CHAPTER- I
INTRODUCTION

1.1 GENERAL

An Electrochromic (EC) material is able to change its optical properties when a voltage is applied across it. The optical properties should be reversible, i.e. the original state should be recoverable if the polarity of voltage is changed. The change is induced due to the intercalation and deintercalation of small ions into the EC material. These properties make electrochromic materials of considerable interest for optical devices of several different types, such as elements of information display, light shutters, smart windows, variable reflectance mirrors and variable – emittance thermal radiators.

The term electrochromism was first used by Platt [1] in 1961, to represent electric field dependent changes in optical absorption spectra of organic dye molecules. The electrochromism is welknown in numerous organic and inorganic substances. Among the inorganic class, almost all the interesting materials are oxides that are employed in the form of thin films. Copper oxide films are promising anodic electrochromics.

The practical use of electrochromism has been known since 1970. During the middle of 1970's many small digital information displays were developed, but the technology could not compete with the advance of liquid crystals for displays. Renewed interest in the area of electrochromism started in the mid 1980's for large area

applications such as automotive mirrors and windows for cars and buildings. This area of development has been growing ever since that time.

Electrochromic devices used for display applications have been discussed since the discovery of electrochromism, but so far such displays have not been turned into large scale consumer items. The reasons for this are not entirely clear but poor long-term durability is often forwarded as an explanation. Today's electrochromic technology has demonstrated excellent durability in some cases, and it appears that no major technological obstacles are now holding back electrochromic display systems.

Electrochromic film can be used to produce a mirror with variable specular reflectance. Antidazzling rear view mirrors built on electrochromic oxide films are currently available for cars and trucks. Work on variable reflectance mirrors was pioneered at Schott in Germany and at Donnelly Corporation in the USA.

Electrochromic optical switching devices known as 'smart windows', can be used for variety of applications. One of the most promising applications is for the regulation of incident solar energy and glare in buildings, vehicles, aircrafts, spacecrafts and ships. Electrochromic products already in market place are automobile mirrors, which can automatically regulate glare according to light

levels. Prototypes are being tested for automobile sunroofs and visors; further applications include automobile side and rear windows, architectural glazing and aircraft windows.

The function of electrochromic device used in a window is to control the flow of light or solar energy according to desire of user. Such windows can lead to energy efficiency as well as comfortable indoor climate. It is well known that due to the fast depletion of conventional energy sources the world continues to be in the grip of energy crisis. In India this problem is more severe. Hence it is necessary to realize the importance of energy savings in this perspective. 'Smart windows' technology is a more attractive way for substantial energy saving and is in practical use, to some extent in many developed countries. From privacy point of view, this technology has significant advantage over existing blinds and draps. In the last few years there has been significant growing interest in this technology and it is expected to be used in products in near future.

1.2 SURVEY OF ELECTROCHROMIC OXIDE FILMS

Electrochromism (EC) has been well documented for oxides of the transition elements, indicated in the periodic table in figure 1.1. Different shading is used to denote cathodic and anodic electrochromism. Cathodic colouration is found in oxides of Ti, Nb, Ta and W and anodic colouration is found in oxides of Cr, Mn, Fe, Co,

Ni, Rh and Ir. Vanadium is exceptional for the pentoxide (with V^{5+}) exhibits anodic and cathodic electrochromism within different wavelength ranges, while the dioxide (V^{4+}) has only anodic electrochromism. Only some of the oxides mentioned above can be fully transparent to visible light, notably the oxides based on Ti, Ni, Nb, Mo, Ta, W and Ir. The other oxides show some residual absorption either across the full visible range or in the blue part of the spectrum.

It is important to note that the EC oxides are based on transition metallic elements that are located in well defined region of the periodic table and different parts of this region pertain to oxides with cathodic and anodic colouration. From this observation one may conclude that the electrochromism is closely related to the electronic structures of the oxides.

The study on EC in copper oxide is sparse and not much work has been done previously. However, recently it is appreciated that copper oxide could serve as the best EC material. In addition to the materials discussed above, EC is known to occur in many binary and ternary mixed oxides and in oxyfluorides. There are also some simple oxides that have been reported as displaying electrochromism, which involves oxides based on Cu, Sr-Ti, Ru and Pr.

ELECTROCHROMIC OXIDES:

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac															

Cathodic coloration

Anodic coloration

Fig. 1.1 The Periodic Table of the elements, excepting the lanthanides and Actinides. The shaded boxes refer to the transition metals whose oxides have well-documented cathodic and anodic electrochromism.

Essentially all of the electrochromic oxides are constructed from one type of building blocks viz, M_eO_6 octahedra with a central transition metal atom (M_e) surrounded by six almost equi-distant oxygen atoms. The building blocks are connected by either by corner-sharing or by a combination of corner- sharing and edge sharing and many different crystal structures are known. Detailed discussion on the crystal structures can be found in the standard text by Wells [2] and by Hide and Anderson [3].

Table 1.1 summarizes a number of key properties of the electrochromic oxides. The first column indicates the nominal composition of the oxide. The second and third column list the overall optical properties, fourth column lists the structure of the oxides.

Table 1.1 Summary of key features for the main electrochromic oxides, showing oxide type, whether the coloration is cathodic C or anodic A, whether full transparency can be achieved (yes = Y; no = N), and whether the general structure type embodies a framework F or layers L of MeO_6 octahedra.

Oxide type	Coloration	Full transp.	Structure type
TiO_2	C	Y	F
V_2O_5	C/A	N	L[a]
Cr_2O_3	A	N	F
MnO_2	A	N	F
"FeO_2"	A	N	F
"CoO_2"	A	N	L?
"NiO_2"	A	Y	L.
Nb_2O_5	C	Y	F
MoO_3	C	Y	F/L
RhO_2	A	?	F
Ta_2O_5	C	Y	F
WO_3	C	Y	F
IrO_2	A	Y	F

[a] Layer structure with VO_5 units.

1.3 THE SURVEY OF LITERATURE ON COPPER OXIDE

Copper oxide exists majorly in two forms- cupric oxide (CuO) and cuprous oxide (Cu_2O). Cuprous oxide (Cu_2O) is a nonstoichiometric p-type semiconductor having nontoxicity. It is a potentially attractive material for solar cells, sensing gas and superconductor applications [4]. Cupric oxide (CuO) is a p-type semiconductor studied for photoconductive and photo-thermal applications [5]. In recent years, it has attracted much interest because it is the basis of several high-Tc superconductors [5]. CuO composites such as CuO-ZnO and $CuO-SnO_2$ systems also find applications in humidity and gas sensors [5]. In recent years, there is an increased interest in the synthesis and characterization of nanoparticles and nanocrystalline Cu_2O thin films for the realization of n-type conductivity [5]. This will make nanocrystalline Cu_2O an attractive semiconductor material for the fabrication of low cost solar cells and other opto-electronic and photovoltaic devices.

P. V. Plunkett et al. [6] determined the stresses in sputter-deposited copper oxide thin films. For copper-oxide films, the stresses were determined as functions of the film thickness and the oxygen partial pressure during the deposition cycle. They found that copper-oxide films could be readily produced in tension or in compression, depending on the amount of oxygen present during the deposition. Both

the nickel and the copper oxide films approached constant stress values for films thicker than approximately 0.7 μm [6].

(001) cuprous oxide (Cu_2O) films were epitaxially grown by Ch. Tsiranovits et al. [7]. From the two methods which were used (the oxidation of the copper films and the direct evaporation of bulk Cu_2O)only the oxidation of copper yielded good single crystal films. It was found that the optimum conditions were an oxidation temperature of 450 $^{\circ}$C with a partial pressure of oxygen of 2 x 10^{-5} Torr and, after oxidation, a further annealing at a pressure of 10^{-8} Torr [7].

J. P. Hiernaut et al. [8] studied stoichiometry and structure of copper-oxide films on glass. The physical properties of copper-oxide films on glass obtained by oxidation of the copper metal depend strongly on the thickness of the original metal and on the rate of oxidation. An apparent nonstoichiometry is observed for films obtained from copper deposits less than 500 A^0 thick and oxidized rapidly. This apparent nonstoichiometry is correlated with extensive modifications of the crystallographic structure [8].

M.T. San Jose et al. [9] studied the electrochemical behaviour of copper oxides (Cu_2O and CuO) in solid state at a carbon paste electrode with an electrolytic binder. They carried out several experiments to elucidate the electrochemical transformation of copper oxide in 10 M KOH medium occurring at +300 to -1400 mV (sce).

The voltammograms have been employed to propose several charge-transfer mechanisms. In addition, they recorded the voltammograms of the superconductor. YBaCuO at the same experimental conditions in order to elucidate the oxidation states of the copper in the solid [9].

The behaviour of the extrapolated copper film electrode on tin oxide / glass or glass carbon surface was studied by Shaojun Dong et al. [10] in potassium hydroxide medium by cyclic voltammetry and in situ transmission electrochemistry. The results indicate that the electroplated copper film electrode is similar to a copper electrode and cyclic voltammetry with this electrode affords more resolution. The anodic peaks were found to correspond successively to the adsorption of oxygen, the formation of a surface layer of Cu_2O, the formation of a surface layer of $Cu(OH)_2$ or CuO and formation of a thick film of CuO. It has been proposed that a surface layer of $Cu(OH)_2$ or CuO is formed from the oxidation of surface layer of Cu_2O. Similarly, a clear interpretation is presented that the cathodic peaks correspond successively to the reduction of CuO to Cu_2O, the reductions of Cu_2O to CuO and the soluble Cu (II) species to Cu. On the other hand, a shoulder peak related to the chemical transformation of $Cu(OH)_2$ to CuO was observed [10].

Sahab Dass et al. [11] studied photoelectrochemical properties of copper oxide thin films (p-type) on the SnO_2 - F coated glass

(conducting glass). X-ray diffractogram pattern of thin films confirm the cupric oxide (CuO) phase [11].

Novel spray pyrolysis deposition of cuprous oxide (Cu_2O) thin films on glass substrates was studied by Tsuyoshi Kosugi and Shoji Kaneko [4]. S. Kaneko et al. [13] attempted preparation of different photovoltaic compound thin films for solar cells by Spray pyrolysis technique. The aqueous solution of copper acetate with glucose was used for cuprous oxide (Cu_2O) thin films [13].

Electrochromism in copper oxide thin films was studied by T. J. Richardson et al. [14]. They predicted that these cathodically colouring films may be useful as counter electrodes for anodically colouring electrode films such as nickel oxide or metal hydrides. They reported large electrochemical storage capacity and tolerance for alkaline electrolytes for these copper oxide films [14].

B. Balamurugan and B. R. Mehta [5] synthesized nanocrystalline Cu_2O thin films using an activated reactive sputtering technique. These studies indicated the stability of cubic Cu_2O phase in these films [5].

Switching effects in thin anodic copper oxide (Cu_xO) films of different structures, compositions, order-disorder ratios and thicknesses was investigated in films formed by anodisation by V. P. Severdenko et al. [15].

A. J. Arvia and N. R. Detacconi [16] studied solid films and interfaces in fused salt electrochemical systems. These films occur at different metal molten electrolyte interfaces and their average composition depends on how they are formed i. e. anodically or cathodically. A thin film of cuprous oxide is formed when copper is immersed in lithium potassium chloride eutectic containing oxide ions, in the temperature range 400-500 °C. The anodic oxidation of copper in molten sodium tetraborate results in the formation of cuprous oxide solid film if either the divalent copper ion concentration in the melt or the current density is increased [16].

F. P. Koffyberg and F. A. Benko [17] studied photoelectrochemical determination of the position of the conduction and valence band edges of p-type CuO. They detected that lithium doped p- type CuO is a low mobility semiconductor with an indirect band gap of 1.35 eV and a flatband potential of +0.55 V, with respect to saturated calomel electrode (SCE), when in contact with an electrolyte at a pH of 9.4. Its valence band lies 5.42 eV below the vacuum level and is made up mainly from the Cu^{2+}-3d wave functions. An oxygen-2p type band is at 7.33 eV, in agreement with a semi-emperical estimate. Its performance as a photoelectrode for the solar photoelectrolysis of water is rather poor, due to the presence of recombination centers in the bandgap and its chemical instability. As photoelectrolysis electrodes, oxides with 3d-type valence bands may

have advantages over the more common oxides with 2p-type valence bands [17].

Da-ling Lu and Ken-ichi Tanaka [18] showed electrodeposition of Cu^{2+} ion resulted in the growth of Cu_2O single crystal particles on an amorphous carbon electrode in solution. Cu_2O single crystals grow at potentials higher than -0.55 V vs. saturated calomel electrode (SCE). The oxygen in the Cu_2O may come from water via cuprous hydroxide intermediate. The effect of anions on crystal habit of the Cu_2O particles was investigated by changing anions. Hexahedral Cu_2O single crystal particles were preferentially formed in $CsClO_4$ solution, but in the presence of sulphate ion the Cu_2O particles grow in a polyhedral form. Y-shape particles of Cu_2O were obtained in presence of chloride ion, which may be due to the effect of stronger adsorption of Cl^- on the surface of growing particles [18].

H. H. Afify et al. used spray pyrolysis technique for deposition of CuO film on glass and aluminium substrates and detected photothermal application. The film morphology and composition were carefully optimized, so that the film was highly absorbing over the majority of the solar spectrum and transparent in the infrared region. The CuO films with such optimized properties were deposited on aluminium sheets to achieve low emittance. Preliminary test was carried out to determine the performance of the prepared CuO film,

relative to commercially matt black paint. It was found that deposited CuO film retained the absorbed heat for a larger period of time [12].

M. Ivill et al. studied structural and magnetic properties of Mn-doped Cu_2O semiconducting thin films grown by pulsed laser deposition. Squid magnetometry was employed to characterize the magnetic properties. Ferromagnetism was observed in selected Mn-doped Cu_2O films, but appears to be associated with Mn_3O_4 secondary phases. In phase-pure Mn-doped Cu_2O films, no evidence for ferromagnetism is observed [19].

Alvin A. Milgram [20] made study of the mechanism of spectral absorbance in anodic copper oxide films. It is shown that the solar absorption is due to the unique surface structure of the anodic oxide film in combination with the optical properties of the basic film component, CuO. The surface structure also affects the spectral absorption in the 4-10 micron region contributing to the thermal emittance values of less than 0.10 [20].

Fujinaka and A. Berezin [21] studied thin films of cuprous oxide deposited on glass coated with transparent conducting indium-tin oxide (ITO) films, both Cu_2O and ITO deposited by rf sputtering in an Ar-O_2 gas mixture. To produce an ohmic electrode, gold was evaporated on the top of the Cu_2O film and hence the resulting structure of the photocell could be specified as ITO- Cu_2O-Au. Photovoltaic characteristics of the fabricated photo-cells were studied [21].

1.4   PURPOSE OF DISSERTATION

Electrochromism is known to be present in numerous organic and inorganic substances. Inorganic electrochromic materials offer promising candidature for information display devices, light shutters, smart windows and variable reflectance mirrors, as they exhibit various favourable properties such as high contrast with continuous variation of transmittance, storage information without energy supply (open circuit memory), ultraviolet stability, no limitation to view angle, large operating temperature range, little power consumption in producing image and no limit to size. Out of all the inorganic materials, cathodically colouring copper oxide is the most studied and the best EC material. Copper oxide is insoluble in many media, shows reasonable response times and reversible colouring and bleaching, and so appears to be promising system for electrochromic devices. Moreover the excellent stability of Cu towards corrosion in alkali hydroxides suggests that this material should form stable systems.

Various deposition techniques such as thermal oxidation, electrodeposition, chemical conversion, etching, spraying, chemical vapour deposition, plasma evaporation, reactive sputtering and molecular beam epitaxy have been used to prepare copper oxide films. It is observed that the physical and electrochemical properties of these films are strongly dependent on method of preparation. Optical and

electrical properties of the film are critically sensitive to the preparative parameters. It is possible to tailor the properties of the film by controlling the preparative parameters, which in turn make the film suitable for a particular application. Therefore selection of a preparation technique and preparative parameters play vital role.

Spray Pyrolysis technique has many attractive features for practical thin film manufacturing because of its simplicity, low cost and feasibility to produce large area thin films. Various other applications are discussed in chapter - III. Therefore in the present research work an attempt has been made to deposit copper oxide thin films by using spray pyrolysis technique (SPT). The preparative parameters like nozzle to substrate distance, spray rate and concentration of solution are optimized and substrate temperature was varied in order to obtain good quality films. The films have been deposited on amorphous glass and FTO coated glass substrates. The structural, electrical and optical charactarisation of the film have been carried out using X-ray diffraction (XRD), optical absorption and two probe electrical resistivity techniques.

The purpose of the work undertaken was to test the applicability of the SPT to prepare electrochronic copper oxide thin films, suitable for smart window prototype device fabrication. This technique is simple and inexpensive which has a great potential to scale-up the

production of large area (100 cm^2) thin film coatings on to glass substrates, provided the said coating has attained maximum possible colouration efficiency and durability. Hence in this investigation an attention has been given on these aspects.

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