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A novel study on augmented physical parameters of nickel doped stannic oxide film

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Abstract

A novel study on the fabrication of virgin and nickel (Ni) doped stannic oxide (SnO2) thin films with different doping extent have been conducted to augment the properties of stannic oxide thin films to incorporate into the electric cell which utilizes sun’s energy. The influence of the Ni doping with various extents on the structural, optical and magnetic properties of the different synthesized samples of stannic oxide thin films are investigated by X-ray diffraction (XRD), Scanning electron microscopy (SEM), UV-Visible spectrophotometer and Vibrating Sample Magnetometer (VSM). All the fabricated samples of SnO2: Ni (1at%, 2at%, 3at% and 4at%) exhibited tetragonal structure of stannic oxide. The fusion of Ni into the stannic oxide lattice makes imperfection in the crystal and the presence of additional peaks confirms that the nickel domination is well observed. Increase in the extent of Ni doping causes diminution in optical band gap. The magnetic study reveals that the ferromagnetic signal is gradually diminished in optical band gap. The magnetic study reveals that the ferromagnetic signal is gradually enhanced with augment in doping concentration.

1. Introduction

From the beginning of the origination of nano structured dye-sensitized solar cell (DSSC), several researches have been undertaken to enhance the efficiency of the device which produces electricity by utilizing solar energy. Innovative and cost-effective technologies are used in the production of thin film solar cells. The translucent conductor usually made of transparent conductive oxides (TCO), is the hypercritical part of the thin film based solar cell and there has been crucial significance on improving the potential of new semiconducting material for ultra-thin layered solar cells [1]. In2O3 is considered to be the leading TCO in concerned with their properties as well as its commercial success. However, indium tin oxide (ITO) is playing a major role in electronics market; it is of high cost and limited availability [2].

SnO2 is economically cheap compared to indium oxide. It is one among the n type semiconductor having wide band gap of 3.6–4.0 eV [3]. The tetragonal rutile structure of SnO2 in which the center of an encircling core consists of a tin atom composed of six oxygen atoms placed approximately at the corners of a quasi-regular octahedron as in figure 1. Three tin atoms surround each oxygen atoms forming an equilateral triangle having the lattice parameters \( a = 4.737 \text{ Å} \) and \( c = 3.186 \text{ Å} \). Solar cells based on tin demonstrates optical properties which are superior and good efficiency solar cell materials are exhibited by its alloys [5] with elevated photosensitive transparency in the wavelength region of 700 nm to 400 nm and high level of specific conductance which are considered to be the most needed properties for solar cells applications, gas sensors and liquid crystal displays [6]. It is a suitable candidate for many applications. Its high chemical stability is considered to be an inherent advantage of SnO2 [7] and it makes SnO2 as a suitable candidate in the most challenging conditions of being a transparent as well as a conductive electrode on photo electrodes or as a selectively solar transmitting coating [8]. In addition to these properties SnO2 exhibits ferromagnetism and finds applications in
novel magnetic optoelectronic devices. Doping of SnO$_2$ with metal ions has been used to enhance its properties which results in an improvement of the device performance [9].

Various methods are employed for the synthesis of SnO$_2$ thin films for example, spray pyrolysis [10], laser removal procedure [11], sol-gel [12], wet chemical method [13], co-precipitation [14], hydrothermal [15], solid state calcinations [16]. Among these methods the most convenient method is spray pyrolysis method. It is simple with inexpensive experimental arrangement and having huge possibility of changing the properties of the film by varying the composition of the starting solution. Using this method many transparent conducting oxides films have been successfully synthesized [17–19].

SnO$_2$ finds its applications in various fields due to the addition of dopant such as noble metals and transition metals. Among these dopants, the transition metal nickel has been extensively selected to improve the ability of SnO$_2$ [20]. As the ionic radius of Ni$^{2+}$ (69 pm) and Sn$^{2+}$ (71 pm) are very close to each other, the particles of Ni can be easily doped into the sites of Sn. Depending on the doping level there occurs decrease in electron density and increase in oxygen vacancies [21]. SnO$_2$: Ni the transparent conducting oxide semiconductor is a direct band gap energy material with nontoxic constituent materials and having abundance in nature. As the authors believed that few groups only reported on Ni doped SnO$_2$ semiconductors, fabrication of Ni doped SnO$_2$ thin films has been made and the influence of nickel doping on its physical parameters are studied.

2. Experimental methods

2.1. Synthesis of Ni doped SnO$_2$ thin film

In the blended mixture of doubly de-ionized water, and methyl alcohol in the ratio 1:1, a suitable quantity of the precursor material, SnCl$_4$.5H$_2$O (Merck) is dissolved to obtain 0.1 M starting solution and few drops of hydrochloric acid to get a clear solution. To the precursor well grained nickel (Ni) powder (Merck) is added in ratio of 0, 1, 2, 3 & 4 at%. A reservoir filled with precursor solution is mounted on stand. The area of the substrate is 2.5 $\times$ 7.5 cm$^2$. Formerly cleaning of the substrates are achieved by Hydrochloric acid, propanone and de-ionized water using supersonic cleaner for 35 min to remove organic materials and other moistures present in the surface of the substrate. The spray pyrolysis experimental setup designed by the authors shown in figure 2 consists of a syringe needle having the diameter of 0.6 mm connected to the reservoir and its height can be altered to get 0.002 ml Min$^{-1}$ at the needle tip. Distance of 8 cm is kept between the needle and the surface of the substrate. Substrate attracts the precursor solution as high voltage of about (9.65 KV) is applied between needle and hot-plate. To optimize the thickness different volume of precursor solution was sprayed and found that to have 500 nm thickness for all the samples and are verified using trail and error method. A timer was connected to high voltage power supply, relay and hot plate. The timer is set in such way that when hot plate is on, high voltage will be in off condition and vice-versa. The charge present in substrate holder and syringe needle is grounded by using relay. The distance of the syringe needle is adjusted up and down to obtain a continous thin film. Five consecutive sets of virgin and Ni (1at%, 2at%, 3at%, 4at%) doped SnO$_2$ films are fabricated by regulating the temperature of the substrate at 500 °C. For each sample the optimized time for deposition is 44 min including the spray intervals. The recurrent spray process of 5 s of spray and an interval of 10 s for each cycle is employed.

![Figure 1. The rutile structure of SnO$_2$.](image-url)
2.2. Characterization techniques

In our present study the surface morphology of the prepared samples are characterized by employing scanning electron microscope EVO18 (CARL ZEISS). The lattice parameters are examined by (SHIMADZU-XRD 6000 diffractometer system with (Cu K-alpha) beam having the wavelength range of 1.5406 Å). The SurfTest SJ-301 profilometer is used find the dimension between the two surfaces of the films and the weight gain method is also used to find the thickness. Unico 4802 Ultraviolet visible spectrophotometer with two beams in the wavelength range: 300 nm – 1100 nm is used to measure the photosensitive absorption and transluency of the fabricated thin films. FTIR spectra are recorded by means of SHIMADZU1800-UV Fourier transform infrared spectrometer. Magnetic study is made using a sensitive Vibrating Sample Magnetometer (VSM 7410).

3. Result and discussion

3.1. Structural properties

XRD spectra are recorded for virgin and Ni doped SnO2 thin films using Cu K-alpha radiation of wavelength 1.54 Å. Figure 3 shows the diffraction peaks of the fabricated thin films. The highest diffraction peaks are (110), (101), (200), (211), (220) and (301). The diffracted peaks with tetragonal rutile structure of SnO2 well matched with JCPDS card number: 41–1445 is observed for the recorded peaks of virgin and Ni doped SnO2 thin films. Ni doping causes no change in the tetragonal rutile structure of SnO2. No change in the position of the peak has been observed in XRD spectra which indicates that there is no considerable change in the structure. Until 3at% doping of nickel in SnO2 thin films, host SnO2 lattice dominates dopant and the results suggested that nickel was incorporated into the host SnO2 lattice as the peaks related to nickel and nickel oxides are not identified. The fusion of Nickel into the SnO2 lattice makes imperfection in the crystal for 4at% of the dopant concentration and the presence of additional peak (contaminant) which proves the existence of an extraneous material and confirms that the nickel domination is well observed which is evident from the SEM image and the diffraction pattern. For the predominant plane (110) the intensity of the peak in the primary phase is increased until 3at% of doping concentration and further addition of 1at% doping concentration the intensity decreases due to the replacement of Sn4+ ions with Ni ions in the lattice of SnO2 film, whereas the intensity of the plane (211) in the
secondary phase rapidly increases. Which shows better atomic arrangement and lower scattering in these planes.

The crystallite size of virgin SnO$_2$ and Ni: SnO$_2$ films with various nickel extent is calculated by using Debye–Scherrer formula $[22]$

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

Where $D$ is the mean crystallite size, $k$ is a particle size dependent constant whose value is 0.9, $\lambda$ is the diffraction wavelength of Copper k-alpha ($\lambda = 1.54$ Å), $\beta$ is the full width at half maximum (FWHM), and $\theta$ is the diffracted angle, respectively. For the virgin SnO$_2$ and Ni (1, 2, 3, 4) at% doped SnO$_2$ thin films synthesized at 500 °C, the corresponding position and the crystallite size of the predominant peak (110) is summarized in table 1.

### Table 1. XRD analysis of the virgin SnO$_2$ and Ni: SnO$_2$ thin films for the predominant peak.

| Predominant peak | Angle$2\theta$ (degree) | d Spacing (Å) | FWHM | Crystallite (nm) |
|------------------|------------------------|---------------|-------|------------------|
| 0% Ni (110)      | 26.799                 | 3.3239        | 0.201 | 45               |
| 1% Ni (110)      | 26.915                 | 3.3100        | 0.220 | 40               |
| 2% Ni (110)      | 26.805                 | 3.3232        | 0.203 | 35               |
| 3% Ni (110)      | 26.898                 | 3.3119        | 0.200 | 30               |
| 4% Ni (110)      | 26.784                 | 3.3257        | 0.184 | 31               |

3.2. Morphological analysis

Figure 4 shows the surface morphology of virgin SnO$_2$ thin films and SnO$_2$: Ni thin films deposited at a calcined temperature of 500 °C with different nickel content concentration. It is observed that there is a significant...
change in the morphology of the films. The presences of uniform sized grains are seen in the virgin SnO$_2$ film. The change in the morphology of the films with increase in the dopant extent is evident from the recorded micrographs of SEM. The presence of the dopant nickel and the quantity that goes into each sample influences the change in microstructure. 1at% of nickel doping influences the change in the morphology of SnO$_2$ film. In the recorded image of 2at% of Ni doped SnO$_2$ thin films grain size decreases and there occurs agglomeration at certain places due to attractive forces between Ni doped SnO$_2$ nano particles and the dopant is not well incorporated into the host SnO$_2$ lattice. Thin film of good surface morphology with a smooth surface having smaller grain size is observed for 3at% of Ni: SnO$_2$ films. This may be due to the well incorporation of nickel ions into the host lattice. Above 3at% of doping concentration, lot of large irregular grains with different shapes have been identified as nickel domination is more effective which is also evident from the XRD pattern.

### 3.3. Optical properties

Optical transmittance spectra of virgin and nickel doped tin oxide thin films are shown in figure 5. From the recorded spectra it is observed that translucency in the visible region (400–700 nm) is about ~30%–90%. Minimum transmittance is observed for virgin SnO$_2$ thin films. Due to homogenous and smooth surface as evident from the SEM image, maximum transmittance is observed for 3at% Ni doped SnO$_2$ thin film indicating a high-quality thin film for disposing it in photovoltaic cell as an electrode. According to Beena et al [23] the decrease of transmittance arises due to many factors like increase in thickness, existence of oxygen vacancies and defects, roughness of the surface, permeable nature of the films, scattering in grain boundary etc but in the present case the decrease of transmittance may be due to the irregular grains. The observed absorbance modulated spectra of virgin SnO$_2$ and Ni : SnO$_2$ thin films at various concentrations are depicted in figure 6. The recorded spectra shows an ultraviolet cut-off in the region of 300 nm–400 nm due to the excitation of sub atomic
particle: electrons from the outer most orbit to the conduction band. The quantity of the light absorbed by the sample is high in the ultraviolet region and low absorption is observed in the visible region. The observed absorbance is almost constant over the higher wavelength region. The band gap is an important property which determines the quality of the deposited thin films. Figure 7 displays $(\alpha h\nu)^2$ versus $h\nu$ using Tauc’s plot for determining the band gap energy. The energy band gap values ranges between 3.46 eV to 3.65 eV. Kuppan et al [24], found the energy band gap of Ni:SnO$_2$ lies between 3.70 eV and 3.76 eV and this is contrary to our present findings. The effect of doping on the band gap energy is associated to either the Burstein–Moss effect (band gap widening) or many body effects (band gap shrinkage), such as electron–electron interactions (EEIs) and electron–impurity interactions (EIIs) [25, 26]. In the present case band gap shrinkage is observed. It may be due to the increase of EEIs as Ni content in SnO$_2$ increased. Good quality film is obtained in 3at% of nickel doping concentration with the band gap energy of 3.43 eV.

3.4. FTIR spectral analysis
To find the occurrence of different functional groups present in the sample FTIR spectra are recorded in the range 500 cm$^{-1}$ to 4000 cm$^{-1}$ of virgin SnO$_2$ and Ni:SnO$_2$ thin films and are displayed in figure 8. Usually the range between 300 cm$^{-1}$ and 800 cm$^{-1}$ have been detected as Sn–O stretching vibration [27]. The bands appear at 440, 560 and 750 cm$^{-1}$ belong to vibration of SnO$_2$. The peak appearing around 490 cm$^{-1}$ seems to be O–Sn–O and Ni bond vibration. Peaks observed at 1050 cm$^{-1}$ and 1320 cm$^{-1}$ may be assigned to stretching vibrations.
of Ni–O. The broad band appearing in the region 1620 cm$^{-1}$ to 2200 cm$^{-1}$ may be due to the HO–H vibration of adsorbed water. All the spectroscopical impression illustrates the strong coupling of Ni on SnO$_2$ configuration.

3.5. Magnetic properties

Figure 9 shows the curves of magnetization versus field of the virgin SnO$_2$ and Ni:SnO$_2$ samples. The nanoparticles of SnO$_2$ are diamagnetic in nature and this is confirmed by several groups [28]. While Hays et al found that nanoparticles of SnO$_2$ are non-ferromagnetic [29]. In the present case virgin SnO$_2$ exhibits diamagnetic property. Doping of Ni results in the change of magnetization as the property transforms from

![Figure 8. FTIR spectra of virgin SnO$_2$ and Ni:SnO$_2$ thin film.](image1)

![Figure 9. Magnetic property study (M-H curve) at room temperature for virgin and Ni doped SnO$_2$ samples.](image2)
Virgin SnO$_2$ and SnO$_2$:Ni diamagnetic to ferromagnetic state due to substitution of Ni ion with SnO$_2$ matrix. The strong magnetic (ferromagnetic) signal is gradually increased up to 3at% of dopant concentration. The saturation magnetization ($M_s$), coercivity ($H_c$), and retentivity ($M_r$) are summarized in Table 2. From the table it is observed that for 3at% dopant level the saturation magnetic moment was high. This is because of the replacement of Sn(4$^+$) ion with Ni(2$^+$) ion leading to the formation of more oxygen vacancies which causes electron trapping and hence there is an increase of saturation magnetic moment ($M_{sat}$). Due to the presence of contaminants the magnetic moment decreases with further addition of 1at% Ni doping. As the magnetic moment decreases, there is a decrease of the saturation magnetization. Low retentivity ($M_r$) and coercivity ($H_c$) for 3at% concentration implies that resistance of the ferromagnetic material to become demagnetized is low.

4. Conclusion

Virgin SnO$_2$ and SnO$_2$:Ni (1at%, 2at%, 3at%, and 4at%) films, are successfully prepared by using self-assembled low cost spray pyrolysis method. The surface morphology of the films revealed that the grain size depended on the dopant concentration. Many superior characters such as well-crystallinity, high transmittance (~90%), band gap value of 3.43 eV, enhanced ferromagnetic behavior, low retentivity ($M_r$) and coercivity ($H_c$) were observed in our results. Hence doping extent of nickel in SnO$_2$ film with 3at% of nickel extent can be suggested as a potential candidate for an solar based devices that converts solar radiation directly into electricity.

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Table 2. Summary of doping concentration, Saturation Magnetization, Coercivity, Retentivity of virgin and Ni doped SnO$_2$ thin films.

| Doping concentration | $M_s$ (emu cm$^{-3}$) | $H_c$ G | $M_r$ (emu cm$^{-3}$) |
|----------------------|-----------------------|--------|---------------------|
| 0at%                 | 2.34                  | 188.35 | 1.09                |
| 1at%                 | 3.08                  | 165.22 | 1.89                |
| 2at%                 | 8.62                  | 276.92 | 2.69                |
| 3at%                 | 20.03                 | 96.71  | 2.16                |
| 4at%                 | 15.24                 | 146.37 | 4.76                |
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