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Effect of Process Variables on Deposited Cupric Oxide Thin Film by Sol-Gel Spin Coating Technique

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Abstract. Cupric oxide were prepared by sol-gel technique and deposited onto glass substrates as thin films using spin coating method. The aim of this research was to study the effects of different spin coating speeds and solution concentrations of cupric oxide thin films on the structural, optical, electrical and physical properties of thin films. Thin films were deposited with concentration variation of the solution ranging from 0.5 M-1 M and speed variation from 1200 rpm-2400 rpm. X-ray diffraction (XRD) and UV-Vis spectrophotometer were used to characterize the structural and optical properties of the deposited films, respectively. The as-synthesized CuO thin films were also characterized using SEM. The dc electrical properties were characterized using nano-electrometer. Based on the results obtained, it was found that the electrical resistivity of the cupric oxide thin films increases as spin coating speeds increase. The optical band gap values of CuO thin films for concentration variation were found 1.47-1.27 eV and for speed variations, it was observed 1.45-1.95 eV. Decreased values of the optical energy gap were observed with increasing concentration while reverse effect was found with increasing speed of spin coating.

1. Introduction

Cupric oxide (CuO) is a black color compound with slight translucence. CuO is a promising candidate for many applications owing to the abundance of its components in nature, low-cost production, good thermal stability, and electrochemical properties. This combined property enables CuO thin films to be an excellent semiconductor for several applications such as high-temperature superconductors [1], solar cells [1], gas sensors [2], magnetic storage media [3], catalyst etc. It has direct optical band gap energy in the range of 1.2 to 1.9 eV [4]. CuO has a monoclinic structure with the lattice parameters a = 4.684A, b = 3.425A, c = 5.129A, and β = 99.28A. The transparent conductive cupric oxide thin films had been developed by several techniques such as electrodeposition, thermal evaporation, sol-gel technique [5] and wet chemical method [6] which could be deposited on various substrates [7]. However, the most prepared technique used is sol-gel method due to its simplicity, lower cost, reproducibility, ease

of composition control and large area deposition [8]. Sol-gel method easily to deposit on different types of substrates that could be performed under non-vacuum environment. Therefore in this research, sol-gel method was used to form the solution of cupric oxide which then deposited on glass substrates using spin coating technique. The main goal of this paper was to study the effects of different spin coating speeds and solution concentrations of the cupric oxide thin films on the optical, structural, electrical and physical properties on glass substrates which were characterized using UV-Vis spectrophotometer, X-ray diffraction pattern, Nano-electrometer and Scanning Electron Microscope (SEM), respectively.

2. Experimental details

The procedures for preparing cupric oxide thin films were summarized in the following.

2.1. Preparation of substrates

In this work, the substrates were initially cleaned with detergent soap in tap water. Then they were cleaned using methanol, acetone and deionized water and allowed to dry with dryer.

2.2. Preparation of cupric oxide solution using sol-gel method

In the sol-gel process, the materials used were copper acetate powder [9], diethanolamine, isopropanol and ethylene glycol without any further purification. 0.5 M, 0.75 M and 1 M of solution were formed by dissolving 0.5 g, 0.75 g and 1 g of copper acetate powder in 9 ml isopropyl alcohol and 0.5 ml diethanolamine which act as precursor, solvent and complexing agent, respectively. Then, 0.5 ml ethylene glycol was added into the solution. Next, the cupric oxide solutions were stirred at room temperature until a transparent solution were obtained. The solutions with concentration of 0.5, 0.75 and 1 M were a clear and dark blue without any suspension of particles.

2.3. Preparation of cupric oxide thin films deposition by spin coating technique

Prior to the thin films deposition process, quarter area of the substrate was covered with capton tape while the other area of the substrate was left uncovered for the layer thickness measurements. After stirring process, a double step spinning program was applied to obtain the homogenous precursor films. In this step, the solutions were spread onto the substrates at 100 rpm for 10 seconds. The solutions were spin coated with concentration of 0.5 M, 0.75 M and 1 M with spinning speed of 1200 rpm and with spinning speed of 1200, 1800 and 2400 rpm of 0.75 M for 3 minutes each. Immediately after coating process, the sample was dried for 5 minutes at 250°C for each layer. Five layers of cupric oxide thin film were coated one over the above. After the drying of the last layer, sample was annealed for 30 minutes at 600°C.

2.4.Samples Characterization

UV-Vis spectrophotometer was used to observe the absorbance of cupric oxide thin films. To determine the crystallinity, X-ray diffraction (XRD) was used. Current-voltage measurements for concentration variation and speed variation were performed by using 6517B Electrometer with applied voltage -5 to 5 V. Prior to the measurements, the thin films were coated with silver (Ag) as the metal contacts. The width of metal contacts deposited onto cupric oxide thin films were 2.3 mm. The morphology of the deposited CuO thin films was observed by SEM (Scanning Electron Microscope).

3. Results and discussion

3.1. Optical properties of cupric oxide thin films

Figures 1 and 2 show the optical properties of deposited CuO thin films at various solution concentrations and spinning speeds on glass substrates have been determined by using absorbance spectra in the region of (300-1100) nm. It was observed that film's higher

absorption on the shorter wavelength side (ultraviolet region), and lower absorption on the higher wavelength side (visible region) [10].

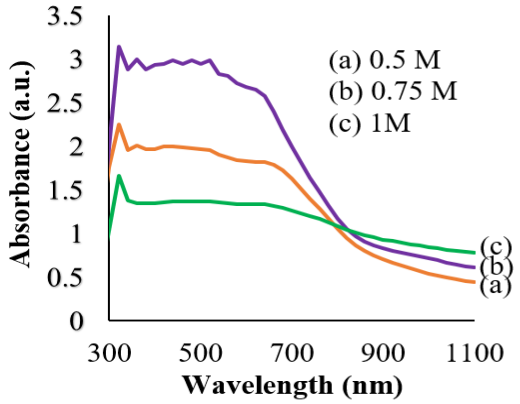

Figure 1. Optical absorbance vs. wavelength for various concentration of CuO at 1200 rpm.

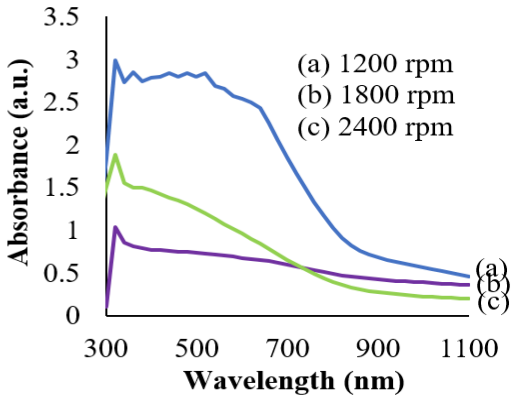

Figure 2. Optical absorbance vs. wavelength for 0.75 M of CuO at various spinning speed.

From figures 1 and 2, the highest absorbance was observed for 0.75 M in case of concentration variation at 1200 rpm and for speed variation of 0.75 M, highest absorbance was found for 1200 rpm. Because, the absorption was occurred when electron made the transition from a lower energy state in valence band to high energy state in conduction band while absorbing the excess energy as photon. It was observed that almost absorption edges were found around 319-321 nm present in the spectra indicating the absorption properties of cupric oxide in the UV region. The optical absorption at absorption edge related to the transition from valence band to conduction band and was closed with band gap energy [11]. The absorption coefficient (α) for the prepared thin films was calculated by the following equation.

$$\alpha = \{ln\,(100/(\%T))\}/d \qquad (1)$$

Where T is the transmittance spectrum of the thin film and d is the thin film thickness.
The absorption coefficient, α of the cupric oxide thin films was related to the photon energy, hν [12], where hν is the photon energy (eV). These optical band gap were obtained by tangent line intersection with energy axis on the photon energy (hν) of the $(\alpha h\nu)^2$ versus photon energy plot [13]. The photon energy (hν) was calculated using equation 2:

$$h\nu = hc/\lambda \qquad (2)$$

Where h is the Plank constant which is 6.626×10^{-34}, c is the light constant that is 3×10^{8} and λ is wavelength. Optical band gap was calculated and showed in figures 3 and 4.

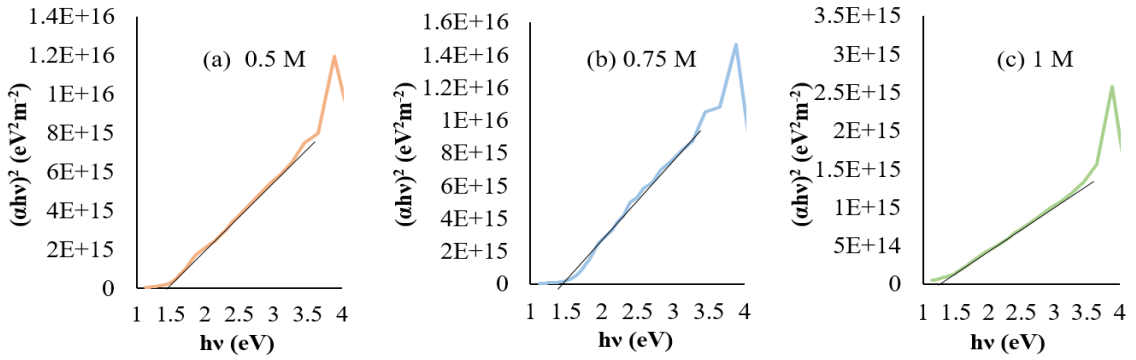

Figure 3. The plot of optical band gap energy versus photon energy at 1200 rpm for (a) 0.5 M, (b) 0.75 M and (c) 1 M CuO thin films.

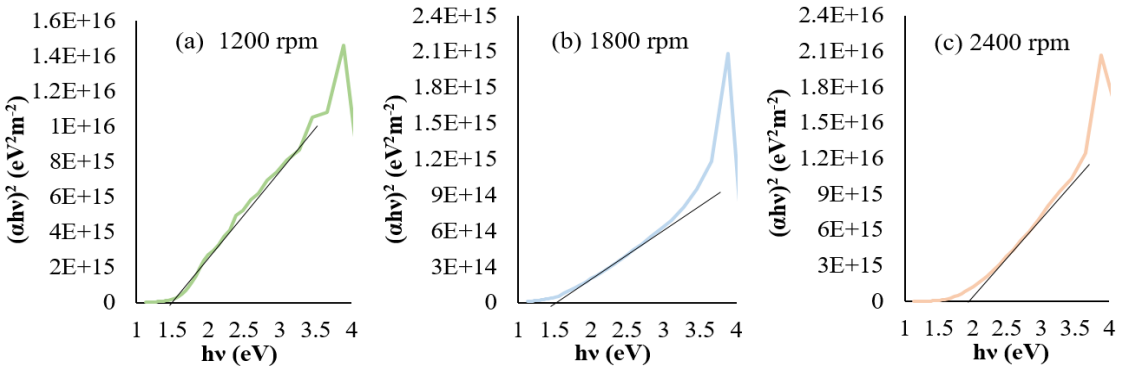

Figure 4. The plot of optical band gap energy versus photon energy at (a) 1200 rpm, (b) 1800 rpm and (c) 2400 rpm for 0.75 M CuO thin films.

From figures 3 and 4, the values of the optical band gap of CuO thin films were tabulated in tables 1 and 2. The optical band gap energy for concentration variation were found to be in the range of 1.47 to 1.27 eV which were decreased as the solution concentration increased, while for speed variation were found to be in the range of 1.45 to 1.95 eV which were increased as the spin coating speeds increased and also were found to be affected by film thickness. It was reported that the optical band gap decreased with the increased of the grain size [13, 14] and crystallinity.

Table 1. Thickness of thin films and optical band gap at different solution concentrations.

Solution concentration (M)	Thickness (nm)	Optical band gap (eV)
0.5	184.694	1.47
0.75	220.99	1.45
1	293.77	1.27

Table 2. Thickness of thin films and optical band gap at different spin coating speeds for 0.75 M concentration.

Spin speed (rpm)	Thickness (nm)	Optical band gap (eV)
1200	220.99	1.45
1800	183.35	1.53
2400	117.24	1.95

3.2. Structural properties of CuO thin films

In figures 5 and 6, it was reported that the X-ray diffraction patterns (XRD) of prepared CuO thin films at annealing temperatures (600)°C (30 min.) for different precursor concentrations ranged from 0.5 M to 1 M at 1200 rpm and for different spin coating speeds of 0.75 M ranged from 1200 rpm to 2400 rpm. Prepared thin film samples using 0.5 M and 0.75 M show two important peaks were observed at 35.5° and 38.6° corresponds to the (-111) and (111) diffraction planes. With increasing the molarity to 1 M, the two dominant peaks assigned to (-111) and (111) and more intense. It was also observed that CuO thin film at 1200 rpm for 0.75 M show two more intense peaks than 1800 and 2400 rpm. It was also noticed the emergence of some small peaks related to (-202) (020)(202) (-113) (-311) (113) (311) and (-222) planes. All the apparent atomic plans reveal that the deposited films are composed of a single CuO phase with monoclinic crystal structure.

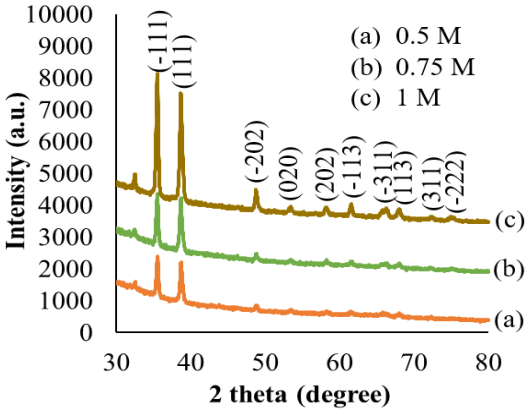

Figure 5. X-ray diffraction of CuO thin films elavorated with concentration variations at 1200 rpm.

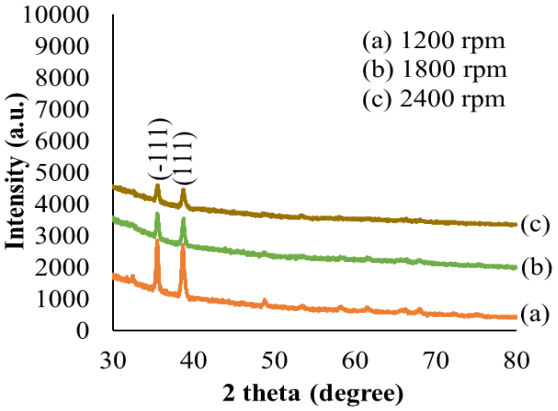

Figure 6. X-ray diffraction of CuO thin films elaborated with spin coating speed variations for 0.75 M.

3.3. Electrical properties of cupric oxide thin films

Figure 7 shows three curves for different concentrations and figure 8 shows another three curves for different spin coating speeds of CuO thin films on soda lime glass deposited by spin coating method which shown that all films indicated the Ohmic behavior with linear curve.

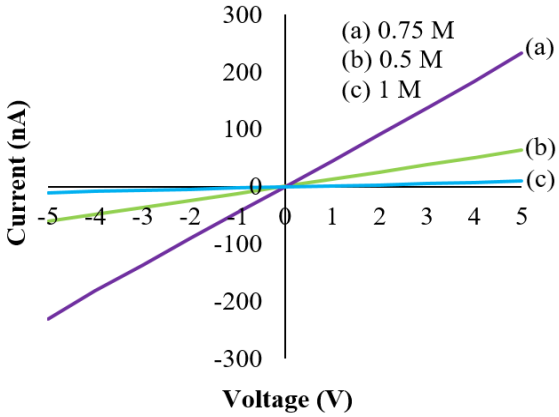

Figure 7. The plot of curves for concentration variation at 1200 rpm.

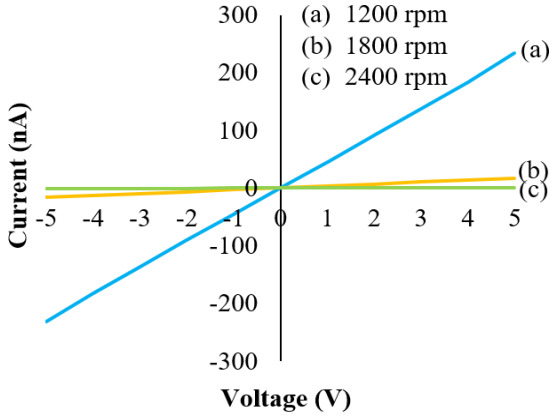

Figure 8. The plot of curves for 0.75 M at speed variation.

It was observed that slope of curves increased with decreasing of speed and the curves revealed that the current at 2400 rpm was the lowest while the current at 1200 rpm was the highest among the other curves. On the other hand, higher slope of curves was found at 0.75 M in case of concentration variation and it was found that the current for 1 M was the lowest while the current for 0.75 M was the highest at 1200 rpm. CuO thin film for 0.75 M at 1200 rpm have active layer uniformly on the glass substrates [15]. As a result, the recombination process took place effectively as more holes and electrons were transported to the active area, which translated into better electrical characteristics [15].

The calculated resistivity obtained in this work to be 3.34, 1.09 and 31.82 Ωm for thin films prepared at 1200 rpm for 0.5, 0.75 and 1M, respectively, while 1.09, 13.03 and 134.68 Ωm were obtained as the calculated resistivity for 0.75 M at 1200,1800 and 2400 rpm, respectively. The lowest resistivity was about 1.09 Ωm for 0.75 M, while the highest resistivity was about 31.82 Ωm for 1 M at concentration variation. Again, the lowest resistivity was about 1.09 Ωm for 0.75 M at 1200 rpm while the highest resistivity was about 134.68 Ωm for 0.75 M at 2400 rpm. This

was due to increase of electron and hole as carrier concentration and hence decreased the resistivity [9]. Therefore, it was observed that CuO thin film with highest concentration and spin coating speed with the decreased carrier concentration produced the highest resistivity.

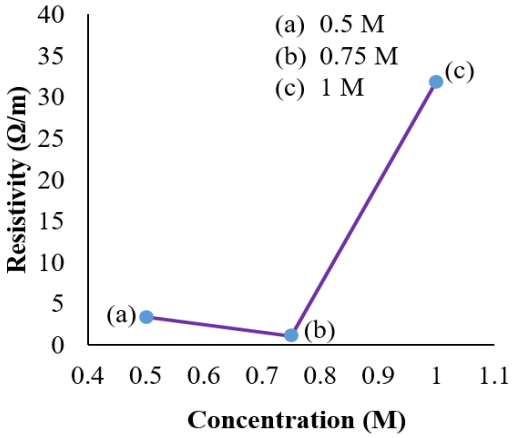

Figure 9. The plot of resistivity of CuO thin films vs. concentrations at 1200 rpm.

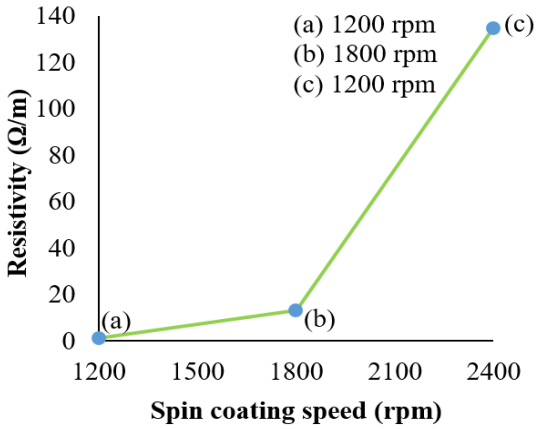

Figure 10. The plot of resistivity of CuO thin films vs. spin coating speeds for 0.75.

3.4. Physical properties of CuO thin films

The surface morphology of as-synthesized CuO thin films was investigated using Scanning Electron Microscope (SEM). The SEM photographs of concentration variation and speed variation of CuO thin films are shown in figures 11 and 12. On comparison of the three concentration photographs at 1200 rpm, it was observed that 0.5 M coated CuO thin film has more pore than that of 0.75 M thin film and it's particle size is greater than that of 0.75 M thin film. Again, 0.75 M CuO thin film coating show highly homogeneous layer of reduced particle size, improved texture, lowest void and pore. On the other hand, 1 M thin film is not homogeneous and it's particle size is greater than that of other films. So, it was found that in case of concentration variation at 1200 rpm, 0.75 M coated CuO thin film is the best thin film among 0.5 M, 0.75 M and 1 M coated thin films.

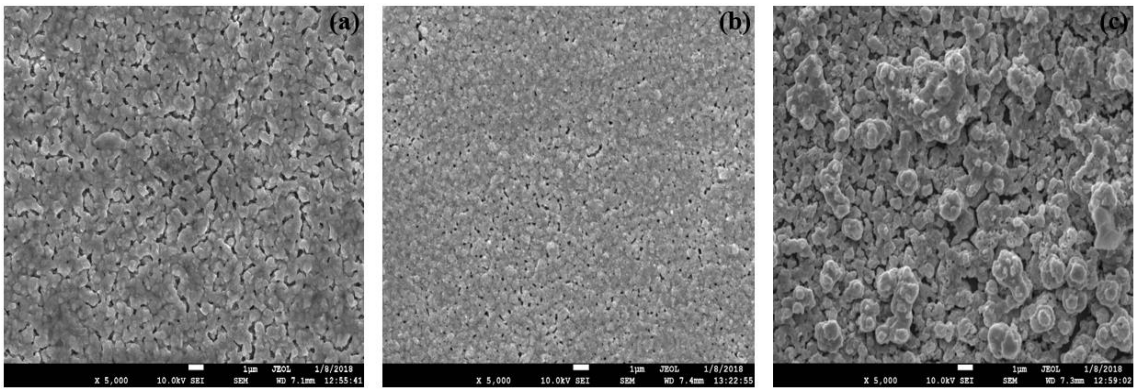

Figure 11. The FE-SEM images for CuO films deposited with: (a) 0.5 M, (b) 0.75 M and (c) 1 M at 1200 rpm.

On comparison of speed variations for 0.75 M, CuO thin film coated at 1200 rpm shows good homogeneous layer, besides it has good crystallinity according to XRD and highest absorbance. Again, thin film prepared at 1800 rpm shows more homogeneity but according to XRD, it's crystallinity is less than that of film at 1200 rpm and it's absorbance is lower than that

of thin film at 1200 rpm and 2400 rpm. On the other hand, CuO coated film at 2400 rpm has more pore and it's pore is greater than that of prepared films at 1200 rpm and 1800 rpm, besides it's crystallinity is less than that of other two films. Thus it was concluded that CuO coated thin film at 1200 rpm for 0.75M is an excellent semiconductor and would be more suitable for photovoltaic applications.

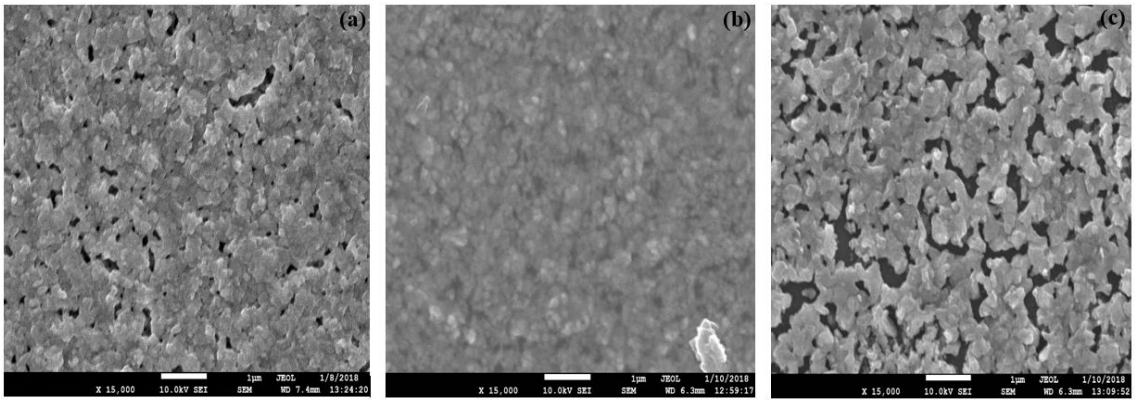

Figure 12. The FE-SEM images for CuO films deposited with: (a) 1200 rpm (b) 1800 rpm and (c) 2400 rpm for 0.75 M.

4. Conclusion

In summary, thin film of CuO was deposited using spin coating method on glass substrate with different thickness by varying solution concentrations and spin coating speeds. The optical, structural, electrical and physical properties of thin films were measured by UV-Visible spectrophotometer, X-ray diffraction, Electrometer and FE-SEM. Film with 0.75 M at 1200 rpm showed the highest absorbance. The decrease of the optical band gap with the increased of the thickness might attributed by the increased of crystallinity. CuO thin film with 0.75 M at 1200 rpm showed the lowest of electrical resistivity. The XRD analysis indicates that the obtained films have a monoclinic structure. Crystallinity for films prepared increased with increasing of concentration and decreasing of spinning speed. The SEM micrographs show that deposited films are homogeneous except 1M sample. From SEM micrographs, it was concluded that film elaborated at precursor concentration and spin coating speed equal to 0.75 M at 1200 rpm shows good quality. Finally from our research, it was observed that 0.75 M at 1200 rpm CuO thin film would be more suitable for solar cells conversion. Future investigation should be done on the optical, structural, electrical and physical properties of CuO thin films using doping technique.

5. Reference

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