Journal of Advanced Scientific Research

Available online through http://www.sciensage.info/jasr

ISSN
0976-9595
Research Article

SYNTHESIS AND CHARACTERIZATION OF COPPER OXIDE THIN FILMS USING SIMPLIFIED SPRAY PYROLYSIS TECHNIQUE

K. Saritha[1], V. Senthamil Selvi[2*], N. Nisha Banu[1]

[1]*PG and Research Department of Physics, K. N. Government Arts Science College, Thanjavur, Tamil Nadu, India.*
[2]*Rajaha Serfoji Government College, Thanjavur, Tamil Nadu, India.*
**Corresponding author: senthamilser1984@gmail.com*

ABSTRACT

By using simplified spray pyrolysis technique CuO thin films have been fabricated at different substrate temperatures with 300, 350 and 400 °C at 0.05M. The structural, morphological and optical properties of the fabricated films were investigated. The structural analysis by using X-ray diffraction (XRD) shows that all the samples are polycrystalline with monoclinic crystal structure. Under the characterization by UV-Visible-NIR spectrophotometer the optical properties of the films were studied, which depicts that the films show high transmittance in the visible region. When the substrate temperature increases from 300 to 400°C gradually optical band gap decreases.

Keywords: Thin film, Spray pyrolysis technique, Copper oxide, X-ray diffraction

1. INTRODUCTION

Copper oxide (CuO) is a semiconductor material for fabrication of photovoltaic solar cells [1]. The salient features of copper oxide semiconductors are high optical transmission and nontoxic and low cost in fabrication [2]. CuO having its monoclinic structure naturally exhibits P-type conductivity and the band gap values of 1.3 eV-2.1 eV have been reported in literatures [3]. CuO thin films have been prepared using various thin film deposition techniques such as chemical vapor deposition, vacuum evaporation, electro deposition, thermal oxidation, sputtering process, electron beam evaporation, chemical solution deposition [4-7] , chemical bath deposition [8], sol-gel [9], plasma evaporation [10], Pulsed laser deposition [11], molecular beam epitaxial [12, 13] and spray pyrolysis [14]. Referring to the spray pyrolysis technique, the spray parameters like spray rate, substrate temperature, spray nozzle distance, solution concentration and volume of the sprayed solution play a crucial role on the physical, electrical and optical properties of the thin films. Owing to its simplicity in making the films over a large area and its inexpensiveness, the spray pyrolysis technique is a better suited method among the other methods for the preparation of thin films. Spray technique facilitates better orientation of crystallites with improved grain structure. Hence in this work, we have optimized the different substrate temperatures to prepare copper oxide thin films with preferred phase. For this copper acetate precursor solution was used to deposit films on glass substrate at 300, 350 and 400°C. The effects of substrate temperature on the structural, morphological and optical properties of the CuO films were investigated.

2. EXPERIMENTAL

Copper oxide thin films have been prepared on glass substrates by simplified spray pyrolysis technique. The precursor solution was prepared by dissolving 0.05M of cupric acetate ($Cu(CH_3COO)_2 \cdot H_2O$) salt in 40 ml of deionized water and was stirred for 30 min at room temperature. During deposition, the substrate temperature kept at 300, 350 and 400°C for three different runs. To study the structural property, X-ray diffraction (XRD) patterns were obtained with a Philips (PRO Analytical) diffractometer with a Cu (λ = 1.54060Å) target. The surface morphological study was accomplished using a Scanning electron microscope (SEM) JEOL JSM-6360. The Fourier transform infrared spectra (FTIR) of the CuO thin film deposited were recorded using PerkinElmer RX-1 FTIR in transmission mode over 500-4000 cm^{-1}. The optical absorption spectra of the films were obtained by Hitachi UV-Vis-NIR spectrophotometer, in the 300-1200 nm wavelength range with glass substrate as a reference.

3. RESULT AND DISCUSSION

3.1. Structural studies

Fig. 1 shows the X-ray diffraction patterns (XRD) of CuO thin films deposited at different substrate temperatures. There are two diffraction peaks which confirm formation of crystalline CuO, in comparison with the JCPDS (Joint Committee on Powder Diffraction Standards) card for CuO [card No. 48-1548]. The diffraction peaks detected at 35.5° and 38.7° correspond to (1 1 1) and (2 0 0) crystal planes, respectively. From XRD reports, increasing the substrate temperature increases the film thickness which results the rise in peak intensity during the film formation. The (1 1 1) and (2 0 0) diffraction peaks are observed for all three samples. All the peaks in the XRD pattern represent the monoclinic structure of CuO. The crystallite size (D) can be determined using Scherrer's formula,

$$D = \frac{k\lambda}{\beta\cos\theta} \tag{1}$$

Where λ is the wavelength of X- ray, β is the full width at half maximum (FWHM in radians) of the peak corrected for instrumental broadening and θ is the Bragg angle, k is the Scherrer's constant, equal to 0.9. The lattice parameters ($a \neq b \neq c$, $\alpha = \gamma = 90^\circ \neq \beta$) of CuO thin films have been calculated from the following equations:

$$\frac{1}{d^2} = \frac{1}{\sin^2\beta}\left(\frac{h^2}{a^2} + \frac{k^2\sin^2\beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl\cos\beta}{ac}\right) \tag{2}$$

Where a, b, c and β are the lattice parameters for the monoclinic structure (h, k, l) are the miller indices and d is the inter planer distance [15]. The calculated lattice parameters values of (2 0 0) plane are given in Table 1. It is seen that the largest crystallite grown up at the substrate temperature of 400°C and gradually decreases as the substrate temperatures decreases. The calculated values of micro structural parameters such as lattice constant 'a', 'b', and 'c', strain 'ε', dislocation density 'δ' and the number of crystallites per unit area 'N' of the CuO films are presented in Table 2. The deviations in the lattice parameters values of the CuO films coated with different substrate temperatures might be due to the small shift in 2θ (2 0 0) diffraction towards higher Bragg's angle. The number of crystallites per unit area N, dislocation density δ and strain ε of the films was calculated using the following formula:

$$N = \frac{t}{D^3} \tag{3}$$

$$\delta = \frac{1}{D^2} \tag{4}$$

$$\varepsilon = \frac{\beta\cot\theta}{4} \tag{5}$$

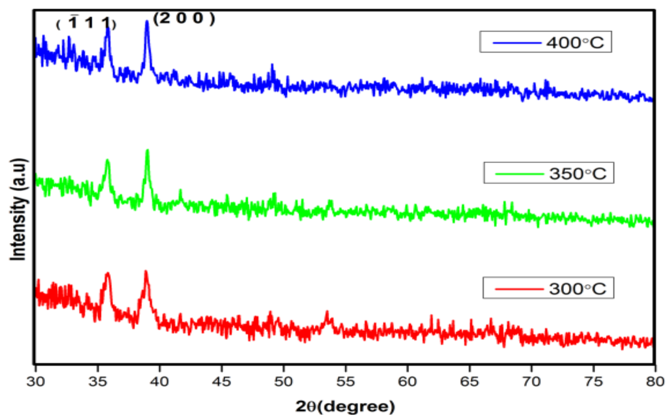

Fig. 1: X-ray diffraction patterns of CuO thin films fabricated at different substrate temperatures

Table 1: Structural parameters of CuO films

Substrate temperature	a(Å) value		b(Å) value		c(Å) value	
	Calculated	Standard	Calculated	Standard	Calculated	Standard
400°C	4.6952	4.6837	3.4310	3.4226	5.1413	5.1288
350°C	4.6954		3.4318		5.1427	
300°C	4.6897		3.4226		5.1353	

Table 2: Micro structural parameters of the CuO films

Substrate Temperature	D(nm)	Strain $\varepsilon\times10^{-3}$	Dislocation density $\delta\times10^{15}$ lines/m^2	Number of crystallites $N\times10^{16}$
400°C	21.42	4.850	2.1795	10.82
350°C	42.17	2.426	0.5413	1.95
300°C	57.12	1.818	0.3064	1.36

3.2. Morphological studies

Fig. 2 shows the surface morphology of CuO films coated with different substrate temperatures. All the films show the polycrystalline nature. For 300 °C and 350 °C the grain size are not well defined and seems to be surface has agglomerated. At 400 °C, the grain size is smaller and of different shapes. The grain size decreases with increase in substrate temperatures. The smaller in grain size which is useful for the enhancement of solar cell applications. This decrease in grain size is inconsistent with the XRD results.

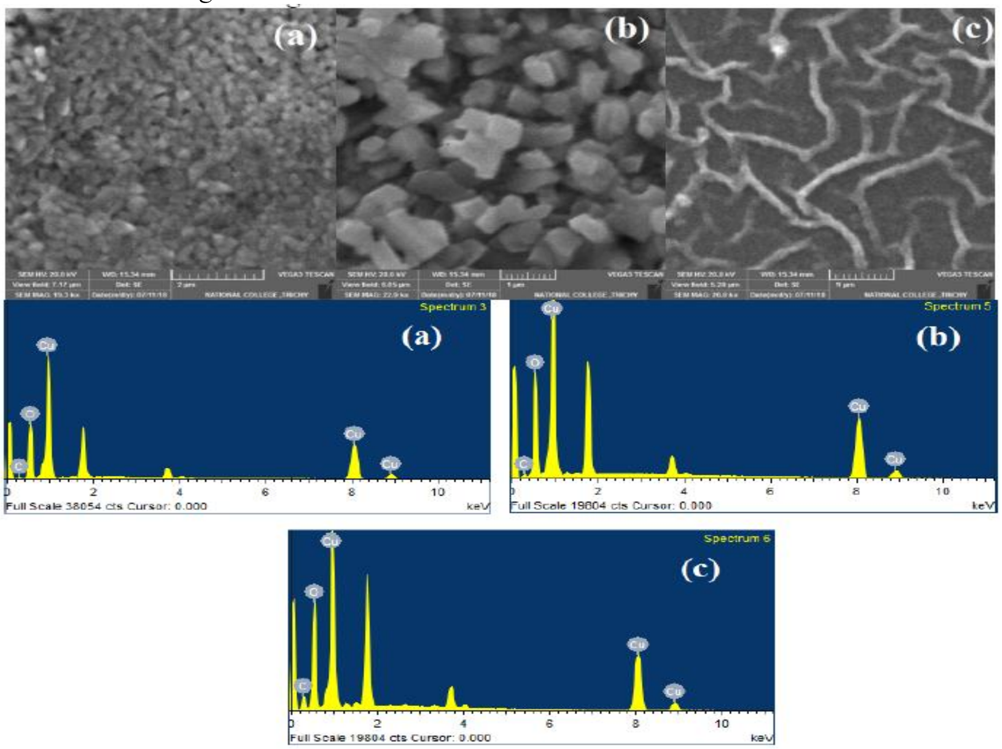

Fig. 2: SEM and EDAX images of CuO films fabricated at different substrate temperatures (a) 400°C, (b) 350°C and (c) 300°C.

Table 3. Result of quantitative of element analysis

Substrate Temperature	Elemental Composition Weight and atomic (%)				
	Cu	**O**	**Cu**	**O**	**O/Cu**
400°C	59.45	35.92	26.24	62.96	2.399
350°C	58.51	37.88	25.65	65.97	2.571
300°C	45.80	39.18	16.31	55.41	3.397

3.3. Elemental analysis

The EDAX spectra of the CuO thin films coated by the simplified spray technique with different substrate temperature**.** All the films contain the elements Cu and O as deposited components. The weight ratio and atomic ratio compositions of Cu and O in the films are presented in Table 3.

3.4. FTIR studies

Fig. 3 shows the FTIR spectra of the prepared CuO thin films. The peak in the range of 1800 cm^{-1} to 1850 cm^{-1} can be assigned to the strectching vibration of C = O.

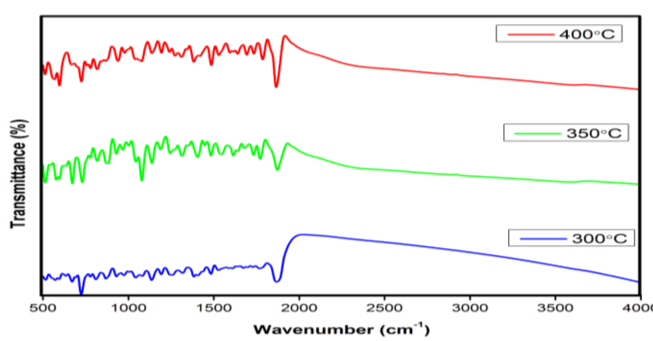

Fig. 3: FTIR spectrum of CuO thin film with different substrate temperatures (400, 350 and 300°C)

The peak at 1489 cm^{-1} indicated the formation of C = C stretching vibration .The peak at 726.18 cm^{-1} are related to bending vibration of C – H. The absorption frequency increases with increasing temperature from 300°C to 400°C which can be attributed to bond length related to crystalline size.

3.5. Optical studies

The optical trasmittance spectra, recorded in the wavelength range from 300-1200 nm , the copper oxide thin films prepared using different substrate temperatures are shown in Fig. 4. The films prepared at substrate temperature 400°C showed a maximum transparancy of 82 % in the visible region.The transmittance increases with increase in substrate temperatures.

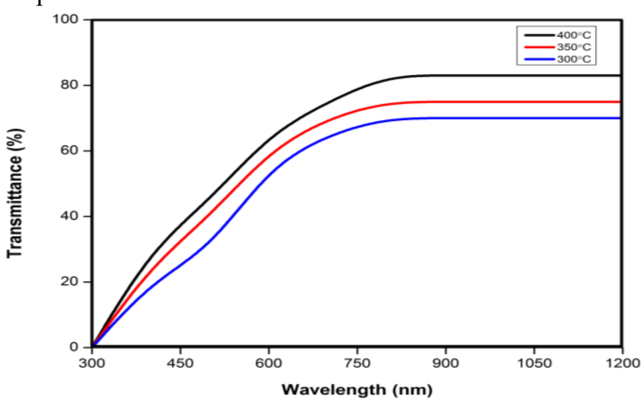

Fig. 4: Optical transmission spectra for CuO thin films coated at different substrate temperature

The direct optical band gap (E_g) is expressed as: [16]

$$\alpha h\nu = (h\nu - E_g)^{1/2} \quad (6)$$

where, α is the absorption coefficient, ν is the photon frequency and h is the Planck's constant. From the Tauc's plots shown in Fig. 5, the band gap values are substrate temperatures and are given in Table 4. It is found that there is substrate temperatures increase in the E_g value with the decrease in the deposition temperatures.

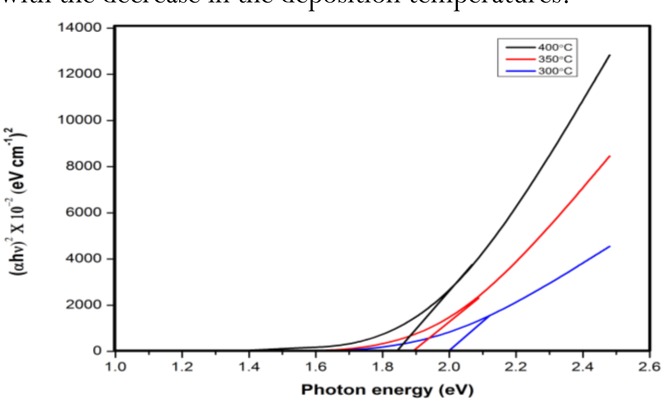

Fig. 5: Optical band gap of CuO thin films for different substrate temperatures

Table 4. Optical parameters of the deposition CuO thin films

Substrate Temperature	Transmittance	Band gap (E_g) (eV)
400°C	82	1.84
350°C	74	1.90
300°C	69	2.00

4. CONCLUSION

CuO thin films were fabricated at different substrate temperatures using simplified spray pyrolysis method. XRD analysis indicates that all deposited films are polycrystalline in nature with monoclinic structure. The increase in optical transmittance with the increase of substrate temperature was attributed to the increase of the film thickness. We have noticed that CuO films exhibit high transmittance in the visible spectrum. The increasing substrate temperature causes the decrease in band gap energy from 2.10 eV to 1.9 eV.

5. REFERENCES

1. Ray SC, *Solar Energy Materials & Solar cell,* 2001; **68:** 307-312.
2. Kidowaki H, Oku T, Akiyama T, Suzuki A, *Journal of Materials Science Research,* 2012; **1 (1):** 138-139.
3. Yahia IS, Farag AAM, EI- Faify S, Yakuphanogle F, et al. *International Journal for light and Electron Optics,* 2016; **127 (3):** 1429-1433.
4. Lim YF, Chua CS, Lee CJJ, Chi D, *Physical Chemistry Chemical Physics,* 2014; **16 (47):** 25928-25934.
5. Lin CY, Lai YH, Mersch D, Reisner E, *Chemical Science,* 2012; **3 (12):** 3482-3487.
6. Zhang Z, Wang P, *Journal of Material Chemistry,* 2012; **6 (22):** 2456-2464.
7. Paracchino A, Mathews N, Hisatomi T, Stefik M, et al. *Energy & Environmental Science,* 2012; **5:** 86738-681.
8. Tcc-Yam S, Potino R, Oliva AI, *Curr. Appl. Phys,* 2011; **11:** 914.
9. Oral, AY, Mensur E, Aslan MH, Basaran E, *Mater Chem Phys,* 2004; **83(1):** 140.
10. Santra K, Sarker CK, Mukherjee MK, Ghosh B, *Thin solid films,* 1992; **213:** 226.
11. Kikuchi N, Tanooka K, *Thin Solid Films,* 2005; **486:** 33.
12. Darvish DS, Atwater HA, *J. Cryst. Growth,* 2011; **319:** 39.
13. Kawaguchi K, Kita R, Nishiyama M, Morishita T, *J. Cryst. Growth*, 1994; **143:** 221.

14. Julia' n Morales, Luis Sa'nchez, Francisco Marti'n Jose R. Ramos-Barrado, et al. *Electrochimica Acta,* 2004; **49:** 4589-4597.
15. Singh I, Bedi RK, *Applied Surface Science,* 2011; **257 (17):** 7592-7599.
16. Pankove JI, *Englewood cliffs, MJ,* 1971; 34-42.