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Research Article (Araştırma Makalesi)

Effect of Thermal Annealing Time on The Optical Characteristics of CuO Thin Films

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Article Info

Recieved: 22.07.2019
Accepted: 24.11.2019
Online Published December.2019

Keywords
CuO,
Thin film,
Annealing time
Optical Property

Abstract: In this study, annealing time effect has been investigated on the optical characteristics of copper oxide thin films prepared by spray method. X-ray diffraction (XRD) measurements determined that the copper oxide films, produced on glass substrate using the 0.1 M copper-II-acetate monohydrate [$Cu(CH_3COO)_2H_2O$] precursor solution at 250 °C were in the tenorite phase. The films produced at 250 °C were annealed at 450 °C for half an hour intervals and were optically characterized. When the film annealed at 450 °C; it was observed that after the first annealing process the film transmittance and band gap energy were decreased, longer annealing process did not change significantly the optical transmittance and the band gap of CuO film. Optical band gap values; for non-annealed and 0.5 h, 1 h, 1.5 h, 2 h, 2.5 h annealed CuO films, it was calculated as 1.71 eV, 1.60 eV, 1.59 eV, 1.61 eV, 1.58 eV, 1.58 eV.

Isıl Tavlama Süresinin CuO İnce Filmlerin Optiksel Özelliklerine Etkisi

Makale Bilgileri

Geliş: 22.07.2019
Kabul: 24.11.2019
Online Yayınlanma Aralık.2019

Anahtar Kelimeler
CuO,
İnce film,
Tavlama süresi
Optiksel özellik

Öz: Bu çalışmada, püskürtme yöntemi ile hazırlanan bakıroksit ince filmlerde tavlama süresinin filmin optik karakteristikleri üzerindeki etkisi araştırılmıştır. X ışını kırınımı (XRD) ölçümleri, 0.1 M bakır-II-asetat monohidrat [Cu (CH_3COO) $2H_2O$] öncül çözeltisi kullanılarak cam alttaş üzerinde 250 °C 'de üretilen bakır oksit ince filmlerin tenorit fazda olduğunu belirlemiştir. 250 °C 'de üretilen filmler yarım saatlik aralıklarla 450 °C 'de tavlandı ve optiksel olarak karakterize edildi. Film 450 °C 'de tavlandığında; ilk tavlama işleminden sonra, film geçirgenliğinin ve bant aralığı enerjisinin azaldığı, daha uzun tavlama işleminin, CuO filminin optik geçirgenliğini ve bant boşluğunu önemli ölçüde değiştirmediği gözlenmiştir. Optik bant aralığı değerleri; tavlanmamış ve 0.5 saat, 1 saat, 1.5 saat, 2 saat, 2.5 saat tavlanmış CuO filmleri için sırasıyla 1.71 eV, 1.60 eV, 1.59 eV, 1.61 eV, 1.58 eV, 1.58 eV olarak hesaplanmıştır.

1. Introduction

Thin film applications are important for semiconductor material because of its use of low material, high production potential and widespread (Ray, 2001; Izaki, 2012; Chand et al., 2015). Copper oxide (CuO/Cu_2O) is a widely used material in thin film applications due to its elemental abundance, non-toxicity, electrical and optical properties (Halin at al., 2014). CuO; crystallizing in monoclinic form and having a band gap ranging from 1.0-2.1 eV. Cu_2O is a semiconductor compound that crystallizes in the cubic structure and whose band gap ranges from 2 to 2.6 eV (Korkmaz et al., 2016). Various techniques are used to produce thin films of copper oxide. Solution-based sol-gel techniques (spin coating, dip-coating, and spray-coating), electro-deposition, radio frequency (RF), sputtering, thermal evaporation, and bath techniques are some of these (Hashim et al., 2012; Radhakrishnan and Beena, 2014; Hashim et al., 2018; Wang et al., 2007; Salazar et al., 2019; Atta and Makki Hiba, 2016; Raship et al., 2017). The physical properties of copper oxide as the thin film layer are firmly attached to the fabrication conditions and the growth technique. In addition, the physical properties of copper oxide as a thin film can vary considerably with annealing. In the process of copper oxide thin film fabrication, the annealing temperature and time are parameters that have a significant effect on the film phase and quality. Among the various thin film deposition techniques, sol-gel techniques are widely used for deposition of metal oxide thin films. Metal oxide semiconductors such as ZnO, CdO, TiO_2 and SnO_2 can be deposited using the spray pyrolysis method (Manjula et al., 2015; Ali et al., 2015; Marikkannanet al., 2015; Zhao et al., 2018). In this method; substrate temperature, annealing conditions, molarity of solution, interaction between the substrate and atomizer are some of the important factors affecting the film properties (Nadarajah et al., 2013&Aparnna et al., 2012). In the sol-gel techniques temperature and time play an important role in the growth of the thin films.

Thin films can be formed at various substrate and annealing temperatures. Saravanan et al., (2015) studied effect of annealing temperatures in the copper oxide thin films growth by spray method. It is found that substrate temperature of 350 ℃ was found to be optimum factor for the growth of copper oxide thin films with tenorite phase. Johan et al., (2011) reported annealing effects on the characteristics of copper oxide thin films via chemical deposition method. The authors have reported that annealing the sample at 200 ℃ does not crystalline the composition. At 300^{o}C temperature two phases coexist (CuO/Cu_2O) while above 400 ℃, CuO prevails. Similarly, Sahin&Kaya, (2016) have reported the annealing effecton the material properties of CuO films by SILAR method. The results of the study showed that annealing process led to a decrease in energy band gap. In a recent study, Singh et al., 2019 reported the effect of annealing time at 450 ℃ annealing temperature on the structural and optical characteristics of n-CuO thin films deposited by sol-gel spin coating technique. From the results obtained in the work, for 15 min, 30 min, 45 min and 1 h annealed CuO thin films, the optical bandgap 1.72 eV, 1.91 eV, 2.09 eV and 2.28 eV are estimated, respectively.

Therefore, this present work focuses on the effect of annealing time on optical characteristics of copper oxide (CuO) thin film produced on glass substrate by spray method. The deposited film has been subjected to different annealing time for 0.5 h, 1 h, 1.5 h, 2 h and 2.5 h at 450 ℃ substrate temperature. The effects of various annealing times have been examined in term of the change in optical properties of the film.

2. Materials and Methods

Copper oxide thin films were prepared by using an airbrush sprayer onto glass substrate at 250 ℃ constant temperature. Copper acetate monohydrate [$Cu(CH_3COO)_2H_2O$, Sigma Aldrich, 99.99 %] was used as starting material. 0.1 M precursor solution was prepared by dissolving 0.98 grams of copper acetate powder salt in 50 ml de-ionized water and was stirred for 1 hour with a magnetic stirrer at room temperature. A homogeneous solution of blue color was obtained at the end of the mixing process. The glass substrates heater previously set to 250 ℃ and an air compressor connected to the device. At the next stage, about 10 ml of the prepared the precursor solution was loaded the reservoir of the spraying atomizer. Dark brown colored films obtained at the end of this process were allowed to dry for one hour at room temperature (Serin et al., 2005). In order to study the effect of the annealing time, the films were annealed at 450 ℃ for different times (0.5 h, 1 h, 1.5 h, 2 h and 2.5 h). A schematic experimental procedure is shown in Fig. 1.

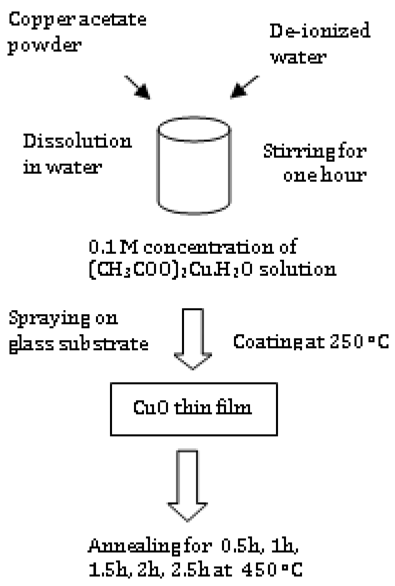

Figure 1.Schematic experimental diagram of spray coating system for CuO thin films.

The optical absorption analyses were carried out with Shimadzu UV-Vis- spectrophotometer (UV-2450). X-Ray Diffraction studies were carried out using Rigaku Diffractometer (Ultima-IV model) with monochromatic CuK_α (λ = 0.15 nm) radiation was used to determine the crystal structure and phase of the CuO thin films.

3.Results and Discussion

The optical transmittance spectra of copper oxide thin films were measured with a UV-Vis spectrophotometer. Figure 2 shows the value of copper oxide optical transmittance curves. In this figure, the transmission of the as deposited copper oxide film is approximately 75% and it appears that there is a significant decrease in transmission after the first annealing. This may be attributed to the scattering effect associated with higher surface roughness and crystallographic defects due to the annealing process (Mohammed, H.A. and Hadia, N.M.A., 2015)

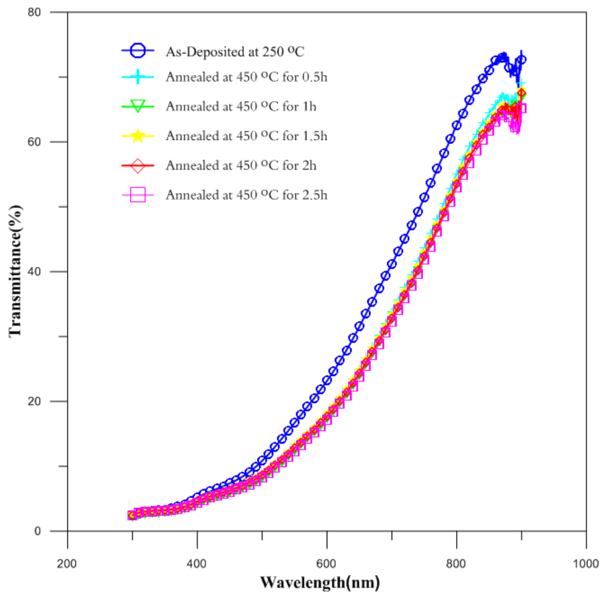

Figure 2. The optical transmission (T %) spectra of CuO thin film as deposited and annealed at 450 °C temperature.

The optical absorption coefficient (α) was evaluated using $\alpha = (\, lnT - 1/t)$ where t is the film thickness and T is the transmittance. The absorption coefficient (α) is directly depending on the optical band gap (E_g) with the $(\alpha h\nu)^2 = A(h\nu - E_g)$equation. Here; A is a constant, hν incident photon energy, E_g band gap energy of the material and h is Planck's constant. The optical band gap (E_g) is calculated from the energy axis cutting point of the linear part of the curve by means of the Tauc equation. Figure 3 depicts a $[\alpha(h\nu)]^2$ versus hυ plot of film as deposited and annealed at 450 ℃ temperature.

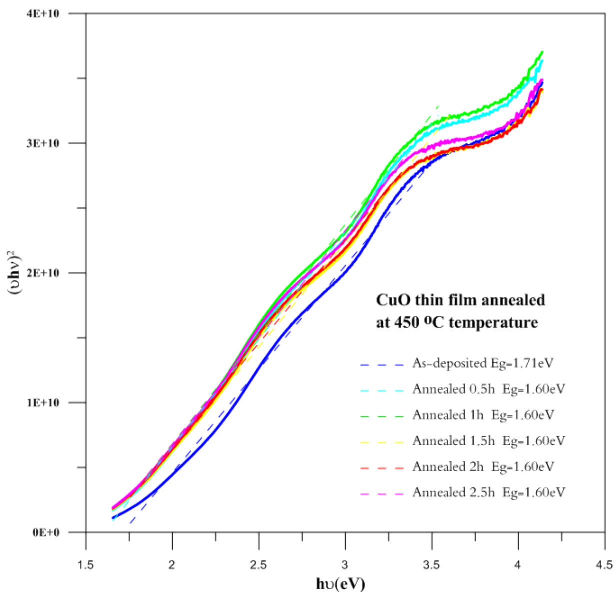

Figure 3. The plots of $[\alpha(h\nu)]^2$ versus $h\nu$ curves of CuO thin film.

At the next step, the annealing process was continued at intervals of half an hour and UV measurement was taken at the end of each interval. This process lasted for two and a half hours. As a result of the optical characterization, the direct band gap values were calculated between 1.58-1.61 eV. The resulting band gap values are in good agreement with literature (Asl and Rozati, 2018). The optical parameters of the films are given in Table 1.

Table 1. Characteristics obtained by annealing CuO thin film at 450 ^oC.

Annealing Condition	Molarity (M) of Precursor Solution	Annealing temperature(^oC)	Annealing time (h)	Band gap (eV)
As deposited	0.1	-	-	1.71
Annealed	0.1	450	0.5	1.60
Annealed	0.1	450	1	1.59
Annealed	0.1	450	1.5	1.61
Annealed	0.1	450	2	1.58
Annealed	0.1	450	2.5	1.58

When the film annealed at 450 ℃; it was observed that after the first annealing process the film transmittance and band gap energy was decreased, the longer annealing process did not change significantly the optical transmittance and the band gap of CuO film.

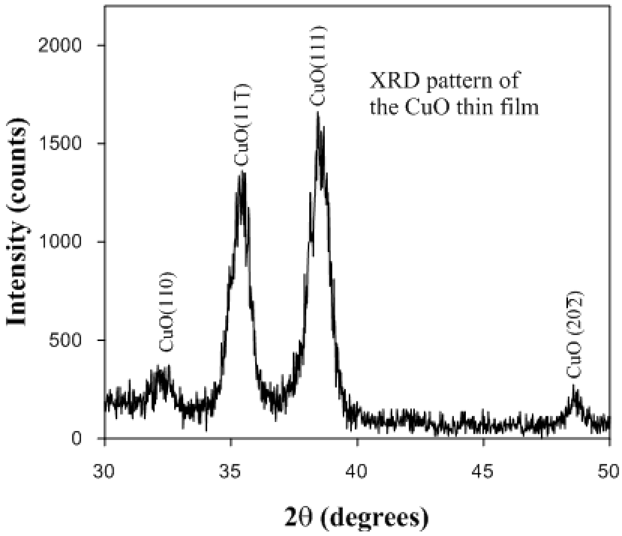

Figure 4. X-ray diffraction (XRD) measurements of CuO film produced at 250 ℃ substrate temperature.

Figure 4 illustrates the XRD spectrum of CuO thin film produced by spray method at 250 ℃ substrate temperature. Plane orientations of the atoms are obtained from the peaks in the graph. There are four peaks positions observed from the XRD analyses for 32.52°, 2θ =35.44°, 38.42° and 48.74° angles that associated with the reflection from (110), (11-1), (111) and (20-2) planes, respectively. These peaks and their corresponding angles are characterized by the CuO crystal structure which is a copper oxide in the tenorite phase. The peaks observed in X-ray diffraction analyses are identified by PDXL program, COD file 1011194, Quality:C card of the standard CuO data. The two peaks of XRD pattern are clear; in the (11-1) and (111) planes at 2θ = 35.44° and 2θ = 38.42° angles, respectively (Kayani et al., 2013; Oral et al., 2004). According to the literature, pure tenorite (CuO) phase has been obtained at 450 ℃ annealing temperature (Raship et al., 2017).

4. Conclusion

Copper oxide films were produced by the spray method using a 0.1 M copper acetate starting solution at substrate temperature of 250 ℃. X-ray diffraction (XRD) measurements determined that the copper oxide, produced on glass substrate were in the tenorite phase (CuO). According to the literature, pure tenorite (CuO) phase has been obtained at 450 ℃ annealing temperature [21]. In this study, after the films were annealed at 450 ℃, it has been observed that there was an approximately 10% decrease in the film optical transmission. Optical band gap values of film obtained from absorption measurements; for as deposited and 0.5 h, 1 h, 1.5 h, 2 h and 2.5 h annealed film; 1.71 eV, 1.60 eV, 1.59 eV, 1.61 eV, 1.58 eV, 1.58 eV was calculated respectively. Optical band gap of as deposited film produced at 250 ℃ found 1.71 eV. When the same film annealed at 450 ℃ for 30 minutes band gap of the film was found 1.60 eV. That is, while the decrease in the optical parameters reaches the peak by the first annealing process, it is observed that it is relatively small in the subsequent annealing processes.

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