Substrate Temperature Effect on the Structure, Morphological and Optical Properties of CuO/Sapphire Thin Films Prepared by Pulsed Laser deposition

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Abstract

This paper addresses the substrate temperature effect on the structure, morphological and optical properties of copper oxide (CuO) thin films deposited by pulsed laser deposition (PLD) method on sapphire substrate of 150nm thickness. The films deposited at two different substrate temperatures (473 and 673)K. 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 films. The surface characteristics were studied by using AFM. It is found that as the substrate temperature increases, the grain size increased but the surface roughness decreased.

The FTIR spectra showed strong band at about 418 $cm^{-1}$and 530 cm^{-1}related to CuO. From the UV-VIS transmission, the energy band gap decreased from 2.2eV to 1.7eV as the substrate temperature was increased 473 and 673K.

Keyword: thin films, Copper oxide, Pulsed laser deposition, effect of substrate temperature

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]. These two oxides have different physical properties, different colors, crystal structures and optical properties. CuO is a black semiconductor with a monoclinic structure belongs to space group 2/m, it displays a wealth of interesting properties, it is abundant, nonhazardous source materials.

Because of their optical and electrical properties (1.2–1.5 eV band gap) [1-3], 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 optimised surface morphology and crystallinity to prevent the surface roughness from affecting carrier transport in the cells.

Many researchers had 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 [4,5], thermal evaporation, oxidation [6], molecular beam epitaxial [7], and electrochemical deposition [8]. Although 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 (0001) substrates at different temperatures 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 was characterized by atomic force microscopy (AFM).The optical transmittance and reflectance spectra, Fouriertransform 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 different substrate temperatures (473and 673) K, at an oxygen background pressure of 20×10^{-2} mbar, and a laser fluence of 1.5 J/cm^2. Before deposition, each 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 by 10 to 100 pulses through (10–20) min to get a singlelayer 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 thesapphire 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 measurementis performed at spectral range (200–1100) nm by 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 for the prepared CuO films deposited at both substrate temperatures to establish the dependence of their surface quality on the growth conditions of the PLD process.

Atomic Force Microscopy

The AFM image is obtained for the CuO films grown at both substrate temperatures (473 and 673) K as shown in Fig.(1) which indicates that the average surface roughness decreased dramatically as the growth temperature is decreased [7]. 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 as compared to the temperature of the PLD plume. A binary feature (formed of small and large grains) is observed on surfaces of the substrate which was heated to temperature 473K, while the size of the grains is approximately the same and the grains are distributed uniformly at 673K that can be attributed to the increase of surface energy at high temperature[9] . In addition, this result can explaine low roughness of surface at high temperature.

FTIR Analysis

The FTIR spectra were taken on the two deposited films which shown in Fig.(2): The substrate temperature (a) at 473K and (b) at 673K. the strong band is at about 418 cm^{-1} and 530 cm^{-1} which can be associated to CuO, this result is good agreement with ref. [10], whereas the wide absorption band around 640cm^{-1} is attributed to Cu_2O which is in an agreement with ref.[11].

For the film deposited at substrate temperature 473K, 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 Cu_2O), but the films deposited at substrate temperature 673K broader peaks at about 535cm^{-1} are also attributed to the CuO stretching. It was also observed that an obvious peak is at about 1120cm^{-1}.

Optical Properties

UV-VIS

Figure (3): showed the combination of optical transmittance spectra of copper oxide thin films deposited at both substrate temperatures with 150nm films thickness, for the range of wavelength (200-1100)nm

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 by using the Eq.

$$\alpha = \frac{lnT - 1}{t} \qquad (1)$$

$$\alpha = \frac{2.303A}{t} \qquad (2)$$

$$A = \log\frac{1}{T} \qquad (3)$$

Where t is the film thickness and T is the transmittance [6]. The best linear relationship is obtained by plotting α^2 against hυ, based on Eq. (4) below.

$$\alpha h\upsilon = \alpha(h\upsilon - E_g)^r \qquad (4)$$

A is constant (independent from υ) and r is the exponent that depends upon the quantum selection rules for the particular material.
The energy gap can be calculated by using the equation:

$$E(ev) = \frac{1240}{\lambda(nm)} \qquad (5)$$

A straight line as showed in Fig.4 is obtained when $(\alpha h\upsilon)^2$ is plotted against photon energy (hυ), which indicates that the absorption edge is due to a direct allowed transition (r = 1/2 for direct allowed transition). The intercept of the straight line on hυ axis corresponds to the optical band gap (E_g).

The band gaps of films that were obtained at both substrate temperatures had different microstructures which do not differ significantly. However, the band gap values are in the expected range for copper oxide thin films [12].

In the case of the films deposited at 473K, the band gap is shifted to lower energies due to the change in the composition from Cu_2O to CuO, the optical band gap at 2.40 eV is due to their possess of similar cuprite structure with Cu_2O phase.

The films deposited at substrate temperature at 673K and possessing CuO composition show a band gap of 1.7eV, corresponding to an optical absorption threshold of ∼900 nm. CuO is the predominant phase at 673K.

Conclusions

Copper oxide thin films at 150nm thickness were produced by pulsed laser deposition on sapphire substrate at both substrate temperatures (473K and 673K). The morphology, roughness and grain size were investigated by atomic force microscopy (AFM). The result obtained of AFM showed the increase of the size of the grains. The surface roughness decreases by the increase of substrate temperatures. The FTIR spectroscopic measurements further proved that the conversion from copper (II) oxide into copper (I) oxide at (673K) substrate temperature. Optical band gap of the films, measured by employing a UV-VIS spectrophotometer, lies at 2.2 eV and 1.7 eV.

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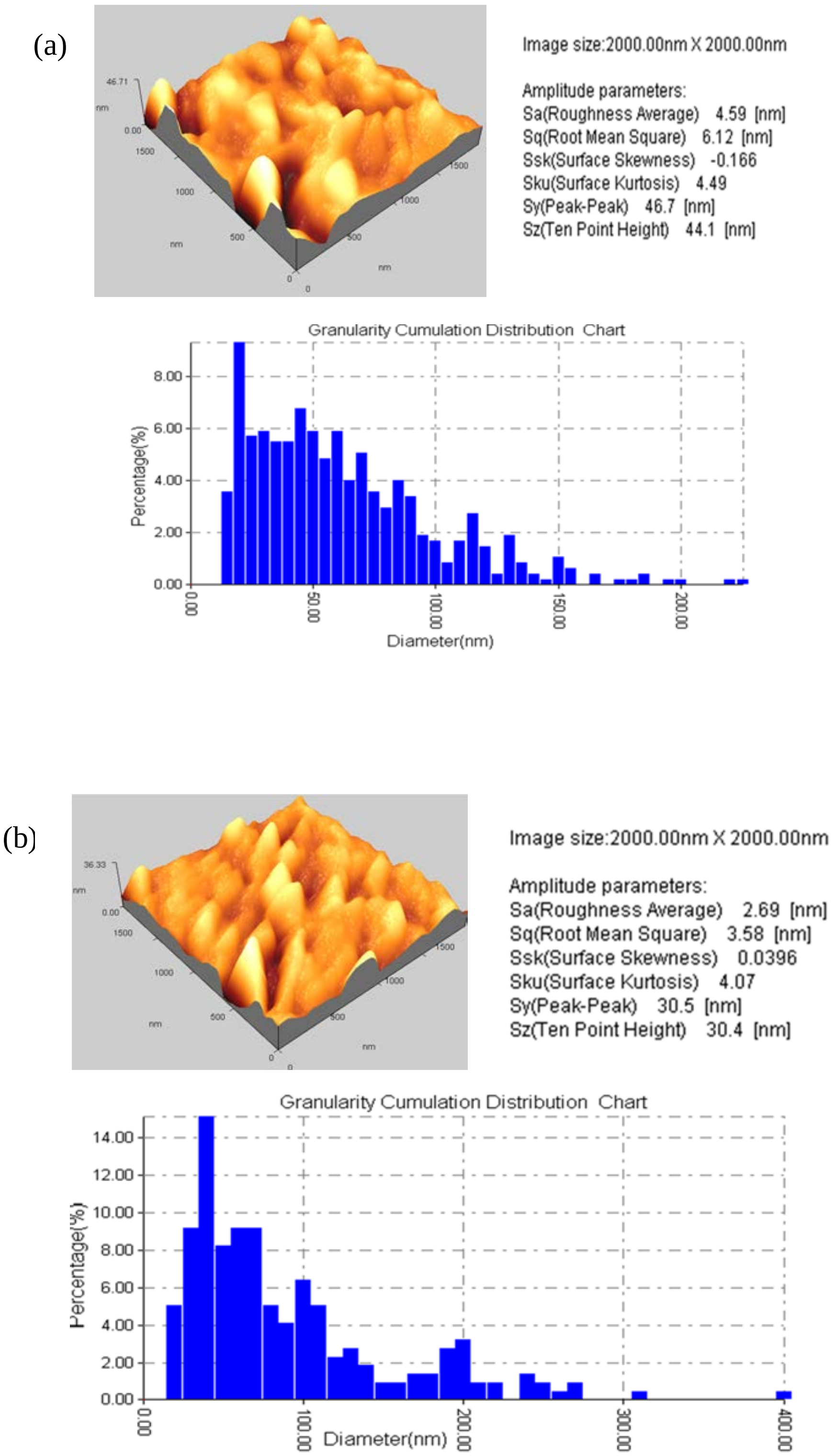

Figure No.(1): 3D AFM pictures of CuO/Sapphire a) at 473K b) at 673K

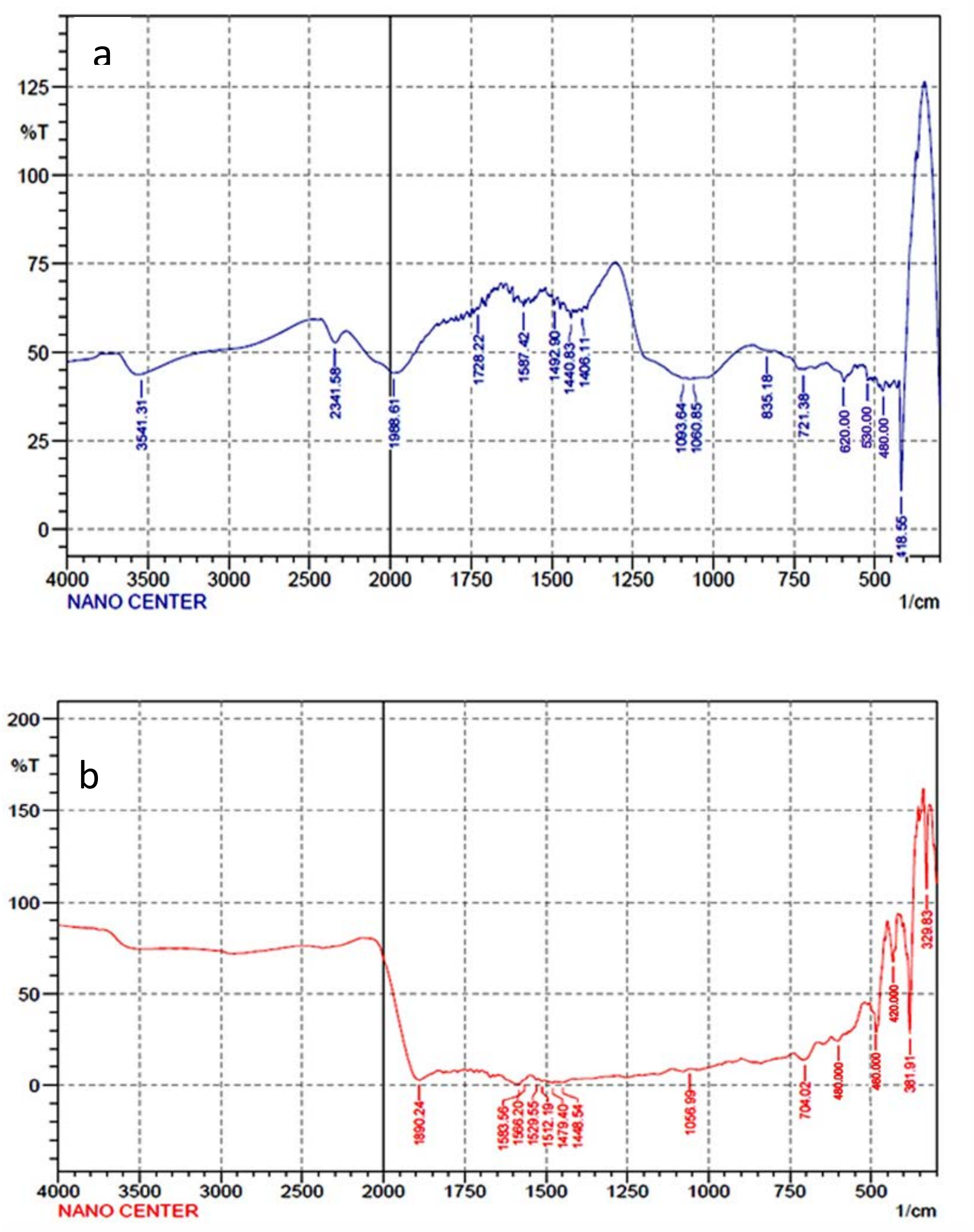

Figure No.(2) FTIR spectra of CuO/Sapphire a) at 473K b) at 673K

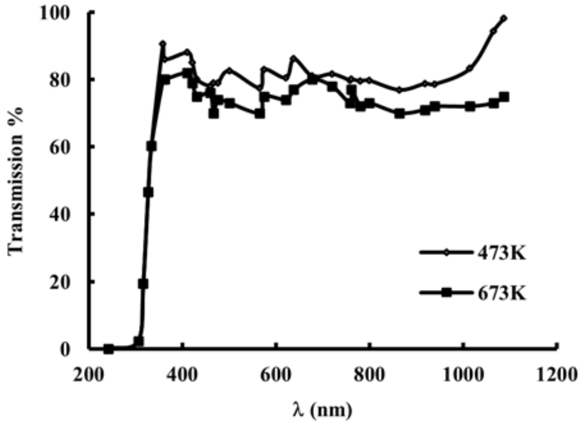

Figure No.(3): Optical transmittance spectra of CuO/Sapphire films at different substrate temperature

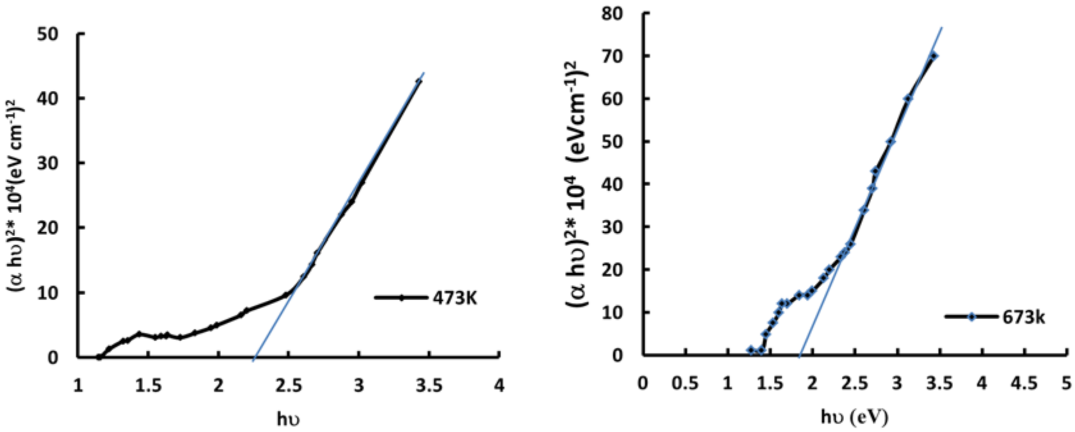

Figure No.(4): Plot of $(\alpha h\upsilon)^2$ versus hυ curve of CuO/Sapphire deposited at both substrate temperatures

تأثير حرارة القاعدة في الخصائص التركيبية والطوبوغرافية والبصرية لاغشية CuO/Sapphire الرقيقة المرسبة بالليزر النبضي

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الخلاصة

في هذا البحث، درس تأثير درجة حرارة القاعدة في الخصائص التركيبية والطوبوغرافية والبصرية لاغشية اوكسيد النحاس المحضرة بتقنية الترسيب بالليزر النبضي (PLD) على قواعد الالومينا بسمك غشاء 150 نانومتر. رسبت الاغشية بدرجات حرارة (473 و 673) كلفن. استخدم مجهر القوة الذرية (AFM)، مطياف فورير للاشعة تحت الحمراء، ومطياف النفاذية للاشعة المرئية –فوق البنفسجية (UV-VIS) لتحديد خصائص الحجم و المورفولوجي والبناء البلوري وكذلك الخصائص البصرية للاغشية المحضرة. درست خصائص السطح باستخدام مجهر القوة الذرية وقد وجد ان البناء متعدد التبلور والحجم الحبيبي يزداد بزيادة درجة حرارةالقاعدة، بينما تقل خشونة السطح. أظهرت اطياف FTIR حزمة قوية عند $418\ cm^{-1}$ و $530\ cm^{-1}$ العائدة لـCuO. ومن قياس طيف الاشعه المرئية – وتحت النبفسجية حسبت فجوة الطاقة من طيف الاشعة وتبين انها تقل بزيادة درجة حرارة القاعدة من2.2eV الى 1.7eV عند تغير درجات حرارة القاعدة من 473 الى 673 كلفن .

الكلمات المفتاحية: الاغشية الرقيقة ، اوكسيد النحاس، الترسيب بالليزر النبضي، تاثير درجة حرارة القاعدة