International Journal of Science and Research (IJSR)
ISSN: 2319-7064
ResearchGate Impact Factor (2018): 0.28 | SJIF (2018): 7.426

Effect of Ni-Doping on the Optical and Electrical Properties of Tin Oxide Thin Films Deposit by Spray Pyrolysis Method

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Abstract: ***In this study, un-doped and Ni-doped SnO_2 have been prepared on glass substrate by low cost spray pyrolysis technique. The films were deposited at a temperature of 350°Cusing starting materials of $SnCl.5H_2O$ and $NiCl.6H_2O$in air ambient. To study the effect of Ni doping on $SnO_2$the samples were characterized by using various techniques like XRD, SEM, UVIR Spectrophotometer and Hall effect measurement. Ni has been doped upto 9% and found that the optical transparency decreases from 84% to 72% with the increase of Ni concentration. The optical band gap of the fabricated samples was found to decrease from 3.55 eV to 3.50 eV for un-doped and 9% Ni-SnO_2. It is observed from the XRD study that the films are polycrystalline in nature. Hall Effect measurement shows that the films are n-type in nature and it is observed that the carrier concentration increases with the doping concentration.***

Keywords: Ni-doped SnO_2, Band gap, Carrier concentration, Hall mobility

1. Introduction

Transparent conducting oxides (TCO) have been attracted much attention in the research area over the last decade due to their interesting properties like high electrical conductivity and optical transparency. These properties make them suitable for various applications such as photovoltaic applications. Transparent oxides like In_2O_3, ZnO_2, SnO_2, TiO_2, CdO etc. have various applications in optoelectronic devices, green energy devices, smart sensors, high temperature electron devices[1-3]. Among these oxides SnO_2 has attracted more attention due to ease of fabrication, good adhesion to substrate, stability, low deposition temperature and low starting material costs. Although, their high transparency and low band gap energy, the electrical conductivity is not sufficient enough to use as photovoltaic and other applications. To improve the electrical conductivity many materials are used as dopant like In, Co, Al, Fe, Cu, F, Ni etc. with SnO_2 [4]. A variety of deposition techniques such as reactive electron beam evaporation [5], DC magnetron sputtering [6], reactive thermal deposition [7], spray pyrolysis technique [8-9], sol gel technique [10] have been used for SnO_2 thin films preparation. Among these techniques spray pyrolysis has some advantages such as low cost, lower temperature and air ambient deposition, large area deposition and convenient to control the deposition conditions and possible to deposit homogeneous and smooth films. In this work Ni doped SnO_2 has been fabricated on glass substrate using spray pyrolysis technique and studied optical and electrical properties.

2. Experimental Details

Ni-doped SnO_2 thin films have been prepared by low cost spray pyrolysis technique. Tin chloride ($SnCl.5H_2O$)and Nickel chloride6-hydrate ($NiCl.6H_2O$) are used for precursor solutions. Samples are prepared with 0.07M concentration. Both materials are dissolved with distilled water and ethanol at 1:1 ratio. In this investigation, SnO_2 films were prepared with various amount of Ni (0%, 1%, 5% and 9%) doping concentration. In spray pyrolysis technique, precursor solutions were supplied from a solution container and sprayed through a nozzle with compressed air. The solutions were sprayed uniformly over the entire substrate at a rate of 0.4 ml/min.

After deposition the films were investigated using several techniques. Optical transmittance and absorbance studies were performed using UV-VIS spectrophotometer (UV-1601, SHIMADZU, Japan). Structural study was performed using X-ray diffraction(XRD) and surface morphology was studied by SEM. Resistivity of the films has been measured within the temperature range 320 K to 370 K using Van der Pauw configuration and Hall measurement is performed to reveal the type of the semiconductor.

3. Results and Discussion

Structural study:

Structural properties of the deposited Ni:SnO_2 films are studied by X-ray diffraction (XRD). Figure 1 shows the XRD pattern of the Ni:SnO_2 films deposited on glass substrate by spray pyrolysis technique. The XRD pattern was taken with Cu-K_α radiation of wavelength λ=1.5405 Å with anode voltage 30 kV, current 10 mA within 2θ values 20° to 60°. From the figure it is observed that the films are polycrystalline in nature. Four diffraction peaks are obtained for the characteristic planes (110), (101), (200) and (211) with a tetragonal unit cell which are in agreement with the standard JCPDS data (Card No. 88-0287).

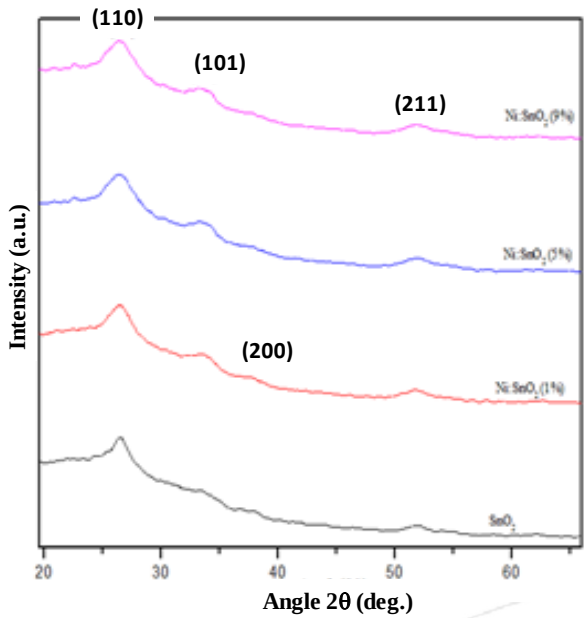


Figure1: XRD output waveform for both Ni-dope and un-doped SnO_2 thin films

Crystallite size of the SnO_2 samples were calculated using Debye Scherer formula [11],

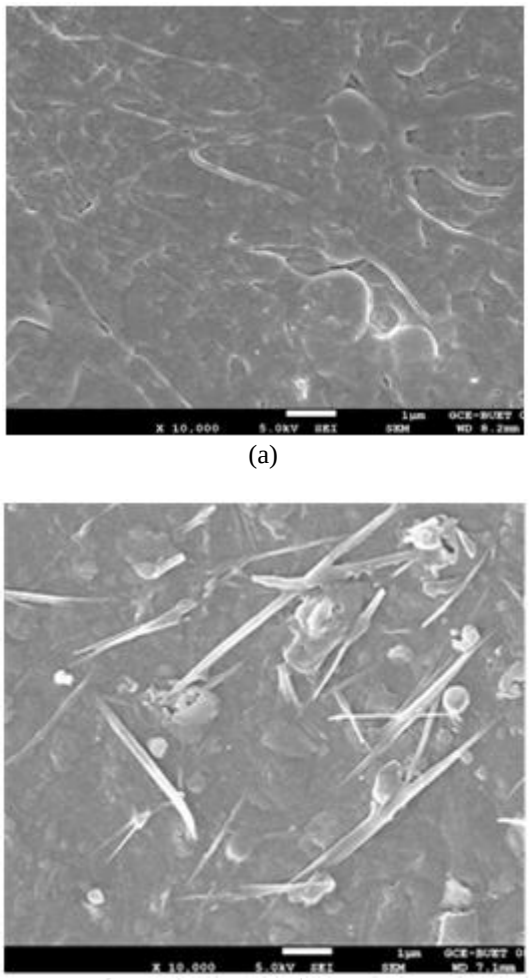
$$D = \frac{k\lambda}{\beta\cos\theta}$$

Where, λ is the wavelength of radiation used (Cu-K_α, λ=1.5405 Å), k is the Scherrer constant (k=0.94 is used), β is the full width at half maximum (FWHM) intensity of the diffraction peak for which the crystallite size is to be calculated, θ the diffraction angle and D the crystallite dimension. The crystallite size, lattice spacing (d), and lattice constant (a) determined from the main peak are summarized in the table-1 below. It is observed that the crystallite size decreases with Ni doping incorporation in SnO_2 films which might be due to the strain introduced in the samples due to excess Ni interstitials in the samples.

Table 1: Structural parameters of Ni-doped SnO_2

Ni-doping (wt %)	(h k l)	Lattice spacing (Å)	Average crystallite size, D (nm)	Average lattice constant, a (Å)
0	(110)	3.35	18.20	3.5362
1	(110)	3.35	17.31	3.5573
5	(110)	3.37	17.64	3.4911
9	(110)	3.37	16.67	3.5650

Surface morphology of the deposited samples were studied by scanning electron microscope and illustrated in Figure 2. From the figure it is observed that the film surfaces are rough and the roughness increases with the Ni-doping. Moreover, some spikes like structure are found in Ni-doped SnO_2 films as shown in Figure 2 (b).



(a)

(b)

Figure 2: SEM images of (a) undoped SnO_2 and (b) Ni doped SnO_2.

Optical Properties:

Optical properties of SnO_2 and Ni:SnO_2 thin films

Figure 3(a) and Figure 3(b) show the transmittance and absorbance spectra of the undoped and Ni-doped SnO_2 thin films as a function of wavelength range 300 nm to 1100 nm. It is observed that the optical transmittance is very high up to 84% in the visible region for undoped SnO_2. A sharp increase in transmittance is observed at around 350 nm and attributed to the band edge absorption. But the transparency decreases with the increase of the amount of Ni doping concentration. At 9% Ni concentration, the transparency falls to 72%. This may due to be the effect of scattering of photons due to the defects produced by the Ni atoms in the SnO_2.

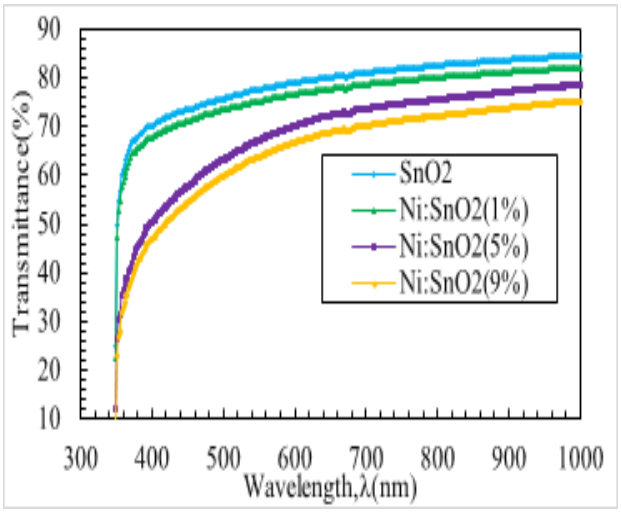


Figure 3(a): Variation of optical transmittance with wavelength for undoped and Ni-doped SnO_2 thin films.

The absorption spectra of Ni doped SnO_2 are illustrated in Figure 3(b). It is observed that the absorbance of the films is high at the band edge and decreased sharply. After the band edge wavelength, the absorbance observed almost constant over the higher wavelength region. It is also seen that the absorbance increases with the increase of Ni doping concentration.

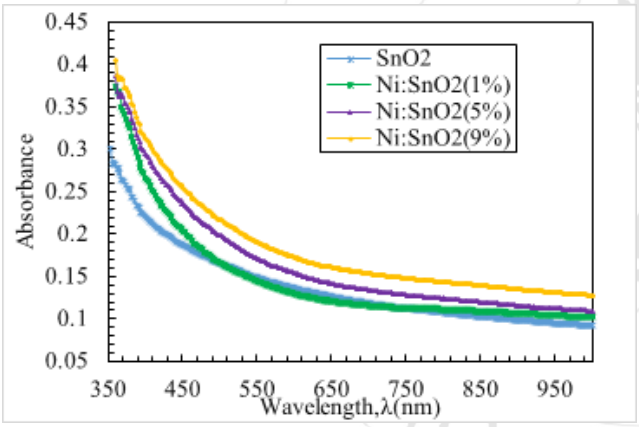


Figure 3(b): Absorbance spectra ofSnO_2 and Ni:SnO_2 thin films

The absorption coefficients of the Ni-doped SnO_2 are studied as shown in the Figure 4. The absorption coefficient (α) has been calculated as follows [12],

$$\alpha = \frac{1}{t} ln(\frac{1}{T}) \quad \text{..... (2)}$$

Where, t is the film thickness and T is the transmission coefficient of film.

Absorption coefficient decreases with the increase of wavelength because at higher wavelength the photons have lower energy hence mainly transmitted up to band gap energy is not exceeded [4].

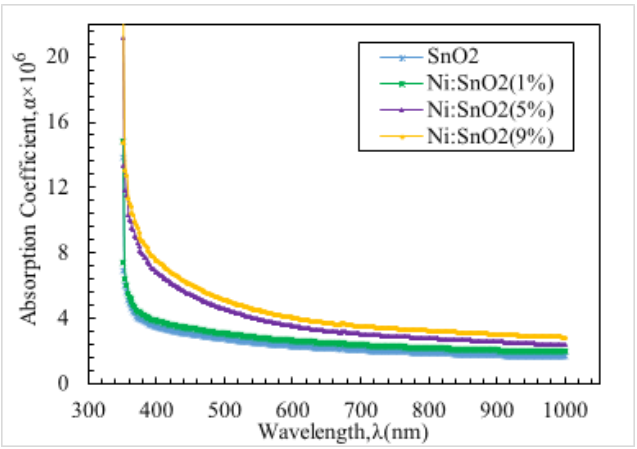


Figure 4: Absorption coefficient versus wavelength

Figure 5 demonstrates that the skin depth is dependent on the wavelength and increases with the increase of wavelength. Skin depth determined from absorption coefficient values and it inversely proportional to the absorption coefficient. In this investigation, films skin depth, χhas been calculated by,

$$\chi = \frac{1}{\alpha} \quad \text{..... (3).}$$

Here, α is absorption coefficient. Skin depth is useful in analyzing transmission characteristics. High skin depth material has lower conductivity. Pure SnO_2 film has higher skin depth but its value decreases with the incorporation of Ni into SnO_2 film. This result is supported by the electrical measurement which shows that the electrical conductivity increases with the increase of Ni doping.

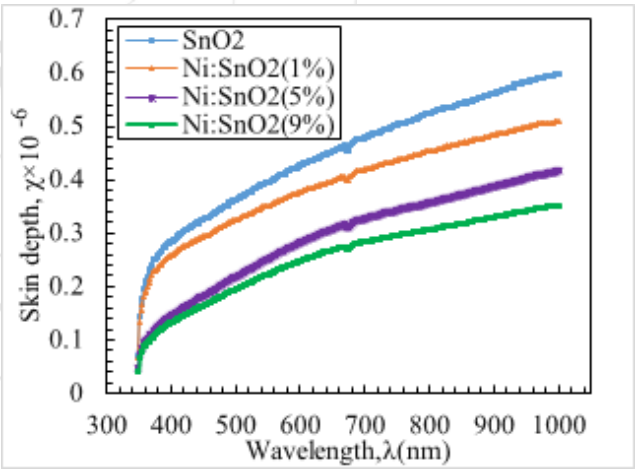


Figure 5: Skin depth versus wavelength

Extinction coefficient (k) of the deposited films are obtained [13],

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

Where, α is absorption coefficient, λ is incident light wavelength. Extinction coefficient is directly proportional to the absorption coefficient and wavelength. Increasing the doping percentage of Ni in SnO_2, extinction coefficient value has been increased because lower transparency of Ni:SnO_2 films comparing with un-doped SnO_2 thin film shown in Fig:6.This is occurred due to the present of highly charge

carriers in Ni:SnO_2 thin films than un-doped SnO_2. Therefore, Ni:SnO_2 films show lower transparency because incident light absorbed by the highly charge carriers films surface and hence lower transparent films unveil slightly higher absorbance than pure SnO_2 film.

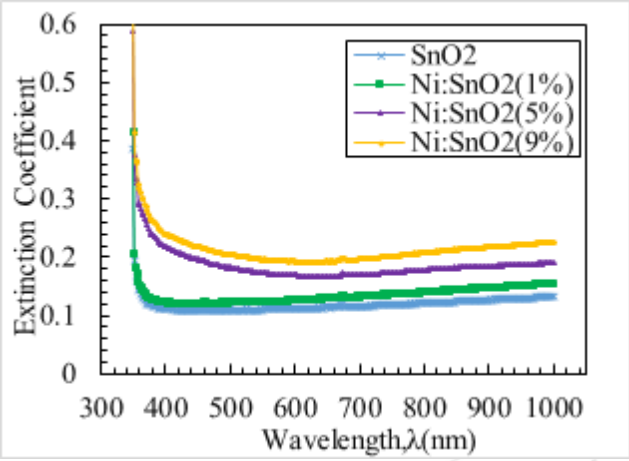


Figure 6: Extinction coefficient characteristics

Optical energy band gap of Ni-doped SnO_2 thin films have been determined by using Tauc's relation [14]

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

Where α is the absorption coefficient, A is an energy independent constant, hυ is the photon energy and E_g is the optical energy band gap and n is an index related to the density of states for the energy band. Figure 7 shows the variation of $(\alpha h\upsilon)^2$ as a function of photon energy, hυ. The band gaps of the samples are obtained from the intercepts of energy axis after extrapolation of the straight line of the slope of the curve to zero.

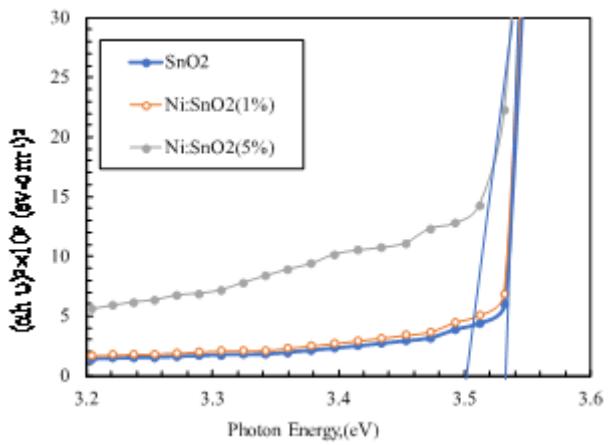


Figure 7: Variation of $(\alpha h\upsilon)^2$ with photon energy for undoped and Ni:SnO_2 thin films

It is observed that the band gap energy is due to direct transition and decreases with the increase of doping concentration. The estimated bandgap energies depending on the doping concentration vary from 3.50 eV to 3.53 eV. It was observed tin oxide doped with different concentration of Ni, band gap increases by increasing doping concentration of Ni. Similar results were obtained by Syed Zafar et. al., [15].

Electrical properties:

Temperature dependent resistivity of Ni:SnO_2 films have been studied by four-probe Vander Pauw's method in air ambient. Figure 8 illustrates conductivity of SnO_2 films deposited on glass substrate. It is observed that the conductivity of the films increases with the increase of temperature indicates semiconducting nature of the SnO_2 films. Moreover, the resistivity of the films decreases with the increase of doping concentration. Both the resistivity and sheet resistance decrease with the increase of charge carriers due to the increase of Ni concentration.

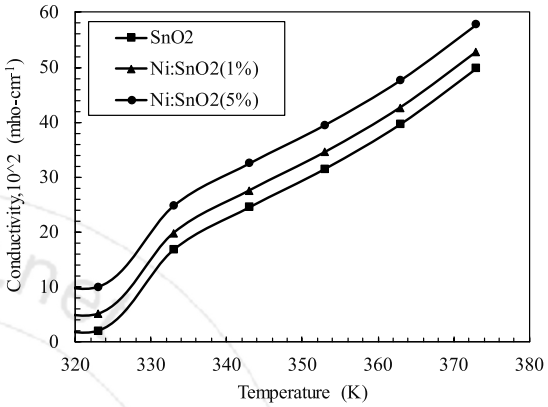


Figure 8: Variation of conductivity with temperature for undoped and Ni:SnO_2 thin films.

Activation energy of the samples are determined from the relation $\sigma = \sigma_0(-\frac{\Delta E}{2k_B T})$

Where ΔE is the activation energy, k_B is the Boltzmann constant. Figure 9 shows the variation of lnσ as a function of 10^3/T.

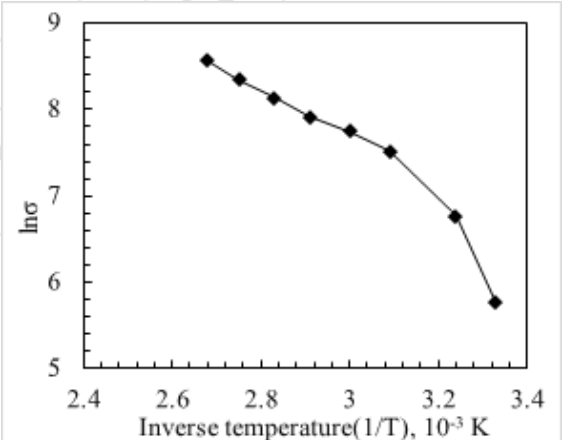


Figure 9: Variation of lnσ with 1/T of Ni-doped SnO_2 thin films.

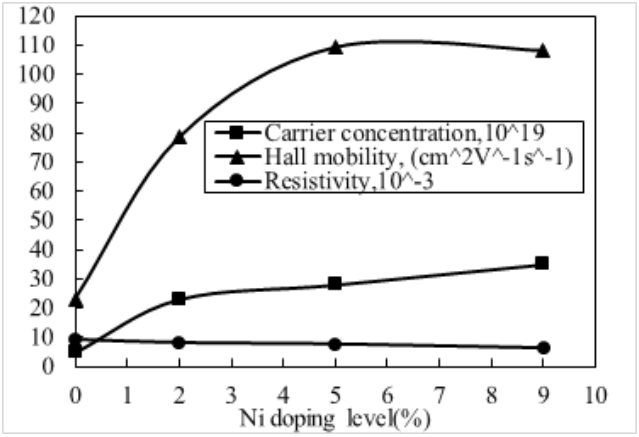


Figure 10: Variation of resistivity, carrier concentration and Hall mobility with the amount of Ni.

Various Hall measurement parameters such as Hall constant (R_H), Carrier concentration (N), Resistivity and Hall mobility (μ_H) have been determined as shown in Figure 10 for undoped and doped SnO_2 films. The hall measurement reveals the n-type nature of the Ni:SnO_2 films. The obtained values are suitable for photovoltaic applications.

4. Conclusion

Undoped SnO_2 and Ni:SnO_2 thin films deposited on a glass substrate by spray pyrolysis technique at temperature around 320~330^{0}C. Homogeneous and uniform films are obtained in this technique on the glass substrate. It is observed that film transparency decreases and optical band gap energy increases with the increase of the amount of Ni in the SnO_2 films. XRD investigation shows the polycrystalline nature of the deposited samples. Crystallite size decreases after Ni incorporation in SnO_2.Electrical measurement exposes that films conductivity increases with Ni doping. Carrier concentration and hall mobility augmented by incorporation of Ni which sort out by hall experiment.

Acknowledgement

This work is performed with the financial support of the ministry of national science and technology. The authors are grateful to the department of Physics, Rajshahi University to use some experimental facilities.

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