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Investigation of Structural, Morphological and Electrical Properties of SnO_2 Thin Film Grown by SILAR Method

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ABSTRACT

Due to its wide band gap value and large applications, tin dioxide (SnO_2) is useful multifunctional material. In this study, SnO_2 thin film was grown by the Successive Ionic Layer Adsorption and Reaction (SILAR) method for 40 cycles on the silver interdigital contact. Structural and morphological properties were investigated by XRD, SEM, and UV analysis. XRD analysis was taken using Cu Kα source in the range of 20- 80 two theta and it was observed that the crystal structure was formed. SEM analysis showed that the SnO_2 material grew homogeneously on the glass surface. The Tauc graph was plotted using the absorbance data. It was determined from the graph that the forbidden energy range was 3.81 eV. Urbach energy graph was also plotted which value was calculated as 0.46 eV. For electrical characterization, I-V and resistivity measurements were also taken depending on temperature by Keithley 2400 source meter and Lakeshore temperature controller. The temperature-dependent resistance graph was plotted. The temperature-dependent resistance graph showed that the resistivity decreased with increasing temperature. Activation energies were calculated by drawing the temperature-dependent Arhenius graph. The results showed that the SnO_2 thin film could be used in future electrical applications.

SILAR Yöntemiyle Üretilen SnO_2 İnce Filmin Yapısal, Morfolojik ve Elektriksel Özelliklerinin İncelenmesi

ÖZ

Geniş bant aralığı değeri ve geniş uygulamaları nedeniyle kalay dioksit (SnO_2) çok işlevli, kullanışlı bir malzemedir. Bu çalışmada, SnO_2 ince film, gümüş interdigital kontak üzerine 40 döngüde Ardışık İyonik Tabaka Adsorpsiyon ve Reaksiyon (SILAR) yöntemiyle büyütüldü. Yapısal ve morfolojik özellikler XRD, SEM ve UV analizleri ile incelendi. XRD analizi 20 ila 80 iki teta aralığında Cu Kα kaynak kullanılarak alındı ve kristal yapının oluştuğu gözlemlendi. SEM analizi SnO_2 malzemesinin cam yüzey üzerine homojen biçimde büyüdüğünü gösterdi. Tauc grafiği, absorbans verileri kullanılarak çizildi. Grafikten yasak enerji aralığının 3.81 eV olduğu belirlendi. Urbach enerji grafiği çizildi ve Urbach enerji değeri 0.46 eV olarak hesaplandı. Elektriksel karakterizasyon için Keithley 2400 kaynak ölçer ve Lakeshore sıcaklık kontrolcüsü cihazı ile sıcaklığa bağlı olarak I-V ölçümleri yapıldı. Sıcaklığa bağlı direnç grafiği çizildi. Sıcaklığa bağlı direnç grafiği, artan sıcaklıkla direncin azaldığını gösterdi. Sıcaklığa bağlı Arhenius grafiği çizelerek aktivasyon enerjileri hesaplandı. Sonuçlar, SnO_2 ince filmin gelecekteki elektriksel uygulamalarda kulanılabilir olduğunu gösterdi.

Anahtar Kelimeler: SnO_2, SILAR, Elektriksel Karakterizasyon

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1. Introduction

Tin dioxide (SnO_2) is an easily available material with a wide band gap. These features allow it to be used in wide areas such as gas sensor applications [1], catalysts [2], optoelectronic device applications [3,4], etc. SnO_2-based semiconductors present significant potential in gas sensors used to detect combustible gases due to their high sensitivity and detection accuracy [5].

SnO_2 has a wide bandgap (3.6 eV) and is an n-type semiconductor oxide. Compared to other elements in the Group-IV periodic table, the element Sn is a unique property that combines transparency and conductivity properties. These properties make it suitable for optically passive components in many devices. Application areas such as catalytic support materials in solar cells and sensor applications etc. activate the study of SnO_2 material [6]. It is very important to produce SnO_2 thin film with the appropriate method with its wide usage area. The selection of the appropriate one among many production methods also affects the cost.

Thin films are grown using physical and chemical techniques in academic and industrial studies. Physical, chemical, technological, technical and economic properties play a role in the selection of magnification technique. Physical vapor deposition method, sol-gel, chemical vapor deposition, spray pyrolysis, etc. these techniques require high temperatures and pressures, hence using these techniques thin film magnification becomes very costly.

SILAR is one of the newest thin-film growth methods. It is an aqueous solution technique that involves a series of sequential reactions at the solution and substrate interface. It is a simple method that allows thin films to be formed by immersing the substrate in a certain sequence in aqueous solutions containing ions of each species and precipitating it on the substrate. The SILAR technique is inexpensive, simple, and suitable for a wide range of precipitation. Since the reaction is carried out at or around room temperature and under pressure that envelops the solutions, various base materials such as insulators, semiconductors, metals and temperature-sensitive (such as polyester) can be used [7].

Compared to other growth techniques, SILAR is a thin film growth method that is simple, applied at low temperatures, does not require expensive equipment and does not waste material. By varying the number of cycles, the film thickness and deposition rate can be easily controlled [8].

In this work, we prepared SnO_2 thin film grown by the SILAR method. The electrical properties of the thin film are investigated.

2. Material and Method

In this work, the glass substrate was used. After cleaning the glass substrate, the interdigital contact has evaporated on the glass substrate's side. Then interdigital contact has been annealed under a nitrogen atmosphere (300◦C, 15 min). After this process, SnO_2 material was grown by the SILAR method on the ready contacts.

To prepare the thin film, $SnCl_4$ of 0.1 M as a source for Sn and aqueous ammonia solution (NH_3-28%) were used. As solvent deionized water was chosen and $[Sn(NH_3)_4]^{4+}$ complex was obtained for producing process. SnO_2 material was successfully grown on the substrates in the same order that we used in our previous work [9].

One SILAR cycle includes four steps and each step is shown in Figure 1. Yıldırım et. al. were investigated the characteristics of SnO_2 thin films prepared by SILAR for 60, 80, 100 and 120 SILAR cycles [10]. Alfaro Cruz et. al. were studied the development of SnO_2–ZnO thin films as a photocatalyst for obtaining alternative fuels through photocatalytic reactions and they were used 60 SILAR cycle to produce SnO_2-ZnO thin films [11]. Based on the studies and our observations, 40 cycles is an optimized number enough to grow SnO_2 thin film on the glass substrate. Thus, SnO_2 material was grown on both sides of the glass substrate.

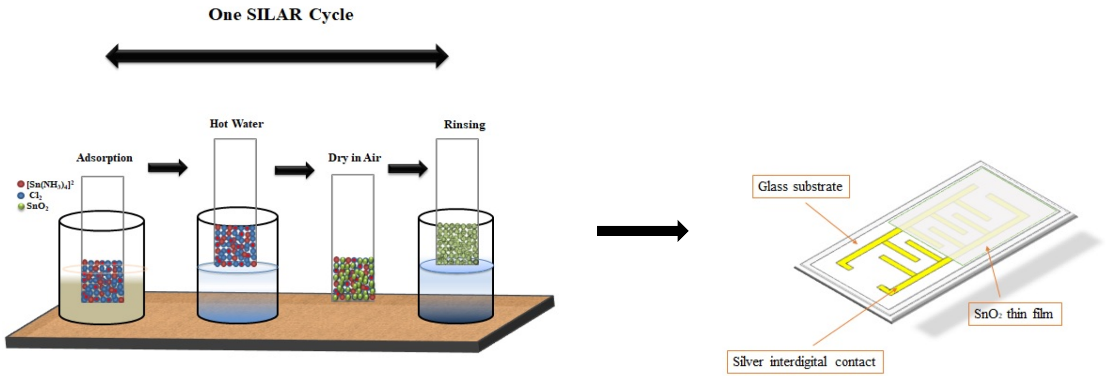

Figure 1. The schematic diagram of one SILAR cycle

3. Results and Discussion

The XRD pattern of the SnO_2 thin film was given in Figure 2. The measurement was taken between 20 and 80 two theta degrees. The pattern indicates the existence of a SnO_2 single phase as shown in Fig. 2. The XRD pattern is in good agreement with the 01-078-1063 PDF card of the orthorhombic phase. The peaks at 2θ = 25, 26.89 and 29.7° correspond to the (111), (112) and (113) planes of SnO_2, respectively.

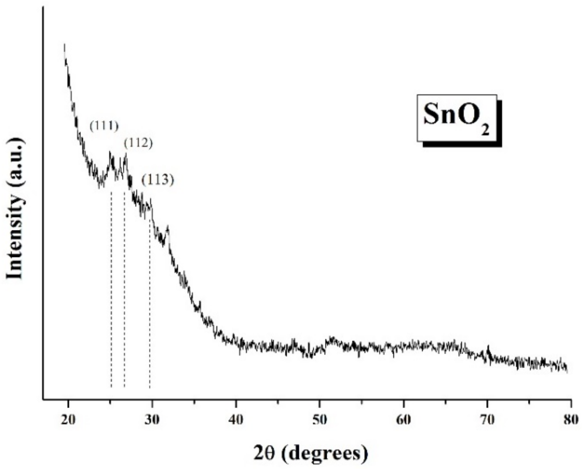

Figure 2. XRD pattern of SnO_2 thin film

Figure 3 shows SEM images taken using the FEI Quanta FEG 450 model SEM for different magnitudes of SnO_2 thin film. The images show that the SnO_2 material covers the entire surface. It was also observed that cracks formed on the surface as a result of 40 SILAR cycles. In addition to the bright regions, relatively dark regions are also seen in these images. Formations in dark areas consist of smaller grains or blanks. In addition, it is observed that an intense layering is formed on the surface of the base material. Besides, EDX results given in Table 1, also support the healthy growth of the structure.

Fig. 4 shows the band gap graph of the SnO_2 thin film. The transition was plotted using the relative Tauc plot given in formula 1.

$$\alpha = \frac{A(h\vartheta - E_g)^n}{h\vartheta} \quad (1)$$

Here α is the absorption coefficient, hυ is the photon energy, A is constant and n is an exponent depending on the nature of the electronic transition (n = 1/2 indicates a permissible direct transition in SnO_2 nanoparticles) [12]. The bandgap energy is identified by extrapolating the linear part of the Tauc plot to the energy axis. The Tauc plot was plotted using $(\alpha h\nu)^2$ versus hν. The band gap energy was determined as 3.81 eV at the point where the line drawn on the straightest part of the graph intersects the hν energy axis. The band gap energy value calculated using the absorption data is compatible with the literature [13].

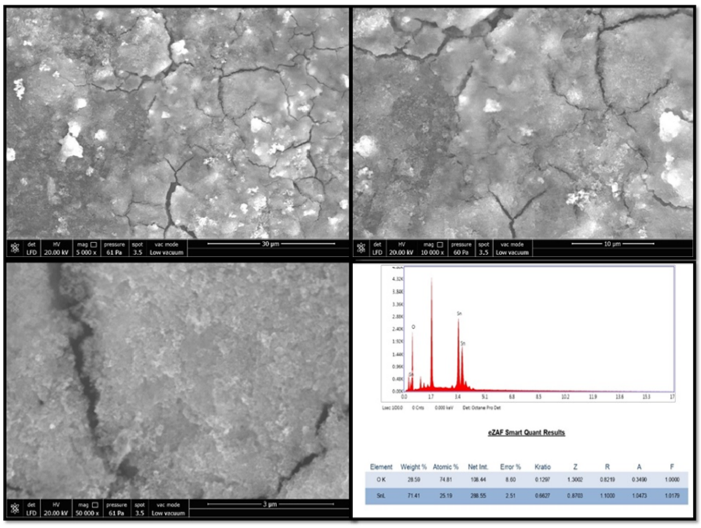

Figure 3. SEM and EDX images of SnO_2 thin film

Table 1. Elements and their percentages in SnO_2 thin film.

Elements (%)	**SnO_2 Thin Film**
O	74.81
Sn	25.19

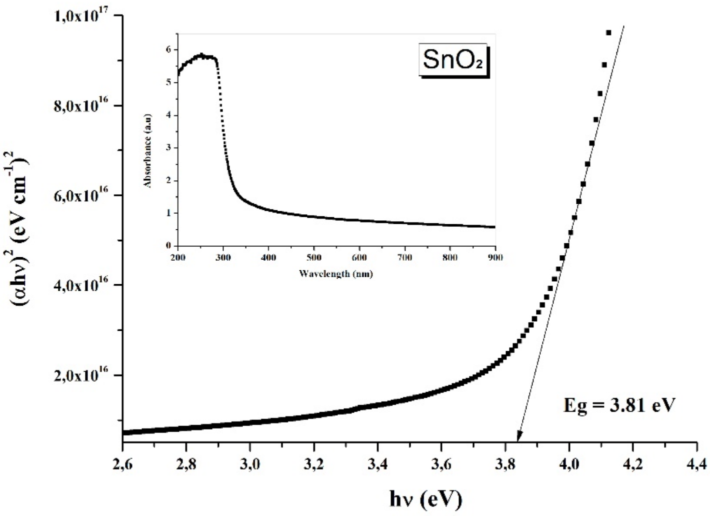

Figure 4. Tauc's plot of optical bandgap for SnO_2

The Urbach energy is related to the disorder of the particles under analysis. Figure 5 shows the Urbach energy graph. The band tail energy or Urbach energy is related to the energy disorder at the band edge of a semiconductor. The Urbach Tail values can be calculated with using formula 2 [14].

$$\alpha = \alpha_0 e^{(E/E_u)} \qquad (2)$$

where, α is the absorption coefficient, α_0 is constant, E is the photon energy, and E_u is the Urbach energy. The Urbach energy was obtained by plotting ln α versus. hν. SnO_2 thin film Urbach energy value calculated to 0.46 eV. However, the calculated value was found to be compatible with the literature [15].

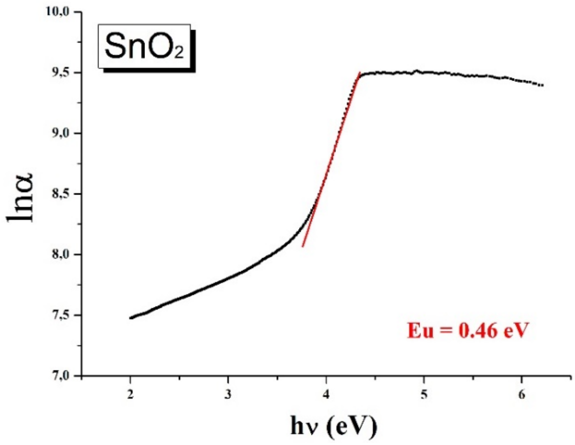

Figure 5. Band tail energy graph for SnO_2 thin film

Figure 6 shows the current-voltage characteristics for the different temperatures of SILAR-deposited SnO_2 thin films. The results show linear I–V relations under both forward and reverse bias indicating a good Ohmic contact behavior of the studied film. It's clearly seen that the electrical characteristics of SnO_2 thin film getting stabilized at high temperatures. All measurements were taken between -5 volt and + 5 volts.

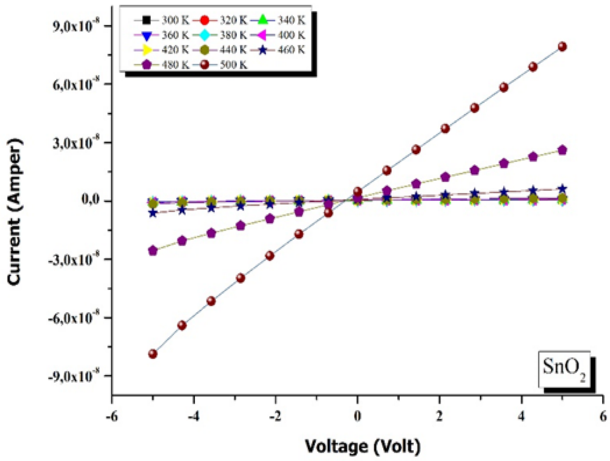

Figure 6. Current –Voltage characteristic of SnO_2 thin film

If the number of charged particles in the environment increases and their kinetic energy is increased by heat, the charges in the valence band will pass to the conduction band and move in the lattice, thus initiating the electric current as well as increasing the current intensity. Thus, the resistance value of the material decreases with increasing temperature. The resistance values of the SnO_2 thin film was calculated from the slope of each temperature-dependent curve in the current-voltage graph and is given in graph 7. It was observed that the resistance of the SnO_2 material decreased with increasing temperature.

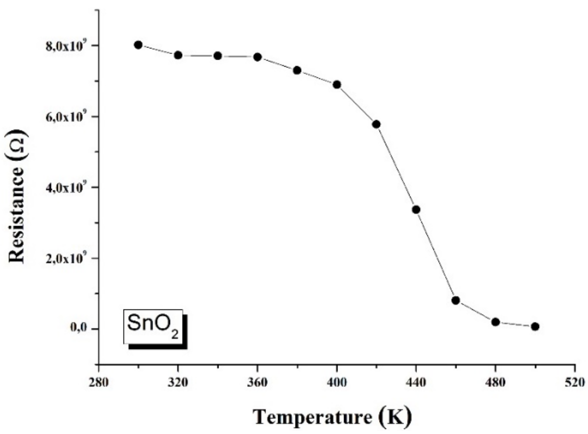

Figure 7. The plot of Resistance versus Temperature of SnO_2 thin film

An increase in the energies of the particles or a decrease in the activation energy means that the charges move more easily and contribute to easier conduction. Therefore, the electrical conductivity equation is empirically the Arrhenius equation, and the graph of ln(σ) – 1000/T drawn for conductivity can be called the Arrhenius curve. The activation energies were estimated using the Arrhenius formula 3 [16]:

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \tag{3}$$

where σ_0 is a pre-exponential factor and E_a is the activation energy of the DC conductivity and k_B is the Boltzmann constant. Figure 8 depicts lnσ against temperature. It can be clearly stated that the conductivity increases with increasing temperature. At low temperatures below 400 °K, the graph stabilized [17]. The activation energies of the SnO_2 thin film in the high-temperature and low-temperature regions were calculated from the slopes of the graph in Figure 8. The calculated activation energies are compatible with the literature [18].

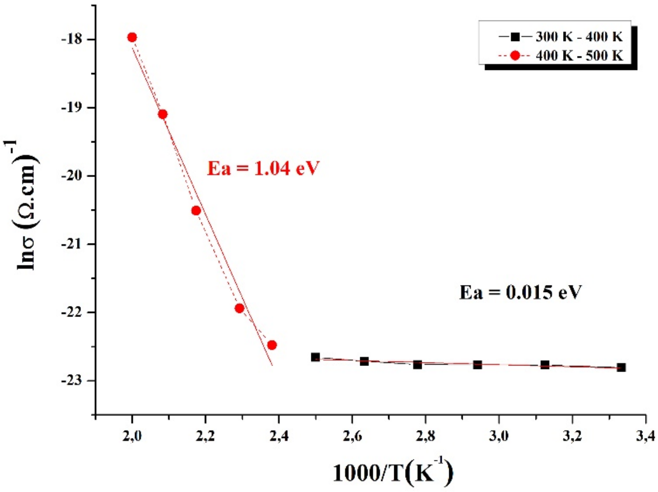

Figure 8. The plot of lnσ against 1000/T of SnO_2 thin film

3. Conclusion

In conclusion, SnO_2 thin film was produced by the SILAR method on glass substrate. XRD and SEM studies have shown that the SnO_2 thin film has a semi-crystalline structure with orthorhombic phase and covers the entire surface. The electrical properties were examined and the current-voltage results showed linear curves showing that the thin film has ohmic properties. The resistance values decreased with the increase in temperature. Using the Arrhenius formula, the activation energies for the two temperature regions were calculated as 0.015 eV and 1.04 eV at 300 °K - 400 °K and 400 °K - 500 °K, respectively. Thus, SnO_2 and its relatively low cost make it preferred in some applications that require a conductive layer on glass. As a result, SILAR was found to be a suitable method for coating SnO_2 thin films. The thin film results show that tin dioxide material is successfully grown on silver interdigital contact and it could be used in future electrical applications.

Conflict of Interest Statement

The authors declare that there is no conflict of interest

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