Print ISSN : 0022-2755
Journal of Mines, Metals and Fuels
Contents available at: www.informaticsjournals.com/index.php/jmmf

Effect of Substrate Temperature on Properties of Copper Oxide Thin Films Coated by Spray Pyrolysis

Ben Jos[1,2], K J Saji[3] and E I Anila[1,4*]

[1]Optoelectronics and Nanomaterials Research Laboratory, Department of Physics, Union Christian College, Aluva, Kerala, India 683102
[2]Sree Sankara College, Kalady, Kerala, India 683574
[3]International School of Photonics, Cochin University of Science and Technology, Kochi, India 682022
*[4]Christ (Deemed to be University), Bengaluru, Karnataka, India 560029. *E-mail: anilaei@gmail.com*

Abstract

Copper oxide shows a wide range of optical as well as electrical characteristics depending upon the preparation parameters. This wide range turning capability makes it a preferable candidate for effective use in various application fields like optical filters, light energy harvesting, gas sensing and semiconducting device fabrication. Spray pyrolysis technique with manual spray system was used to deposit a thin layer of copper oxide on glass substrates at temperatures of 300°C, 350°C, and 400°C. X-ray diffraction analysis shows that all the thin films obtained have monoclinic phase. A change of grain size from 15 nm to 25 nm was observedas the substrate temperature was varied from 300°C to 400°C.The Hall coefficient analysis confirms p-type conductivity in films obtained at 300°C and 350°C and N type conductivity with high resistivity for film coated at 400°C. Optical band gap increases from 1.75 to 2.17 eV with the increase in substrate temperature due to energy band tailing.

Keywords: *Spray pyrolysis, surface morphology, bandgap energy, Urbach tailing.*

1.0 Introduction

Oxides of copper are used in the fabrication of solar energy harvesting devices, gas sensors, and superconductors (Diachenko et al., 2021; Shinde et al., 2006). Various deposition techniques such as sputtering, (Abinaya et al., 2020), electrodeposition, (Kondrotas et al., 2015) thermal evaporation (Huang et al., 2004) and chemical bath deposition (Godbole and Tiwary, 2017) are employed to prepare films as cost effective methods (Khatami et al., 2015). The properties of the thin-film are governed by a number of parameters such as aerosol formation and transport, solvent evaporation, droplet impact with substrate and its subsequent spreading, and precursor decomposition (ZareAsl et al., 2018). The role of substrate temperature on electrical, morphological, and optical properties of copper oxide thin film synthesized by spray pyrolysis of aqueous solution of copper (II) acetate monohydrate, $Cu(C_2H_3O_2)\ 2{\bullet}H_2O$, was examined in this study. We had noted a change from P type conductivity to N type conductivity for film coated with a substrate temperature of 400°C.

2.0 Experimental Details

2.1 Film Deposition

A clear solution of 0.05M copper acetate was prepared in double distilled water using copper (II) acetate-monohydrate, $Cu(C_2H_3O_2)2{\bullet}H_2O$, (Merck, 99.9%). The solution was

---

*Author for correspondence

manually sprayed onto the substrate using a pneumatic sprayer, keeping the substrate temperature constant. Filtered normal air with pressure kept constant at 0.2Kg cm^{-2} above atmospheric pressure was used as carrier gas. The distance between the spray gun and the substrate was 20 cm and the flow rate of solution was kept as 30 ml per minute. Samples were prepared for substrate temperatures 300°C, 350°C and 400°C. All samples were then annealed at 450°C in air for two hours.

2.2. Characterization Techniques

The structural properties of the films were determined by using PAN alytical Aeris bench-top XRD instrument. The diffraction intensity was taken by varying 2θ values in the range 10–90°. Film morphology was analyzed by using field emission scanning microscope (FESEM), (JEOL-JSM-7610F). Investigation in optical transmission was performed with Agilent Cary 60 UV-vis spectro-photometer. Film thicknesses were estimated with near normal spectroscopic reflectometer (HO-NNSR-01). Electrical characterization of the films was carried out at room temperature using a custom-made Hall effect measurement system with probes in Vander Pauw configuration witha magnetic field of 5000 G.Keithley's 2450 source measure unit (SMU) was also used to determine electrical conductivity using the two probe method.

3.0 Results and Discussion

3.1 Structural Properties

3.1.1 XRD analysis

The samples' patterns obtained with X-ray diffraction are consistent with COD file number 00-901-6057. All the samples are poly crystalline with strong orientation along $[\bar{1}11]$ plane having a monoclinic lattice structure (Figure 1A). The average grain size of CuO thin films were calculated using Scherer's equation (Cullity et al. 2001). The result obtained is tabulated in Table 1. It is clear that the grain size increases with substrate temperature. As the temperature of the substrate increases the thickness was found to be decreasing. This may be due to the increased upward air current at the higher temperatures which resists droplets from reaching the substrate.

3.1.2 Raman analysis

Raman analysis was carried out to get more information about the structure of the samples prepared. CuO can have Raman modes at frequencies 296 cm^{-1}, 346 cm^{-1} and 631cm^{-1} in bulk samples corresponding to A_g and two B_g vibrations. In the present case we got intense peaks at 302 cm^{-1} and 614 cm^{-1} and a feeble peekat 346 cm^{-1} (Fig.1B). The peak at 302 cm^{-1} corresponds to A_g mode vibrations, while the peak at 614 cm^{-1} corresponds to B_{g2} mode vibrations (Reichardt et al., 1990). Peak at 346 cm^{-1} is comparatively less intense, indicating that oscillation along B_{g1} mode of vibrations is less likely in this sample.

3.2 Surface Morphology Analysis

FESEM images of CuO thin films produced at various substrate temperatures are shown in Figure 2 (a), (b), and (c). Image of the film coated at 300°C, Figure 2(a), revealed that the film has an inhomogeneous surface morphology with fine particles distributed on the surface. Figure 2(b) and 2(c) show that samples coated at 350°C and 400°C have bigger irregular flat structures formed due to agglomeration of particles. Figure 2(d) confirms that the film contains Cu and O elements and the element overlay figure (inset of Figure 2(d)) revealed

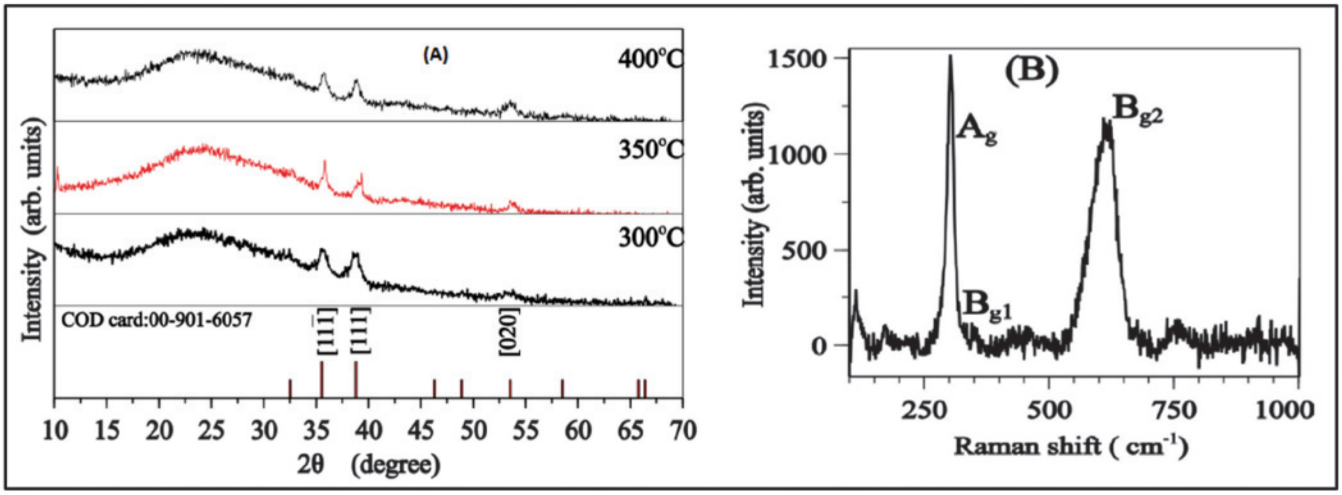

Figure 1: (A) XRD patterns of the samples prepared at different substrate temperatures, (B) Raman shift of sample synthesized at 350°C

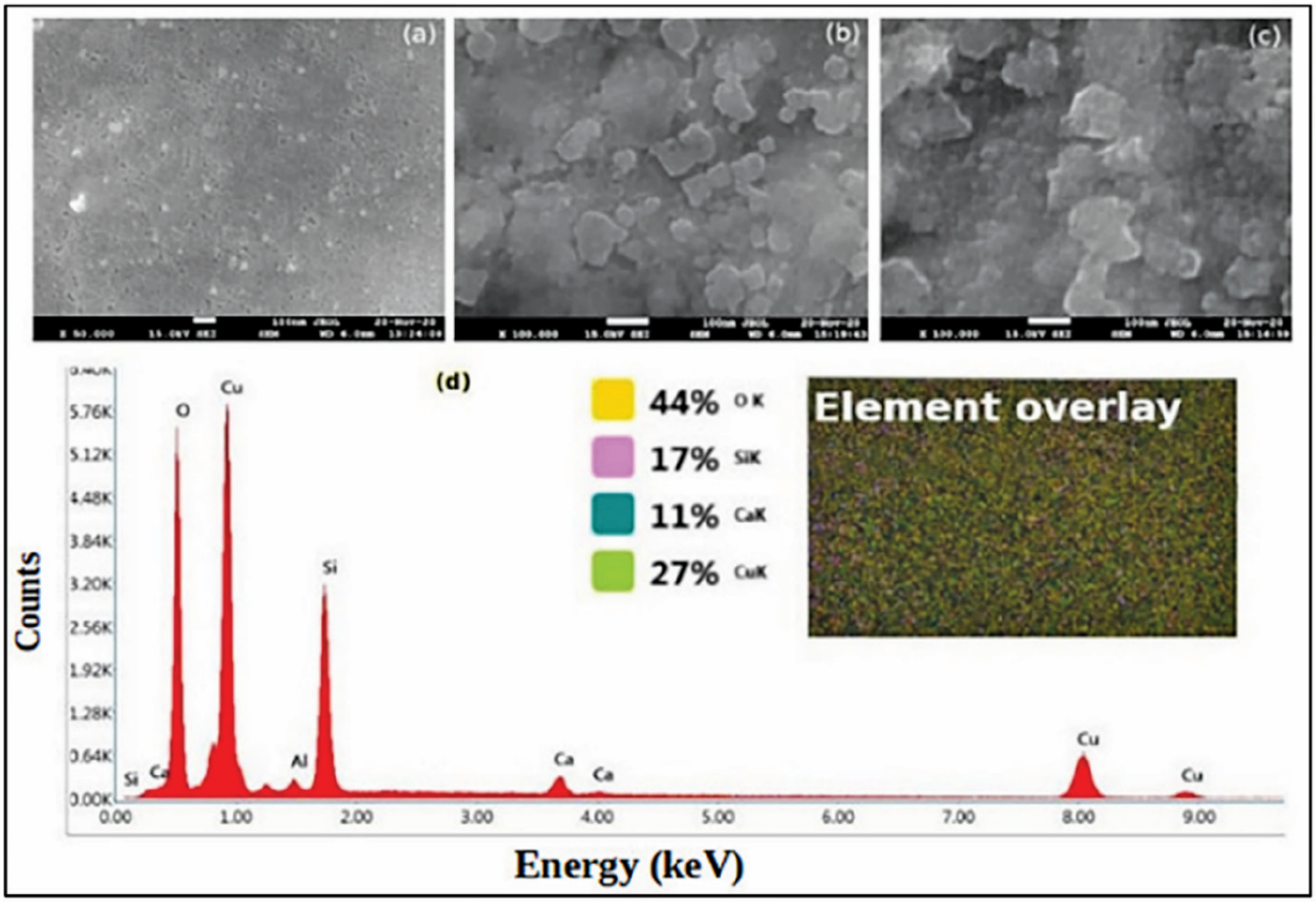

Figure 2: FESEM images of sample coated with substrate temperature (a) 300ºC (b) 350ºC (c) 400ºC (d) EDAX of sample coated at 350ºC

that they were dispersed uniformly across the film. The occurrence of Ca and Si peaks in the EDAX spectrum are owing to the presence of these elements in the substrate used.

3.3 Optical Properties

The optical transmission of the prepared films was investigated in the wavelength region 400 to 1100 nm (Figure 3A). All the samples showed a significant increase in transmission percentage on increasing the wavelength from visible to near infrared region. The optical band gaps were calculated assuming direct band gap for the material with the help of Tauc plot shown in Figure 3B. The band gap values are tabulated in Table 1. There is a blue shift in band gap with increase in temperature. This observation is unexpected since larger grain size should result in smaller band gap (Srividhya et al. 2014). The exponential component near the optical band edge of an absorption curve of a poor crystalline or disordered material is known as Urbach tail. Variations from ideal crystalline nature as well as other sample flaws, cause this tailing effect. To validate tailing of band gap energy, an Urbach energy calculation was done. For this, a plot with ln (α) on Y axis and photonenergy in eV on X axis was drawn. Figure 3C illustrates the results achieved. Urbach energy was calculated for all the samples at straight line portions of the graphs. The inverse ofthe slope of this linear part yielded Urbach energy, EU. (Hassanien and Akl, 2016; Dhineshbabu et al. 2016). Band tailing width was 0.38 eV for specimens produced at 400°C and 0.39 eV for samples made at 350°C, whereas band tailing width was 0.40 eV for samples prepared at 300°C. A higher value of Urbach tailing indicates that sample prepared at 300°C had poor crystalline structure or more disorder states and local defects. This enhanced Urbach band tailing could explain why the sample processed at 300°C had a narrower band width.

3.4 Electrical Properties

CuO is a P-type semiconducting material. (Li et al., 2011) The P-type conduction mechanism is explained with the help of copper vacancy formation (Jeong & Choi, 1996) analyzing the Hall effect in the sample as shown in Table1. From Table 1, we can assert that even though the sample processed at

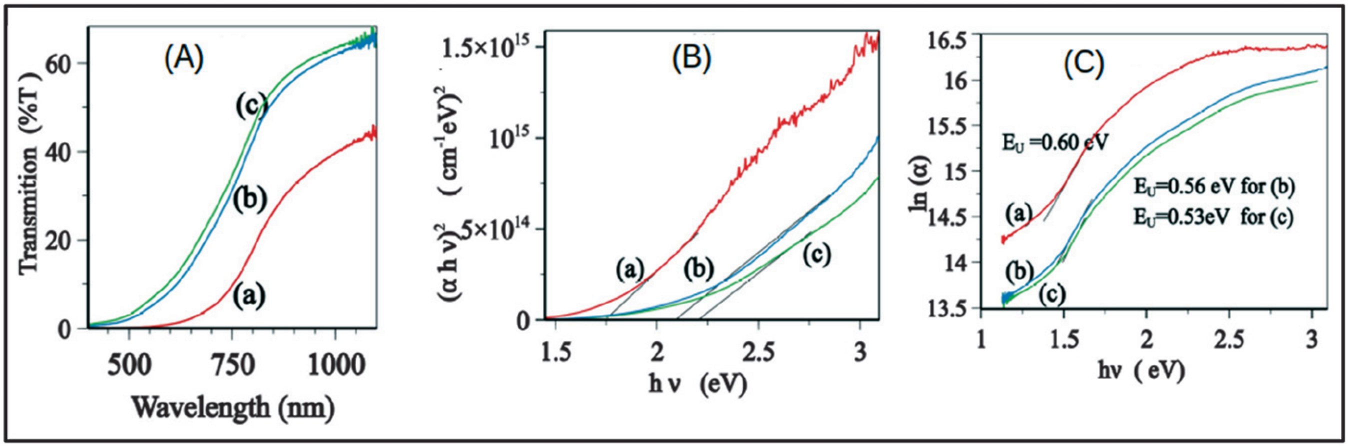

Figure 3: (A) Transmission (%T) (B) Tauc plot for band gap calculation (C) Graph for band tailing energy calculation of CuO thin film prepared at (a) 300°C (b) 350°C (c) 400°C substrate temperatures

Table 1: Structural, optical and electrical properties obtained for samples prepared with different substrate temperatures

Substrate temperature	Thickness [nm]	Grain size [nm]	Band gap [eV]	Carrier concentration[cm^{-3}]	Mobility [$cm^2V^{-1}s^{-1}$]	Resistivity [Ω cm]	Carrier Type
300°C	230	15	1.75	2×10^{14}	25.6	$1.2x10^3$	P
350°C	189	20	2.1	3.3×10^{19}	0.05	3.94	P
400°C	187	25	2.17	1.3×10^{16}	2.22	222	N

350°C had lowest mobility, it had the highest carrier concentration, and showed lowest resistivity. The sample prepared at 300°C had a remarkable decrease of carrier concentration, by the order of 10^5 than sample prepared at 350°C which caused a significant increase of resistivity.

Again, though the sample processed at 300°C has greater mobility, a lower carrier concentration as well as a lower grain size or increased grain boundaries caused a higher resistivity. Higher grain size as well as better carrier concentration obtained for sample prepared at 400°C caused a less resistivity compared to sample prepared at 300°C. It is evident that the sample prepared at 350°C possess maximum number of charge carriers available for conduction compared to films coated at 300°C and 400°C. Film coated at 350°C had shown the least resistivity of 3.94Ω cm. despite, the mobility of the carriers decreased considerably for this sample. For the sample coated at 400°C, majority charge carries change from P type to N type. Du et al. reported the possibility of N type conduction in CuO thin films fabricated at a substrate temperature 500°C (Du et al., 2019). At higher substrate temperatures the Cu atoms gets more mobility while forming CuO and the chances of forming Cud eficiency, which causes P type conduction, in the lattice gets reduced. They had also suggested the possibility of desorption of oxygen form the surface at higher substrate temperature which may lead to the formation of oxygen vacancies. (Du et al., 2019). Thus the increase in mobility when moving from 350°C to 400°C may be that of N type charge carrier.

4.0 Conclusions

X-ray diffraction studies established the formation of polycrystalline phases of CuO with a monoclinic lattice structure. SEM analysis made it clear that the film had homogeneous surface morphology with fine particles distributed over the surface. Films coated at 350°C and 400°C have agglomeration of particles. EDAX has demonstrated consistent particle distribution and the presence of both Cu and O as well as a lower percentage of impurity for films made using this technique. UV studies showed that as the substrate temperature changed from 300°C to 400°C there is an increase in direct band gap from 1.75eV to 2.17eV.

The results of the Urbach energy calculation showed that the bandgap is influenced by the Urbach tailing effect.The sample treated at 300°C has a lower band gap due to more disorder states and local defects. The sample processed at 350°C had the highest carrier concentration, according to the Hall effect study. Granting the fact that the sample processed at 300°C has greater mobility, it has a lower carrier concentration and a lower resistivity. Films fabricated by spray pyrolysis method for substrate temperatures 300°C and

350°C shows ptype conductivity whereas the sample coated at 400°C exhibited N type conductivity. Reduction in number of copper vacancies due to high mobility of copper atoms at high temperature led to N type conduction. Conditions to get better N type conductivity in this material has to be investigated.

5.0 Referances

1. Abinaya, C., Bethke, K., Andrei, V., Baumann, J., Beatrix Pollakowski-Herrmann, Kanngießer, B., Beckhoff, B., Vásquez, G. C., Mayandi, J., Finstad, T. G., & Rademann, K. (n.d.). The effect of a. post-deposition annealing conditions on structural and thermoelectric properties of sputtered copper oxide films. RSC Advances, 10(49), 29394–29401. https://doi.org/10.1039/d0ra03906c
2. Cullity, B. D., Stock, S. R., & Stock, S. (2001): Elements of X-Ray Diffraction (3rd Edition). Prentice Hall.
3. Dhineshbabu, N. R., Rajendran, V., Nithyavathy, N., and Vetumperumal, R. (2016): Study of structural and optical properties of cupric oxide nanoparticles. *Applied Nanoscience*, 6(6), 933–939. https://doi.org/10.1007/s13204-015-0499-2
4. Diachenko, O., Kováè, J., Dobrozhan, O., Novák, P., Kováè, J., Skriniarova, J., and Opanasyuk, A. (2021): Structural and Optical Properties of CuO Thin Films Synthesized Using Spray Pyrolysis Method. Coatings, 11(11), 1392. https://doi.org/10.3390/coatings11111392
5. Godbole, B. and Tiwary, S. (2017): CuO Thin Film Prepared by Chemical Bath Deposition Technique: A Review. *International Journal of Nanoscience and Nanotechnology*, 8, 11–15.
6. Hassanien, A. S. and Akl, A. (2016): Effect of Se addition on optical and electrical properties of chalcogenide CdSSe thin films. Superlattices and Microstructures, 89C, 153–169. https://doi.org/10.1016/j.spmi.2015.10.044
7. Huang, L. S., Yang, S. G., Li, T., Gu, B. X., Du, Y. W., Lu, Y. N. and Shi, S. Z. (2004): Preparation of large-scale cupric oxide nanowires by thermal evaporation method. Journal of Crystal Growth, 260(1–2), 130–135.
8. Jeong, Y. K. and Choi, G. M. (1996): Nonstoichiometry and electrical conduction of CuO. *Journal of Physics and Chemistry of Solids*, 57(1), 81–84. https://doi.org/10.1016/0022-3697(95)00130-1
9. Khatami, N., Ilegbusi, O. and Trakhtenberg, L. (2015): Mathematical Modeling and Experimental Validation of Mixed Metal Oxide Thin Film Deposition by Spray Pyrolysis. *Materials Sciences and Applications*, 06. https://doi.org/10.4236/msa.2015.61009
10. Li, F. M., Waddingham, R., Milne, W. I., Flewitt, A. J., Speakman, S., Dutson, J., Wakeham, S. and Thwaites, M. (2011): Low temperature (<100°C) deposited P-type cuprous oxide thin films: Importance of controlled oxygen and deposition energy. Thin Solid
11. R. Kondrotas, Juðkënas, R., Naujokaitis, A., Niaura, G., Mockus, Z., Kanapeckaitë, S., Èechavièius, B., Juðkevièius, K., Saucedo, E. and Sánchez, Y. (2015): Investigation of selenization process of electrodeposited Cu–Zn–Sn precursor for Cu2ZnSnSe4 thin-film solar cells. Thin Solid Films, 589, 165–172. https://doi.org/10.1016/j.tsf.2015.05.012
12. Reichardt, W., Gompf, F. and Wanklyn, B. M. (1990): Lattice dynamics of cupric oxide. Zeitschrift Fr Physik B Condensed Matter, 81(1), 19–24. https://doi.org/10.1007/BF01454208
13. Shinde, V. R., Mahadik, S. B., Gujar, T. P., and Lokhande, C. D. (2006): Supercapacitive cobalt oxide (CO_3O_4) thin films by spray pyrolysis. *Applied Surface Science*, 252(20), 7487–7492.
14. Tauc, J. (1968): Optical properties and electronic structure of amorphous Ge and Si. Materials Research Bulletin, 3(1), 37–46. https://doi.org/10.1016/0025-5408(68)90023-8
15. ZareAsl, H., Mohammad Rozati, S., ZareAsl, H., & Mohammad Rozati, S. (2018): Spray Deposited Nanostructured CuO Thin Films: Influence of Substrate Temperature and Annealing Process. Materials Research, 21(2). https://doi.org/10.1590/1980-5373-mr-2017-0754.