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CHARACTERIZATION OF COPPER OXIDES BY EDS-SEM DEPTH PROFILING, EIS AND XRD

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Abstract

Study of surface and subsurface interfacial chemistry of metallic and similar systems has its enormous technological importance. Copper, for example, is a common component of many alloys and bulk amorphous systems. It is being increasingly studied today because of its use for electronic interconnect systems where processing is done below 200 °C. Since several types of copper oxides exist, and the degree of their formation is dependent on temperature, perhaps characterization by EDS-SEM depth profiling and EIS might delineate one type of oxide from another. In this paper, we described our work on transformation of copper oxides with temperature ranging from 70 to 350 °C and their characterization by SEM, EDS, and XRD. We also showed the use of the phase angle portion of the impedance as a means to identify the predominant structure and the transition through Cu_3O_2 between the predominant stable CuO and Cu_2O.

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Introduction

Copper oxides are semiconductors and have been studied for several reasons such as: the natural abundance of starting material (Cu); the easiness of production by Cu oxidation; their non-toxic nature and the reasonably good electrical and optical properties exhibited by Cu_2O. Cupric oxide (CuO) is a *p*-type semiconductor having a band gap of 1.21–1.51 eV and monoclinic crystal structure. Cuprous oxide (Cu_2O) is also a *p*-type semiconductor having a band gap of approximately 2.0 eV and a cubic crystal structure. Its high optical absorption coefficient in the visible range and reasonably good electrical properties constitute important advantages and render Cu_2O as the most interesting phase of copper oxides.

Several methods such as thermal oxidation, chemical vapor deposition, plasma evaporation, reactive sputtering and molecular beam epitaxy have been used to prepare copper oxide thin films (1-3). In most of these studies, a mixture of phases of Cu, CuO and Cu_2O is generally obtained and this is one of the nagging problems for non-utilizing Cu_2O as a semiconductor. Pure Cu_2O films can be obtained by oxidation of copper layers within a range of temperatures followed by annealing for a small period of time.

Metal oxides undergo an interfacial evolution when grown thermally (4). According to Cocke and associates, temperatures less than about 100°C are thought to create Cu_2O on a copper surface(5). This is illustrated in the Figure 1 adapted from (6).

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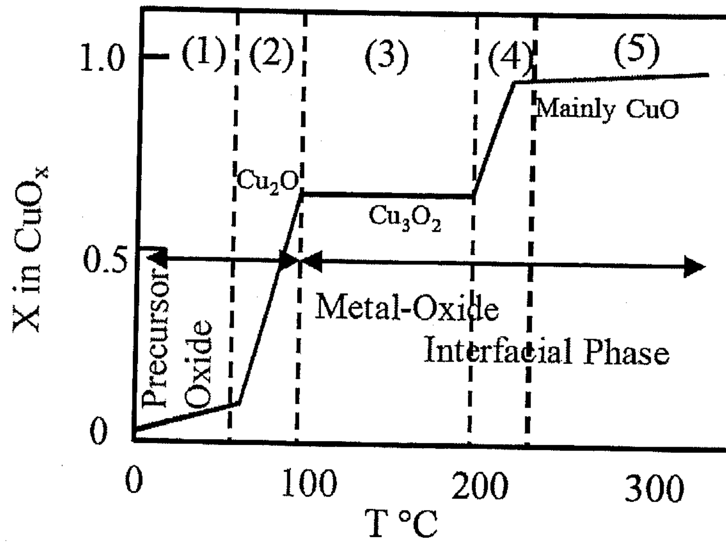

Figure 1. Schematic of the temperature dependent development of the oxides on copper. the horizontal arrows show the evolution of the precursor metal-oxide interfacial phase from the precursor phase.

As a sample of copper is heated, a larger fraction of the oxide is transformed into Cu_3O_2 until another transformation occurs near 200°C. After the temperature exceeds this milestone, the kinetically more energetic copper and the growing oxide prefer to form CuO. This is also displayed in Figure 2 from (5). The work here strongly supports the growth mechanism (a) over that of (b) of Figure 2 (7-10). The greatest slope in Figure 1 infers the largest degree of inhomogeneity in the structure corresponds to the transition realm between Cu_2O and CuO. This suggests the use of the phase angle portion of the impedance as a means to identify the predominant structure and the transition through Cu_3O_2 between the predominant stable CuO and Cu_2O.

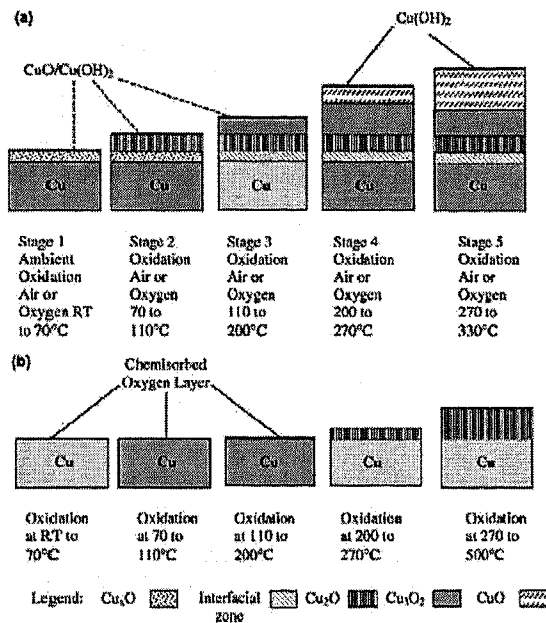

Figure 2. The complex oxide layer structures that form on cu during oxidation with the model (a) improvement by cocke and associates compared to the previous (b) proposed model.

Experimental

Two copper disks, each 0.4 inches in diameter and 0.04 inches thick, were inserted between two gold coated titanium end plates. These disks were kept at room temperature and lightly polished to a luster to remove naturally occurring oxide, as well as other deposits from the atmosphere. To keep the conditions as similar as possible, the disks were placed in the end plate set under 40 lb-in torque. Since there was such a change in resistance and inductance associated with copper disks heated to 350°C, it seemed important to examine the effect of heating identical disks for the same time interval for several different temperatures. Since it is known that several types of copper oxides exist, and that the degree of their formation is a function of temperature, perhaps there might be a relatively simple characterization by EIS that may be performed that delineatesone type from another.

Identical copies of polycrystalline copper disks with a diameter of 0.4 inch and a thickness of 0.04 inch have been oxidized in air for 4 hours at (70, 100, 150 200, 250 and 350) °C. This range of temperatures covers the changes in speciation observed by Weider and Czanderna, and oxide thicknesses that range over the probe depth. The samples were all prepared by removing any existing oxide layers by polishing them prior to heating them up in an oven that was already preheated to the desired temperature. Two disks were placed upon a large clean copper mass to ensure close to uniform heating occurred from the onset. The disks were removed after four hours and allowed to come to thermal equilibrium with the ambient room temperature.

Energy dispersive analysis by x-rays (EDAX) also known as (EDS) was used in conjunction with the SEM to determine the elemental composition of the oxide layer as a function of temperature to characterize the type of copper oxide. In this study a Hitachi 3400N SEM was used to analyze thin films of copper oxide at various stages of thermal growth. The elemental composition was accomplished via EDS with a matrix correction for atomic number absorption fluorescence (ZAF) performed. A worst-case relative error of 30 % is assumed based upon the comprehensive NIST statistical and experimental error methodologies (11). The instrumental parameters were fixed to reduce error except for varying the accelerating voltage (V_{acc}) from 3 KeV to 30 KeV. The working distance was fixed at 10mm and the X-ray analysis take off angle (TOA) was 35 degrees. No interferences were seen from escape peaks or edge adsorption. To properly probe the surface, a low V_{acc} was chosen for the 200 ^{0}C and below samples. At elevated temperatures the oxide layer is thicker and can be profiled at multiple depths. The beam energy used will be related to the depth of analysis. The less energetic the field, the more representative the results will be of the near surface layer as seen in the results. The higher 10 and 20 keV trials overestimate the copper present at the surface since they are capable of penetrating beneath the oxide layer and report the almost pure copper. Alternatively, this implies that these higher energies underestimate the oxygen to copper ratio.

Electrochemical Impedance Spectroscopy (EIS) measurements were made upon the thin metal oxide layer samples (12). Solartron Analytical equipment, consisting of a 1470E CellTest System used in conjunction with a 1252A Frequency Response Analyzer were employed to examine the response of the material to small excitation, time-varying voltages. The polarization resistance was determined from a slow potential sweep of 0.1667 mV/s which was carried out from (-0.015 to 0.015) V. It is from the current measured as this is performed that a plot of current (I) as a function of electric potential (V) that will allow for a determination of the material object resistance.

The impedance may be determined from the single frequency, sinusoidal voltage applied to a material object from the phase shift and amplitude of the resulting current that is associated with it. Displaying the impedance as real and imaginary parts allows for the resistive nature of the material to be separated from the reactive portion. Allowing for the frequency then to sweep logarithmically, recording the resulting impedance components will yield spectral data that may be displayed.

Results and Discussion

EIS were performed for all the six copper discs heated at various temperature over 1-100 kHz as shown in Figure 3. It appears from Figure 3 as though there are three distinct slopes from 1000 to 10,000 Hz, each corresponding to a pair of curves for (70 and 350) °C, (150 and 200) °C and (100 and 250) °C. The steepest pair, although their phase angles are separated by about two degrees at 1000 Hz, accompanies the two middle temperature disks. The slightest correspond to the two extreme temperatures while the remaining two are associated with (70 and 100) °C.

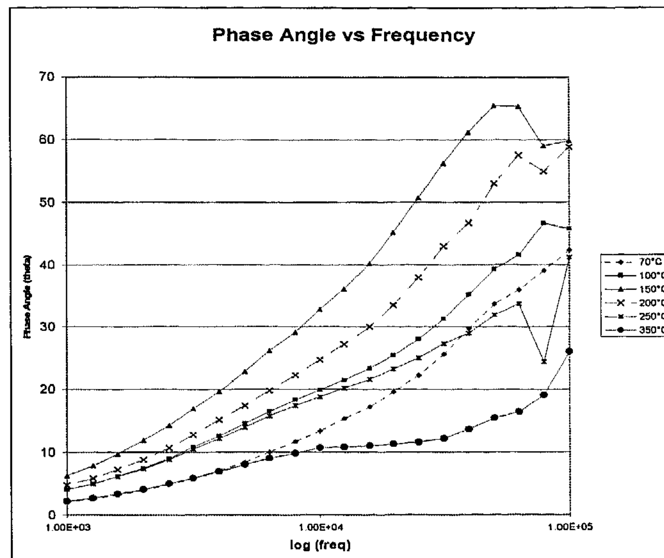

Figure 3. Comparison of all six copper disks heated to various temperatures for four hours and then analyzed with eis over an identical (1-100) KHz spectrum.

Table I shows the impedance phase angle for copper oxide as a function of different heating temperature (70 °C, 100 °C, 150 °C, 200 °C, 250 °C, and 350 °C) heated for four hours at various EIS frequencies. The difference in phase angles in Table I suggests that a quick measurement may be made based upon the type of copper oxide present.

SEM, EDAX, and XRD Characterization of Oxidized Copper Disks

In this study a Hitachi 3400N SEM was used to analyze thin films of copper oxide at various stages of growth. The elemental composition was accomplished via EDS with a matrix correction for atomic number absorption fluorescence (ZAF) performed. A worst-case relative error of 30 % is assumed based upon the NIST methodology.

The instrumental parameters were fixed to reduce error except for varying the accelerating voltage (V_{acc}) from 3 KeV to 30 KeV. The working distance was fixed at 10mm and the X-ray analysis take off angle (TOA) was 35 degrees. To properly probe the surface, a low V_{acc} was chosen for the 200 ^{0} C and below samples. At elevated temperatures the oxide layer is thicker and can be profiled with higher beam energies.

From the EDAX data derived from SEM profiling, the ratio of oxygen to copper was generated as shown in Figure 4. These were then averaged and plotted as functions of temperature for each of the probe energies. The beam energy used will be related to the depth of analysis. The less energetic the field, the more representative the results will be of the near surface layer as seen in the results. The higher 10 and 20keV trials overestimate the copper present at the surface since

they are capable of penetrating beneath the oxide layer and report the almost pure copper. Alternatively, this implies that these higher energies underestimate the oxygen to copper ratio.

Table I. Impedance phase angle for copper oxide as a function of heating temperature for four hours and eis frequency

Frequency (Hz)	70°C	100°C	150°C	200°C	250°C	350°C
100,000	42.3	45.7	59.7	58.8	41.1	26.1
79,433	39.1	46.6	59.0	55.0	24.5	19.1
63,096	36.0	41.5	65.3	57.5	33.8	16.4
50,119	33.7	39.3	65.4	53.0	31.9	15.4
39,811	29.8	35.2	61.1	46.7	29.1	13.7
31,623	25.6	31.4	56.2	42.9	27.4	12.2
25,119	22.4	28.1	50.6	38.0	25.1	11.6
19,953	19.7	25.5	45.1	33.5	23.3	11.3
15,849	17.3	23.4	40.2	30.1	21.6	11.0
12,589	15.3	21.5	36.1	27.3	20.3	10.8
10,000	13.4	19.9	32.8	24.8	18.8	10.7
7,943	11.7	18.3	29.2	22.3	17.4	9.9
6,310	10.0	16.5	26.1	19.9	15.7	9.0
5,012	8.5	14.6	22.9	17.4	14.0	8.0
3,981	7.1	12.6	19.6	15.1	12.2	6.9
3,162	5.9	10.8	16.9	12.8	10.5	5.9
2,512	4.8	9.0	14.2	10.7	8.8	4.9
1,995	3.9	7.5	11.9	8.8	7.4	4.1
1,585	3.2	6.1	9.7	7.2	6.1	3.3
1,259	2.6	5.0	7.8	5.9	5.0	2.7
1,000	2.1	4.0	6.3	4.8	4.1	2.2

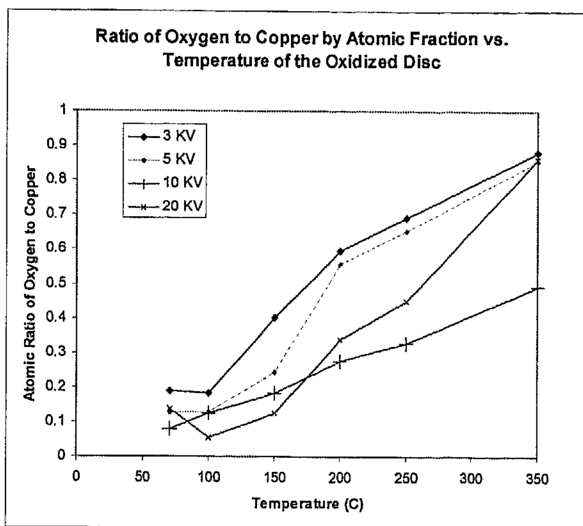

Figure 4. Atomic ratio of oxygen to copper versus temperature

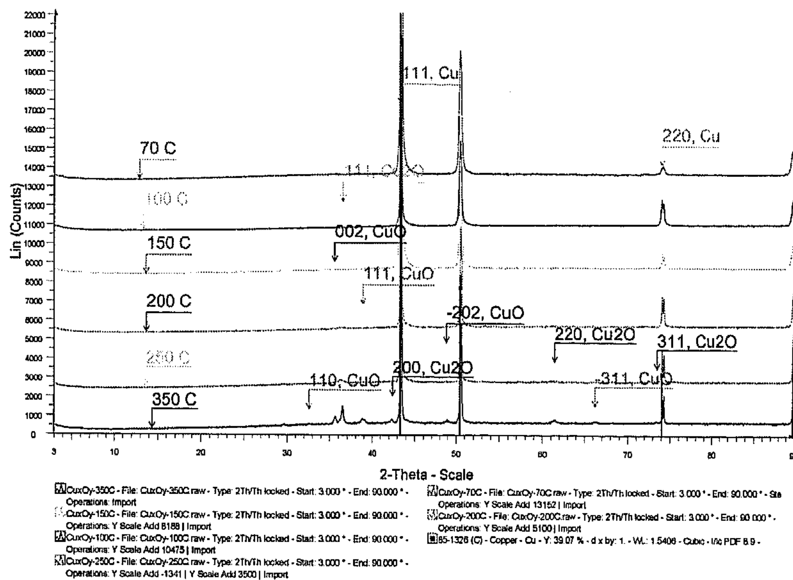

Figure 5. XRD 2-theta data for copper disks oxidized for 4 hours in air at (70, 100, 150, 200, 250, 350) °C. X-ray analyses reveals existence of Cu, CuO and Cu_2O for various expected peaks.

The powder x-ray diffraction analysis of the sample was carried out with a Bruker D4 Endeavor diffractometer. The data as seen in Figure 4.49 confirms the presence of CuO and Cu_2O with the Cu_2O transitioning to CuO as the temperature of preparation increases. The inclusion of XRD with the EDAX provided by the SEM strongly supports the hypothesis of determining the type of copper oxide that dominates a surface layer.

Conclusion

EIS strongly suggests the presence of the compound Cu_3O_2 in the copper oxide layers. It can be used to determine the types of copper oxides that are formed after heating them at various temperatures. From the phase angle determination in EIS, it suggests that a quick measurement may be made based upon the type of copper oxide present and a good LCR (inductance, capacitance, and resistance) meter may be used in-situ easily. SEM-EDS measurements on copper oxides at various potentials may be used to determine the depth profiling of copper oxide layers.

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