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1.1 General

An Electro chromic (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 the voltage is changed. 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 wellknown in numerous inorganic and organic substances. Among the inorganic class almost all the interesting material are oxides that are employed in the form of thin films. Niobium oxide films are promising cathodic electrochromics that in many aspects can compete with the more frequently studied WO_3 films.

The practical use of electrochromism has been known since 1970. During the middle of the 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 a 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 the 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 an electrochromic device used in a window is to control the flow of light or solar energy according to the desire of the user. Such windows can lead to energy efficiency as well as a 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 saving 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 into the next century.

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, Mo, 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 (with 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.

ELECTROCHROMIC OXIDES:

H																				Ho
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																		

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.

It is important to note that the EC oxides are based on metallic elements that are located in a 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 structure of the oxides.

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.

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 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 Hyde 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 Survey of literature on niobium oxide

Niobium oxide belongs to the class of transition metal oxides and is one of the promising electrochromic materials. This oxide, which is insoluble in many media, shows a reasonable response time and reversible colouring and bleaching, and so appears to be a promising system for electrochromic devices. Moreover it has excellent chemical stability and corrosion resistance in both acid and base media, which suggests that this material should form stable systems. Recently Nb_2O_5 oxide dielectric films are extensively used as capacitors in microelectronic circuits, insulators in active devices such as FET. It has attracted a great deal of interest and has been most extensively investigated. In this investigation, an extensive literature survey was done on niobium oxide to identify their importance as EC material.

In the earlier work on niobium (1960), Young [4] determined certain electrical properties of the niobium oxide by specular reflectivity studies. Dielectric properties of niobium oxide films formed by vacuum evaporation of Nb_2O_5 were studied by Goswami[5]. The dielectric constants of these films vary from 12-130 were found to be thickness dependent.

A report on preparation and optical properties of niobium oxide films was made by A.Goswami and A.P.Goswami [6]. They studied vacuum deposited niobium oxide films, formed at room temperature and at 300°C substrate temperatures. By electron diffraction studies, the films at room temperature

were found to be amorphous and deposits at higher substrate temperatures were crystalline. The optical energy band gap estimated from the absorption edge shows thickness dependency and decreases with increase of film thickness.

M.R.Arora and Roger Kelly (1977) [7] studied the structure and stoichiometry of anodic films on Nb in H_2SO_4 based electrolyte. They found that thick anodic films on Nb have amorphous structure and stoichiometry is Nb_2O_5 . Al-Ismail et al. [8] prepared Nb oxide films by evaporation at a rate up to 1nm/s. Electron diffraction did not show any signs of crystallinity. Reactive evaporation in the presence of oxygen has been used to make NbO like films [9]; they were subsequently transformed to pentoxide by annealing post treatment. The temperature dependent electrical conductivity for anodic Nb oxide films, prepared at least above $900^{\circ}C$ were interpreted in terms of small polaron hopping by G. Jouve (1991) [10].

While undertaking review of literature on electrochromism (EC) in niobium oxide, one is compelled to start with Palatniks work in 1974 [11]. He reported that sintered tablets of Nb_2O_5 were coloured when brought in contact with hydrogen loaded graphite rods under H_2SO_4 electrolyte. They also found that colouration and bleaching of anodically formed Nb oxide layers took place under cyclic electrochemical treatment in H_2SO_4 . Electrochromism in Nb was mentioned in 1977 by Witzke and Deb [12].

Riechmann and Bard [13] and Gomes et al. [14] found a blue colouration in opaque Nb_2O_5 grown thermally at about 500°C on niobium metallic disk. Alves [15] has confirmed the possibility to insert Li^+ ions in Nb_2O_5 ceramic prepared from commercial powder sintered at about 800°C . Hayashi et al. [16] analyzed anodic Nb oxide films treated in H_2SO_4 and D_2SO_4 and clear evidence was found for ion intercalation across the entire film with a density that was larger at a more negative intercalation potential. Kumangi et al. [17] have measured emf in electrolytes of $\text{LiClO}_4 + \text{PC}$ for Nb oxide films made by thermal oxidation and found that emf falls off upon increasing Li^+ intercalation in approximately the same way as for W oxide. Cabnel et al. [18] reported Cyclic Voltammograms for films obtained by reactive sputtering in the presence of N_2 followed by oxidation post-treatment. The voltammograms are rather featureless and in this respect resemble corresponding data for heavily disordered electrochromic W oxide films. Analogous voltammograms have been reported for H^+ intercalation into films made by anodization [16] and thermal oxidation [14] and for Li^+ intercalation into films made by sol-gel technology [18].

The first attempt to fabricate sol-gel Nb_2O_5 for electrochemical purpose has been reported by Lee and Crayton [19] using a sol made of a mixture of NbCl_5 dissolved in ethanol. However the 5-10 μm thick film presented substantial cracking and peeling due to shrinkage during drying process. Avellaneda et al. [20,21] using a sol prepared with niobium pentachloride via the Na process

have obtained homogenous films without cracks and defects presenting good and promising electrochromic properties. Ohtani et al. [22] reported the preparation of Nb_2O_5 films exhibiting good electrochromic properties by using sol prepared from Nb ethoxide. Nilgun Ozer et al. [23] prepared Nb_2O_5 coatings by the sol-gel spin coating and D.C. magnetron sputtering techniques. The electrochemical behavior and structural changes were investigated in 1M LiClO_4 / Propylene Carbonate solution and found that sol-gel spin coated Nb_2O_5 films exhibiting high colouration efficiency comparable with that of D.C. magnetron sputtered niobia films. M.Schmitt et al. [24] studied electrochemical properties of sol-gel prepared niobium oxide films in LiClO_4 electrolyte. The colouring efficiency determined at $\lambda = 600 \text{ nm}$ was $22 \text{ cm}^2/\text{C}$. The same route was used in [25]. The EC devices exhibited colouring / bleaching changes up to 40-50%.

1.4 Purpose of dissertation

Electrochromism (EC) 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

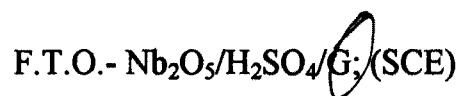
view angle, large operating temperature range, little power consumption in producing image and no limit to size. Out of all the inorganic materials, cathodically colouring WO_3 is the most studied and the best EC material. However the slow dissolution of WO_3 in aqueous electrolytes has prevented application of this system to practical devices. Niobium 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 Nb towards corrosion in mineral acids suggests that this material should form stable systems [25].

Various deposition techniques such as vacuum evaporation, sputtering, chemical vapour deposition, sol-gel process, and electron beam evaporation are being used to deposit niobium 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 films 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 niobium oxide thin films by using spray pyrolysis technique (SPT). The preparative parameters like nozzle-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 characterization of the films have been carried out using scanning electron microscopy (SEM), X-ray diffraction (XRD), optical absorption and two probe electrical resistivity techniques.

Electrochemical properties were studied using a three-electrode electrochromic cell of the form,



Where F.T.O. – Nb_2O_5 was used as a working electrode. H_2SO_4 was used as an electrolyte and graphite as a counter electrode. The voltages were measured with reference to saturated calomel electrode (SCE). The electrochromic properties of the cell were studied by using cyclic voltammetry, chronoamperometry and spectral transmittance technique.

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