Cuprous oxide thin films obtained by dip-coating method using rapid thermal annealing treatments

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ABSTRACT

The transformation of cupric oxide (CuO) into cuprous oxide (Cu_2O) thin films by rapid thermal annealing (RTA) treatments is studied. The CuO films were obtained by dip-coating from a precursor solution containing copper (II) acetate. The films are formed of ten coats, where each one was deposited with a withdrawal speed of 8 cm/min and dried in air at 250 °C for 5 min; after that, the films were sintered in air at 250 °C for 1 h. Under these conditions an average thickness of 240 nm is obtained. The RTA treatments on the CuO films were performed for 10 s with a heating ramp of 5 °C/s in vacuum at temperatures (T_A) in the 325–450 °C range with steps of 25 °C. As revealed by X-ray diffraction data, the composition of the polycrystalline films depends upon the applied T_A: i) CuO + Cu_2O for T_A < 375 °C, ii) only Cu_2O for T_A = 375 and 400 °C, and iii) Cu_2O + Cu for $T_A \geq 425$ °C. Some physical properties of Cu_2O films are: crystallite size ranging between 6.5 and 8.5 nm, direct forbidden band gap energy of 2.36 eV, and optical transmission around 75% for wavelengths larger than 520 nm. Cu_2O films obtained at T_A = 400 °C are p-type with resistivity of 9.9×10^1 Ω-cm, mobility of 0.52 cm^2 V^{-1} s^{-1}, and carrier concentration of 1.2×10^{17} cm^{-3}. These properties of the RTA obtained Cu_2O films make them a good candidate for application in solar cells of transparent conductive oxide (n-type)/Cu_2O heterostructure type.

1. Introduction

Copper oxides are attractive as thin film photovoltaic materials due to their high absorption coefficients in the visible region, low toxicity and great availability given that Cu is one of the most earth-abundant elements. Generally, Cu_2O and CuO show natural p-type conductivity attributed to copper vacancies within the crystal lattice [1–4]. Solar cells have been investigated implementing CuO and Cu_2O as absorber layers, nevertheless for CuO low conversion efficiencies have been reported, which is attributed to small short-circuit current densities and low carrier lifetimes [5,6]. On the other hand for Cu_2O, a theoretical maximum efficiency around 20% has been estimated for homojunction devices attributed to its band-gap value (~2 eV). However, due to the difficulty to obtain n- type Cu_2O films, Schottky barrier and heterojunction devices have been investigated, the later showing efficiencies above 2% [7–9]. A maximum efficiency of 8.1% has been reported for a MgF₂/AZO/ Zn$_{0.38}$Ge$_{0.62}$-O /Cu_2O:Na heterostructure, using Cu_2O as substrate (thickness ~ 0.2 mm) [10]. For this type of cell, the large thickness and low conductivity of the Cu_2O can decrease the fill factor (FF) values. Due to this fact, Cu_2O thin films may contribute to increase the efficiency of this type of cells [11].

Several techniques have been used for fabrication of bulk and thin film Cu_2O, these include thermal oxidation, electrodeposition and r.f. sputtering [12–18]. However, few works have been reported in the literature using the dip or spin coating method based on a simple precursor solution, despite it presents advantages such as, low cost and less demanding processing conditions, among others. Using this method, Cu_2O films are obtained after thermal treatments in controlled atmospheres at temperatures in the 275–900 °C range and times from 30 min to 5 h [18–21]. Depending on the as-deposited material, the atmospheres might be N_2, O_2, Ar, forming gas, or vacuum to either reduce CuO or to oxidize Cu. In this work from our knowledge, for first time, CuO thin films were subjected to rapid thermal annealing (RTA) in vacuum in order to obtain Cu_2O films. One advantage of using RTA is the lower treatment times and other effects not achieved through conventional annealing. Structural, optical and morphological properties were studied at different annealing temperatures (T_A) at fixed heating ramp and treatment time. Electrical parameters of resistivity, mobility, and carrier (holes) concentration are reported too. In this way, this work contributes to a better understanding of the electrical

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Table 1
Molar proportions and specifications of the reagents used in the precursor solution.

Reagent	Brand	Semi-structural formula	Molar proportion
copper (II) acetate monohydrate	Sigma-Aldrich	$(Cu(CH_3COO)_2) \cdot H_2O$	1 mol
methanol	J.T. Baker	CH_4O	72 mol
triethylamine	Merck	$N(CH_2CH_3)_3$	1 mol
glycerol	Merck	$CH_2OHCHOHCH_2OH$	0.4 mol
lactic acid	J.T. Baker	$CH_3CH(OH)COOH$	1.64 mol

properties of Cu_2O films deposited by the spin or dip-coating method, which is scarce [22].

2. Experimental procedure

A copper acetate (II) precursor solution was prepared at room temperature with the proportions shown in Table 1. The CuO films were deposited on glass substrates (Corning 2947) by the dip-coating method. Prior to deposit, the glass substrates were washed with a residue-free detergent and left in chromic acid solution for a 24 h period to remove any organic material residue. After that, a chemical attack with nitric acid is performed for 3 h at 75 °C. Ten cycles of immersion-withdraw-drying and a final sintering were required to obtain films of the target thickness which was 240 nm. The withdrawal speed was 8 cm/min and the drying was performed at 250 °C for 5 min in air. After that, the samples were sintered at 250 °C for 1 h, also in air, using a conventional heating ramp of 7.5 °C/min.

Rapid thermal annealing (RTA) treatments were performed in a closed chamber at a vacuum pressure of $\sim 1 \times 10^{-4}$ Torr on the CuO films obtained as described previously. The sample heating configuration is shown in Fig. 1, the sample was placed between two graphite plates which absorb radiation, generated by halogen lamps. One side of the sample is resting on the graphite plate and the other is in direct contact with the atmosphere. The heating profile used during the thermal treatments is shown in Fig. 2. An initial degassing treatment stage (DS) was applied to the sample at 200 °C for 5 min. After that, the samples were rapidly heated at different T_A's in the 325–450 °C range through a non-conventional heating ramp of 5 °C/s. Once the T_A set-point was reached, the sample remained during 10 s at this temperature. The inset of Fig. 2 shows the temperature profile with more detail around T_A, for the case of 400 °C. The samples were kept in the chamber under vacuum, until a temperature below 100 °C was reached.

Structural characterization was performed with a Rigaku D/Max 2100 diffractometer with $K_{\alpha 1} = 1.54$ Å. Crystallite mean size (CS) was estimated with Scherrer's formula Eq. (1), using Jade 5® analysis software, calibrated with a Si standard. The crystallite shape factor k has a value of 0.94 and $FWHM(S)$ represents the value of full width at half maximum after subtracting the instrumental error contribution.

$$CS = \frac{k \times \lambda}{FWHM(S) \times \cos \theta}, \tag{1}$$

The different Cu oxidation states were identified from their respective power patterns, Cu:PDF04-0836, CuO:PDF48-1548 and Cu_2O:PDF05-0667 number cards. Film thickness was determined with a Dektak II profilometer. Resistivity measurements were obtained by the four-point probe system using a Loresta GP MCP-T600. Mobility and carrier concentration were obtained from Hall Effect measurements. Reflectance (R) and transmittance (T) spectra in the 240–840 nm range
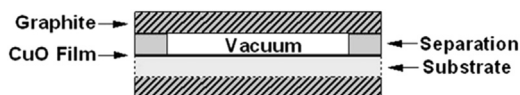

Fig. 1. Heating configuration for CuO thin films using rapid thermal treatments.
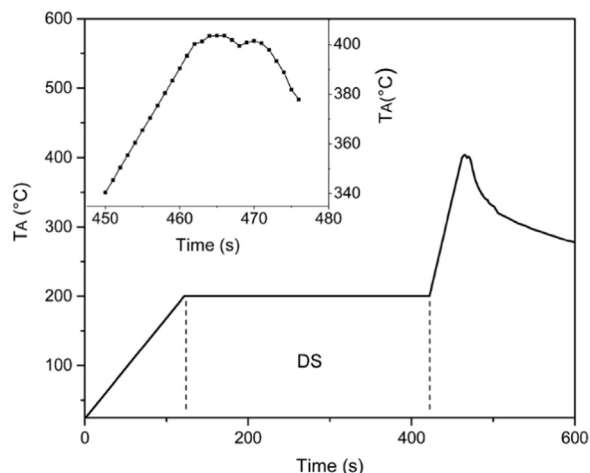

Fig. 2. a) Temperature profile used for the RTA including degassing treatment stage and b) broaden profile in the region of T_A.

were acquired using a FilmTek 3000 system (SCI, Inc.). Also, T measurements were performed with a Cary-5000 (Agilent Technologies) spectrophotometer in the 240–2600 nm range. As both sides of the substrate are film-coated, only the film exposed to the vacuum during the RTA was characterized. The film at the back side was removed with a 10% HCl solution previously to the T and R measurements.

Morphological properties were determined by scanning electron microscopy (SEM) using a JEOL electron probe microanalyzer model JXA-8530F, further compositional analysis was performed by scattering energy dispersive X-ray spectroscopy (EDS). X-ray photoelectron spectroscopy (XPS) high resolution scans were acquired with a system assembled by Intercovamex equipped with a monochromatized Al $K\alpha_1$ (hν = 1486.7 eV) X-ray source, and an Alpha 110 hemispheric spectrometer (pass energy of 50 eV), with a seven channel electron multiplier detector (Thermofisher). The spectra were referenced to adventitious carbon peak C 1s at binding energy 284.5 eV.

3. Results and discussion

3.1. Crystalline structure and surface morphology

The presence of CuO in the films deposited by the ten cycles of immersion-withdraw-drying and final sintering was confirmed by XRD data (Fig. 3). Their dark-brown appearance is also consistent with band gap energy below 1.5 eV [23]. After the RTA treatments in vacuum, the CuO films changed in tonality to yellow, suggesting a phase transformation to Cu_2O which has a band gap in the range 2.17–2.4 eV [24]. Fig. 3 shows the XRD patterns of the films after RTA at different T_A's. As a guide for a quick identification, the expected diffraction lines according to PDF cards for CuO and Cu_2O are displayed. It can be seen for $T_A \leq 350$ °C, polycrystalline films are constituted of a mixture of two phases, CuO and Cu_2O, indicating a partial phase transformation. The CuO phase is identified by the small contribution of diffraction peaks corresponding to the $(11\bar{1})$ and (111) planes. For films RTA-treated at T_A's 375 °C and 400 °C, the patterns show diffraction lines belonging only to the Cu_2O phase indicating a complete transformation of the CuO phase. Therefore, polycrystalline films of Cu_2O with a preferential orientation on the (111) plane are obtained by the reduction process carried out in vacuum using RTA. Thermal treatments at higher T_A's further reduce Cu ions to the extent that the formation of metallic copper is detected by small peaks of (111), (200) and (220) crystallographic planes.

The average crystallite size values calculated from the full width at half-maximum (FWHM) of the Cu_2O (111) diffraction peak are shown in Fig. 4. As it can be noticed, the crystallite size of Cu_2O is in the range of 6–10 nm and with a trend to increase with T_A. Thus, nanocrystalline