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Sn doped ZnO Thin Films Prepared by Pulsed Laser Deposition for Photovoltaic Applications

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Abstract: The objective of the present research work is to prepare various compositions of Sn doped ZnO thin films on a single crystal silicon (1 0 0) substrate via pulsed laser deposition technique, for investigation of valuable structural and optical properties. For this purpose, targets of pure and Sn-ZnO were prepared in the form of compressed, sintered and densified pellets by solid state reaction method. A KrF excimer laser (λ=248 nm, τ=20 ns, E_l = 20 mJ and Φ_l=1 J/cm^2) was employed to deposit various thin films on silicon substrate. Post deposition annealing of all the Sn-ZnO thin films was carried out at 300 ˚C, and their structural and optical properties were investigated by X-ray diffraction (XRD) and Spectroscopic Ellipsometry (SE), respectively. It was observed from XRD results that ZnO (0 0 2) and SnO_2 (2 1 0) were preferred planes orientations for all the Sn-ZnO thin films. The presence of SnO_2 peak showed that SnO_2 was epitaxialy included in ZnO matrix. The crystallite size of all the thin films was measured with the help of Scherrer formula and it was decreased with the increase of Sn concentration in ZnO. Spectroscopic ellipsometry analysis showed that the values of refractive index *(n)* and extinction coefficient *(k)* were increased and optical band gap of the thin films was decreased with addition of Sn contents in ZnO thin films. The modification in band gap energy could be attributed to the crystallites size of the thin film; the decrease in crystallite size decreased the band gap energy, which makes the thin films valuable for variety of photovoltaic applications.

Keywords: Pulsed laser deposition; KrF excimer laser; thin films; structural and optical properties

1. Introduction

ZnO is an n-type semiconductor from II-VI group having wurtzite crystal structure, with direct and wide band gap of 3.37 eV. It is widely used in optoelectronic devices especially for blue and UV emissions, like in laser diodes [1, 2]. ZnO thin films have exciton binding energy 60 meV which is much greater than the binding energies of gallium nitride (21 meV) and zinc sulfide (20 meV), and this property makes it preferable to gallium nitride and zinc sulfide. Excitonic devices are fabricated from ZnO thin films due to its higher values of excitonic energies at room temperatures [3]. ZnO thin films are widely used in transparent conducting coatings, varistors, solar cell panels and thin film gas sensors [4]. Due to all these distinctive applications, ZnO thin films have drawn much attention among the modern researchers and scientists.

Different techniques like molecular beam epitaxy (MBE), sol-gel method, metal organic chemical vapor deposition (MOCVD), radio frequency (RF) sputtering, pulse laser deposition (PLD), etc. can be used to prepare stichiometric and epitaxial thin films of ZnO [5]. PLD is used as a deposition technique due to its matchless advantages like stoichiometric deposition, an essentially clean process and simple control of experimental parameters. During deposition of ZnO thin films, the parameters such as laser light fluence, pulse length, substrate surface temperature and back ground pressure have large affect on the ZnO thin film crystalline quality [6]. The optical properties of ZnO thin films can be tuned by fundamental doping process and mostly transition metals are used for this purpose [7]. In present research work, Sn doped ZnO thin films with different Sn proportions were deposited on Si (1 0 0) substrate and their structural and optical properties were investigated.

2. Experimental Work

The targets with compositions $(ZnO)_{1-x}(SnO_2)_x$ (x = 0.00, 0.01, 0.02, 0.04) were synthesized via solid state reaction method. For this purpose, the required proportions of ZnO and SnO_2 in powder form having purity level 99.99% were mixed together and grinded properly. The uniformly mixed powder was calcined at 800 °C for 8 hours and the final product was further grinded and collected into a steel dye. Mechanical hydraulic press was used to compress the powder material at 150 bar to obtain high dense pellets. These pellets were sintered at 900 °C for 10 hours to make them more compact.

The thin films were deposited on single crystal silicon (1 0 0) substrates using KrF excimer laser (λ=248 nm, τ=20 ns, E_l = 20 mJ and Φ_l=1 J/cm^2). KrF excimer laser was focused on to the target surface at an angle of 45˚ using UV lens having a focal length of 40 cm. A single crystal silicon (1 0 0) substrate having dimensions 1×1×0.2 cm^3 cleaned with acetone in ultrasonic bath, was placed parallel to the target material at distance of 18 mm. The base pressure ≈10^{-5} mbar was created inside the PLD chamber using rotary and turbo molecular pumps. A DC Stepper motor was used to rotate and translate the target material during deposition for uniform ablation from the target surface, which helped to avoid the crater formation on the target's surface. The schematic diagram of the experimental setup has been shown in Fig. 1.

Ten thousand laser pulses were incident on each target to irradiate them during the thin film deposition, and the temperature of the substrate surface was kept at 300 °C for all depositions. Post deposition annealing was performed at 300 °C for 2 hours to improve the crystallinity of the thin films. The structural analysis of thin films was carried out using X-ray diffractometer (XRD) whereas the optical properties were studied by spectroscopic ellipsometry (SE).

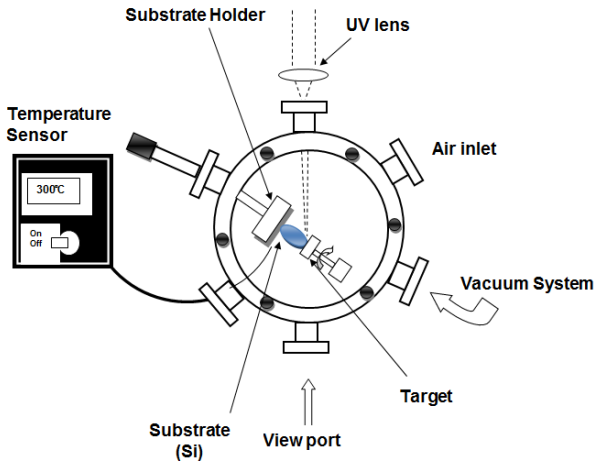

Fig. 1: Schematic diagram of Experimental Setup

3. Results and Discussion

3.1 Structural Analysis

The structural properties of Sn-ZnO thin films were investigated by X-ray diffractometer (D8 discover, Bruker Germany). Fig. 2 shows diffraction patterns of Sn doped ZnO for all deposited thin films, and it is clear from the Figure that all the films have ZnO (0 0 2) preferred plane orientation, like single crystal structure. The c-parameters of the silicon substrate (c = 5.430 Å) is very close to the c-parameters of the ZnO (c = 5.206 Å) which makes the growth of ZnO (0 0 2) plane favorable. A peak for SnO_2 (2 1 0) plane was observed in XRD patterns, given in Fig. 3, showing that SnO_2 was epitaxialy present in ZnO thin film matrix.

The average value of crystallites size was calculated using Scherrer formula [8, 9]:

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

In this relation, k is shape factor having value ≈ 0.94, λ is wavelength of the Cu K_α (1.5414 Å), β is FWHM and θ is the Bragg's angle.

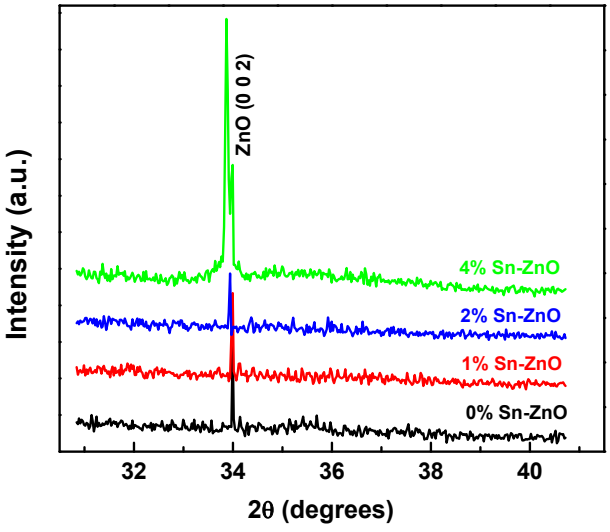

Fig. 2: XRD patterns of compositions $(ZnO)_{1-x}(SnO_2)_x$ (x = 0.00, 0.01, 0.02, 0.04)

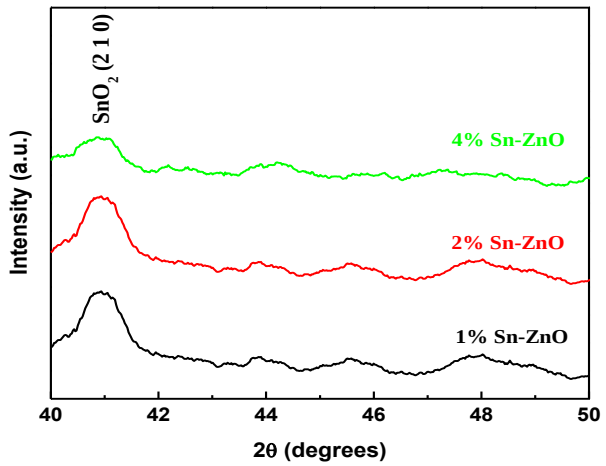

Fig. 3: XRD patterns showing plane (2 1 0) for Sn in Sn-ZnO thin films

Figure 4 and 5 show the variation in FWHM and crystallites size of ZnO and SnO_2, respectively. The value of FWHM was increased and that of crystallite size was decreased with addition of Sn contents in ZnO thin films, which can be attributed to the production of more lattice defects and lattice strains in the thin films [10].

The amount of defects produced in Sn-ZnO thin films can be estimated by calculating the dislocation line density $'\delta'$ which is related to particle size, as follow [10]:

$$\delta = \frac{1}{D^2} \qquad (2)$$

This relation shows that dislocation line density is increased with decrease in crystallite size, as was observed in the recent case.

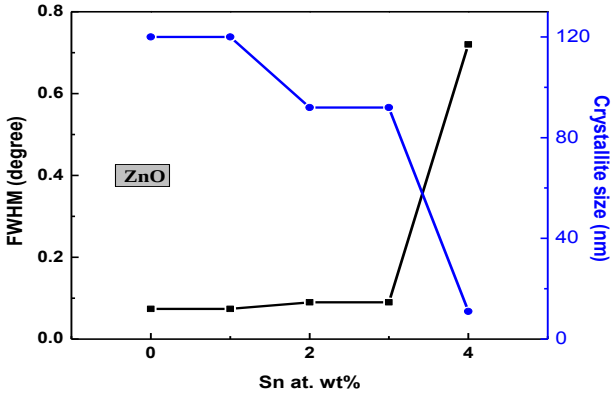

Fig. 4: FWHM and crystallites size of ZnO as a function of Sn at. wt%

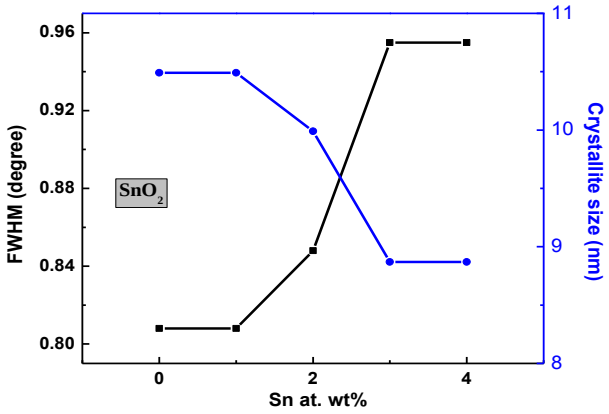

Fig. 5: FWHM and crystallites size of SnO_2 as a function of Sn at. wt%

In the present research work, the addition of Sn contents in ZnO thin films increased the dislocation line density which directs that defects are increased and crystallinity of the ZnO thin films is reduced.

3.2 Optical Properties

The optical properties of Sn doped ZnO thin films were studied by spectroscopic ellipsometry from which changes in amplitude and phase of light before and after interaction with the thin films, can be determined. In the recent work, refractive index (n) and extinction coefficient (k) of all the thin films for different regions of wavelength were measured from spectroscopic ellipsometry. Fig. 6 shows the variation in refractive index whereas Fig. 7 gives the variation in extinction coefficient with respect to wavelength for pure and Sn doped ZnO thin films. The values of refractive index for all Sn doped ZnO thin films were greater than the value for pure ZnO thin films in a wavelength range 600 to 1000 nm. For pure ZnO thin films, the value of refractive index was found to be 0.9 in a wavelength range 600 to 900 nm. For Sn doped (at. wt. 1%, 2%, 4%) ZnO thin films, this value was increased from 1.5 to 1.7 with increase in Sn contents, through the wavelength range 600 to 1000 nm.

Fig. 7 shows the influence of Sn doping on extinction coefficient of Sn-ZnO thin films. The value of extinction coefficient was increased with addition of Sn contents in ZnO thin films within a wavelength range 600 to 1000 nm, resulting in more absorption of wavelengths. In our work, the highest value of extinction coefficient was obtained at Sn doping level of wt. 4% which proved that Sn doped ZnO thin films have become more suitable for fabrication of various optoelectronic devices [1, 10-13].

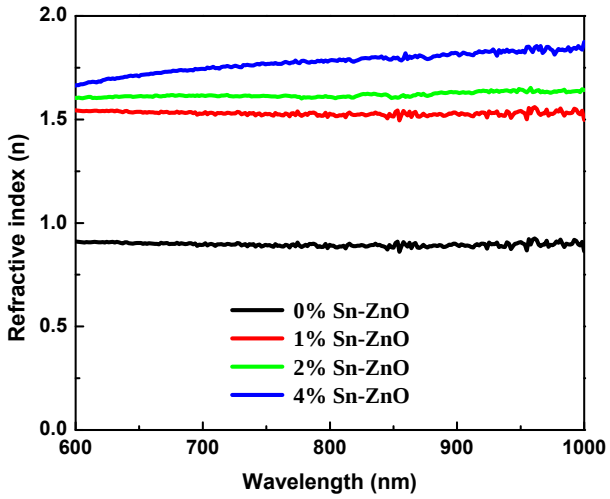

Fig. 6: Refractive index (*n*) of Sn-ZnO thin films as a function of wavelength

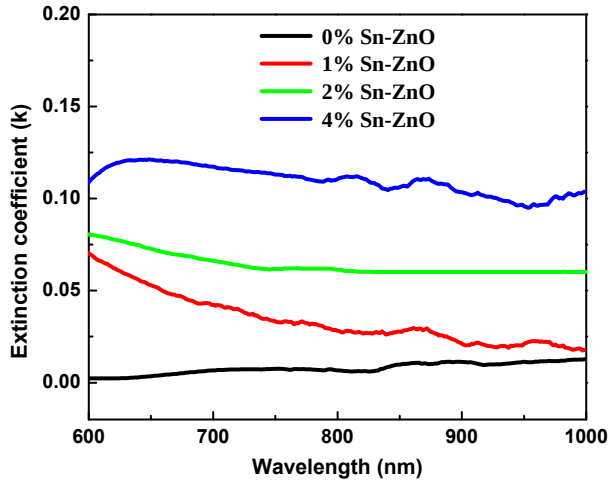

Fig. 7: Extinction coefficient (*k*) of Sn-ZnO thin films as a function of wavelength

Fig. 8 shows the Tauc's curves for all deposited thin films from which band gap energy of these films can be measured using Tauc's model. According to this model, the extension of linear portion of the plot between $(\alpha h\upsilon)^n$ and $h\upsilon$, up to the energy axis at $\alpha = 0$, gives the value of band gap energy. For direct and indirect band gap materials, the values of *n* are 2 and 0.5, respectively. As ZnO is a direct band gap material, hence the value of *n* was taken as 2 during the measurements of band gap energies for all thin film [10].

Fig. 9 illustrates that the value of optical band gap energy is decreased with increase in Sn contents that produce material disorders, resulting in the development of redistributed states between valence and conduction bands, and hence enhancement in photoelectric properties of the thin films [10].

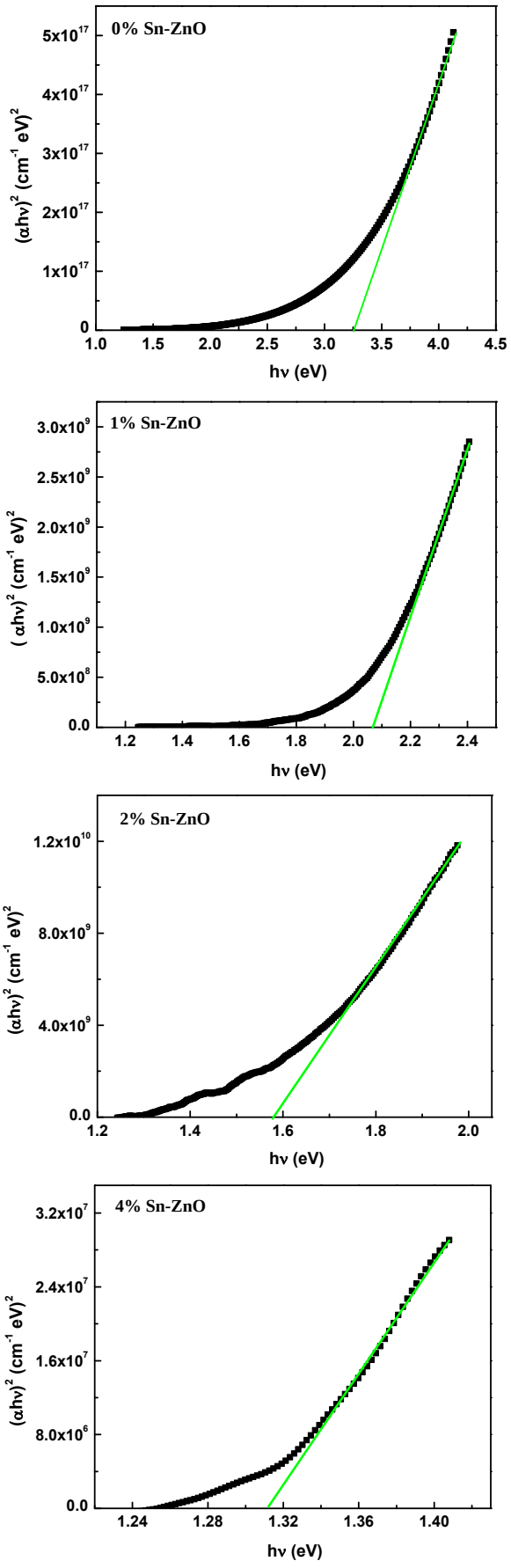

Fig. 8: Tauc curves for all deposited Sn-ZnO thin films

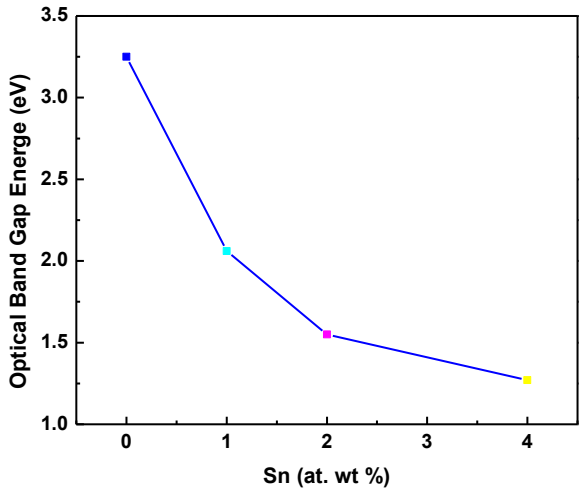

Fig. 9: Influence of Sn doping on optical band gap of ZnO thin films

4. Conclusions

Sn doping effects the properties of ZnO thin films meritoriously. XRD analysis showed that Sn doped ZnO thin films have preferred plane orientation (0 0 2), whereas SnO_2 (2 1 0) was also epitaxialy included in the thin films. The value of FWHM was increased and that of crystallite size was decreased with increase in Sn concentrations. SE results showed that the values of refractive index (*n*) and extinction coefficient (*k*) were increased with addition of Sn content in ZnO thin films throughout the wavelength region 600 to 1000 nm. Contrary to this, the optical band gap of ZnO thin films was reduced with addition of Sn contents that can be attributed to the decrease in crystallite size. Smaller is the crystallite size, smaller will be the optical band gap energy, which is consistent with the previous results. These Sn doped ZnO thin films of tunable band gap can be efficiently utilized in wide range applications of optical industries.

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