*Journal of Ceramic Processing Research. Vol. 20, No. 2, pp. 139~142 (2019)*

J O U R N A L O F
Ceramic
Processing Research

# Effect of thickness and annealing temperature on the structural properties of CuO thin films prepared by sol-gel spin coating technique

**Fouzia Saadaoui, Abdelilah Rjeb, Badr Akharkhach, Aziz Nfissi and Salaheddine Sayouri***

*Laboratory of Theorical and Applied Physics, Faculty of Sciences Dhar el Mahraz, University Sidi Mohammed Ben Abdellah, PO Box 1796 Atlas Fez, 30000, Morocco*

**In this work, CuO thin films were deposited by sol gel spin-coating technique on microscope glass substrates. Copper acetate was used as the starting salt material source, ethanol as solvent and monoethanolamine as stabiliser. The as-coated films were preheated at 300 °C for 10 min and then annealed using two different temperatures. As the annealing temperature was increased from 500 °C to 600 °C, along with thickness, an improvement of the structural properties was concluded from XRD and SEM analyses. I-V characteristics of the films corroborated this result and showed existence of a normal Ohmic behaviour of these films. The average crystallite size estimated from XRD analysis was found to increase from 28.06 to 37.68 nm with the increase of both thickness and annealing temperature. On the other hand, the two parameters dislocation density and strain followed an opposite trend and decreased from 1.27 to 0.704 ($10^{15}$ lines /$m^2$) and from $1.29 \times 10^{-3}$ to $0.961 \times 10^{-3}$, respectively.**

**Key words: CuO thin films, Sol gel, Structural properties, I-V characteristics.**

## Introduction

Cupric oxide (CuO) known as p-type semiconducting material has attracted much attention because of its interesting properties and promising applications in batteries, superconductors, gas sensors, bio sensors, nanofluid, catalysis, thin film photovoltaic material, etc. [1-4]. There are many methods for synthesizing CuO thin films such as reactive sputtering [5], molecular beam epitaxy [6], spray pyrolysis deposition [4], and sol gel processing [7-10]. The sol gel process is one of the versatile methods to prepare thin films without complicated instruments; it is simple, inexpensive and has a general advantage of easy-control of composition, large area deposition and uniformity of film thickness [7, 11]. It is known that CuO (tenorite) single phase can be obtained either by using high oxygen pressure, inert atmosphere of nitrogen or simply in air, while $Cu_2O$ (cuprite) single phase can be obtained in low pressure oxygen atmosphere or in nitrogen atmosphere but with prolonged treatment (up to 5 hr).However, the co-existence of the two phases was always reported in all the previous conditions, at least on the films surfaces [3, 7], which may alter the desired properties of each phase [5, 12]. In this work, sol gel method was used to prepare CuO sol, and CuO thin films were produced from the spin coating of the sol on glass substrates. The effect of annealing temperature, in ambient air, and thickness on the structural properties and phase purity of the as-prepared CuO thin films was investigated and the I-V characteristics of the films were also reported.

*Corresponding author:
Tel : +212-6-73-78-52-88
Fax: +212-5-35-73-33-49
E-mail: ssayouri@gmail.com

## Experimental

The CuO precursor solution was obtained by first dissolving copper acetate in an ethanol solvent for 30 min. Afterwards, monoethanolamine (MEA) as a stabilizer was added to the solution with continuous stirring. The molar ratio of Cu ions to MEA in the as-prepared sol was maintained at 1.0 and the Cu ions concentration was controlled at 0.5 mol/L. The complex solution was stirred for 4h at 70 °C to yield a homogenous and stable sol. A CuO sol served as the coating solution after aging for at least 24hrs at room temperature. CuO thin films were coated onto pre-cleaned glass substrates using the spin coating technique at a speed of 3000 rpm for 30sec. Each as-coated layer was pre-heated at 300 °C for 10 min, and this cycle was repeated three, five and seven times in order to obtain thin films with different thicknesses (three, five and seven layers). The samples were subsequently heated to 500 °C, or 600 °C, at a heating rate of 10 °C/min, and then maintained at this temperature for 1hrs in a tube furnace in air ambiance. The crystal structure of CuO thin films was determined by X-Ray diffraction (X'PertHighScore Report) with CuKα radiation (λ = 1.54 Å). The surface morphology of the thin films was characterised by scanning electron microscope (FEI Quanta 200).The I-V characteristics were carried out using Picoammeter/Voltage Source-Keithley Model 6487 system.

## Results and Discussion

Fig. 1 shows the XRD patterns of the as-prepared copper oxide films annealed at 500 and 600 ºC, respectively for three different thicknesses (corresponding to three layers: 3; 5 and 7).For samples consisting in less than seven layers, the majority of peaks could be assigned to monoclinic (tenorite) structure of CuO. Furthermore, the presence of multiple peaks of the CuO phase revealed the polycrystalline nature of the films. In addition to the reflections due to the tenorite phase, which is the predominant phase, two weak diffraction lines at $2\theta = 41.965^{\circ}$ and $43.6012^{\circ}$ were also observed and attributed to the $Cu_2O$ phase (ICDD No. 05-0667) and metallic copper (ICDD No. 04-0836), respectively. Irrespective of the annealing temperature, increased thickness with seven layers led to a disappearance of those phases along with the rise of CuO reflections intensity. Structural parameters such as crystallite size, dislocation density and strain for all thin films were evaluated using the XRD patterns and are presented in table 1.The average crystallite size of the deposited films was estimated from the line broadening using Scherrer formula [2]:

$$D = D=\frac{K\lambda}{\beta\cos\theta} \qquad (1)$$

Where K = 0.94 is the shape factor, $\lambda$ is the wavelength of $CuK_{\alpha}$ radiation, $\beta$ is the full width at half maximum (FWHM) and $\theta$ is the angle of Bragg diffraction. The dislocation density, $\delta$, and strain, $\varepsilon$, of the thin films were estimated from the following equations [4, 13-15]:

$$\varepsilon=\frac{\beta\cos\theta}{4} \qquad (2)$$

$$\delta=\frac{1}{D^2} \qquad (3)$$

The average crystallite size was found to increase from 28.06 to 37.68 nm with the increase of both thickness and annealing temperature. The dislocation density and strain exhibited an opposite trend and decreased from1.27 to 0.704 ($10^{15}$ lines /$m^2$) and from $1.29 \times 10^{-3}$ to $0.961 \times 10^{-3}$ , respectively. These changes may be attributed to the improvement of crystallinity and the decrease in the concentration of lattice defects with the increase of thickness and annealing temperature. The increase of the crystallite size could be due to the decrease in grain boundaries, and hence the amount of defects in the films. Furthermore, the thermal energy produced by annealing led to an enhancement of mobility of active species by filling the micro-voids or defects in the structure and formation of more packed and large crystallites [2]. It is worth noting that if we increase the annealing temperature of thin films with the same thickness or by maintaining constant the annealing temperature while increasing the thickness of the thin films, an increase of the crystallite size as well as a decrease of strain and dislocation density are observed, with an exception for the sample with maximum deposited layers but annealed at lower temperature. In this case, the values of dislocation density and strain were still relatively high which in turn constraint the growth of large crystallites. This indicates that both thickness and annealing temperature contribute to the decrease in lattice imperfections and the formation of high quality films.

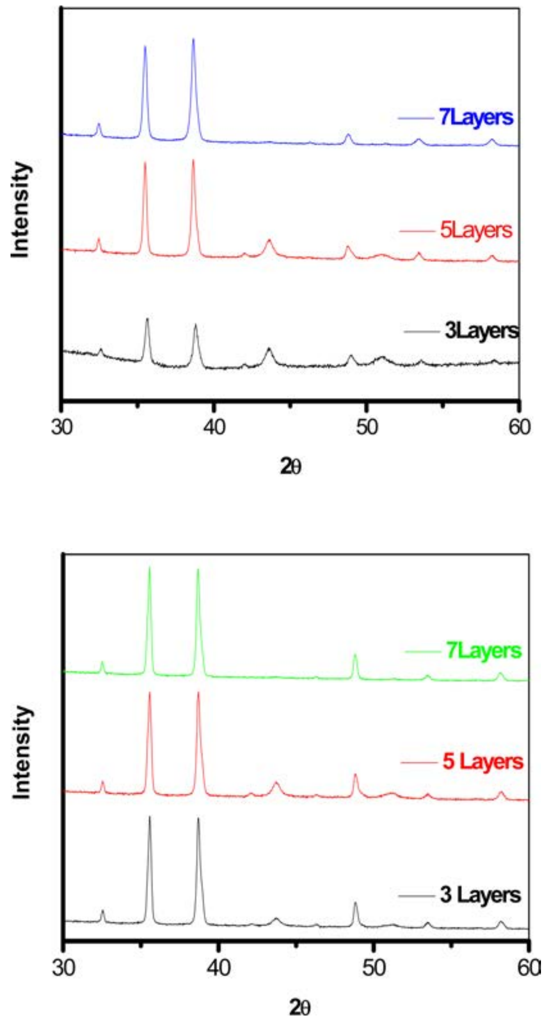


**Fig. 1.** XRD patterns of CuO thin films on glass substrate annealed at (a) 500 ºC and (b) 600 ºC with different thicknesses.

Fig. 2 shows the SEM images of the synthesised CuO thin films annealed at 500 and 600 ºC for three different film thicknesses. Regardless of the number of the deposited layers, it can be seen that the films have a better and a uniform surface morphology when annealed at higher temperature. Furthermore, the grains size has become larger, their shape more homogenous

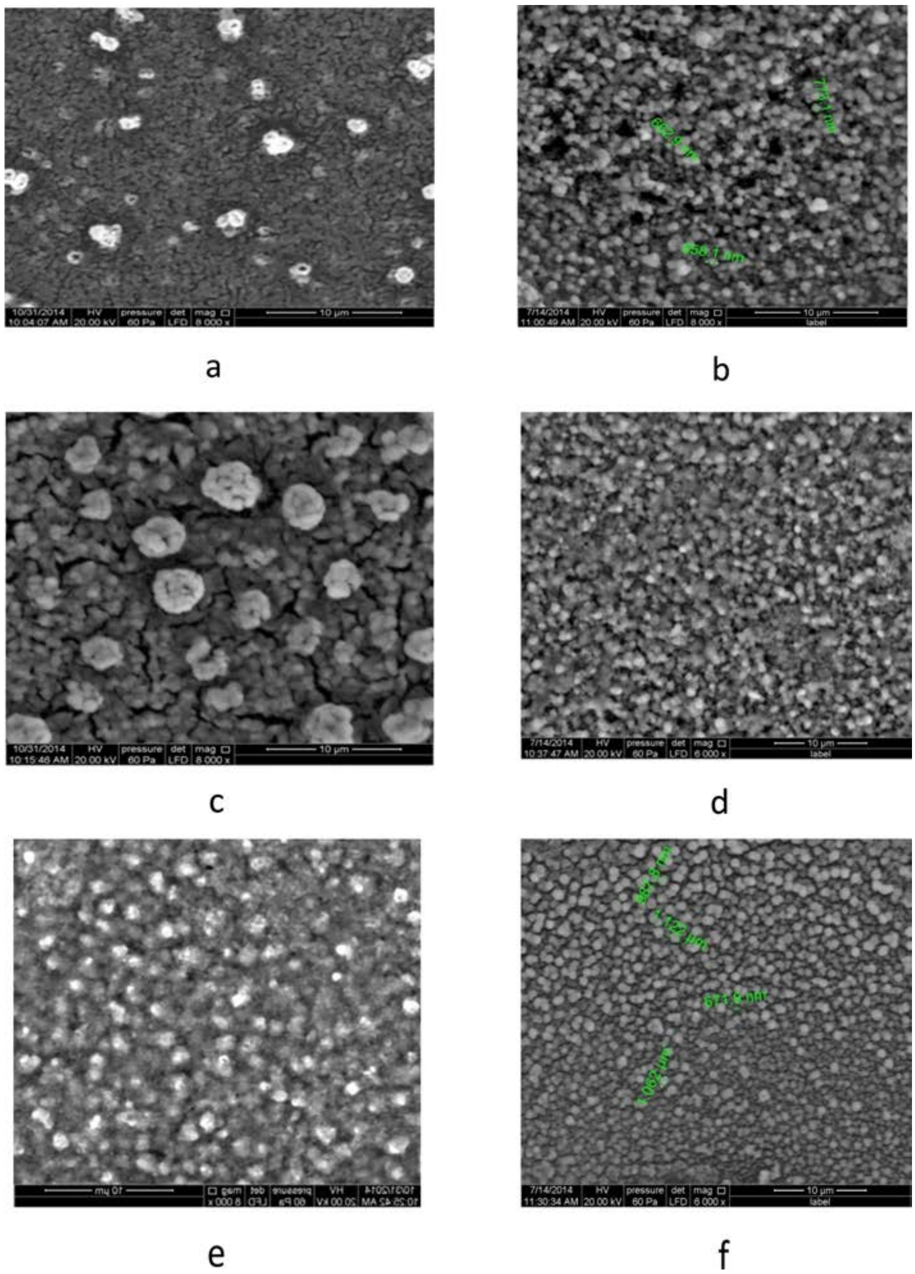


**Fig. 2.** SEM images of CuO thin films on glass substrate. (a) Three layers annealed at 500 °C. (b) Three layers annealed at 600 °C (c) Five layers annealed at 500 °C. (d) Five layers annealed at 600 °C. (e) Seven layers annealed at 500 °C. (f) Seven layers annealed at 600 °C.

and quasi-spherical and the distinct crystals formed on top of the film surface (grains clusters on the surface) disappear, which contributes to the increase of smoothness. Simultaneously, the increased thickness, together with the increased annealing temperature, yield films with dense, smooth and more compact morphology which is essential for the application in thin film solar cells, since leakage of photo-current can be avoided [15].

Fig. 3 shows the I-V curves of the CuO thin films on glass substrate. From a qualitative point of view, when the thickness is increased, the curves exhibit the ohmic behaviour characterizing CuO thin films [16]. Otherwise, a nonlinear behaviour takes place. This may be attributed to the high amount of scattering of carriers through the films, that is, as grain size decreased, the grain boundary density of the films increased. Subsequently, the scattering of carriers at grain boundaries increased which in turn decreased carrier mobility and hence caused the I-V curves to deviate from their normal behaviour. However, as thickness and annealing temperature increased, lattice imperfections decreased and the structure became denser which reduced grain boundary scattering and

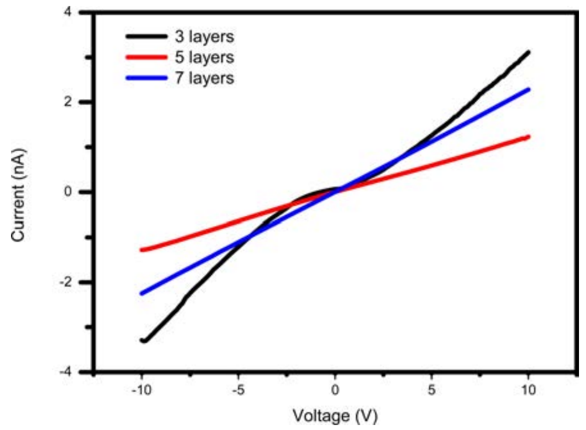


**Fig. 3.** I-V characteristics of CuO thin films on glass substrate annealed at 600 °C with different thicknesses.

**Table 1.** Structural parameters of CuO thin films on glass substrate for different annealing temperatures and thicknesses.

| No. of layers/ annealing temp. | FWHM | D (nm) | $\varepsilon$ ($10^{-3}$) | δ ($10^{15}/m^2$) |
|---|---|---|---|---|
| 3/500 | 0.3135 | 28.06 | 1.29 | 1.27 |
| 3/600 | 0.26 | 33.82 | 1.07 | 0.874 |
| 5/500 | 0.2768 | 31.77 | 1.139 | 0.991 |
| 5/600 | 0.2625 | 33.50 | 1.08 | 0.891 |
| 7/500 | 0.3298 | 26.66 | 1.357 | 1.407 |
| 7/600 | 0.2334 | 37.68 | 0.961 | 0.704 |

increased carrier mobility of the films [2].

## Conclusions

CuO thin films were successfully synthesized on glass substrates in ambient air using sol gel method. Both of thickness and annealing temperature have a great influence on structural properties and phase purity of the films, that is, increased thickness with seven deposited layers led to a disappearance of diffraction lines belonging to other phases than the CuO phase. In addition, with the increase of both annealing temperature and thickness, strain and dislocation density were found to decrease while crystallites size increased, which gave rise to thin films with good quality as confirmed by SEM images, and by I-V characteristics which exhibit normal Ohmic behaviour when both of the two conditions were fulfilled.

## References

1. Q. Zhanga, K. Zhang, D. Xu, G. Yang, H. Huang, F. Nie, C. Liu, S. Yang, Prog. Mater. Sci. 60 (2014) 208-337.
2. D. Gopalakrishna, K. Vijayalakshmi, C. Ravidhas, Ceram. Int. 39 (2013) 7685-7691.
3. A. Chen, H. Long, X. Li, Y. Li, G. Yang, P. Lu, Vacuum 83 (2009) 927-930.
4. R. Shabu, A. Moses, E. Raja, C. Sanjeeviraja, C. Ravidhas, Mater. Res. Bull. 68 (2015)1-8.
5. L. Guo, M. Zhao, D.-M. Zhuang, M. Cao, L. Ouyang, X. Li, R. Sun, Z. Gao, Appl. Surf. Sci. 359 (2015) 36-40.
6. K.-G. Yang, P. Hu, S.- X. Wu, L.- Z. Ren, M. Yang, W.- Q. Zhou, F.- M. Yu, Y.- J. Wang, M. Meng, G.- L. Wang, S.- W. Li, Mater. Lett. 166 (2016) 23-25.
7. L. Armelao, D. Barreca, M. Bertapelle, G. Bottaro, C. Sada, E. Tondello, Thin Solid Films 442 (2003) 48-52.
8. H. Qin, Z. Zhang, X. Liu, Y. Zhang, J. Hu, J. Magn. Magn. Mater. 322 (2010)1994-1998.
9. A. Yildiz, S. Horzum, N. Serin, T. Serin, Appl. Surf. Sci. 318 (2014) 105-107.
10. A. Nalbant, Ö. Ertek, İ. Okur, Mater. Sci. Eng. B 178 (2013) 368-374.
11. D. Raoufia, T. Raoufi, Appl. Surf. Sci. 255 (2009) 5812-5817.
12. M. Farbod, N. Meamar, G. Kazeminezhad, Ceram. Int. 40 (2014) 517-521.
13. Y. Akaltun, Thin Solid Films 594 (2015) 30-34.
14. P. Chand, A. Gaur, A. Kumar, U.- K. Gaur, Appl. Surf. Sci. 307 (2014) 280-286.
15. K. Mageshwari R. Sathyamoorthy, Mater. Sci. Semicond. Process. 16 (2013) 337-343.
16. A.-H. Jayatissa, K. Guo, A,- C. Jayasuriya, Appl. Surf. Sci. 255 (2009)9474-9479.