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Sb Katkılı CuO Filmlerinin Yapısal ve Optik Özellikleri

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Öz

(111) tercihli yönelimli Sb katkılı CuO ince film, çeşitli ağırlık oranlarında (ağırlıkça % 0, 1, 2 ve 3 Sb), soda kireç cam alttaşı (SLG) üzerine dönel kaplama tekniği kullanılarak büyütüldü. Farklı Sb katkısının CuO filmlerin yapısal, morfolojik ve optik özellikleri üzerindeki etkisi, X-ışını difraksiyon (XRD) ünitesi, taramalı elektron mikroskobu (SEM) ve UV-vis spektrofotometresi kullanılarak kapsamlı bir şekilde incelenmiştir. Filmlerin X ışını kırınım spektroskopi çalışmaları, ince filmlerin tercihli yönelim boyunca polikristal doğaya sahip olduklarını göstermektedir. Tüm CuO ince film morfolojisi yüzeyde kusur olmaksızın homojen doğaya sahip olduğunu göstermektedir. Elde edilen CuO filmlerin geçirgenliği, Sb içeriğindeki artışla değişmiştir. Ultraviyole görünür bölge spektrofotometre ölçümleri, elde edilen filmlerin enerji bant aralığında 1.70'den 2.37 eV'ye kadar radikal bir şekilde artış olduğunu göstermektedir. Sb katkılı CuO ince film optik özelliklerinin önemli ölçüde değiştiği söylenebilir.

Anahtar Kelimeler: İnce film, Geçirgenlik, Enerji bant aralığı, XRD

Structural and Optical Properties of Sb Doped CuO Films

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Abstract

Preferentially (111) oriented Sb-doped CuO thin film with various weight fractions (0, 1, 2 and 3 wt% of Sb) have been grown on soda-lime glass substrate (SLG) by spin coating technique. The effect of Sb doping in different amounts on the structural, morphological and optical properties of CuO films was comprehensively investigated via X-ray diffraction (XRD) unit, scanning electron microscopy (SEM) and UV–vis spectrophotometer. X-ray diffraction spectroscopy studies of the films indicate that thin films are polycrystalline nature along the preferential direction. The morphology of all CuO thin film is uniform with no cracking in the surface. The transmittance of the CuO films changed with an increase in Sb content. Ultraviolet–visible spectrophotometer measurements indicate that a radical increase in the energy band gap of the films with an increase in Sb content from 1.70 to 2.37 eV. It can be said that the optical properties of the Sb doped CuO thin film were significantly changed.

Keywords: Thin film, Transmittance, Energy band gap, XRD

1. INTRODUCTION

Technological advancements and nanoscience have played an important role both in encouraging the invention of a new phenomenon, industrial revolutions and in the development of economy for the 21st century [1, 2]. In recent years, transition metal oxides have attracted the researchers' interest owing to their unique properties for technological point of view. Among all the transition metal oxides such as iron oxide and zinc oxide nanostructures, copper oxide (CuO) films have attracted a wide interest because of their immense potential applications in various field of science and technology including optics, optoelectronics, biosensor, solar cell technology, gas sensing, catalysis, transducers and capacitors [2-12]. Transition metal oxides have novel electronic, magnetic and optical properties that are different from their conventional bulk counterparts [11].

Copper oxide thin films are important monoclinic p-type transition metal oxide semiconductor, having a narrow band

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gap of 1.21 – 2.1 eV [13-15]. CuO has an important advantage in device applications since it has several attractive features such as favorable capacitive, easily produced in different shapes, low cost, non-toxicity and available resources [16].

CuO thin films also play an important role in catalysis and solar energy conversion applications because of their several advantages such as high activity and selectivity in reactions [17]. A broad variety of physical and chemical techniques have been used for the fabrication of CuO films, such as molecular beam epitaxy [18], hydrothermal process [19], thermal evaporation [20], thermal decomposition [21], magnetron sputtering [22], pulsed laser deposition [23]. In this study, the spin coating method is employed to get high-quality films to control crystalline growth and amorphous surfaces.

This technique has been proved to be a very efficient method in producing thin films such as relatively homogenous deposition in air condition, easy control of film thickness at different concentrations and fine composition [24, 25]. Besides, a number of metal atoms can be used as doping elements of nanostructured films to improve the physical and chemical properties of materials to meet the specific demand and device applications. Generally, doping elements make radical variation in optical, electrical, structural and magnetic properties of CuO films by changing electronic properties. Cu has hole doping and electron doping mechanisms owing to its different oxidation states such as Cu^+, Cu^{2+} and Cu^{3+} [26, 27].

In recent years, a number of studies have been carried out on doping elements of CuO thin films however it maintains a difficulty to get high quality of thin films with excellent physical and chemical behavior. Among p-type nanostructured metal oxides, CuO doped with transition elements has attracted considerable attention for its excellent device application in gas sensor applications, catalysts and spintronic devices owing to high activity and selectivity in reactions and Curie temperature [28]. Many authors have shown that the changes in the material's physical and chemical properties are associated with CuO doping with various dopants [29-33]. Yun et al. have prepared Sb doped p-type Cu_2O films by electro deposition method [34]. They showed that the addition of Sb dopants in the Cu_2O significantly improved the characteristic properties of the film.

In this study, Sb doped CuO films were grown by using spin coating technique. Then, all films were annealed at 450 ºC to develop their properties. The optical, structural and morphological properties of Sb doped CuO thin films have not been comprehensively investigated and the knowledge in the literature about this study is very limited. Therefore, the concentration effect on CuO film was comprehensively investigated in this study.

2. EXPERIMENTAL

Pure and Sb doped CuO thin films with different weight fractions (0, 1, 2 and 3 wt% of Sb) were grown by spin coating technique using a solution containing 0.1 M copper (II) acetate ($Cu(CH_3COO)_2 \bullet H_2O$), 0.01 M antimony (III) chloride fabricated under optimized condition. To obtain a clear and homogenous blue solution, copper (II) acetate and antimony (III) chloride solutions with a high purity of about 98% were prepared. 0.1 M copper (II) acetate and 0.01 M antimony (III) chloride solution was separately stirred in ethanol for 24 h. Then, an adequate amount of antimony (III) chloride was slowly mixed into the copper (II) acetate solution to obtain various doping concentrations (i.e. 0, 1, 2 and 3 %) and then the solutions were stirred for 8 h until a clear and homogeneous blue solution was attained. In this study, it has been reported that various Sb doping concentrations have effects on CuO thin film.

Prior to deposition process, the used SLG substrates were firstly boiled in the solution of 5:1:1 H_2O (water), NH_3 (ammonia) and H_2O_2 (hydrogen peroxide) for 15 min at 90 ºC and then in the solution of 5:1:1 H_2O (water), H_2O_2 (hydrogen peroxide) and HCl (hydrogen chloride) for 15 min at 90 ºC to obtain a clear surface. Then, these SLG substrates were stirred in acetone for 5 min to obtain a clear surface. Finally, these substrates were cleaned by double distilled water and then dried.

After drying the substrates and preparing the solutions, the thin films were fabricated using spin coating technique at a spin rate of 2000 rpm for 63 s for 10 layers of deposition and then, each layer of the thin films was preheated at 220 ºC for 12 min on a hot plate. The Sb-doped CuO thin films were annealed at 450 ºC for 1 h in a furnace. The effect of Sb doping in different amounts on the optical, morphological and structural properties of CuO thin film was studied in this work. The crystalline properties and phase purity of the acquired Sb-doped CuO thin film were investigated by an X-Ray Diffractometer (XRD) unit. The surface morphology of all thin films was obtained by scanning electron microscopy (SEM). The optical measurements such as transmittance and energy band gap of all thin films were analyzed using a UV-Vis spectrophotometer in the 300-1100 nm wavelength range.

3. RESULTS AND DISCUSSION

3.1. Structural analysis

For structural and phase purity analysis, pure and Sb doped CuO films were deposited on soda-lime glass substrate using spin coating technique, XRD spectrum of all the films was investigated by an X-ray diffractometer and the results are shown in Fig.1. The XRD patterns were investigated at a scan rate of 0.02º and an operating voltage (V) with current (I) of 40 keV and 30 mA, respectively.

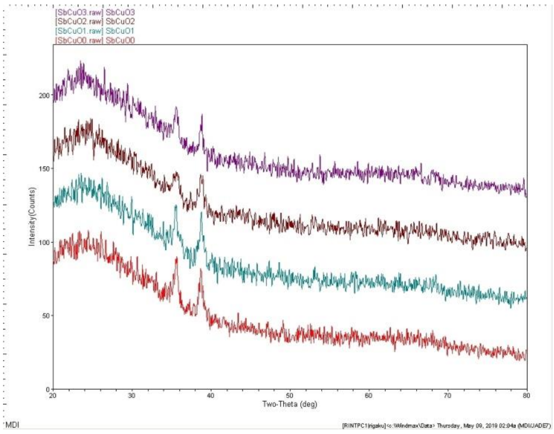

Figure 1: XRD patterns of the films

Table1: Structural parameters derived from XRD measurements of pure and Sb doped CuO thin film films.

Sample	2 theta (Degree)	FWHM (degree)	Grain Size (Å)	d-Spacing (Å)	Dislocation Density (δ)x10^{14} (m^{-2})	Strain (10^{-4})	Orientation
Pure CuO	35.56	0.546	160.2	2.5225	38.97	22.62	002
	35.68	0.543	160.3	2.5143	38.92	22.61	- 111
	38.70	0.468	187.3	2.3248	28.51	19.34	111
1% Sb:CuO	35.62	0.543	161.9	2.5185	38.15	22.61	-111
	38.82	0.541	163.5	2.3180	37.41	22.16	111
2% Sb:CuO	38.68	0.682	129.1	2.3259	60.00	28.07	111
	39.00	0.610	145.0	2.3076	47.56	25.10	200
3% Sb:CuO	38.88	0.468	148.4	2.3144	45.41	19.33	111

It can be seen in Fig.1 that all films have polycrystalline nature, giving the formation of monoclinic structure. The peak positions of the XRD pattern were located at around 2θ = 35.5, 35.6, 38.7 and 39.00° corresponding to (002), (-111), (111) and (200) planes for Sb (0, 1, 2 and 3%) doped CuO film, respectively. Furthermore, we can see from the XRD data that there are clear changes in the peak positions in the spectra, which may be attributed to the substitution of Cu atoms by Sb atoms affecting the monoclinic structure of the parent CuO thin films. Sekhar indicated that CuO thin film has (002) and (111) planes when thin films were deposited at 400–500°C temperature [35]. Maruyama reported that both Cu_2O and CuO phases using chemical vapor deposition method grown Cu_2O thin films fabricated at a substrate temperature of 300°C [36]. Yoon et al. reported a dominant phase of CuO prepared using ion beam sputtering method at a different baking temperature ranging from 25 to 400 °C [37]. Luzeau et al. also reported that a mixture of Cu, CuO and Cu_2O phases fabricated via an oxygen plasma source at a different baking temperature from 450 to 600°C [38]. Increasing the Sb doping caused a decrease in the intensity of all diffraction peaks at first as the intensity of (002) and (-111) observed to gradually decrease. However, the peak (111) is still seen even for the highest Sb doping. It is important to note here that the intensities of XRD peaks declined as Sb was doped in CuO and increasing Sb doping in CuO thin films caused degenerate the crystalline quality of films. For the Sb (0, 1, 2 and 3%) doped CuO thin film, crystallite size (*D*) was calculated by measuring the peak full width at half maximum (FWHM) using the Scherrer's equation [10].

$$D = \frac{0.94\lambda}{\beta cos\theta} \tag{1}$$

where λ is the wavelength of the X-ray beam (1.5418Å), θ is the Bragg diffraction angle and β is the angular width of the peak at half-width maximum (FWHM) and D is the calculated crystalline size of the CuO films, as indicated in Table 1.

It can be seen in Table 1 that the crystallite size of Sb doped CuO films was found to be in the range of 12.9–18.7 nm. This shows that the crystallite size changes with the increase of Sb doping in CuO film, which may be owing to high radius (121.76 Å) of Sb ions in solution. Balamurugan and Mehta indicated that as the oxygen flow rate increases, the crystallite size of the film decreases [13]. Gülen et al reported that the crystallite size of 0.02% Mn-doped CuO film decreases while the crystallite size of 0.06 and 0.10 Mn-doped CuO film increases [39].

The dislocation density value δ (the number of defects in CuO films) is calculated using the following equation:

$$\delta = \frac{1}{D^2} \quad (2)$$

where D is the crystallite size. Strain (ε) of the pure and Sb-doped CuO films is calculated from the following equation:

$$\varepsilon = \frac{\beta}{4tan\theta} \quad (3)$$

Both strain and dislocation density in our work changed with increasing of Sb concentration in the solution. The changing of the dislocation density shows deterioration of the crystallinity with an increase in Sb doping effect. We can see in Table 1 that the main cause of change in crystallite size for all orientation is associated with a change in strain. These changes indicate the proof of the strain in the pure and Sb-doped CuO films.

3.2. Surface morphology studies

The SEM images of pure and 1, 2, 3% Sb-doped CuO thin film with various Sb concentrations are shown in Fig 2 (a, b, c and d), respectively.

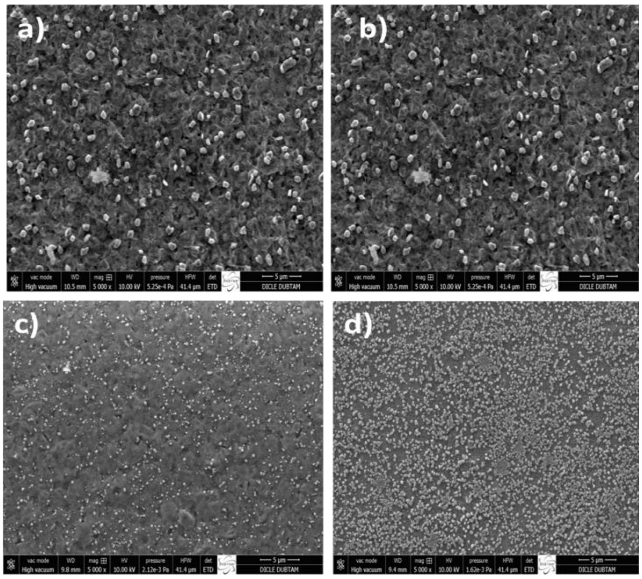

Figure 2: SEM image of **a)** pure CuO film, b) 1% Sb-doped CuO film, **c)** 2% Sb-doped CuO film, **d)** 3% Sb-doped CuO film

As seen in Fig. 2, the surface topology of the thin films has uniform surfaces without any cracks or pinholes for all CuO films. The surface topology of the films has comparatively smooth surfaces and grains are spherical. It can be said that all thin film surface is also composed of densely packed nanoparticles and the coverage rate of the nanoparticles comparatively increased with Sb. A similar change in the SEM images was reported in our previous work [40]. Additionally, it can be said that the doping concentration of Sb affected the appearance of the Sb-doped CuO film's surface topology.

3.3. Optical studies

The optical properties of CuO films fabricated onto soda-lime glass substrates were analyzed to observe the effect of doping on the energy band gap $E_g(\lambda)$ and the transmittance $T(\lambda)$ by using a UV–visible spectrophotometer in the wavelength range from 300 to 1100 nm. There was not seen any other peak in the UV-vis area because all thin films have a good quality (clear and homogenous). Fig. 3 indicates the optical transmission spectra of CuO films for various concentrations.

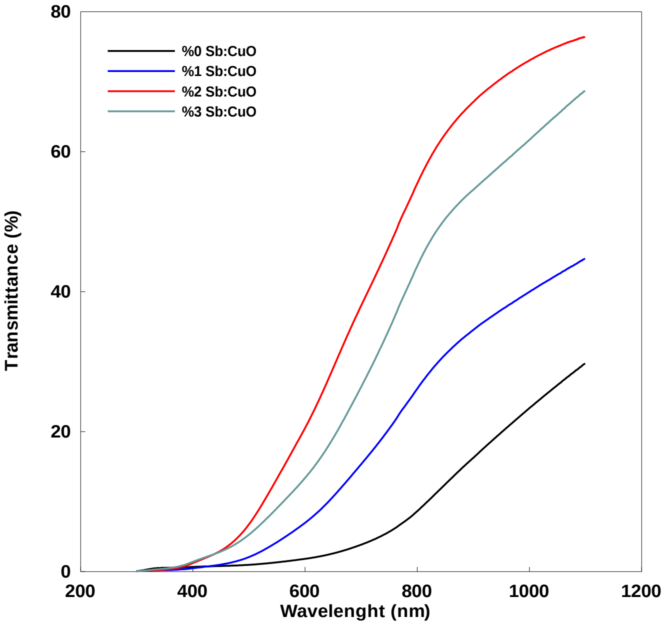

Figure 3: Transmittance of pure and Sb doped CuO thin films

Pure CuO thin film has a minimum transmittance value compared to the other thin films. Gülen et al. indicated that pure CuO transmits the higher wavelengths at small percentages using SILAR method and they showed that Mn-doped CuO film exhibited transparency around 80% [39]. Also, Joseph et al. indicated an enhancement in the transmittance for the spray fabricated 10% Fe-doped CuO films [41]. As seen in Fig. 3, the transmission of Sb doping in the solution increases with increasing of incorporation concentrations and the highest transmittance value for films was obtained at 2% as compared to the others. It can be said that the transmittance value of Sb-doped CuO thin film changed with Sb doping level owing to the differences in the microstructure. The energy band gap of pure and Sb-doped CuO thin films in the wavelength range of 300–1100 nm was investigated and illustrated in Fig. 4. For such materials, optical absorption theory shows that the absorption coefficient (α) and incident photon energy (hν) are correlated as follows:

$$\alpha h\upsilon = K(h\upsilon - E_g)^n$$

where K is an energy-independent constant related to the material, $h\upsilon$ is the photon energy and E_g is the energy band gap. A curve of $(\alpha h\upsilon)^2$ vs. photon energy ($h\upsilon$) for the 0, 1, 2, 3% Sb-doped CuO thin film as shown in Fig. 4 (a, b, c and d) indicates the effect of different concentration fractions on the energy band gap (E_g).

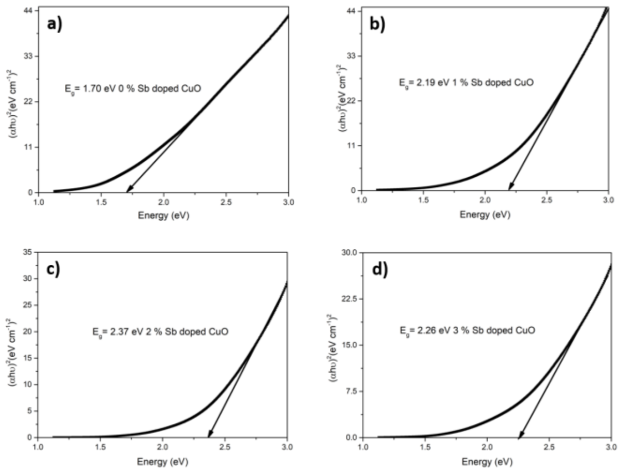

Figure 4: Energy band gap of **a)** pure CuO film, **b)** 1% Sb-doped CuO film, **c)** 2% Sb-doped CuO film, **d)** 3% Sb-doped CuO film

The calculated energy band gap of the films found from this curve was 1.70, 2.19, 2.37 and 2.26 eV for 0, 1, 2, 3% Sb doped CuO films, respectively. Sb doping has changed the energy band gap owing to the band tailing effect [31], which indicates that Sb could be used to regulate the optical band gap of CuO films. Joseph et al. reported that the values of Eg for the CuO thin films on doping with Fe increased [41]. Gülen et al indicated that energy band gap of Mn-doped CuO films increased from 1.98 to 2.20 related to increasing of Mn doping fractions [39]. Yıldız et al. showed that energy band gap of In doped CuO thin films using sol gel dip coating method increases from 1.24 to 1.46 eV with the increasing doping fractions [42].

4. CONCLUSION

In summary, we have investigated the structural, morphological and optical properties of pure and Sb doped CuO thin film via spin coating technique. The X-ray diffraction pattern study indicates that all thin films have polycrystalline nature and the crystallite size of CuO films has changed with increasing of Sb doping.

The SEM images of all thin films demonstrate that the morphological properties of all thin films are dependent on Sb doping fractions. One can easily see that the energy band gap of 1, 2 and 3% Sb doped CuO film increased compared to pure CuO film. The transmittance value changed depending on Sb doping fractions and the highest transmittance value was found to be for 2% Sb-doped CuO film in the visible range.

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