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Research Article

The Effect of Deposition Platform Speed on Structural and Optical Properties of CuO Thin Films Prepared by Home-Made Fully Computerized Spray Pyrolysis Deposition System

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Abstract

This study presents the effect of the heated platform speed during spray process on the structural and optical properties of copper oxide thin films deposited by spray pyrolysis technique. Copper oxide (CuO) thin films were sprayed on heated microscopic slide substrates by using home-made Fully Computerized Spray Pyrolysis Deposition (FCSPD). Fixed substrate temperature of 450 ℃, nozzle to substrate distance (NSD) was kept at 30 cm, and fixed molar concentration of copper (II) chloride as a precursor was used. In addition to that Sprayed this film were carried out at different deposition speed 3, 4, 5, and 6 mm/s. The structural, optical properties, were determined by using X-ray diffraction method, and UV-Vis spectrophotometer. The XRD spectra showed that all sample polycrystalline structure with different quality structure depending on deposition speed, the better crystallinity was found at 6mm/s, and all sample have two preferred orientations along the (111), (-111). The grain size and lattice parameter were investigated as a function of deposition speed. Transmittance spectra exhibit small divergence in transmittance value along the sample at different examined position and deposition speed was measured the transmittance on it. A lower value to this variance in the divergence detected at 3, 6 mm/s. The CuO films were optical direct band gap calculated from optical transmittance measurements within the range of 1.422 to 2.395 eV, which are quite compatible with the solar absorber values. The results show that the compact design is better than the conventional SPD, also, that exhibit the obvious effect of deposition platform speed on the CuO properties. The advantages of (FCSPD) design are the advance performance of precise 3D motion, spraying, with specific location and high homogeneity in deposition layer.

Keywords: *Fully computerized spray pyrolysis deposition, CuO, Deposition speed, structural properties, optical properties*

1. Introduction

Copper oxide thin films semiconductors have attracted increasing interest of researchers. They are reasons behind it, Abundant in nature, low coast and non-toxic properties suitable and ideal energy gap material for solar application because of their direct band gap =1.2-2.0 eV (Yin *et al*. 2005; Gan *et al*. 2004; Jayatissa *et al*. 2009). in addition to of their its important application in many fields such as a solar cell(Abd *et al*. 2015; Kidowaki *et al*. 2012; Oku *et al*. 2011). Magnetic behavior of copper oxide have been reported (Borzi *et al*. 2001). it has been used as anode material of lithium-ion battery(Fu *et al*. 2007; Mohapatra *et al*. 2016). This molecule regard as an interesting material used in environmental catalysis (Zhang *et al*. 2014; Zhou & Li 2012; Karadimitra *et al*. 2004; Al-Ghamdi *et al*. 2016). Although widely used as a different Gas sensor (Asad & Sheikhi 2016; Park *et al*. 2014; Hsu *et al*. 2016). Copper oxide have been prepared by using a different technique such as chemical vapor deposition(Maruyama 1998; Nair *et al*. 1999), Sol-gel (Ray 2001), thermal oxidation of copper(Papadimitropoulos *et al*. 2006), Plasma evaporation(Santra *et al*. 1992), R F & dc magnetron sputtering (Hammoodi *et al*. 2014; Mugwang'a *et al*. 2013),copper oxide were prepared by using fully computerized chemical spray pyrolysis deposition technique (FCSPD) .it has been aimed at preparing CuO thin films of different controlled preparation parameter but exception temperature was kept at 450 °C. the purpose of the present study was to synthesized CuO thin film based on atmospheric deposition as absorber layer by (FCSPD), and to characterized the variation of changing both speed and nozzle height on the optical and structural properties of this layer.

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2. Experimental Procedure

Materials and Methods

The Copper Oxide thin films were prepared by homemade fully computerized spray pyrolysis deposition (FCSPD) with pneumatic spray jet on glass slides substrate with a different dimension that does not exceed of (20 X 20) cm^2 deposition platform area. The glass substrates were cleaned carefully by immerging in chromic acid and washing in distilled water for 1min and ultrasonically in ethanol for 2 min finally leave it to dry in the oven. The starting solution was prepared of pH value equal 2 by dissolving copper (II) chloride in distilled water containing a number of a few drops of concentrated HCL. The concentration of spray solution was 0.1 M. the films were prepared by spraying 50-80 mL of precursor depending on deposition speed, at fixed substrate temperature T_S is 450 °C where this temperature was controlled by using microcontroller type Arduino UNO and A/D converter type MAX6679 with K-type thermocouple for precise control, with real-time monitoring and recording the temperature through the deposition process every 1 sec. Compressed air used as a carrier gas with a flow equal to 4 kg/cm^2 through the pressure – monitoring gauge and the solution flow rate was 2-3 mL/min. .The spray jet was adjusted to fixed nozzle to substrate distance (NSD) 30 cm by using custom Graphical User Interface GUI to controlling the 3D motion system, (X, Y) stage stepper motor speed, X to Y displacement, Z-axis stepper motor to obtain the accurate nozzle height, Defining the substrate position on the platform, sit on X-Y movable hot plate stage (carriage), as shown in Fig. 1 and by using GUI pattern interface to ensure the spray cone fit on the surface area of the substrate. Setting preparation temperature, delimitation, and the preparation method such as scanning or repeated line, in this work repeated line was kept at all process, finally, a visual monitoring using Logitech camera type, controlling, and recording the temperature. These experimental parameters were used, deposition speed 3,4,5,6 mm/s, while the deposition speed refers to the solution deposition rate per unit area per unit time, X-Y displacement 4mm, and setting temperature 450 °C with adjustable or user defined accuracy ±5 °C. Hand-made resistive heater from tungsten wires of diameter 1.5mm is employed to alter the temperature of the substrate deposition on our requirement. Table 1 shows the optimized values that were used in this research. The structural properties of CuO thin films were characterized using x-ray diffractometers type Shimadzu – 6000 of Cu Kα radiation (λ=1.54060A°), all CuO samples were scanned in the 2θ range of (25-70) deg. and the diffraction pattern recorded with continuous scan mode and scanning speed 5deg/min and scan step of0.1 deg. The average size of crystallites was calculated according to the Scherrer formula. Optical transmittance spectra versus wavelength are recorded in the range of 300nm-1100 nm by using UV-Visible spectrophotometer type UV Mate SP8001.

$$CuCl_2 + H_2O \rightarrow CuO + 2HCL$$

Table 1: Optimized spray parameter

Spray Parameter	Values
molarity	0.1M
Solvent	Distilled water
Carrier gas	Compressed air
Nozzle height	30 cm
Substrate temperature	450 °C
Spray Rate	2-3 mL/min

Figure 1 Hot plat surface platform exact match on GUI machine program. (a) Hot plat dimension. (b) Stainless steel hot plat. (c) GUI exact match the design

3. Result and discussion

A. Structural properties

Fig. 2 Shows the X-ray diffraction pattern for CuO films prepared at deposition speed 3 to 6 mm/s and 450°C substrate temperature. The pattern matches with the JCPDS card no: 05-0661. Denote the formation of CuO was monoclinic with a preferred orientation along (-111) (002) and (111) (200) plans located at a 2θ value of (35.511) and (38.696) respectively at 6 mm/s deposition speed. The preferred growth along (-111) (002) and (111) (200) remained in all pattern irrespective of alteration in preparation speed in addition to the intensity of 2θ at preferred orientation has been found to increase with increasing deposition speed, and observed an enhancement in crystal structure at the speed 6 mm/s Fig 2d.

While some studies used various annealing temperature to enhance the crystal structure of CuO film (Saravanan *et al*. 2015). For the spray solution with flow around 2 mL/min at 6 mm/s speed that the net heat absorbed by the number of droplet and or the density of droplet per deposition area was quite enough to pyrolysis the material on the hot glass substrate surface correctly to complete process of Chemical Vapor Deposition (CVD) to produce the CuO phase, whereas at low speed the density of the droplet is much more delivered to the surface leading to the steady decline in temperature in the surface causes low crystalline structure formation. Table 2. Show the position of three strongest peaks measured by XRD, also that the average grain size and d-spacing observed compared with d-spacing from JCPD card at specific hkl. These peak positions which is in good agreement with previous work (C. Ravi Dhas, Dinu Alexander, A. Jennifer Christy, K. Jeyadheepan 2014).

Table 2 XRD parameter at nozzle height 30 cm and different deposition speed

Deposition Platform Speed mm/s	2 θ deg.	I/Io	FWHM deg.	d ops. ⁰A	d Std. ⁰A	Avg. Grain nm	h-k-l
3	35.597	100	0.5476	2.521	2523	21.23	(111)(200)
	38.865	73	0.6738	2.315	2.323		(-111)(002)
	30.443	47	0.3	2.933			(202)(020)
4	35.577	100	0.48	2.521		24.11	--
	38.839	61	0.4997	2.316			--
	28.302	28	0.2857	3.15			--
5	38.785	100	0.8764	2.319		12.8	--
	35.584	94	0.856	2.52			--
	32.470	12	0.6083	2.755			--
6	38.793	100	0.5054	2.319		21.93	--
	35.629	56	0.4391	2.517			--
	58.266	14	0.6461	1.582	1.581		--

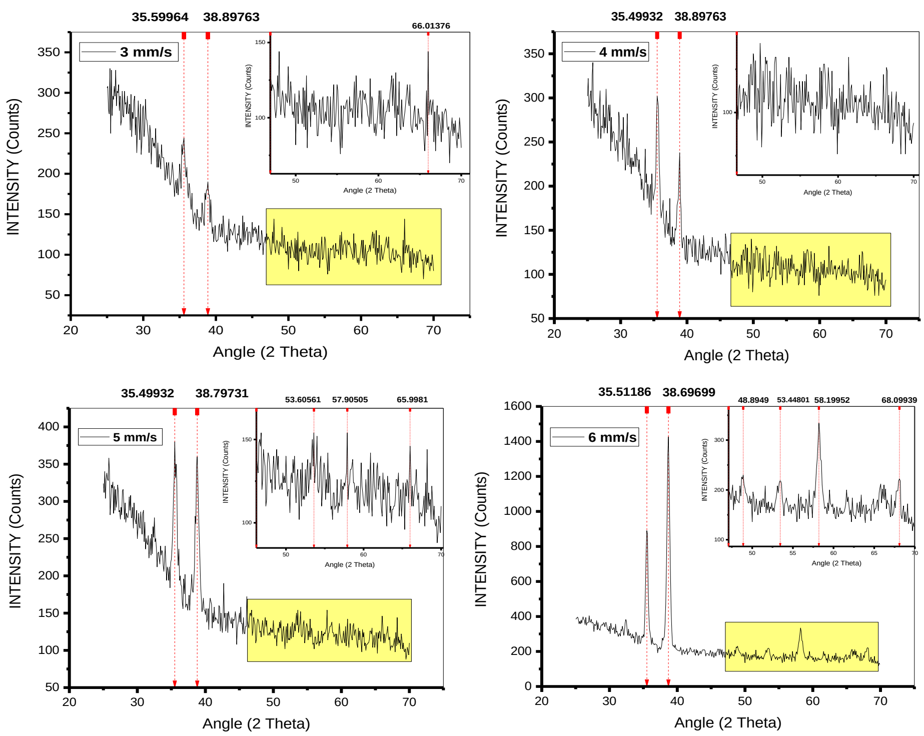


Figure 2 (a-d) XRD pattern of CuO layer prepared at different deposition speed and NSD equal 30 cm

B. Thickness measurement

It was measured the thickness of the CuO layer prepared using non-contact film thickness measurement system for single and multilayer structure *TF*-**C-UVIS-SR** *StellarNet* USA with wavelength 220-1100 nm and resolution < 2.5 nm, thickness measurement range 50 A°-20μm, where the results showed that the thickness of the copper oxide films decreases with increasing deposition speed, these results are consistent with the literature (Lamri Zeggar *et al*. 2015), as shown in Table 3.

Table 3: shows CuO layer thickness prepared at different deposition speed

Deposition condition	Thickness (nm)
3 mm/s	4111
4 mm/s	304.4
5 mm/s	202
6 mm/s	136.1

C. Optical properties

Fig.3 displays the transmittance spectra of the CuO thin film as a function of wavelength at different deposition platform speed. It appears in the spectrum that the transmittance decreasing with increasing deposition speed (Lamri Zeggar *et al*. 2015). Fig. 4(a-d) shows the transmittance spectrum as a function of wavelength at two positions examined on the sample at specific deposition platform speed on the form the transmittance change depending on the change in the thin film thickness. Since the results were presented to show another measure express the film homogeneity and a good distribution of the coating over the entire sample area. The results showed that the speed 6 mm/sec a convergence of thickness unlike speed 3, 4, 5. Where the disparity in thickness is clear, thus the homogeneity of the thin films increases with increasing deposition platform speed. In contrast with decreased deposition speed, non-homogeneity are clear and the reason behind this is due to the high of droplets density deposited a specific area per time, causes the formation of crystalline defects and get pinholes in the thin films, as displayed in the results of the thickness in table 3. The optical gaps of these films were estimated with Tauc's equation below

$$(\alpha h\upsilon)^2 = A\,(h\upsilon - E_g)$$

Where $h\upsilon$, α, A and E_g are incident photon energy, absorption coefficient, a constant, and the optical gap respectively. Fig. 5 shows the plot of $(\alpha h\upsilon)^2$ versus $h\upsilon$, the intercept of the straight line on $h\upsilon$ axis corresponding to the optical band gap and were found to be in the range of 1.422 - 2.395 eV, these values agree with previous study (Senthil Kumar *et al*. 2010). Clearly, the Fig.5 is that at increasing deposition speed the energy band gap decreased, these results also led to the increased deposition platform speed will be in enhancements in films structure. In addition to, the above results the, deposition platform speed can be adopted according to the proper application, especially in the field of solar energy (Bhaumik *et al*. 2014; Afify *et al*. 1999), which is an area of interest.

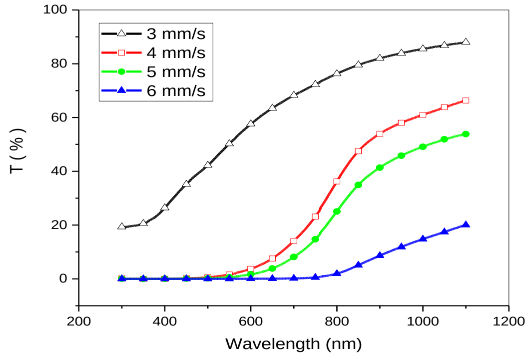
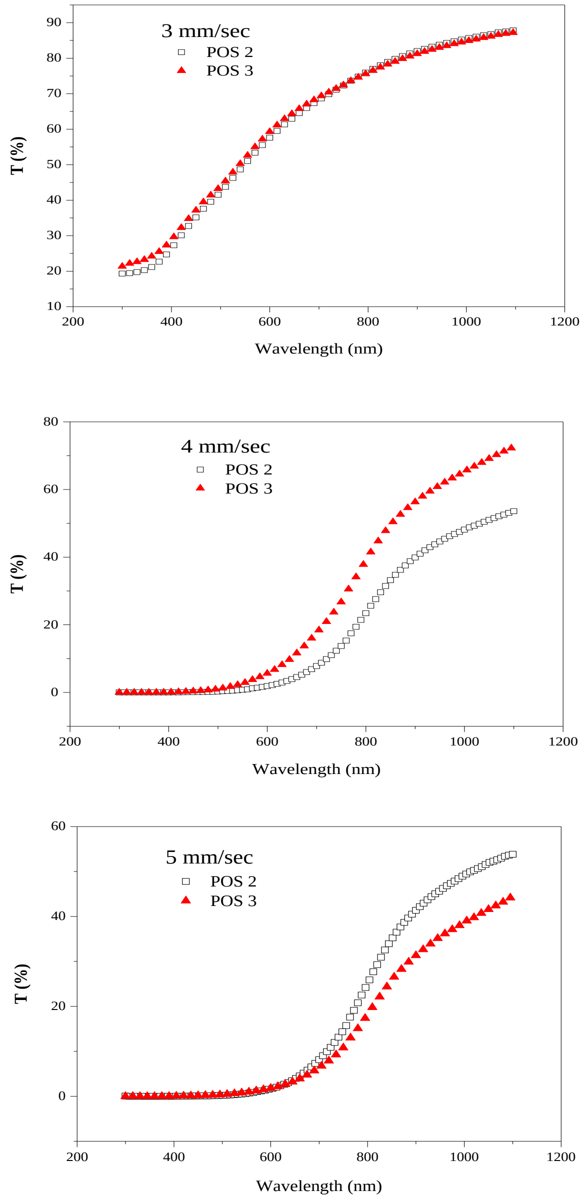


Figure 3 Transmittances spectra of CuO as a function of deposition platform speed at 30 cm NSD



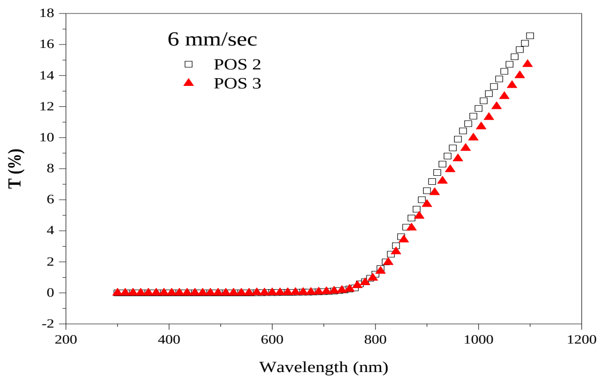


Figure 4 (a-d) Transmittance spectra of CuO as a function of examined position (POS) and deposition speed at 30 cm NSD

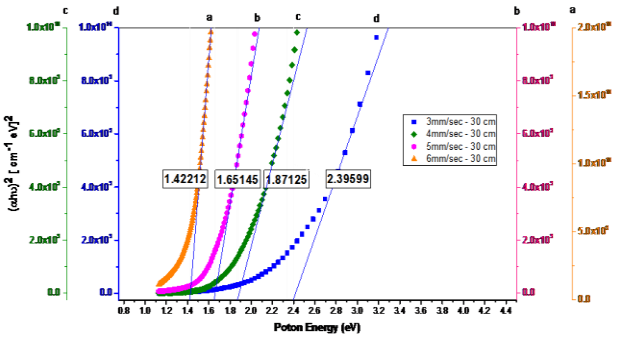


Figure 5 Optical band gap as a function of deposition speed at 30 cm nozzle height

Conclusion

The results showed a clear impact of the change one parameter certified and kept other deposition parameters fixed on the thin films formation. The spray deposition of CuO layers onto glass substrates at different deposition platform speed and nozzle-to-substrate distances equal 30 cm shows polycrystalline in nature with monoclinic structure. The Transmittance spectra reveal that the transmittance decreasing with increased preparation speed. The higher speed exhibits an improvement on the structural and optical properties over preparation speed. The as- deposited film, which changes to a smooth and uniform at the speed (6 mm/s), Band gap, thickness, found to be increased with decreasing of deposition speed. The energy band gap varies from 1.422 to 2.395 eV pursuant to change in deposition speed.

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