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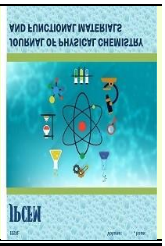

The Synthesis and Opto-Electrical Chracteristics of Cadmium doped Tin Oxide Thin Films by the Sol-Gel Method

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ABSTRACT

In this study, undoped and Cd doped SnO thin films at different atomic rates (0, 2, 4 and 6%) were synthesized by the Sol-Gel method. The changes in the opto-electrical properties of the samples produced with Cd dopant were investigated by means of the UV-VIS-NIR spectroscopy. The effect of Cd doping on the optical properties of SnO films was investigated by spectrophotometric measurements. Optical constants (refractive index, n, and absorption index, k) of the samples were obtained in the wavelength range of 300-800 nm. Dispersion parameters were determined and discussed according to the single oscillator model. The optical band gaps of the samples were calculated using Tuac equation. It was observed that Eg values of the samples increased from 3.57eV to 3.60 eV depending on the Cd dopant. As a result of the investigations, it was determined that Cd doping has significant effects on the optical properties of SnO films and the produced samples can be used in transparent conductive electrode applications, optoelectronic devices, and sensor production.

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sol-gel, spin coating
optical properties
band gap

1. Introduction

Tin is the oldest metal known by the human being. Tin has been used increasingly in several areas such as the coatings, compounds, alloys with high technology from the ancient ages to the present. For instance in the optical and electrical applications, the conductive materials are opaque (light proof), the permeable materials are insulating. However, it is not valid for Tin Oxide (SnO2). Because the Tin oxide is both permeable and conductive. High permeability and semi-conductor characteristics of SnO2 enables keeping the conductivity and permeability properties together. SnO2 is the most common Tin compound. SnO2 is n-type semi-conductor with a wide band rage (3.6-3.8 eV) [1] and has large optical transmittance in the visible region. Moreover, it has several good properties such as low electrical conductivity, high reflection for the infrared lights, high mechanical hardness, chemical and thermal stability [2]. SnO2 has a wide usage area in the Li-ion batteries, gas sensors, solar batteries, optoelectronic devices, light emitting diodes, architectural glasses, aircraft glasses due to these outstanding properties [3]. The structural, physical and chemical properties of the SnO2 can be improved with dopant of with the different transition metals, therefore the usage of these material has gradually increased. Among all transition metals, Cd is among the mostly preferred ones due to the wide solid solubility and a stable compound in the range of various Sn/Cd rate [4]. Several scientific studies have been conducted on this material since SnO2-based nano materials can be produced by many different methods. It is reported in the literature that since SnO2 based materials can be produced by the physical vapour deposition (PVD), chemical vapour deposition (CVP), sol-gel, hydrothermal method, co-precipitation method and spray pyrolysis [5]. In this study, undoped and Cd doped SnO2 thin films were synthesized by the Sol-Gel spin coating method using Tin and Cadmium Acetate. Then, the effect of the synthesizing parameter and Cd dopant on the optical properties of the thin films synthesized was investigated.

2. Experimental Details

All chemicals for this research were analytical purity and were used as received from Sigma Aldrich, without further purification. Tin (II) Acetate ($Sn(CH_3CO_2)_2$), Cadmium Acetate Dihydrate ($Cd(CH_3COO)_2$ $2H_2O$), 2-metoxyethanol ($CH_3OCH_2CH_2OH$) and monoethanolamine (MEA) were used as a starting material, dopant source, solvent and stabilizer, respectively. All solutions were prepared as 1 M, 10 ml. The starting materials with calculated substance quantities were weighed and placed in the test tubes containing the solvent. These mixtures were stirred by the magnetic stirrer at room temperature and then stirred in an ultrasonic mixer. Finally, the solution was stirred at 60 °C for 2 h to obtain the gel form. In the formation of thin films from

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the prepared gels, microscope glass was used as the substrate. Expanding the thin films on the glass substrates was made with the help of spin coater. The coating process was conducted at 1000 rpm for 30 sec. The substrates were placed on a heater pre-set to 150 ˚C and kept for 10 min. At the last stage, the obtained films were heat treated at 600˚C for 1 h. For all dopant rates, the thin films were prepared under the same conditions.

The optical spectra which used for determine the optical properties and to calculate the band gap of the nano electroceramics were obtained with a SHIMADZU UV-vis-NIR 3600 spectrophotometer in the wavelength range from 300 to 800 nm at room temperature.

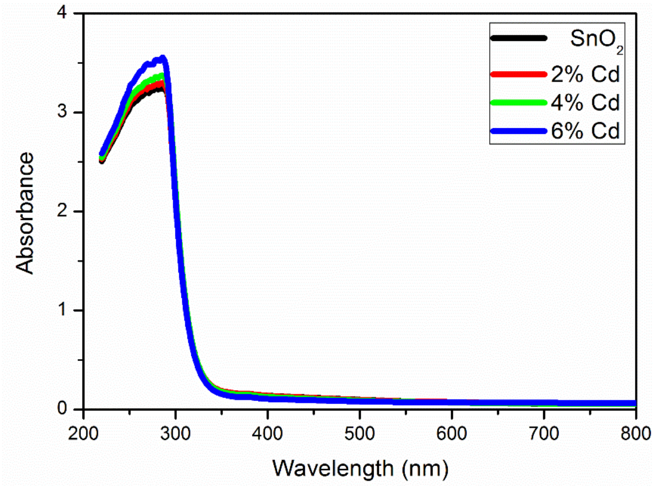

Figure 1. Absorbance spectra of undoped and Cd-doped tin oxide films.

3. Results and Discussion

The absorption spectrum of the prepared thin film samples is presented in Figure 1. In Figure 1, Cd doped SnO thin films exhibit strong absorbing characteristics at 300 nm and lower wavelengths, and a continuous increase in absorption is observed. This can be explained by the fact that photons absorb more at low wavelengths [22].

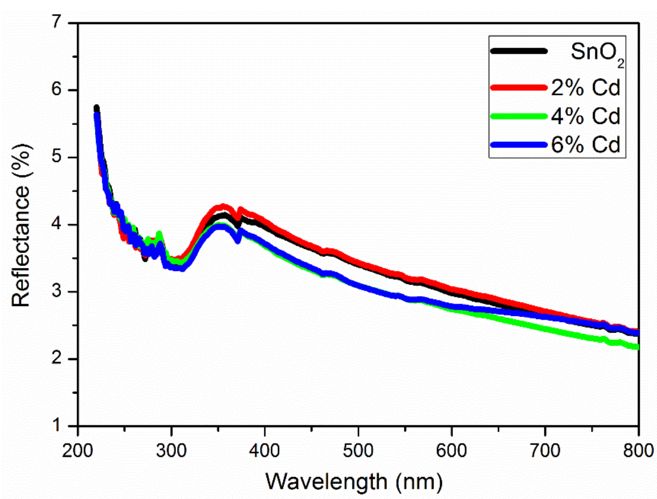

Figure 2: The reflectance spectra of the undoped and Cd-doped thin oxide thin films.

Reflection spectra of undoped and Pd-doped ZnO samples are presented in Figure 2. As shown in Figure 2, the reflection curves of the samples show a peak at a wavelength of approximately 350 nm. This peak varies depending on Cd doping. This confirms that the optical band gaps of the films change with Cd doping. With Cd doping, the reflectance values of the samples decrease compared to the undoped SnO sample. The sample with the highest reflectance value is the 2% Cd doped SnO sample. Furthermore, the reflectance values increased at shorter wavelengths. The reason for this may be the reflection of photons due to the increase in their energy and thus more interaction with electrons, atoms, or crystal molecules.

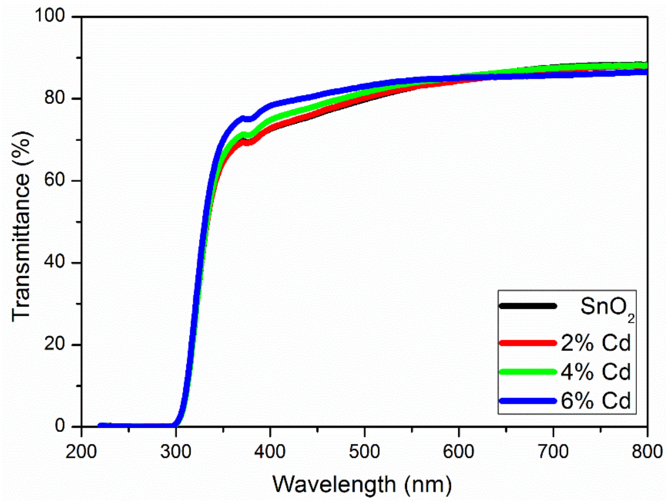

Figure 3. The transmittance spectra of the undoped and Cd-doped tin oxide thin films.

The *T* spectra in the gap of 300-800 nm of the evaluated current samples are presented in Figure 3. The produced samples exhibited permeability of over 80% in the visible region. For all of the samples, the transparency value increases with the increase in the amount of Cd doping compared to the undoped SnO sample. This increase is related to the structural properties of films because changes in permeability depend on the material properties of the films. When evaluated in this regard, the produced samples are good transparent semiconductors. In Figure 3, a sharp absorption band is observed at wavelengths of 300-400 nm in the transmittance spectrum of the thin films. This band edge is decreasing in parallel with the increasing Cd concentration.

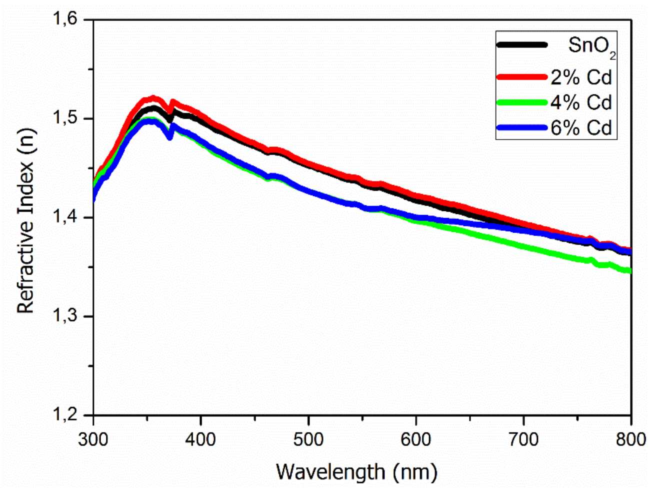

Figure 4. Refractive index (n) of undoped and Cd doped SnO films.

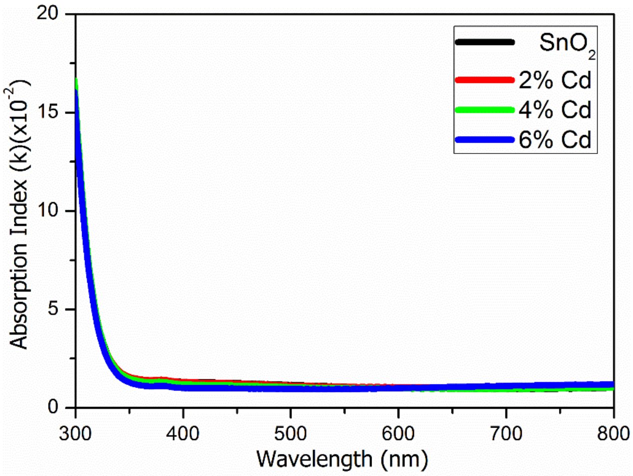

Figure 5. Absorption index (k) of undoped and Cd doped Tin oxide films.

The determination of the refractive index of semiconductor materials, by utilizing the optical properties of the material, plays a vital role in determining the appropriate application area, in the design of the device, and in the accurate modeling. The n and k values of the nanostructured thin films produced by the sol-gel technique were determined from the permeability and reflection spectra. The complex refractive index of SnO-based thin films can be expressed by the following relation [6-9]:

$$\check{n} = n(\lambda) + ik(\lambda) \quad (1)$$

where, n is the real part and k is the imaginary part of the complex refractive index. By using the reflection values of the samples, the following formula called the Fresnel formula is used to calculate the refractive index (n)[10-13]:

$$n = \frac{(1+\mathrm{R})\sqrt{4R-(1-R)^2k^2}}{1-R} \quad (2)$$

The following formula can be used to obtain the damping coefficient (k) [14-16]:

$$k = \frac{\alpha\lambda}{4\pi} \quad (3)$$

where, λ and α represent the wavelength and absorption coefficient, respectively. The change in the n and k values, calculated by the Fresnel formula, with the wavelength is shown in Figure 4 and Figure 5, respectively.

As seen in Figure 5, in general, the refractive index value increases with the increasing wavelength and then decreases. The sample with the highest refractive index value is 2%Cd doped SnO. The gradual decrease in n and k originates from the decrease in surface optical dispersion and optical losses due to the increase in carrier concentration and the decrease in surface roughness as a result of the change in the chemical composition of the samples with doping.

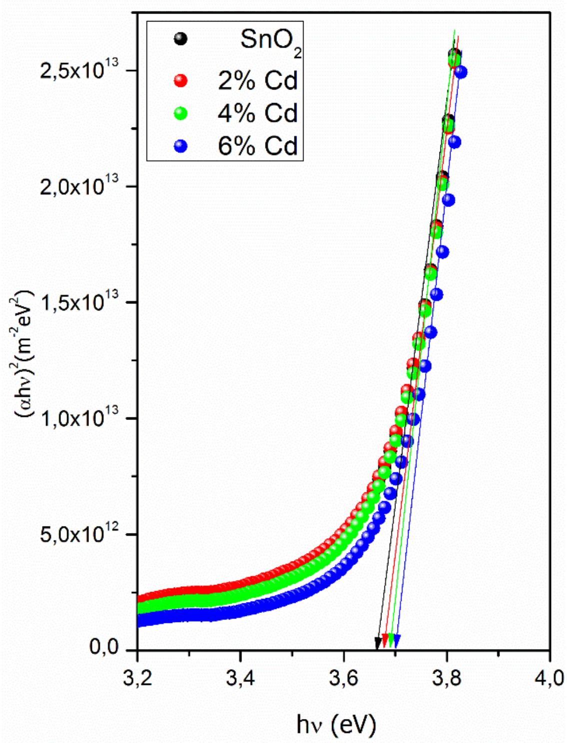

Figure 6. Plotting of $(\alpha h\nu)^2$ versus $(h\nu)$ of undoped Cd doped SnO films.

The optical band gap of the produced semiconductor thin films was determined from the *$(\alpha h\nu)^2$-$h\nu$* exchange graph which is drawn using the basic absorption spectrum. The energy value of the point, at which the direction of the linear part of this change cuts the $h\nu$ axis at $(\alpha h\nu)^2 = 0$, gives the optical band gap of the semiconductor. In the calculation of the band gap, the formula known as the Tauc equation is used [7, 17-19]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (4)$$

here, α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap, and A is the constant. The graphs of $(\alpha h\nu)^2$-$h\nu$ drawn for determining the optical band gap of undoped and Cd doped SnO nanostructured thin films produced are shown in Figure 6. The optical band gaps (E_g) of the samples that were calculated with the help of the curves in Figure 6 were found as 3.67, 3.68, 3.69 and 3.70 eV for SnO, 2, 4 and 6% Cd, respectively. it is observed that the sample with the lowest band gap is undoped SnO. The E_g of the samples increased in general with the increasing Cd ratio.

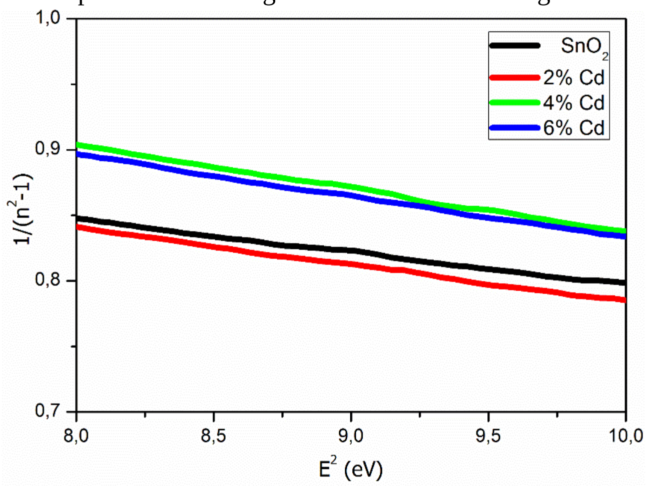

Figure 7. Plots of $(n^2\text{-}1)^{-1}$ versus $(h\nu)^2$ of undoped and Cd doped SnO films.

Refractive dispersion plays an important role in the investigation of optical materials because it is an important factor in the design of devices to be used for image distribution in optical communication. The refractive index distribution of the nanostructured thin films obtained in this study was analyzed by using the Wemple-Didomenico (WD) model.

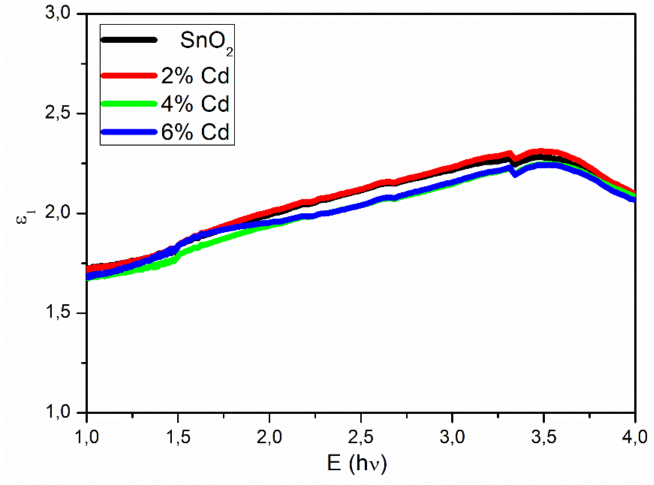

Figure 8: The variation of real parts of the dielectric constant of the undoped and Cd doped SnO thin films with photon energy.

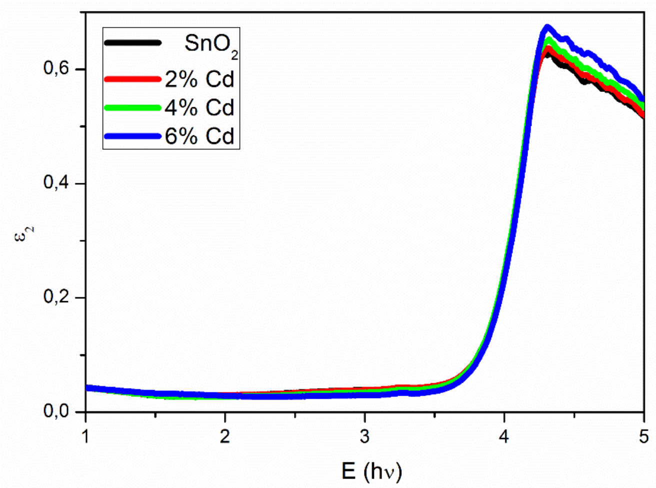

Figure 9: The variation of imaginary parts of the dielectric constant of the undoped and Cd doped SnO thin films with photon energy.

It is known that the polarizability of any solid material is proportional to the dielectric constant. This is related to the position density within the optical band gap. In this context, it is important to examine the real and imaginary parts of the complex dielectric constant. The dielectric constant is defined as $\mathcal{E} = \mathcal{E}_1 + i\mathcal{E}_2$, in other words, as the real and imaginary parts of the complex dielectric constant. This situation is expressed as follows [5, 11, 20, 21]:

$$\varepsilon_1 = n^2 - k^2 \qquad (5)$$

and

$$\varepsilon_2 = 2nk \qquad (6)$$

Dependence of the real ($\mathcal{E}_1$) and imaginary parts ($\mathcal{E}_2$) of the dielectric constant on photon energy ($h\nu$) is shown in Figure 8 and Figure 9, respectively.

When Figure 8 and Figure 9 are examined, it is observed that the real and virtual dielectric constant for all nano-structured thin films changes in the visible region. Conductivity values of the samples increase with the increasing energy. This increase in optical conductivity is thought to originate from electrons stimulated by photon energy . In the graph of $\mathcal{E}_2$ in Figure 9, there is a peak point that reflects the general band structure. This peak presence is due to the photo-excitation process in which electrons are stimulated from the valence band to the conduction band . The optical conductivity of the films has changed due to Cd doping.

4. Conclusion

Undoped and Cd doped SnO thin films were grown on glass base plates with the sol-gel spin coating technique. The effect of Cd concentration properties on optical properties was investigated. Optical spectroscopy spectra show that the optical band gaps of the samples increase with Pd doping that is attributed to the Burstein-Moss shift. The results have indicated that the optical properties of the produced SnO thin films are improved by Cd doping. These highly featured materials produced may be evaluated as potential candidates for use in transparent conductive electrode applications, photovoltaic devices, and optoelectronic devices.

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