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Annealing effects on the properties of copper oxide thin films prepared by chemical deposition

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Abstract

We have investigated the annealing effect on the structural, optical and electrical properties of copper oxide films prepared on glass substrates by chemical deposition. The films were annealed in air for different temperatures ranging from 200 to 350 °C. X-ray diffraction patterns showed that the films as-deposited and annealed at 200 and 250 °C are of cuprite structure with composition Cu_2O. Annealing at 300 °C converts these films to CuO. This conversion is accompanied by a shift in the optical band gap from 2.20 eV to 1.35 eV. Also this conversion was obtained by the dc electrical conductivity and FTIR spectroscopy measurements.

1. Introduction

Cu_2O (cuprite or cuprous oxide) and CuO (tenorite or cupric oxide) are two important compounds of copper. The crystal structure of Cu_2O is cubic and mostly exhibits p-type semiconductor characteristics. Since it has a 2.0 eV band gap [1, 2] Cu_2O is a suitable material for photo-voltaic energy conversion. Thus Cu_2O is very promising for solar cell applications [3, 4].

CuO has a monoclinic crystal structure and presents p-type semiconductor behaviour with a band gap of 1.21–1.51 eV [5, 6]. CuO composites such as CuO/ZnO, CuO/Cu_2O and CuO/SnO_2 could be employed in humidity and gas sensors [7–11]. In recent years, copper oxide systems have also attracted much interest because of their superconduction properties [12, 13].

Copper oxide can be prepared by many techniques. These are listed as the thermal oxidation method [14], reactive magnetron sputtering [15], reactive evaporation [5], sol–gel method [3, 16] and chemical depositions [17, 18]. The deposition conditions and techniques play a major role in the physical properties of copper oxide thin films.

In our investigation we have studied the annealing effect on the structural, optical and electrical properties of Cu_2O thin films deposited by successively dipping the glass substrate in a solution of NaOH and in copper complex ions.

2. Experimental details

For depositing thin films of copper oxides on a glass substrate a NaOH 1 M solution was prepared in a 100 ml pyrex beaker and heated to 70 °C. A colourless solution of copper thiosulfate complex was prepared by adding just enough (approximately 125 ml) of 1 M sodium thiosulfate ($Na_2S_2O_3$) to 25 ml of 1 M copper sulfate pentahydrate ($CuSO_4$ $5H_2O$). The final volume of the solution prepared in this way was made up to 250 ml with the addition of de-ionized water. In order to deposite the metal oxide film, about 80 ml of the solution of the metal ion complexes was transferred to a 100 ml beaker and maintained at room temperature. As a first step, the glass substrates cleaned in acetone and ethanol were immersed in the hot NaOH solution using a sample holder where two glass substrates could be held together back to back for 20 s, which was found as the optimum duration for obtaining uniform thin films. When the substrate is immersed in the hot NaOH solution, the OH^- ions adhere to the substrate surface forming an ionic layer. Then the substrates with the holder are manually transferred to the beaker containing the copper ion complexes for 20 s. The Cu(I) ions formed by the dissociation in equilibrium of thiosulfatocuprate(I) ions, $[Cu(S_2O_3)]^- \leftrightarrow Cu^+ + S_2O_3^{2-}$, react with OH^- ions present on the glass surface and adhere to the substrate to form Cu_2O by the reaction $2Cu^+ + 2OH^- \rightarrow Cu_2O + H_2O$. These two steps, OH^-

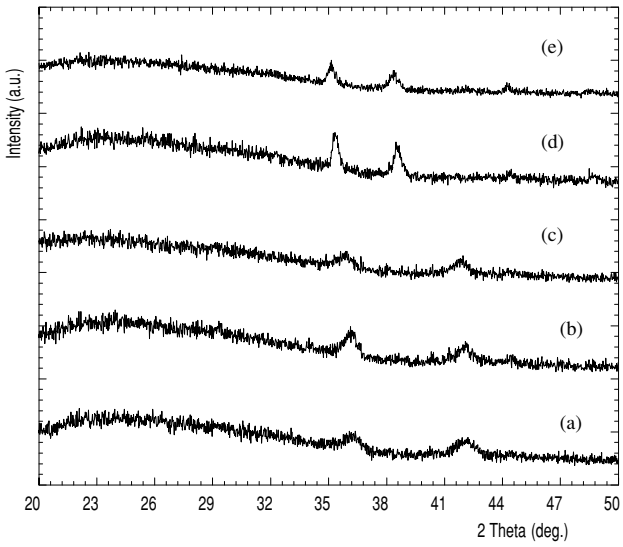

Figure 1. XRD patterns of copper oxide thin film (*a*) as-deposited and annealed at various temperatures (°C), (*b*) 200, (*c*) 250, (*d*) 300 and (*e*) 350.

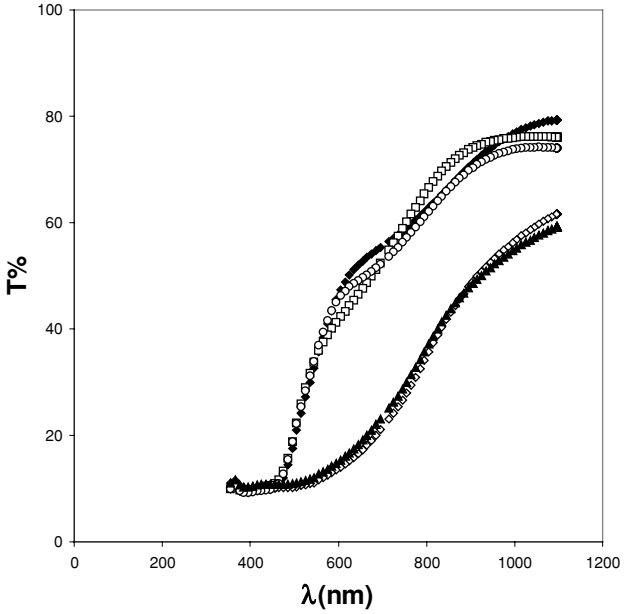

Figure 2. Optical transmittance (*T*%) spectra of a copper oxide thin film (○) as-deposited and annealed at various temperatures (°C), (♦) 200, (□) 250, (◊) 300 and (▲) 350.

adsorption and Cu^{+} reaction over the glass surface complete one cycle. At the end of three immersion cycles, the thin film shows silvery reflection. The cycle can be repeated to increase the thickness of the film. Repeated immersions of up to ten cycles resulted in a film thickness of $\cong 0.15$ μm. Then substrates are washed with distilled water and dried. In this way all the samples showed good homogenity and good adhesive property to the glass.

In order to investigate the annealing effect on the copper oxide films, films were prepared on five separate glass substrates under the same conditions. Systematically, the first sample was not annealed and the four others were annealed from 200 °C to 350 °C in steps of 50 °C during 1 h in air atmosphere. Then the films were characterized by means of structural, optical and electrical techniques. The x-ray diffraction studies were carried out by using a Rigaku D/Max 2200 diffractometer to investigate the structure of the annealed films. Cu Kα radiation with a wavelength of 1.54 Å was used and the scanning range of 2θ was restricted to the range 20–50° (figure 1).

The optical band-gap determination is based on UV–VIS transmission measurements performed with a Perkin Elmer Lambda 2 UV/VIS spectrometer in the 300–1100 nm range (figure 2). The FTIR transmission spectra were recorded using a Mattson 1000 FTIR spectrometer in the spectral range 400–1800 cm^{-1}(figure 3). In order to record IR patterns, the first copper oxide films on the glass substrates were scratched and copper oxide powder was mixed into KBr powder then a pellet was prepared for each annealed film.

The electrical conductivity of the films was determined by the two-point probe method in the temperature range 300–373 K. A constant voltage (20 V) was applied between the two probes on the film and the change in current with respect to the change in temperature of the film was measured by using an amperemeter. High quality silver paste was used for the contacts to minimize the contact resistance. The variations of the electrical conductivity as a function of temperature for the films as-deposited and annealed at 350 °C are given in figure 4.

3. Results and discussion

Figure 1 shows the glancing angle x-ray diffraction patterns of the copper oxide film deposited and annealed in atmosphere. When the film was deposited the crystalline character of the Cu_2O phase was observed. In the x-ray diffraction pattern, XRD peaks at $2\theta = 36.40°$ and $2\theta = 42.30°$ corresponding to the (1 1 1) and (2 0 0) planes of Cu_2O are seen. Since the two peaks are sharp it is evident that the deposited films are polycrystalline. Annealing the samples at 200 and 250 °C (figure 1) does not affect the composition of the film. For the sample annealed at 300 °C, the XRD pattern shows peaks near $2\theta = 35.50°$ and 38.70° which match reflections from the $(-1\,1\,1)$ planes and (2 0 0) planes respectively of CuO. When the sample is annealed at 300 °C the films get converted completely to CuO. The composition CuO is maintained after annealing at 350 °C. The conversion of Cu_2O into results from the diffusion of oxygen into the films. Cu_2O starts reacting with O and forms the CuO phase by the following reaction $2Cu_2O + O_2 \rightarrow 4CuO$. From thermodynamic considerations, Gibbs free energy of the reaction is around -3.73 kcal mol^{-1} at about 200 °C. Therefore, the formation of the CuO phase at a temperature of 300 °C can easily be explained by this reaction [19]. The crystallite size is calculated by using the Scherrer formula [20], neglecting peak broadening due to residual stresses in the films, $D = 0.9\lambda/\beta\cos\theta$ ($\lambda = 1.54$ Å for Cu Kα, β is the full width at half maximum (FWHM) of the peak corrected for the instrumental broadening in radians and θ is the Bragg angle). All samples as-deposited and annealed at 200 °C and at 250 °C resulted in an average crystallite size of approximately 14 nm. The annealing at 300 °C causes an increase in average crystallite size from

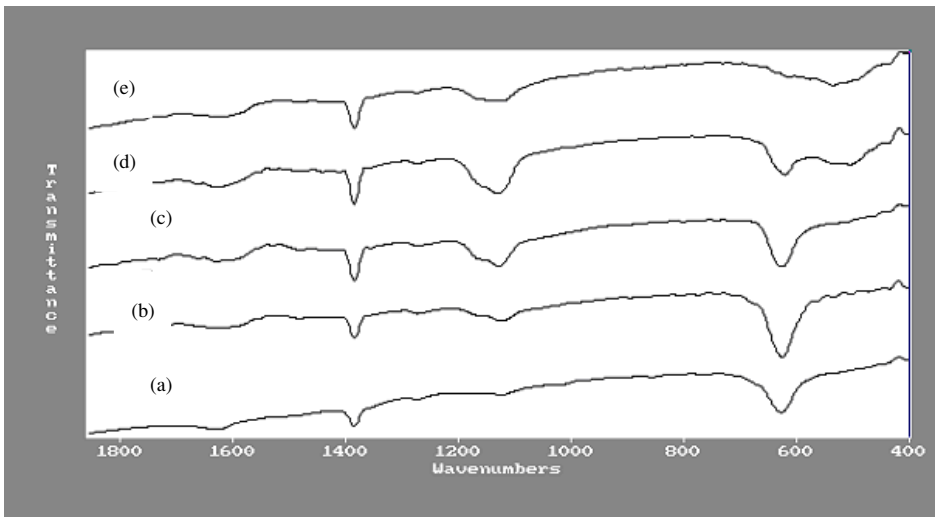

Figure 3. FTIR spectra of (*a*) as-deposited, and annealed at various temperatures (°C), (*b*) 200, (*c*) 250, (*d*) 300 and (*e*) 350.

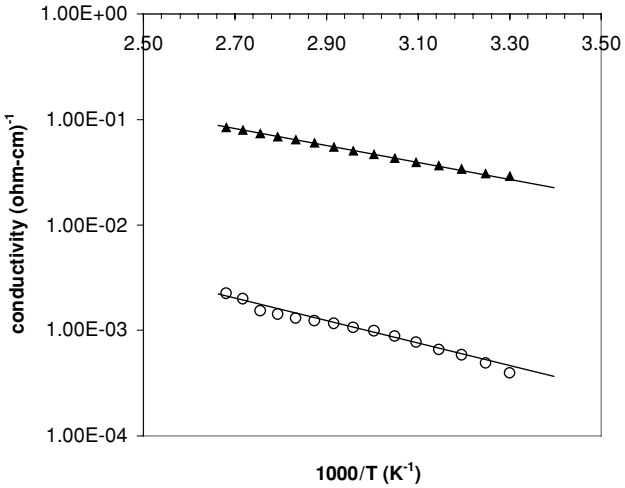

Figure 4. Temperature dependence of the conductivity for the films (○) as-deposited and (▲) annealed at 350 °C.

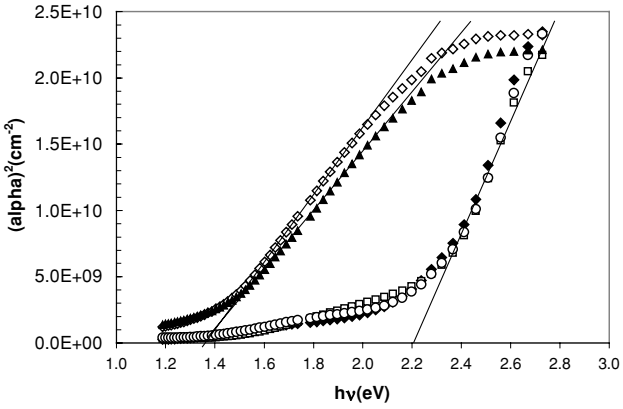

Figure 5. The plots of α^2 versus $h\nu$ curves for copper oxide films (○) as-deposited and annealed at various temperatures (°C), (⧫) 200, (□) 250, (◊) 300 and (▲) 350.

14 nm to 26 nm. The increase in grain size can be attributed to the change in crystallographic phase from Cu_2O to CuO. Our XRD results were compared with those obtained by Nair *et al* [17], Valtierra *et al* [18] and Pierson *et al* [15]. The similarities and differences of results can be summarized as follows: Cu_2O is the dominant phase before air annealing in all studies. Our deposited films have no preferred orientation but their films have a strongly preferred orientation along the (1 1 1) plane [17, 18] and the (2 0 0) plane [15]. Nair *et al* and Valtierra *et al* have observed a dominant phase of CuO in films grown by the same method as ours after annealing at 350 °C and 375 °C, respectively. Pierson *et al* have observed a mixture of Cu_2O and CuO phases in films grown by the dc magnetron sputtering method after annealing in air at 350 °C. Although our film thickness is almost the same as Nair's [17] and Valtierra's [18] the phase conversion temperature was found to be different. This result shows that the orientation of the films influences the conversion temperature.

The conversion of Cu_2O into CuO can also be shown by the determination of the optical band gap. The optical band gap of the material of the films has been determined on the basis of UV–VIS transmission measurements (figure 2). For this, in the fundamental absorption region the optical absorption coefficient (α) was evaluated using $\alpha = (\ln T^{-1})/t$ where t is the film thickness and T is the transmittance. Figure 5 shows a α^2 versus $h\nu$ plot of films as-deposited and annealed at different temperatures. The best linear relationship is obtained by plotting α^2 against $h\nu$, indicating that the optical band gap in these films is due to a direct allowed transition. The value of the optical band gap has been determined from the value of the intercept of the straight line at $\alpha = 0$. The films as-deposited and annealed at 200 °C and 250 °C have the same optical band gap 2.20 eV. In the literature Cu_2O film band gaps are listed: about 2 eV [1, 2], 2.1 eV [3], 2.35 eV [21] and 2.45 eV [15]. For 300 °C and 350 °C annealed films, when the diffraction peaks of CuO are detected in the x-ray pattern, the optical band gap decreases close to 1.35 eV. This value is close to the band gap of bulk CuO 1.30 eV given in the literature [15] and is lower than the optical band gap of tenorite films deposited by various techniques [3, 15, 17, 19]. After the annealing in atmosphere at 300 °C, CuO is the predominant phase. This is in agreement with the XRD results given in figure 1.

The results of FTIR measurements of as-deposited and annealed films are summarized in figure 3. The spectra of deposited films, annealed at 200 °C and 250 °C, are characterized by a strong band with one transmittance minimum of about 617 cm^{-1}. Balamurugan and Mehta [5], Maruyama [21] and Draou *et al* [22] observed the same band assigned to the phonon spectrum of Cu_2O. For the films annealed at 300 °C there are two peaks at about 617 cm^{-1} (the phonon spectrum of Cu_2O) and 500 cm^{-1} (the phonon spectrum of CuO). For the films annealed at 350 °C, broader peaks at about 500 cm^{-1} are also attributed to the phonon spectrum of CuO. The results of FTIR spectroscopic measurements also showed the conversion of Cu_2O into CuO after annealing at 300 °C.

Figure 4 presents the Arrhenius plots at temperatures between 300 and 373 K of dc conductivity σ of as-deposited Cu_2O and CuO films annealed at 350 °C. As shown in figure 4 the electrical conductivity of CuO is higher than the conductivity of Cu_2O and both of them are dependent on measurement temperatures. That result suggests that the thermoionic emission plays a major role in the carrier transport in this temperature range. The conductivity σ is given by $\sigma = \sigma_o e^{-E\sigma/kT}$, where E_σ is the activation energy. The activation energy values are obtained from the slopes by best fitting as 0.22 eV for Cu_2O and as 0.15 eV for CuO. Although film preparation methods are different these values are quite comparable with the reported values [23–25] for CuO. The activation energies of Cu_2O and CuO are much less than the actual band gaps. The conductivities are extrinsic in these materials.

4. Conclusions

Copper oxide films are prepared on glass substrates by chemical deposition. All prepared oxide films carry the crystalline character of the Cu_2O phase. The Cu_2O film has mainly (1 1 1) and (2 0 0) crystalline orientations. The direct band gap of Cu_2O and activation energy were found to be 2.20 eV and 0.22 eV, respectively. While the crystal structure did not change by annealing below 300 °C, it was observed, through using electrical conductivity, XRD, UV–VIS and FTIR transmission measurements, that Cu_2O converted to CuO (with band gap 1.35 eV) for annealing at 300 °C or greater temperatures.

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