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Research Article

Effect of Hydrothermal Reaction Temperature on the Structural and Optical Properties of CuO Thin Films

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Abstract

Copper oxides are one of the first semiconductors studied for device applications. In the present work, CuO thin films were deposited on fluorine-doped tin oxide (FTO) substrates via hydrothermal method without using any surfactant and the effects of reaction temperature on the properties of the films were studied. CuO thin films deposited at different reaction temperatures were characterized for their structural and optical properties using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDAX), Raman spectroscopy, and optical absorption measurements. XRD results revealed that all the films consisted of polycrystalline CuO with a monoclinic crystal structure without any impurity phase. SEM images showed that chrysanthemum-like structures were formed, the number of which increased with increasing hydrothermal reaction temperature. EDAX measurements proved the existence of Cu and O elements and showed that all the films have Cu/O ratios close to unity. The Raman spectra confirmed the formation of crystalline CuO in all the films. From the optical absorption measurements, the direct forbidden energy gap values of the CuO thin films were found to be between 1.34 eV and 1.41 eV, depending on the hydrothermal reaction temperature.
Keywords: CuO thin films, hydrothermal method, reaction temperature.

Hidrotermal Reaksiyon Sıcaklığının CuO İnce Filmlerin Yapısal ve Optik Özelliklerine Etkisi

Öz

Bakır oksitler cihaz uygulamaları için incelenen ilk yarı iletkenlerden biridir. Bu çalışmada, CuO ince filmler, herhangi bir yüzey aktif madde kullanılmadan, hidrotermal yöntemle flor katkılı kalay oksit (FTO) altlıklar üzerine büyütülmüş ve reaksiyon sıcaklığının filmlerin özellikleri üzerine etkisi araştırılmıştır. Farklı reaksiyon sıcaklıklarında büyütülen CuO ince filmler, X-ışını kırınımı (XRD), taramalı elektron mikroskobu (SEM), enerji dağılımlı X-ışını analizi (EDAX), Raman spektroskopisi ve optik soğurma ölçümleri kullanılarak yapısal ve optik özellikleri açısından karakterize edilmiştir. XRD sonuçları, tüm filmlerin herhangi bir safsızlık fazı içermeyen, monoklinik kristal yapıya sahip, polikristal CuO'dan oluştuğunu ortaya çıkarmıştır. SEM görüntüleri, krizantem benzeri yapıların oluştuğunu ve hidrotermal reaksiyon sıcaklığının artmasıyla bu yapıların sayısının arttığını göstermiştir. EDAX ölçümleri Cu ve O elementlerinin varlığını kanıtlamış ve tüm filmlerin Cu/O oranlarının bire yakın olduğunu göstermiştir. Raman spektrumları tüm filmlerde kristal CuO oluşumunu doğrulamıştır. Optik soğurma ölçümlerinden CuO ince filmlerinin doğrudan yasak enerji aralığı değerlerinin hidrotermal reaksiyon sıcaklığına bağlı olarak 1,34 eV ile 1,41 eV arasında olduğu bulunmuştur.
Anahtar Kelimeler: CuO ince filmler, hidrotermal method, reaksiyon sıcaklığı.

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1. Introduction

Metal oxides are important materials for engineering and scientific applications due to their distinctive physical and chemical properties. Among various metal oxides, copper oxides are one of the first semiconductors studied for device applications and widely used in a range of fields, such as solar cell technology [1, 2], electrochromic devices [3], gas and humidity sensing applications [4, 5], electrochemical energy storage devices [6], and photocatalytic degradation of biological pollutants and organic dyes [7, 8]. In addition, copper oxides are of interest because of their chemical stability, low production cost, and non-toxic nature. Copper oxides are known to have p-type conductivity and two familiar forms of copper oxides are cupric oxide or tenorite (CuO) with the reported direct optical band gap ranging from 1.0 eV to 2.1 eV and cuprous oxide or cuptite (Cu_2O) with the reported direct optical band gap ranging from 2.0 eV to 2.6 eV [7, 9]. Specifically, relatively narrow optical band gap of the CuO makes it an important material for the absorption of ultraviolet–visible to near-infrared radiation. For the deposition of copper oxide thin films, a variety of physical and chemical processes have been proposed including sputtering [8, 9], chemical-thermal oxidation [7], electrodeposition [2], chemical vapor deposition [10], chemical bath deposition [6, 11], spin coating [12], successive ionic layer adsorption and reaction [13, 14] and hydrothermal method [15], etc. Among these processes, the hydrothermal method attracts intensive attention because of its low cost, simple operating procedure, and low process temperatures, which improves surface coverage on the substrates and reduces the possibility of film cracking [16, 17]. Therefore, this method is known to be one of the most important soft solutions chemical processes and suitable for large-scale production. Because the process is controlled by dissolution / precipitation of reactants in an aqueous solution, the nature and properties of the product can be controlled by different process parameters such as reaction temperature and time, properties of precursor solution, and the types of additives such as surfactants, templates, or mineralizers used [15, 16]. Although the use of surfactant has some advantages such as controlling particle size, morphology and size distribution of the final product, the introduction of surfactant means a more complicated reaction process and can cause an increase of impurity concentration in the final product.

In this paper, we report the synthesis of CuO thin films via hydrothermal method without using any surfactant. To evaluate the effect of reaction temperature on the structural and optical properties of the films, CuO thin films were synthesized by varying the reaction temperature while keeping the reaction time constant.

2. Material and Methods

The copper (II) sulfate pentahydrate ($CuSO_4.5H_2O$) and ammonia solution (NH_4OH) 32% were used as precursor materials for deposition of CuO thin films using hydrothermal route. All raw materials were analytical grade and purchased from Sigma-Aldrich Company. Deionized water was used as a solvent. Fluorine-doped tin oxide (FTO) glass slides (20 mm × 10 mm × 3 mm) were chosen as substrate material. Prior to the deposition process, FTO substrates were cleaned ultrasonically in the commercial detergent, acetone, 1:1 ethanol-water solutions, and finally deionized water for 15 min sequentially. To obtain the precursor solution, first 50 mM $CuSO_4.5H_2O$ solution was prepared by dissolving a proper amount of material in 30 ml deionized water under magnetic stirring for 15 min at room temperature. Then NH_4OH was slowly added dropwise to the above solution under constant stirring. Initially a pale blue and then a clear, dark blue solution was obtained. At this point, the pH of the solution reached 10.5. The solution was stirred for a further 30 min, then transferred into a teflon-lined stainless-steel autoclave with 50 ml capacity. FTO substrates were vertically dipped into the precursor solution and the autoclave was sealed and placed in a hot oven for 24 h at different reaction temperatures (120ºC, 140ºC, 160ºC, and 180ºC). At the end of the growth process, the autoclave was cooled to room temperature naturally. The coated substrates were removed, washed with deionized water several times, and dried in air overnight. The films on the non-conductive sides of the FTO substrates peeled off during washing, but the films obtained on the conductive sides were well adherent, nearly uniform and, dark brown in color.

Structural, morphological, compositional, and optical properties of the CuO thin films deposited at different reaction temperatures were analyzed. The determination of the crystal structure and phase was carried out using Panalytical Empyrean X-ray diffractometer using Cu-Kα radiation with the wavelength λ=1.5405 Å at 45 kV and 40 mA. The diffraction patterns were recorded in the 2θ range 20°–80° at a scanning rate of 1.50° min^{-1}. The surface morphology and elemental compositional analysis of the films were investigated with FEI Quanta FEG 450 scanning electron microscopy (SEM) coupled with Amatek energy dispersive X-ray analysis (EDAX) attachment. Raman spectroscopy was further used as a supplementary method to prove the phase purity of the CuO thin films, and the spectra were obtained using Witec alpha 300R Raman module in the spectrum range 200–800 cm^{-1}. Optical absorption spectra of the CuO thin films were obtained with UV-1810 DASPC UV-VIS double beam spectrophotometer. The spectra were recorded in the wavelength range of 500–1100 nm at room temperature. Optical band gap energies of the films were estimated through the Tauc method.

3. Results and Disscussion

A series of CuO thin films were obtained on FTO substrates using hydrothermal method for 24 h by varying the reaction temperature from 120ºC to 180ºC with 20ºC steps. The formation mechanism of CuO thin films can be explained as follows. When NH_4OH is added into the $CuSO_4.5H_2O$ solution, initially $Cu(OH)_2$ occurs according to the following reaction:

$$\mathrm{CuSO_4} + 2\mathrm{NH_4OH} \rightarrow \mathrm{Cu(OH)_2} + \mathrm{(NH_4)_2SO_4} \tag{1}$$

Addition of excess NH_4OH dissolves $Cu(OH)_2$:

$$\mathrm{Cu(OH)_2} + NH_4\mathrm{OH} \rightarrow (NH_4)CuO_2^- + H_2O + H^+ \tag{2}$$

Under hydrothermal conditions, the ionic product exceeds the solubility product and CuO film forms on the FTO substrate by the following reaction [6]:

$$(NH_4)CuO_2^- + H^+ \rightarrow \mathrm{CuO} + NH_4OH \tag{3}$$

XRD method was used to analyze the phase composition and crystallographic structure of the CuO thin films, and Figure 1 shows the diffraction patterns of the films deposited at different hydrothermal reaction temperatures. The patterns revealed that all the films had a polycrystalline nature and observed diffraction peaks were in closely match with the standard pattern of monoclinic CuO (JCPDS No.:45-0937) along with the diffractions from the FTO substrate which were marked with *. Two characteristic peaks of CuO corresponding to reflections from (11-1) and (111) planes were clearly observed in all the patterns, and no peaks from impurities such as Cu_2O or $Cu(OH)_2$ were seen.

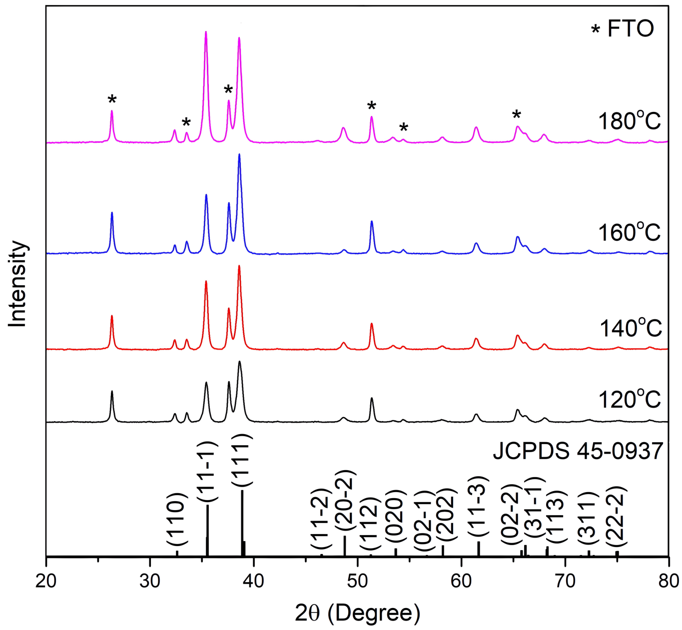

Figure 1. XRD patterns of CuO thin films deposited at different hydrothermal reaction temperatures

XRD analysis also showed no remarkable changes in the crystallographic structure and phase composition of the films depending on hydrothermal reaction temperature. Increasing hydrothermal reaction temperature generally increased the intensity and sharpening of the observed peaks, which means the crystallinity increases with the increasing reaction temperature.

With the help of XRD measurements, interplanar distances (d) of the planes and average grain size values (D) of CuO thin films were calculated for prominent (11-1) and (111) planes, using Bragg's diffraction condition [18] and Scherrer Equation [19]:

$$D = \frac{K\lambda}{\beta Cos\theta} \tag{4}$$

where K is a constant which is referred as the shape factor (K=0.9 was used), λ is the wavelength of the X-ray, β is the full width at half maximum of the peak in radian, and θ is the Bragg angle that corresponds to the peak analyzed. Obtained results are shown in Table 1 along with the standard values of the interplanar distances. It can be seen from the table that the calculated d values are compatible with the standard values and increasing the hydrothermal reaction temperature from 120ºC to 160ºC increased the grain size from 15.2 nm to 18.7 nm, while further increasing the reaction temperature to 180ºC caused a slight decrease in grain size. Differences between the relative X-ray diffraction intensities of the samples and the standard

JCPDS data indicate that a preferential orientation is present, and the preferential orientation can be determined considering the texture coefficient (T_c). T_c values for all planes of randomly oriented materials are approximately 1. Values of T_c greater than 1 indicate preferential orientation, while values less than 1 indicate the absence of grains oriented in that direction [20]. The T_c values of the CuO thin films were calculated using the equation [19]:

$$T_c(hkl) = \frac{I(hkl)/I_0(hkl)}{\frac{1}{N}\sum I(hkl)/I_0(hkl)} \tag{5}$$

where I is measured X-ray diffraction intensity, I_0 is standard JCPDS intensity and N is the reflection number. Calculated T_c values of CuO thin films deposited under different hydrothermal reaction temperatures are shown in Table 1. As can be clearly seen from the table, increasing reaction temperature caused a periodic change in preferential orientation.

Table 1. Standard and calculated interplanar distances with average grain size and texture coefficient values

Reaction Temperature	2θ (observed)	hkl	d(Å) (standard)	d(Å) (calculated)	D (nm)	T_c
120ºC	35.49	11-1	2.529	2,527	15.2	0.91
	38.69	111	2.322	2.325		1.09
140ºC	35.46	11-1	2.529	2.529	18.4	1.03
	38.64	111	2.322	2.328		0.97
160ºC	35.49	11-1	2.529	2.527	18.7	0.87
	38.67	111	2.322	2.326		1.13
180ºC	35.44	11-1	2.529	2.531	16.8	1.15
	38.64	111	2.322	2.328		0.85

The film's surface morphology was studied by SEM and the images of the films deposited at different hydrothermal reaction temperatures are shown in Figure 2. To illustrate the shape of CuO structures distinctly, higher magnification (30000×) images are displayed in inset of all the SEM images. Close examination of the SEM image reveals that, in the early stage of the hydrothermal process, randomly oriented rod-like nanostructures completely cover the surface of the FTO substrates without any voids, pinhole or cracks and numerous CuO nanostructures assemble together possibly to reduce the excess interfacial energy and form the micrometer-sized spherical, chrysanthemum-like structures [21]. As the reaction temperature increases, chrysanthemum-like structures become more compact, and the number of these structures increases.

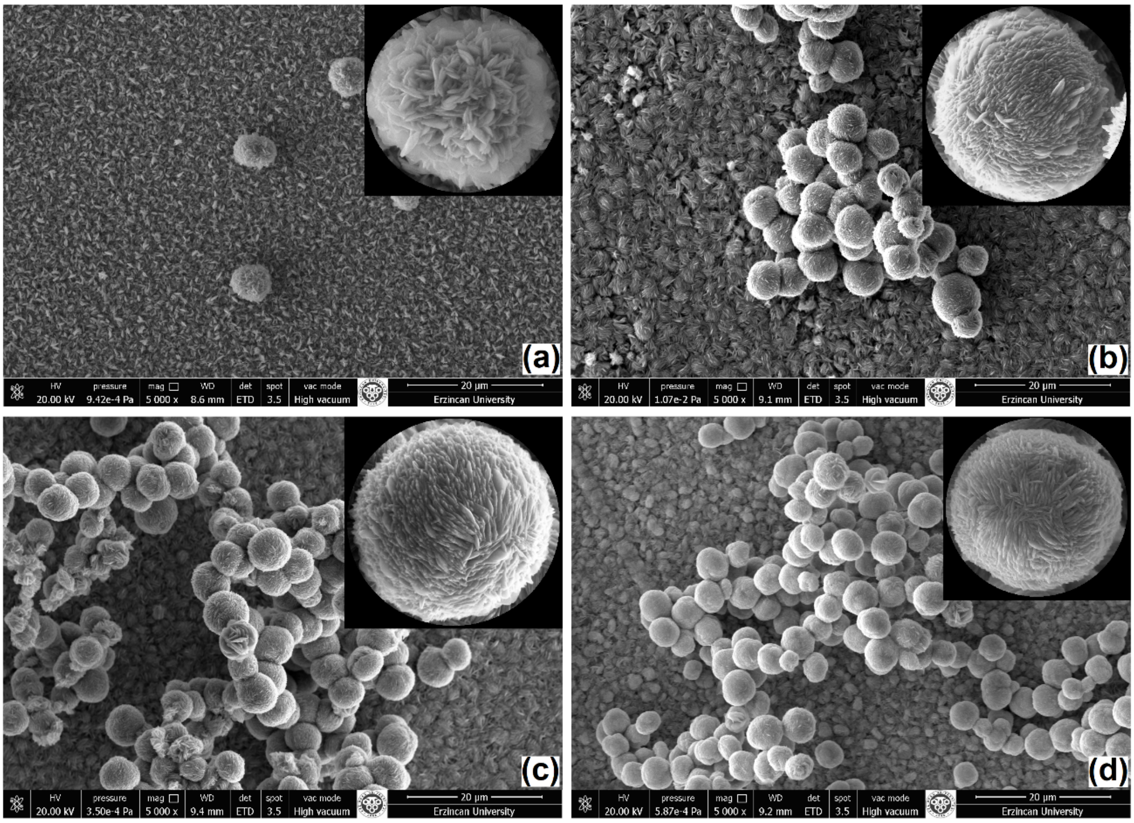

Figure 2. SEM images of CuO thin films deposited at different hydrothermal reaction temperatures, (a) 120ºC, (b) 140ºC, (c) 160ºC, (d) 180ºC.

The elemental compositional analysis of the CuO thin films were estimated by EDAX and the spectra are given in Figure 3. All EDAX spectra show the existence of Cu, O, and Sn elements. The Cu/O ratios of the films were determined from the spectra and found to be 0.95, 1.07, 1.02, and 1.04 for hydrothermal reaction temperatures of 120ºC, 140ºC, 160ºC, and 180ºC respectively. Although Cu/O ratios change in a non-regular manner with increasing hydrothermal reaction temperature, the variations are very small and all the films have Cu/O ratios of unity, which is in agreement with the XRD results. The appearance of weak Sn peaks in the EDAX spectra is due to the FTO substrate and the spectra show that increasing reaction temperature resulted in a decrease in relative Sn content, which may be due to the increasing film thickness.

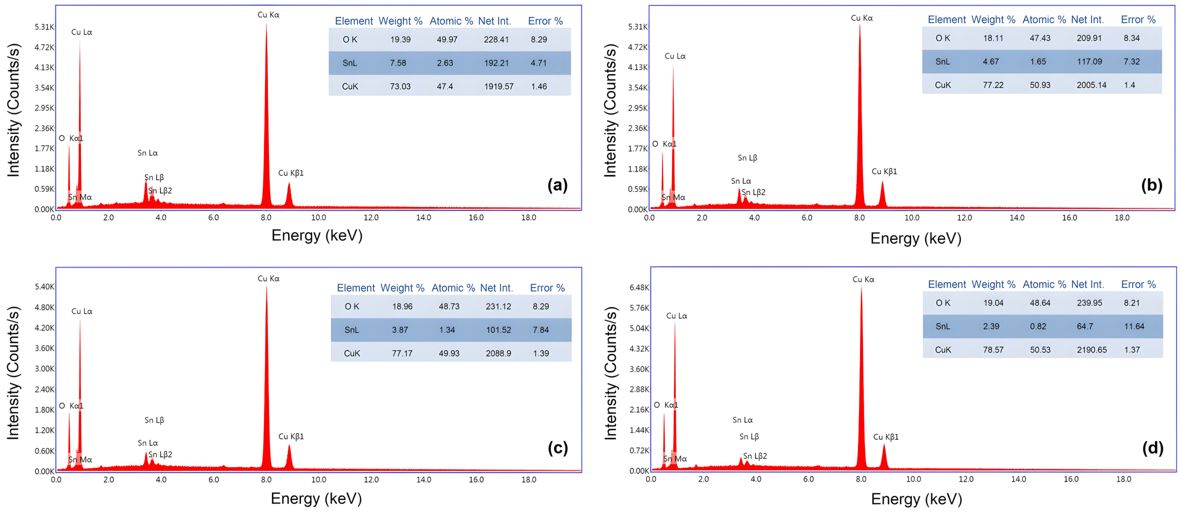

Figure 3. EDAX spectra of CuO thin films deposited at different hydrothermal reaction temperatures, (a) 120ºC, (b) 140ºC, (c) 160ºC, (d) 180ºC.

For the structural analysis of materials, Raman scattering has proven to be an appropriate alternative and/or complementary method to XRD studies [22]. The films were further analyzed using Raman analysis and Figure 4 shows the Raman scattering spectra of the CuO thin films, obtained at different reaction temperatures. All films are characterized by an intense peak at 274 cm^{-1}, a less intense peak at 323 cm^{-1}, and a rather weak and broad peak at about 605 cm^{-1}. These three Raman peaks can be assigned to A_g and the two B_g modes of CuO respectively, and are comparable with the reported values [11, 23]. The trend in intensity of the prominent Raman peak at 274 cm^{-1} is consistent with the XRD results. Furthermore, all three peaks are red shifted as compared to reported values for the CuO single crystal [24]. This relative shift to lower frequencies can be attributed to size effects [25]. The weak peak observed at 249 cm^{-1} may be caused by FTO substrate [26]. Due to the relatively low thickness of the films, this peak is more clearly observed in the Raman spectra of the films obtained at reaction temperatures of 120ºC and 140ºC that is agreement with the EDAX results. No vibrational mode belonging to any impurity phase was identified in all Raman spectra, which indicates the purity of the CuO thin films and is consistent with XRD results.

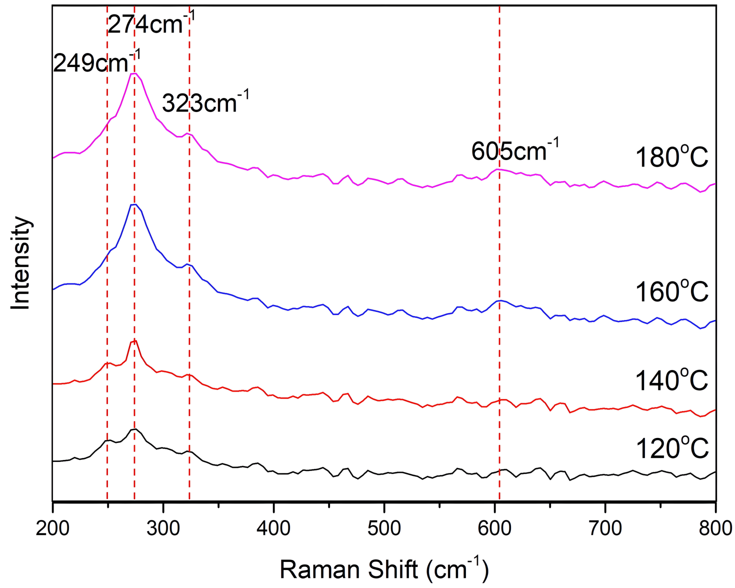

Figure 4. Raman scattering spectra of CuO thin films deposited at different hydrothermal reaction temperatures.

The equation between the absorption coefficient (α) and the optical band gap energy (E_g) is given by;

$$\alpha = \frac{A(h\upsilon - E_g)^n}{h\upsilon} \quad (6)$$

where A is a constant dependent on the effective masses associated with the valence and conduction bands and hv is the photon energy. The value of n is related to the type of the transition (n=2 for indirect allowed, n=½ for direct allowed transition). According to equation 6, the direct band gap energy values of the materials are determined by extrapolating the linear part of the $(\alpha hv)^2$ versus hv graphs onto the horizontal axis. Figure 5 shows the optical absorption spectra and variations of $(\alpha hv)^2$ as a function of photon energy for CuO thin films deposited at different hydrothermal reaction temperatures. From the absorption spectra, it can be seen that all the films exhibit high absorbance at wavelengths < 750 nm, which is very useful for applications of solar cell devices. The linear nature of the all $(\alpha hv)^2$ - Energy plots confirm the direct optical transition in CuO thin films. It is clear from the figure that optical band gap values were all found to be similar and 1.34 eV, 1.41 eV, 1.37 eV, and 1.40 eV for hydrothermal reaction temperatures of 120ºC, 140ºC, 160ºC, and 180ºC respectively. The obtained direct band gap values are in the good agreement with the literature values [27, 28].

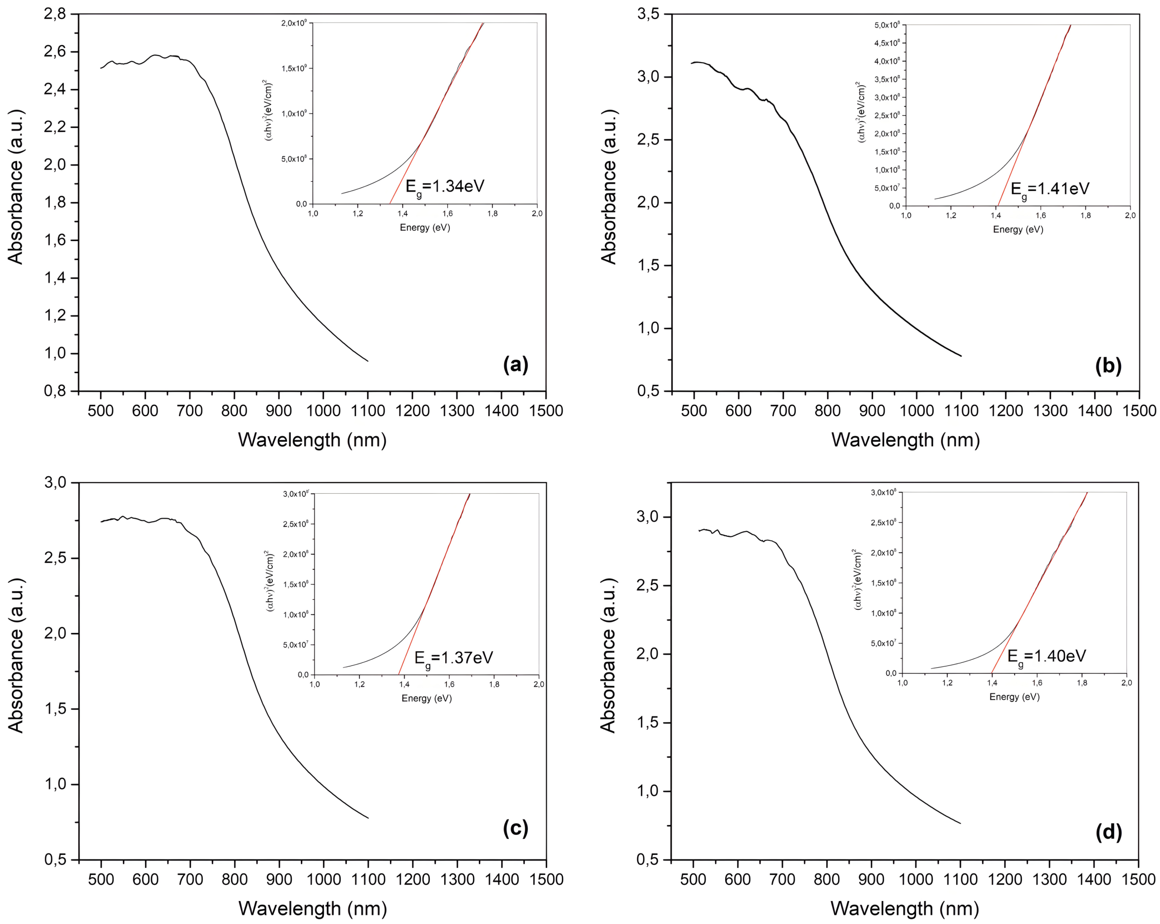

Figure 5. Optical absorption spectra with the variations of $(\alpha h\nu)^2$ as a function of photon energy for CuO thin films deposited at different hydrothermal reaction temperatures, (a) 120ºC, (b) 140ºC, (c) 160ºC, (d) 180ºC.

4. Conclusion

In the present study, CuO thin films were deposited on FTO substrates via hydrothermal method and the effect of reaction temperature on some structural and optical properties of the films were reported. XRD results showed that all the films had a polycrystalline nature with monoclinic symmetry and revealed no significant variations in the crystallographic structure and phase composition of the films deposited at different reaction temperatures. Increasing hydrothermal reaction temperature generally improved the crystallinity and caused a change in the texture coefficient of the films. The films deposited at 160ºC hydrothermal reaction temperature showed better crystallinity with a grain size of 18.7 nm. SEM images revealed the formation of micrometer-sized chrysanthemum-like structures, the number of which increased with increasing hydrothermal reaction temperature. It was confirmed with the help of EDX measurements that all films had stoichiometric ratios very close to CuO. Phase purity and crystalline nature of the films were further proved through the Raman scattering measurements. The estimated direct optical band gap energies of the films were in the range of 1.34 eV-1.41

eV, depending on reaction temperature. Obtained results demonstrated that CuO thin film, which has been considered as a potential absorber material for low-cost photovoltaic applications, could be successfully deposited using facile hydrothermal method under mild conditions without using any surfactant.

Ethics in Publishing

There are no ethical issues regarding the publication of this study.

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