Morphological studies of p-type Mn-doped SnO$_2$ nanostructure

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SnO$_2$ thin films doped with various manganese concentrations were prepared on glass substrates by sol–gel dip coating method. The decomposition procedure of compounds produced by alcoholysis reactions of tin and manganese chlorides was studied by thermogravimetric analysis (TGA). The effects of Mn doping on structural, morphological, electrical and optical properties of prepared films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), Hall effect measurement, Fourier Transform Infrared (FTIR) spectral analysis, UV–Vis spectrophotometry, and photo- luminescence (PL) spectroscopy. The results of the X-ray diffraction show that the samples are crystalline with a tetragonal rutile structure and the grain size decreases with increasing the doping concentration. The SEM and AFM images demonstrate that the surface morphology of the films was affected from the manganese incorporation. The Sn$_{1-x}$Mn$_x$O$_2$ thin films exhibited electrically p-type behavior in doping level above $x = 0.035$ and electrical resistive increases with increase in Mn doping. The optical transmission spectra show a shift in the position of absorption edge towards higher wavelength (lower energy). The optical constants (refractive index and extinction coefficient) and the film thickness were determined by spectral transmittance and using a numerical approximation method. The oscillator and dispersion energies were calculated using the Wemple–DiDomenico dispersion model. The estimated optical band gap is found to decrease with higher manganese doping. The room-temperature PL measurements illustrate the decrease in intensity of the emission lines when content of Mn is increased in Mn-doped SnO$_2$ thin films.

Keywords: SnO$_2$; Doping; Structural.

1. INTRODUCTION
SnO$_2$ thin films are wide band gap n-type semiconductors with unique properties, including high electrical conductivity, high transmittance at near-IR and visible wavelengths and high chemical (thermal) stability. These properties make them useful for functional applications such as gas sensors, transparent conductive electrodes in devices such as solar cell and flat panel displays [1–3]. There is considerable interest in the development of tin oxides based diluted magnetic semiconductors (oxide) (DMS(O)) because of their high Curie temperature which is essential for spintronic de- vices [4]. A number of experiments have revealed magnetic properties of SnO$_2$ thin films doped with transition metal such as Fe [5], Cr [6], Co [7] and Mn [8] at room temperature. Numerous efforts were made in enhancement of n-type conductivity of SnO$_2$ thin films by Sb and F [9], but little research was reported on fabrication of p-type conducting SnO$_2$ using elements with a lower valence cation such as Al [10], Ga [11], In [12], Li [13], Sb [14] and In–Ga co- doped [15] as the acceptor impurity, which increases the hole concentration. Recently, transition-metal-doped SnO$_2$ thin films such as Fe [16, 17] and Co [18] were prepared as possible candidates for p-type transparent conducting thin films. These materials can offer simultaneous ferromagnetic and p-type conduction and new research prospects. Among the transition metals much emphasis is being put on Mn due to its large equilibrium solubility and nearly the same ionic adii compared to Sn$^{4+}$ ion for substitution. So far, there has been only one report on the Mn:SnO$_2$ ceramics as p-type ox- ide semiconductor prepared by conventional solid state re- action [19], but there is no report discussing p-type conduction of Mn-doped SnO$_2$ thin films. Various techniques, such as spray pyrolysis [20], pulsed laser deposition (PLD) [21], thermal evaporation [22] and sol–gel spin coating method (SGSC) [23], have been used to deposit Mn-doped SnO$_2$ (Sn$_{1-x}$Mn$_x$O$_2$) nanostructured thin films. The results of properties of Sn$_{1-x}$Mn$_x$O$_2$ thin films strongly depend on the preparation conditions and growth methods.

Sol–gel process is advantageous compared to other techniques, such as low processing temperatures and possibility of tailoring the starting solutions resulting in better compositions and better control of the final structure. So far, the major focus of studies on Sn$_{1-x}$Mn$_x$O$_2$ thin films has been on the magnetism induced by the incorporation of Mn ion into the SnO$_2$ lattice. However, to the best of our knowledge, there have been no complete reports on the study of the electrical, photoluminescence and optical properties of Sn$_{1-x}$Mn$_x$O$_2$ thin films besides the fact that the evaluation of optical constant of a transparent DMS is considerably important for the applications in magneto-optical devices. In the present study, Mn-doped SnO$_2$ thin films were fabricated on glass substrates by a sol–gel dip coating (SGDC) method from chloride precursor. Doping concentration was taken as the experimental parameter to study the alterations in structural, electrical, optical and morphological properties.

2. EXPERIMENTAL

Sn$_{1-x}$Mn$_x$O$_2$ thin films were prepared by the sol–gel dip coating method. The following procedure was adopted for the preparation of thin films. The sol was prepared by dissolving (0.5 mol) of SnCl$_2$·2H$_2$O in 50 ml absolute ethanol (99.7 %). The mixture was well stirred and refluxed at 80 °C for 2 h. Manganese chloride (MnCl$_2$, 99 %) was then added into the solution as an Mn precursor and Mn concentration was varied for each experiment as $x = 0.000, 0.015, 0.035, 0.070$ and 0.120. This was refluxed at 80 °C for 4 h for the homogeneous mixing of the solution and then aged in air for 48 h, i.e. until the formation of
a clear and homogeneous sol with a stabilized viscosity and pH. The Sn$_{1-x}$Mn$_x$O$_2$ thin films were deposited on glass substrates ultrasonically cleaned with acetone using the dip coating method. The withdrawal speed of the substrate from the coating is 90 mm/min. Then the films were dried at 120 °C to evaporate the solvent and remove organic residuals. This coating and drying procedure was repeated several times to produce layers of solution on substrate. Then for crystallization, the samples were annealed in a furnace at 500 °C for 1 h in air. Upon annealing, the thin film was ready to be analyzed for its characteristics. Thermogravimetric-derivative thermogravimetry (TG- DTG) of powder sample was performed with Perkin Elmer (Pyris Diamond) thermal analyzer. The analysis has been carried out in N$_2$ atmosphere at a heating rate of 20 °C/min. Infrared spectrum of sample was recorded by using Fourier transformed infrared (FT-IR) spectrophotometer (Shimadzu model 8900) to identify the chemical structure. The structural investigations were performed with a Philips PW-1840 diffractometer by using Cu K$_{α}$ radiation ($λ$Cu K$_{α}$ =0.15406 nm). The surface morphology of films was characterized using scanning electron microscope (SEM), LEO, 1430VP. AFM experiment was carried out in the ambient condition with Veeco CP Research instrument using Si cantilever. The electrical properties including resistivity, carrier concentration, Hall mobility of the films were determined with Hall effect measurements system (RH2010) by using the four-probe van der Pauw method. The ohmic contacts were made with silver-spot electrodes. The transmission spectra of films were measured with Varian Cary100 UV–Visible spectrophotometer. The optical constants (refractive index and extinction coefficient) of the films were calculated from the experimental spectral transmittance by using pointwise unconstrained minimization approach [24]. The Wemple–DiDomenico (WD) model and Urbach’s relation were used in the analysis of the obtained spectral data. The photoluminescence spectra of thin films were investigated by Perkin Elmer (LS 55) Fluorescence spectrometer under excitation at 297 nm.

3. RESULTS AND DISCUSSION

A concentrated gel material was prepared for TGA by evaporating the solvent of a small volume of the original gel. Figure 1 shows TG curves of the dried Mn-doped SnO$_2$ gel. Two weight losses were observed at about 70–100 °C and 110–150 °C in the TG curve and the most of weight loss happened below 200 °C. The first weight loss may be from the evaporation of water and alcohol and the following weight loss by the combustion of resultant organics. No other weight loss in TG was observed over 500 °C, confirming that the organic materials were burned out at 500 °C. The results reveal some chemical changes during thin film preparation from sol. All IR band has been assigned to the absorption peak of Sn–O and (Sn, Mn)–O, Sn–OH or OH bond vibrations. The band at 1100 cm$^{-1}$ is attributed to the O–H deformation mode. The absorption in the range of 3000–3600 cm$^{-1}$ is assigned to O–H stretching vibration [25]. The absorption peaks in the range of 500–700 cm$^{-1}$ are assigned to Sn–O and (Sn, Mn)–O bands (antisymmetric Sn–O–Sn stretching mode of the surface–bridging ox- ide formed by condensation of adjacent surface hydroxyl.
The incorporation of Mn at Sn site was found to influence the surface morphology of the films. The microstructure of pure SnO$_2$ film has uniformly distributed nanocrystallites (Fig. 2a). It may be noted from Fig. 2 that the grain size decreases with an increase in Mn concentration. This reduction can be explained by the fact that Mn$^{3+}$ ion has a smaller radius and contraction of the lattice structure than Sn$^{4+}$ ion. The root-mean-square (RMS) surface roughness is generally used to study the morphology of surfaces. The RMS roughness contributes to light scattering and also gives an idea about the quality of the surface for optical device designing. AFM images of pure SnO$_2$ and Sn$_{1-x}$Mn$_x$O$_2$ (x = 0.035, 0.070 and 0.120) films are respectively presented in Fig. 3(a)–(d), and roughness parameters (average surface roughness, Ra, and root mean square roughness, Rq) are measured. The surface of pure SnO$_2$ film is more uniform than that of Mn-doped SnO$_2$ films. The roughness parameters increase with increasing of Mn contents from the x = 0.000 (Rq = 0.44 nm and Ra = 0.35 nm) to x = 0.120 (Rq = 1.04 nm and Ra = 0.65 nm). There are signs of hump
formation in top surface of the SnO2 film deposited, probably because of particle or grain coalescence.

The Hall effect experiment results showed that the resistivity of pure tin oxide films is much higher than that of thin films prepared by other conventional methods [9, 26] and this is related to slight deviation from stoichiometry. As can be seen in Table 2, in low doping level, below \( x = 0.035 \), the films showed n-type behavior and above this level, conversion to p-type conduction (when majority carriers are holes) has occurred. This behavior can be attributed to the substitution of Sn4+ by Mn3+ as an acceptor [19]. Regarding the Hall effect measurement results, the resistivity showed increase by enhancement of the Mn concentration (x). This effect is due to the increase in disorders and amorphous phase, which can be explained based on the XRD patterns. Another reason for increasing resistivity is attributed to the fact that Mn3+ ions are substituted into Sn4+ sites and act as an acceptor in SnO2 lattice. This trend is accompanied by decrease of carrier concentration because of the presence of carrier traps. A decrease in mobility of p-type thin films is caused by the decrease of grain size (grain boundary enhancement) and increased disorder of the tin oxide crystalline lattice, which corresponds to phonon and ionized impurity scattering. Optical transmission spectra of the Sn1–xMnxO2 films in the wavelength region of 300–800 nm.

![AFM micrographs of films prepared with various doping concentrations at (a) \( x = 0.000 \), (b) \( x = 0.035 \), (c) \( x = 0.070 \) and (d) \( x = 0.120 \).](image_url)

**Fig. 3** AFM micrographs of films prepared with various doping concentrations at (a) \( x = 0.000 \), (b) \( x = 0.035 \), (c) \( x = 0.070 \) and (d) \( x = 0.120 \).

The spectra show a high transmittance (>80 %) for the pure tin oxide thin film and lower transmittance for the films prepared by doping of various Mn concentrations. The higher transmittance observed in the pure SnO2 film was attributed to less scattering effects, structural homogeneity and better crystallinity, whereas the lower transmittance in the Mn-doped SnO2 thin films can be due to a lesser crystallinity, increase in scattering centers
(grain boundaries, defects, etc.) and enhanced surface roughness, which is consistent with the AFM results. Further, the fundamental absorption edge was shifted towards higher wavelengths with the increase of Mn concentration, suggesting the narrowing of energy band gap in the films due to sp–d exchange effect. It was reported that similar shift has resulted from the incorporation of transition metal ions into the SnO2 nanoparticles [21, 27–29].

The optical constants (refractive index and extinction coefficient) of the films prepared at different dopant concentrations were calculated from the experimental transmission spectra by using pointwise unconstrained minimization. The variations of refractive index and the extinction coefficient with the wavelength for all the films. The refractive index of the samples increases with the doping concentration. The observed variation of refractive index with doping concentration for SnO2 :Mn thin films can be explained on the basis of the contribution from both disorder of the films and lattice contraction [30] that were deduced from XRD results. The increase in values of the extinction coefficient can result from the absorption and grain scattering due to the decrease in grain size, according to XRD patterns results, and so the

4. CONCLUSIONS

Undoped and Mn-doped SnO2 thin films with different Mn doping concentrations were successfully deposited on glass substrates by sol–gel dip coating technique. The X-ray diffraction pattern indicates that pure SnO2 films possess a tetragonal crystalline structure. Upon increasing the Mn concentration, the crystalline quality was found to be deteriorated. SEM images reveal reduction of granule size with increase in Mn content. AFM results proved that the surface roughness of the films has increased with Mn content. The Hall effect measurements have shown that above a particular percentage of manganese, the doping the conduction type changes from n-type to p-type and in this region, resistivity is high because of the enhancement of lattice disorder and defects in SnO2 thin films. The optical transmittance measurements of the films confirmed that the films are transparent in the visible region. Upon Mn concentration, the optical band gap $E_g$ of the films was found to decrease from 3.93 to 3.75 eV. The bowing of band gap is accompanied with a broadening of the Urbach tail. The optical constants (refractive index and extinction coefficient) tend to increase with increasing doping concentration. It was shown that the dispersion parameters of the films obey the single oscillator model.

References

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