CHAPTER-IX

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In recent years there is a considerable interest in oxide materials as these show the electrical behaviour ranging from insulators to superconductors. Oxide materials have predicted their possible potential applications in high Tc superconductors and photoelectrolysis of water.

Among the many oxide semiconductors Mn-oxide in film form has been paid very less attention. Recently some workers have studied electrical properties of Mn-oxide films. Oxide semiconductors are attracted due to their potential applications in ECPV cell, photoelectrolysis of water, photoluminescence, as an insulator, thermistor, superconductor, etc. The efficiency of many transition metal oxides is found to be poor and their band gap energies are higher which do not match with the solar spectrum. In the present investigation the attempts have been made to deposite uniform large area Mn-oxide films with the use of spray-pyrolysis and chemical bath deposition techniques. The studies have been made on Mn-oxide films to characterize them by structural, electrical and chemical methods. The films of Mn-oxide are deposited on non-conducting and conducting glass substrates.

The structural and electrical properties of these films are studied systematically and the preparative parameters of the film are optimised. Also the electrochemical properties are studied. Lastly an attempt has been made to prepare the Mn-oxide films by chemical bath technique to study superiority of these films over the films deposited by spray-pyrolysis technique. The whole quantum of work carried out in the present course and the learned work from others research are described into eight chapters and the highlights of the work are briefly summarised and concluded in this IXth chapter.

Chapter-I opens with a brief survey of types of oxides. Out of these oxides one type is transition metal oxide which is described therein. Synthesis, structural, electrical properties and uses of manganese oxides are explained in detail. The statement of the problem is given in Chapter-I.

The theoretical background of transition metal oxides based on the existing literature is given in Chapter-II. Different models explaining the nature of transition metal oxides are described in detail. Also the transport properties of these oxides are explained therein.

Third chapter gives the details of experimental procedure for the deposition of Mn-oxide films by spray-pyrolysis technique. This method is relatively simple and economically feasible to prepare thin films of oxides, sulphides, chalcogenides and mixed films. With the help of this method Mn-oxide films are prepared by spraying solution of manganese chloride. While preparing these films we have optimized the preparative parameters such as spray rate, air pressure, concentration of ingradient solutions, substrate temperature. The spray rate is changed with solution level height as well as pressure. The optimum spray rate 12 cc/min. is achieved by adjusting the solution level height with reference to the tip of the nozzle and also the pressure at their respective values. At higher concentration the films are found to be non-uniform and powdery whereas at very low concentration the films formed are of negligible thickness. The optimum concentration revealed is 0.25 M. Using this optimum concentration the temperature of substrate was varied from 250°C to 500°C. The sdubstrate temperature is kept 400°C and spray rate is maintained at 12 cc/min, concentration of the solution has been changed from 0.1 M to 1 M.

Mn-oxide films deposited on amorphos and FTO glass substrates at various substrate temperatures and concentrations of the spraying solution have been employed for structural characterisations. The transmission micrographs showed that the gain size decreases with the increase in temperature. Also the grain size decreases if the conducting glass substrate is used instead of nonconducting glass substrate. Comparison of films deposited on non-conducting and conducting glass substrates showed decrease in grain size for the film deposited on conducting glass substrate. Annealing effect showed decrease in grain size for the film deposited on conducting glass substrate. XRD patterns of films having different substrate temperatures are compared with each other. Also XRD patterns of films deposited with the spraying solution having different concentrations are compared with each other. The comparison showed that there is no significant change in the composition of Mn-oxide, only the stoichiometry changes. The 'd' values are determined from these patterns. It is found that calculated values match very well with the standard 'd' values (taken from XRD data book). XRD patterns showed that the films are polycrystalline in nature and had composition Mn_3O_4. As Mn_3O_4 may contained the composition MnO. Mn_2O_3, the percentage of MnO and Mn_2O_3 present in the film along with Mn_3O_4 is calculated for films deposited at different substrate temperature and with spraying solution having different concentrations. It is found that the film which is deposited at 400°C substrate temperature with the spraying solution of concentration 0.25 M has more percentage of Mn_2O_3 than MnO and Mn_3O_4.

Dark conductivity is studied in the temperature range between 300°K to 550°K. The conductivity is found to be of the order of 10^{-3} to 10^{-4} per ohm per cm. It is increased with increase in temperature predicting that material is a semiconductor. It is found that the substrate temperature, concentration of spraying solution and spray rate affects the conductivity. The film deposited at 400°C substrate temperature with the spraying solution having concentration 0.25 M has the maximum conductivity. There is increase in condutivity with the spray rate. Activation energy determined from the resistivity measurement is 0.15 to 0.84 eV. The activation energy for the film deposited at 400°C with spraying solution having concentration 0.25 M and spray rate 12 cc/min is 0.6 eV. It is in good agreement with the values reported by others. The thermoelectric power measurement revealed Mn-oxide is of p-type. Thickness measurement is done for all films which are characterized by different substrate temperatures, concentrations of spraying solution and spray rates. The thickness increases with concentrations of spraying solution as well as substrate temperatures. Maximum thickness attained in this case is 4 um and 3.2 um for concentrations of spraying solution and substrate temperatures respectivly. Thickness increases with increase in spray rate but for 10 and 12 cc/min. spray rate it decreases with increase in spray rate. It is also found that the thickness of the film deposited on conducting glass substrate is less than the film deposited on non-cionducting glass substrate.

Optical absorption and transmission measurements are carried out within wavelength range from 400 nm to 750 nm. Absorption coefficient determined from above measurement is found to be of the order of 10^3 to 10^4 cm^{-1} and the optical transitions are found to be of direct type. The straight line nature of the graph of α vs $(h\nu - Eg)^2$ gave the Mn-oxide as allowed direct transition, indirect band gap semiconductor. The graph of $(\alpha)^{\frac{1}{2}}$ vs $h\nu$ revealed the bandgap energy equal to 1.9 eV. The transmission vs wavelength plots showed that the transmissioin increases with wavelength but beyond 6500 A° it is nearly constant. The effect of concentration of spraying solution, substrate temperature and spray rate showed that the transmission is found to be decreasing with increase in concentration cf spraying solution, decrease in substrate temperature and decrease in spray rate. Refractive indices are calculated with the ellipsometric measurements which are made with the help of the Gaertner Ellipsometer, Model L_{119}. The refractive index is found to be of the order of 1.86 to 2.1. For all the substrate temperatures except 450°C the refractive index remain constant (i.e.1.92). The refractive index increases with spray rate but remain constant for 10 cc/min. and 12 cc/min. spray rate.

The ECPV cell with the configuration FTO Mn-oxide/0.5 NaOH + 0.01 M K_4/K_3 $Fe(CN)_6$/C is formed with Mn-oxide thin film as a photoelectrode, 0.5 NaOH + 0.01 K_4/K_3 Fe $(CN)_6$ as an electrolyte and carbon as a counter electrode.

To study the type of conductivity of carriers in the Mn-oxide film the cell is illuminated with 100 mW/cm^2 illumination intensity. Cathodic behaviour of the photovoltage is observed which indicates p-type conductivity of the semiconductor. The charge transfer across semiconductor electrolyte interface is defined by the Butler-Volmer relation and the analysis of the data showed that junction is rectifying in nature. The photovoltaic power output characteristic of the cell under 100 mW/cm^2 light excitation has been studied. Shifting of the I-V curve in the second quadrant indicates the cell is generator of electricity. From the photovoltaic output curve the fill factor and efficiency are calculated and found to be 38.4% and 0.005% respectively. The lower efficiency obtained in this investigation may be due to i)absence of post preparative treatments to photocathode ii)absorption losses of the light in the electrolyte iii)the reflection losses from glass and photoelectrode surfaces iv)nonoptimised photoelectrode thickness v)high resistivity of films, etc. Therefore to improve the efficiency, attempts have been made first to increase thickness of the film, to fix the geometry of the cell and then to select a proper redox couple. Different aqueous and non-aqueous electrolytes such as ferrous-ferric chloride, ferri-ferrocynide, hydroquinone, polysulfide and ferrocene in DMSO have been tried with Mn-oxide photoelectrode. For aqueous electrolytes KCl solution and NaOH solution is used as a supporting electrolyte. However, it is observed that ferri-ferrocynide in NaOH electrolyte is a suitable electrolyte. In other electrolytes, the film corrodes. Mott-Schottky graph is plotted by measuring capacitance with applied bias in the dark. The nature of the graph showed that the films are of p-type. The flat band potential for the film deposited at 400°C substrate temperature and with spraying solution having concentration 0.25 M is (-0.1 eV) vs SCE. Flat band potential is found to be affected by the concentration of the spraying solution.

Mn-oxide films are also deposited by chemical bath method. The films are deposited at different substrate temperatures from 30°C to 90°C on glass substrates, with optimized speed of rotation of substrates (110 rpm) and concentration of reaction mixture $MnCl_2$ (0.02 M) + HN_4Cl (0.8 M) + NH_3 (0.28M). At 80°C substrate a good quality films of Mn-oxide are formed. Due to very low thickness the study of structural characterization is not possible. The films are highly resistive. The conductivity is of the order of 10^{-4} per ohm per cm and it is maximum for the film deposited at 40°C substrate temperature. Conductivity is found to be decreasing with increase in substrate temperature. The activation energy is of the order of 0.68 to 0.83 eV. Thermoelectric power measurement revealed Mn-oxide is of p-type. The thickness of the film is found to be increasing with substrate temperature. The optical absorption showed that the optical absorption is of the order of 10^3 to 10^4 cm^{-1} and the optical transitions are found to be of direct type. Bandgap is found to be of the order of 2.62 eV. Transmission graphs showed that transmission increases with wavelength but beyond certain wavelength remains constant for all the films except the film deposited at 30°C substrate temperature. The refractive index measurement is not possible due to very low thickness. For electrochemical characterizatioin different electrolytes in the aqueous and non-aqueous solvent have been tried for p-Mn-oxide based ECPV cell. These include ferri-ferrocynide, ferrous-ferric chloride polysulfide, hydroquinone, formaldehyde and ferrocene in DMSO. For aqueous electrolytes KCl solution and NaOH solution are used as a supporting electrolyte. Corrosion took place in all electrolytes and showed very poor response in electrolyte ferri-ferrocynide in NaOH due to poor junction formation as the thickness of the film is very low. Hence these films are not found suitable for their applications in ECPV cells.

It is found that the Mn-oxide films prepared by spray pyrolysis technique are superior than the Mn-oxide films prepared by chemical bath technique as the Mn-oxide films deposited by spray pyrolysis are thick and suitable for the use in electrochemical photovoltaic cell than the Mn-oxide films deposited by chemical bath method. In the deposition of Mn-oxide films the chemical bath deposition method is more expensive and time consuming method than the spray pyrolysis method of deposition.