Chapter – VII

Summary and Conclusions

The salient features of the present investigations are:

i) Polyacrylamide route has been employed for the first time for the deposition of In$_2$O$_3$, SnO$_2$ and ITO films

ii) ITO films have been used for the first time in DSSC solar cells as the active photoelectrode, though ITO has been used as counter electrode.

iii) ITO films with different concentrations of tin in the range 5 – 70 % have been prepared by sol gel for the first time.

Results on In$_2$O$_3$ films

➢ Indium oxide films were deposited by the sol gel dip acrylamide route.

➢ The films exhibited single phase indium oxide. Microstructural properties of the films formed at different temperatures

➢ The RMS value of the surface roughness increases from 0.15 nm to 1.08 nm with increase of formation temperature. Fine grains are observed for the films formed at lower temperatures. Higher formation temperatures result in larger grains.

➢ The energy band gaps of the films are found to vary from 3.53 to 3.68 eV. Such a shift in band gap to higher energies is attributed to the increased carrier density due to Burstein–Moss effect. Refractive index was 1.995.
The room temperature electrical resistivity was found to decrease from the value of 40 ohm cm to 10 ohm cm for the films formed in the temperature range 350 – 500°C.

Room temperature carrier concentration values in the range of $1.67 \times 10^{16}$ to $37.2 \times 10^{16}$ cm$^{-3}$ with increase of formation temperature was observed.

Room temperature mobility values were observed in the range of $9.35 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ to $1.25 \, \text{cm}^2 \, \text{V}^{-1} \, \text{s}^{-1}$ with increase of formation temperature.

Two distinct peaks in the PL spectrum were observed in the blue region, i.e. at wavelengths of 415 and 440 nm wavelengths under the excitation wavelength of 375 nm at room temperature.

Characteristic Raman peaks corresponding to indium oxide are observed at 496 and 627 cm$^{-1}$ for all the films.

All the In$_2$O$_3$ films were sensitized in a dye solution of cis-di (thiocyanate) bis (2, 2'-bipyridyl-4,4'-di-carboxylate) ruthenium (II) (R535, N3-dye, Solaronix) for 12 h at room temperature. Carbon paste coated on a FTO substrate was used as a counter electrode. The Dye sensitized solar cell (DSSC) was fabricated by clamping the dye-sensitized indium oxide photoelectrode against carbon counter-electrode and filling the inter-electrode space by the electrolyte of 0.5M.
KI, 0.05M I₂ and 0.05M 4-tert-butylpridine. The photoelectrodes formed at 500°C exhibited an efficiency of 0.86 %.

- The DSSC shows reasonably high IPCE value. The IPCE spectrum shows two peaks at 410 and 526 nm, which are close to ruthenium-based dye (N₃-dye) absorbance.

- The indium oxide gas sensors were sensitive to H₂S gas at an operating temperature of 115°C. Response and recovery times were in the range of 19s – 26s and 34s – 91 s respectively.

**Results on SnO₂ films**

- Tin oxide films were deposited by the sol gel dip acrylamide route.

- The films exhibited single phase tin oxide. Microstructural properties of the films formed at different temperatures

- Roughness increases and the amount of island grains increase significantly.

- The energy band gaps of the films are found to vary from 3.68 to 3.88 eV. Refractive index was in the range of 2.05 – 2.18.

- The room temperature electrical resistivity was found to decrease from the value of 60 ohm cm to 20 ohm cm for the films formed in the temperature range 350 – 525°C.
Room temperature carrier concentration values in the range of $2 \times 10^{16}$ to $30 \times 10^{16}$ cm$^{-3}$ with increase of formation temperature was observed.

Room temperature mobility values were observed to be in the range of $3.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ to $1.00 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with increase of formation temperature.

An intensive UV-violet peak at 390 nm (about 3.18 eV) and a shoulder at 430 nm (about 2.88 eV) are observed. In addition, there is a broad peak at 520 nm (about 2.38 eV).

Three fundamental Raman peaks at 474, 632, and 774 cm$^{-1}$ corresponding to the $E_g$, $A_{1g}$, and $B_{2g}$ vibration modes, respectively, are observed, in good agreement with those for the rutile bulk SnO$_2$.

All the SnO$_2$ films were sensitized in a dye solution of cis-di(thiocyanate) bis(2,2'-bipyridyl-4,4'-di-carboxylate) ruthenium (II) (R535, N3-dye, Solaronix) for 12 h at room temperature. Carbon paste coated on a FTO substrate was used as a counter electrode. The Dye sensitized solar cell (DSSC) was fabricated by clamping the dye-sensitized indium oxide photoelectrode against carbon counter-electrode and filling the inter-electrode space by the electrolyte of 0.5M KI, 0.05M $I_2$ and 0.05M 4-tert-butylpyridine. The photoelectrodes formed at 500°C exhibited an efficiency of 1.375%.
The DSSC shows reasonably high IPCE value. The IPCE spectrum shows two peaks at 410 and 526 nm, which are close to ruthenium-based dye (N₃-dye) absorbance.

The responses to 10 ppm H₂S gas of SnO₂ at 120°C were all very fast, but the recovery times were 82, 70 and 40 s, respectively for the films formed at 525°C, 450°C and 350°C, indicating that SnO₂ formed at 350°C was of remarkably improved recovery characteristics, but they are not permanent changes. After a long time, they recovered to the original state.

Results on ITO films

ITO films were formed with different concentrations of tin in the range of 5 % to 70 %.

The films were single phase with bixbyte structure. Microstructural parameters were determined from the XRD data. The crystallite size decreased with increase of tin concentration.

The SnO₂ content was determined to be 68.0 at %, 58 at %, 47 at %, 38 at %, 29 at %, 19 at %, 14 at %, 9 at %, 5 at % respectively for the films with different concentration of SnO₂ starting from 95 % to 30 % from EDS studies.

Surface roughness increased from 0.20 nm to 1.25 nm as the tin concentration decreases. The film surface is porous.
The resistivity of the films decreased from 20 ohm cm (In$_2$O$_3$ films formed at 450°C) to 0.01 ohm cm as the tin concentration increases to 10 %. Further increase of tin oxide content caused increased in resistivity. Beyond 10 % tin the resistivity increases from 0.1 ohm cm to 250 ohm cm at 70 % tin concentration.

The $N_d$ increased from $3.85 \times 10^{17}$ cm$^{-3}$ (In$_2$O$_3$ films formed at 450°C) to $1.25 \times 10^{20}$ cm$^{-3}$ up to 10 at %, beyond this value of SnO$_2$ content, the carrier density decreases.

The value of mobility increased from $1.35 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ to $49.93 \text{ cm}^2 \text{ V}^{-1} \text{s}^{-1}$ up to 10 at % SnO$_2$, beyond which the mobility decreases.

Three PL bands appeared at 423, 486, 529 nm with a small broad peak at 439 nm.

In this work, the Raman vibration modes appeared at 144, 175, 248, 476 and 584 cm$^{-1}$ in the ITO spectrum

All the ITO films were sensitized in a dye solution of cis-di(thiocyanate) bis (2, 2'-bipyridyl-4,4'-di-carboxylate) ruthenium (II) (R535, N3-dye, Solaronix) for 12 h at room temperature. Carbon paste coated on a FTO substrate was used as a counter electrode. The Dye sensitized solar cell (DSSC) was fabricated by clamping the dye-sensitized ITO photoelectrode against carbon counter-electrode and filling the inter-electrode space by the electrolyte of 0.5M KI, 0.05M I$_2$ and 0.05M 4-tert-butylpridine. Films formed with 10 % tin exhibited maximum efficiency of 2.294 %. The photocurrent peaks occurring at
approximately 410 nm are due to direct-light harvesting by SnO$_2$ semiconductor, in which the photogenerated electrons diffuse through SnO$_2$, and the holes in the valence band are replenished directly by charge transfer from the I$_3^--/I^-$ electrolyte. The IPCE value at around 526 nm has contributed by the dye absorption.

- ITO sensors with 70 % tin concentration exhibited maximum sensitivity to H$_2$S gas at an operating temperature of 100°C. Sensors with lower tin concentrations up to 40 % exhibited sensitivity to H$_2$S gas at an operating temperature of 110°C and 120°C. The maximum response values are 38, 33, 29, 23.5. The responses to 25 ppm H$_2$S gas of ITO films with different concentration of tin at the operating temperature corresponding to the maximum response for that tin concentration (120°C, 110°C and 100°C) were all very fast, but the recovery times were higher than the response times, it was in the range of 70s to 90s for the ITO films with different concentrations of tin formed at 450°C, but they are not permanent changes. After a long time, they recovered to the original state.

The results of this work clearly demonstrate that nanocrystalline ITO films can easily be prepared by the sol gel dip coating method. Results obtained on DSSC solar cells are very encouraging. Further increase in efficiency should be aimed in future work. Moreover, the results obtained with sensors point toward the possibility of using them for sensing hazardous gases. The operating temperature has to be decreased further for industrial application.