Structural, Morphological and Optical Characterization of Tin Doped Zinc Oxide Thin Film by (SPT)

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Abstract.
Thin films of tin doped zinc oxide (ZnO: Sn) with thickness 300 ± 30 nm prepared by spray pyrolysis method at substrate temperatures of 400°C. The structure, surface morphological and optical properties were studied, for Two weight ratios of doping (2 and 4) wt %. The results of X-Ray measurements showed that all deposit samples have a polycrystalline pattern with hexagonal wurtzite type structure. The films crystallites were oriented along (002) plane. The morphology measurements obtained by scanning electron microscope (SEM) showed that there is a change in the surface texture by the increasing of tin weight ratios with the rate of porosity of the surface when treating with 4wt %. The measurement of Atomic force microscopy (AFM) revealed nano particles sized and the roughness of the surface decrease to increase deflection, while optical measurements showed a decrease The energy gap of the models that are expected in the undoped samples.

Key word: Thin films, ZnO: Sn, Spray pyrolysis, photon energy graph, Grain size, X-Ray, SEM, AFM.

1. Introduction
Recently, many researchers have direct their research on metal oxide nanostructures due to their safe, easy, environmentally friendly [1], cheap synthesis procedure and technological applications [2]. Metal oxide nanostructures such as (zinc, indium, copper and titanium) oxides can be synthesized in various morphologies such as nanoparticles [3], nano cubes [4], nanorods [5], nano wires, nano belts, tetra pods, flower like using various physical and chemical routes. Also, they can be fabricated on different type of substrates such as semiconductors, metals, crystalline, amorphous and polymers. [6] Metal oxides, such as
ZnO, SnO$_2$ and In$_2$O$_3$ have been found to be very useful for gas-sensing applications, in which the surface conductivity changes depending on the absorption of the absorbed gas which makes the membrane suitable for applications of gas sensors [7]. The development of nanostructures fabrication These methods have a great deal in the applications of Nanoscience and nanotechnology. Several methods have been investigated for nanostructures materials [8]. These include sole-gel [9], hydrothermal [10], thermal evaporation [11], electro spinning [12], Anodization, solid-state chemical reaction [13], chemical vapor deposition [14], RF sputtering [15], molecular beam epitaxy [16], vapor-phase transport [17].

The dependent of nano material properties on the size and shape, raising expectations for a better performance is generally a consequence of large surface area and effective percentage of active surface atoms [18]. The size control is within the nanometer, the shape, the chemical composition and the precise structural structure. One of the important factors in understanding the unique qualities of nanoparticles. Thus adding new and unique properties in scientific applications. [19] They represent an important class of materials in the development of devices that can be used in various applications such as: optoelectronic device, photo-thermal therapy, bio sensors, solar cells, cooling system, nano Photonics devices, antibacterial against, catalysis, cancer treatment, chemical sensor [20].

Metin Yurddaskal and et.al. Sn doped ZnO nanoparticles were synthesized through flame spray pyrolysis (FSP) technique. The Sn dopant concentrations were 1, 3, 5, 7 and 9 at. % in producing ZnO nanoparticles The models showed that the photochemical activity of the structure of the zinc oxide was increased after cyanide abrasion and that the best cyanide abrasion rate was 1%, where the increase was more than the standard value. The performance of the optical coating was decreasing. The best performance was explained based on the generation of the cargo space [21]. Nadia Chahmat et. al. The optical transmission increases and becomes important for $\lambda > 380$ nm, which proves that the ZnO thin films Sn doped have an excellent transparency in the visible game while the optical gap is reduced with increasing in Sn/Zn doping ratio. The study showed high penetration in the visual region with a decrease in the value of the energy gap at the increase of the Sn deflection in addition to increasing the reflection intensity of the level (002) and increase the crystalline volume with the increase of deflection Sn, and the energy gap increased at a rate almost constant to 8% Energy gap values [22]. The aim of this work is to study the morphology and optical properties of tin doped zinc oxide thin films.

2. Materials and Methods

Chemical spray pyrolysis was used to prepare ZnO thin films doped with Sn. The films prepared from O.1 M Zinc Chloride (ZnCl$_2$) (provide by Shubha Chemicals Industry –India) was dissolved in deionized water to prepare undoped ZnO. The doping agent (Sn) gets from SnCl$_2$ (provide by Sigma-Aldrich – German) that dissolved in deionized water. Few drops of HCl were added to the solution in order to get clear solution. The films were prepared on substrate glass slides. The preparation conditions that used to prepare the films are: Substrate temperature 400 OC, distance between the nozzle and the substrate was 28 cm, spraying period 8 s lasted by 60 s to avoid cooling, spray rate was 4ml/min, and Nitrogen gas was used as a carrier gas. Thickness of the films was estimated by gravimetric method and it is about 300 ± 30 nm. The XRD (SHIMADZU XRD-6000) was used to determine the nature of the film structure, while the SEM (Jeol JSM 6335F) and AFM (AA3000 SPM) that used to determine the morphology of the films. UV-Visible photometer (UV SPECTROPHOTOMETER SHIMADZU MODEL UV-1800) used to determine the absorption spectra to calculate the optical properties.
3. Results and discussion

Figure (1) shows the X-ray diffraction pattern of the pure ZnO and Sn doped with 2wt % and 4wt %, and prepared by the chemical spraying on the substrate of glass. It is noted that all the samples showed hexagonal wurtzite have a polycrystalline diffraction pattern and the Sn doping process does not result in any significant change in the microstructural, which may be due to variation in the ionic radius of Zn$^{2+}$ and Sn$^{2+}$ which made the substitution of Zn$^{2+}$ easy with Sn$^{2+}$ and no remarkable shift in the diffraction angle to the substitution of zinc and tin in the hexagonal structure [21] and that all reflections fall within the international card for zinc oxide and tin oxide is No. 36-1451 and No. 41-1445 respectively. The reflection in the pure and doped models is the same as the reflection (002) corresponding to the angle $34.56^\circ$. Note that the intensity of the reflection increases with the increase of the intensity of refraction up to 4wt %, and that the crystallite size of this reflection ranges from 43.53 nm to 46.67 nm according to Shearer equation (1) [22]. The attached form (1-a) represents the magnifying image of the reflection (002). The reflection (112) is observed at the angle $67.68^\circ$, which disappears with the increase of deflection in the models that are disrupted by 2wt % and 4wt %. A number of secondary reflections are observed in the pure and viscous models (100), (101), (102), (110), (103), 32.05$^\circ$, 36.33$^\circ$, 47.71$^\circ$, 56.58$^\circ$, 62.96$^\circ$, respectively. The reflection (301) at angle 66.10$^\circ$ represents the phase SnO$_2$ according to card No. 41-1445. Microstrain ($\varepsilon$) has calculated by equation (2) [23]. Microstrain ($\varepsilon$) drop And resulting from the displacement at the sites of the atoms of the sites centered. Figure (2) shows the Microstrain in the films, This increase is due to increased doping concentration. Dislocation density ($\delta$) is a deficiency in the crystal connected with the misregistry of the lattice in one portion of the crystal with another portion. The dislocation density ($\delta$) has been calculated by using the equation (3) [23] and Figure (2) shows the dislocation density decreases as the doping concentration.

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D = \frac{k \lambda}{\beta \cos\theta} \quad (1)
\]
\[
\varepsilon = \frac{\beta \cos\theta}{4} \quad (2)
\]
\[
\delta = \frac{1}{D^2} \quad (3)
\]
Figure 1. X-Ray diffraction pattern for pure ZnO, 2wt % and 4wt % Sn doped (a) Magnifying image of the reflection (002).
Figure 2. Grain size, Microstrain and dislocation density for ZnO:Sn

Figure (3) represents the images of the SEM and the inset images of the AFM. The accumulation distribution chart of atoms on the surface shows that the atoms in the images of AFM grow in the form of columns of the surface of the films and the average of height 32.65 nm and average diameter was about 70 nm – 80 nm. The distribution of these columns is regular in the pure model and with increasing doping concentration, it was noted that the columns are decrease in height and the diameter of these columns is increased, which corresponds to the XRD measurements and the average size of the particles ranges from 60 nm to 80 nm, when increasing the doping concentration from pure to 4 wt wt %. From the measurements of the accumulation distribution chart of the atoms in the inset figure (3), the particle size is 60 to 80 nm. From the SEM images, much cannot be observed from being a micrometer scale. In these measurements it is difficult to determine the nanostructure.
Figure 3. SEM image and the inset image of AFM and accumulation distribution chart of pure and Sn doped ZnO.

Figures (4,a) show Transmittance as against wavelength graph. The measurements of transmittance of pure and tin doped models showed that the transmittance is located in the visual region at the limits of percentage transmittance (50 to 80) % and in the ultraviolet region at the rate of the percentage transmittance (70 to 81) % as the doping concentration increasing up to 4wt % due to the improvement in crystallization and an increase in the roughness of the surface by increasing the diameter of the developing columns on the
surface. From the relationship (4) representing Tauc formula [24,25], absorption coefficient $\alpha$ is related to the energy gap of a semiconductor as:

$$\alpha = \frac{2.303 \cdot \left( \frac{A}{t} \right)}{\Delta t}$$  \hspace{1cm} (4)

Here, “$t$” represents the thickness of the films

$$\left( \alpha h\theta \right) = b \left( h\theta - E_g \right)^n$$ \hspace{1cm} (5)

Where $h\theta$ is the photon energy, $n$ is an index related to the density of state ($n=1/2$ for direct transition and $n=2$ for indirect transition) and $E_g$ is the optical band gap of the semiconductor films. Fig. (4,b) shows the plot of $(\alpha h\theta)^2$ vs photon energy, the extrapolations of the straight portion of the graphs were used to estimate the band gap of pure and Sn doped ZnO film, which decreases from 2.17 eV to pure models to 2.35 eV of the model is 4wt %. The reason is due to the increase of the intensity of reflection with increasing crystallization and to the low levels of secondary in the energy gap reduces the level Fermi Energy.

**Figure 4.** (a) Transmittance as against wavelength graph (b) $(\alpha h\nu)^2$ versus photon energy graph for pure and Sn doped ZnO thin films

**4. Conclusion**

The results of XRD obtained for Sn doped zinc oxide with different concentration indicate the absence of change in the phase of zinc oxide, but with an improvement in crystallization and an increase in crystallite size from 43.53 nm in the undoped sample to 46.67 nm for 4 wt% sample, The images of AFM shows grow in the columns of the surface about 70nm – 80 nm in height and regular distribution of these columns are in the pure model and with increasing doping concentration, and the columns are decrease in height and the diameter ranges from 60 nm to 80 nm, the band gap of pure and Sn doped ZnO film decreases from 2.59 eV to pure models to 2.0 eV of the model is 4wt %.
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