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Structural and annealing studies of potentiostatically deposited Cu_2O thin films

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Abstract

Cuprous oxide (Cu_2O) thin films were deposited on Cu and tin oxide coated glass substrates through potentiostatic electrodeposition. The optimum range of deposition parameters was experimentally investigated. X-ray diffraction studies revealed the formation of single-phase cubic Cu_2O films in the deposition potential range from -0.355 to -0.555 V versus SCE. Studies revealed that an optimum pH of 9.0 yielded single-phase cubic films with improved crystallinity. The preferential orientation of (2 0 0) cubic Cu_2O peak was found to increase with bath temperature in the range 30–70 °C. The effects of annealing on the preferred orientation, grain size and optical band gap were studied. The energy conversion efficiencies of as-deposited and annealed p-Cu_2O films as photocathodes in photoelectrochemical (PEC) solar cells were studied and the results were discussed.

Keywords: Cu_2O films; Structural properties; Photoelectrochemical solar cells

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1. Introduction

Cuprous oxide (Cu_2O) is a non-toxic, semiconducting material potentially attractive for solar cell and sensor applications [1,2]. Cu_2O thin films are prepared by several deposition methods including anodic oxidation [3], thermal oxidation [4], electrodeposition [5], reactive sputtering [6] and chemical bath deposition [7]. Among various methods employed for the preparation of Cu_2O films, electrodeposition is attractive due to its simplicity, low-cost and low-temperature process. Electrodeposited Cu_2O film normally exhibits high resistance and the efficiency of photovoltaic and photoelectrochemical (PEC) solar cells was low. The structural properties of semiconducting thin films are found to influence the orientation, grain size and in turn the performance of solar cell devices. In this paper, we report our work on the structural, annealing behavior and PEC solar cell studies of electrodeposited Cu_2O thin films.

2. Experimental details

Cuprous oxide films were electrodeposited on copper and tin oxide coated glass slides ($\sim 10\,\Omega$/square) in an electrochemical cell containing an aqueous solution mixture of lactic acid (3.25 M), cupric sulphate (0.45 M) and sodium hydroxide (NaOH). The counter and reference electrodes were a graphite foil and saturated calomel electrode (SCE), respectively, and electrodeposition was carried out using a PAR Potentiostat/Galvanostat (EG&G, model 362). Cuprous oxide thin films were prepared at various solution pH (5.0–11.0) and bath temperatures (30–90 °C) at a deposition potential of -0.555 V versus SCE for durations ranging from 30 min to 2 h to obtain films of various thickness.

Cuprous oxide films were annealed in air at various temperatures (150–550 °C) for 30 min. An X-ray diffractometer (JEOL-JDX 8030), with CuK_α radiation ($\lambda = 1.542$ A) was used for structural studies. Optical studies were carried out with a Hitachi U-2000 spectrophotometer. The surface morphology and EDAX measurements were carried out using a scanning electron microscope (JEOL JSM 35). Electrical resistivity measurements were carried out using a four-probe technique in the temperature range from 27 to 330 °C.

A PEC solar cell was formed using Cu_2O as photocathode in a three electrode geometry consisting of a platinum foil and SCE as counter and reference electrodes, respectively, in an electrolyte containing 0.5 M Na_2SO_4. The spectral response measurements were carried out using a 150 W tungsten-halogen lamp with monochromator (Jasco-CT 10) and filters (Toshiba IRA).

3. Results and discussion

3.1. Effect of deposition potential and solution pH

The deposition potential plays an important role on the structure of electrodeposited Cu_2O films. X-ray diffraction patterns of Cu_2O films prepared at various

deposition potentials (−0.355, −0.455, −0.555,−0.655 and −0.755 V versus SCE) are recorded. It is found that the XRD patterns of films deposited at −0.355, −0.455 and −0.555 V versus SCE showed Cu_2O peaks with preferential orientation along (2 0 0) axis. However, films deposited at more negative potentials (−0.655 and −0.755 V versus SCE) indicated the presence of Cu peaks in addition to Cu_2O peaks with a preferential orientation along (3 1 1) direction. The grain sizes of films along preferred orientations are estimated from FWHM data and Debye–Scherrer equation [8]. The grain sizes are estimated as 26, 31, 55, 25, and 20 nm for films deposited at −0.355, −0.455, −0.555, −0.655 and −0.755 V versus SCE, respectively. The above results indicate an optimum deposition potential of −0.555 V versus SCE to prepare Cu_2O films with a larger grain size.

The effect of solution pH on the structure of Cu_2O film is also studied. Fig. 1 shows the XRD spectra of Cu_2O films prepared at a deposition potential −0.555 V versus SCE at various pH values (7.0, 9.0, and 11.0) on tin oxide coated substrates at 70 °C. Even though no change in crystal structure is observed, films deposited at solution pH 7.0 exhibits extra Cu peaks in addition to Cu_2O peaks. The effect of pH is mainly in controlling the concentration of the freely diffusing Cu^+ ions. At lower pH value (7.0 and below), besides Cu_2O, crystalline Cu was also found which may be due to the rapid crystallization of Cu compared with that of Cu_2O. It is found that the XRD spectra of films deposited at solution pH 9.0 exhibits good crystallinity with higher peak intensities and taken as the optimum solution pH to synthesize Cu_2O thin films.

3.2. Effect of bath temperature

Films deposited below 50 °C are poorly crystallized and at higher bath temperatures well-crystallized cubic Cu_2O films are found. It is observed that the current densities at higher bath temperatures are higher (1 mA cm^{-2}) than at low temperatures (400 μA cm^{-2}). It is observed from Fig. 2 that as the deposition temperature increases the peak intensities and grain size along the preferential orientation direction (2 0 0) increases which indicates an improvement in the crystallinity of the samples. This improvement may be caused by the effective mass transfer and increased rate of deposition at higher temperatures. However, at a bath temperature of 90 °C, partial evaporation of bath solution hinders uniform growth of Cu_2O films which is evidenced by surface morphological studies.

3.3. Annealing studies

Cuprous oxide films were annealed at various temperatures in air for 30 min. Fig. 3 shows the XRD spectra of films annealed in the temperature range from 150 to 450 °C. It is clear from Fig. 3 that there is no change in the crystal structure for films annealed at 150, 250 and 350 °C. However, for the sample annealed at 400 °C a peak corresponding to cupric oxide (CuO) appeared in addition to peaks of cuprous oxide (Cu_2O) whereas annealing at 450 °C shows mainly CuO peaks. This indicates a conversion of cuprous to cupric oxide which is evidenced by a color change from

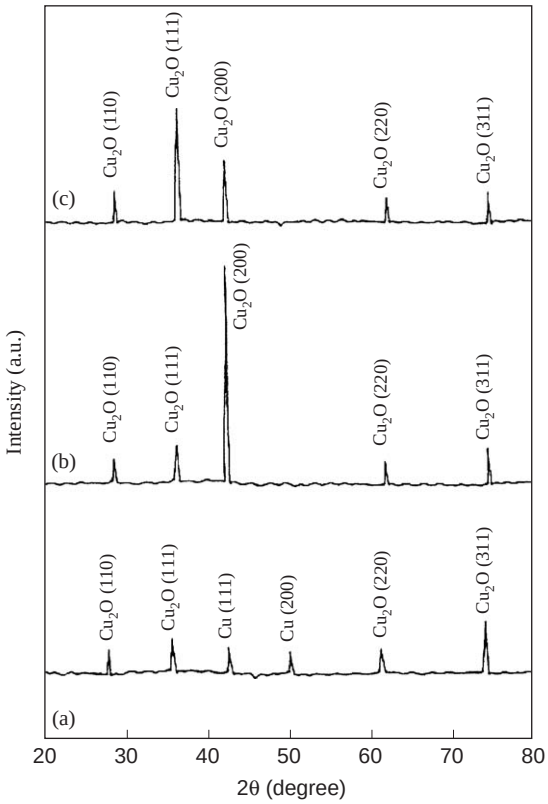

Fig. 1. XRD patterns of Cu_2O films deposited at various solution pH values. (a) pH: 7.0 ± 0.1 (b) pH: 9.0 ± 0.1 (c) 11.0 ± 0.1; deposition potential: -0.555 V vs SCE, bath temperature : 70 °C, deposition time: 30 min.

brick red (Cu_2O) to black (CuO). CuO may be obtained by oxidation of cuprous oxide at higher temperature as represented by the equation

$$Cu_2O + \tfrac{1}{2}O_2 \rightarrow 2CuO.$$

Similar behavior has been reported for films annealed at 550 °C and annealing above 550 °C causes peeling off the films from the substrates. However, it is found that the intensity of (2 0 0) cubic phase increases with annealing temperature and it is found to be maximum for a film annealed at 350 °C. The increase of peak heights of XRD spectrum for annealed sample suggests the crystallization of some amorphous Cu_2O in the polycrystalline material.

The grain sizes, on the other hand, are also found to increase with annealing temperature and found to be 100 nm for a typical film annealed at 350 °C. The above results indicate that the optimum annealing temperature for Cu_2O film is 350 °C in air. Scanning electron micrographs of an unannealed and annealed (350 °C in

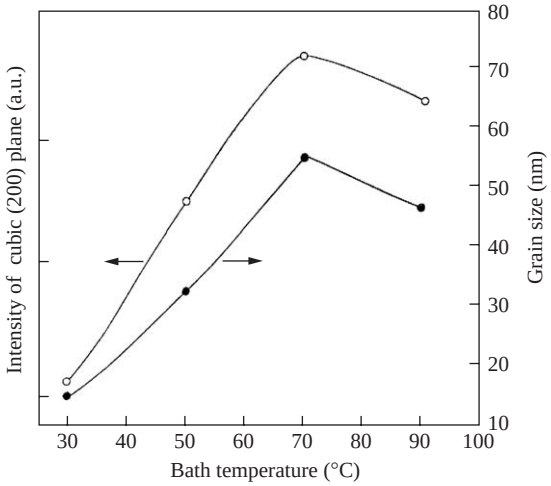

Fig. 2. Variation of XRD signal intensity of Cu_2O (200) and crystallite size with bath temperature for typical Cu_2O film.

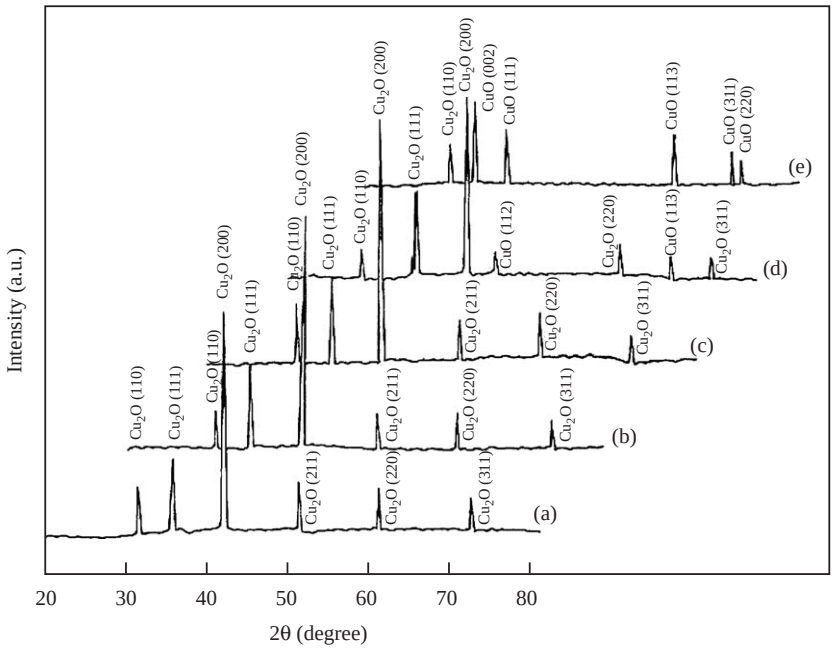

Fig. 3. XRD spectra of typical Cu_2O films annealed at various temperatures (a) 150 °C, (b) 250 °C, (c) 350 °C, (d) 400 °C and (e) 450 °C.

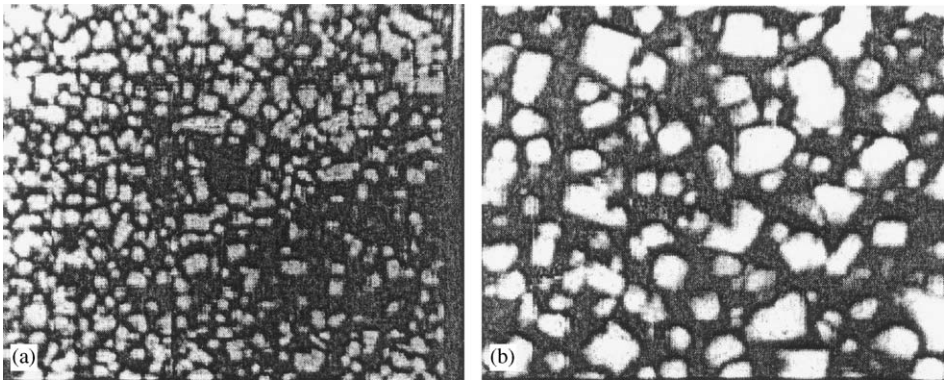

Fig. 4. Scanning electron micrographs of typical Cu_2O films (a) as-deposited, (b) annealed at 350 °C in air.

air for 30 min) samples revealed grain sizes 50 and 100 nm, respectively, (Fig. 4) which indicates an increase in grain size due to annealing process.

Optical absorption spectra are recorded for as-deposited and annealed samples and the band gaps of Cu_2O films are evaluated from $(\alpha h\gamma)^2$ versus $h\gamma$ plots. The band gaps estimated for as-deposited and annealed samples are 1.97 and 2.00 eV, respectively, which are in good agreement with literature value of 1.97 eV for Cu_2O single crystals [9]. The studies indicate that the band gap of Cu_2O films is unaffected by annealing treatment in air at 350 °C. However, annealing at 450 °C showed the change in band gap from 1.97 to 2.25 eV which corresponds to the band gap of CuO. The refractive index 'n' and extinction coefficient 'k' of as-deposited and annealed films were evaluated by a continuous descent derivative method [10]. The refractive index corresponding to as-deposited and annealed films (350 °C) is found to be 2.73 and 2.71, respectively, which is in close agreement with the earlier reports for Cu_2O [11]. The refractive index of films annealed at 450 °C is found to be 2.55, which agrees with the refractive index of CuO film. The extinction coefficient, on other hand, decreases with increase in wavelength. It is noted that variation of n and k with wavelength is similar to the absorbing semiconducting materials.

3.4. Photoelectrochemical studies

As-deposited and annealed samples are used as photocathodes in a three-electrode PEC solar cell. Fig. 5 shows the photocurrent variation with wavelength for Cu_2O photoelectrodes. It is observed that the maximum photocurrent exhibited a peak near the absorption edge of Cu_2O. The energy conversion efficiencies of the PEC cells were estimated to be 0.2% and 0.05% for annealed and as-deposited films, respectively. The lower values of conversion efficiency may be due to the defect structure of Cu_2O film. Even though the conversion efficiencies estimated are low, the efficiencies of the PEC cells estimated in the present work are larger than the values reported earlier for Cu_2O electrodes [12]. The conversion efficiency of

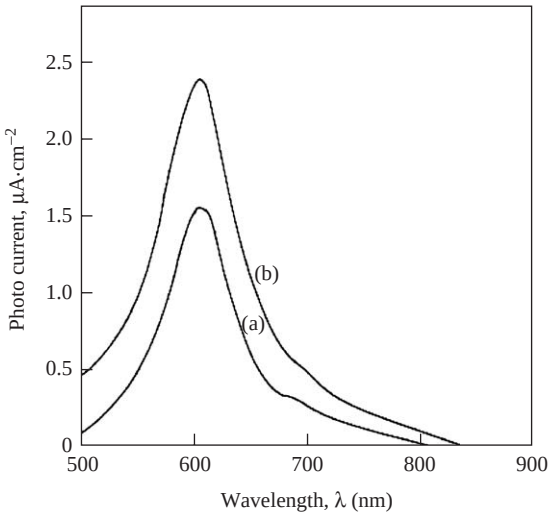

Fig. 5. Variation of photocurrent with wavelength for p-Cu_2O solar cell (a) as-deposited, (b) annealed at 350 °C in air.

Cu_2O-based PEC solar cell may be improved by preparing doped Cu_2O films and suitably modifying the surfaces to achieve lower resistivity values.

4. Conclusions

Polycrystalline Cu_2O thin films with cubic structure were deposited potentiostatically on Cu and SnO_2 substrates. The optimized deposition conditions to synthesize good quality Cu_2O films are derived as: bath temperature, 70 °C; deposition potential, −0.555 V versus SCE, and solution pH, 9.0 ± 0.1. The resistivity, band gap and activation energy of as-deposited and typical Cu_2O film are estimated to be $5 \times 10^6\,\Omega$ cm, 1.99 and 0.85 eV, respectively. No change in band gap is observed during annealing below 350 °C. However, annealing increases the crystallite size and lowers the electrical resistivity of the film from 10^7 to $10^3\,\Omega$ cm. The changes in band gap from 1.97 to 2.25 eV and color from brick red to black showed the conversion of Cu_2O into CuO during annealing at 450 °C. PEC solar cell studies employing p-Cu_2O as photocathodes exhibited a higher conversion efficiency for annealed films.

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