Research Article

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Investigation of SnO_2 and Ti-Doped SnO_2 Thin Films for Morphological, Structural and Electrical Characterization

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ABSTRACT: In this work, SnO_2 and Ti-doped SnO_2 thin films were produced by successive ionic absorption and reaction methods on platin interdigital contacts. The thin films produced were not annealed. Structural properties of amorphous thin films were investigated using X-ray Diffraction (XRD), morphological properties using Scanning Electron Microscopy (SEM), optical and electrical properties of Ultraviolet-visible Spectrophotometer (UV-VIS) and Keithley 2400 instruments. From the XRD results, it was determined that the thin films were an amorphous structure. Surface analysis by SEM shows that all films are coated and smooth. The current-voltage measurements show that thin films are ohmic. Lnρ results also show that the lowest resistance value for SnO_2 thin films is after 320 °C temperature and after 360 °C temperature for Ti-doped SnO_2 thin films.

Keywords: Successive ionic layer adsorption and reaction (SILAR), Tin dioxide (SnO_2), Characterization

1. INTRODUCTION

There have been extensive studies on their use in semiconductor technology for transparent conductive oxides (TCOs). There are many TCOs such as zinc oxide, indium oxide, tin oxide, etc [1], [2]. Tin oxide thin films are widely used as, photoconductors, transparent conductors, catalysts, gas sensors and solar cells due to their numerous electrical and optical properties such as high electrical conductivity and transparency[3][4][5][6]. The most commonly observed phases of tin oxide are tin dioxide (SnO_2) and tin monoxide (SnO). In recent years, SnO_2 thin films have become a promising material because they exhibit many properties such as n-type conductors, long life, a band gap in the range of 3.0- 4.0 eV, low cost, good reproducibility and ease of fabrication [7]. SnO_2 thin films are materials with higher mechanical and chemical stability compared to other transparent conductive oxides[8]. SnO_2 thin films are materials with low resistivity and high optical transparency in the visible region. From the studies, it is found that the SnO_2 thin films can be further improved by doping with suitable materials such as Co, F, Zn, Cd and Fe [9][10][11][3][12][13]. Many methods such as successive ionic layer adsorption and reaction (SILAR), sputtering, chemical vapor deposition and ultrasonic spray pyrolysis are used to produce SnO_2 thin films [14][15][16]. The SILAR method is a low-cost, flexible, and easy-to-manufacture method. Although there are many studies on titanium-doped

tin oxide thin film in the web of science database like sol-gel [17], and ultrasonic spray technique [18], the SILAR method was not used in any of these studies.

The growth method affects the structural, optical and electrical properties of the films produced. Liu et. al. have studied the characteristics of nano Ti-doped SnO_2 powders prepared by sol–gel method [17]. Khelifi et. al. have investigated influence of Ti doping on SnO_2 thin films properties prepared by ultrasonic spray technique [18].

The main purpose of this study is to use the SILAR method and examine its effects compared to the commonly used methods for Ti-doped SnO_2 thin films. Along with the innovative production method in this field of study, it will show structural, optical and electrical changes on its difference from the traditional production method.

We prepared pure SnO_2 and Ti-doped SnO_2 thin films as a new approach using the SILAR deposition method. Then, structural properties of thin films were investigated by X-ray Diffraction (XRD), morphological properties using Scanning Electron Microscopy (SEM), for optical and electrical properties using ultraviolet-visible spectrophotometer (UV-VIS) and Keithley 2400 instruments.

2. Materials and Methods

SnO_2 and titanium-doped SnO_2 thin films were grown on platinum IDT substrates using the SILAR method. First, platinum contacts are grown on glass substrates with a thickness of 100 nanometers by thermal evaporation. Then, the grown platinum contacts were annealed at 300 °C for 15 minutes in a nitrogen environment. After the annealing process, the SnO_2 material was successfully grown by the SILAR method on the substrates. The SILAR method consists of four basic steps. These;

1) Immersion of the substrate in the prepared solution for a certain period of time and the accumulation of the ions in the solution on the substrate (adsorption).

2) Immersion in water at a certain temperature for a specified time in order to remove weakly bonded molecules that accumulate on the substrate and are not desired to grow from the surface.

3) Drying at room temperature for a specified time in order to increase the adhesion of the material desired to be enlarged to the surface.

4) Rinsing the substrate in pure water at room temperature for the specified time in order to completely purify the material from pollution atoms.

The growth process parameters were used in the same order that we used in our previous studies[19]. The same process is used for Ti-doped SnO_2 thin film. One SILAR cycle was given in Figure 1. Both thin-film productions were scaled up by completing the 40 SILAR cycles.

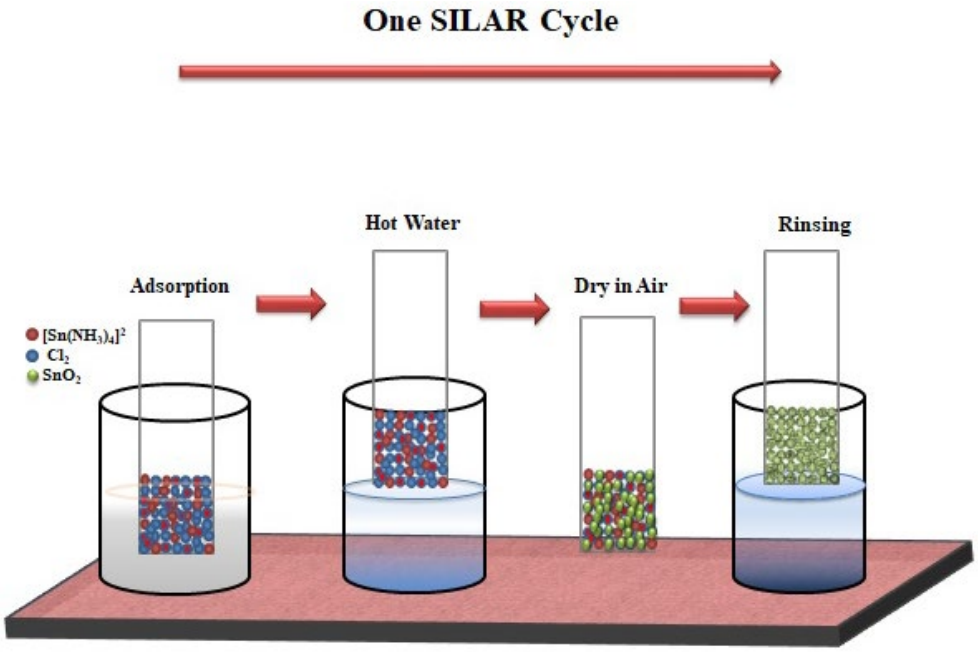

Figure 1. One SILAR cycle

3. Results and Discussions

3.1. XRD Results

The XRD patterns of SnO_2 and Ti-doped SnO_2 thin films grown by SILAR method, are shown in Figure 2. It is seen that undopped SnO_2 thin film has in semi-crystal structure. Addition of titanium, the XRD pattern of $SnTiO_2$ changed the SnO_2 structure and a transition from semi-crystalline to the crystalline structure was observed. The peaks belonging to the TiO_2 anatase phase confirmed 00-021-1272 PDF card occurred the different Bragg's peaks positioned at 2θ ~25.8°, 37.8° and 48.05° corresponds to crystal planes as (101), (004) and (200). $SnTiO_2$ thin film has also in good agreement with 01-078-1063 positioned at 2θ~26.83° and 29.74° corresponds to (112) and (113) crystal planes.

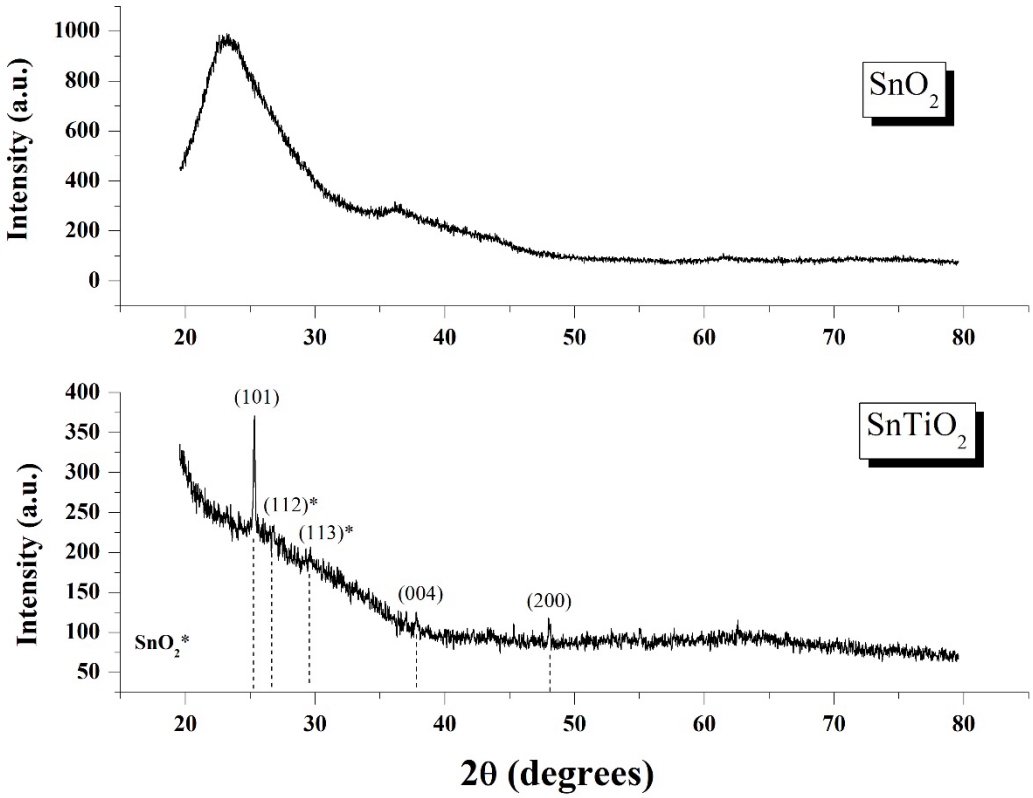

Figure 2. XRD patterns of SnO_2 and Ti-doped SnO_2 films

3.2. SEM Results

It is known that the surface properties affect the electro-optical properties of thin films. For example, it is a desired feature in gas sensor applications to ensure that the target gas adheres to the sensor surface. The surface properties of thin films are very important [2]. Figure 3 show SEM images of SnO_2 and Ti-doped SnO_2 thin films for 5 000x magnitude and 50 000x magnitude. It is seen that the un-doped films have a smooth surface morphology, but the smoothness of the thin film decrease with the titanium additive. Even if the decrease in homogeneity and smoothness has a negative effect in some applications, it is thought to be beneficial in optoelectronic applications as the surface area expands [3], [4].

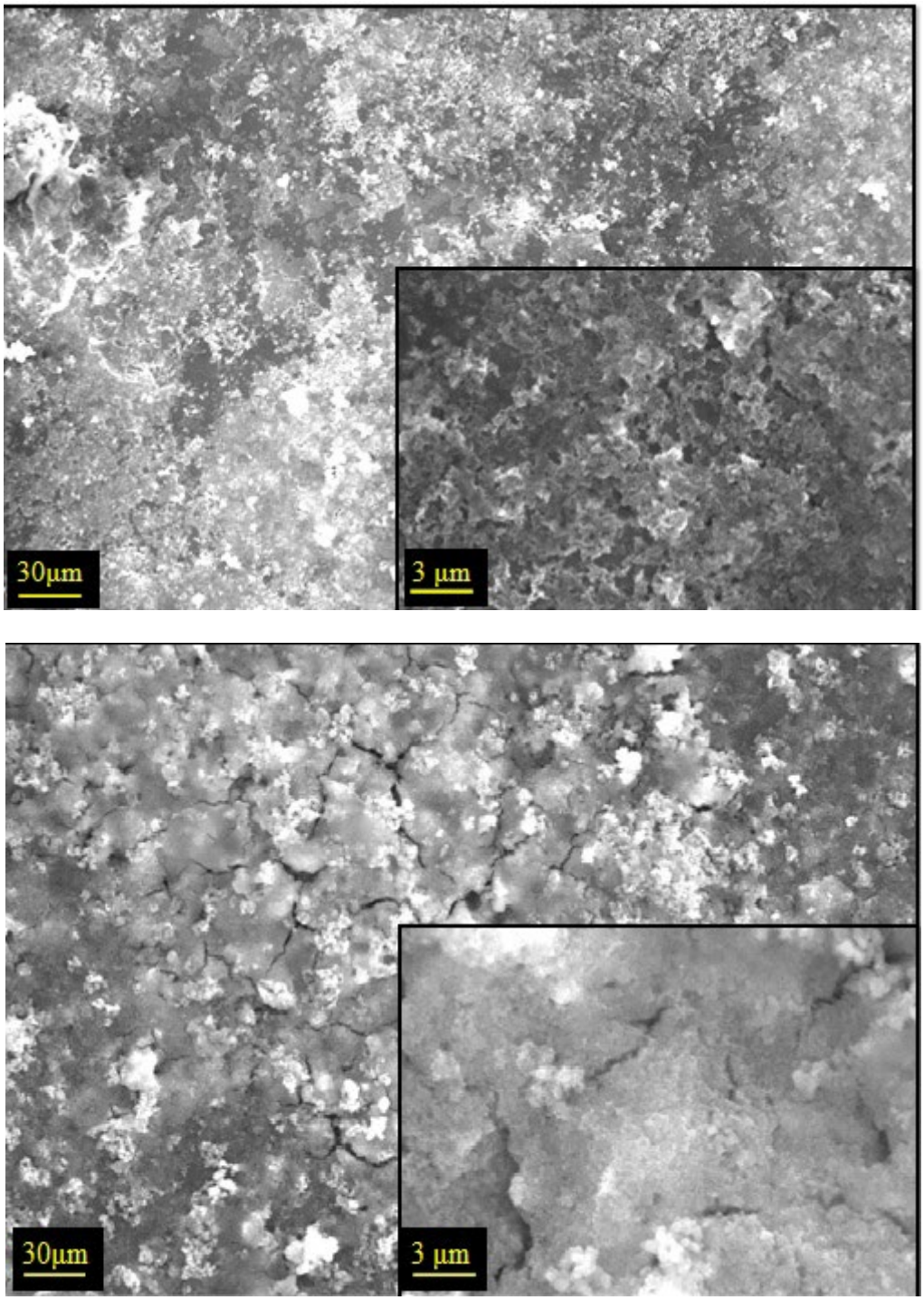

Figure 3. SEM images of SnO_2 and Ti-doped SnO_2 thin films

The EDS image of SnO_2 and Ti-doped SnO_2 thin films and the graphs showing the composition of the elements are shown in figures 4. The peaks of Sn and O belonging to the SnO_2 can be clearly observed in the spectrum, which shows a purity phase of SnO_2. Also, Ti can be clearly seen in the second spectrum. It is known that the other noticed idle peaks, such as Si and Na come from the glass substrate. The percentage values of the elements measured in thin films are given in Table 1.

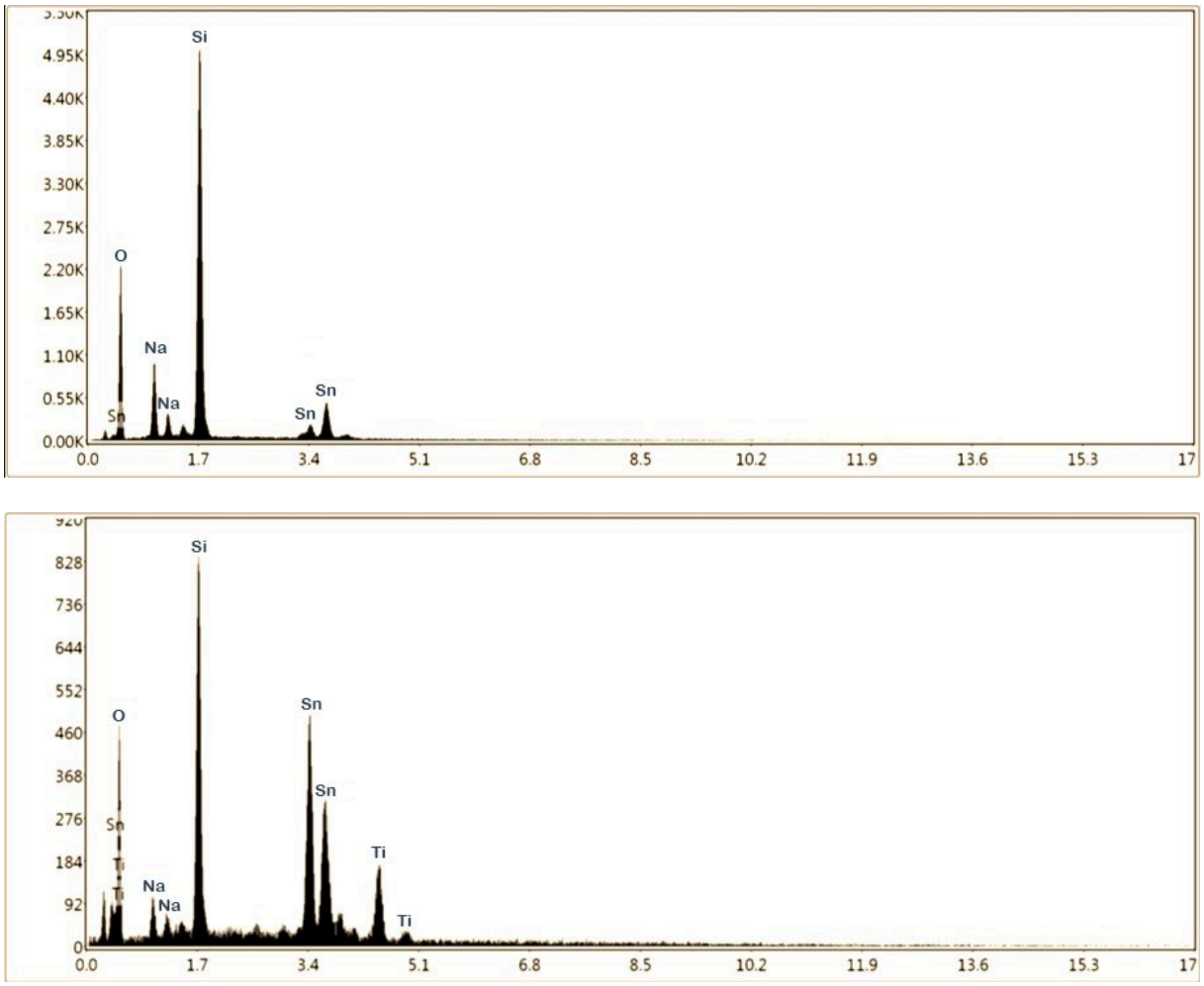

Figure 4. EDS plots of SnO_2 and Ti-doped SnO_2 thin films.

Table 1. Elements and their percentages in SnO_2 and $SnTiO_2$ thin films.

Elements (%)	**SnO_2 Thin Film**	**$SnTiO_2$ thin film**
O	76.09	35.82
Sn	23.91	50.62
Ti	0	13.56

3.3. UV-Visible Results

Band gap values of thin films were calculated using the data obtained as a result of UV-Visible measurements.

$$(\alpha h\nu)^n = A(h\nu - E_g)$$

where α is the absorption coefficient, hν is the incident energy of the photon, A is constant, Eg is the band gap energy and n is the value defined by the indirect and direct band gap. Since SnO_2 has a direct band gap in band gap calculations, the n value is used 2[20]. UV-Visible measurements UV-visible absorption spectroscopy and band gap of SnO_2 and Ti doped SnO_2 thin films are shown in figures 5. The calculated optical band gap of undoped and Ti-doped thin films are 3.92 eV and 3.81 eV, respectively. The band gap decreases with Ti doping. The results were found to be compatible with the literature[18].

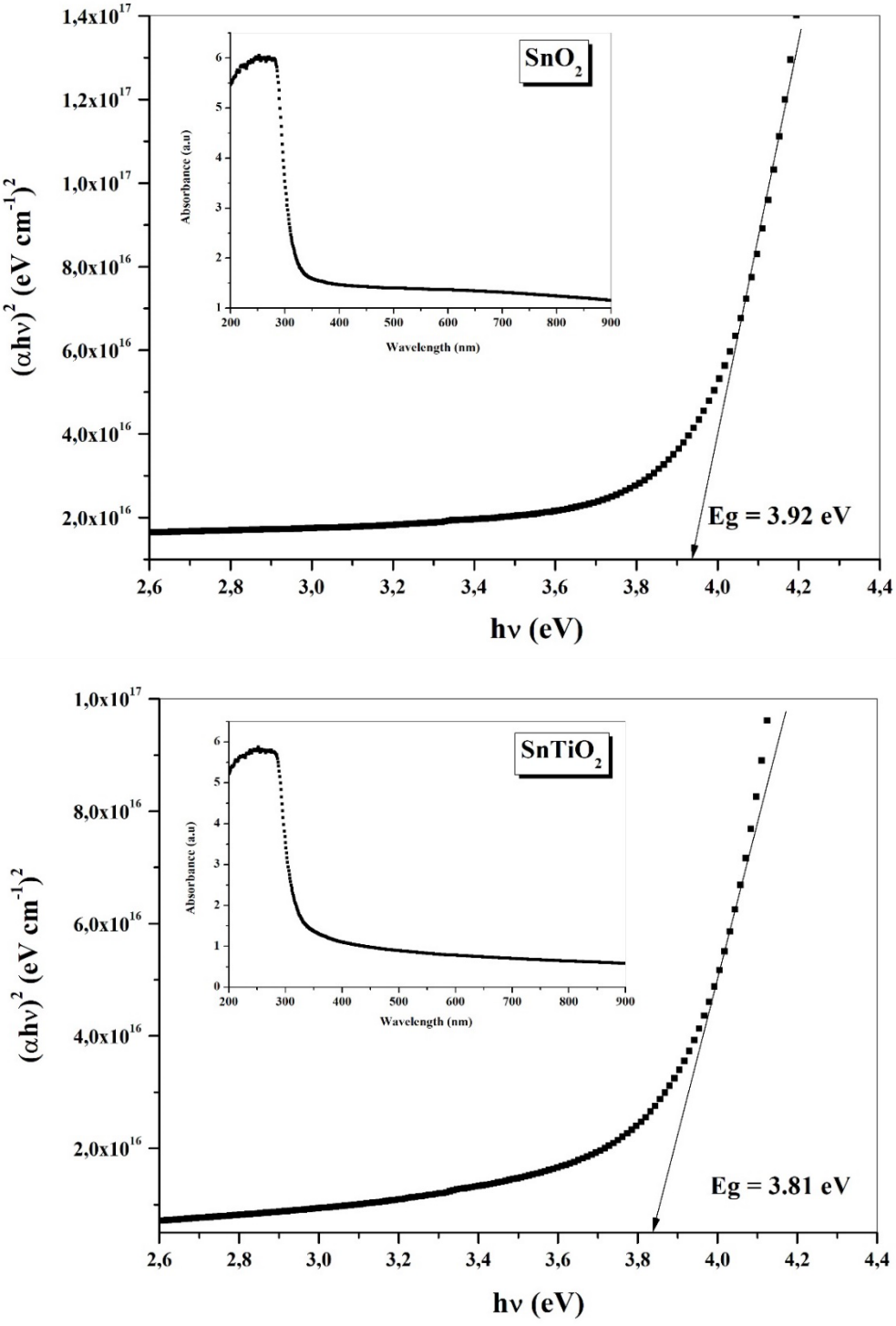

Figure 5. Tauc's plot of optical bandgap for SnO_2, Ti doped SnO_2

Urbach energy plots were given in Figure 6. Band tail energy or Urbach energy characterizes the degree of absorption edge contamination due to crystal lattice irregularity. In short, it is a measure of energy disorder at the band edge. The Urbach Tail values can be calculated with using formula 2 [21].

The equation for Urbach energy is given by,

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

where, α_0 is constant, E is the photon energy, α is the absorption coefficient, and E_u is the Urbach energy. The Urbach energy were obtained by plotting ln α vs. hν. SnO_2 thin film Urbach energy value calculated to 0.43 eV and Ti-doped SnO_2 calculated value is found to be 0.44 eV. This values are almost close. However, the calculated values were found to be compatible with the literature [22][23].

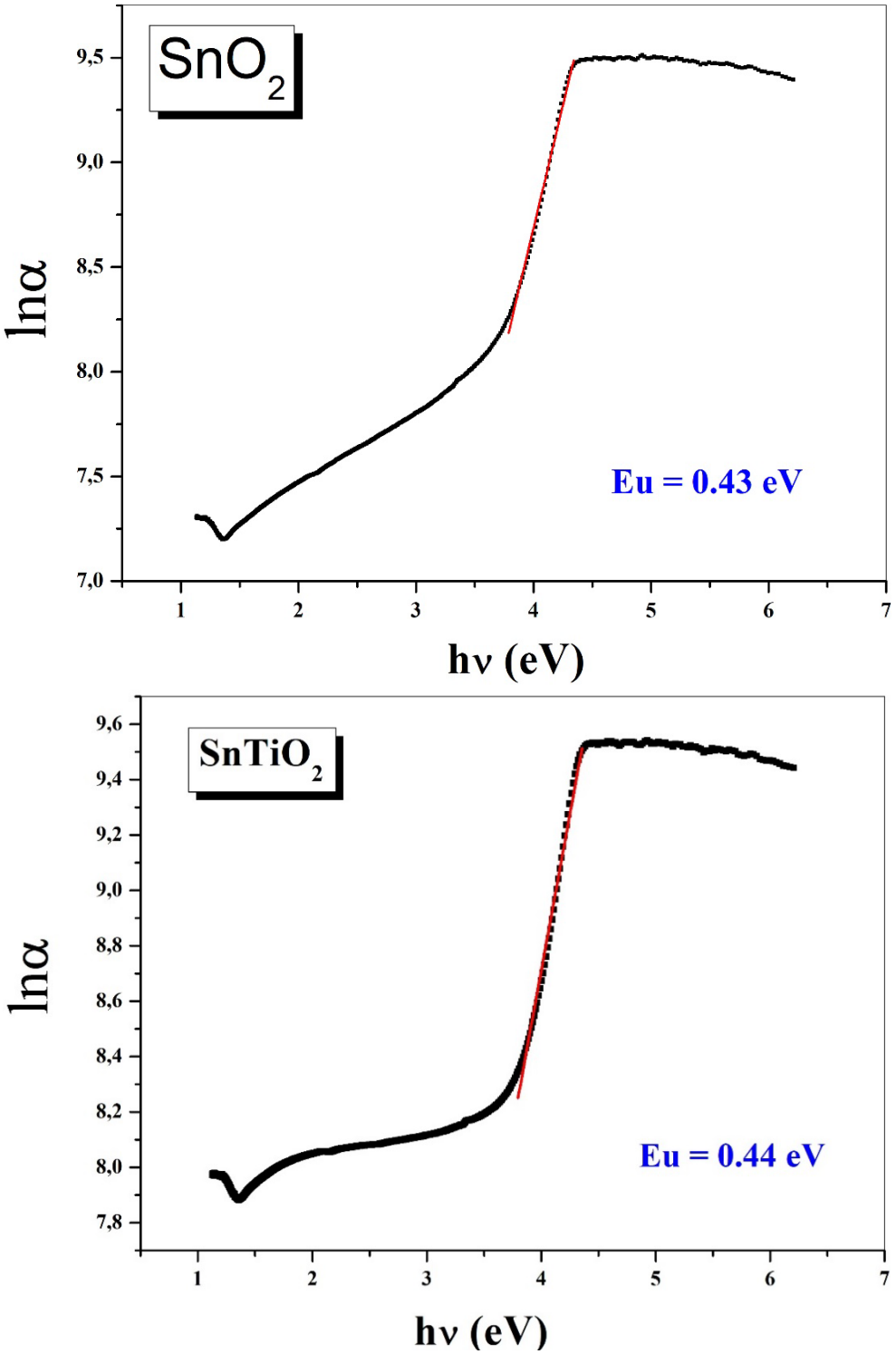

Figure 6. Urbach energy graphs for thin films.

The current-voltage graphs at various temperatures were given in Figure 7. In both graphs, it is seen that the current-voltage curves are linear and symmetrical. Linear curves indicate that thin films have ohmic properties. Although the decrease in the resistance values of the materials with the increase in temperature is clearly seen in the graph, the temperature-dependent resistance change graph in the structure is plotted for a more detailed examination and is given in figure 8.

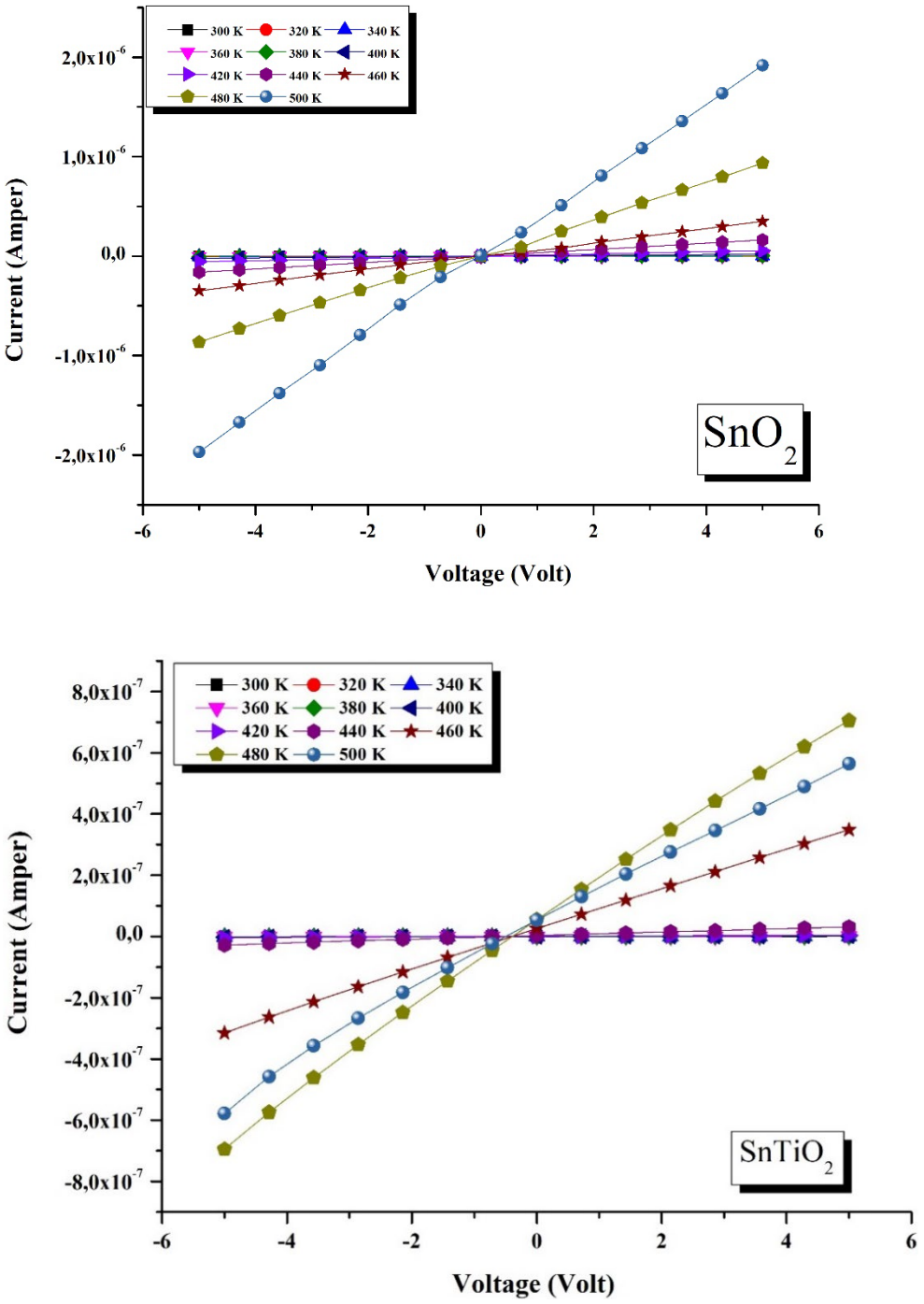

Figure 7. Current-Voltage plots at versus temperatures for SnO_2 and Sn-doped TiO_2 thin films

Figure 8 depicts the Lnρ versus 1000/T plot of the thin films produced. At the graph of the undoped SnO_2 thin film, it is seen that there is a linear decrease in resistivity after 320 °C. The

resistivity value of SnO_2 material at 500 °C was calculated as 9,22 Ω.cm. While it was observed that the resistivity value of the material decreased after 360 °C with titanium additive, the resistivity value of SnO_2 with Ti-doped at 500 °C was calculated as 10,45 Ω.cm.

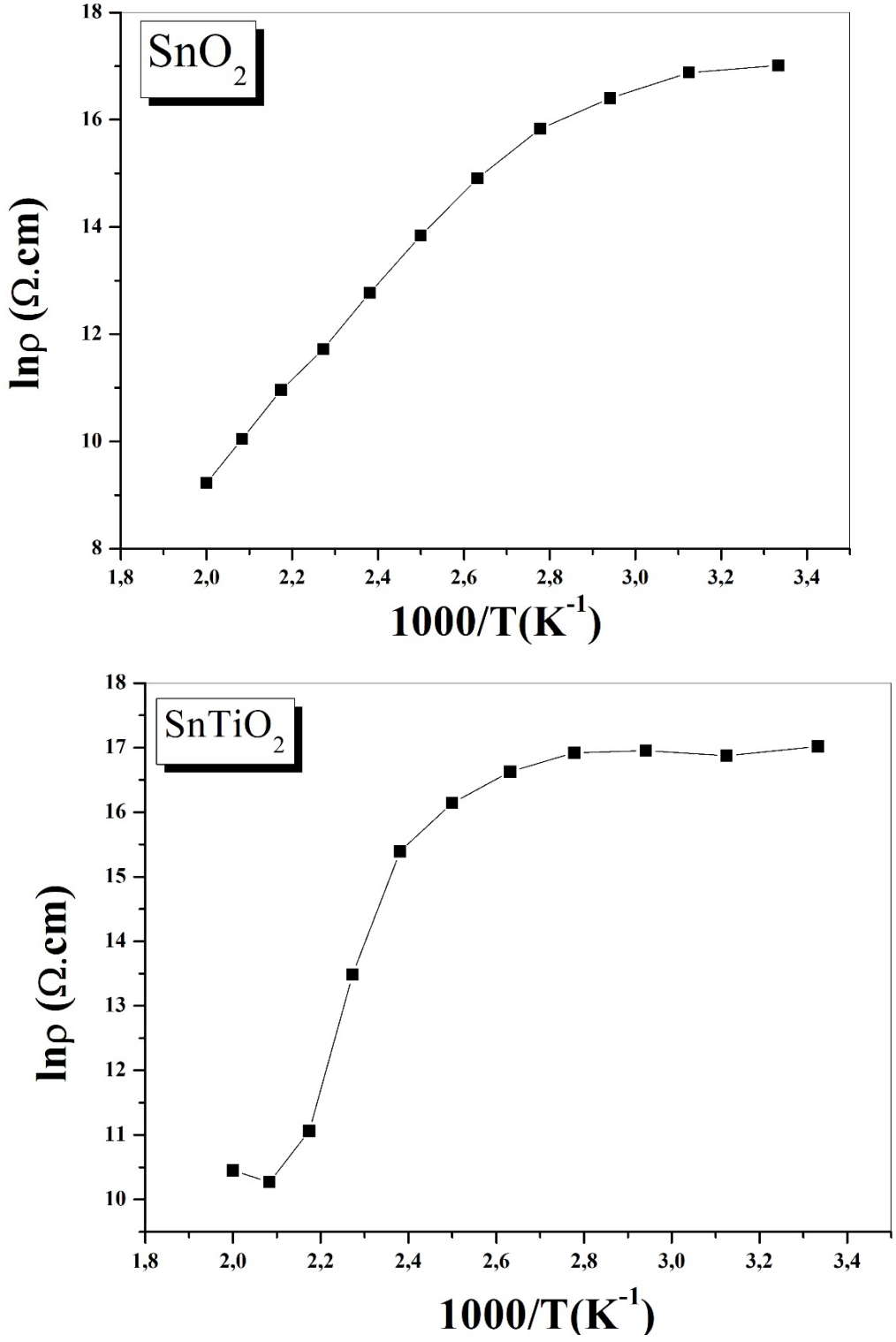

Figure 8. Lnρ-1000/T plots at versus temperatures for SnO_2 and Sn-doped TiO_2 thin films

6. CONCLUSIONS

SnO_2 and Ti-doped SnO_2 thin films successfully growth on the platinum interdigital contacts by SILAR method. The XRD patterns show that the structure transitioned from the semi-crystalline phase to the crystalline phase with the addition of titanium. Band gap energies calculated as 3.92 eV for undoped SnO_2 and 3.81 eV for Ti-doped SnO_2. Urbach energy results are in agreement with band gap values. The thin films current-voltage results have linear curves which indicate that thin films have ohmic properties. The resistivity values at 500 °C were calculated as 9,22 and 10,45 Ω.cm for undoped and Ti-doped thin films, respectively. It has seen that there are changes in the properties of the thin films depending on the use of titanium material. Depending on the usage area, titanium-doped SnO_2 thin films may show promise in commercial applications.

Conflict of Interest

No conflict of interest was declared by the authors.

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