Effect of doping on the Structural and Optical Properties of SnO₂ Thin Films fabricated by Aerosol Assisted Chemical Vapor Deposition

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Abstract. In order to achieve high conductivity and transmittance of transparent conducting oxide (TCO), we attempted to fabricate Mg doped SnO₂ (MgₓSn₁₋ₓO₂) thin films and characterized them for their structural and optical properties. The MgₓSn₁₋ₓO₂ thin films have been deposited on glass substrate by using aero-sole assisted chemical vapor deposition (AACVD). The molar concentration of Mg concentration was changed from 0 to 8%. The confirmation of tetragonal structure and particle size (32 to 87nm) has been calculated of thin films by XRD. The surface roughness is decreased with the increase of the dopant concentration, which has been investigated by atomic force microscopy (AFM). The optical transmission has increased from 54 to 78% and the band gape of pure SnO₂ has been found to be in the range of 3.76eV and it is shifted to 3.69eV for 6Wt % Mg doping and then increase on further increasing the Mg doping.

Keywords: Mg Doped SnO₂; Thin Films; AACVD; RBS; XRD

1. Introduction
Nanometre size materials are great insert in the recent year due to the promising technological application in various fields. Among these materials, tin oxide (SnO₂) is a very important material, due to its attractive properties like optical transmittance, uniformity, low resistivity, mechanical hardness, stability to heat treatment and piezoelectric behaviour [1-2]. These properties make SnO₂ a suitable candidate for device such as for gas sensor application, Li- ion batteries, photovoltaic, super capacitor, Light emitting diode, display devices and solar cell [3-4].

SnO₂ thin film has been prepared by various techniques such as RF magnetron sputtering [5-6], electron beam evaporation [7], sol gel coating [8], chemical vapour deposition [9], etc. Among them AACVD is very simple technique for the growth of SnO₂ due to its simplicity and low cost. In comparison of other deposition techniques which required to maintains high vacuum during deposition, in AACVD the deposition is performed under atmospheric pressure.

To improve the quality of film as well as the physical and chemical properties of thin films, the addition of some metal ions as impurities is expected to play an important role in changing the charge carriers concentration of the metal oxide matrix, catalytic activity, the surface potential, the phase composition, the size of crystallites, and so on [10-11]. In literature we have found that Cu [12],
Fe [13], Mn [14], Sb [15], Cs [16] and F [17] were doped to improve the properties of SnO$_2$. In the literature, no one has reported the deposition of Mg$_x$Sn$_{1-x}$O$_2$ thin films by AACVD. The Mg$^{2+}$ has ionic radius of 0.67 Å, which is close to the ionic radius of Sn$^{4+}$ that is 0.71 Å. Therefore replacement of Sn by Mg does not change in lattice constants and crystal structure. It is possible to change the band gap by doping SnO$_2$ with suitable ratio of Mg.

In this study, we have grown SnO$_2$ thin film with different concentration of Mg (2-8 wt%) and study the effect of Mg doping on the structure and optical properties of the growth film using X-ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR), Rutherford back scattering (RBS), UV-Vis transmission spectroscopy and atomic force microscopy (AFM).

2. Materials and Methods

The schematic diagram of AACVD apparatus is shown in figure 1. The 0.2 M solution of Mg$_x$Sn$_{1-x}$O$_2$ (x=0-0.08) in ethanol was prepared and stirred with magnetic stirrer on hotplate for 30 minutes. The glass slides (1 x 2 cm) were washed ultrasonically prior to deposition with ethanol, propanol and mixture of acetone-propanol before deposition. The slides were placed in distilled water. Before the deposition, the glass slides were taken from the distilled water and placed inside the quartz tube and heated to the required temperature (450 °C). The temperature of the glass slides were continuously monitored by the K-type thermocouple. The 0.2 M solution of Mg$_x$Sn$_{1-x}$O$_2$ (x = 0-0.08) in a two neck flask was placed on the humidifier. The aero-sol was generated at room temperature were transported to the heated substrate by an inert gas (Argon gas). The deposition was performed for 30 mints and then deposited thin films were allowed to cool down to the room temperature under the inert gas passage.

The phase crystallinity and structural analysis of the deposited Mg$_x$Sn$_{1-x}$O$_2$ was analyzed by X-ray diffraction patterns using X’pert PRO (PAN analytical) with Cu-K$_{α}$ source radiation. The optical transmission of the thin films were recorded at room temperature by a Perkin Elmer UV/VIS/NIR Lambda19 spectrometer in the wave length 300-850nm. FTIR transmission spectra were recorded at room temperature on a Nicolet 6700, Thermo electron Co. USA in the range of 500-1800 cm$^{-1}$. Surface morphology of the thin films were investigated by atomic force microscopy (Quesant Universal SPM, Ambios Technology) in non connected mode. An AFM tip of silicon nitride was used having an approximate radius of curvature of 10nm. Rutherford backscattering (RBS) was performed to confirm the layer structure across the thickness of the thin films. Incident particles were the He$^{+}$ ions accelerated by 5UDH Tandem Accelerator to energy of 2.84MeV. The scattering angle was 170°, which is most common for conventional RBS. However, required depth resolution was
achieved by maintaining the surface normal of the sample to 0° with respect to incident beam and 10° with respect to the scattered beam.

3. Result and Discussion

Non-destructive X ray diffraction technique was used to determine the phase crystallinity and structural analysis of the Mg$_x$Sn$_{1-x}$O$_2$ deposited thin films as shown in figure 2(a) and 2(b). As shown in figure 2(a), the d$_{hkl}$ (inter planer distance) values of their corresponding <hkl> have been identified as (110), (101), (200), (211), (220), (310), and (321) of the pure SnO$_2$ thin film which indicate the tetragonal structure of SnO$_2$. The lattice parameter are a = b = 4.67 Å, c = 3.19 Å respectively with unit cell volume 69.57 Å$^3$. The lattice parameters were not change by Mg doping because Sn$^{4+}$ have the close radii to the Mg$^{2+}$, might be due to the substitution of metal ions in the crystallite structure and therefore no structure strain is generated. These results comply with the standard SnO$_2$ XRD pattern of the JCPDS line [18]. The Mg$_x$Sn$_{1-x}$O$_2$ XRD spectrum shows in figure 2(b) that the thin film retain the tetragonal structure but peaks slightly shifted towards the lower angle, this is due to the substitution of Sn$^{4+}$ ions at the lattice sites with the Mg$^{2+}$ ion.

For calculate the crystallite size of the deposited thin films, the Debye Scherer formula was employed on the XRD spectra which is given by

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$

Where $\lambda$ is the wave length of the X-rays employed which in this case is 0.1548 nm for Cu-K$_\alpha$. 0.9 is the correction factor in the Debye Scherer equation, $\beta$ is the FWHM (full width and half maxima) in radian and $\theta$ is the Bragg's angle in degree. The calculated crystalline size from the Scherer formula is in the range of 32 nm for the deposited thin films.

The depth profile study and the elemental concentration of the deposited Mg$_x$Sn$_{1-x}$O$_2$ thin films by AACVD have been examined by Rutherford Back scattering analysis. Figures 3(a), (b), (c) and (d) show the simulation and experimental data of the thin films with the energy of the incident He$^{4+}$ beam was 2.084MeV. The counts come from the Mg in the thin films overlap with the substrate Si because of minor difference in their atomic weight. The O, Mg and Sn are simulated at the channel energies corresponding to 0.82, 1.05 and 1.69MeV respectively. The elemental composition of the thin films and their thickness examined by RBS simulated spectra are presented in Table 1.
Figure 3. RBS and depth profile spectra of Mg$_x$Sn$_{1-x}$O$_2$ thin films with increasing concentration of dopant shown in (a), (b), (c) and (d), respectively.

FTIR spectra of Mg$_x$Sn$_{1-x}$O$_2$ thin films are shown in fig.4. The stretching/vibrational peaks corresponding to 595, 760 and 850 cm$^{-1}$ of deposited pure SnO$_2$ thin films. The peaks assigned at 595 cm$^{-1}$ to O-Sn-O and 760 cm$^{-1}$ to Sn-O-Sn stretching vibration, while the peak at 850 cm$^{-1}$ is due to the phonon vibration. These peaks shifted to 620, 775 and 880 cm$^{-1}$ in case of Mg doping. B. Zhang et al [17] reported the peaks at 468 and 619 cm$^{-1}$ which assign to O-Sn-O and Sn-O. K.K. Purushothaman et. al. [19] reported the band at 437, 536, 586 and 642 cm$^{-1}$ belongs to the vibration of SnO$_2$. The shape of the FTIR and position of the peaks have been shown to vary with synthesis routes and particle size [20].
Atomic force microscopic analysis was performed to determine the grain size of the deposited Mg$_x$Sn$_{1-x}$O$_2$ thin films. For an optical surface, roughness is normally considered as an important parameter. Surface roughness not only the light scattering but also give an idea about the quality of the surface under investigation, in addition to providing some insight on the growth morphology. A systematic description of various analytical method used for roughness characterization can be found in ref [21]. Root mean square roughness ($R_{\text{rms}}$) which is defined as standard deviation of the surface height profile from the mean height, is the most commonly reported measurement of the surface roughness and is given by,

$$R_{\text{rms}} = \left( \frac{1}{N} \sum_{i} (h_{i} - \langle h \rangle)^2 \right)^{\frac{1}{2}}$$

Where $N$ is the number of pixels in the image, $h_{i}$ is the height of $i^{th}$ pixel and $\langle h \rangle$ is the mean height. Two dimension AFM images of the Mg$_x$Sn$_{1-x}$O$_2$ as shown in the figure 5(a) and 5(b). The value of $R_{\text{rms}}$ decreases (54 – 23nm) with increasing the Mg doping.

The transmission spectra of Mg$_x$Sn$_{1-x}$O$_2$ were recorded in UV-visible near the infrared region (300-850nm). Figure 6 shows the variation of transmittance with the wave length for Mg$_x$Sn$_{1-x}$O$_2$ thin films. The average transmission in the visible region was found to range of 55 to 78% depend on the Mg concentration with the increase in transmission was observed.
Figure 5. Surface morphology of pure and Mg doped TiO$_2$ thin films. The surface roughness increase with the increase of Mg concentration confirmed by AFM images (5µm x 5µm).
Figure 6. Transmission plot of pure and Mg doped SnO$_2$ thin films with increasing dopant concentrations.

The absorption coefficient ($\alpha$) was calculated from the transmission spectra using equation [12],

$$ \alpha = \frac{1}{t} \ln \left( \frac{1}{T} \right) $$

Where $T$ is the optical transmission and $t$ is the film thickness. The direct band gap of thin films were calculated from figures 7(a), (b), (c) and (d) respectively using the formula [22],

$$ \alpha h \nu = A(h \nu - E_g)^m $$

Where $\alpha$ is the absorption coefficient, $h$ is the Planck’s constant, $\nu$ is the frequency of incident light, $E_g$ is the energy band gap of material and $m$ is the factor governing the direct/indirect, etc. transition of electron from the valance band to the conduction band.
It was found that the band gap of pure SnO$_2$ that the band gaps of un-doped SnO$_2$ is 3.76eV which is larger to the typical value quoted for bulk SnO$_2$ (3.6eV). It is related with the oxygen vacancies and the structural defects. The value of band gap decreases with increase in the Mg doping for low concentration and increase at doping concentration (i.e. 8 wt %) as shown in figure 8.
The increasing of the band gape as usually observed for oxide semiconductor doped with donors, and reduces if doped with acceptors. The decreasing in the band gap was attributing to the presence of holes in Mg\textsubscript{x}Sn\textsubscript{1-x}O\textsubscript{2}. Each substitution Mg atom will create two holes in O 2p state because of the lower-valence than Sn\textsuperscript{+4}. They form the impurity band inside the forbidden gap region. The electrons in the valence band are exited, and they can be combining with the holes in the impurity band first. However they are not stable. The trapped electrons will recombine with the hole in the conduction band, resulting the shrinking of the band gap. At the 8% doping of Mg sample has a larger band gap than the 6% Mg doping as shown in Figure 8. It is due to the Mg interstitials because of the limiting solubility of Mg in SnO\textsubscript{2}.

| Sample          | Thickness (nm) | Stiochiometry      |
|-----------------|----------------|--------------------|
| Pure SnO\textsubscript{2} | 350            | Sn\textsubscript{1.02}O\textsubscript{2} |
| 4% Mg/SnO\textsubscript{2} | 424            | Sn\textsubscript{1.00}O\textsubscript{2}Mg\textsubscript{0.13} |
| 6% Mg/SnO\textsubscript{2} | 300            | Sn\textsubscript{1.00}O\textsubscript{2}Mg\textsubscript{0.18} |
| 8% Mg/SnO\textsubscript{2} | 320            | Sn\textsubscript{1.06}O\textsubscript{2}Mg\textsubscript{0.23} |

4. Conclusions

Mg\textsubscript{x}Sn\textsubscript{1-x}O\textsubscript{2} (x = 0-0.08) thin films have been prepared on a glass substrate by aero-sol assisted chemical vapor deposition. The tetragonal structure of pure and Mg doped SnO\textsubscript{2} was conformed and lattice parameters and volume of unit cell were calculated by XRD. The thickness of the deposited thin films are in the range of 300nm, where as the elemental composition of the Mg and Sn in the thin films are in accordance with the proposed composition of the deposited material, conformed by the RBS and XRD analysis. The transmission was increased from 55 to 78% and energy band gap (3.67 to 3.69eV) was decreased by increasing the Mg (0 to6%) doping. The refractive index (1.61 to 1.53) is increased as the Mg concentration increase. The Mg doped SnO\textsubscript{2} transparent conducting oxide is very useful for window layer of solar cell due to high reflectance of infrared radiation and transparent of visible light.

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