Studies on XPS Valence State Analysis of Copper Materials

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Abstract

XPS analysis technique can be used for valence state analysis. However, due to the limitation of the energy resolution of XPS, it can be difficult to differentiate the valence state of some elements. In this study, the Scanning XPS Microscope PHI Quantera II was used to analyze and identify Cu_2O from Cu. Although the equipment possesses good energy resolution (0.48 eV), it is still difficult to distinguish Cu^+ from Cu as their difference of the 2p3 energy (0.20 eV) is less than the energy resolution of the XPS tool. In this paper, we will study the method to identify and distinguish Cu^+ from Cu by using LMM energy peak in XPS spectra.

1. Introduction

For Copper material analysis, it is very important to identify different valence states. XPS analysis technique can be used for valence state analysis. However, due to the limitation of the energy resolution, certain valance states of individual element can be difficult to separate. For example, it is difficult to identify Cu_2O from Cu as their difference of the 2p3 energy is less than the best energy resolution of the present machine. In this study, Scanning XPS Microscope PHI Quantera II is used for the study of the method to identify Cu^+ from Cu by using LMM energy peak in XPS spectra.

2. Physical/Theoretical Studies

It is well-known that Cu has three common oxidation states: Cu, Cu^+ and Cu^{2+}. Their 2p3 energy are Cu^{2+} (CuO) 933.7 eV, Cu^+ (Cu_2O) 932.5 eV and Cu (0) (metal) 932.6/932.7 eV [1]. The energy resolution of Scanning XPS Microscope PHI Quantera II is 0.48 eV. As such, we are able to distinguish Cu^{2+} (CuO) from Cu^+ (Cu_2O) or Cu (0) (metal), as the peak position difference of the 2p3 peaks are 1.2 eV and 1.0-1.1 eV, respectively. However, it is difficult to identify Cu^+ (Cu_2O) from Cu (0) (metal) as the difference is only 0.1-0.2 eV.

In order to identify all three chemical states (Cu, Cu^+ and Cu^{2+}), the Cu Auger LMM energy peak from XPS spectra are used. From the Auger peak, we can obtain the LMM energy of three oxidation states (Cu, Cu^+ and Cu^{2+}), since the Auger LMM peak positions of Cu^{2+} (CuO), Cu^+ (Cu_2O), Cu (0) (metal) are 568.5 eV, 570.4 eV and 567.9/568.0 eV at XPS spectra, respectively, and the difference of LMM peak energy for Cu^+ (Cu_2O) and Cu (0) (metal) is 2.4-2.5 eV which is much larger than machine's energy resolution.

3. Experimental, Results and Discussion

The depth profiling analysis of Copper Oxide layer on Cu pad surface was conducted by using Scanning XPS Microscope PHI Quantera II (Al source, 1486.6 eV). XPS depth profiling was performed to observe the changes of the copper chemical state. The sputtering rate was calibrated by using SiO_2 standard.

High resolution scans of Cu 2p3 and Cu LMM for depth profiling are shown in Figure 1 and Figure 2, respectively. From Figure 1, it can be seen that there was no obvious peak position shift among the spectra at different depths ranging from as received condition to 4nm sputtered condition for Cu 2p3. It can be concluded that there was no CuO existing on the sample surface, since no peak at 933.7 eV (CuO) was detected.

In comparison, Cu 2p3 peak positions for Cu_2O (932.5 eV) and Cu (932.6/932.7 eV) are very closed, with a difference of merely 0.1-0.2 eV. Therefore, they cannot be distinguished from Cu 2p3 peaks. However, obvious position shift for Cu LMM peak during the depth profiling, can be detected as shown in Figure 2, since the difference of the peak positions for Cu (567.9/568.0 eV) and Cu_2O (570.4 eV) is 2.4-2.5 eV. The evolution of the spectra with increasing sputtering depths could also provide useful thickness information about the constituents. This can be seen from the quantified result of the XPS depth profile based on Cu LMM peak as shown in Figure 3. It can be determined that there was a Cu oxide (Cu_2O) layer with thickness of ~2 nm on the sample surface.

3. Conclusions

Due to the limitation of the energy resolution of XPS, it is difficult to identify Cu_2O from Cu as their difference of the 2p3 energy is less than the energy resolution of the XPS tool. In this paper, we study the method to identify Cu^+ from Cu by using LMM energy peak in XPS spectra. Cu

Auger LMM energy peak from XPS spectra can be used to identify all three chemical states (Cu, Cu^+ and Cu^{2+}).
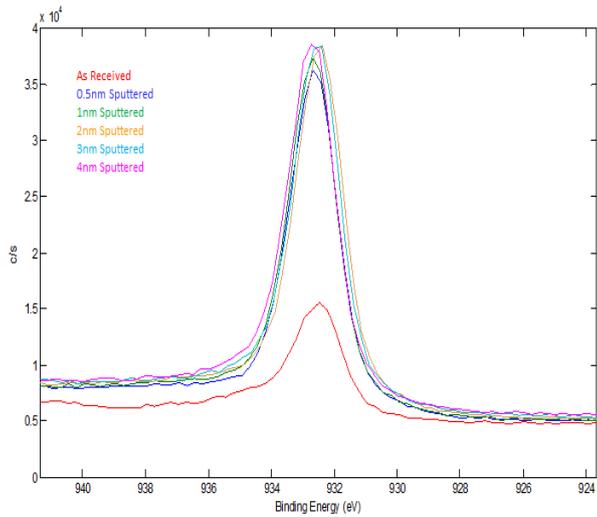
Figure 1: XPS high resolution scan of Cu2p3 at various depths
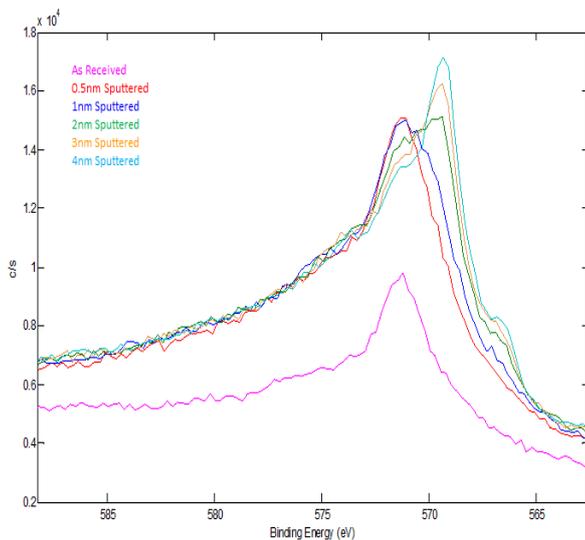
Figure 2: XPS high resolution scan for CuLMM at various depths
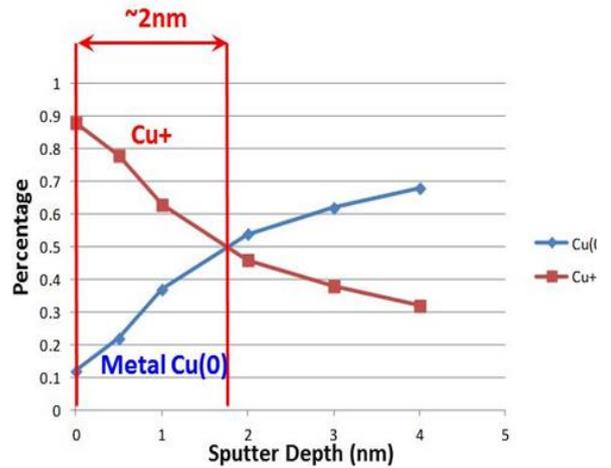
Figure 3: XPS depth profile of Cu^+ and Cu(0)

Depth (nm)	Cu(0)	Cu^+
0	12	88
1	22	78
1	37	63
2	54	46
3	62	38
4	68	32

Figure 4: Atomic% table of Cu^+ and Cu(0) at various depths

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