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Research Article

Band-gap Control of Nanostructured CuO Thin Films using PEG as a Surfactant

Halit ÇAVUŞOĞLU [1*]

[1]Selcuk University, Faculty of Science, Department of Physics, 42075, Konya/TURKEY, E-mail: hcavusoglu@selcuk.edu.tr

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Abstract

Nanostructured copper oxide thin films were fabricated on glass substrates at room temperature by a facile and cost-efficient Successive Ionic Layer Adsorption and Reaction (SILAR) method with varied amounts of polyethylene glycol (PEG). The effects of PEG on the optical properties of the CuO thin films were investigated by means of ultraviolet-visible (UV-Vis) spectroscopy analysis. By UV–Vis analysis at the room temperature, it was seen that the optical band gap values and transmission characteristics of the CuO thin films vary with the increasing PEG concentration in the growth solution. The optical band gap energy of the CuO thin films was found to increase from 1.30 eV to 1.42 eV with the increasing PEG concentration. The thickness of the CuO thin films was also found to vary in between 137 nm and 680 nm depending on the PEG concentration. Other significant parameters including refractive index (n), high frequency dielectric constant (ε_∞) and optical static (ε_0) values of the thin films were calculated by using the optical band gap energy values as a function of the film thickness. The investigations revealed that the PEG concentration has a remarkable impact on the optical properties of SILAR grown CuO thin films.

Keywords: CuO thin films; SILAR method; PEG; Optical properties

1. Introduction

During the past few decades, scientists have drawn attention to the transition metal oxide thin films due to their unique properties which enable promising applications in the field of nanotechnology. Among different transition metal oxide thin films, cupric oxide (CuO) is a significant p-type transition-metal–oxide semiconductor, which has a narrow bandgap (optical band gap energy E_g= 1,2-1.8 eV) (Sun et al., 2013). It has monoclinic structure and exhibits many properties such as high thermal conductivity, stability, and photovoltaic performance. Owing to these versatile properties, CuO can be used in several diverse applications, including fabrication of optoelectronic devices (Yu et al., 2016), heterogeneous catalysts (Chary et al., 2005), selective gas sensors (Samarasekara et al., 2006, Nayan et al., 2016), and solar cells (Chang et al., 2011, Shabu et al., 2015, Kidowaki et al., 2012). Up to now, CuO thin films have been synthesized using a variety of deposition techniques (Morales et al., 2005, Lim et al., 2014, Koh et al., 2013, Chen et al., 2009, Nair et al., 1999, Balamurugan et al., 2001, Mageshwari et al., 2013). Among these techniques, SILAR has a number of advantages, does not require vacuum at any step, can be performed at room temperature, have no restrictions on substrate materials, deposition equipment is simple and cheap (Pathan et al., 2004).

Physical characteristics of the thin films can be improved by the addition of surfactant materials to the growth solution in the solution-phase deposition techniques. Surfactants in solutions are also known to reduce the surface activity and modify the growth kinetics of the films (Zhang et al., 2006). Polyethylene glycol (PEG) is one of the important surfactant material. It has recently attracted much attention because of non-toxicity, nonflammability, and easy-to-handle. It also prevents the aggregation of particles (Jozefczak et al., 2011). In the literature, PEG has been widely used in the deposition processes of the several metal oxide thin films (Inamdar et al., 2008, Bertus et al., 2013, Deng et al., 2014).

To the best of my knowledge, the impact of the PEG on the optical properties of the CuO thin films has not been investigated yet. Herein, the role of PEG content on the optical band gap values and other optical parameters of the CuO nanostructured thin films obtained by SILAR method was investigated comprehensively.

2. Materials and Experimental Procedure

All reagents used in the study were analytical grade and purchased form Merck KGaA, Darmstadt, Germany. All glassware was cleaned with hydrochloric and chromic acids followed by rinsing with ultrapure water and dried in an oven before use. Four series of nanostructured CuO thin films were deposited on glass substrates by using the SILAR technique at room temperature. To synthesize the nanostructured CuO thin films, aqueous copper-ammonia complex ions ($[Cu(NH_3)_4]^{2+}$) were chosen for the cationic precursor, in which using analytical reagents of $CuCl_2$•$2H_2O$ (99.999%) and concentrated ammonia (NH_3) (25%) were used. 0.1 M copper (II) chloride solution was prepared with $CuCl_2$•$2H_2O$.The molar ratio of Cu:NH_3 is 1:10 obtained following the several experimental findings. The anionic precursor was hot deionized water maintained at 90 °C. The temperature was kept constant in both reactions. CuO thin films were deposited on glass slides by alternate immersion in$[Cu(NH_3)_4]^{2+}$ complex and hot water. The substrates were immersed in the solution vertically for the 30 s and then into hot water (90 °C) for 30 s. This deposition cycle was repeated for 10 times. To investigate the effect of PEG as a surfactant, different volume percentages (1%, 2%, and 4%) of PEG were added to the growth solutions. Before characterization process, the deposited films were annealed at 623 K (350 °C) for an hour in an air atmosphere. Characterizations of the CuO thin films were carried out at room temperature. Optical band gap and spectral transmittance measurements were performed using a JASCO V-670 spectrophotometer in the wavelength range of 190–1100 nm. The thickness of films was measured with a NanoMap-500LS contact surface profilometer.

3. Results and Arguments

To determine the optical band gap energies and examine the transmittance properties of the produced films, a UV-Vis spectrophotometer (JASCO V-670) was used. The optical transmittance spectra of the CuO thin films as a function of PEG concentration recorded in the wavelength range of 400-1100 nm was shown in Figure 1. As clearly seen in Figure 1, the average transmittance values of the films were less than about 5%. The CuO thin film without PEG content has the lowest transmittance. The average transmittance of the thin films increased gradually with the increasing PEG concentration. The materials with low transmittance value may be applicable in photovoltaic applications (Roblesa et al., 2014).

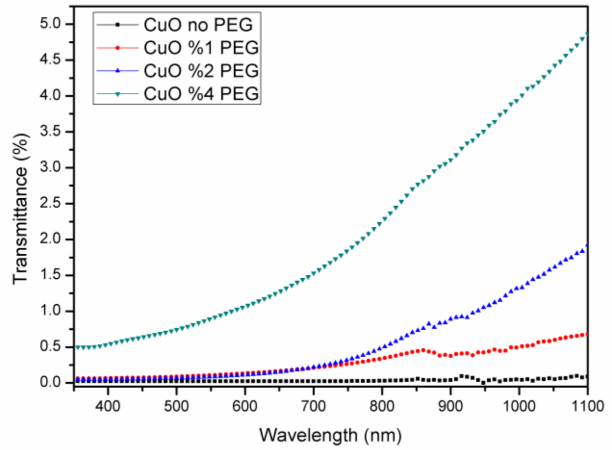

Figure 1. *Transmission spectra of the CuO thin films as a function of PEG concentration.*

The optical energy band gap values of the CuO thin films were determined by using the relationship between the absorption coefficient (α) and the photon energy (hν) given by the following equation (Shinde et al., 2006),

$$\alpha h\nu = A\,(h\nu - E_g)^m \qquad (1)$$

where A is an energy-independent constant. It is well known that the exponent m is equal to 1/2, 2, 3/2 and 3 for the allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions, respectively (Maity et al., 2006). The allowed transitions occurred in CuO, which corresponds to 1/2. Thus, in order to observe the effect of the PEG concentration on the optical band gap energies, Figure 2 was plotted with $(\alpha h\nu)^2$ versus hν as a function of the PEG concentration. E_g values were found to be 1.30, 1.32, 1.34 and 1.42 eV for the CuO thin films which were grown in the growth solution having 0, 1%, 2% and 4% volume percentages of the PEG, respectively. The obtained E_g values of the CuO thin films were presented in Table 1.

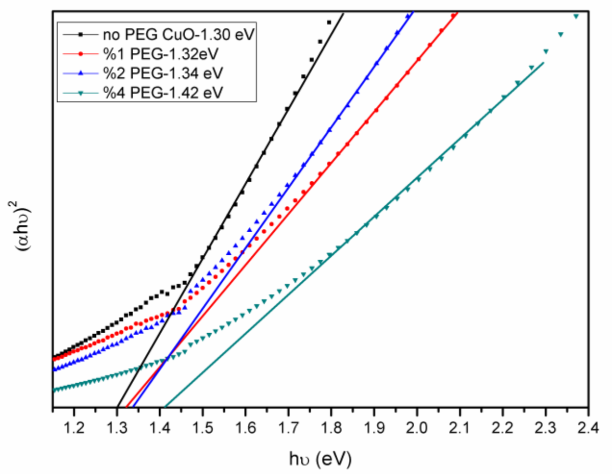

Figure 2. *Comparison of $(\alpha h\nu)^2$ versus hν plots of the CuO thin films as a function of PEG concentration.*

It was also observed that increasing the PEG concentration resulted in a decrease in film thickness of the CuO thin films from 680 nm (0% PEG) to 137 nm (4% PEG) as shown in Table 1. Moreover, as can be clearly seen from the Table 1and Figure 3, the band gap values of the

CuO thin films decreased from 1.42 to 1.30 eV with increasing the film thickness. The decrease in the band gap value with increasing the film thickness can be ascribed to the morphological alteration of the films, improvement in crystallization and changes in interatomic distances of the films (Ateş et al., 2007, Akaltun et al., 2011, Yıldırım et al., 2010, Akaltun et al., 2015).

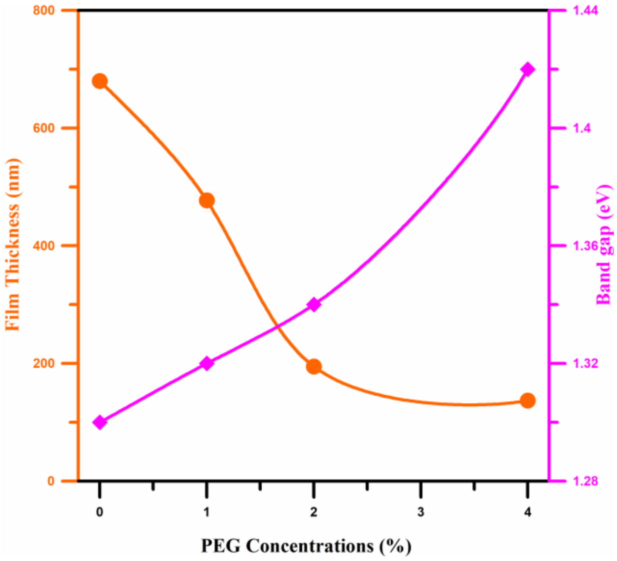

Figure 3. *Film thickness and band gap variation of the CuO thin films with different PEG concentrations.*

The refractive index of the thin films was determined according to the Moss relation (Hannachi et al., 2009) which is directly associated with the fundamental energy band gap,

$$E_g n^4 = k \qquad (2)$$

where k is a constant which corresponds to 108 eV. Another relevance between the band gap energy and the refractive index was introduced by Herve and Vandamme in the following equation (Herve et al., 1994),

$$n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2} \qquad (3)$$

where A and B are numerical constants which are equal 13.6 and 3.4 eV, respectively. The alteration of refractive index (n) as a function of the film thickness of the CuO thin films was also shown in Table 1 for these two models.

Table 1. *Optical parameters for the CuO films having different PEG concentrations.*

PEG Concentration CuO Film	Film Thickness (nm)	Moss relation		Herve &Vandamme		Band gap (eV)	Static Dielectric Constant
		n	ε∞	n	ε∞		ε0
% 0	680	3.02	9.12	3.06	9.36	1.30	14.52
% 1	477	3.00	9.00	3.04	9.24	1.32	14.45
% 2	195	2.99	8.94	3.03	9.18	1.34	14.39
% 4	137	2.95	8.70	2.99	8.94	1.42	14.15

One can see clearly from the Table 1, values of the refractive index increased from 2.95 to 3.06 with increasing the film thickness. Nevertheless, the increase rate appears to be related to the used models. It may be remarked that refractive index of the materials strongly depends on the band gap energy.

Identification of the dielectric characteristics of the metal oxide semiconductors is very crucial for various electron-device properties. Either static or high-frequency dielectric constants were calculated for all the films. The high-frequency dielectric constant (ε_0) value was obtained from the following relation (Hannachi et al., 2009),

$$\varepsilon_\infty = n^2 \qquad (4)$$

where n is refractive index. The static dielectric constant (ε_0) of the CuO thin films was obtained by using an equation which states the energy band gap dependence of ε_0 for semiconductors compounds in the following form (Mezrag et al., 2010, Adachi 2010);

$$\varepsilon_0 = 18.52 - 3.08E_g \qquad (5)$$

The calculated n, ε_∞ and ε_0 values of the CuO thin films which correspond to the different film thicknesses were given in Table 1. As can be seen from the Figure 4, the refractive index values of the CuO thin films increased with increasing the film thicknesses.

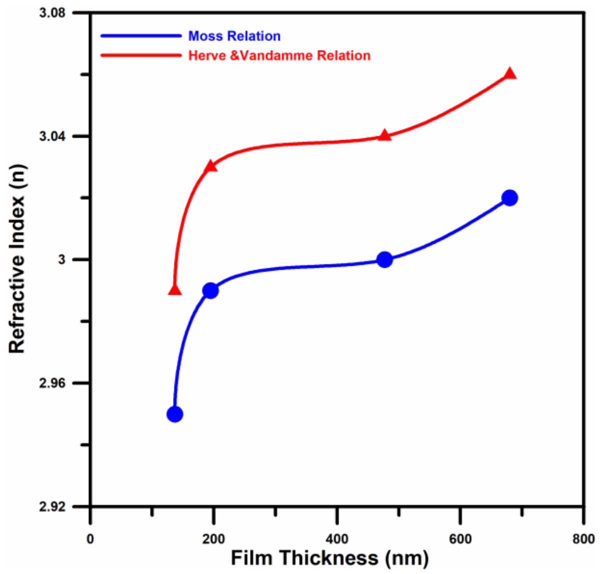

Figure 4. *Comparison of $(\alpha h\nu)^2$ versus $h\nu$ plots of the CuO thin films as a function of PEG concentration.*

4. Conclusion

In summary, nanocrystalline thin films of CuO have been synthesized using a relatively simple and cheap SILAR method using the PEG as a surfactant. The effect of the PEG on the band gap energies and other optical characteristics of the CuO thin films were broadly investigated. Optical band gap energy values of the thin films were found to be increasing from 1.30 eV to 1.42 eV by the addition of PEG concentration. It was also observed that the PEG added CuO thin films were more transparent than the CuO thin films without PEG, which points out that they are feasible for optoelectronic device applications. As a result, the PEG concentration plays an essential role on the characteristic parameters of the CuO thin films, and the SILAR is a convenient technique for depositing CuO thin films. It is anticipated that one can easily use the PEG as a surfactant to adjust the band gap of a semiconductor.

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