



Original Article

Effect of Annealing Temperature on Cu_2O Thin Films Prepared by Thermal Oxidation Method

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Abstract: We report a facile process to fabricate cuprous thin films by thermal oxidation of copper substrates. Structure and phase identification were studied by X-ray diffraction measurement and Raman spectroscopy. Scanning electron microscopy was utilized to study surface morphology of the as-fabricated thin films and optical properties of the samples were investigated by diffused reflectance spectroscopy. The study shows that cuprous thin films could be obtained by controlling annealing temperature in the region of 200-300 °C.

Keywords: Copper oxide, thin films, thermal oxidation, Raman.

1. Introduction

Cuprous oxide (Cu_2O) is a semiconductor with bandgap of around 1-2 eV [1], which finds many applications in fields of sensor, photocatalyst and especially photovoltaics [2–8] thanks to their interesting properties such as: earth abundant composition, environment friendly, high absorption coefficient in visible region, p type conduction. Even though the efficiencies of solar cell based on copper oxide is often quite low of around 1 to 2%, the ratio of efficiency to cost of Cu_2O is still very competitive to other materials. Hence, preparation of Cu_2O thin film is an interesting topic for study in view of both fundamental and application.

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Various techniques were developed to fabricate Cu_2O thin films for example: electro-deposition, chemical oxidation, reactive sputtering, reactive chemical deposition [4,9–14]... However, to realize such applications, a cost effective fabrication process is very important. In this paper, we report a one-step process to fabricate high quality cuprous thin films by thermal oxidation and investigate the influence of annealing temperature on the structure and some material properties.

2. Experiment

Cuprous oxide thin films were prepared on high purity copper substrates. Diluted HCl acid (10%) solution was first used to remove native oxide layer on copper substrate. The substrates were then rinsed thoroughly with distilled water. Thermal oxidation of copper substrate was performed in an high temperature furnace XD-1600MT. The annealing time was set at various temperatures in range of 200-300 °C. Surface morphologies of the as-produced thin films were studied by using Nova Nano SEM 450, and Energy dispersive Xray spectroscopy integrated on SEM system was used to verify the sample composition . Raman spectra of samples were acquired on Labram 800 spectrometer (Horiba), as the samples were excited from He-Ne laser at the wavelength of 632.8 nm. All the spectra were taken at room temperature with acquisition time of 30s and low laser power of 0.5 mW at the surface sample. Structure and phase identification of the samples were investigated by X-ray diffractometer Bruker D500, using monochromatic wavelength 1.54056 Å of Cu K_α radiation. Optical properties of the samples were characterized with diffuse reflectance spectroscopy.

3. Results and Discussion

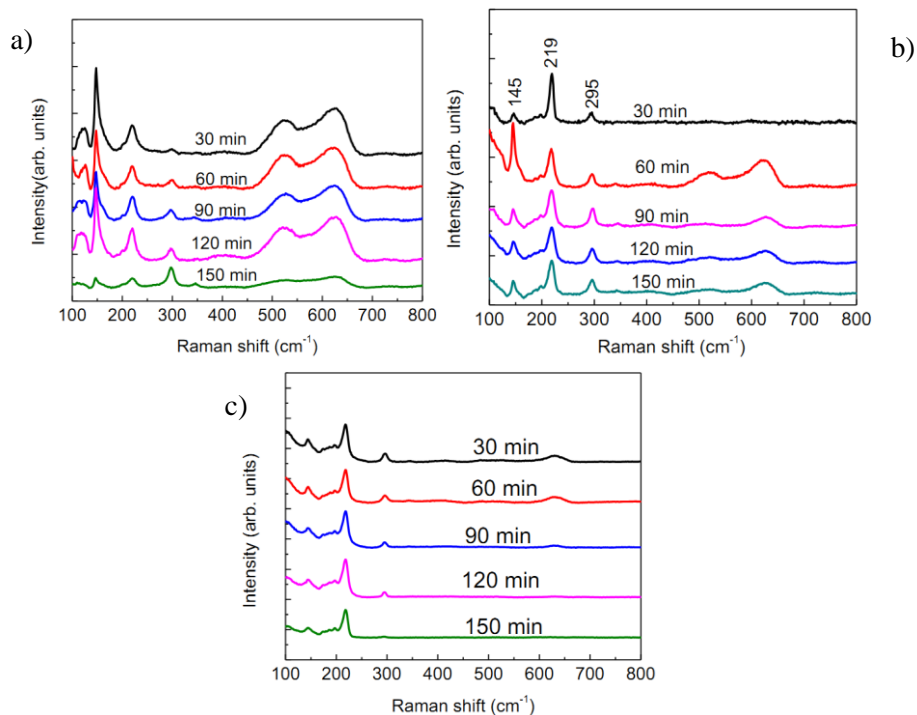


Figure 1. Raman spectra of copper oxide thin films prepared at 200 °C (a); 250 °C (b) and 300 °C in different times.

Figure 1 shows Raman spectra of copper oxide thin films prepared at different temperatures and oxidation times. Several Raman features were observed in the region from 100 to 600 cm^{-1} . Three characteristic peaks of CuO appeared at 288 cm^{-1} , 330 cm^{-1} and 621 cm^{-1} , which can be assigned to the well-known A_g , B_{1g} and B_{2g} modes, respectively [15,16]. Other Raman peaks in region 100-300 cm^{-1} belong to Cu_2O as reported [17–19]. It should be noted that according to group theory, cuprous oxide has one Raman active mode at 600 cm^{-1} . However this Raman mode was not observed in the spectra of these samples. Some other Raman features were observed at around 200 cm^{-1} . These Raman modes are believed to relate to defects in Cu_2O material, which are responsible for p type conduction in Cu_2O [19,20].

As can be seen from Raman spectra in Figure 1, after 30 min of annealing, both CuO and Cu_2O were formed. As increasing annealing time to 60 min, the intensity of the Raman peaks of Cu_2O increased notably and became dominant. At longer annealing time and higher temperature, the CuO related peaks became weaker and weaker. At annealing time of 150 min, the most intense peak of CuO at 290 cm^{-1} almost disappeared for samples annealed at 300 °C. We understand that the crystal growth rate of Cu_2O is higher than that of CuO at 300 °C, even though the obtained thin films are composed of both Cu_2O and CuO, Cu_2O becomes dominant at the latter stage of the growth and might form a layer of Cu_2O on top of the films.

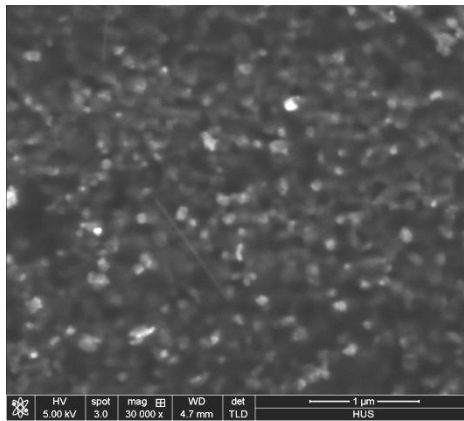


Figure 2. SEM image of copper oxide thin film prepared at 300 °C in 150 min.

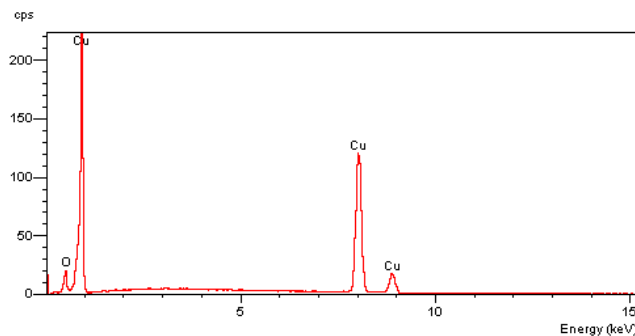


Figure 3. Energy dispersive spectrum of copper oxide thin film prepared at 300 °C in 150 min.

SEM image of copper oxide thin film annealed in 150 min is shown in Figure 2. It can be seen that the obtained film contains no crack or holes. The top view image demonstrates that the film is

composed of nanocrystals. The purity of the sample is verified by the fact that only oxygen and copper peaks appear in the EDS spectrum.

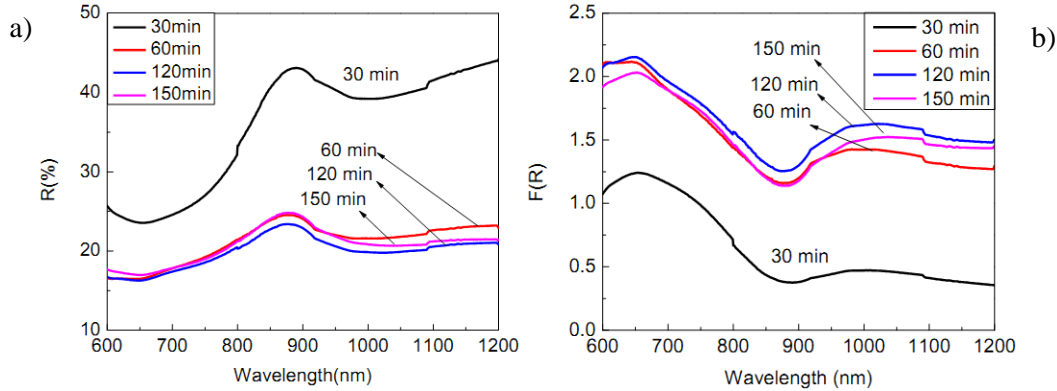


Figure 4. Diffuse reflectance spectra (a) and $F(R)$ vs wavelength plot (b) of thin films prepared at 300 °C in different oxidation times.

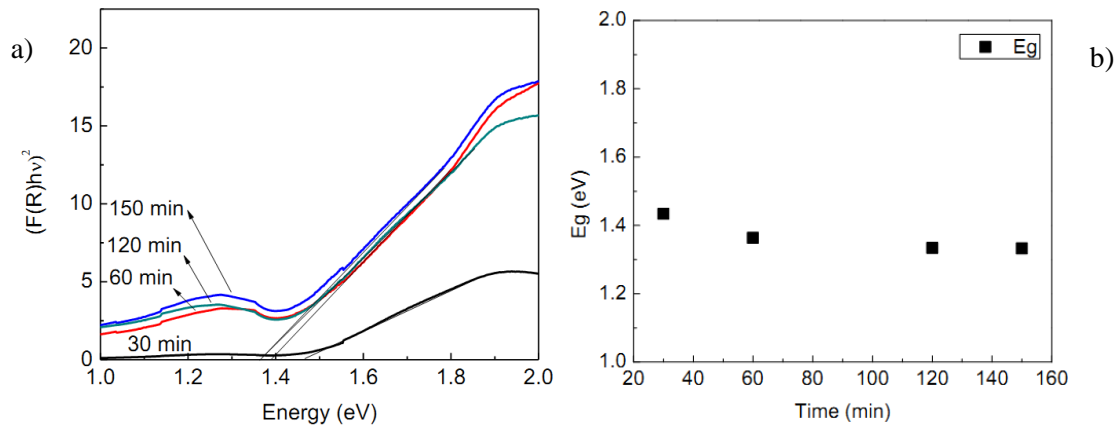


Figure 5. Plot of $(F(R).hv)^2$ vs hv (a) and bandgap values (b) of the samples annealed at 300 °C in different oxidation times.

Figure 4 shows diffuse reflectance spectra and the plot of absorption coefficient $F(R)$ calculated from reflectance data by using Mubelka Munk function. From the absorption coefficient, the plot of $(F(R)hv)^2$ vs. hv was established to estimate the bandgap of the as-prepared films. Band gap values are extrapolated from intersection between the linear fit of the graphs with the energy axis.

The results show that energy bandgap gradually decreases as heating time is reduced. Bandgap of the films tends to remain unchanged when the heating time is greater than 120 min. The results can be understood that at long annealing time, Cu_2O is the dominant phase in the sample as shown by Raman data. The bandgap value of the films is closed to the optimal value for solar absorber layer of solar cell.

4. Conclusion

High quality thin films of cuprous oxide were successfully fabricated on copper substrate by thermal oxidation method. The results showed that annealing temperature and annealing time are critical parameters to get thin films of pure phase. The as-prepared copper oxide thin films has band gap of around 1.4 eV, which is optimum for solar absorbing materials and hence are very promising in electronic and photovoltaics applications.

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