CuO Thin Films Deposition by Spray Pyrolysis: Influence of Precursor Solution Properties

M. Lamri Zeggar, F. Bourfaa, A. Adjimi, F. Boutbakh, M. S. Aida, N. Attaf

Abstract—CuO thin films were deposited by spray ultrasonic pyrolysis with different precursor solution. Two staring solution slats were used namely: copper acetate and copper chloride. The influence of these solutions on CuO thin films proprieties of is instigated. The X rays diffraction (XDR) analysis indicated that the films deposed with copper acetate are amorphous however the films elaborated with copper chloride have monoclinic structure. UV- Visible transmission spectra showed a strong absorbance of the deposited CuO thin films in the visible region. Electrical characterization has shown that CuO thin films prepared with copper acetate have a higher electrical conductivity.

Keywords—Thin films, cuprous oxide, spray pyrolysis, precursor solution.

I. INTRODUCTION

METAL OXIDE thin films used in various technological application are predominantly governed by their properties. Among these, cuprous oxide (CuO) thin films have been intensely studied as a promoting materiel for many industrial applications.

CuO has a monoclinic crystal structure and important p-type semiconductor with an optical band gap ranged from 1,2 to 1,6 eV and a high absorption coefficient [1]. CuO thin films were utilized in different applications such as: gas sensor for detection of CO and CO_2 [2], absorber layers for solar cells with theoretical predicted efficiency of 20% [3], lithium battery [4] and material for the magnetic storage [5]. Several techniques have been employed to prepare CuO thin films for example: sol-gel [6], electrode position [7], chemical vapor deposition [8], thermal oxidation [9] and reactive sputtering [10]. Among these techniques CuO thin films have been grow typically by spray pyrolysis on diverse type of substrates. It is a simple and easy technique for deposition of various metal oxide thin films. Two major interests in this method are the operating at atmospheric pressure and the deposition on a large surface. Investigations of deposition parameters influence on CuO thin films properties have been intensively carried. Parameters such as: substrates temperature [11], substrate nature [12] and doping [13]. However fewer studies have been devoted to the influence of precursor solution on the proprieties of CuO thin films.

M. LamriZeggar is with the Department of Physics, Laboratory of Thin Films and Interface, University Constantine 1, Algeria (e-mail: meryemlamri@gmial.com).
M. S. Aida is with the Faculty of Science, Department of Physics, Laboratory of Thin Films and Interface, UniversityConstantine1, Algeria (e-mail:aida_salah2@yahoo.fr).

In the present paper we address a comprehensive study of the influence of the solution nature and properties on the characteristics of CuO thin films deposited by spray pyrolysis technique.

II. EXPERIMENTAL

CuO thin films were deposited by spray ultrasonic pyrolysis on clean glass substrates using 0,05M of two aqueous solution of copper chloride ($CuCl_2.2H_2O$) and copper acetate ($C_4H_6O_4Cu.2H_2O$).To prepare 40 ml of the precursor solution the required quantity of salt is dissolved in double distilled water. The substrate temperature was kept at 300°C and the deposition time was fixed for 30 min.

Films structural properties were determined by XRD using PhilipsX'Pert system with CuKα radiation (λCu=0.154056nm). The diffract meter reflections were taken at room temperature and the 2θ value were varied in the range 20–80°. Films morphology was analyzed using scanning electron microscope Jeol5400SEM microscope. The optical transmission in the UV–visible range (200–2400nm) measurements was performed using ShimadzuUV-3101PC spectrophotometer. Films thicknesses were estimated from fitting optical transmission data. Films electrical characterization was performed using Hall Effect measurement system at room temperature (27°C), to determine electrical conductivity.

III. RESULTS AND DISCUSSION

A. Deposition Rate

In Table I, we have reported the film thickness and the deposition rate with different precursor solutions used. The deposition rate is estimated from the ratio of the thickness of the layer on the deposition time. As can be seen the deposition rate of CuO thin films deposited with copper chloride is almost three times greater than the deposited rate of the films obtained with copper acetate.

TABLE I
THICKNESS AND DEPOSITION RATE WITH DIFFERENT PRECURSOR SOLUTION

Precursor	Thickness (μm)	Deposition rate (nm/min)
Copper chloride	2.8	192
Copper acetate	1	67.3

The difference in thickness originates from the difference in the precursor properties that may alter the films growth mechanism. The formation of the films is produced by the pyrolytic reaction on the surface of substrate. When using copper chloride the reaction on surface is spontaneous.

However, when using copper acetate as starting solution the pyrolytic reaction is slowly. In fact, the decomposition of copper acetate in water leads to the formation of compound copper hydroxide $Cu(OH)_2$. Therefore, Copper ions (Cu^{+2}) are trapped by the hydroxide, the decomposition of this compound release requires else intermediate reactions which delays the formation of CuO phase in the case of copper acetate. On contrary to the solution prepared with copper chloride the copper ions are free which leads dialectally to the growth of CuO thin films.

B. Structural Proprieties

Fig. 1 shows XRD spectra of CuO thin films deposited with the two studied salts. As can be seen, the films deposited with copper chloride solution are polycrystalline in nature. Two most prominent peaks can be clearly located at 2θ value 35.5° and 39.1° corresponding to atomic planes (111) and (200), respectively of CuO phase. This indicated that the obtained CuO films have a monoclinic structure with the preferential orientation normal to the (200) direction. However the films deposited with copper acetate are amorphous in nature, since no peaks corresponding to monoclinic CuO planes were observed in the XRD pattern (Fig. 1 (b)).
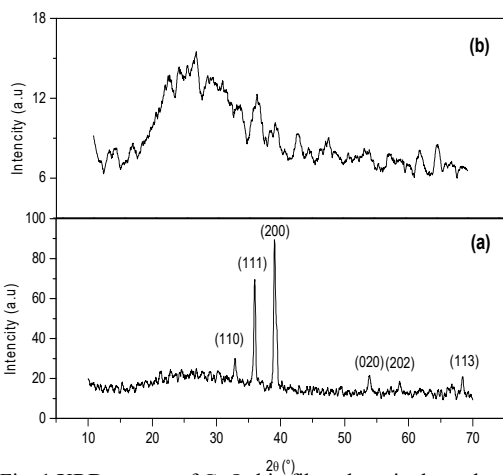

Fig. 1 XRD spectra of CuO thin films deposited at substrate temperature equal to 300°C with different solutions: (a) Copper chloride and (b) Copper acetate

Fig. 2 shows the Raman spectra of the as-prepared CuO thin films with different precursor solution. The Raman spectra are composed with three main phonon modes (Ag and 2Bg) located at 295,343 and 605 cm^{-1}. These peaks are largely reported in the literature [14]–[16]. This confirms the presence of a single phase CuO for all deposited films.

Fig. 3 shows typical SEM images of films deposited with the tow studied precurs or solutions. As can be seen, the film morphology depends strongly on the nature of the used precursor. The films elaborated with copper acetate are characterized by a rough, granular surface, consisting of crystallites distributed randomly with the presence of a needle structures. While films prepared with copper chloride salt gave a densely packed structure with uniformly distributed grains.
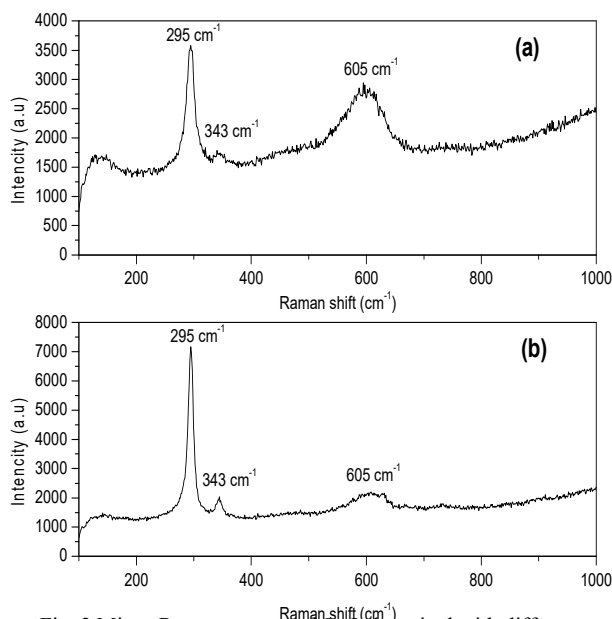

Fig. 2 Micro-Raman spectra of CuO deposited with different solutions: (a) Copper acetate and (b) Copper chloride
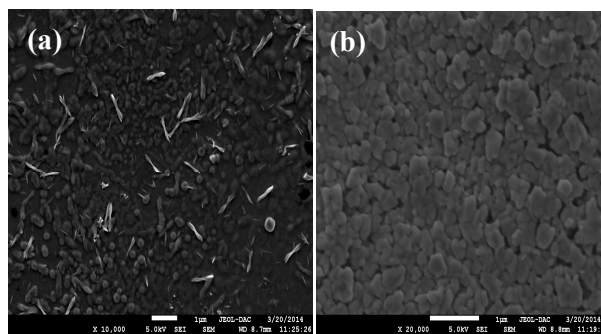

Fig. 3 SEM images of CuO thin films deposited at substrate temperature equal to 300°C with different solutions: (a) Copper acetate and (b) Copper chloride

C. Optical Proprieties

The transmittance spectra in UV–visible region of the prepared CuO films are shown in Fig. 4. As deposited CuO thin films exhibit a strong absorption in visible region. Films deposited with copper chloride have low transparency than films prepared with acetate due to the difference in thickness of the deposited films.

The optical band gaps of films have been estimated, as shown in Fig. 5, from the plot of their absorption coefficient as a function of photon energy and using Tauc formula for direct band gap semiconductors [17]:

$$(\alpha h\upsilon)^2 = B\,(E_g\text{-}h\upsilon) \qquad (1)$$

where α is a absorption coefficient, B is a constant, h is Planck constant, E_g is the energy band gap and υ is incident photon frequency.
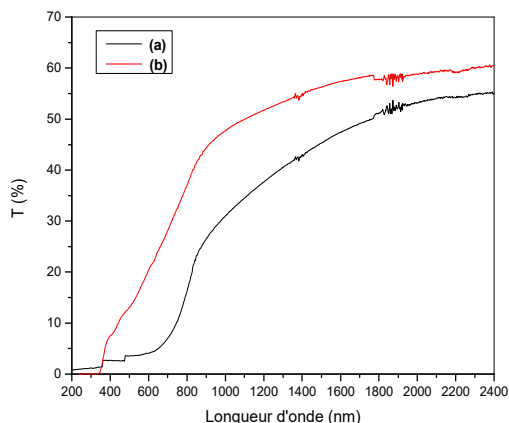
Fig. 4 UV-visible transmittance spectrum of CuO thin films deposited at 300 °C using different salts: (a) Copper chloride and (b) Copper acetate
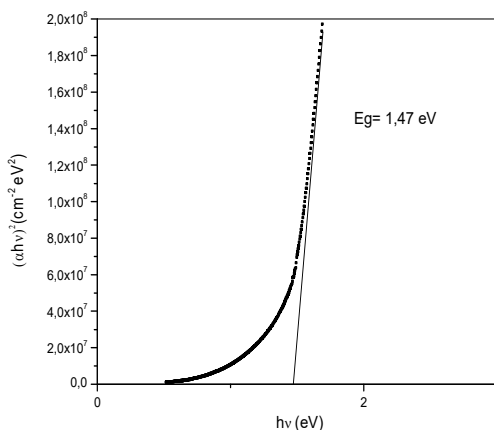

Fig. 5 Typical variation of the quantity $(\alpha h\nu)^2$ as a function of photon energy, for the sample prepare with copper chloride used for the determination of the optical gap

The obtained values of optical band gap and band tail width are reported in Table II. Films optical band gap are found equal to 1.47 and 1.30 eV for films prepared with copper chloride and copper acetate respectively which is in good agreement with CuO band gap values reported by [18]. These values are required for absorber layer in solar cells since it matches well with solar spectrum.

Due to the disorder in film network, localized states appear near the bands edges which cause band tails formation. These band tail states are responsible for the photon absorption in the low energies range. In this range the absorption coefficient is given by [19]:

$$\alpha \, (h\nu) = \alpha_0 \exp \, (h\nu/E_{00}) \qquad (2)$$

where α_0 is the pre-exponential factor, $h\nu$ the photon energy and E_{00} is the band tail width or disorder energy commonly called Urbach tail. E_{00} can be estimated from the inverse slope of the linear plot of $\ln(\alpha)$ versus $h\nu$.

The values of the band tail width E_{00} with various precursor solutions are reported in Table II. As can be seen value of the band tail width for the films prepared with copper acetate is more important is due to the presence of the amorphous phase in these films. This confirms the presence of amorphous phase as deduced from XRD analysis. The variation of the band tail and the optical band gap are opposite. This suggests that the variation of the optical gap is governed by the disorder in the film network.

TABLE II
OPTICAL BAND GAP AND BAND TAIL WIDTH WITH DIFFERENT PRECURSOR SOLUTIONS

Precursor	E00 (eV)	Eg (eV)
Copper chloride	0.40	1.47
Copper acetate	0.75	1.30

D. Electrical Proprieties

The films electrical conductivity was characterized by mean of Hall Effect measurements in order to determine the dark conductivity, free carriers concentration and mobility. In Table III we have reported the electrical conductivity and free carriers concentration of the deposited CuO thin films. As can be seen, the electrical conductivity follows faithfully the trend of the carriers' concentration. This indicates clearly that the conductivity is rather controlled by the free carrier concentration. The whole prepared films have p type conductivity according to Hall constant sign. The free carriers concentration in film prepared with copper chloride is three decades lower than in film prepared with the copper acetate indicating that using copper chloride as precursor yields to a film with low density of defects such as copper vacancies or oxygen in interstice sites since the latter are a source of free carriers.

TABLE III
ELECTRICAL CONDUCTIVITY AND FREE CARRIERS CONCENTRATION WITH DIFFERENT PRECURSOR SOLUTION

Precursor	σ ($\Omega.cm^{-1}$)	Free carriers concentration (cm^{-3})
Copper chloride	3.46×10^{-3}	7.73×10^{17}
Copper acetate	1.46×10^{-4}	9.37×10^{13}

IV. CONCLUSION

In present work, CuO thin films have been synthesized using spray pyrolysis technique. The influence nature of precursor solution on films properties has been investigated. The obtained results indicate that CuO films properties are sensitive to staring solution slats. The films deposited with copper chloride are crystalline with monoclinic structure. While films deposited with copper acetate are composed with micros-crystallites embedded in an amorphous phase. SEM image reveals that films elaborated with copper acetate are characterized by the presence of a needle structures. All CuO thin films have direct band gaps and strong absorption in visible region this property is suitable for photovoltaic applications.

REFERENCES

[1] F. Marabelli, G. B. Parravicini, F. Salghetti-Drioli, Phys. Rev. B52 (1995) 1433–1436.

[2] A. Chowdhuri, V. Gupta, K. Sreenivas, R. Kumar, S. Mozumdar, P. K. Patanjali, Appl. Phys. Lett. 84 (2004) 1180–1182.

[3] K. Han, M. Tao, Sol. Energy Mater. Sol. Cells 93 (2009) 153.

[4] X. P. Gao, J. L. Bao, G. L. Pan, H. Y. Zhu, P. X. Huang, F. Wu, D. Y. Song, J. Phys. Chem. B 108 (2004) 5547–5551.

[5] R. V. Kumar, Y. Diamant, A. Gedanken, Chem. Mater. 12 (2000) 2301–2305.

[6] A. Y. Oral, E. Mensur, M. H. Aslan, E. Basaran,MaterChemPhys, 83(1), 140 (2004).

[7] E. R. Kari, K. S. Brown, Choi, Electrochemical synthesis and characterization of transparent nanocrystalline Cu2O films and their conversion to CuO films, Chem. Commun. (2006) 3311–3313.

[8] T. Maruyama, Copper oxide thin films prepared from copper dipivaloylmethanate and oxygen by chemical vapor deposition, Jpn. J. Appl. Phys. 37(1998) 4099–4102.

[9] J. H. Benjamin, K. Nikolai, L. Ganhua, L. I. - Khan, C. Junhong, Z. Xin, Transport, analyte detection and optoelectronic response of p-type CuO nanowires, J. Phys. Chem. C 114 (2010) 2440–2447.

[10] V. F. Drobny, D. L. Pulfrey, Properties of reactively-sputtered copper oxide thinfilms, Thin Soild Films 61 (1979) 89–98.

[11] D. Gopalakrishna, K. Vijayalakshmi, C. Ravidhas Effect of pyrolytic temperature on the properties of nano-structured Cuo optimized for ethanol sensing applications, J Mater Sci: Mater Electron (2012).

[12] V. Dhanasekaran, T. Mahalingam, Physical properties evaluation of various substrates coated cupric oxide thinfilms by dip method, Journal of Alloys and Compounds 539 (2012) 50–56.

[13] S. Kose, E. Ketenci, V. Bilgin, F. Atay, I. Akyuz, Some physical properties of In doped copper oxide films produced by ultrasonicspray pyrolysis, Current Applied Physics 12 (2012) 890-895.

[14] D. P. Volanti, D. Keyson, L.S. Cavalcante, A.Z. Sim~oes, M.R. Joya, E. Longo, J. A. Varela, P. S. Pizani, A. G. Souza, J. Alloys Compd. 459 (2008) 537.

[15] H. Fan, B. Zou, Y. Liu, S. Xie, Nanotechnology 17 (2006) 1099.

[16] T. Yu, C.-H. Sow, A. Gantimahapatruni, F.-C. Cheong, Y. Zhu, K.-C. Chin, X. Xu, C.-T. Lim, Z. Shen, J.T.-L. Thong, A.T.-S. Wee, Nanotechnology 16 (2005) 1238.

[17] J. J. Tauc, Amorphous and Liquid Semiconductors, Plenum, London, 1974.

[18] L. Chabane, N. Zebbar, M. Lamri Zeggar, M. S. Aida, M. Kechouane a, M. Trari, Effects of CuO film thickness on electrical properties of CuO/ZnO and CuO/ZnS hetero-junctions Materials Science in Semiconductor Processing 40 (2015) 840–847.

[19] F. Urbach, Phys. Rev. 92 (1953) 1324.