Morphological and Optical Properties of Pure and Mg Doped Tin Oxide Thin Films Prepared by Spray Pyrolysis Method

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Abstract: Pure Tin Oxide (SnO_2) and Magnesium (Mg) doped SnO_2 thin films have been deposited onto glass substrates by spray pyrolysis technique at the substrate temperature of 450°C. The doping concentration of Mg was varied from 1 to 9 wt% (with 2 wt% step) while all other deposition parameters such as substrate temperature, spray rate, carrier gas pressure and distance between spray nozzle to substrate were kept constant. The surface morphology and optical properties of the deposited thin films have been studied by Scanning Electron Microscopy (SEM) and UV visible spectroscopy. Average optical transmittance in the 400–900 nm range varies from 18.21% to 58.99% with varying Mg concentration in the film. Maximum band gap value of 3.90 eV is obtained for undoped SnO_2.

Keywords: Thin Films, Spray Pyrolysis, Mg Doped Tin Oxide, Optical Properties, Scanning Electron Microscope

1. Introduction

In recent years, there has been considerable interest in metal oxides because of their many industrial applications, especially transparent conducting oxides (TCO). Tin oxide belongs to a transparent conductive oxide (TCO) family which are the most studied [1]. Transparent conducting oxides are semiconductors produced from a combination of metal and Oxygen. The study of SnO_2 transparent conducting oxide thin films are important due to its unique attractive properties like high optical transmittance, uniformity, nontoxicity, good electrical, low resistivity, chemical inertness, stability to heat treatment, mechanical hardness, piezoelectric behavior, and its low cost. So, SnO_2 is used in solar cells, sensor gas, display devices and in other important applications [2-3].

Tin Oxide is an n-type semiconductor with wide band gap energy (E_g = 3.5-4 eV) [4]. Tin Oxide has a tetragonal structure. Its unit cell contains two Tin and four Oxygen atoms as is shown in Figure 1. The Tin atom is at the center of six Oxygen atoms placed at the corners of a regular octahedron. Every Oxygen atom is surrounded by three Tin atoms at the corners of an equilateral triangle [5, 6].
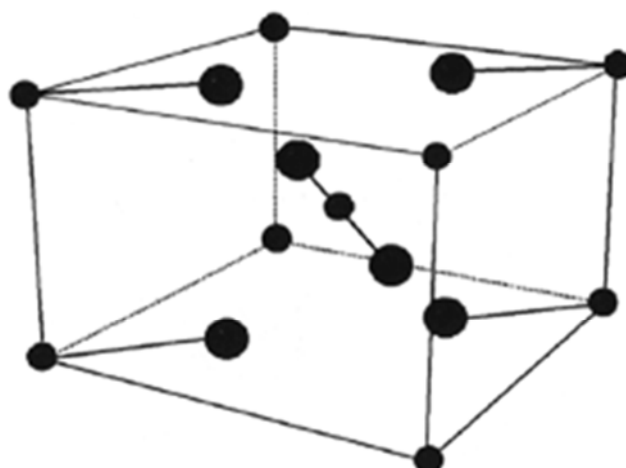

Figure 1. *Unit cell of crystalline structure of SnO_2. big circles represent Oxygen atoms and small circles represent Tin atoms (from [7]).*

The structure of this material in its bulk form is tetragonal with lattice parameters of a = b = 4.737 A° and c = 3.186 °A. However, in thin film form, depending on the deposition technique, its structure can be polycrystalline or amorphous. The grain size is highly dependent on the deposition technique, substrate temperature, post heat treatment and doping level [8].

So nowadays we notice the importance of thin films in our practical life and from this point many techniques in depositing thin films have appeared with high Accurate qualities such as: thermal vacuum evaporation, sputtering, pulsed laser ablation, chemical vapor deposition, chemical bath, dip coating, spin coating and spray pyrolysis [9]. The spray pyrolysis is the simplest, cheapest alternative method to manufacture thin films that is used in industrial applications [10]. There are many characteristics of this method such as: it is suitable for preparing doped and pure thin films because of their simple experimental manufacturing, we can prepare films from high melting temperature materials that we can't prepare in other methods, economic technique because the used devices don't need vacuum or complicated devices, we can add several dopants that are different in concentration, we can change deposition factors (type of used substrates – temperature of substrate – composition of solution – flow rate solution – distance between the spray nozzle and substrate) to get films that have special electrical and optical properties [11].

The undoped and Mg doped SnO_2 thin films were deposited by using a homemade spray pyrolysis apparatus in Albaath university. Starting solution of SnO_2 was prepared by dissolving 1M Stannous Chloride ($SnCl_4$, 99%, Merck, Germany) in 25 ml of Ethanol (C_2H_6O, 99.8%, Sigma-Aldrich, Germany) and distilled water with ratio 7/3 (7 for distilled water and 3 for Ethanol) and with adding few drops of HCl in this solution. For Mg doping, Magnesium Chloride ($MgCl_2$, 98%, Riedel-de haen, Germany) was dissolved in solution as dopant material source.

In order to grow undoped and Mg doped SnO_2 films varied from 1 wt% to 9 wt% by weight percentage (with 2 wt% step), the necessary amounts of these solution were prepared. All spray solutions were stirred to obtain homogenous solutions. The resultant solutions were sprayed on glass substrates (Citoglas, 7.5cm * 2.5cm * 0.1cm). The glass substrates were rinsed with HCl and then cleaned with ethanol. Finally, they were cleaned with distilled water by using an ultrasonic cleaner (Trans sonic 700/H) and then dried with air compressor.

Figure 2 shows the schematic diagram of the spray pyrolysis apparatus. The substrate temperature was fixed as 450°C on hot plate and controlled by temperature control unit. The nozzle to substrate distance was 25 cm and the time for the film deposition was about 15 min. after the deposition operation, the substrates was kept cooled at room temperature. All experiments were done under approximately similar conditions.

2. Experimental Procedure

1. Air compressor   2. Stand   3. Spray nozzle   4. substrate   5. substrate heater   6. Temperature control unit

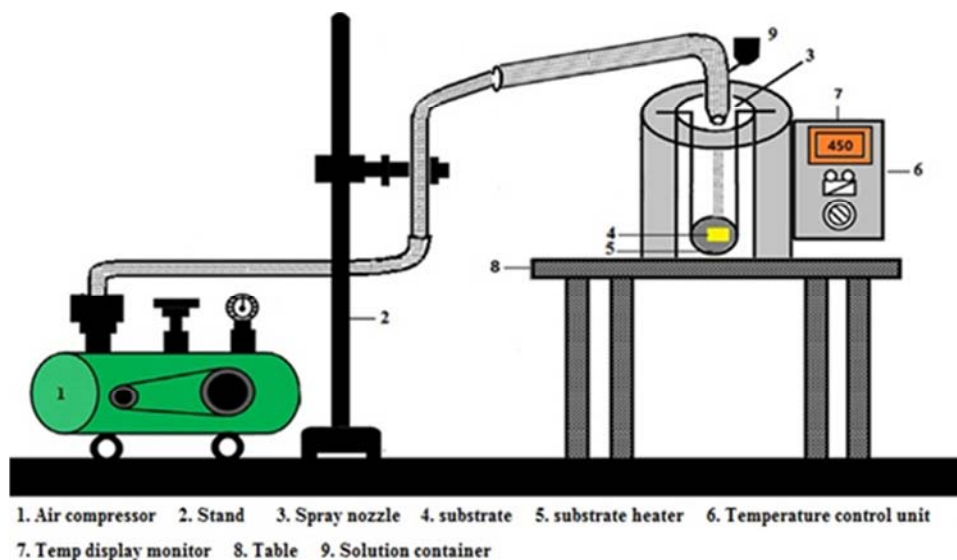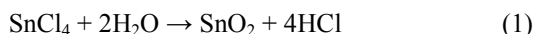7. Temp display monitor   8. Table   9. Solution container

Figure 2. Schematic diagram of the spray pyrolysis apparatus.

A close control of the spraying parameters such as doping, substrate temperature, uniformity of temperature throughout the substrate etc., produces films with the required properties like high visible transmittance and low resistivity.

Generally in spray pyrolysis, the chemical reaction of thin film formation of SnO_2 is as follows [12]:

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl \qquad (1)$$

3. Results and Discussion

3.1. Optical Properties

The optical transmission spectra of the films (T%), were recorded using a UV–VIS–NIR double beam spectrophotometer (Jasco V-570). In order to compare the

transparency of SnO$_2$:Mg thin films with various Mg-doping levels, six samples (0, 1, 3, 5, 7 and 9 wt%) were selected and then their optical spectra in the VIS–NIR region were measured (400 – 900 nm). The optical transparency and absorbency of SnO$_2$:Mg thin films for various Mg-doping levels are shown in Figure 3 and Figure 4 respectively.
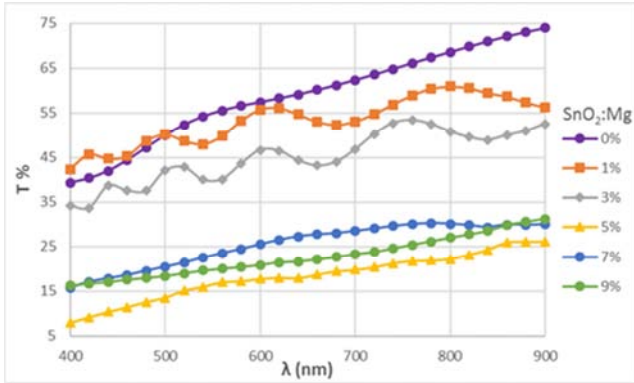

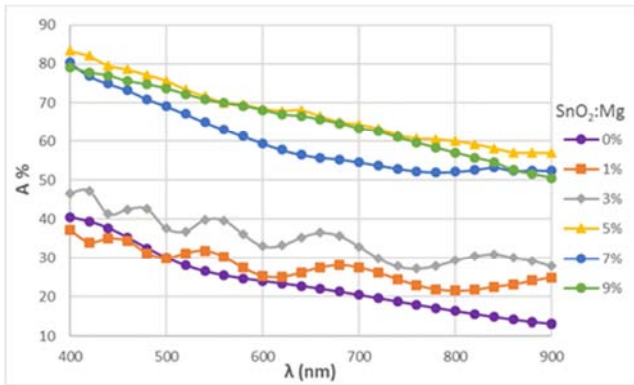*Figure 3. Optical transmission spectra of the SnO$_2$:Mg films.*

Figure 4. Optical absorption spectra of the SnO$_2$:Mg films.

The average optical transmittance of samples in the wavelength region (400–900 nm) decreases with values (58.99%, 53.34%., 45.14%, 25.44%, 22.63%) by increasing Mg – doping level (0, 1, 3, 7, 9 wt%) respectively, except Mg-doping level 5wt% (18.21%).

The interpretation as the film with 5wt% doping level which has the lowest transmittance and the highest absorbance will be explained by scanning electron microscope graphs.

The optical absorbance values are calculated using the relation [13]:

$$A = Log(1/T) \qquad (2)$$

Optical band gap (E$_g$) of SnO$_2$ and Mg: SnO$_2$ thin films was estimated using the relation in the region [300-900 nm] [13]:

$$(\alpha h\nu)^2 = A(h\nu - E_g) \qquad (3)$$

where A is a constant, α is the absorption coefficient and hν is the photon energy.

The absorption coefficients (α) were determined by means

of the optical transmittance spectra using the relation [14]:

$$\alpha = (1/d)\ln(1/T) \qquad (4)$$

where d is the thickness and T is the transmittance of the film at a particular wavelength.

The direct allowed transition energy of the prepared films was estimated from the plot drawn between $(\alpha h\nu)^2$ and energy of the photon by extrapolating in order to extend the linear portion of the curve to reach the photon energy axis. The E$_g$ values are in the range of 3.76–3.90 eV (Figure 11). The optical band gap of undoped SnO$_2$ thin film is 3.90 eV and it decreases with increasing Mg doping concentration except 5wt% doping level whereupon E$_g$ increases up to 3.88eV and then it decreases gradually again (5 to 9 wt%). Undoped SnO$_2$ thin film has the maximum band gap (3.90 eV) and the low band gap (3.76 eV) is obtained for 9 wt% Mg:SnO$_2$ thin film.
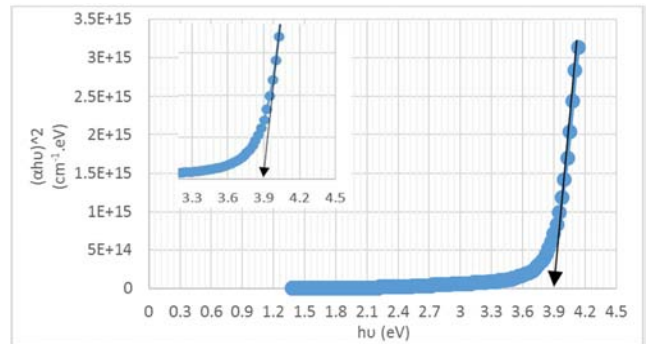

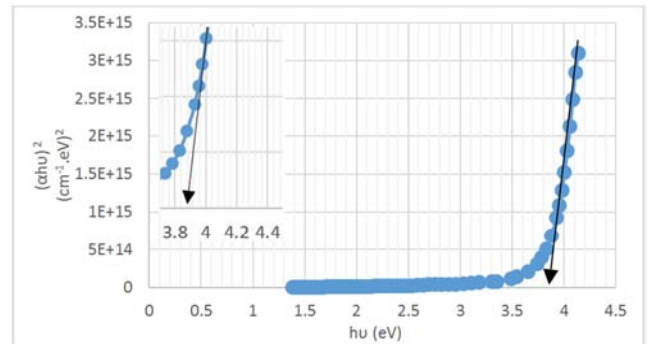*Figure 5. The variation of $(\alpha h\nu)^2$ versus hν for undoped SnO$_2$ film.*

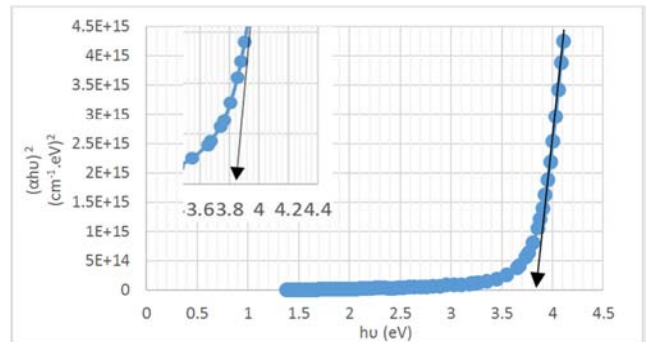*Figure 6. The variation of $(\alpha h\nu)^2$ versus hν for Mg:SnO$_2$ (1wt%) film.*

Figure 7. The variation of $(\alpha h\nu)^2$ versus hν for Mg:SnO$_2$ (3wt%) film.
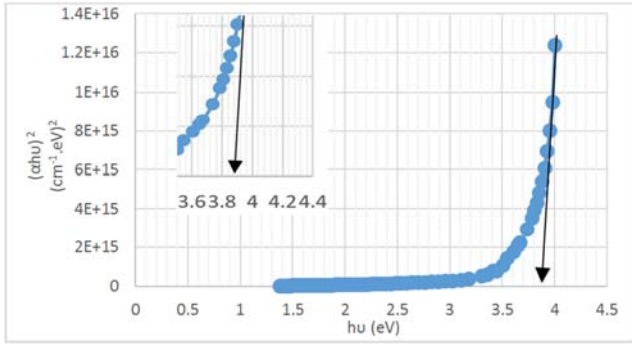
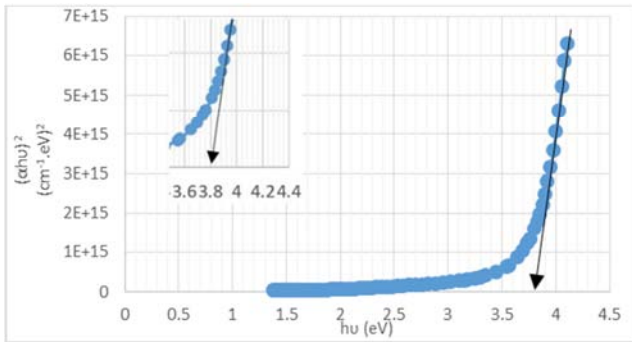**Figure 8.** *The variation of (αhv)^2 versus hv for Mg:SnO$_2$ (5wt%) film.*

Figure 9. *The variation of (αhv)^2 versus hv for Mg:SnO$_2$ (7wt%) film.*
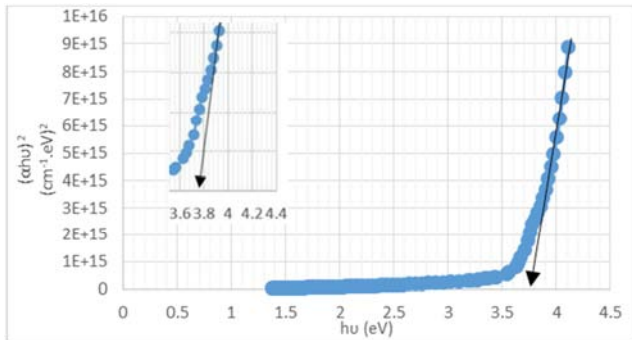

Figure 10. *The variation of (αhv)^2 versus hv for Mg:SnO$_2$ (9wt%) film.*
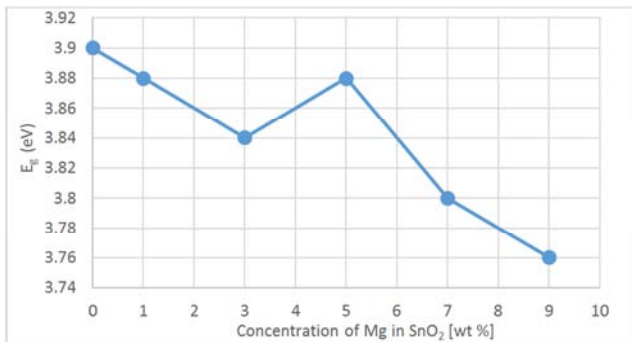

Figure 11. *The variation of optical band gap with different concentrations of Mg dopant.*

3.2. SEM Analysis

The undoped and Mg doped SnO$_2$ thin films were studied by scanning electron microscope (Quanta 200) with magnification 1600x. SEM micrographs of undoped and Mg doped SnO$_2$ thin films are shown in Figure 12.
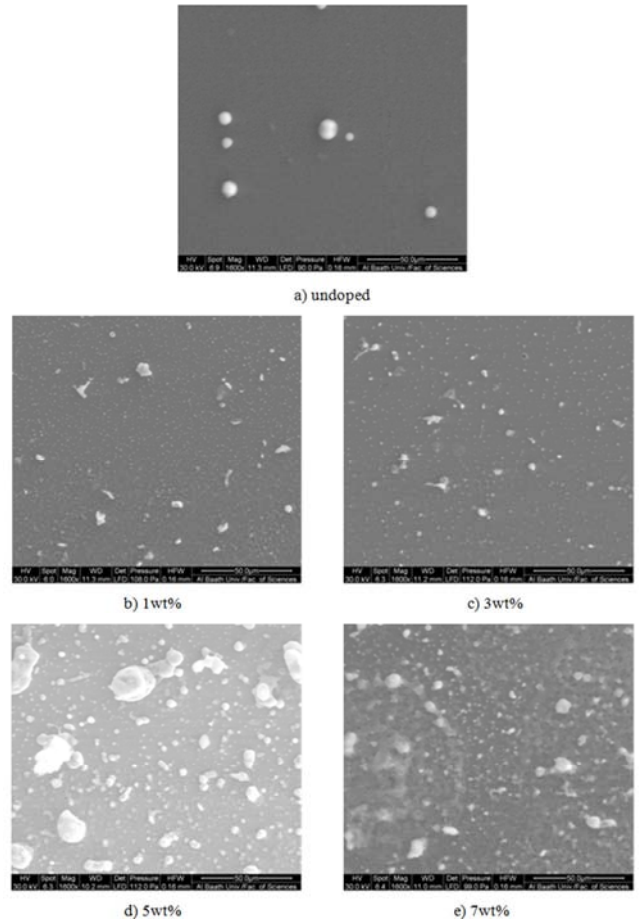

Figure 12. *SEM micrographs of (a) undoped, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, (e) 7 wt% Mg doped SnO$_2$ thin films.*

It can be observed from Figure 12, Figure 3 and Figure 4 with increasing grains size that the transmittance decreases and the absorbance increases. This explains the fact that 5wt% film has the lowest transmission and the highest absorption.

4. Conclusions

Effect of Mg-doping on the properties of SnO$_2$ thin films prepared by the spray pyrolysis method was studied by varying the dopant concentration. The Mg-doped SnO$_2$ films were deposited on glass substrates with dopant concentrations ranging from 0 to 9 wt% (with 2 wt% step). The average transmittance of the undoped and doped SnO$_2$ films decreases with increasing Mg concentration except 5wt% doping level. The optical band gap of undoped SnO$_2$ thin film is 3.90 eV and it decreases with increasing Mg doping concentration except 5wt% doping level where E$_g$ increases up to 3.88 eV and then it decreases again with increasing dopant concentration till 3.76 eV at 9 wt%. SEM micrographs show that the grains have different sizes and they also confirm the relation between decreasing in transmittance values and increasing in grains size.

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