XPS Study on Changes of Lead on the Channel Surface of Microchannel Plate Reduced by Hydrogen

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Abstract. Lead silicate glass has excellent conductivity after hydrogen reduction, which plays an important role in improving the dynamic range of micro-channel plates. X-ray photoelectron spectroscopy was used to determine the valence state and distribution of lead on the surface of the channel surface of MCPs reduced by hydrogen. The results showed that Pb²⁺ reacted with hydrogen and reduced to Pb atom gradually. When the temperature increases or the time extends during the hydrogen reduction process, Pb⁰ gradually increases on the surface, which leads to the changes of MCP resistance during reduction. Furthermore, the bismuth has the same change trend as lead during hydrogen reduction.

1. Introduction
Micro-channel plate (MCP) was wildly used in low light level night vision, particle counting, nuclear detection and other fields, because of its excellent performance in electron multiplication with high gain, high resolution, low noise, and other characteristics [1-3]. As the first choice for preparing MCPs, lead silicate glass materials has high yield of secondary electron, easy prepared, and can obtain suitable resistance after reduced by hydrogen [4-5].

When the MCPs were reduced by hydrogen, there are some changes on the surface, such as morphology and composition. As the experimental results showed, the surface conductivity of reduced glasses increases, when the temperature increases or the reduction time extends, while the resistance of MCPs decrease [5]. Moreover, the spectral transmittance and XRD patterns showed that Pb²⁺ was gradually reduced to Pb⁰ [5]. The X-ray photoelectron spectroscopy (XPS) also confirmed that the valence state of lead changed before and after reduction [6-7].

However, the research on the valence state and distribution of lead on glass surface by reduction reaction is not enough. This work uses the XPS method to investigate the changes of lead element on the channel surface of MCPs during hydrogen reduction process, aims to further reveal the cause of resistance changes of MCP after hydrogen reduction, and to find the optimum process parameters in order to improve the performance of MCPs.

2. Experimental
The lead silicate glass used in this study has the following composition: 66% of SiO₂, 18% of PbO, 8% of (Na₂O+K₂O), 5% of (MgO+BaO) and 3% of Bi₂O₃. The raw materials with analytical reagent grade were used to prepare glass samples by melting at 1400°C~1460°C for 1h~3h, then the molten
glass was annealed at 480°C~550°C for 4h~6h to reduce the thermal stress. Finally, MCPs with channel diameter of 6 μm and aspect ratio of 40 were prepared.

The MCPs samples were reduced in a furnace. The reduced temperature changed from 300°C to 600°C, while the reaction time changed from 0h to 3.5h. After hydrogen reduction, all samples should be vacuum-packaged immediately to avoid the secondary pollution.

XPS (ESCALAB 250, Thermo Fisher Scientific, USA) measurements were performed with Al Kα radiation (1486.6 eV, analyzed area diameter is 500 μm), pass energy of 30 eV and energy resolution of 0.80 eV. In order to avoid the shift of binding energy caused by charge accumulation, the neutralization was used. The binding energy of C 1s (284.8 eV) was used to compensate the energy shift caused by surface charging effect. Atomic concentrations of lead and bismuth were determined from the XPS spectra by calculating the relative area of photoelectron peaks.

3. Results and Discussion

3.1. XPS spectra of Pb4f on the channel surface of MCPs reduced by hydrogen

As the XPS spectra showed in Figure 1a, Pb ion keeps the divalent state with the binding energy of 4f7/2 and 4f5/2 at 138.9 eV and 143.8 eV respectively before hydrogen reduction. There is no binding energy shifting, which means that the lead ion keeps in the state of Pb-O, so that the MCPs have very high resistance. However, the binding energy of Pb4f shifts towards lower energy after hydrogen reduction, see Figure 1b. When decomposing Pb4f into two peaks, the binding energy of 137.4 eV is associated with Pb2+4f7/2, and the 136.4 eV is associated with Pb04f7/2, indicating that Pb2+ and Pb0 are coexisted on the surface of reduced samples. Obviously, the content of Pb0 is higher than that of Pb2+.

![Figure 1. XPS spectra of Pb ion before (a) and after (b) hydrogen reduction](image)

3.2. XPS spectra of Pb4f on the surface of MCPs reduced at different temperature

As shown in Fig.2, when the reduction temperature increases, the photoelectron peak of Pb04f gradually appears and dominates. We can also find that the binding energy of Pb2+ shifts towards lower energy, for example, the binding energy of Pb2+4f7/2 is 138.5 eV at 300 °C, and 137.9 eV at 600 °C. However, the binding energy of Pb04f is almost unchanged. From the area of Pb2+4f and Pb04f in XPS spectra, it can be seen that the content of Pb0 increases gradually on the surface of lead silicate glass reduced at different temperature. The calculated content changes are shown in Figure 3. When the reduction temperature increased from 300 °C to 500 °C, the content of Pb0 rises gradually. This is because the higher the temperature, the more complete the reduction reaction. However, when the reduction temperature increased to 600 °C, the content of Pb0 decreased, which can be attributed to the lead volatilize at high temperatures [5]. Therefore, the XPS measurements are consistent with the spectral transmittance and XRD results [5], and further explain that the surface conductivity of the glass samples increases while resistivity of MCPs decreases firstly and then increases according to the change of reduction temperature.
3.3. XPS spectra of Pb4f on the surface of MCPs reduced with different time

MCP samples reduced at 500 °C with different time were measured by XPS, the spectra shows in Figure 4 and the changes of content of Pb shows in Figure 5. The binding energy of Pb2+ 4f shifts slightly towards the low energy direction, as the results shown, from 138.9 eV to 137.4 eV. The content of Pb0 increases gradually, while the content of Pb2+ decreases, with the prolongation of reduction time. Moreover, when the reduction time exceeded 2 hours, the content of Pb0 increased slowly, indicating that the reduction reaction on the surface of the sample was carried out sufficiently. All the XPS test results are consistent with the resistance variation of lead silicate glass and MCP [5].
Figure 4. XPS spectra of Pb4f on the surface of MCPs reduced with different time.

Figure 5. The content of Pb on the surface of MCPs reduced with different time.

3.4. XPS spectra of Bi4f on the surface of MCPs before and after hydrogen reduction

Bi ion can also be reduced to atom by hydrogen in MCPs as shown in Figure 6. Before reduction, the spectra is a typical XPS spectra of Bi$^{3+}$. But after reduction, the spectra changed to a typical XPS spectra of Bi$^{0}$ [6]. The results of this measurement demonstrate that the Bi ions on the surface of lead silicate glass are completely reduced to atoms, which plays an effective role in improving the resistance of MCPs.
4. Conclusions

The transition from Pb$^{2+}$ to Pb$^0$ on the channel surface of MCPs during hydrogen reduction was studied by XPS method. When the temperature increases and the time extends, Pb$^{2+}$ reacted with hydrogen and gradually reduced to Pb atom. The binding energy of Pb$^{2+}$ 4f shifts slightly towards the low energy direction, while the binding energy of Pb$^{0}$ 4f is almost unchanged. The Bi ions on the surface of lead silicate glass can be reduced to atoms completely during hydrogen reduction process. XPS measurements are consistent with the spectral transmittance and XRD results, and further explain that the surface conductivity of glasses increases according to the change of reduction temperature or time, while the resistivity of MCPs decreases firstly and then increases.

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