

## CHAPTER - VI

### SUMMARY AND CONCLUSIONS

During the last two decades the electrochromism (EC) in different materials has attracted interest on account of 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.  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{NiO}$ ,  $\text{IrO}_x$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{Cu}_2\text{O}$  and

$\text{Co}_3\text{O}_4/\text{CoO}$ ). 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 whose EC properties have been documented but still are dormant. One such example is copper oxide. This oxide is insoluble in many media, 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 copper oxide thin films, viz. thermal oxidation, electrodeposition, chemical conversion, chemical brightening, etching, spraying, chemical vapour deposition, plasma evaporation, reactive sputtering and molecular beam epitaxy. 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 view of this, the present work has been planned and the subject matter has been organized in five chapters. The emphasis has been given on the preparation and characterization of copper 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 copper 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 copper oxide are described.

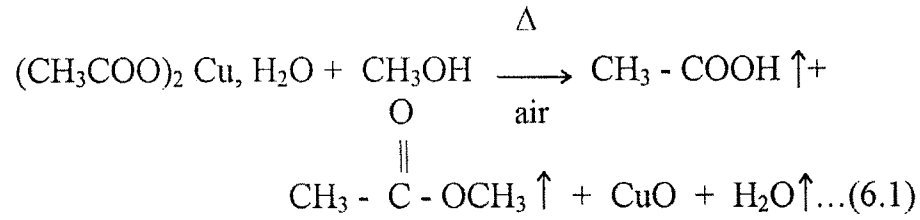
CHAPTER THREE begins with the description of the pneumatic spray pyrolysis technique (PSPT). The advantages of PSPT over other techniques are given. The scheme of pyrolysis of the precursor with respect to the substrate temperature is given. The necessary theoretical background and detail description of the characterization techniques such as X-ray diffraction (XRD), 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 copper oxide thin films has been given. The preparative parameters to obtain copper oxide thin films with desired properties are optimized and their values are given in Table 6.1.

**Table 6.1** : Optimized preparative parameters for copper oxide thin films

Sr. No.	Preparative Parameter	Optimized values
1.	Solution concentration	0.01 M
2.	Solution quantity	30 cc
3.	Spray rate	6 cc/min
4.	Nozzle to substrate distance	25 cm
5.	Air pressure	1 kg/cm <sup>2</sup>

CHAPTER FOUR deals with the preparation and characterization of copper oxide thin films by PSPT. Copper oxide thin films were deposited by spraying 0.01 M methanolic solution of cupric acetate onto the preheated amorphous glass substrates. The substrate temperature was maintained at 250, 300 and 350<sup>0</sup>C. When sprayed droplets reach to the hot substrates, pyrolytic decomposition of precursor occurs and results into the formation of copper oxide thin films according to reaction 6.1.



The films of different temperatures are denoted by  $C_{250}$ ,  $C_{300}$  and  $C_{350}$  where subscripts denote the substrate temperature. The samples were further annealed in air at  $500^\circ\text{C}$  for half an hour. The annealed samples are denoted by  $C_{A250}$ ,  $C_{A300}$  and  $C_{A350}$ .

Film 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 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  $2\theta$  between  $10^\circ$  and  $100^\circ$ . It was found that as prepared sample  $C_{250}$  was amorphous, whereas the samples  $C_{300}$  and  $C_{350}$  were slightly crystalline. All the annealed samples  $C_{A250}$ ,  $C_{A300}$  and  $C_{A350}$  were crystalline, consisting of monoclinic CuO composition. This result suggests that the copper oxide films prepared at low substrate temperature were amorphous and films prepared at higher substrate temperature were crystalline.

An IR transmission spectrum of the as deposited films (samples C<sub>300</sub> and C<sub>350</sub>) were recorded in the spectral range 400 - 4000 cm<sup>-1</sup>. The IR spectra for sample C<sub>300</sub> contains only one peak at 620 cm<sup>-1</sup>, corresponding to Cu<sub>2</sub>O phase and the sample C<sub>350</sub> showed absorption peaks at 416, 455, 517 and 568 cm<sup>-1</sup> corresponding to CuO phase only.

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  $(\alpha h\nu)^2$  versus  $h\nu$  plots to zero absorption coefficient gives rise to the band gap energy  $E_g$ . It was found that the sample with low substrate temperature (C<sub>250</sub>) has higher  $E_g$  values. The decrease in band gaps with increase in substrate temperature may be due to homogeneity and crystallinity of the films. The  $E_g$  value decreases due to annealing. The  $E_g$  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 (C<sub>250</sub> to C<sub>350</sub>) was found to be attenuated from 10<sup>6</sup> Ω cm to 10<sup>4</sup> Ω cm and for annealed films (C<sub>A250</sub> to C<sub>A350</sub>) it was attenuated from 2.5 x 10<sup>5</sup> Ω-cm to 8.0 x 10<sup>3</sup> Ω-cm. The decrease in electrical resistivity is due to the improvement in crystallinity of the film. From the Arrhenius plots (log ρ versus 1/T) it was found that resistivity decreases with rise in ambient temperature suggesting

semiconducting nature of copper oxide films. The values of resistivity and activation energy for all the samples are given in Table 6.2.

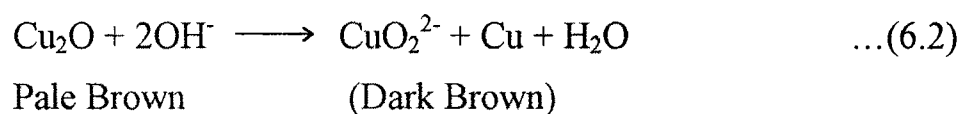
The thermoelectric emf measurements were used to determine the conductivity type exhibited by copper oxide films. The polarity of the thermally generated voltage at the hot end was negative indicating that copper oxide films are of p-type. The observed value of thermoemf for sample C<sub>250</sub> was 770  $\mu\text{V/K}$ .

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

Sample	Thickness ( $\mu\text{m}$ )	Band gap $E_g$ (eV)	Electrical resistivity at 300 K ( $\Omega\text{-cm}$ )	Activation energy $E_a$ (eV)
C <sub>250</sub>	0.131	1.87	$1.0 \times 10^6$	0.30
C <sub>300</sub>	0.049	1.78	$6.0 \times 10^5$	0.39
C <sub>350</sub>	0.045	1.00	$1.0 \times 10^4$	0.34
C <sub>A250</sub>	0.129	1.10	$2.5 \times 10^5$	0.26
C <sub>A300</sub>	0.047	1.51	$2.0 \times 10^5$	0.25
C <sub>A350</sub>	0.043	1.20	$8.0 \times 10^3$	0.17

CHAPTER FIVE is devoted to the EC properties of annealed copper oxide thin films. It includes EC properties of copper oxide 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 copper oxide 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 NaOH. The CVs were carried out for all the annealed samples ( $C_{A250}$  to  $C_{A350}$ ) at 50 mV per second scan rate. A cathodic scan to the extreme potential of -1.0 V (SCE) caused the films to turn brownish and at anodic scan to + 1.0 V (SCE) the films became almost transparent. The general features of the CV are similar to those obtained for copper oxide films deposited by other techniques. The colouration and bleaching of the copper oxide thin film is associated with intercalation and deintercalation of  $\text{OH}^-$  ions in the film according to the equation 6.2.



Different parameters associated with ion intercalation and deintercalation of  $\text{OH}^-$  into and out of copper oxide host lattice are given in Table 6.3. The magnitudes of both the anodic and cathodic peak currents were maximum for sample  $C_{A250}$  among all the samples. This suggests that extent of  $\text{OH}^-$  ion intercalation as well as deintercalation is maximum for relatively less crystalline sample, which wanes for highly crystalline samples. The diffusion constant of  $\text{OH}^-$



ions was calculated and found to lie between  $53 \times 10^{-16} \text{ cm}^2/\text{s}$  and  $2.7 \times 10^{-16} \text{ cm}^2/\text{s}$  for  $C_{A250}$  to  $C_{A350}$  samples.

The CA was used to measure the speed of EC response of copper oxide films in NaOH 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  $C_{A250}$  sample is about 4 seconds and bleaching time is about 2.5 seconds, suggesting slow colouration and fast bleaching. The behaviour is same for all the samples. The colouration and bleaching times 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.

$$CE = \frac{\Delta OD}{\Delta Q} \quad \dots (6.3)$$

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).

$$OD(\lambda) = \ln [T_o(\lambda) / T_x(\lambda)] \quad \dots (6.4)$$

Where  $T_o(\lambda)$  is the transmittance of the bleached state and  $T_x(\lambda)$  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  $C_{A250}$  exhibits maximum CE than other samples. It suggests that CE is better for  $C_{A250}$  sample than  $C_{A300}$  and  $C_{A350}$  samples. The films were found to be stable upto 5000 colour/ bleach (c/b) cycles.

**Table 6.3 :** Different parameters associated with intercalation and deintercalation of  $\text{OH}^-$  ions from NaOH electrolyte into and out of sprayed copper oxide thin film samples

Sample	Structure	Epa (mV)	Ipa ( $\mu\text{A}$ )	D $\text{cm}^2/\text{sec}$	$t_c$ sec	$t_b$ sec	$\Delta\text{OD}$	% CE ( $\text{cm}^2/\text{C}$ )
$C_{A250}$	CuO	-65	140	$53 \times 10^{-16}$	4	2.5	0.51	32
$C_{A300}$	CuO	-100	115	$3.58 \times 10^{-16}$	3.9	3.4	0.39	25
$C_{A350}$	CuO	-95	100	$2.7 \times 10^{-16}$	2.5	8	0.46	29

Epa : Anodic peak potential; Ipa : Anodic peak current;  
 D : Diffusion coefficient ;  $t_c$  : Colouration time;  
 $t_b$  : Bleaching time and CE : Colouration efficiency

It is finally concluded that the spray deposited copper oxide thin films offer promising candidature to fabricate smart windows. However it is further mandatory to enhance the electrochemical stability in liquid electrolyte, which can be addressed in future.