lead silicate glasses during hydrogen reduction. The results showed that the binding energy of silicon, sodium, potassium, magnesium, barium and cesium did not change. However, the content of metal elements is gradually increased increases, while the alkali metal ions and alkaline earth metal ions migrate to the surface. At the same time, the bridge oxygen and non-bridge oxygen content also changed. All the changes of valence and content of elements on glass surface eventually lead to the change of electrical properties of MCPs.

1. Introduction
Lead silicate glasses based on R$_2$O-PbO-SiO$_2$ system are currently the most employed glasses for micro-channel plates (MCP) \cite{1-4}. They are also used for other applications: electrical vacuum devices, sealing glasses, radiation protection, optical glasses, for example. Hydrogen reduction is an important chemical reaction in the preparation of MCP based on lead silicate glasses. After this process, lead silicate glasses have higher secondary electron emission coefficient and conductivity.

As the study by A M Then et al \cite{5} showed, the outer layer of the inner wall of MCPs channel is the segregated alkali metal ion layer with a thickness of only 1.0-1.5 nm, followed by the electron emission layer of rich SiO$_2$ with a thickness of 10-20 nm, and the conductive layer with lead and bismuth atoms has a thickness of 150-300 nm. Gases are adsorbed in the range of 200 nm from the surface, mainly H$_2$, H$_2$O, N$_2$, CO$_x$, etc \cite{6-7}. And some studies have shown that the composition, chemical state and morphology of glass surface changed obviously before and after hydrogen reduction treatment \cite{8-9}.

Knowledge of surface composition during hydrogen reduction is of great importance for a proper understanding of these materials and their applications. The effect of hydrogen reduction on properties of lead silicate glass for MCPs has been studied \cite{3}. In this work, we investigated the changes of
surface composition of lead silicate glasses during hydrogen reduction by X-ray photoelectron spectroscopy method, in order to explain the reasons for the change of its performance.

2. Experimental

Lead silicate glasses were synthesized in 500g batches in a corundum crucible using reagent-grade silica, lead oxide and sodium, potassium, cesium, magnesium, calcium, barium carbonate powders or nitrate powders. The mixture with 66% of SiO\textsubscript{2}, 18% of PbO, 8% of R\textsubscript{2}O, 5% of RO and other oxide was melted at 1450°C, and refined for 2h at the same temperature. It was quenched by pouring onto a stainless steel plate, and annealed at 500°C for 4h to reduce the thermal stress. Finally, flake glass samples were prepared for hydrogen reduction treatment and performance testing.

The glass samples were reduced in hydrogen atmosphere by a furnace. The reduced temperature was as follows, non-reduction, 300°C, 400°C, 500°C, 600°C, and the reaction time was as follows, 0h, 0.5h, 2h, and 3.5h, respectively.

After hydrogen reduction, all samples were measured by XPS (ESCALAB 250, Thermo Fisher Scientific, USA) with Al K\textalpha radiation (1486.6 eV). The test conditions were as follows: pass energy of 30 eV, analyzed area diameter of 500 μm, and energy resolution of 0.80 eV. The neutralization was used to correct the shift of binding energy caused by charge accumulation, and the energy shift was compensated by the binding energy of C 1s (284.8 eV).

3. Results and Discussion

3.1. Surface composition of reduced MCPs glass under different time

Atomic concentrations of surface elements were calculated from the relative area of photoelectron peaks from XPS spectra, as showed in Table 1. There is no change in the binding energy of Si 2p\textsubscript{3/2} at 103.15 eV, while the content of Si elements increases from 26.92% to 37.84%. With the increase of reduction time, lead and bismuth ions are gradually reduced to metal atoms, and the content of metal elements is gradually increased, which can reduce the resistivity of MCPs [3]. At the same time, alkali metal ions and alkaline earth metal ions aggregate to the surface, this is conducive to the secondary electron’s emission. Due to the complexity of glass microstructure, there are two chemical states of oxygen in glass, bridge oxygen and non-bridge oxygen. From the table, we can see that as the reduction reaction continues, the bridge oxygen content and the non-bridge oxygen content decreased gradually.

| Elements          | Content under different time (mol%) |
|-------------------|-----------------------------------|
|                   | 0h  | 0.5h | 2h  | 3.5h |
| Si\textsuperscript{4+} | 26.92 | 33.52 | 35.83 | 37.84 |
| Bridge oxygen     | 34.85 | 31.60 | 29.82 | 27.79 |
| Non-bridge oxygen | 30.89 | 26.94 | 23.85 | 22.23 |
| Pb\textsuperscript{2+}  | 2.90  | 0.78  | 0.28  | 0.29  |
| Pb\textsuperscript{0}   | 0    | 1.12  | 2.15  | 2.10  |
| Bi\textsuperscript{3+}  | 1.44  | 0.00  | 0     | 0.00  |
| Bi\textsuperscript{0}   | 0    | 1.09  | 1.65  | 1.70  |
| Na\textsuperscript{+}  | 0.65  | 1.53  | 2.13  | 2.75  |
| K\textsuperscript{+}   | 0.84  | 1.60  | 2.13  | 2.62  |
| Cs\textsuperscript{+}  | 0.49  | 0.65  | 0.81  | 1.10  |
| Mg\textsuperscript{2+} | 0.49  | 0.58  | 0.62  | 0.76  |
| Ba\textsuperscript{2+} | 0.53  | 0.59  | 0.73  | 0.82  |
The changes of chemical states of oxygen were further studied by XPS spectra. With the increase of reduction temperature, the binding energy at the peak of O1s orbital electron increases gradually. It is found that O1s is composed of oxygen ions in bridge oxygen bond (≡Si-O-Si≡), non-bridge oxygen bond (≡Si-O-M) and hydroxyl (-O-H). Hydroxyl groups are caused by the contact of glass samples with air. The binding energies of O 1s of the three chemical states have no chemical shifts themselves. With the prolongation of reduction time, the total content of bridge oxygen, non-bridge oxygen and surface oxygen decreased, and the reduction of non-bridge oxygen was faster than that of bridge oxygen. The reason is that when the reduction reaction takes place, hydrogen mainly reacts with non-bridge oxygen to produce water.

Figure 1. XPS spectra of O 1s on reduced glasses surface at different time

3.2. Surface composition of reduced MCPs glass under different temperature

The changes of chemical states of oxygen were shown in Table 2. With the increase of reduction temperature, the binding energies of O 1s of the three chemical states have no chemical shifts themselves. However, due to the different content of the three chemical states, the whole O 1s peak moves toward the high energy direction. The calculation results show that the bridge oxygen content is relatively stable, but the non-bridge oxygen content decreased slightly. See Table 3.

The composition distribution of other elements on the glass surface after reduction at different temperatures is also listed in Table 3. There is no change in the binding energy of silicon, sodium, potassium, magnesium, barium and cesium, while the content of these elements changed. As the reduction reaction continues, lead and bismuth ions are gradually reduced to metal atoms, and the content of metal elements is gradually increased to reduce the resistivity of MCPs [3]. At the same time, the alkali metal ions and alkaline earth metal ions migrate to the surface of glass, which is beneficial to increase the gain of MCP.
Table 2. The binding energy of O1S varies with the reduction temperature

| Bond | unreduced | 300℃ | 400℃ | 500℃ | 600℃ |
|------|-----------|-------|-------|-------|-------|
|      | BE/eV     | Area  | BE/eV | Area  | BE/eV | Area  | BE/eV | Area  | BE/eV | Area  |
| ≡Si-O-Si≡ | 532.3 | 51314 | 532.3 | 98494 | 532.3 | 125982 | 532.3 | 109012 |
| ≡Si-O-M  | 531.4 | 45315 | 531.4 | 75986 | 531.4 | 90394  | 531.4 | 96065 |
| -O-H    | 532.9 | 3214  | 532.9 | 7983  | 532.9 | 8091  | 532.9 | 8034  |

Table 3. Content of elements on the surface of reduced MCP glass under different temperature

| Elements | Content under different temperature (mol%) |
|----------|------------------------------------------|
|          | unreduced | 300℃ | 400℃ | 500℃ | 600℃ |
| Si^{4+}  | 26.92     | 34.35 | 32.93 | 35.83 | 34.23 |
| Bridge oxygen | 34.85 | 30.97 | 30.50 | 29.82 | 31.36 |
| Non-bridge oxygen | 30.89 | 25.99 | 26.67 | 23.85 | 24.61 |
| Pb^{2+}  | 2.90      | 1.14  | 0.46  | 0.28  | 0.25  |
| Pb^{0}   | 0         | 1.53  | 1.93  | 2.15  | 1.54  |
| Bi^{3+}  | 1.44      | 0.61  | 0     | 0     | 0     |
| Bi^{0}   | 0         | 1.06  | 1.62  | 1.65  | 1.06  |
| Na^{+}   | 0.65      | 1.36  | 2.05  | 2.13  | 2.28  |
| K^{+}    | 0.84      | 1.22  | 1.79  | 2.13  | 2.30  |
| Cs^{+}   | 0.49      | 0.62  | 0.77  | 0.81  | 0.88  |
| Mg^{2+}  | 0.49      | 0.52  | 0.59  | 0.62  | 0.68  |
| Ba^{2+}  | 0.53      | 0.63  | 0.69  | 0.73  | 0.81  |

3.3. Effects of metal ions migration on secondary electron emission coefficient of glasses

The gain and resistance of MCPs reduced under different temperature and time were shown in Figure 2 and Figure 3 respectively. The resistance decreases and the gain increases. This is closely related to the distribution and variation of surface composition of glass [3].

![Figure 2. Resistance and gain of MCPs reduced under different temperature](image)

The gain and resistance of MCPs reduced under different temperature and time were shown in Figure 2 and Figure 3 respectively. The resistance decreases and the gain increases. This is closely related to the distribution and variation of surface composition of glass [3].
4. Conclusion
The changes of surface composition of lead silicate glasses during hydrogen reduction were studied by XPS method. With the increase of reduction temperature or time, there is no change in the binding energy of silicon, sodium, potassium, magnesium, barium and cesium, while the content of these elements changed. The content of metal elements is gradually increased to reduce the resistivity of MCPs. At the same time, alkali metal ions and alkaline earth metal ions migrate to the surface to increase the gain of MCP.

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