Effect of Different Dopants in Structural, Electrical and Optical Properties of SnO_2 Thin Films Prepared by Sol Gel Technique

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Abstract:- **SnO_2 is a typical n-type wide band gap semiconducting material. It is chemically inert, mechanically hard and can resist high temperature. In order to improve the electrical, optical and magnetic properties of SnO_2 thin films, dopants such as antimony, manganese, indium etc. are incorporated. The structural properties were studied using the X- ray diffraction pattern (XRD). A fine crystallinity was observed for manganese doped SnO_2 films (MTO). Compared with antimony doped SnO_2 films (ATO) and indium doped SnO_2 films (ITO), crystallite size was greater for MTO films. The lattice parameters were calculated and the variations were observed with respect to pure SnO_2 film. This variation was due to the difference in the ionic radii of different dopants and the host.The surface morphology (SEM) studies reveals homogenous and crack free appearance of the films. The electrical properties of the films were studied using four probe method. ATO films gave n type conductive films, whereas, ITO films gave p type films. MTO films were less conductive compared with ATO and ITO films. The optical properties of films with different dopants were studied using transmittance spectra. All the films showed transparency ~ 80 % in the visible region of the electromagnetic spectra. The band gap value was greater for ATO films and less for ITO films compared with MTO films. Magnetic study was performed inSnO_2 film by doping Mn in the film. MTO films showed room temperature ferromagnetism. Such films with structural, optical and electrical properties finds suitable applications in optoelectronic devices and light emitting diodes. MTO films can be applied in dilute magnetic semiconductors which are now becoming an integral part of modern technology.**

1. INTRODUCTION

SnO_2 is a typical n-type wide band gap semiconducting material. It is chemically inert, mechanically hard and can resist high temperature. In order to improve the electrical, optical and magnetic properties of SnO_2 thin films, dopants such as antimony, indium, manganese etc. are incorporated. For obtaining cost effective transparent conducting oxides (TCO), antimony doped tin oxide (ATO) and indium doped tin oxide (ITO) thin films can be used. TCOs are used in transparent conducting electrodes, static electric charge shielders , soft touch screen controllers etc. Antimony exist in both +3 and +5 oxidation states in the Sb doped SnO_2 structures. The +5 oxidation state is in particularly tight association with sites inside the SnO_2 particle. For low doping concentrations, Sb^{5+} is dominant. Doping n type dopants like Sb in SnO_2 , creates oxygen vacancies surrounding Sb^{5+} ions, located at grain boundary layer and results in decrease of the potential barrier . This increases the charge carrier mobility, which can increase the electrical conductivity of ATO films [1] .

Indium has one less valance electron than tin, so substitutional doping; indium in SnO_2 can act as an acceptor and giving rise to p type films [2] . Xu et al. [3] have observed that low particle size (~ 6 nm), high gas sensitivity and short response times can be achieved in ITO films. This criteria is satisfied in the prepared ITO film(Table 1) and hence this ITO thin film is a potential material suitable for gas sensing applications. Also, ITO films find wide applications in LEDs, like organic light emitting diodes (OLEDs) are , one of the most promising candidates for flat panel displays. ITO has been widely used as the anode contact for organic light emitting devices. These devices usually consist of a sandwich structure with the organic thin film deposited onto the ITO-coated glass substrate and covered by patterned top metal cathode contacts.

Studies involving materials that involve both the charge and spin of electrons in a single substance, have paid special attention on SnO_2 based diluted magnetic semiconductors (DMS) realized through transition metal (TM) doping. In recent days, thin films of manganese doped tin oxide (MTO) films have become an integral part of modern electronic technology. Magnetic semiconductors are materials that exhibit both ferromagnetism and semiconductor properties.

Doped SnO_2 films are very sensitive to the preparation techniques. These films have been prepared by various techniques such as chemical vapor deposition (CVD), spray pyrolysis, reactive RF sputtering, sol-gel technique. Sol–gel fabrication has gained much interest because of its simplicity, low processing temperature, stoichiometry control and its ability to produce uniform, chemically homogenous films over large areas that can provide integration with other circuit elements. The sol–gel method can be successfully used for the preparation of pure oxide films applied in electronics and optics [4]. The main advantage of the sol-gel process is the ability to form inorganic structures at relatively low temperature. Moreover, incorporation of dopant is easier in this technique.

In this study, doped SnO_2 thin films were deposited on glass by sol–gel dip-coating method using metal salt $SnCl_2 \cdot 2H_2O$ doped with 5 mol% of $SbCl_3$, $InCl_3$ and $MnCl_2$ respectively , as precursors giving three sets of films . The structural, electrical and optical properties of doped SnO_2 films were examined in relationship with the various dopants.

2. EXPERIMENTAL DETAILS

SnO_2 solution was prepared by dissolving 8.37 g of Tin (II) Chloride dihydrate ($SnC1_2. 2H_2O$) (Alfa Aesar, purity :98%) in 100 ml of absolute ethanol. The dopant solution of antimony (for Sb/Sn ratio 3 mol%) were simultaneously prepared by dissolving antimony trichloride ($SbCl_3$), in 20 ml of absolute ethanol. Both mixtures were separately stirred and heated at 70 °C for 2 h in a closed vessel. Then, the vessels were opened, and the solutions were again stirred and heated until the solvent was completely evaporated. We finally obtained two powders that were mixed in 50 ml of absolute ethanol .The mixture was finally stirred and heated at 50 °C for 2 h. Deposition of the film from the solution (sol) was performed using the dip-coating process. Similar procedure was used for preparing indium and manganese doped SnO_2 films by using the precursors $InCl_3.4H_2O$ and $MnCl_2.4H_2O$ respectively. Sol-gel dip-coating technique is able to produce homogeneous films with crystallites regular in size. The cleaned glass substrates were dipped in the solution and then withdrawn at a constant speed of 80 mm/min. The deposited films were first dried at 100 ºC for 15 min and then heat treated at 500 °C for 15 min. This process of coating and drying was repeated to obtain films of appropriate thickness suitable for XRD analysis. The dip-coated films were then sintered at 500ºC.

The XRD patterns of the films were measured by Philips X'pert Materials Research diffractometer operated at a voltage of 40 kV and a current of 30 mA,using Cu Kα radiation (λ=1.54 Å) . Optical transmittances of the films were studied using a spectrophotometer (Model – JASCO-V550). From the transmission spectra, Swanepoel's envelope method [5] was used to calculate the thickness and optical band gap of the samples**.** The resistivity of the films were determined by four-point probe measurements with a Keithley 6200 source meter and a cylindrical four point probe head. The magnetic properties were measured using the VSM (Lakeshore VSM 7410).

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction studies

The X-ray diffraction (XRD) pattern of sol-gel derived doped SnO_2 thin films (5 layer coatings) on glass substrates annealed in air at 500 ºC are shown in Fig 1. The XRD patterns revealed that all the samples posses tetragonal rutile structure with orientation along (110), (101), (200) and (210) reflections(JCPDS No. 41-1445). The crystallite size 'D' of films were calculated using Scherrer's formula [6].

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

where D is the crystallite size, β is the full width at half-maximum (FWHM) of the most intense diffraction peak, λ is the X-ray wavelength (1.5406 A°) and θ is the Bragg angle. Table 1: Crystallite size, FWHM, Lattice constants, Thickness and Band gap of 3 mol% of the respective dopants. It can be seen that the diffraction peaks get broadened in ATO films. Broadened peaks indicate the nanosizing of the grains. The intensity of ITO diffraction peaks are low compared with that of ATO and MTO films (Fig. 1). It can also be seen (Table 1) that the crystallite size changed, corresponding to the FWHM of the peaks with different dopants.

The lattice parameters a and c were calculated using the formula

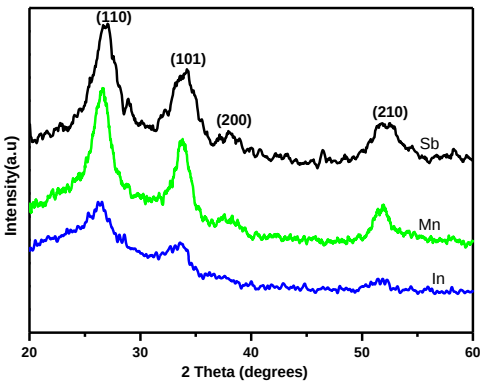

Fig 1: XRD spectra of various dopants in SnO_2 films

$$\frac{1}{d^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2} \qquad (1)$$

Where'd' is the interplanar distance, (h k l) are the Miller indices and 'a' and 'c' are the lattice constants. The calculated values of lattice parameters of the doped films are lower than that of SnO_2 films. This change may be related with the difference in the ionic radii between the dopants and the host SnO_2.

Hence, the dopant atoms incorporate rather easily in the SnO_2 matrix by substitution to Sn atoms leading to a lattice parameter modification. Dopants does not form a second phase either in or with the SnO_2 indicating that all dopant ions were embedded into the crystal lattice of SnO_2.

Dopant	D (nm)	FWHM (rad)	Lattice constants		T(nm)	Eg (eV)
			a	c		
Antimony	3.69	0.038	4.721	3.159	309	3.84
Indium	6.02	0.023	4.751	3.299	426	3.53
Manganese	7.62	0.0187	4.716	3.200	455	3.66

Table 1: Crystallite size(D), FWHM, Lattice constants, Thickness(T) and Band gap (Eg)
of 3 mol% of the respective dopants in SnO_2 films

3.2 Surface Morphology

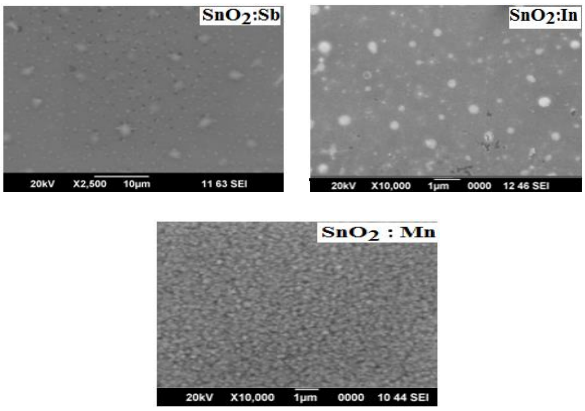

Fig 2: SEM micrograph of dopants (Sb, In, Mn) in SnO_2 film

The figures show the surface morphology of different dopants on SnO_2 film. The grains of various sizes exist in all films and are distributed evenly in some ranges. In addition, the grains possess different irregular shapes and separations.The micrographs shows that films are devoid of cracks. All the micrographs shows different appearance. This shows the effect of incorporation of dopants in SnO_2 film.

3.3 Electrical properties

The variation of electrical conductivity of the various dopants in SnO_2 films are as shown in Fig. 3. The electrical conductivity in films is controlled by the grain size, grain boundary scattering, mobility of charge carriers, by the presence of the dopant and its valence state in the tin oxide lattice**.** The electrical conduction in SnO_2 samples is correlated with non stoichiometry and oxygen deficiency during deposition. When SnO_2 is doped with dopants, single ionized donor is formed. The ionic radius of dopants is compatible with that of tin and hence the dopants get substituted in the lattice sites. In ATO films, Sn^{4+} ions in the lattice are replaced by Sb^{5+} ions. This substitution results in the generation of conduction electrons and thereby decreases resistivity in the lattice. The nature of the semiconductor was confirmed using hot probe method. Hence, by the addition of Sb^{5+} as a dopant, ATO films acquired n-type conductivity. In ITO films, a decrease in resistivity in the film was observed. Substitution of tin (Sn^{4+}) tetravalent by trivalent indium (In^{3+}) may cause a deficiency of one electron or creation of a hole. This gives one extra charge carrier, giving rise to increased conduction.

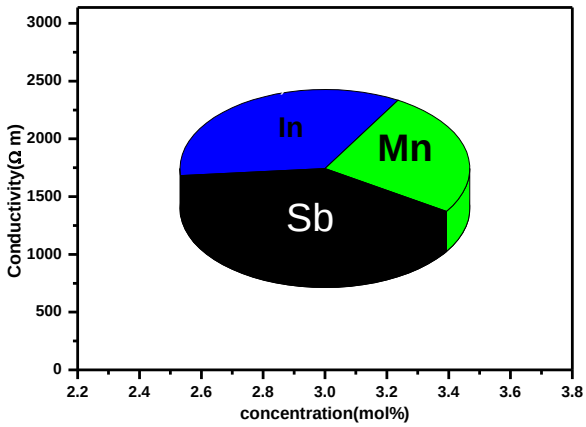

Fig 3 : Schematic diagram of conductivity of various dopants in SnO_2 films

It is observed that this substitution increases the carrier concentration. Such low resistivity is one of the key requirements for TCO films to be used in many optoelectronic and electro-optic devices. Compared with ATO and ITO films, the conductivity of MTO films are low. This may be due to the some type of scattering effects in the film.

3.3 Optical Studies

The optical transmission spectra of various dopants in SnO_2 thin films are as shown in the fig 4. All the films are highly transparent in the visible region of the electromagnetic spectrum. An average transmittance greater than 80 % was observed for all the films in the visible region. The high average value of transmittance in the visible region is indicative of relatively good homogeneous film formed by nanometer-sized small grains. Compared with ATO and

ITO films, the transmittance of MTO film is more. This high transmittance may be due to the enhancement in the crystallinity . The greater grain size reduces light scattering and increases transparency. This is clear from grain size as seen in Table 1.High transmittance at visible-light wavelengths is a key factor for the semiconducting material in a transparent device, such as the SnO_2 thin film solar cell or transistor.

The optical band gap of semi-conductor materials can be deduced from transmission measurements using Wood-Tauc relation[7]. Eg values obtained by extrapolating the linear portion of $(\alpha h\nu)^2$ versus hν plots to intercept the photon energy axis (inset- Fig.3), the calculated Eg values are given in the Table 1. In all the films, the plots of $(\alpha h\nu)^2$ as a function of energy(hν) for films tend asymptotically towards a linear section, which shows that the investigated films have a direct optical band gap. The bandgap energy of the films depends on

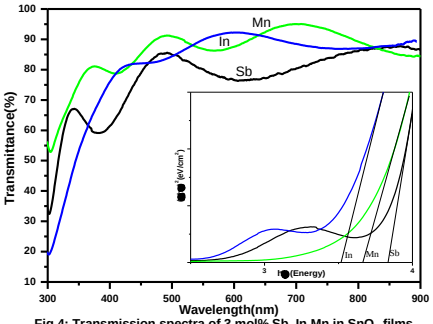

Fig 4: Transmission spectra of 3 mol% Sb, In,Mn in SnO_2 films
(Inset fig: plot of hν versus $(\alpha h\nu)^2$ (eV/cm)^2

many factor like the, presence of dopants and its properties, valence electrons etc. In this comparative study of SnO_2 films using different dopants, the band gap energy is found to vary from 3.53 – 3.84 eV. Such wide gap films are suitable in optoelectronic applications.

3.4 Magnetic property

Magnetization of MTO film is due to Mn-doping in SnO_2 film. The M–H curves of MTO films , shown in fig 5, exihibit room temperature ferromagnetism . The presence of Mn^{3+} ($3d_4$) with magnetic states m = 1 and magnetic moment = 3 μB/cell is a result of the four manganese spin-up electrons and one spin-down electron provided by the neighboring atoms[8]. The magnetization can be ascribed to the F-center exchange coupling, in which both oxygen vacancy and TM doping involved [9]. Such MTO films find wide applications in DMS.

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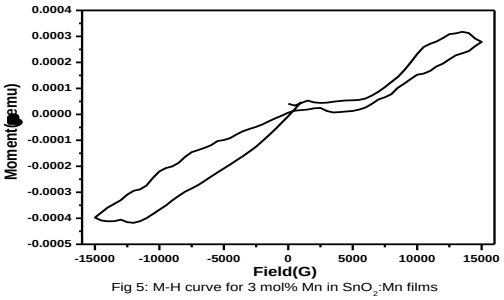

Fig 5: M-H curve for 3 mol% Mn in SnO_2:Mn films

CONCLUSION

SnO_2 films were doped with different dopants like Sb, In and Mn . These films were deposited by dip coating technique onto glass substrate. Different dopants show variation in the XRD spectra, of which, MTO films showed better crystallinity. ATO films produced n type conductivity and ITO films produced p type conductive films. All the films showed a good transparency in the visible region of electromagnetic spectrum. MTO films showed magnetic property, which finds wide applications. Such transparent oxide semiconductors are essential requisites for short-wavelength luminescent devices, such as blue and ultra-violet light-emitting diodes and laser diode. In addition to this, MTO thin films indicated its excellent quality suitable for application as dilute magnetic semiconductor devices.

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