CHAPTER- IX

Summary
9.1 Summary of Results

Electrochromic materials are potentially useful due to their low power consumption, high contrast and memory effects under open conditions. The commercialization of NiO based devices has been affected due to its rapid degradation on cycling and residual optical absorption in the 400 to 500 nm region due to hydrated nickel oxide films, thereby precluding a fully transparent state in the entire range of visible spectrum. In this work conducting layer (FTO) on glass substrate has been prepared using spray pyrolysis method, the step by step optimization has been done to enhance the EC properties of the NiO films via cheaper route and the effect of the addition of cobalt to nickel oxide is also studied and reported. The smart widows based on NiO has been fabricated and tested.

Low cost dip coating and spray pyrolysis units have been developed to prepare uniform thin films. The dip coating unit has been constructed using stepper motor and a stepper controller IC L297. The spray pyrolysis unit has been designed and constructed using tubular furnace and homemade spray nozzle.
Fluorine doped tin oxide (FTO) films have been prepared as a part of the work via spray pyrolysis method. The condition under which the best performance could be obtained is identified. For the entire work FTO films on glass were prepared under these optimized conditions.

The effect of fluorine concentration on the optical, structural and electrical properties of SnO$_2$ thin films prepared via spray pyrolysis route has been studied. X-ray diffraction pattern reveals the presence of SnO$_2$ films in the rutile structure with a preferential growth along the [200] direction. EDS was used to estimate the fluorine concentration. SEM reveals the surface of FTO to be made of nano-crystalline particles. The sheet resistance was found to decrease with increase in fluorine concentration to a minimum of 6.35 $\Omega/\Box$ for 7.5 mole % of NH$_4$F and it showed an increase beyond this concentration. The 7.5 mole % of F doped film had a lower resistance and higher carrier density, mobility. The same film has been used for electrochromic applications.

The first step in the optimization process is the optimization of thickness by varying the number of layers at an annealing temperature of 400$^\circ$C. Nickel oxide films have been deposited from nickel acetate precursor using sol-gel dip coating method onto glass and conducting FTO substrate. XRD analysis reveals an amorphous structure for 2-6 layered films and
cubic crystalline structure with preferential growth along (111) and (200) plane for 8 and 10 layered nickel oxide films with a particle size of 12 nm and 20 nm respectively. FTIR spectrum confirms the formation of Ni-O. Electrochromic properties of the nickel oxide coatings were studied using cyclic voltammetry (CV) technique. The 8 layered NiO film exhibit the anodic/ cathodic diffusion coefficient of $16.7/5.73 \times 10^{-13}$ cm$^2$/s and the change in optical transmission is $\Delta T_{630nm}=53\%$. The 8 layered film exhibits better electrochromic behavior.

The second step of the optimization process is the optimization of annealing temperature at an optimized thickness. The 8 layered NiO films has been prepared and annealed at different temperatures ranging from 250°C - 450°C. The XRD patterns reveals that the crystallinity along the planes (111) (200) and (220) increases as the temperature is increased from 250°C-450°C. The SEM images indicate the formation of nano rods in the temperature range of 350°C-450°C. The film prepared at 300°C with a thickness of 306 nm exhibits maximum anodic/cathodic diffusion coefficient of 11 / $6.44 \times 10^{-12}$ cm$^2$/s and the same film exhibits the maximum colour change of 68 %. The films annealed at 300°C exhibit the optimum electrochromic behaviour.
The final step of the optimization process is the optimization of duration of annealing at an optimized thickness and temperature. The NiO films have been prepared at 300°C followed by annealing them at 300°C for different durations (15-45 min). The XRD patterns reveal the annealed films to be amorphous in nature. The field emission SEM images indicate the films annealed for 30 min to contain good amount of porosity with the average pore size of 46 nm. The films annealed for 30 min exhibit maximum anodic/cathodic diffusion coefficient value of $12.33 \times 10^{-11}$ cm²/s and the same film exhibits the maximum colour change of 82.5%.

The step by step optimization greatly enhances the electrochromic behavior. The amorphous porous NiO films exhibit excellent electrochromic behavior compared with nanocrystalline NiO films with a particle size of 12 nm and 7 nm.

The mixed mode Ni-Co oxide $\{Ni_xCo_{1-x}O \ (x=0.95, 0.75, 0.50, 0.25)\}$ films were prepared at the optimum conditions. The XRD patterns exhibit the crystalline nature for $Ni_{0.75}Co_{0.25}O$ and $Ni_{0.5}Co_{0.5}O$ films while $Ni_{0.95}Co_{0.05}O$ and $Ni_{0.25}Co_{0.75}O$ films show amorphous nature. The field emission SEM images show that nanochannels like structure for $Ni_{0.95}Co_{0.05}O$ films and exhibit the formation of nano crystallites in the $Ni_{0.75}Co_{0.25}O$ and $Ni_{0.5}Co_{0.5}O$ films. The $Ni_{0.95}Co_{0.5}O$ films exhibit maximum
anodic/cathodic diffusion coefficient value of \(10/8.86 \times 10^{-11}\) \(\text{cm}^2/\text{s}\). The diffusion coefficient increases with cycling and reaches maximum at 100 cycles and the value of same is nearly twice that of pure NiO films. The same film exhibits the bleached/coloured state transmission of 90.42 / 7.21%.

The 6 layered tungsten trioxide films were prepared by sol-gel dip coating method. The structural and electrochemical studies were made and reported. The electrochromic Smart window has been built with the structure of

(i) \(G/\text{FTO}/\text{NiO}/\text{PMMA-PC-H}^+/\text{WO}_3/\text{FTO}/G\),

(ii) \(G/\text{FTO}/\text{NiO}/\text{PMMA-PC-Li}^+/\text{WO}_3/\text{FTO}/G\),

(iii) \(G/\text{FTO}/\text{Ni}_{0.95}\text{Co}_{0.05}\text{O}/\text{PMMA-PC-H}^+/\text{WO}_3/\text{FTO}/G\),

(iv)\(G/\text{FTO}/\text{Ni}_{0.95}\text{Co}_{0.05}\text{O}/\text{PMMA-PC-Li}^+/\text{WO}_3/\text{FTO}/G\)

and the electrochromic property of the devices was studied and reported.
9.2 Suggestions for further works

A suitable dopant has to be found to enhance the cyclic stability of the NiO films. The large area EC devices have to be fabricated. Along with electrochemical behaviour, the uniformity of the film thickness may be studied. Since gas evolution is a major problem, suitable ion transfer layer may be identified so that effective device fabrication is made possible.