CHAPTER - IX

SUMMARY, CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Materials possessing the remarkable combination of high electrical conductivity and optical transparency form the foundation of many important technological applications like flat panel displays, solar energy conversion, gas sensors and many other optoelectronic devices. Thin films having the nature of both transparent to visible region of solar spectrum and electronic conduction are called transparent conductors. There is ever growing interest in the development of transparent conducting oxides (TCOs) with n-type conductivity. Many inorganic transition metal oxides and metal oxides of binary compounds in thin film form are largely studied. The field of solar electricity or photovoltaic (PV), is rich in that there are many materials and concepts for converting sunlight into electricity. In the last twenty years, advance scientific and engineering efforts have been focused on the development of solid state solar cells. Although the solid-state solar cells are technologically very satisfactory, they are very expensive.

In 1991, Gratzel and his research group made a breakthrough in preparing an efficient dye-sensitized solar cell (DSSC) utilizing, a relatively non-pure raw material and an inexpensive preparation procedure and chemical route. The dye solar cell has potential for becoming a cost-effective means for producing electricity, capable of competing with current conventional solar electric technologies and, eventually, with today’s conventional power technologies. The photoelectrode of a dye-sensitized solar cell consists of a nanocrystalline TiO₂ thin film electrode that contains a monolayer of adsorbed dye molecules; the dye-coated particles are supported on a transparent conducting glass substrate (Tin doped Indium Oxide, ITO). Although a few studies have explored semiconducting oxides such as SnO₂, ZnO, Nb₂O₅, CeO₂ and SrTiO₃, the preponderance of work has focused on the anatase form of TiO₂ for DSSCs.

The demand for gas sensing devices used in safety applications where combustible or toxic gases are present, in buildings and vehicles is increasing quite rapidly. Most of the gas sensors are based on metal oxide semiconductor types of devices where electrical properties of the devices changes when exposed to a gas whose
concentration variations need to be monitored. In n-type semiconductor materials, like TiO₂, oxygen from air is adsorbed on the oxide surface and stronger oxidizing reaction will take place, which results in an increase in the resistance. When a reducing type of gases is sensed, oxygen will be removed from the surface of the oxide material leading to the formation of oxygen vacancies, which will reduce the resistance. In this regard, recently TiO₂ films have been intensively studied for developing gas sensors to sense combustible ethanol gases.

For these applications, the presence of uniform nano crystalline anatase (nc-TiO₂) is essential. It is well known that intrinsic properties of titanium are strongly dependent on the techniques experimental conditions, and the selection of crystallite size. Many different deposition techniques have been used to prepare nc-TiO₂ thin films, which include chemical vapor deposition (CVD), sol-gel, Physical vapor deposition, sputtering and liquid-phase deposition.

In the present work, TiO₂ films have been prepared by three different techniques: (1) Electron beam evaporation, (2) DC reactive sputtering and (3) Chemical spray pyrolysis techniques. SnO₂:F/ITO films were used as transparent as well as back contact electrodes for TiO₂ films in developing DSSC and gas sensor devices. The properties of the three different TiO₂ films and the parameters of the devices developed using them are studied and compared.

The EBE technique has been engaged to deposit nano crystalline TiO₂ films on glass substrate. TiO₂ power was made into pellets and used to deposit the films by keeping the substrates at temperatures RT, 50, 100 and 150°C. The deposition time was adjusted differently so that the thickness of the TiO₂ films was always about 0.95 μm for all studies. As the as-deposited films show non-crystalline phase only, the TiO₂ film deposited at 150°C was given a post annealing treatment in air at 300°C and 400°C for 1 hr. XRD results of these films show the presence of (101) prominent peak confirming the formation of anatase TiO₂ films with tetragonal structure. Electrical studies showed n-type nature and high resistivity of about 10⁷ Ωcm for the as deposited films. TiO₂ films annealed at 300 °C and 400 °C in air showed 5.2x10⁶ Ωcm and 4.3x10⁵ Ωcm respectively. The carrier concentration measured is about 10¹⁹-10²⁰ cm⁻³ and the mobility values are very low. Compositional and stoichiometry analysis by EDX and XPS confirmed TiO₂
film formation. Optical studies showed the presence of both direct bandgap and indirect bandgap transition in the TiO$_2$ lattice. Direct bandgap values are 3.42, 3.35 and 3.30 eV for the films as-deposited at 150$^\circ$C and annealed at 300 and 400$^\circ$C respectively, which is due to the increased grain size of the films at high temperature treatment. The refractive index value is about 2.1 - 2.4 in the visible region. TEM analysis showed the presence of nano crystalline grain of size 25-40 nm. Raman scattering and PL studies also confirmed the formation of anatase TiO$_2$ films. SEM and AFM studies revealed the formation of uniform surface morphology with nano grains.

TiO$_2$ films with anatase phase alone showing tetragonal structure were deposited by DC reactive sputtering (DCRS) technique. The TiO$_2$ films deposited at 200$^\circ$C and annealed in air at 200 and 300$^\circ$C for 1 hr have been characterized for their structural optical, electrical and morphological properties. XRD results showed the presence of (101) oriented crystallites along with other small intensity peak planes (004), (112) and (211), which confirmed the deposition of TiO$_2$ films with tetragonal anatase phase. The electrical resistivity values are about 2.0 - 8.0 $\times 10^3$ $\Omega$cm. The activation energy for the TiO$_2$ film deposited at 200$^\circ$C is about 0.72 eV, whereas it is 0.60 eV for the film annealed at 300$^\circ$C. EDX and XPS analysis show the formation of TiO$_2$ films without any impurities. TiO$_2$ films deposited at RT, 200$^\circ$C and 250$^\circ$C have shown direct bandgap values of 3.43, 3.41, 3.37 eV respectively showing a grain size dependence. Further, as-deposited and 200$^\circ$C, 300$^\circ$C annealed films showed both direct and indirect bandgap values. The refractive index value is increasing from 1.8 to 2.1 with temperature revealing densification of the TiO$_2$ films. SEM and AFM analysis showed uniform surface morphology with grain size in the range of 100-250 nm, increasing with temperature. Raman scattering study confirmed the formation of anatase TiO$_2$ films. TEM showed the presence of 15-30 nm sized crystallites and PL studies confirmed the formation of pure TiO$_2$ films with direct bandgap values of about 2.96-3.30 eV.

Nano grained TiO$_2$ films have been deposited in detail at different substrate temperatures between 300 and 500 $^\circ$C using titanium acetylacetonate (TiAcAc) as the precursor metal salt. The spray solution was prepared by dissolving 0.05, 0.1, 0.15, 0.20, and 0.25 M of TiAcAc in 100% ethanol and used to prepare TiO$_2$ films. The substrate temperature was fixed as 450$^\circ$C and the molarity of TiAcAc was fixed at 0.15 M and the
properties were studied. Films deposited under these conditions showed anatase phase with tetragonal structure, having the prepared orientation along (101) direction. Microstrain and grain size variations show a temperature dependent nature. The resistivity is about $10^4 \, \Omega \text{cm}$. The carrier concentration in about $10^{20} - 10^{21} \, \text{cm}^{-3}$ and the mobility values are very low of the order of $10^{-16} \, \text{cm}^2/\text{Vs}$, which is due to the high resistivity of the TiO$_2$ films. Optical studies show that the band gap values are temperature as well as precursor concentration dependent. The direct bandgap values increased form 2.84 eV to 3.66 eV when the temperature varied from 300$^\circ \text{C}$ to 500$^\circ \text{C}$. The refractive index value varies between about 1.9 and 2.5 in the wavelength region of 400-1000 nm. SEM and AFM morphological studies show uniform surfaces. Raman scattering and TEM studies have shown agglomerated grains with nanoparticles. PL studies showed a direct band gap of 3.26 eV and an indirect band gap of 2.95 eV.

Dye Sensitized Solar Cells (DSSCs) have been fabricated using the TiO$_2$ films deposited by EBE, DCRS and CSP techniques. The configuration of the solar cells is: Glass/ITO/TiO$_2$ + EOSIN B dye + KI + I$_2$ /Pt/SnO$_2$:F. The current-voltage (I-V) output by these solar cells are: open circuit voltage, $V_{oc}=0.46, 0.58, 0.06 \, \text{V}$, short-circuit current density, $I_{sc} = 0.17, 0.37, 0.55 \, \text{mA/cm}^2$, solar conversion efficiency $\eta = 0.06, 0.14, 0.22 \, \%$ respectively. The higher output parameters are due to the porous nature and the reasonably lower resistivity of the TiO$_2$ films deposited by the chemical spray pyrolysis technique.

Sensing elements, using TiO$_2$ films of thickness about 0.8-1.0 $\mu$m, were prepared by the EBE, DCRS and CSP techniques. The active area is 5 mm x 5 mm and an annealing step at 400$^\circ \text{C}$ for 1 hr in air was adopted. Sensitivity to ethanol gas was studied by fixing the operating temperature at 30, 100, 200, 300 and 400$^\circ \text{C}$. Maximum sensitivity has been observed for the CSP prepared TiO$_2$ film operating at 300$^\circ \text{C}$. The sensor response and recovery times are faster for this CSP prepared films, which is attributed to the porous morphology.

These are lot of scopes for the future work to improve the DSSC solar cell output characteristics. The TiO$_2$ films deposited using different techniques may be given extra annealing treatment at vacuum or under reducing atmosphere like hydrogen or inert gas like nitrogen heat treatment, to reduce the resistivity. This treatment will improve the
mobility of electrons in the TiO$_2$ thin films. Different dyes may be tried like natural dyes or copper based low cost dyes to reduce the cost. As far as gas sensor development is concerned, porous silicon structures with silicon nano pillars may be made on n-type/p-type silicon wafers engaging electrochemical anodic etching technique and used as template for introducing TiO$_2$ into the pores. This will increase the surface area of the sensing element, which may increase the sensitivity of the sensor, reduce the operating temperature and also the selectivity to various toxic gases.