Eng. &Tech.Journal, Vol. 32,Part (B), No.5, 2014

Morphological and Optical Properties of Cuo/Sapphire Thin Films Prepared by Pulsed Laser Deposition

Dr. Afnan k. Yousif
Applied Sciences Department, University of Technology / Baghdad
Email: Afnan_kamal@ yahoo.com
Ban A. Bader
Applied Sciences Department, University of Technology / Baghdad
Rana O. Mahdi
Applied Sciences Department, University of Technology / Baghdad

Received on: 29/5/2013 & Accepted on: 28/1/2014

ABSTRACT

This paper addresses the structure, morphological and optical properties of copper oxide (CuO) thin film deposited by pulsed laser deposition (PLD) method on Sapphire substrate of 150nm thickness. The film deposited at substrate temperature (400ºC). The atomic force microscopy (AFM), Fourier transform infrared spectroscopy (FTIR) and UV-VIS transmission spectroscopy were employed to characterize the size, morphology, crystalline structure and optical properties of the prepared thin film. The surface properties were characterized using (AFM), indicate that the average grain size less than 100nm, the surface roughness (2.69nm) and the root mean square is (3.58nm). The FTIR spectra shown strong band at about 418 $cm^{-1}$and 530 cm^{-1} related to CuO. From the UV-VIS transmission the energy band gap (1.7eV).

Keywords: Thin Films, Copper Oxide, Pulsed Laser Deposition, Effect of Substrate Temperature

الخصائص الطوبوغرافية والبصرية لاغشية اوكسيد النحاس المرسبة على الالومينا الرقيقة المحضرة بالليزر النبضي

الخلاصة

تم في هذا البحث، دراسة تأثير درجة حرارة القاعدة على الخصائص التركيبية والطوبوغرافية والبصرية لاغشية اوكسيد النحاس المحضرة بتقنية الترسيب بالليزر النبضي (PLD) على قواعد الالومينا بسمك غشاء 150 نانومتر. تم ترسيب الغشاء بدرجة حرارة (400ºC). استخدم مجهر القوة الذرية (AFM) ومطياف فورير للاشعة تحت الحمراء ومطياف النفاذية للاشعة المرئية – فوق البنفسجية (UV-VIS) للاغشية المحضرة لدراسة الخصائص التركيبية والطوبوغرافية والبصرية لها من خلال مجهر القوة الذرية وجد ان البناء متعدد التبلور وان معدل الحجم الحبيبي اقل من 100 نانومتر وكذلك خشونه السطح

(2,69 نانومتر) ومعدل مربع الجذر هو (3,58 نانومتر). أظهرت اطياف FTIR حزمة قوية عند $418\ cm^{-1}$ و $530\ cm^{-1}$ العائدة لاغشية CuO. ومن قياس طيف الاشعه المرئية – وتحت النبفسجية تم حساب فجوة الطاقة من طيف الاشعة ووجد ان قيمتها تساوي (1.7eV).

INTRODUCTION

Among other compound semiconductors, copper oxide is of great interest in semiconductor physics. Copper forms two well-known stable oxides, cupric oxide (CuO) and cuprous oxide (Cu_2O)[1,2]. These two oxides have different physical properties, colors, crystal structures and optical properties. CuO is a black semiconductor with a monoclinic structure belongs to space group, it displays a wealth of interesting properties, it is abundant, nonhazardous source materials.

Because of their optical and electrical properties (band gap 1.2–1.5 eV) [3-5], CuO have attracted interest as promising materials for solar cells and gas sensor. In practice, solar cells require proper layering of very-high-quality thin films with optimized surface morphology and crystallinity to prevent the surface roughness from affecting carrier transport in the cells.

Many researchers have been reported on the structural analysis and characterization of the physical properties of copper oxide thin films, using different methods, the most important deposition techniques used are sputtering [6, 7], thermal evaporation and oxidation [8], molecular beam epitaxial [9], and electrochemical deposition [10]. Although pulsed laser deposition (PLD) is widely used for the growth of oxide films because of its advantage in the stoichiometry conservation of complex materials, only few studies have grown cupric oxides by this technique. The PLD of CuO can yield films with improved qualities; however, there is no straightforward theoretical or experimental model for the deposition processes or the resulting film properties.

In this work we report the fabrication of copper oxide films on Sapphire (1000) substrates at different temperature by PLD technique. The results show that the single-phase CuO and Cu_2O thin films can be obtained. Furthermore, the morphology of the deposited films were characterized by atomic force microscopy (AFM), the optical transmittance and reflectance spectra, Fourier transform infrared spectroscopy were used to investigate the optical properties of the films.

EXPERIMENTAL WORK

Crystalline CuO films were grown on polished Sapphire substrates (0001) (from MTI Corp.) by Pulsed Laser Deposition with substrate temperature (400ºC), at an oxygen background pressure of 20×10^{-2} mbar, and a laser fluence of 1.5 J/cm^2. Before deposition, the substrate was cleaned with acetone and ethanol and dried under nitrogen gas flow. Then the substrate was loaded into the PLD chamber, the substrates were placed at 4 cm distance from CuO target. The chamber was kept at vacuum pressure of 10^{-3} mbar. The CuO target was ablated from 10 to 100 pulses (10–20 min) to get single layer thin films.

During the deposition, Nd: YAG laser (532 nm, pulsed width 7 ns and the repetition rate 10 Hz), which was operated at various energies, was used to ablate a commercial CuO target (99.99% from MTI Corp.). The laser beam was focused on the target at an incidence angle of 45° through a UV-grade quartz window. The ablated species of CuO were ejected with high kinetic energies and deposited on the sapphire substrates. During deposition, O_2 gas (99.99% purity) was purged into the chamber through a mass flow controller and a variable leak valve at various pressure ranges. The structure of the grown films was determined by Fourier transform infrared (FTIR) measurements. Film transmission measurement is performed at spectral range 200–1100 nm using UV–VIS-PV-8800 (Perkin Elemer Company) spectrophotometer. The surface morphology was examined by Atomic Force microscopy (AFM).

RESULTS AND DISCUSSION

The present study focused on the investigation of the surface morphology of the CuO films deposited at different substrate temperature to establish the dependence of their surface quality on the growth conditions of the PLD process.

The AFM image obtained from the CuO films grown on Sapphire at substrate temperature (400ºC) as show in Figure (1) indicate that the average surface roughness (2.69nm) and the root mean square is (3.58nm) [9], This improvement occurs because the film species at high temperatures have enough kinetic energy to collide strongly with each other and simultaneously re-evaporate because of the low melting point of CuO compared to the temperature of the PLD plume. a binary feature (formed of small and large grains) was observed at surfaces, while the size of the grains is approximately the same and the grains are distributed uniformly that can be attributed to the increases of surface energy at high temperature[11] . In addition, this result can be explained low roughness of surface at high temperature.

The FTIR spectra taken on the CuO/Sapphire deposited film is shown in Figure (2): the strong band at about 418 $cm^{-1}$and 530 cm^{-1} can be associated with CuO [12], where as the wide absorption band around 640cm^{-1} is attributed to Cu_2O [13].

For the film deposited on sapphire substrate at temperature 400ºC there are two peaks at wave number of about 418 cm^{-1} and 530 cm^{-1} (the phonon spectrum of CuO) and 620cm^{-1} (the phonon spectrum of Cu2O),

Figure (3) shows the combination of optical transmittance spectra of copper oxide thin films deposited on the different substrate temperature with 150nm films thickness.

Because of the crystallinity and higher transparency, the copper oxide films are suitable for optical analysis from which the absorption coefficient and energy band gap may be determined. The conversion of Cu_2O into CuO can also be shown by the determination of the optical band gap. For this, in the fundamental absorption region the optical absorption coefficient (α) was evaluated using the Equation.

$$\alpha = (\ln T\text{-}1)/t \qquad \ldots(1)$$

Where t is the film thickness and T is the transmittance [8]. The best linear relationship is obtained by plotting α^2 against hν, based on Eq. (2) below.

$$\alpha h\nu = A(h\nu - E_g)^{n/2} \qquad \ldots(2)$$

Where α is absorption coefficient, A a constant (independent from ν) and n the exponent that depends upon the quantum selection rules for the particular material.

The photon energy (hν) for y-axis can be calculated using Equation (3).

$$E = h\nu = hc/\lambda \qquad \dots (3)$$

Where h is Plank's constant ($6.626x10^{-34}$), c is speed of light ($3x10^{8}$) and λ is the wavelength.

A straight line shown in Figure (4) is obtained when $(\alpha h\nu)^2$ is plotted against photon energy (hν), which indicates that the absorption edge is due to a direct allowed transition (n = 1 for direct allowed transition). The intercept of the straight line on hν axis corresponds to the optical band gap (Eg).

The band gaps of film that was obtained. However, the band gap values are in the expected range for copper oxide thin films [14].

The films deposited at substrate temperature at 400 °C and possessing CuO composition show a band gap of 1.7 eV, corresponding to an optical absorption threshold of ∼900 nm. CuO is the predominant phase at 400ºC.

CONCLUSIONS

Copper thin films at 150nm thickness were produced by pulsed laser deposition on sapphire substrate at substrate temperature (400ºC). The morphology, roughness and grain size were investigated by atomic force microscopy (AFM). The result obtained of AFM showed the uniformed of the size of the grains and the average grain size less than 100nm, the surface roughness (2.69nm) and the root mean square is (3.58nm). The FTIR spectroscopic measurements further proved that the conversion from copper (II) oxide into copper (I) oxide at (400ºC) substrate temperature. Optical band gap of the films, measured by employing a UV-VIS spectrophotometer, 1.7 eV.

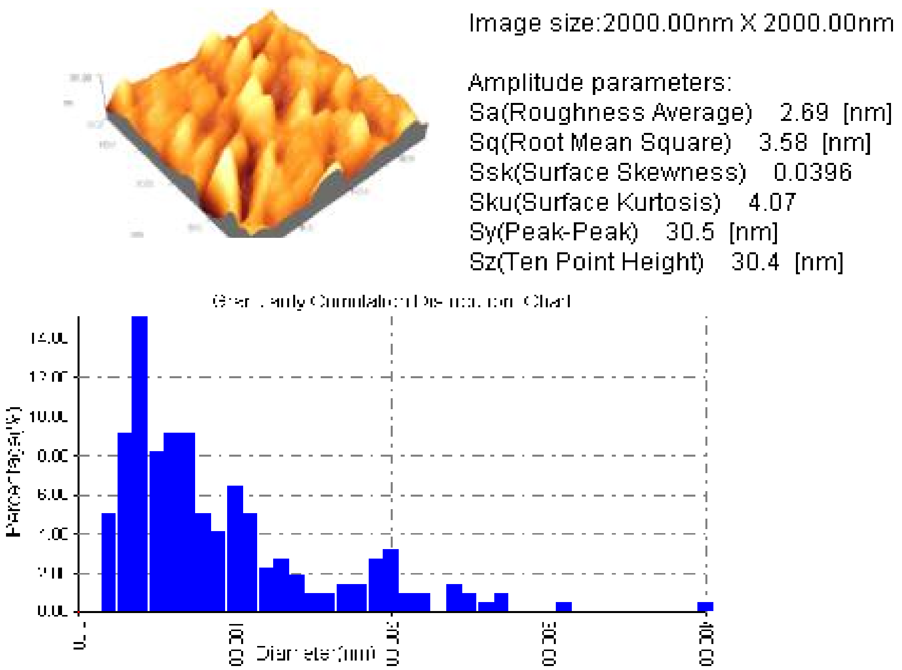

Figure (1) 3D AFM pictures of CuO/Sapphire.

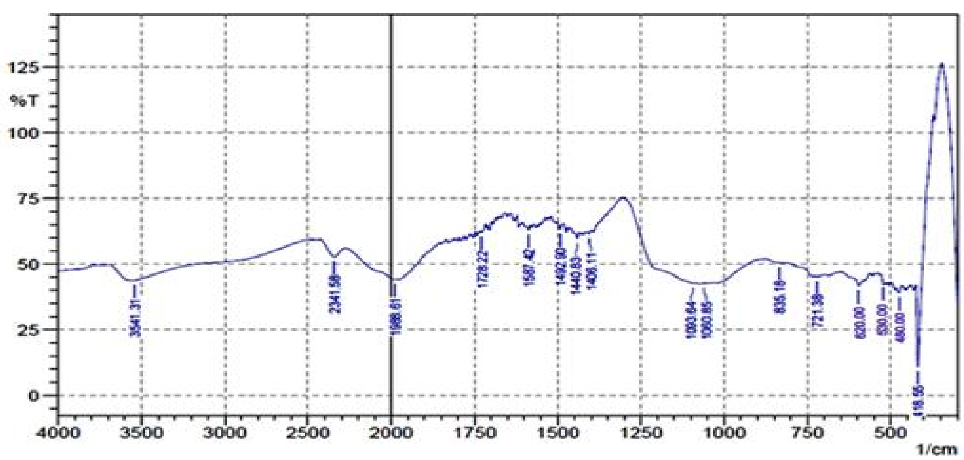

Figure (2) FTIR spectra between wave number and transmission of CuO/Sapphire thin film

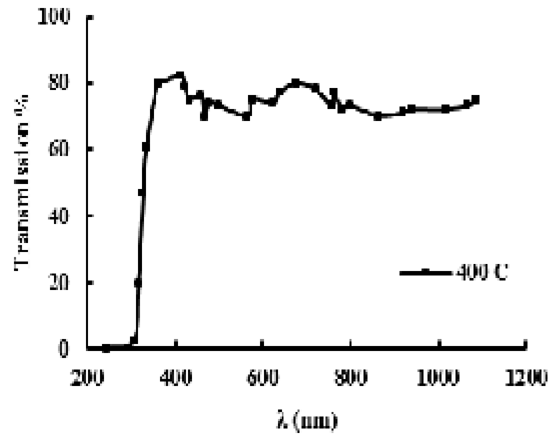

Figure (3) Optical transmittance (T) spectra of CuO/Sapphire thin film.

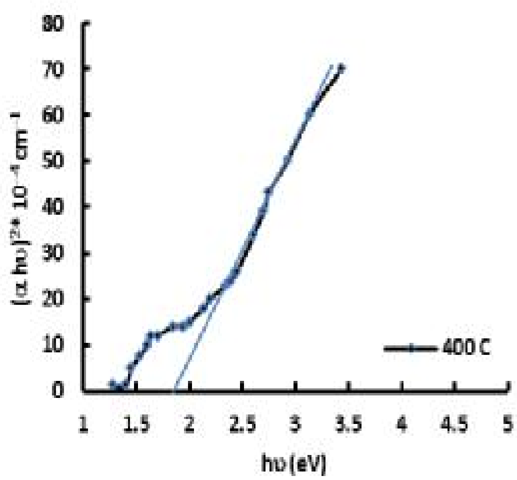

Figure (4) Plot of a^2 versus hυ curve of CuO/Sapphire thin film.

REFERENCES

[1]. Jayatissa,A. K. Guo, A. Jayasuriya, Fabrication of cuprous and cupric oxide thin films by heat treatment, (2009) Applied Surface Science 255, 9474–9479.

[2]. Bari1,R. H. S. B. Patil, A. R. Bari, Spray-pyrolized nanostructured CuO thin films for H2S gas sensor, (2013) International Nano Letters 3:12.

[3]. Dhanasekaran,V. T. Mahalingam, V. Ganesan, SEM and AFM Studies of Dip-Coated CuO Nanofilms, (2013) MICROSCOPY RESEARCH AND TECHNIQUE 76:58–65.

[4]. Rocquefelte, X. M. Whangbo, A. Villesuzanne, S. Jobic, F. Tran, K. Schwarz, P. Blaha, Short-range magnetic order and temperature-dependent properties of cupric oxide, (2010) Journal of Physics: Condensed Matter 22, 045502.

[5]. Hoa,N. S. An, N. Dung, N. Van Quy, D. Kim, Synthesis of p-type semiconducting cupric oxide thin films and their application to hydrogen detection, (2010), Sensors and Actuators B: Chemical 146, 239–244.

[6]. Darma, T. A. Ogwu, F. Placido, Effects of sputtering pressure on properties of copper oxide thin films prepared by rf magnetron sputtering, (2011) , Materials Technology: Advanced Performance Materials 26, 28–31.

[7]. H. Lu, C. Chu, C. Lai, Y. Wang, Property variations of direct-current reactive magnetron sputtered copper oxide thin films deposited at different oxygen partial pressures, (2009), Thin Solid Films 517, 4408–4412.

[8]. Papadimitropoulos,G. N. Vourdas, V. Vamvakas, D. Davazoglou, Optical and structural properties of copper oxide thin films grown by oxidation of metal layers, (2006), Thin Solid Films 515, 2428–2432.

[9]. Muthe, K. J. Vyas, S. Narang, D. Aswal, S. Gupta, D. Bhattacharya, R. Pinto, G. Kothiyal, S. Sabharwal, A study of the CuO phase formation during thin film deposition by molecular beam epitaxy, (1998), Thin Solid Films 324, 37–43

[10]. Morrison, E. D. Gutiérrez-Tauste, C. Domingo, E. Vigil, J. Ayllón, One step room temperature photodeposition of Cu/TiO_2 composite films and its conversion to CuO/TiO_2, (2009), Thin Solid Films 517, 5621–5624.

[11]. Khojier, K. A. Behju. Annealing temperature effect on nanostructure and phase transition of copper oxide thin films, (2012), Int.J.Nano Dim. 2(3): 185-190.

[12]. Balamurugan, B. B.R. Mehta, D.K. Avasthi, F. Singh, A.K., Modifying the nanocrystalline characteristics—structure, size, and surface states of copper oxide thin films by high-energy heavy-ion irradiation (2002) J Appl Phys., 92, 3304.

[13]. Joha , M. R. M. S. Mohd Suan, N. L. Hawari1, Annealing Effects on the Properties of Copper Oxide Thin Films Prepared by Chemical Deposition,(2011), Int. J. Electrochem. Sci., 6, 6094 - 6104

[14]. Banerjee and K. Chattopadhyay, A.N. Progress in Crystal Growth and Characterization of Material. (2005) 50, 52-105.