# CHAPTER- VI

## SUMMARY AND CONCLUSIONS

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During the last two decades the electrochromism (EC) in different materials has attracted interest on account their potential applications in light modulation displays, smart windows for buildings and cars and variable reflectance mirrors. The electrochromic effect is related to a reversible colouration and bleaching process by means of an electrochemical procedure, which gives rise to simultaneous injection and / or extraction of ions and electrons due to applied voltage. An electrochromic device is a multilayer device, which consists of two conducting electrodes, an electrochromic layer, an ionic conductor and a passive or active counter electrode. In an early stage, electrochromism has been studied in the context of high contrast non-emissive display. Currently there are vigorous research efforts to develop EC coatings specially for the energy saving 'Smart windows' technology.

The EC materials may be divided into two types (a) cathodic EC materials, which are coloured by a reduction process and (b) anodic EC materials which are coloured by oxidation process. EC is a multifaceted phenomenon exhibited by a number of inorganic and organic materials. In inorganic class, EC is reported in many transition metal oxides (e.g. $WO_3$, $MoO_3$, $V_2O_5$, NiO, $IrO_x$, $Nb_2O_5$ and $Co_3O_4$/CoO) of these, tungsten oxide and iridium oxide are the most extensively investigated. However, these materials encounter some problems like durability

large area coating capability dissolution, irreversible colouring and slow response. Alternative to above materials is to use other materials whole EC properties have been documented but still are dormant. One such example is niobium oxide. This oxide is insoluble in many medial shows reasonable response times, and reversible colouring and bleaching and so appears to be a promising system for electrochromic devices.

Various methods are being currently used to produce EC niobium oxide thin films, viz. vacuum evaporation, sputtering, chemical vapour deposition, ionization and sol-gel. It was found that, the EC properties are very much dependent on a kind of preparation technique and the preparative parameters, used in the deposition of thin films. The inexpensive pneumatic spray pyrolysis technique (PSPT) has been employed for the deposition of the EC thin films.

In a view of this, the present work has been planed and the subject matter has been organized in five chapters. The emphasis has been given on the preparation and characterization on niobium oxide material in thin film form, using inexpensive SPT and its electrochromic properties.

The FIRST CHAPTER begins with general introduction of the subject matter. An information of EC technology in energy saving is highlighted. An extensive survey of literature on niobium oxide is given. The survey of other oxides is given, as well. The purpose of dissertation is stated at the end of the chapter.

CHAPTER SECOND embraces the theoretical background. It includes history and basis of EC. Thereafter application areas of EC devices are given. The configuration of EC cell and ideal requirements of different components of the cell are given. Lastly, the structural features of niobium oxides are described.

CHAPTER THREE begins with the description of the pneumatic spray pyrolysis technique (PSPT). The advantages of PSPT over other techniques are given. The scheme of pyrolysis of the precursor with respect to the substrate temperature is given. The necessary theoretical background and detail description of the characterization techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy (IS), electrical resistivity, thermoelectric power (TEP) and optical absorption is given. The electrochemical tools such as cyclic voltammetry (CV) and chronoamperometry (CA) to characterize the EC materials are given in detail. The procedure for the preparation of the precursor solution for the deposition of niobium oxide thin films has been given. The preparative parameters to obtain niobium oxide thin films with desired properties are optimized and their values are given in Table 6.1.

**Table 6.1:** Optimized preparative parameters for $Nb_2O_5$ thin films

| Preparative parameter | Optimized values |
|---|---|
| 1. Solution concentration | 0.005 M |
| 2. Solution quantity | 50 cc |
| 3. Spray rate | 8cc/min |
| 4. Nozzle to substrate distance | 25 cm |
| 5. Air pressure | 1 $Kg/cm^2$ |

CHAPTER FOUR deals with the preparation and characterization of niobium thin films by PSST. Niobium oxide thin films were deposited by spraying 0.005 M aqueous solution of niobium onto the preheated amorphous glass substrates. The substrate temperature was maintained at 250,300,350,400 and 450°C. When sprayed droplets reach to the hot substrates, pyrolytic decomposition of precursor occurs and results into the formation of $Nb_2O_5$ thin films according to reaction (6.1).

$$2[NbO_4(CHOHCOO^-)_2]^{5-} \xrightarrow[air]{\Delta} Nb_2O_5 + 4H_2O + 8CO_2 \qquad .....6.1$$

The films of different temperatures are denoted by $N_{250}$, $N_{300}$, $N_{350}$, $N_{400}$ and $N_{450}$, where subscripts denote the substrate temperature. The samples were further annealed in air at 500°C for four hours. The annealed samples are denoted by $NA_{250}$, $NA_{300}$, $NA_{350}$, $NA_{400}$ and $NA_{450}$.

Films thickness was determined by using weight difference method. The values of film thicknesses are given in Table 6.2. The film thickness decreases continuously with increase in substrate temperature. This behaviour is attributed to the increase in evaporation rate of initial product before reaching to the substrate, with increase in temperature.

The structural characterization was carried out using XRD in the range of angle 2θbetween 10 and 100°. It was found that as prepared samples N250, N300, N350 were amorphous, whereas the samples N400 and N450 were slightly

crystalline consisting of $Nb_2O_5$ monoclinic phase. All the annealed samples i.e. NA250 and NA450 were highly polycrystalline. The samples NA250, NA300 and NA450 consisting of $Nb_2O_5$ monoclinic phase, where as NA350 and NA400 consisting of $Nb_2O_5$ monoclinic + tetragonal composition. This result suggests that the niobium oxide films prepared at low substrate temperature were amorphous and films prepared at higher substrate temperature were crystalline. The grain size was calculated using well-known Scherrer's formula for the major reflex in XRD. It was observed that the average grain size was varied from 31 to 41 nm for the samples NA250 to NA450. The grain size values are listed in Table 6.2

The surface morphology of the films was studied by scanning electron microscopy. The NA250, NA300 and NA350 samples were found to have asperity and no well-defined grains could be seen. The growth of independent crystallites and their random distribution is visible in NA400 and NA450.

An IR transmission spectrum of the annealed film (sample NA 350) was recorded in the spectral range 400-4000 $cm^{-1}$. The IR spectrum displays three distinctive bands, the first band of 560 $cm^{-1}$ is associated with Nb – O stretching, the second band at 710 $cm^{-1}$ is associated with Nb – O – Nb bridging and third band at 860 $cm^{-1}$ is associated with $Nb_3O$ stretching. The results confirmed monoclinic structure of $Nb_2O_5$ thin films.

The optical absorption studies were carried out in the wavelength range of 350 to 850 nm. The optical absorption analysis suggested the presence of direct

interband transition. The extrapolation of straight-line portion of $(\alpha h\gamma)^2$ versus $h\gamma$ plots to zero absorption coefficient gives rise to the band gap energy Eg. It was found that the sample with low substrate temperature (N250) has higher Eg values. The decrease in band gaps with increase in substrate temperature may be due to homogeneity and crystallinity of the films. The annealed films had lower Eg values as compare to as prepared films. The Eg values are listed in Table 6.2.

The dark electrical resistivity measurements were carried out with two-point probe D.C. method. The electrical resistivity of as deposited films (N250 to N450) was found to be attenuated from $3.2 \times 10^8$ ohm-cm to $6.3 \times 10^6$ ohm-cm and for annealed films (NA250 to NA450) it was attenuated from $1.6 \times 10^8$ to $4.7 \times 10^6$ ohm-cm. The decrease in electrical resistivity is due to the improvement in crystallinity of the film. From the Arrhenious plots ($\log\rho$ versus 1/T) it was found that resistivity decreases with rise in ambient temperature suggesting semiconducting nature of $Nb_2O_5$ films. The plots of $\log\rho$ versus $(To/T)^{1/4}$ are straight lines. This result evinces for variable range hopping of charge carriers between randomly localized electronic states in the system. The values of resistivity and activation energy for all the samples are given in Table 6.2

The thermoelectric emf measurements were used to determine the conductivity type exhibited by $Nb_2O_5$ films. The polarity of the thermally generated voltage at the hot end was positive indicating that $Nb_2O_5$ films are of n – type. The observed values of thermoemf for samples N250 and NA250 were

largest and these values were smallest for samples N450 and NA450. The values of TEP, for all the samples are given in Table 6.2

**Table 6.2:** Effect of substrate temperature on properties of niobium oxide thin films prepared by spray pyrolysis

| Sample | Thickness (μm) | Grain Size (nm) | Band Gap Eg (eV) | Electrical resistivity at 300K (Ω-cm) | Activation Energy Ea (eV) | Thermoelectric power (mV/°C) |
|---|---|---|---|---|---|---|
| N250 | 0.27 | ----- | 2.8 | $3.2 \times 10^{8}$ | 0.84 | 0.16 |
| N300 | 0.21 | ----- | 2.8 | $2.0 \times 10^{8}$ | 0.83 | 0.15 |
| N350 | 0.16 | ----- | 2.7 | $5.1 \times 10^{7}$ | 0.81 | 0.08 |
| N400 | 0.09 | ----- | 2.6 | $3.2 \times 10^{7}$ | 0.80 | 0.04 |
| N450 | 0.06 | ----- | 2.6 | $6.3 \times 10^{6}$ | 0.79 | 0.012 |
| NA250 | 0.19 | 31 | 2.6 | $1.6 \times 10^{8}$ | 0.81 | 0.80 |
| NA300 | 0.14 | 32 | 2.5 | $5.0 \times 10^{7}$ | 0.79 | 0.58 |
| NA350 | 0.06 | 35 | 2.4 | $1.3 \times 10^{7}$ | 0.78 | 0.33 |
| NA400 | 0.05 | 36 | 2.35 | $8.3 \times 10^{6}$ | 0.77 | 0.16 |
| NA450 | 0.04 | 41 | 2.35 | $4.7 \times 10^{6}$ | 0.77 | 0.13 |

CHAPTER FIVE is devoted to the EC properties of annealed $Nb_2O_5$ thin films. It includes EC properties of $Nb_2O_5$ thin films using cyclic voltammetry (CV), chronoamperometry (CA) and optical techniques. A three-electrode electrochemical cell has been formed to study the electrochemical and

intercalation – deintercalation properties. The $Nb_2O_5$ thin films deposited onto the fluorine doped tin oxide (FTO) coated glass substrates, were annealed and used as working electrodes. The counter electrode was graphite and the reference electrode was a saturated calomel electrode (SCE). The electrolyte was 0.1 N $H_2SO_4$. The CVs were carried out for all the samples (NA250 to NA450) at 50 mV per second scan rate. A cathodic scan to the extreme potential of –0.45 V (SCE) caused the films to turn blue and at anodic scan to +0.25 V (SCE) the films became almost transparent. The general features of the CV are similar to those obtained for $Nb_2O_5$ films deposited by other techniques. The colouration and bleaching of the $Nb_2O_5$ thin film is associated with intercalation and deintercalation of $H^+$ ions and electrons in the film, according to equation 6.2

$$Nb_2O_5 + xH^+ + xe^- \rightarrow H_xNb_2O_5 \qquad .....(6.2)$$

(transparent) (blue)

Different parameters associated with ion intercalation and deintercalation of $H^+$ into and out of $Nb_2O_5$ host lattice are given in Table 6.3. The magnitudes, of both the anodic and cathodic peak currents were maximum for sample NA250 among all the samples. This suggests that extent of $H^+$ ion intercalation as well as deintercalation is maximum for amorphous sample, which wanes for crystalline samples. The diffusion constant of $H^+$ ions was calculated and found to lay between $1.7 \times 10^{-7}$ $cm^2$ / s and $0.78 \times 10^{-7}$ $cm^2$ / s for NA250 to NA450 samples. The values in this study are in good agreement with the reported values.

The CA was used to measure the speed of EC response of $Nb_2O_5$ films in $H_2SO_4$ electrolyte. From CA the colouration and bleaching time (time required for the current to stabilize at its lowest value) were calculated. The colouration time of NA250 sample is about 12 seconds and bleaching time is about 9 seconds, suggesting slow colouration and fast bleaching. The behaviour is same for all other samples. The colouration and bleaching time are listed in Table 6.3.

The colouration efficiency (CE) is one of the important parameters to probe EC device performance and is calculated by using following equation.

$$CE = \frac{\Delta OD}{\Delta Q} \qquad .....6.3$$

Where $\Delta OD$ is change in optical density at particular wavelength and $\Delta Q$ is the inserted charge density. $\Delta OD$ was obtained from the optical transmission plots of the coloured and bleached films, using the relation (6.4)

$$OD(\lambda) = \ln [To(\lambda)/Tx(\lambda)] \qquad .....6.4$$

Where $To(\lambda)$ is the transmittance of the bleached state and $Tx(\lambda)$ is the transmittance of the coloured state at particular wavelength $\lambda$. $\Delta Q$ values are estimated from CA curves. The values of CE are given in Table 6.3. Sample NA250 exhibit maximum CE than other samples. It suggests that CE is better for amorphous $Nb_2O_5$ sample than polycrystalline $Nb_2O_5$ sample. The films were found to be stable up to $1 \times 10^3$ colour / bleach (c / b) cycles.

**Table 6.3:** Different parameters associated with intercalation and deintercalation of $H^+$ ions from $H_2SO_4$ electrolyte into and out of sprayed $Nb_2O_5$ thin film samples.

| Sample | Structure | Epa V(SCE) | $E_T$ V(SCE) | $i_{pa}$ (mA) | $i_{pc}$ (mA) | D x $10^{-7}$ ($cm^2$ $s^{-1}$) | $t_c$ (s) | $t_b$ (s) | ΔOD | CE $cm^2$ $c^{-1}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| NA250 | M | 0.37 | -0.05 | 3.2 | 4.8 | 1.7 | 12 | 9 | 0.51 | 26 |
| NA300 | M | 0.33 | -0.05 | 2.8 | 4.3 | 1.4 | 12 | 9 | 0.41 | 24 |
| NA350 | M + T | 0.30 | -0.1 | 2.4 | 3.2 | 1.0 | 12 | 6 | 0.33 | 23 |
| NA400 | M + T | 0.28 | -0.17 | 1.8 | 2.3 | 0.93 | 12 | 6 | 0.31 | 23 |
| NA450 | M | 0.27 | -0.17 | 1.6 | 2.1 | 0.78 | 12 | 5 | 0.21 | 19 |

M: Monoclinic; T: Tetragonal; Epa: Anodic peak potential; $E_T$: Threshold voltage; $i_{pa}$: Anodic peak current $i_{pc}$:Cathodic peak current; D: Diffusion coefficient; $t_c$: Colouration time; $t_b$: Bleaching time and CE: Colouration efficiency.