SECTION A

CHAPTER -III

Preparation and characterization of undoped and Sn- and Cu-doped In$_2$O$_3$ thin films
Preparation and characterization of undoped and Sn- and Cu- doped In$_2$O$_3$ thin films

3.1. Introduction

The properties of indium oxide thin films depend on the preparation methods which play an important role while fabricating a device using these thin films. This chapter describes in detail about the preparation of indium oxide thin films using dip coating technique with two different precursors. It includes cleaning of the substrates and also a comparative study of the films prepared from the two different solutions. The methods used for the characterization of the thin films are thermo gravimetry/differential thermal analysis (TG/DTA), X-ray diffractometer (XRD), Raman scattering analysis, scanning electron microscopy (SEM), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), UV-Vis spectrometer and Photoluminescence analysis (PL).

3.2. Experimental

3.2.1. Selection and cleaning of substrates

Reliable thin film adhesion depends greatly on the cleanliness of the surface upon which the film is deposited. Optimum surface roughness also affects thin film adhesion. So the selection and cleaning of the substrates play an important role on the growth of the films and its adhesion on the substrate. Glass substrate has got the maximum surface smoothness and is also optically plane [1, 2]. Besides it is easily available and economical. The process of substrate cleaning requires that the bonds are broken between the contaminant molecules as well as between the contaminant and substrate. This may be accomplished by chemical means or by supplying sufficient energy to vaporize the impurity. In the present investigation, the following steps are followed for cleaning the glass substrates.
Glass substrates of the required size were cut by using the diamond glass cutter and then dipped in chromic acid for 2 minutes and then thoroughly rinsed with double distilled water.

The glass substrates were then cleaned with soap solution to remove the fatty materials.

They were next rinsed and cleaned with double distilled water in the agitator for about 45 minutes.

They were then dried in an oven.

The dried substrates were cleaned with isopropyl alcohol vapors condense.

The substrates were finally dried in an oven.

3.2.2. Method-I

i) Preparation of the coating solution

Initially, 0.1M of indium chloride (InCl₃, Aldrich) solution was precipitated with aqueous ammonia. The precipitates were centrifugally washed several times (15,000 rpm, 20 min) with double distilled water to remove the contained free ions. A clear transparent solution was prepared by adding glacial acetic acid in drops to the washed precipitates. The pH of the transparent solution was close to 2 and the solution was left without disturbance (i.e. aging) till its pH becomes 4.

ii) Thin film preparation

Cleaned glass substrates were dipped in the aged solution for 3 mins and then dried in a hot air oven at 100°C for an hour. The dried films were then annealed at 400°C for an hour in a muffle furnace. When the dipping time was less than 3 mins the sticking property of the solution over glass substrates was less or island like sticking of the solution over the substrates was observed. Uniform coating of the substrates were observed when the dipping time was 3 min. Thus, the optimized 3 mins dipping time was given to all of the substrates for good adhesion of the film over the substrates. Fig 3.1 shows the schematic representation of the dip coating technique. Step 1 shows the substrate being gradually immersed in the coating solution and step 2 shows the substrate being gradually dragged out of the solution.
Due to the surrounding air the solution coated on the substrate started drying as shown in step 3. Dip coating, can be done either manually or using a programmed controller.

![Fig. 3.1 Dip coating technique]

3.2.3. Method-II

i) Preparation of the coating solution

0.25 g of indium nitrate (In(NO$_3$)$_3$, Aldrich) was dissolved in 10 ml of mixed solvent (n-propanol + 2-methoxy ethanol, 1:1 volume ratio). After complete dissolution of the salt, the solution was stirred continuously for 1 hr to get a homogeneous dispersion. Then the solution was left for 16 hrs aging.

ii) Thin film preparation

Cleaned glass substrates were dipped in the aged solution for 1 min and then dried in a hot air oven at 100°C for an hour. The dried films were then annealed at 400°C for an hour in a muffle furnace. When the dipping time was less then 1 minute the sticking property of the solution over glass substrates was less and when it was increased to more than 1 min the whole substrate gets wetted and the sticking of the film was not proper. This may be due to the usage of organic solvents n-propanol and
2-methoxy ethanol. Thus, for this method the optimized 1 min dipping time was given to all of the substrates for good adhesion of the film over the substrates.

From the characterization analysis, it is observed that In$_2$O$_3$ thin film prepared using method – II is found to have better surface morphology than that to method – I. So the method – II is adopted to prepare Sn and Cu doped In$_2$O$_3$ thin films.

3.2.4. Preparation of Sn doped In$_2$O$_3$ thin films

To prepare Sn doped In$_2$O$_3$, 0.25 g of indium nitrate (In(NO$_3$)$_3$, Aldrich) was dissolved in 10 ml of mixed solvent (n-propanol + 2-methoxy ethanol, 1:1 volume ratio). After complete dissolution of the salt, 5 ml of the mixed solvent (acetic acid and 2-methoxy ethanol, 3:2 volume ratios) has been added to the solution and stirred well. To the mixed solution, 0.03 g of SnCl$_4$ 4H$_2$O has been added (1:0.1 molar ratio) and stirred continuously for 1 hr to get homogeneous dispersion. Then the solution was left for 16 hrs for aging. Thin film coating has been done as discussed in the section. 3.2.3(ii). The same procedure is repeated for 1:0.2 and 1:0.3 molar ratio of In:Sn compositions.

3.2.5. Preparation of Cu doped In$_2$O$_3$ thin films

A similar procedure has been adopted for preparing Cu doped In$_2$O$_3$. By replacing SnCl$_4$ 4H$_2$O, the copper precursor CuCl$_2$ 2H$_2$O has been added with the respective molar ratios. Three molar ratios (1:0.1, 1:0.2 and 1:0.3) have been fixed for both of the dopants and separate coating solutions have been prepared for the doped In$_2$O$_3$ thin films.

3.3. Results and discussion

3.3.1. Thermal analysis

Thermal analysis was performed using the Thermo-Gravimetry/Differential Thermal Analysis (TG/DTA) instrument SDT Q600 V8.3 Build 101 at a heating rate of 20 °C / min under air atmosphere. The precursor solution was dried at 60 °C and then the dried powders were taken for thermal analysis. Fig. 3.2 shows the TG/DTA spectra of the powders prepared from method-I. The TG spectrum shows a weight loss from 172 to 242 °C (about 10%) associated with an endothermic peak at 227 °C in DTA due to dehydration.
Fig. 3.2. TG/DTA spectra of the dried precursor solution of method – I

Fig. 3.3. TG/DTA spectra of the dried precursor solution of method – II
From 242 to 301 °C, the weight loss is about 12% which is due to the phase transformation of indium oxide from the precursor. Again there is a weight loss observed from 301 to 337 °C (about 2%) associated with an exothermic peak at 332 °C due to the crystallization of indium oxide while subject to further heat. The obtained result is in good agreement with the reported result [3].

Fig. 3.3 shows the TG/DTA spectrum of the dried precursor of method-II. The weight loss of 12.34 % that occurred from 188 to 231 °C is due to the loss of water molecules trapped in propanol. The weight loss from 231 to 309 °C (12.46%) is due to the decomposition of nitrates. A major weight loss from 309 to 370 °C (of 32.96 %) associated with an exothermic peak around 370 °C is due to the phase transformation of the precursor to indium oxide. A minor weight loss of 3.4 % from 370 to 407 °C has been observed in association with an exothermic peak around 400 °C due to the crystallization process.

3.3.2. Structural analysis

The structure of the thin film was examined using X-Ray Diffraction (XRD) on a PANalytical XPert Pro diffractometer with Cu Kα radiation (\( \lambda = 1.5406 \) Å). Fig. 3.4 shows the XRD pattern of the film prepared through method-I. The peaks were observed at \( 2\theta = 30.61, 35.45, 51.08, 60.78^\circ \) corresponding to the body centered cubic structure of indium oxide (JCPDS # 06-0416, space group Ia3). The prepared film is highly oriented towards (222) direction, i.e., \( 2\theta = 30.61^\circ \). The average crystallite size calculated using Scherrer’s formula is found to be 22 nm.

Fig. 3.5 shows the XRD pattern of the film prepared through the method-II. The so formed film also crystallized in body centered cubic structure of indium oxide (JCPDS # 06-0416, space group Ia3) and oriented highly towards (222) direction. The peaks were observed at \( 2\theta = 30.63, 35.40, 51.11, 60.67^\circ \). The average crystallite size for the film prepared through method – II is 15 nm.

The average crystallite size, lattice parameter and lattice spacing were calculated using standard formulae and are shown in the table 3.1. The lattice parameter and constant values are in good agreement with the standard values (JCPDS # 06-0416). In both of the films, an amorphous background has been observed upto \( 2\theta = 40^\circ \) which may be due to the substrate effect. Here the films were coated on glass substrates.
Fig. 3.4. XRD pattern of the film prepared through the method - I

Fig. 3.5. XRD pattern of the film prepared through the method - II
Table 3.1. Structural parameters calculated from the XRD patterns

<table>
<thead>
<tr>
<th>Preparation method</th>
<th>$\theta$ (deg.)</th>
<th>hkl</th>
<th>Average crystallite size ‘D’ (nm)</th>
<th>Lattice constant ‘a’ (Å)</th>
<th>Lattice parameter ‘d’ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method-I</td>
<td>30.61</td>
<td>222</td>
<td>22</td>
<td>10.111</td>
<td>2.918</td>
</tr>
<tr>
<td>Method-II</td>
<td>30.63</td>
<td>222</td>
<td>15</td>
<td>10.104</td>
<td>2.917</td>
</tr>
</tbody>
</table>

Raman scattering analysis was also performed to study the structure of the thin films prepared through the two methods using HORIBA JOBIN YVON microRaman spectrometer. Indium oxide belongs to cubic C-type rare-earth oxide structure and for this type of structure the factor group analysis predicts the following modes,

$$4A_g + 4E_g + 14T_g + 5A_u + 5E_u + 16T_u \rightarrow (3.1)$$

in which $A_g$, $E_g$ and $T_g$ are Raman active and infrared inactive, while the $T_u$ vibrations are infrared active and Raman inactive. The $A_u$ and $E_u$ vibrations are inactive in both Raman and infrared measurements [4 and 5]. Raman scattering analysis for indium oxide thin film prepared by method I & II is shown in the Fig. 3.6. Thin film samples were excited with 514.5 nm Ar$^+$ ion laser. The observed spectrum showed a very low frequency peak around 137 cm$^{-1}$, two low frequency peaks around 310 cm$^{-1}$ and 370 cm$^{-1}$ and two high frequency peaks around 499 cm$^{-1}$ and 632 cm$^{-1}$, which are in good agreement with the reported values of bcc-In$_2$O$_3$ [6-8].
3.3.3. Surface morphological analysis

The surface morphology of the thin film was analyzed through a FEI Quanta 200 Scanning electron microscope and the surface roughness of the prepared thin film was calculated using Veeco Caliber Atomic force microscopy. The surface morphology of the prepared films was observed through SEM and AFM analysis. Fig. 3.7(a) shows the SEM image of the film prepared through the method – I which contains spherical grains over the surface. The size of the spherical grains ranges around a few nanometers. Fig. 3.7(b) shows the SEM image of the film prepared through the method – II. The SEM image of the film prepared through method – II shows nearly a smooth surface. Such a smooth surface was observed by Gupta et al [9] for pulsed laser deposited doped In$_2$O$_3$ thin film.

Fig. 3.8(a) shows the 2D-AFM image of the film prepared though the method – I and the RMS roughness has been calculated from the marked area in the figure. Here also a similar morphology has been observed as in the case of SEM analysis. Fig. 3.8(b) shows 3D-AFM image of the film and the RMS roughness is found to be 2.1 nm.
Fig. 3.9 shows the 2D and 3D images of the sample which show that the films and the RMS roughness has been calculated from the marked area in Fig. 3.9(a). 3D AFM image shows the uniform vertical direction growth. The RMS roughness is found to be 2.56 nm. The uniform growth in the vertical direction is a good sign in the aspect of improvement of surface area of the films.

![Fig. 3.7. SEM images of In$_2$O$_3$ thin films prepared using (a) method – I and (b) method - II](image)

Improved surface area with a decrease in crystallite size showed that the method – II prepared thin films can be best used as sensing elements to carry out sensing experiments. Apart from the surface and size of the crystallite, the method – II has an added advantage that the sticking property of the precursor solution to the glass substrates is good when compared with the method – I (it took three minutes to get a good film through the method - I whereas the films can be easily adhered to the substrates when the sticking property was 1 min in method – II). Hence with this good implication of the method – II, it is adopted to carry out the sensing measurements and is also used to prepare doped thin films.
Fig. 3.8(a) 2D and (b) 3D AFM images of In$_2$O$_3$ thin films prepared using method – I
The main material of research in the present study is indium oxide. If the material is doped with Sn and Cu, the two impurities it will occupy the position of metal In in In$_2$O$_3$. Thereby the electrical behaviour of the film changes which should improve the electrical behaviour of In$_2$O$_3$. Thus there might be an improvement in the sensor response of the material. To calculate the effect of dopant on the gas sensing element indium oxide prepared through dip coating method, two different dopants were chosen. One is the well known tin dopant i.e. tin doped indium oxide known as...
ITO and it has been widely used as electrode material. The other is a rare dopant of indium oxide, copper. The difference between these two dopants are the first one (Sn) belongs to the 4th group of the periodic table and Cu belongs to the 1st group. Even though, Cu doped In$_2$O$_3$ is less studied and the sensing behaviour of the material is not yet reported, Cu in its oxide form is sensitive to various gases such as H$_2$S, alcohols, NO$_2$ etc [10-12]. In the present study, a significant change is expected in the sensing behaviour of In$_2$O$_3$ with the addition of Cu dopant.

3.3.4. Structural analysis of the doped In$_2$O$_3$

Fig. 3.10 shows the XRD patterns of Sn-doped In$_2$O$_3$ thin films. The observed patterns showed the peaks corresponding to cubic In$_2$O$_3$ (JCPDS# 06-0416) and highly oriented towards (222) direction as observed for pure In$_2$O$_3$ in Fig. 3.5. But there is a shift observed in 2θ. The observed shift is calculated from the preferentially oriented peak (222). For undoped In$_2$O$_3$ thin film the (222) peak is observed at 2θ = 30.63° and for the molar ratio of In:Sn = 1:0.1 the peak gets shifted to 2θ = 30.58°, as the concentration of Sn increases from 1:0.1 to 1:0.2 the peak again gets shifted towards the lower angle of 2θ, from 2θ = 30.58° to 30.45°. Again there is shift observed in 2θ (30.45° to 30.42°) when the concentration of In:Sn becomes 1:0.3. This type of lower angle shift upon the increase in concentration of Sn in In$_2$O$_3$ clearly depicts the presence of dopant in the synthesized films. The structural parameters calculated using XRD are given in table 3.2.
Doped and Undoped In$_2$O$_3$ thin films

Fig. 3.10. XRD pattern of Sn-doped In$_2$O$_3$ thin films with molar ratios (a) 1:0.1, (b) 1:0.2 and (c) 1:0.3

Table 3.2. Structural parameters calculated from the XRD patterns of Sn-doped In$_2$O$_3$ thin films

<table>
<thead>
<tr>
<th>Molar ratio In:Sn</th>
<th>$\theta$ (deg.)</th>
<th>hkl</th>
<th>Average crystallite size ‘D’ (nm)</th>
<th>Lattice constant ‘a’ (Å)</th>
<th>Lattice parameter ‘d’ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.1</td>
<td>30.58</td>
<td>222</td>
<td>16.47</td>
<td>10.119</td>
<td>2.921</td>
</tr>
<tr>
<td>1:0.2</td>
<td>30.45</td>
<td>222</td>
<td>18.40</td>
<td>10.163</td>
<td>2.934</td>
</tr>
<tr>
<td>1:0.3</td>
<td>30.42</td>
<td>222</td>
<td>19.16</td>
<td>10.171</td>
<td>2.936</td>
</tr>
</tbody>
</table>
Doped and Undoped In$_2$O$_3$ thin films

Fig. 3.11 shows the XRD patterns of the Cu doped In$_2$O$_3$ thin films coated on glass substrates. Here the main peak at (222) position is clearly noticed rather than the other peaks corresponding to In$_2$O$_3$. In this case also the shift in the position of the main peak is observed but here the shifting is towards the higher end of 2θ. Initially for pure In$_2$O$_3$ the position of (222) peak was at 2θ = 30.63° and for 1:0.1 concentration of In:Cu the position of the peak gets shifted to 2θ = 30.68° and as the concentration increases from 1:0.1 to 1:0.2 the position of 2θ = 30.69°. For the concentration 1:0.3 the position of 2θ becomes 30.72°. As the concentration of the dopant increases a considerable change has been observed in the main peak (222), which clearly indicates the presence of the dopant in the film. The XRD parameters calculated using standard formulae is tabulated in table 3.3.

Considering both the dopants Sn and Cu, it is found that as the concentration of the dopant increases the crystallite size also increases. In the case of Sn dopant it is found that as the concentration of Sn increases the lattice parameters increase whereas for Cu they decrease.

![Fig. 3.11. XRD pattern of Cu-doped In$_2$O$_3$ thin films with molar ratios (a) 1:0.1, (b) 1:0.2 and (c) 1:0.3](image-url)
Table 3.3. Structural parameters calculated from the XRD patterns of Sn-doped In$_2$O$_3$ thin films

<table>
<thead>
<tr>
<th>Molar ratio In:Cu</th>
<th>$\theta$ (deg.)</th>
<th>hkl</th>
<th>Average crystallite size $'D'$ (nm)</th>
<th>Lattice constant $'a'$ (Å)</th>
<th>Lattice parameter $'d'$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0.1</td>
<td>30.68</td>
<td>222</td>
<td>12.05</td>
<td>10.087</td>
<td>2.912</td>
</tr>
<tr>
<td>1:0.2</td>
<td>30.69</td>
<td>222</td>
<td>14.04</td>
<td>10.082</td>
<td>2.911</td>
</tr>
<tr>
<td>1:0.3</td>
<td>30.72</td>
<td>222</td>
<td>16.57</td>
<td>10.076</td>
<td>2.909</td>
</tr>
</tbody>
</table>

Fig. 3.12. Raman Spectra of Sn doped In$_2$O$_3$ thin films of (In:Sn) molar ratio (a) 1:0.1, (b) 1:0.2 and (c) 1:0.3
Fig. 3.12 shows the Raman spectrum of Sn doped indium oxide thin films of various concentrations (1:0.1, 1:0.2 and 1:0.3). The spectra showed the peaks which get shifted towards the lower wave number when compared with the Raman spectrum of undoped In$_2$O$_3$. The Cu doped In$_2$O$_3$ also showed such a lower end Raman peak shift, Fig. 3.13. The shift in peak position of Raman spectrum is due to the change of grain size or the change of lattice constant as reported elsewhere [13]. In the present work the change in crystallite size as well as change in lattice constant has been observed due to the addition of Sn and Cu dopants in In$_2$O$_3$ thin films (Table 3.2 and 3.3) through XRD patterns. Thus the obtained Raman results are in good agreement with the XRD results calculated using standard formulae.

Fig. 3.13. Raman Spectra of Cu doped In$_2$O$_3$ thin films of (In:Cu) molar ratio (a) 1:0.1, (b) 1:0.2 and (c) 1:0.3
3.3.5. Surface morphology of the doped thin films

The surface of the Sn doped In$_2$O$_3$ thin films are shown in Fig. 3.14. Fig. 3.14(a) shows the surface morphology of 1:0.1 molar ratio (In:Sn) of Sn doped In$_2$O$_3$ thin film. The dip coated film is found to be uniform with few cubical agglomerates on the surface. Fig. 3.14(b) shows the surface of 1:0.2 molar ratio of Sn-doped In$_2$O$_3$ thin film. Here the formed film is found to be rough and the size of the cubical agglomerate has become larger (~80 nm). When the concentration of Sn is further increased i.e. 1:0.3 molar ratio (Fig. 3.14(c)), a similar type of rough surface has been observed as in the case of 1:0.2 concentration of the film. Also cubical agglomerates were formed at few places as observed for the other two concentrations but the size of the agglomerate becomes larger by about 1 µm.

Fig. 3.15 shows the SEM images of Cu doped In$_2$O$_3$ thin films prepared by the dip coating method. When the concentration of In:Cu is 1:0.1 (Molar ratio) the surface of the film is found to be rough with very minute agglomerations over the film, Fig. 3.15(a). As the concentration of Cu increases from 0.1 to 0.2 i.e. 1:0.2 molar ratios, the surface of the film get a little smooth (Fig. 3.15(b)) when compared with the lower concentration. In this case, clear cubical agglomerates with different sizes are observed over the surface. Fig. 3.15(c) shows 1:0.3 molar ratio of In:Cu dip coated thin film. Here the surface observed seems to be smooth with cubical agglomerates, and the thickness of the films were found to be 4000 nm.

From the SEM images of the different concentrations of Sn and Cu doped In$_2$O$_3$ thin films, it is observed that cube like agglomerates are formed over the surface. But the density of agglomeration is found to be less and as the concentration of the dopant increases the size of the agglomerated particles are found to be larger. For the lower concentration of Cu (1:0.1 molar ratio) the formed surface is slightly different from the other concentration of dip coated films and it showed a rough surface. In order to know more about the surface of the prepared films AFM analysis has been carried out.

Fig. 3.16 shows the 2D and 3D AFM images of 1:0.1 molar ratio of In:Sn doped In$_2$O$_3$ thin film. The observed surface showed a similar vertical growth as in the case of pure indium oxide. The RMS roughness observed for the film is found to be very less i.e. 3 nm. The obtained film is smooth as observed from the SEM image.
of the film. Fig. 3.17 shows the AFM images of the thin films dip coated with 1:0.2 In:Sn concentration. As the concentration increases it is observed that the grass like growth of the film disappears and the surface of the film becomes rough with RMS roughness of 8 nm. When the concentration of Sn is further increased, the RMS roughness is found to increase to 10 nm (Fig. 3.18). The surface roughnesses of the films are calculated from the selected area indicated by red coloured squares in the 2D AFM images. The observed results are in good agreement with the SEM results.

2D and 3D AFM images of Cu doped In$_2$O$_3$ thin film of 1:0.1 molar ratio of In:Cu are shown in Fig. 3.19. In the case of Cu dopant, the vertical growth of the film has been observed with RMS roughness of 3 nm. When the concentration of the Cu dopant increased to 0.2 (Fig. 3.20), shunted growth in the vertical direction has been observed but the RMS roughness becomes 5 nm. As the concentration of Cu increases to 0.3 (Fig. 3.21) the surface RMS roughness increased to 7 nm but the surface observed is similar to that of the surface observed for 0.2 molar concentration of Cu.

The surface morphology observed through 2D AFM images of the prepared Sn doped In$_2$O$_3$ thin films showed nearly spherical and elliptical particles over the surface. For Cu doped In$_2$O$_3$ the particles observed are spherical in shape. A similar morphology for SnO$_2$ film loaded with CuO nanoparticles was observed by Chowdhuri et al [14].
Fig. 3.14. SEM images of the Sn doped In$_2$O$_3$ thin films of (In:Sn)molar ratio (a) 1:0.1, (b) 1:0.2 and (c) 1:0.3 with thickness about 200 nm.

Fig. 3.15. SEM images of the Cu doped In$_2$O$_3$ thin films of (In:Sn)molar ratio (a) 1:0.1, (b) 1:0.2 and (c) 1:0.3 with thickness about 200 nm.
Doped and Undoped In$_2$O$_3$ thin films

Fig. 3.16. (a) 2D and (b) 3D AFM images of the Sn doped In$_2$O$_3$ thin films of (In:Sn) molar ratio 1:0.1

Fig. 3.16. (a) 2D and (b) 3D AFM images of the Sn doped In$_2$O$_3$ thin films of (In:Sn) molar ratio 1:0.1
Fig. 3.17. (a) 2D and (b) 3D AFM images of the Sn doped In$_2$O$_3$ thin films of (In:Sn)molar ratio 1:0.2
Fig. 3.18. (a) 2D and (b) 3D AFM images of the Sn doped In$_2$O$_3$ thin films of (In:Sn)molar ratio 1:0.3
Doped and Undoped $\text{In}_2\text{O}_3$ thin films

Fig. 3.19. (a) 2D and (b) 3D AFM images of the Cu doped $\text{In}_2\text{O}_3$ thin films of (In:Cu)molar ratio 1:0.1

Fig. 3.19. (a) 2D and (b) 3D AFM images of the Cu doped $\text{In}_2\text{O}_3$ thin films of (In:Cu)molar ratio 1:0.1
Fig. 3.20. (a) 2D and (b) 3D AFM images of the Cu doped In$_2$O$_3$ thin films of (In:Cu) molar ratio 1:0.2
Fig. 3.21. (a) 2D and (b) 3D AFM images of the Cu doped In$_2$O$_3$ thin films of (In:Cu)molar ratio 1:0.3
3.3.6. Compositional Analysis

Composition analysis has been carried out by placing the samples on carbon tapes with an X-ray photoelectron spectroscopy (XPS, Kratos analytical, ESCA-3400, Shimazu). The X-ray source (MgKα, 1253.6 eV) was operated at 10 kV and 20 mA. Resolutions for survey analyses, i.e., FWHM of Ag3d₅/₂ spectrum, were 1.15 eV or 0.95 eV, respectively. Step size (eV) or dwell time (sec) for survey analyses were 1 eV, 150 sec or 0.1 eV, 300 sec, respectively. Spectra were corrected by -1.25 eV using standard binding energy of C-C bonds (C 1s, 284.6 eV) in surface contaminations.

Fig. 3.22 shows the survey spectrum of the pure indium oxide thin film. The spectrum exhibits the characteristic spin-orbit split 3d₅/₂ and 3d₃/₂ signals and a O 1s peak. The In 3d signal from the XPS spectra is shown in Fig. 3.22, in which the spin–orbit split is clearly marked. The O 1s XPS signal of the thin film could be deconvoluted into two components – two Gauss peaks at 530.2 eV and the second peak at 531.7 eV. The observed O 1s peak at 530.2 eV can be assigned to the lattice oxygen in the crystalline In₂O₃ and the O 1s peak at 531.7 eV to the adsorbed oxygen species [15]. An impure peak for C is observed from the carbon tape used for support during the analysis. Based on the quantitative analysis of the XPS spectra the In:O composition ratio in indium oxide thin films was found to be 1:1.24. The obtained value is non-stoichiometric and this is due to the oxygen vacancies which might be created during annealing of the film. However non-stoichiometric indium oxide has high free carrier concentration and the film will be more conducting and this is due to oxygen deficiency [16-19].

The XPS survey spectrum of Sn doped indium oxide thin film of 1:0.1 (In:Sn) molar ratio as shown in the Fig. 3.23. From the survey spectrum it is observed that very minute traces of tin are present in the coated thin film. Two peaks observed at 494.95 eV and 486.45 eV are due to Sn 3d₃/₂ and Sn 3d₅/₂, respectively which corresponds to the Sn⁴⁺ bonding of the dopant [20-22]. The deconvoluted XPS spectrum of In 3d doublet shows a clear contribution from two components (Fig. 3.24). The 3d₅/₂ component at the lowest binding energy 443.5 eV is due to the In-Sn bond; the one shifted by 1 eV (444.5 eV) toward higher binding energies is assigned to the In₂O₃ bond [23 and 24]. The O 1s peak observed here also consists of two peaks as observed in pure indium oxide thin film as shown in Fig. 3.25. The peak observed
at 530.33 eV corresponds to the lattice oxygen in the crystalline $\text{In}_2\text{O}_3$ and the peak at 531.56 eV is due to adsorbed oxygen species. The quantitative analysis of the XPS spectra showed the atomic ratio of In:O:Sn in Sn doped indium oxide thin films as 1:1.24:0.03.

Fig. 3.26 shows the XPS survey spectrum of 1:0.2 (In:Sn) molar ratio of Sn doped indium oxide thin film. The inset in XPS spectra of Sn 3d shows the presence of the doublet at 494.95 eV and 486.5 eV. Presence of both lattice as well as adsorbed oxygen species was observed. Here the atomic ratio of In:O:Sn is found to be 1:1.22:0.05. The survey spectrum of 1:0.3 (In:Sn) molar ratio of Sn doped indium oxide thin film is shown in Fig. 3.27. Sn 3d doublets are found at 494.7 eV and 486.3 eV and the atomic ratio of the Sn doped indium oxide is found to be 1:1.19:0.7. In all of the three molar ratio prepared thin films oxygen deficiency has been observed as in the case of pure indium oxide.

Fig. 3.28 shows the XPS survey spectrum of Cu doped indium oxide of molar ratio 1:0.1 (In:Cu). Copper doublet has been found at 953 eV and 933.34 eV corresponding to Cu 2p (inset in Fig. 3.28). The quantitative analysis from the XPS spectra showed that the atomic ratio of In:O:Cu is 1:1.3:0.3. Fig. 3.29 shows the XPS spectrum of Cu doped indium oxide of 1:0.2 (In:Cu) molar ratio. Cu 2p doublet is observed at 952.99 eV and 933.09 eV for Cu $2p_{1/2}$ and Cu $2p_{3/2}$ respectively [25-27]. The XPS analysis showed the composition of In:O:Cu as 1:1.3:0.6. Fig. 3.30 shows the XPS spectra of 1:0.3 (In:Cu) molar ratio prepared thin film of Cu doped indium oxide. Doublet peak at 952.91 eV and 933.04 eV of Cu 2p is shown in the inset of Fig. 3.30. The composition found using XPS quantitative analysis is 1:1.4:0.7. A common inference from the doped and undoped indium oxide thin films XPS is, all are deficient in oxygen and nearly stoichiometric. Also both lattice and adsorbed oxygen are found in the XPS spectra by deconvoluting the observed O 1s peak. Further the presence of oxygen vacancy is confirmed using photoluminescence analysis.
Fig. 3.22. XPS survey spectrum of pure In$_2$O$_3$ and deconvoluted O 1s peak and spin-orbit split of In 3d
Fig. 3.23. XPS survey spectrum of Sn doped In$_2$O$_3$ (1:0.1, In:Sn) and the inset shows observed doublet of Sn 3d.

Fig. 3.24. Deconvoluted XPS spectrum of In 3d spin-orbit split.

Fig. 3.25. Deconvoluted XPS spectrum of O 1s.
Fig. 3.26. XPS survey spectrum of Sn doped In$_2$O$_3$ (1:0.2, In:Sn) and the inset shows the doublet of Sn 3d

Fig. 3.27. XPS survey spectrum of Sn doped In$_2$O$_3$ (1:0.3, In:Cu) and the inset shows the doublet of Sn 3d
Fig. 3.28. XPS survey spectrum of Cu doped \( \text{In}_2\text{O}_3 \) (1:0.1, \text{In}:\text{Cu}) and the inset shows the doublet of Cu 2p.

Fig. 3.29. XPS survey spectrum of Cu doped \( \text{In}_2\text{O}_3 \) (1:0.2, \text{In}:\text{Cu}) and the inset shows the doublet of Cu 2p.
3.3.7. Photoluminescence analysis

Photoluminescence analysis has been carried out using HORIBA JOBIN YVON Spectroflosumax-4. Thin film samples are excited with 390 nm of UV light using a xenon lamp. In general, bulk form of In$_2$O$_3$ does not emit light [28]. Upon size reduction to nanometer scale, In$_2$O$_3$ can emit light. The reason for emission may be due to quantum confinement effect or vacancies. Quantum confinement effect in In$_2$O$_3$ can be observed when the size of the material is comparable with the exciton Bohr radius (2.14 nm for In$_2$O$_3$) [29]. If the particle size is more when compared with exciton Bohr radius, the emission may occur due to vacancies.

In the present case, a strong blue emission around 430 nm and a weak emission around 534 nm have been observed for pure In$_2$O$_3$ (Fig. 3.31). For Sn doped In$_2$O$_3$ thin film, the blue emission has not shifted. Only the peak around 534 nm corresponding to green emission has shifted to 533 nm as shown in Fig. 3.32. For Cu doped In$_2$O$_3$ both the blue and green emission have shifted to the lower wavelength.
region i.e. Blue emission around 429 nm and green emission around 533 nm (Fig. 3.33). The shift observed here in both of the dopant films is as less as 1 nm and this may be due to change in the band gap upon doping. These emissions are induced by oxygen vacancies present in the samples. This type of vacancy induced visible light emission has been reported elsewhere [30]. The presence of oxygen vacancies will improve the gas sensing behaviour of the prepared nanoparticles [31].

In olden days researchers wanted to prepare defect free materials. But now the trend has changed and people have started thinking where the defective structures will work. In many of the cases the defective structure works better than the stoichiometric form of the material. Also, when the size of a material reduces to nanometer scale it is hard to prepare a stoichiometric compound. Stoichiometric defect can be identified using XPS, EDX, photoluminescence etc. For example, a thermal barrier coating material formed of a highly defective cubic matrix structure had the concentration of the stabilizer sufficiently high such that the oxygen vacancies created by the stabilizer interacts within the matrix to form multi-vacancies, thereby improving the sintering resistance of the material [22]. In the present work, it has been identified that the prepared indium oxide is oxygen defective and this deficiency will improve the sensor response of the material [21].

![PL emission spectrum of pure In$_2$O$_3$ thin film at room temperature](image)

**Fig. 3.31.** PL emission spectrum of pure In$_2$O$_3$ thin film at room temperature
Doped and Undoped In$_2$O$_3$ thin films

3.3.8. Optical analysis

The optical band gaps of the prepared pure and Sn and Cu doped thin films are analyzed using UV-Vis spectrometer. The optical spectra observed for the Sn doped thin films are shown in Fig. 3.34. Initially for the first concentration of Sn dopant the transmittance is found to decrease but for further increase in concentration the percentage of transmittance also increased. For pure indium oxide the transmittance percentage is found to be 75 in the visible region and for the higher concentration of Sn doped indium oxide thin film it is found to be 80.
Fig. 3.35 shows the optical transmittance spectra of Cu doped indium oxide. For Cu doped indium oxide initially the transmittance decreases as observed in the case of Sn doped indium oxide thin films and gradually increases as the concentration increases. The transmittance of the higher concentration of copper doped indium oxide thin film is nearly equal to that of the undoped indium oxide thin film.

Fig. 3.36 shows the $(\alpha h\nu)^2$ Vs $h\nu$ plot from the transmittance spectrum of pure indium oxide. The X-intercept of the extrapolation of the line drawn from the linear portion of the curve gives the optical band gap of the prepared indium oxide thin film. The band gap of the dip coated film is found to be 3.58 eV. The $(\alpha h\nu)^2$ Vs $h\nu$ plot of Sn doped indium oxide is shown in the Fig. 3.37. The band gap of the doped thin films is found to increase with increase in concentration of Sn. For 1:0.1 (In:Sn) molar ratio, the band gap is found to be 3.69 eV, for 1:0.2 (In:Sn) molar ratio it is 3.71 eV and for 1:0.3 (In:Sn) it is 3.74 eV. The obtained values are in good agreement with the earlier reported result [33].

Fig. 3.38 shows the $(\alpha h\nu)^2$ Vs $h\nu$ plot of Cu doped indium oxide. As the concentration of copper increases the band gap of the thin film is found to decrease. For 1:0.1 molar ratio the band gap of the film is found to be 3.42 eV, as the concentration was increased further to 1:0.2 molar ratio the band gap of the material get reduced to 3.31 eV and for 1:0.3 molar ratio, it has become 3.25 eV.

For gas sensors working at room temperature, the band gap could be considerably lower and for sensors working at higher temperature (i.e. $T>300 ^\circ$C) the optimal band gap could be higher than 2.5 eV [34]. The current voltage characteristics of the films are discussed in the chapter 4 in detail with the construction of FET using the undoped and Sn ans Cu doped In$_2$O$_3$ thin films.
Fig. 3.34. Optical transmittance spectra of pure and Sn doped In$_2$O$_3$ thin films

Fig. 3.35. Optical transmittance spectra of pure and Cu doped In$_2$O$_3$ thin films
Fig. 3.36. \((\alpha \nu \gamma)^2\) Vs \(\nu\) plot of pure \(\text{In}_2\text{O}_3\) thin film

Fig. 3.37. \((\alpha \nu \gamma)^2\) Vs \(\nu\) plot of Sn doped \(\text{In}_2\text{O}_3\) thin films

Fig. 3.38. \((\alpha \nu \gamma)^2\) Vs \(\nu\) plot of Cu doped \(\text{In}_2\text{O}_3\) thin films
3.4. Conclusion

In conclusion, it has been observed that from the two simple chemical methods, method – II is suitable for making thin films that can be applied to gas sensors. The film prepared using method – II showed a more uniform morphology when compared to that of the film prepared using method – I. Thus the method – II is employed for the preparation of Sn and Cu doped In$_2$O$_3$ thin films. The prepared thin films were characterized using various techniques. It has been found that as the concentration of Sn and Cu increased in the thin films the vertical growth of the films decreased and the RMS roughness increased. From the XPS analysis it has been found that oxygen vacancies are present in the pure and doped films and this is in good agreement with the PL analysis. The prepared thin film emitted a strong blue and a weak green light even with the presence of dopants. The presence of oxygen vacancies can improve the gas response kinetics. The band gaps of the prepared pure and doped films were calculated by analyzing the films using UV-Vis spectroscopy. The increase in Sn concentration of Sn doped indium oxide thin films showed a increase in band gap of the thin film whereas for increase in Cu concentration in Cu doped thin films, a decrease in band gap was observed.
3.5. Reference


