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ROOM TEMPERATURE FERROMAGNETIC BEHAVIOUR OF INDIUM-DOPED SnO_2 DILUTE MAGNETIC SEMICONDUCTOR NANOCRYSTALLINE THIN FILMS

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Pure and Indium (In) doped SnO_2 nanocrystalline thin films have been fabricated using sol-gel technique. The effect of In-doping on structural, optical and magnetic properties has been studied. Scanning electron microscopy (SEM) study reveals that the grains of pure and doped SnO_2 possesses spherical symmetry. X-ray diffraction (XRD) study reveals that pure and In-doped SnO_2 thin films possess rutile structure having tetragonal phase. UV-visible study suggests that with In-doping in SnO_2, the value of the band gap first increases (upto 5% In-concentration) but further increase in concentration of In to 25% leads to decrease in band gap. It has been found from the room temperature magnetic study that pure and In-doped SnO_2 thin films show ferromagnetic behaviour, however with 5% In-doping saturation magnetization value increased. The observed ferromagnetic behaviour may be due to the defects and oxygen vacancies.

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1. Introduction

Nanocrystalline materials are very promising for future devices applications due to their unique and size dependent superior properties than their bulk counterparts. In the search of multifunctional futuristic materials, dilute magnetic semiconductors (DMSs) in which the semiconductor host is replaced by magnetic impurity (rare earth and transition metals) are very promising for Spintronics i.e. spin based electronics. The interest in these futuristic materials is because of their use in new multifunctional devices in which the spin degrees of freedom use to carry information in order to reduce electrical consumption, allow non-volatility, store and manipulate data [1].

Amongst the dilute magnetic oxides, SnO_2 is n-type semiconductor with wide band gap having elite properties such as transparency, chemical and thermal stabilities; it finds applications in solar cells, gas sensors, liquid crystal displays, spintronics, and in transparent conducting electrodes [1-5]. Recently, it had been observed by many researchers that the ferromagnetism in doped-SnO_2 is not due to any magnetic dopant having 3*d* electrons [6-10]. But however, a few reports suggests that observed ferromagnetism is due to the oxygen vacancies, clustering or formation of secondary phase, and/or defects [6-13]. Therefore, although a number of reports on doped SnO_2 thin films with conflicting results both experimentally as well as theoretically [1, 6-10] reported, but still the origin of ferromagnetism in this material is under debate.

In present work, pure and In-doped SnO_2 have been fabricated by sol-gel technique. The effect of In-doping on the structural, optical and magnetic properties also has been explored.

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2. Experimental

2.1 Fabrication of pure and In-doped thin films

Pure and In-doped SnO_2 thin films have been fabricated using sol gel method [11]. In typical procedure, the precursor solution has been prepared by dissolving the appropriate amount of $SnCl_4.5H_2O$ in ethanol and 2-methoxy ethanol. The above solution was stirred for 6 hour at 70^oC, followed by ageing of 12 hours. The doping of In (2, 5 and 25%) has been done by adding In_2Cl_3 during the preparation of sol. The films were deposited on quartz substrates through sol-gel spin coating process with a spinning speed of 3000 rpm for 40 seconds. After the deposition, each layer is dried for 10 min at 200^oC in order to remove the volatile organic solvents used during the synthesis of sol. To obtain the desired thickness, 20 layers of SnO_2 were deposited. The annealing of the deposited layers at 500^0C for 1 hour has been done at the end.

2.2 Characterization technique

Structural and phase analysis of the pure and In-doped SnO_2 thin films has been carried out using (Bruker D8-Focus) glancing angle x-ray diffractometer (XRD) with Cu-Kα (0.15418 nm) radiation operated at 40 kV and 40 mA. The high intense beam was focused over a small area and the gonio scan was recorded for 2θ range $20\text{-}60^o$. UV-Vis transmission spectra of the fabricated thin films on the quartz substrates was recorded on the (Shimadzu UV- visible double beam spectrophotometer model 1601) in the wavelength range of 200-1100 nm. For morphological study scanning electron microscopy (SEM) has been carried out using JEOL, JSM-6510 L. For SEM analysis, the thin films were coated with gold-palladium alloy using JEOL, JFC sputter coater. The magnetization versus applied magnetic field (M-H) hysteresis loop has been carried out using vibrating sample magnetometer (VSM) of Lake Shore at room temperature.

3. Results and discussions

3.1 Structural and phase analysis

Fig. 1 shows the glancing angle x-ray diffraction patterns of the pure and In-doped (2, 5 and 25 %) SnO_2 thin films. The diffraction peaks positioned at angle $2\theta = 26.61^o$, 33.89^o, 51.79^o and 61.87^ocorresponding to the (110), (101), (200) (211) planes respectively, suggest that the synthesized product possess rutile structure having tetragonal phase (JCPDS file no. 41-1445). Additionally two extra peaks (mark as *) corresponds to the orthorhombic phase of SnO_2 have been observed. Tetragonal phase is the more stable phase under ambient conditions, whereas the orthorhombic phase is normally present under high pressure. No additional peaks corresponding to secondary phase (such as In_2O_3) were observed, indicating that Indium gets incorporated into the tin oxide lattice. The average crystallite size of the pure and In-doped SnO_2 thin films has been calculated from Debye-Scherer equation [5]. It has been found that the average crystallite size of pure SnO_2 thin film has been found to be 17 nm. However, with addition of In, the average crystallite size decreases from 17 nm to 14 nm. This is due to the smaller size of the dopant (In) as compare to the host (SnO_2) that leads to lattice contraction.

3.2 Morphological study

Morphological and surface studies of the synthesized pure and In-doped SnO_2 thin films have been carried out using scanning electron microscopy (SEM). It is evident from the figure 2 that the grains of pure and the 5% In-doped SnO_2 thin films possess spherical symmetry. The average grains size of pure SnO_2 thin film is found to be 18 nm. But however with the addition of 5% In (figure 2 (b)), the average grain size decreases to 12 nm, that is also consistent with XRD results (figure 1). Moreover, the porosity of pure SnO_2 thin film is higher than 5% In-doped SnO_2.

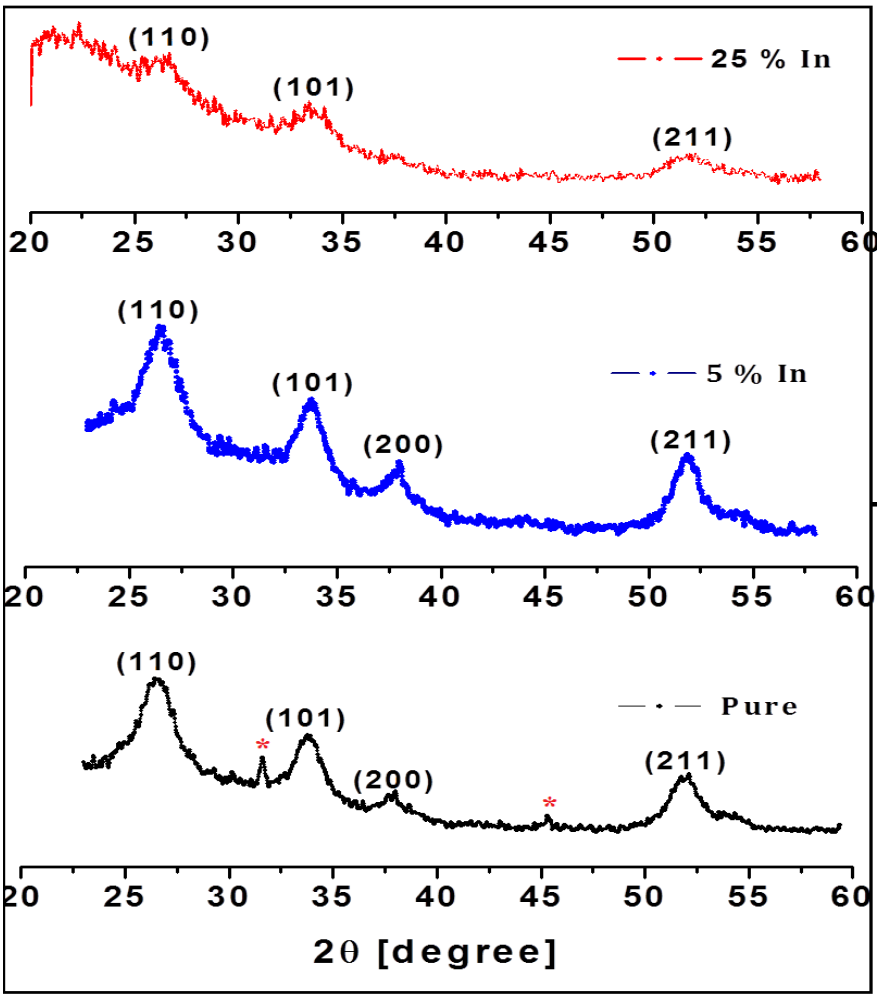

Fig. 1 XRD patterns of pure and In-doped SnO_2 thin films

3.3 Optical study

Figure 3 (a) shows the UV-visible transmission spectra of pure and In-doped SnO_2 thin films clearly reveals that the visible light transmission between 400-700 nm for all the samples is 55-65 % indicating the good transparency of the fabricated thin films. Pure and 5 % In-doped SnO_2 thin films show transmission around 65%. But with 25% In-doping, the transmission decreases to 55 %. The band gaps (E_g) of these thin films have been calculated from transmission spectra using Tauc's relation [12]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^{1/2}$$

where α absorption coefficient, h Planck's constant, υ frequency of incident light and A is constant. Table 1 shows the band gap calculated from Tauc's plots (figure 3 (b)).

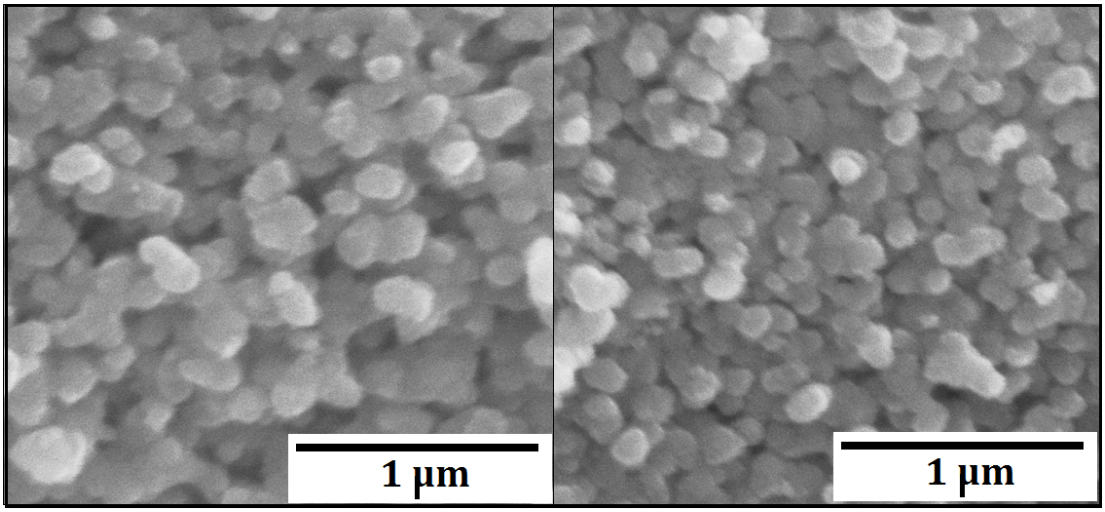

Fig. 2 SEM micrographs of (a) Pure and (b) 5% In-doped SnO_2 thin films.

The band gap of pure SnO_2 nanocrystalline found to be 4.30 eV which further increased to 4.68 eV with 5% In-doping. But, however with further increase in doping concentration up to 25 % band gap decreases to 3.85 eV.

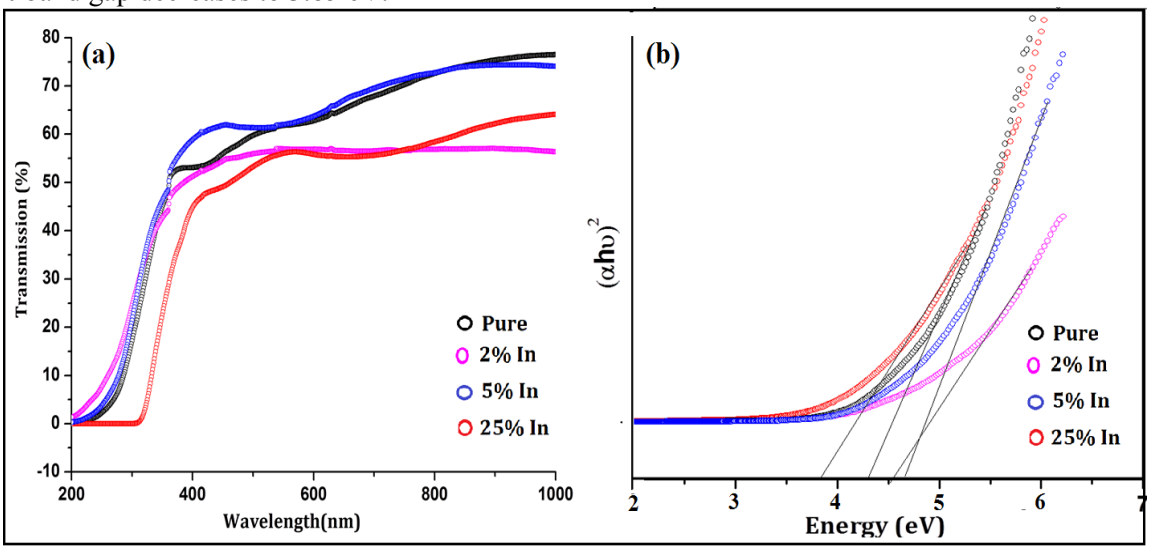

Fig. 3 (a) UV-visible transmission spectra and (b) Tauc's plot of pure and In-doped SnO_2 thin films.

Table 1: Energy band gap of pure and In-doped SnO_2 thin films

Sample	Band Gap (Eg) (±.01eV)
1. Pure SnO_2	4.30
2. 2% In-SnO_2	4.55
3. 5% In-SnO_2	4.68
4. 25% In-SnO_2	3.85

3.4 Magnetic study

Figure 4 shows the applied magnetic field versus magnetization (M-H) hysteresis loop of pure and In-doped SnO_2. It is clear from the figure 4 that pure and 5% In-doped SnO_2 thin films exhibit ferromagnetic behaviour.

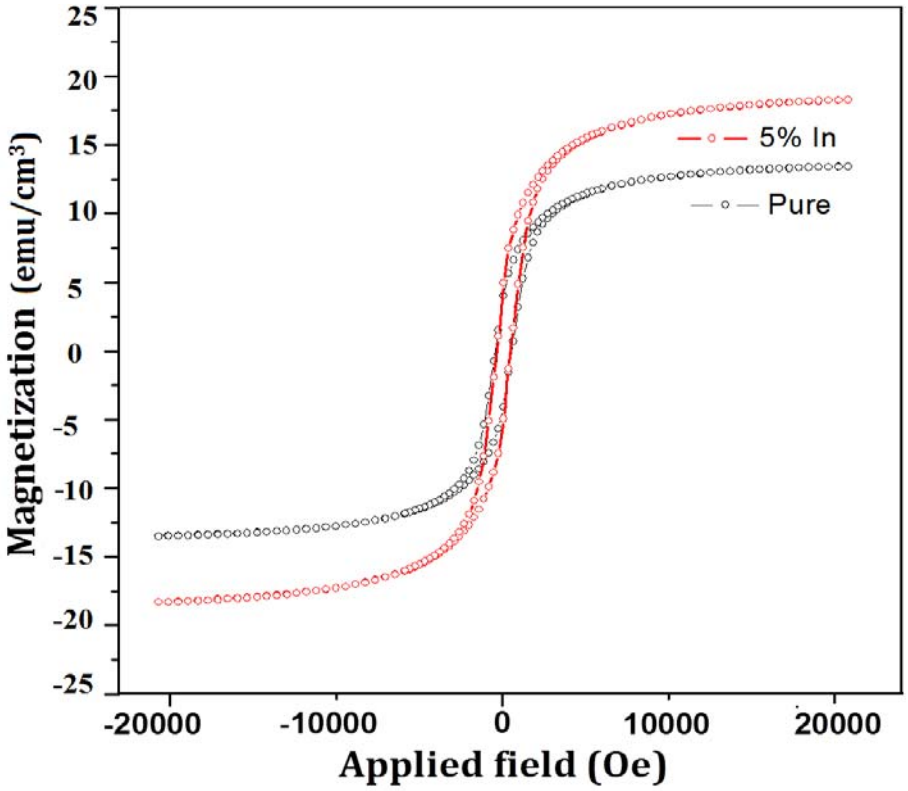

Fig. 4: Magnetization versus magnetic field (M-H) hysteresis loop of pure and 5 % doped-SnO_2 thin films at room temperature.

By increasing the In-doping concentration in SnO_2, the saturation magnetization increased. Similar results were reported by Hong *et al.* [13] that SnO_2 thin film exhibits ferromagnetic behaviours. The RKKY interactions are responsible for the observed ferromagnetic behaviour in SnO_2 thin films since there is no 3d electrons present in this [6-10, 13]. SnO_2 thin films doped with 5% In also show ferromagnetic behaviour, but the saturation magnetization value increased as compare to pure one. The increases in saturation magnetization value in In-doped SnO_2 thin films is may be due to the defects generated by addition of Indium in SnO_2. This confirmed that magnetism in SnO_2 is without the magnetic impurities. The induced ferromagnetism observed in nonmagnetic doped ions is due to the Ruderman-Kittel-Kasua-Yoshida (RKKY) interaction [6-10, 13]. Also, the observed ferromagnetic behaviour in pure and doped samples may be due to oxygen vacancies, surface defects in thin films, and confinement of the dopant in host.

4. Conclusions

Nanocrystalline pure and In-doped SnO_2 thin films have been fabricated by sol-gel spin coating technique. XRD study confirmed rutile structure of pure and doped SnO_2 thin films having tetragonal phase. No additional peaks related to any secondary phase have been observed. Crystallinity of the films also deteriorates on increasing In concentration. UV-visible study reveals that the band gap of the pure SnO_2 thin films is ~ 4.30 eV increases gradually with increasing In-doping upto 5% to 4.68 eV, and then drastically decreases to ~ 3.85 eV with 25% In doping. Magnetic study confirmed the ferromagnetic behaviour of pure and In-doped thin films. Magnetic

saturation value increased with increase in In-doping concentration (5%). The RKKY interactions are responsible for the observed ferromagnetic behaviour. These nanocrystalline pure and In-doped SnO_2 thin films acts as dilute magnetic semiconductors and may find potential applications as transparent conductors, gas sensors and in Spintronics devices.

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