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An effect of temperature on structural, optical, photoluminescence and electrical properties of copper oxide thin films deposited by nebulizer spray pyrolysis technique

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ABSTRACT

In this work, copper oxide thin films were deposited on glass substrate by nebulizer spray pyrolysis technique with different temperatures (i.e. 250–320 °C). All the deposited films were characterized by X-ray diffraction (XRD), atomic force microscopy (AFM), Laser Raman, UV–Vis, Photoluminescence and Hall Effect measurements for the Structural, morphological, vibrational, optical and electrical properties. The XRD studies confirmed that the films deposited with different temperatures from 250 to 300 °C possess single cubic crystal structure phase of cuprous oxide (Cu_2O) whereas the films deposited at 310 and 320 °C were found to have a mixed phase of CuO and Cu_2O. When the temperature reaches above 310 °C the Cu_2O phase become unstable and started to convert as CuO. Laser Raman studies confirmed that the observed peaks at 109, 148, 219, 416,515 and 635 cm^{-1} are belong to Cu_2O phase deposited at 250 and 280 °C. However, the films deposited at 310 °C and 320 °C having additional peaks at 273, 327 and 619 cm^{-1} which conforms the presence of mixed (CuO and Cu_2O) phase. The AFM studies shows that the deposited films has uniformly distributed with homogeneity and the particles extended all over the surface. Optical measurement showed that the band gap of deposited thin films in the range of 2.44–1.97 for 250–320 °C, respectively. A single and strong emission peak at ~ 617 nm is observed in PL spectra, which conforms the copper oxide film. Hall Effect measurements showed that all the films are of p-type conductivity with resistivity (ρ) of $4.61 \times 10^2\ \Omega$ cm, carrier concentration (n) of $13.53 \times 10^{15}\ cm^{-3}$ and mobility of 1.0 cm^2/vs at 320 °C temperature. The low activation energy of 0.012 eV were observed for the film deposited at 320 °C.

1. Introduction

Copper oxide have advantages of nontoxic, economic and good environmental suitability, rather simple formation of oxide makes it as an attractive material [1]. It has considerable attention as a recognized p-type semiconductor. The two possible phases of copper oxide are cupric oxide or tenorite (CuO) and the cuprous oxide or cuprite (Cu_2O) of monoclinic and cubic structures with band gap values of 1.3–2.1 eV and 2.0–2.6 eV, respectively [1], and those phases have suitable properties for certain applications. Although, the preparation of a preferred phase of copper oxide is not an easy task. It has been widely studied for several applications such as solar energy conversion, optoelectronics, batteries, gas sensors, optical switches, semiconductors and photo catalysis [2,3]. Numerous techniques were updated for obtaining copper oxide thin films such as electro deposition [4], chemical vapor deposition [5], SILAR [6], sol–gel [7], sputtering [8], spray pyrolysis [9], thermal oxidation [10], plasma evaporation [11] and nebulizer spray pyrolysis [12] etc. Ahead of various thin film deposition techniques, Nebulizer Spray pyrolysis (NSP) is a versatile, inexpensive, time saving and efficient way of obtaining thin films at room atmosphere. Nebulizer

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technique is used to produce metal oxide thin films as it is cost effective and suitability for mass production. The benefit of nebulizer spray technique is its minimum material consumption with improved control over spray and carrier gas flow allowing deposition of pinhole free smooth films. In the NSP method optimization of various parameters can be done like temperature, the volume of the solution, molarity, distance between the gun and substrate and pressure. Nebulizer was used to prepare mist of the precursor solution for thin film fabrication on a glass substrate. A specially designed glass tube guides the mist of the precursor solution generated from nebulizer onto the substrate kept at desired temperature. As per the detailed reviewed literature by authors on copper oxide thin films, there are few reports available on phase change of copper oxide thin film [10,13–15]. However, there are no reports in the near phase changing temperature or in the temperature range from 250 to 320 °C. Hence, in the present work, for the first time the authors attempts to study the various key properties of copper oxide films fabricated in the temperature range from 250 to 320 °C. The prepared copper oxide thin films were investigated.

2. Experimental detail

2.1. Preparation of precursor solution

Schematic diagram of the nebulizer spray pyrolysis unit is already shown in our previous work [16]. Nebulizer spray pyrolysis technique arrangement has a nebulizer unit, a hot plate, temperature controller, spray gun shaped glass tube and a compressor unit. The copper oxide thin film was deposited on glass substrate by spraying an aqueous solution containing copper (II) acetate monohydrate ($C_4H_6O_4{\cdot}H_2O$) and high pure glucose ($C_6H_{12}O_6$) both with the molar concentration of 0.04 M was dissolved in 10 ml of distilled water. The prepared solution was added with 20 vol% of 2-propanol [$(CH_3)_2$ CHOH] and stirred at room temperature for 30 min. The precipitation of copper particles was done by glucose which is a reducing agent [17]. The wet-ability of the droplet in the substrate is enhanced by the use of 20 vol% of 2-propanol to reduce the surface tension of the solution which improves the homogeneity level of the deposited films [18]. Before the deposition, the glass substrate was chemically cleaned by detergent and kept in the chromic acid for a couple of hours to remove the impurities in the substrate followed by acetone cleaning and then rinsing it with de-ionized water. The volume for the each deposition was 10 ml and the temperature is varied between 250 and 320 °C. The substrate temperature was maintained by the use of highly stable temperature controller. The distance between nozzle and substrate was kept at ~ 5 cm and the air flow rate of ~ 1.0 kg/cm^2 for an area of 5 × 2.5 cm. The sample was kept on the hot plate until it reaches the room temperature after the deposition was over.

2.2. Characterization

The structural properties of copper oxide thin films deposited on a glass substrate were studied using X-ray diffraction (Bruker D8 advance X-ray diffractometer) CuKα (λ = 1.5406 nm) radiation. The diffraction angle for scanning was started from 10° to 80 degrees continuously with a scan rate of two degrees per minute. The Raman spectra for the deposited copper oxide film were recorded using Raman (Princeton Acton SP 2500) instrument at room temperature. The morphology of the deposited copper oxide thin film was studied by using atomic force microscopy (AFM). The Optical characterization was recorded for the various temperature copper oxide films using (Hitatchi-330) in the wavelength range of 300–1100 nm. Photoluminescence spectra were obtained for the copper oxide thin films using Perkin Elmer LS55 fluorescence spectrophotometer used with Xe lamp in the wavelength range 400–900 nm. Hall Effect measurement was used to measure the electrical properties of the copper oxide thin film by the use of four probe method. The thickness of the deposited thin films were measured by marking the scratch off a minute area by a scalpel and step height between substrate and average height within about 1 mm length with a surface profilometer (Alpha step scan system) and found to be in the range of 200–500 nm when the temperature increased from 250 to 320 °C.

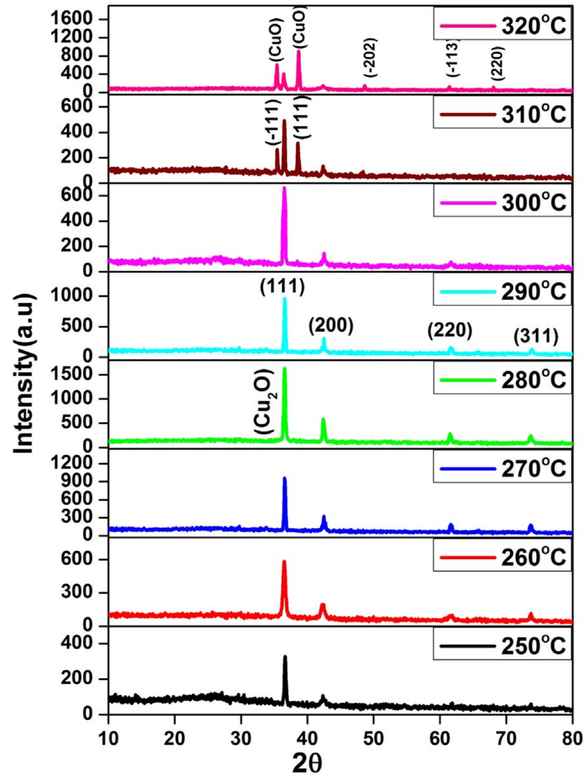

Fig. 1. X-ray diffraction patterns of copper oxide thin films.

3. Result and discussion

3.1. Structural studies

The X-ray diffraction pattern of the deposited copper oxide thin film by varying the temperatures from 250 to 320 °C are shown in Fig. 1. From the figure,the well defined peak at 36.4°corresponding to reflections at (111) plane was observed for all the films. The films deposited between 250 and 300 °C are polycrystalline in nature and matched the characteristic peaks due to the cuprous (Cu_2O) (JCPDS 77-0199). The intensity of (111) plane was increased for the film deposited between 250 to 280 °C,the maximum intensity was obtained at 280 °C with cuprous oxide (Cu_2O) phase. The intensity of the film at (1 1 1) plane for Cu_2O decreases for temperatures 290 and 300 °C. It is noticed that there is a slight change in phase, starts to occur at 310 °C. For the film deposited at 310 °C, Cu_2O (cuprite) become unstable and partially started to convert to CuO (tenorite) which agrees with the film annealing at 300 °C represents the mixed phase of copper reported by Khojier et al. [10]. The XRD pattern shows that the deposited thin films at 320 °C temperature coexist mixed phases: Cu_2O and CuO [19]. XRD patterns shows two extra peaks at angles about 2θ = 35.4° and 38.7° with reflections of (−111) and (111), respectively for the film deposited at 310 °C.The film deposited at 320 °C shows a decreased intensity of Cu_2O (111) peak, while the intensity of other two peaks (−111) and (111) of CuO is increased. The additional peaks were obtained at (−202),(−113) and (−220) for the film deposited at 320 °C which conforms the mixed phase of the film but the CuO peaks were increasing while Cu_2O peaks keeps on decreasing by increasing the temperature. This result can be matched with reference to JCPDS No: