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Copper oxide thin films deposition by spray pyrolysis

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Abstract

CuO thin films have been growth on to heated glass substrates by varying substrate temperatures from 280 to 400°C. The effect of the pyrolysis on structural, optical and electrical proprieties of CuO films has been investigated in the present work. Phase analysis was carried out using Micro-Raman scattering. The optical properties were studied by mean of UV–visible and near infrared spectroscopy. The conductivity was measured by the electrical D.C transport. The structural analysis indicates the presence of a single CuO phase with a monoclinic structure. The optical transmittance spectra show a high absorption of all films in the visible region. The electrical characterization indicates a maximal electrical conductivity of $1{,}03 \times 10^{6}$ $(\Omega .cm)^{1}$.
Keywords: Copper oxide, solar cells, Spray pyrolysis.

1. Introduction

In recent years, copper oxide (CuO) thins films have attracted great interest due to their important applications in many technological fields. This is due, firstly, to the low cost, the non-toxicity and the availability of copper in the nature, secondly to the simplicity of the deposition process of its components. Copper oxide is known to have two stable forms, namely CuO and Cu_2O with different properties. CuO is a p-type semiconductor with a monoclinic structure; it has a relatively low band gap of 1,2-1,9 eV [1,2]. Furthermore, Cu_2O materials, in general, is a p-type semiconductor which crystallizes in cubic structure with a large direct band gap of 2 et 2,6 eV [3]. These two phases were mainly used in the fields of electronics and optoelectronics such as: high Tc superconductors [4], lithium batteries [5], for magnetic storage [6], gas sensors [7] and absorbers layers in solar cells [8].Various techniques have been used for CuO thin films deposition namely: sol-gel [9] chemical vapor deposition [10], plasma evaporation [11] and electrodeposition [12].
Among these techniques, spray pyrolysis is a very attractive and versatile technique; it has been largely used to produce adherent, homogenous and stoichiometric films. The main goal of the present work is to produce CuO thin films with good optoelectronic properties by optimizing the substrates temperature while keeping constant the others operating parameters.

2 Experimental

Copper oxide thin films have been prepared on glass substrates by ultrasonic spray pyrolysis. The precursor solution was prepared by dissolving 0.05 M copper chloride ($CuCl_2.2H2O$) in distilled water. Then, the precursor solution sprayed in fine droplets of 40 µm in diameter, by an ultrasonic generator on heated glass substrate. Films were formed by pyrolytic reaction. During deposition, the substrate temperature is kept at 280, 300, 350, 400 °C for four different runs. The deposition time for each run is 20 min.
The films crystalline phases are analyzed by micro-Raman measurements performed at room temperature using the 514.5 nm line of an argon ion laser as the excitation source (Renishow). The UV–Visible transparence of the films is performed by Shimadzu UV–3101 PC spectrophotometer within the wavelength range of 200–1800 nm. The values of films thickness and refractive index were derived from optical transmission measurement. The electrical characterization of the films was carried out using the electrical D.C transport to measure the conductivity in dark and at room temperature.

3 Results and discussion

3.1 The deposition rate and the refractive index

In Figure.1 we have reported the variation of deposition rate and the refractive index of CuO thin films as a function of substrate temperatures. The deposition rate is estimated from the ratio of the layer thickness on the deposition time, fixed at 20 minutes. As can be seen the deposition rate decreases with increasing of substrate temperature, it is maximal

(Vd=275.15nm/min) at substrate temperature equal to 280 ° and minimal (Vd=216.32nm/min) for the sample prepared at 400 ° C. The reduction of deposition rate can be explained by the phenomenon of densification. The rise in substrate temperatures yields to an increases in the formation energy of the material by the pyrolytic reaction on the surface, which influence on the growth kinetics and produces denser film. This result is in good agreement with the increase of the refractive index from 1,53 to 1,65which is a clear indication of films densification.

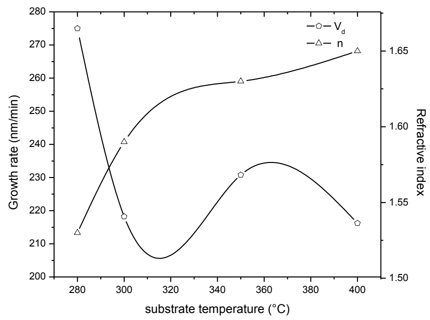

Figure1: Variation of deposition rate and refractive index as a function of substrate temperatures

3.2. Structural properties

Figure.2 shows the Raman spectra of the as-prepared CuO thin films with diverse substrate temperatures. The Raman spectra are composed with three main phonon modes (Ag and 2Bg) located at 297, 334 and 608 cm^{-1} which are assigned to a single phase CuO with a monoclinic structure. These peaks are largely reported in the literature [13-15]. No other secondary phase modes are present as Cu_2O [16].

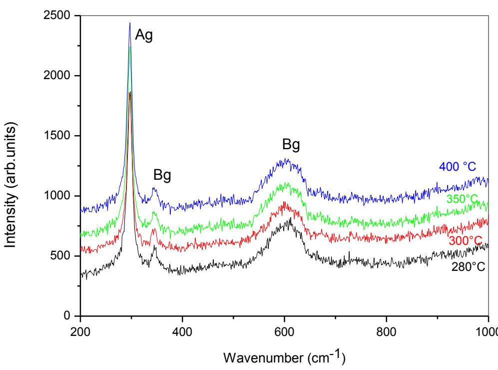

Figure 2: Micro Raman spectra of CuO deposited with various substrate temperatures.

3.3 Optical properties

The transmittance spectra in UV-Visible region of CuO films prepared with different substrate temperatures are shown in figure.3. The measurements were performed in the UV-visible, corresponding to the wavelength range: 200 - 1800 nm. It was determined that all films behaved as transparent materials in the 800-1100 nm wavelength range located in infrared field. On the other hand, in the visible region films transmittance values decreases sharply in the wavelengths range less than 800 nm due to their highly absorbing properties. This wavelength range represents the material fundamental absorption region. Films optical band gap have been estimated, as show in Fig.4 from the plot $(\alpha h\nu)^2$ as a function of photon energy (hν), according to Tauc formula for direct band gap semiconductors [17]:

$$(\alpha h\nu)^2 = B\,(Eg-h\nu)$$

Where α is a absorption coefficient, B is a constant, h is Planck constant, Eg is the energy band gap and ν is incident photon frequency.

The obtained optical gaps increase with substrate temperature increasing from 1.44 eV to 1.76 eV

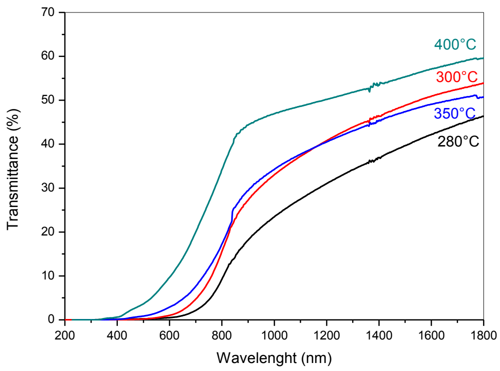

Figure 3: UV-Visible transmittance spectrum of CuO thin films deposited spectra at different substrate temperatures.

which is in good agreement with CuO band gap values reported by Gopalakrishna et al. [18]. They found optical band gap values laying between 1.8 eV and 1.2 eV for substrate temperature ranged from 250 to 400 ° C. However, film prepared at 280 °C have an optical band gap close to 1.44 eV , this value is required for solar cells since it matches well with solar spectrum.

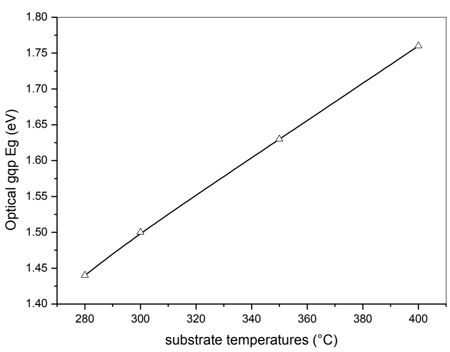

Figure 4: Variation of optical band gap of CuO films with substrate temperature

3.4. The electrical properties

The electrical conductivity variation, measured in the dark and at room temperate, with different deposition temperatures is shown in Figure.5. From this figure we observe that the conductivity increases from 7.11 x 10^{-8} to 1.03 x 10^{-6} (Ω. Cm)$^{-1}$ for substrate deposition temperature increase from 280°C to350 ° C, while at 400 °C the conductivity decreases by one order of magnitude.

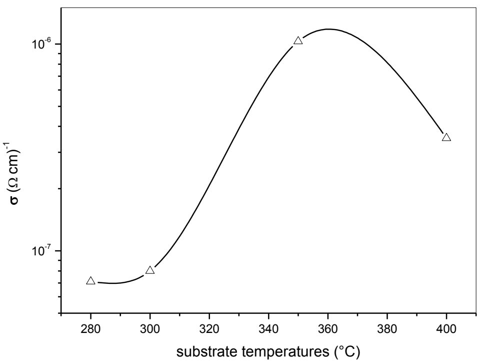

Figure 5: Variation of the conductivity versus the substrate temperatures.

4. Conclusion

CuO thin layers were deposited by ultrasonic spray on glass substrates. The influences of the substrate temperature on structural, optical and electrical properties were studied. The films prepared at different temperatures showed the presence of a single phase CuO with a monoclinic structure. The optical characterization showed a strong absorbance in the visible range with values of optical gap varied from 1.44 to 1.76 eV. All the deposited films exhibit p-type conductivity with a relatively high conductivity. Film deposited at 350°C seems to have suitable optical and electrical properties for efficient thin film solar cell fabrication.

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