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CHARACTERIZATION AND PREPARATION OF COPPER OXIDE THIN FILMS

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ABSTRACT

In the present work we study thin films of copper oxide that were deposited by oxidation of copper thin films on silicon substrates in temperatures varying from 150° C up to 450°C. Copper films were deposited by vacuum evaporation and their thickness was estimated from the evaporated mass. X-rays diffraction (XRD) patterns showed that in the copper oxide films coexist two phases: CuO and Cu₂O their proportion varying with oxidation temperature. At temperatures up to 225 C Cu and Cu₂O is formed while above this temperature CuO forms. Pure Cu₂O was obtained at 225 C while pure CuO above 350 C. FTIR transmittance spectra confirmed the results from the XRD. The index of refraction was calculated from spectroscopic ellipsometry measurements within the energy range 1 to 3 eV, which were analysed using the Forouhi-Bloomer model.

1. 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 Cu₂O. Cupric oxide (CuO) is a p-type semiconductor having a band gap of 1.21–1.51 eV and monoclinic crystal structure. Cuprous oxide (Cu₂O) 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 Cu₂O as the most interesting phase of copper oxides.

Several methods such as: thermal oxidation; electrodeposition; chemical conversion; chemical brightening; spraying; chemical vapor deposition; plasma evaporation; reactive sputtering; and molecular beam epitaxy have been used to prepare copper oxide thin films. In most of these studies, a mixture of phases of Cu, CuO and Cu₂O is generally obtained and this is one of the nagging problems for non-utilizing Cu₂O as a semiconductor. Pure Cu₂O films can be

obtained by oxidation of copper layers within a range of temperatures followed by annealing for a small period of time. In the present work, we deposited thin films of copper oxides, oxidizing thin films of copper vacuum evaporated on silicon substrates. Structure and composition of these films were determined with X-rays diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy in transmittive mode. The optical properties of the thin films were studied with spectroscopic ellipsometry measurements and analysing these measurements with the aid of the Forouhi-Bloomer model. Our aim was to achieve films composed by pure Cu₂O, with final objective its utilization for the construction of electronic devices.

2. EXPERIMENTAL PROCEDURE

Thin films of copper oxide were deposited on 3 inches silicon wafers (resistivity 5-10 Ω . cm) in a thermal vacuum evaporator. The base pressure of the evaporator was 10⁻⁶ Torr, which during deposition was rising to 5. 10⁻⁵ Torr. Calibration experiments have shown that the thickness of the evaporated film was linearly proportional to the evaporated mass. 50 nm thick Cu films were evaporated throughout this study. The thermal oxidation of these evaporated films was done in a horizontal, radiatively heated quartz furnace. Samples at six different temperatures, namely 150, 185, 225, 270, 350 and 450 C were prepared. The gases used for the oxidation of samples were nitrogen (99.9999% pure) and oxygen (99.999% pure) at atmospheric pressure. Above 185 C samples were oxidized within a few minutes while for those at lower temperatures the duration of oxidation was of the order of hours (at 150 o C the oxidation endured 4 ½ hours). During oxidation the colour or the samples was changing. The oxidation was stopping once no more change of colour was observed of half an hour. XRD measurements were made with a D500

SIEMENS diffractometer using Cu K α radiation and a secondary graphite monochromator. FTIR spectra were recorded with a Bruker (model Tensor 27) spectrograph and results were analyzed with the OPUS V. 4.2 software. Before recording each spectrum that of the Si substrate was taken using as reference a Si piece cut from the wafer on which the sample was deposited.

Spectroscopic ellipsometry measurements were made within the 245-1000 nm range using a J.A Woolam Inc. M2000 ellipsometer running the WVASE32 software at an angle of incidence of 75.14o

3. RESULTS AND DISCUSSION

XRD spectra taken on samples deposited at various temperatures are shown in figure 1. At 150 C the observed peaks correspond to Cu and Cu₂O. It may be concluded then, that at this temperature and in spite of the long oxidation time (4 and ½ h), this copper film was not fully oxidized. At 185 C peaks corresponding to Cu₂O and Cu silicide are observed while at 225C a unique peak corresponding to Cu₂O is observed. It is well-known that Cu diffuses easily in Si then the appearance of peaks corresponding to Cu silicide is to be expected. However, the oxidation time seems also to play a major role to the intermixing of Cu and Si. Thus, the film deposited at 225C was oxidized fast so Cu silicide did not have the time to form while in that at 185C, which remained at the oxidation temperature for much longer time, Cu and Si had enough time to intermix. At 280C the peak corresponding to Cu₂O starts to decrease and peaks corresponding to CuO are starting to appear as well a peak corresponding to Cu silicide. The formation of Cu silicide is probably due to the fact that the sample was not withdrawn from the furnace immediately after oxidation but it remained in it for some extra time. Finally, at 350 and 450 C pure CuO films are obtained. Similarly to the conclusion

drawn for the sample at 185 C, and taking into account that at 280C the oxidation time is much longer than at 350 and 450C, it can be concluded that the longer oxidation times favor the formation of Cu silicide.

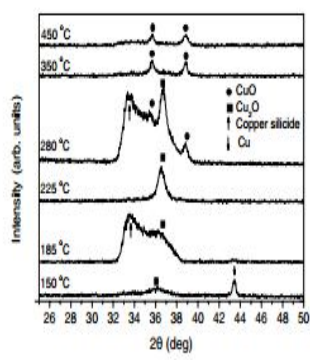


Figure 1. XRD spectra taken on Cu oxide samples obtained at various temperatures of oxidation.

In figure 2 the FTIR transmission spectra taken on samples prepared under the same conditions as for those above are shown. It is observed that for oxidation temperatures up to 225 C the formation of Cu₂O is favored while at higher temperatures that of CuO. More precisely, for temperatures up to 225C the absorption bands of Cu₂O near 615 cm⁻¹ are observed. At 280 C the absorption bands observed correspond to Cu₂O and CuO while at higher oxidation temperatures the bands of CuO only at 480 and 529 cm⁻¹ [1] are observed. The weak bands at 418 cm⁻¹ according to the literature also correspond to CuO. However their magnitude, which is at the limits of noise of the instrument does not permit the extraction of safe conclusions.

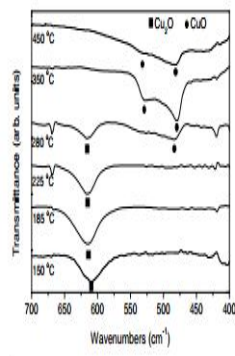


Figure 2. FTIR transmission spectra taken on Cu oxide samples grown at various oxidation temperatures.

In figure 3a the recorded and the theoretical spectra of psi and delta taken on a sample

grown at 225 C, which as shown before is composed by Cu₂O, are shown. It is observed that recorded and theoretical spectra are in good agreement. The theoretical spectra were generated using the ForouhiBloomer model introduced to simulate the refractive index dispersion in disordered solids. This model uses five adjustable parameters, namely n_{∞} , A, B, C and E_g of which the four last are related to the electronic structure of the disordered solid. Therefore, the model except the real and imaginary part of refractive index may also provide information with respect to the density of states near the band gap. The values of the FB parameters are reported in Table 1 and introducing them in the formulae reported in the dependence of n and k on photon energy was plotted and is shown in figure 3b. The values of n compare satisfactorily with those reported earlier while those of k are in general agreement with those reported for single-crystalline Cu₂O. Recorded and theoretical spectra of psi and delta for a CuO sample grown at 350°C are shown in figure 4a. As for the case of Cu₂O theoretical and recorded spectra are in good agreement indicating the suitability of the FB model to describe the dispersion of n and k for the Cu oxide films. The corresponding photon energy variations of n and k are shown in figure 4b. As before, n and k were obtained using the FB parameters reported and formulae reported in reference

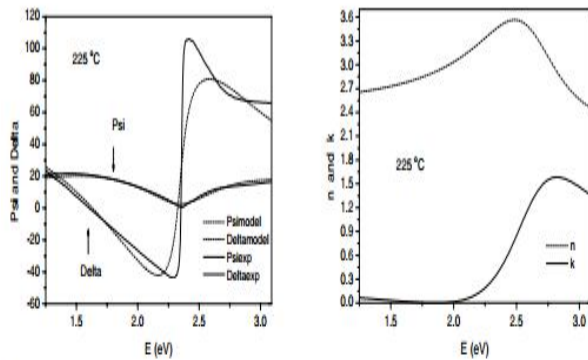


Figure 3. (a, left) Recorded and theoretical spectra of psi and delta for a Cu_2O sample grown at 225°C . (b, right) Photon energy variation of n and k for Cu_2O .

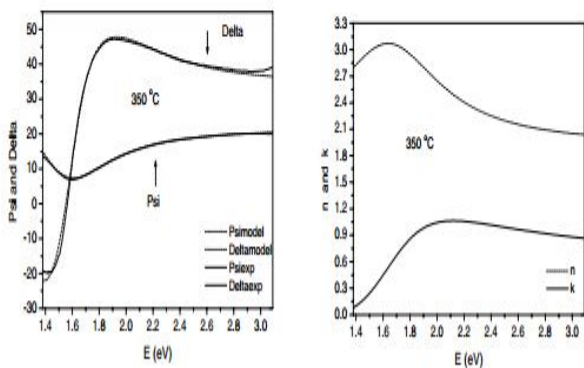


Figure 4. (a, left) Recorded and theoretical spectra of psi and delta for a CuO sample grown at 350°C . (b, right) Photon energy variation of n and k for CuO .

4. CONCLUSION

In the present work, we studied thin films of copper oxide grown by oxidizing vacuum evaporated copper thin films. At temperatures up to 225°C the obtained films were mainly composed of Cu_2O while at above this temperature CuO prevails. It was also shown that the time of oxidation influences the composition of the obtained film. The FB model seems to describe satisfactorily the dispersion of n and k of Cu oxide films and the values of n and k obtained using this model were found in agreement with values found in the literature for Cu_2O .

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