

Oxidation Behavior of Copper at a Temperature below 300 °C and the Methodology for Passivation

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In this study, we investigate the oxidation behavior of copper at temperatures below 300 °C and its mechanism. A methodology to slow down the oxidation rate is then proposed based on the observed mechanism. The oxides formed after oxidation at low temperatures have fine crystal sizes; the rate constants reach 2×10^{-15} m²/s and 6×10^{-14} m²/s at 200 °C and 300 °C, respectively. A passivation treatment at 600 °C in nitrogen produces a thin oxide layer composed of relatively large Cu₂O crystals. The presence of such a layer slows down the oxidation rate constants by an order of magnitude. This study demonstrates that the oxidation of copper at low temperatures is controlled by the grain boundary diffusion. Increasing the crystal size in the surface oxide reduces the oxidation rate significantly.

Keywords: Copper, Passivation, Oxidation, Oxidation kinetics

1. Introduction

The oxidation of copper is an important issue both for academic research and industrial applications. The oxidation behavior of copper has therefore received considerable interest for a very long time¹⁻³. At temperatures above 600 °C, it is believed that the oxidation is controlled by the lattice diffusion of copper ions through a Cu₂O layer^{4,6}. In contrast, the reported kinetic data on the oxidation below 500 °C varied significantly⁷. Zhu et al., conducted a kinetic study on the oxidation of copper over the temperature range 350 °C to 1050 °C. They suggested that the oxidation within a temperature range from 350 °C to 550 °C is controlled by the grain boundary diffusion. Since the impurities tend to segregate at the boundaries of Cu₂O grains, the type of impurities and their amounts at the grain boundaries affect the diffusion rate along the grain boundary. The variation of the previously reported values has been related to this impurity effect⁷.

The oxidation behavior of copper at a temperature below 300 °C has attracted less attention. Nevertheless, the oxidation behavior of copper at such low temperatures is an extremely important issue. Copper has been widely used as bonding wires or interconnects within many electronic components. Due to increasing component density and decreasing line width, the temperature within an electronic device may reach a temperature above 200 °C during operation⁸⁻¹⁰. In this study, the oxidation behavior of copper at 200 °C and 300 °C in air is investigated. The oxidation mechanism at such a low temperature range is also explored.

In previous studies, the weight gain of the oxidized specimens to characterize the extent of oxidation has been measured¹¹⁻¹³. The weight gain after oxidation at temperatures of 200 °C and 300 °C is very small. In this study, the X-ray photoelectron spectrum (XPS) technique was used to evaluate

the composition of oxidation products and their thickness. Through the use of this technique, the oxidation kinetics can be measured, and the oxidation mechanism for copper at low temperatures can be identified. After establishing the oxidation mechanism, a methodology to reduce the oxidation when the temperature is below 300 °C is proposed.

2. Experimental

High purity Cu (99.99%) plates with a thickness of 0.3 mm were used in this study. The dimensions of the plates were 10 mm by 10 mm. The Cu plates were first ground with SiC papers from #400, #800, #1000, #2000 to #4000. After grinding, the plates were cleaned with both alcohol and acetone in an ultrasonic bath. The oxidation was carried out at 200 °C and 300 °C in air for various durations. The heating and cooling rates were 5 °C/min. The surface morphologies of the oxidized Cu plates were inspected using scanning electron microscopy (SEM, FESEM-1530, LEO Instrument, Cambridge, U.K.). The phase of the oxidized Cu plate was analyzed with the X-ray diffraction (XRD, TTRAX-III, Rigaku Co., Tokyo, Japan) technique. The composition of the oxidized surface was evaluated using the X-ray photoelectron spectrum technique (XPS, PHI Quantera SXM, ULVAC-PHI Co., Kanakawa, Japan). The thickness of the oxide layer was also estimated using this technique. Since the oxidation was conducted at relatively low temperatures (200 °C-300 °C), the technique could provide reliable data on the thickness of the oxide layer.

A methodology to prevent oxidation at low temperatures is also proposed in this study. We will show that the diffusion along grain boundaries dominates the oxidation behavior. A layer composed of large oxide crystals was used as the passivation layer for the copper plates. This layer was produced by a pre-oxidation treatment. The pre-oxidation treatment

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was carried out at 600 °C in nitrogen for 3 minutes. After the passivation treatment, the copper plates were oxidized at 200 °C and 300 °C in air for various durations. The surface layer was also characterized using the same techniques aforementioned.

3. Results

Figure 1(a) shows the surface morphology of the Cu plate after oxidation at 200 °C in air for 10 minutes; fine oxide particles are observed on the surface. This demonstrates that the oxidation of copper takes place at a temperature as low as 200 °C for a short duration. The size of the oxide particles is in the range 50 to 100 nm. The size of the oxide particles will remain small after prolonged oxidation, Figure 1(b). In Figure 1(c) the microstructure of the oxide layer formed at 300 °C for 120 minutes is shown. The size of the oxide crystals is around 200 nm. Figure 2 shows the XRD patterns for the Cu plates after oxidation at 200 °C and 300 °C for various durations. The primary phase for the surface oxidation is Cu_2O . A small amount of CuO is found after

prolonged oxidation at both temperatures. The broadened peaks in the XRD patterns confirm that the crystal size of the oxides formed at 200 °C is small, while the crystals formed at 300 °C are slightly larger.

The composition of the oxide layer was evaluated with the XPS technique. Figure 3 shows the oxygen profiles in the surface region of the oxidized Cu plates. A very thin layer of concentrated oxygen is found in the surface region. The oxygen content in this thin layer is around 50 at%, which corresponds to the composition of CuO . A plateau with oxygen content around 30 at% is observed next to the CuO layer for the specimens oxidized at 200 °C. This suggests the phase at the plateau is mainly composed of Cu_2O . The oxygen content then drops slowly from the plateau to zero. The region with decreasing oxygen content is termed an oxygen-containing zone. The oxidized layer is thus composed of three regions, a very thin CuO layer, a thick Cu_2O layer and a region containing oxygen. The total thickness for the ($\text{CuO} + \text{Cu}_2\text{O} + \text{oxygen-containing zone}$) layers increases with an increase in oxidation time. This increase is primarily attributed to an increase in the

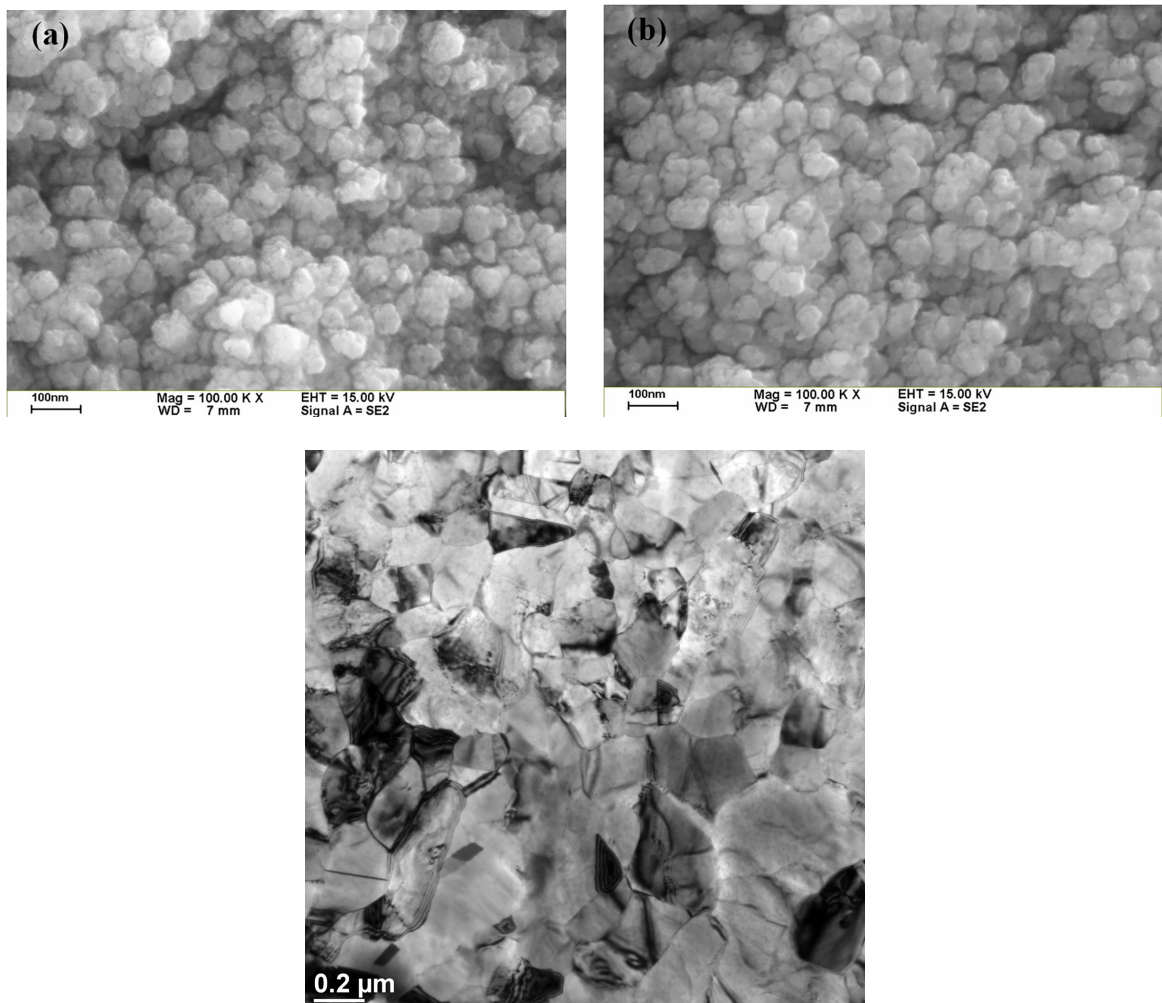


Figure 1. Morphology of the surface of Cu plates after oxidation at 200 °C for (a) 10 minutes and (b) 120 minutes. (c) The sub-surface structure of the Cu plate after oxidation at 300 °C for 120 minutes

thickness of Cu_2O . For the specimens oxidized at 300 °C, the surface oxide is also composed of 3 layers, CuO , Cu_2O and an oxygen-containing zone.

A passivation technique is proposed in the present study. This passivation technique employs a pre-oxidation treatment. The treatment was conducted at 600 °C in N_2 for 3 minutes. Figure 4(a) shows the surface morphology of the Cu plate

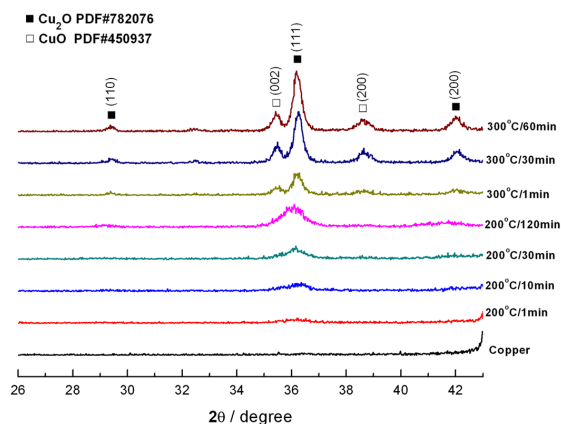
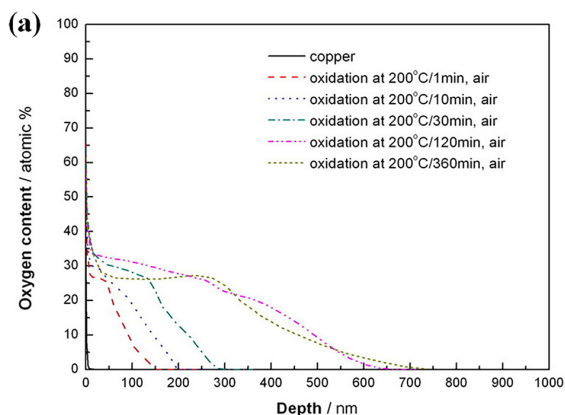


Figure 2. XRD patterns for the Cu plates after oxidation at 200 °C and 300 °C in air for various durations



after the pre-oxidation treatment; faceted oxide particles are observed. The size of these faceted particles is around 1000 nm. Although the oxygen partial pressure in the flowing nitrogen was around 1 ppm, as determined by an oxygen sensor, slight oxidation did take place during this treatment. The phase of these oxide particles consists mainly of Cu_2O , as revealed by its XRD pattern shown in Figure 5. During the treatment at 600 °C in N_2 for 3 minutes, oxygen diffuses into copper to a distance of 300 nm, as shown in Figure 6(a). A layer of approximately 10 nm containing concentrated oxygen, CuO , is also present. Due to its small thickness, no CuO peak is observed in the XRD pattern (Figure 5).

Further oxidation at 200 °C in air produces small oxide particles on the surface of the facet grains, Figure 4(b). The size of the oxide particles formed at this stage is in the range 50 to 100 nm. As shown in Figure 5, the phase of the oxidized layer is mainly Cu_2O after oxidation at 200 °C for a short duration. The CuO is then formed after prolonged oxidation (a period over 120 minutes). For oxidation at 300 °C in air, the CuO peaks were observed after oxidation for only 1 minute. After the pre-oxidation treatment, further oxidation at 200 °C causes minimal increase in the diffusion distance of the oxygen, Figure 6(a). Nevertheless, the subsequent oxidation at 300 °C in air pushes the oxygen slightly further into the interior of the copper plate, Figure 6(b).

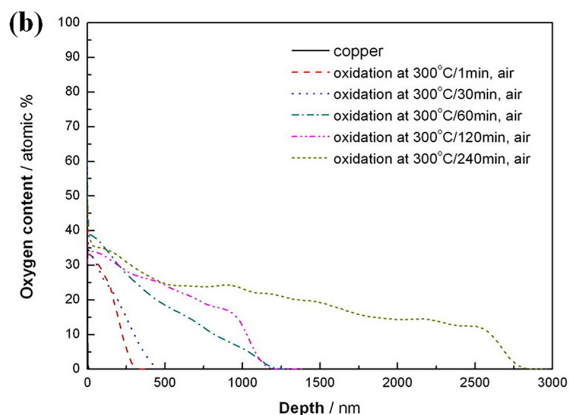


Figure 3. Oxygen profile in the Cu plates after oxidation at (a) 200 °C and (b) 300 °C in air for various durations

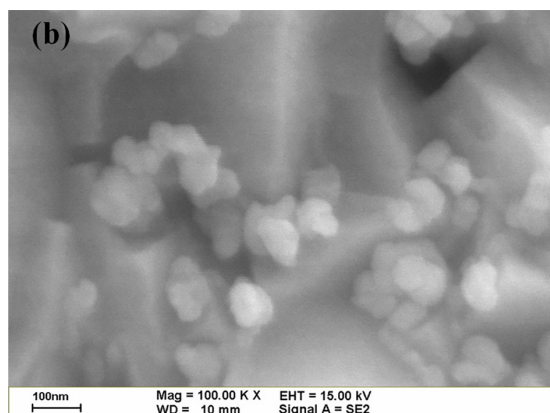
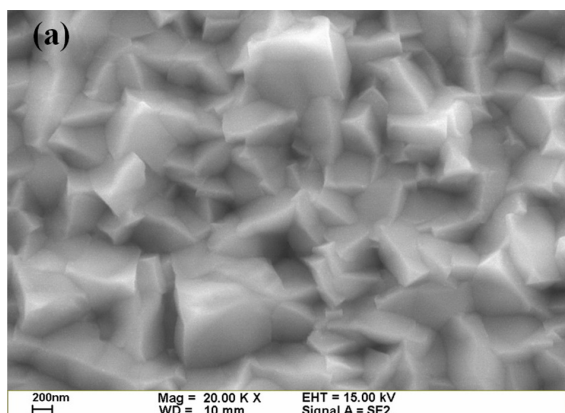


Figure 4. Surface morphology of the Cu plate (a) after the pre-oxidation treatment at 600 °C in N_2 for 3 minutes, then (b) oxidized at 200 °C in air for 10 minutes

In Figure 7 the total diffusion distance as a function of time is shown. A linear relationship is observed between the diffusion distance and the square root of time, indicating that the oxidation at 200 °C and 300 °C is controlled by a diffusional process. The rate constants are 2×10^{-15} m²/s and 6×10^{-14} m²/s at 200 °C and 300 °C, respectively. After applying the pre-oxidation treatment, the rate constants for the passivated Cu plates are 1×10^{-16} m²/s and 9×10^{-15} m²/s at 200 °C and 300 °C, respectively. The oxidation rate has

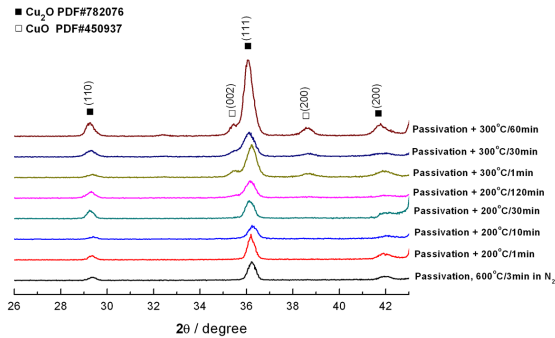


Figure 5. XRD patterns for the passivated specimens after oxidation at 200 °C and 300 °C in air for various durations

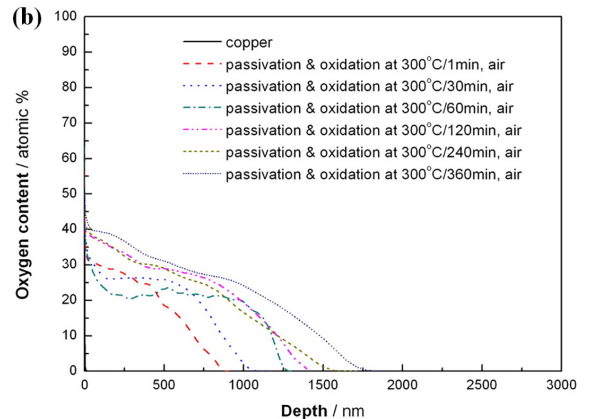
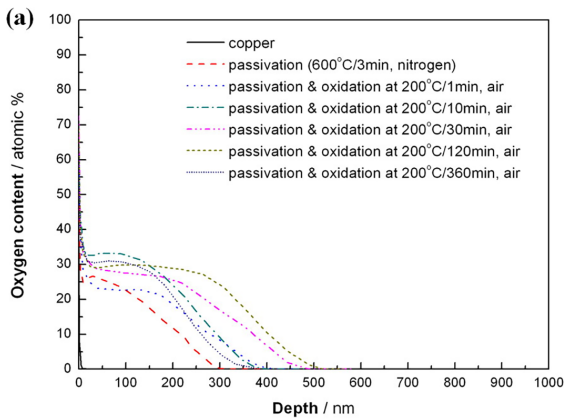


Figure 6. Oxygen profile in the passivated specimen after oxidation at (a) 200 °C and (b) 300 °C in air for various durations

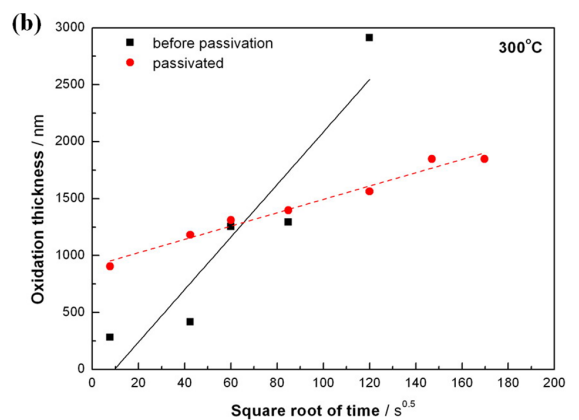
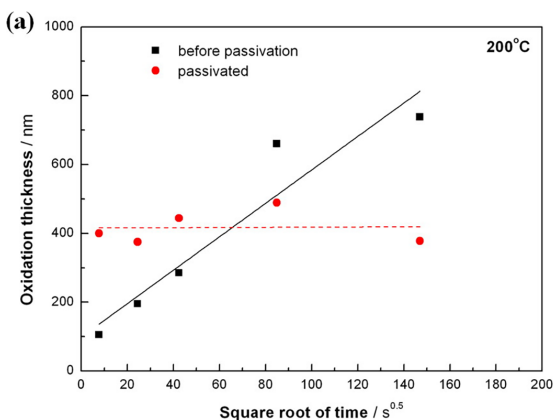


Figure 7. Oxidation kinetics of Cu plates oxidized at (a) 200 °C and (b) 300 °C

dropped by approximately one order of magnitude after the passivation treatment. This indicates that the pre-oxidation treatment is an effective passivation treatment.

4. Discussion

With the increase of component density and decrease of line width, the operation temperature for an electronic device can be very high. As an example, the reported operating temperature of a central processing unit (CPU) can reach temperatures as high as 150 °C⁸⁻¹⁰. However, the oxidation behavior of copper at a temperature below 300 °C has received little attention. This study has demonstrated that oxidation does take place at a temperature as low as 200 °C. The oxygen can diffuse into copper to a distance greater than 100 nm after oxidation at 200 °C in air for only 1 minute, Figure 3(a).

In previous studies the weight gain as the index to quantify the extent of oxidation was used¹¹⁻¹³. To determine the weight gain after every oxidation run is a straightforward technique. However, it is unable to deliver information on the structure of the oxide layer. The resolution of the XPS technique used in the present study is 1 nm¹⁴. The structure of the oxide layer can be determined from the XPS analysis results. After oxidation at 200 °C and 300 °C, the oxidation product is composed

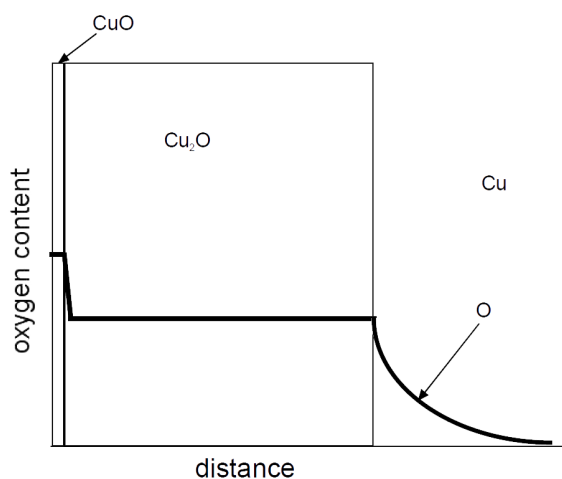
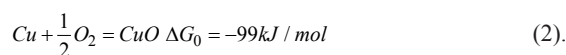
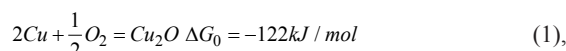
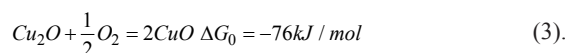


Figure 8. Schematic for the oxygen profile in the Cu plate after oxidation at low temperatures

of three layers, CuO, Cu₂O and an oxygen-containing zone. The CuO layer is very thin; its thickness is in the range of 10 to 50 nm, Figure 3. This corresponds to a size that is even smaller than the size of one surface oxide particle. This may imply each surface oxide particle contains both CuO and Cu₂O phases. The oxidation of copper is possibly contributed by the following reactions^{12,13}



From the values of the Gibbs free energy change at 400 °C, the Cu₂O is likely formed first. Further oxidation is possible on the surface of the Cu₂O particles and can be described as



Therefore, a thin CuO layer is always present on the top of the Cu₂O particles.

From the oxygen profiles shown in Figure 3(a) and Figure 6(a), a plateau at oxygen concentration of 30 at% is well defined for the specimens oxidized at 200 °C. The XRD patterns, Figures 2 and 5, indicate that the primary phase for the oxide layer is mainly composed of Cu₂O. The thickness of the Cu₂O layer varies from 50 nm to several hundred nm. The Cu₂O layer is the primary part of the oxide layer. An increase in oxidation time mainly increases the thickness of Cu₂O. The oxygen concentration then reduces slowly in the oxygen-containing zone. A schematic diagram for the oxidation layer is proposed in Figure 8. There are 3 layers in the surface region of the Cu plate after oxidation at 200 °C: a thin CuO layer, a thick Cu₂O layer, and a layer with decreasing oxygen concentration.

The oxygen profiles in the oxidation products are similar when the oxidation is carried out at 300 °C. The plateau for the Cu₂O phase in some profiles is not so well defined. Therefore, it is not possible to estimate the thickness of each

layer for some oxidized specimens. In these profiles, the oxygen content next to the CuO layer is slightly lower than 30 at%. This may imply that the layer next to the CuO layer is in fact composed of Cu₂O and Cu. Since the solubility of oxygen in Cu is only 0.12 at%¹⁵, the layer next to CuO is still mainly composed of Cu₂O.

The oxygen in the region next to the Cu₂O plateau decreases with an increase in distance. This region is termed an oxygen containing zone. Since the solubility of oxygen in copper is low, this region may also contain some Cu₂O crystals. Along with the increase of oxidation time, the thickness of the Cu₂O increases with an increase in time. In contrast, the thickness of the CuO layer and the oxygen diffusion zone is more or less the same.

In previous studies, it was suggested that the oxidation of copper in the temperature range 350 °C to 550 °C is controlled by the grain boundary diffusion through Cu₂O¹. The oxidation kinetic results shown in Figure 7 indicate that the oxidation of copper below 300 °C is also a diffusional process. Since the oxidation layer is mainly composed of a thick Cu₂O layer, the present study further confirms that the oxidation of copper below 300 °C is also controlled by diffusion through the Cu₂O layer. Since Cu₂O is an oxide, the diffusion species should be either Cu ions or O ions.

The oxide crystals in the oxide layer after oxidation at 200 °C and 300 °C are very small, as can be seen in the microstructure in Figure 1. Many grain boundaries are available for mass transportation in the oxide layer. A higher oxidation temperature, such as 600 °C used in this study, produces an oxide layer composed of large Cu₂O crystals. The grain boundary paths are limited to the layer of large crystals. The oxidation is thus reduced. This suggests the oxidation at a temperature below 300 °C is also controlled by the grain boundary diffusion. The pre-oxidation at a relatively high temperature is thus an effective passivation treatment. This passivation treatment produces a layer composed of large Cu₂O grains, and further oxidation at low temperature is thus prohibited due to the decrease of diffusional paths. In-depth investigation is still required to determine whether the Cu ions or oxygen ions are the primary control of the diffusional process.

Nitrogen is preferred as the atmosphere of the pre-oxidation treatment. Many CuO nanowires may be produced on the surface of copper after oxidation in air¹⁶. The presence of CuO nanowires may not prevent further oxidation. Therefore, a low oxygen partial pressure environment should be used for the passivation treatment.

5. Conclusions

The oxidation behavior and mechanism of Cu at 200 °C and 300 °C is investigated in this study. With the help of the XPS technique, the thickness and structure of the surface oxide on a Cu plate were characterized. The oxide layer is composed of three regions: a thin CuO layer, a thick Cu₂O layer, and an oxygen-containing region. The oxidation at a temperature below 300 °C is controlled by diffusion along the boundaries of the Cu₂O grains. Increasing the size of the Cu₂O crystals in the surface oxide will therefore reduce the paths for mass transportation, so the oxidation rate is hence reduced. Based on this fact, a pre-oxidation treatment at a

relatively high temperature was shown to be an effective passivation technique. This treatment produces large Cu_2O crystals in the surface oxide, and the subsequent oxidation at a temperature below 300 °C is reduced significantly.

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