Journal of Analytical and Applied Pyrolysis 111 (2015) 272–277

Contents lists available at ScienceDirect

Journal of Analytical and Applied Pyrolysis

journal homepage: www.elsevier.com/locate/jaap

Growth and characterization of spray pyrolysis deposited copper oxide thin films: Influence of substrate and annealing temperatures

Vignesh Saravanan [1], Prabakaran Shankar [1], Ganesh Kumar Mani [1], John Bosco Balaguru Rayappan *

Centre for Nanotechnology & Advanced Biomaterials (CeNTAB) & School of Electrical & Electronics Engineering (SEEE), SASTRA University, Thanjavur - 613 401, India

ARTICLE INFO

Article history:
Received 5 February 2014
Accepted 16 August 2014
Available online 27 August 2014

Keywords:
Spray pyrolysis
Crystal structure
Polycrystalline deposition
Nanomaterials
Filters

ABSTRACT

The effect of substrate and annealing temperatures on the structural, morphological, optical and electrical properties of spray deposited copper oxide thin films was investigated. The films were deposited on glass substrates using 0.05 M of cupric acetate precursor at the substrate temperatures of 523, 623 and 723 K. From the structural, morphological and optical characteristics, the film coated at 623 K was found to have better crystallinity with mixed cuprite and tenorite phases. Thus, substrate temperature was fixed at 623 K and films were prepared by increasing the molar concentration of cupric acetate to 0.1 M. Further the effect of annealing on the various properties of the CuO films was investigated. The XRD patterns of the annealed films at 523, 623 and 723 K for 6 h revealed the formation of copper oxide thin films with tenorite phase.

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1. Introduction

Copper oxide, one of the *p*-type semiconducting oxides plays an important role in the fabrication of semiconductor devices in wide range of applications such as solar cells, optoelectronic devices, field emitters, gas sensors, batteries, optical switches, magneto resistance materials, catalysts, high temperature superconductors and soil lignin study [1–8]. Though the low cost and non-toxic nature of the copper oxide material makes it an attractive option for these applications, synthesizing copper oxides of preferred phase still poses a challenge. The two possible phases of this oxide are copper oxide (CuO) and cuprous oxide (Cu_2O) of monoclinic and cubic structures with band gap values of 1.3–2.1 eV and 2.0–2.6 eV, respectively [9].

Among the various thin film deposition methods, spray pyrolysis technique has been widely used to deposit nanostructured metal oxide thin films [4,10–13] owing to its cost effectiveness and suitability for mass production. Thin films with the desired properties can be obtained in this technique by optimizing various deposition parameters such as the molar concentration of the precursor solution, spray rate, nozzle to substrate distance and air pressure. In particular, crystalline property and formation of nanostructures depend mainly on the molar concentration of the precursor [4,14]. Further, temperature plays an important role in the growth of thin films, as it determines the nucleation and further growth of nanostructures. The influence of the temperature on the thin film formation can be analyzed by studying the properties of the films formed at various substrate temperatures and annealing temperatures.

The substrate [10,11] and annealing temperatures [4] are known to be important control parameters for obtaining single phase crystalline copper oxide thin films. Kose et al. studied the crystallinity and structural properties of copper oxide thin films formed at various substrate temperatures [11]. A strong influence of the substrate temperature on the surface, optical and electrical properties of the film has been reported [10–12]. Similarly, heat treatment of the deposited samples was found to have strong effect on the grain size and surface roughness of the copper oxide thin films [4,15,16], and thus affects the optical and electrical properties. Most significantly, the substrate and annealing temperatures would be deciding factors for the selectivity and the composition of the Cu_2O (cuprite) and CuO (tenorite) phases [10,11,15,17,18] in the film. Hence in this work, we have optimized the substrate and annealing temperatures to prepare copper oxide thin film with preferred phase. Towards this, copper acetate precursor solution was used to deposit films on glass substrates at 523, 623 and 723 K. Based on the crystallinity of the film, the substrate temperature was fixed as 623 K for studying the effect of annealing on the structural, optical and electrical properties of the thin films.

* Corresponding author. Tel.: +91 4362 264 101x2255; fax: +91 4362 264120.
E-mail address: rjbosco@ece.sastra.edu (J.B.B. Rayappan).
[1] The authors have contributed equally to this work.

http://dx.doi.org/10.1016/j.jaap.2014.08.008
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Table 1
Optimized deposition parameters of 0.05 and 0.1 M precursor solution.

Parameters	Values
Precursor	Cupric acetate (0.05 & 0.1 M)
Substrate temperature	523, 623, 723 K
Solvent	Deionized water (50 ml)
Carrier gas pressure	2.5 mbar
Solution Flow rate	2 ml min^{-1}
Distance between nozzle and substrate	15 cm
Spray time	45 s
Spray interval	30 s
Spray area	15 cm^2 min^{-1}
Spray angle	90°
Spray nozzle diameter	0.2 mm
Annealing temperature	523, 623 & 723 K

2. Materials and methods

2.1. Thin film deposition

Copper oxide thin films were deposited on glass substrates using spray pyrolysis technique at different substrate temperatures viz. 523, 623 and 723 K using fully automated spray pyrolysis equipment (HOLMARC HO–TH–04, India) with optimized deposition parameters given in Table 1. The precursor solution was prepared by dissolving 0.05 M of cupric acetate (Cu $(CH_3COO)_2{\cdot}H_2O$) salt in 50 ml of deionized water and was stirred for 30 min at room temperature. Then the precursor solution was loaded in the dispenser and sprayed over the substrates prepared for the deposition by drying in hot air oven for 1 h after washing with acetone, isopropanol, and deionized water. The temperature of the substrate was maintained at 523 K during the spraying process. The same procedure was followed with precursor solutions of identical concentration for different substrate temperatures of 623 and 723 K. From the XRD and SEM data, the film deposited at 623 K was found to have better crystallinity with spherical shaped grains. For further enhancement of crystallinity, precursor solution with increased molar concentration of 0.1 M was used to deposit thin films at 623 K. To study the effect of annealing, these films were annealed at different temperatures viz. like 523, 623 and 723 K for 6 h each.

2.2. Characterization

The structural properties of the films were studied using X-ray diffraction (XRD) (D8 Focus, Bruker, Germany) with Cu $K\alpha$ radiation ($\lambda = 1.54$ Å). The average crystallite size was calculated using the Scherrer equation (Eq. (1)),

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where, k is the shape factor, λ is the wavelength of the X-ray, β is the full width half maximum of the diffraction peak and θ is the angle of the diffraction peak.

The film thickness (t) was measured from weighing method using digital weigh balance (AX 200, Shimadzu, Japan). Film thickness was calculated using the density relation (Eq. (2)),

$$t = \frac{\Delta w}{\rho l b} \quad (2)$$

where, Δw is the difference in weight of the substrate before and after film deposition, ρ is the density of ZnO (5.61 g cm^{-3}), l and b are the bare length and breadth of the substrate, respectively. Thickness of the films deposited using 0.05 M concentration at the substrate temperatures of 523, 623 and 723 K was 340, 320 and 295 nm, respectively.

Field emission scanning electron microscope (FE-SEM) (JSM-6701F, JEOL, Japan) was used to study the surface morphology of the films. The optical characteristics of the films were studied in the 200–800 nm region using UV–vis spectrophotometer (Lambda 35, Perkin Elmer, USA). Electrical conductivity of the samples was measured using high resistance electrometer (Keithley 6517A, USA).

3. Results and discussion

3.1. Structural studies

The XRD patterns of copper oxide thin films prepared using 0.05 M concentration of precursor at different substrate temperatures are shown in Fig. 1(a). The patterns clearly depict the amorphous nature of the as-deposited thin films at the substrate temperature of 523 K and 723 K. But in the case of film deposited at 623 K, significant peaks at 36.03°, 39.25° and 42.37° corresponding to (1 1 1), (0 0 2) and (2 0 0) planes, respectively indicate the crystallinity and the presence of mixed phases of the copper oxide viz. CuO and Cu_2O. At lower substrate temperature (523 K), the insufficient thermal energy required for the pyrolysis process lead to the incomplete decomposition of precursor salts, which in turn resulted in the formation of film with amorphous nature [12,19]. On the other hand, at higher deposition temperature (723 K), the premature decomposition of precursor before reaching the substrate [12,19,20] might be the reason for the amorphous nature of the film. In this context, we identified the substrate temperature of 623 K among the three trials as the optimum temperature, as it provided the thermal required energy for proper decomposition of the precursor salt and the crystallization of CuO thin films. To deposit films with enhanced crystallinity, 0.1 M concentration of precursor solution was used. Fig. 1(b) shows the XRD patterns of CuO thin films deposited using 0.05 M and 0.1 M concentration of precursor. The patterns clearly show the increase in the intensity of the peaks confirming the increased crystallinity due to higher molar concentration. Further, increase in the number of metal ions favoured the monoclinic phase of CuO with better crystallinity [4,14]. The increase in metal ion concentration may lead to the formation of Cu_2O rather than CuO. But it depends on the concentration of the metal ions which in-turn depends on the molar concentration of the precursor salt used for the film preparation. Gopalakrishna et al. [4] and Srinivasa et al. [14] have reported the influence of molar concentration on the synthesis of copper oxide films with tenorite and cuprite phases. They observed the formation CuO film when the molar concentration was varied from 0.05 to 0.15 M. At the same time, Cu_2O film was formed when the concentration was varied from 0.3 to 0.45 M [21]. With reference to these reports, one can conclude that the precursor concentration of 0.05 to 0.1 M was not enough to form Cu_2O phase.

Fig. 1(c) shows the XRD patterns of as-deposited and annealed thin films prepared using 0.1 M precursor concentration. The diffraction peaks detected at 35.5°, 38.73° and 53.53° correspond to ($\bar{1}$ 1 1), (2 0 0) and (0 2 0) crystal planes, respectively were found to be in agreement with the XRD standard for CuO, ICDD file No. 48-1548. The absence of change in the position of diffraction peaks ($\bar{1}$ 1 1) and (2 0 0) with annealing temperature implies annealing has no effect on the lattice parameters. In addition to the increase in the intensity of the diffraction peaks at ($\bar{1}$ 1 1) and (2 0 0) with the annealing temperature, an additional peak at 57° corresponding to (0 2 0) crystal plane of CuO was observed indicating the increase in the crystallinity. The trend of the increase in the peak intensity for the three peaks with the annealing temperature is shown in Fig. 1(d).

The average crystallite size calculated from the XRD data using Scherrer formula is given in Table 2. The crystallite size of the films prepared using 0.05 M and 0.1 M precursor concentration was found to be 10.5 nm and 16 nm, respectively. The increase in

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