Synthesis of Nickel Oxide Nanostructures for the **Application of Smart Windows**

M.Tech. Thesis

By Kaushal H. Parmar (1702105007)



DISCIPLINE OF METALLURGICAL ENGINEERING AND MATERIAL SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE

June 2019

Synthesis of Nickel Oxide Nanostructures for the Application of Smart Windows

A THESIS

Submitted in partial fulfillment of the Requirements for the award of the degree Of

Master of Technology

By Kaushal H. Parmar (1702105007)



DISCIPLINE OF METALLURGICAL ENGINEERING AND MATERIAL SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE June 2019



INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **Synthesis** of Nickel Oxide Nanostructures for The Application Of Smart Windows in the partial fulfillment of the requirements for the award of the degree of MASTER OF TECHNOLOGY and submitted in the DISCIPLINE OF METALLURGICAL ENGINEERING AND MATERIAL SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July, 2018 to June, 2019 under the supervision of Dr. Rupesh S. Devan, Associate Professor Discipline of Metallurgy Engineering and Materials Science (MEMS) Indian Institute of Technology (IIT) Indore and Dr. Parasharam M. Shirage, Associate Professor, Head, Discipline of Metallurgy Engineering and Materials Science Indian Institute of Technology (IIT) Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

Kaushal H. Parmar

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Dr. Rupesh S. Devan Dr. Parasharam M. Shirage

Kaushal H. Parmar has successfully given his M.Tech. Oral Examination held on **26th June, 2019**.

Signatures of Supervisors of M.Tech. Thesis Date:

Convener, DPGC Date:

Signature of PSPC Member 1 Date: (**Dr. Kiran Bala**)

Signature of PSPC Member 2 Date: (**Dr. Hemant Borkar**)

ACKNOWLEDGEMENTS

First and foremost, I want to thank my Guides, Dr. Rupesh S. Devan and Dr. Parasharam M. Shirage, whose support and guidance have driven me to do this work. Their friendly nature gave me the freedom and opportunity to interact with them as much as I wanted to.

I also want to thank my PSPC members Dr. Kiran Bala and Dr. Hemant Borkar, for their valuable suggestions in assessing my work during the mid-term and end-term presentations. I am thankful to Dr. P.M. Shirage, Head of the Department- MEMS for providing facilities that I required throughout the project work. I am also thankful to the faculties of this Department for their support and effort in teaching the concepts in Materials Engineering. I would also thank Sophisticated Instrument Center, IIT Indore for the FESEM facility; Saniya Ayaz and Prashant Sharma for helping me with XRD facility; and Central workshop staff for helping me with manufacturing stuff.

I also like to thank Dr. Yuan Ron Ma, for helping me in Electrochromic Characterization in their laboratory in Taiwan. I express my gratitude to Lab supervisors and technicians Mr. Mayur Dhake, Mr. Kinny Panday, and Mr. Rishiraj Chauhan for helping me in carrying out the experiments. I thank all my colleagues - Param Chikate, Narasimharao Kitchamsetti Vishesh Manjunath, Sameena Mulani, Madhuri Patil, and Santosh Bimli for helping me out with experiments.

I thank my classmates and friends at the Institute for the good time I had here. I am very happy to attribute my sincere thanks to the Director Indian Institute of Technology, Indore for providing me the necessary research facilities. I am grateful to MHRD for providing me teaching assistantship. I want to acknowledge my family for their affection, care, and untiring support. Finally, I would like to express my sincere gratitude to the Almighty.

Kaushal Parmar

In memory of loving brother Rajan Dedicated to my parents

Abstract

Nickel Oxide is a very well known anodic electrochromic oxide used in an ECD. Nickel oxide nanostructures have received huge attention because of its several properties, i.e. high (and low) transparency of colored and bleached (and colored) state, fast coloration and bleaching times; and good coloration efficiency. Nanostructures offer a larger surface area and more capillary pathways for the ion insertion and deinsertion. Because of the insertion and deinsertion of anions with NiO nanostructures of thin films, bleaching and coloration takes place

In this research work, we have demonstrated the two different types of nanostructures synthesized by the physical and chemical method. HFMOVD and hydrothermal method are the physical and chemical method used for this work. Nanobelts were obtained from Hydrothermal method, and thin films were synthesized by the physical method. The characterization of these samples and performance tests from which we have obtained the electrochromic properties. The coloration efficiency is ~74% and for the physically synthesized samples are ~13 % at ~354 nm. The coloration and bleaching times at this wavelength are 2-6 seconds and 0.39-0.45 seconds respectively.

TABLE OF CONTENTS

List	of Figures	K
List	of Tables	xi
List	of Abbreviation	xii

Chapter 1	Introduction	1
-----------	--------------	---

1.1 Overview	1
1.2 Comparison between the Existing and New	
Technologies	3
1.3 Electrochromism and Electrochromic Device	4
1.4 Principle of Operation	6
1.5 Performance Parameters	8
1.5.1 Contrast Ratio (CR)	8
1.5.2 Cycle Life and Write-Erase Efficiency	9
1.5.3 Response Time (τ)	9
1.5.4 Coloration Efficiency	10

Chapter 2 Review of Past Work and Problem Formulation

11	
 11	Ĺ.

2.1 Smart Windows Review Papers	1
2.2 Review papers on Electrochromism1	3
2.3 Research papers on ECD based on Nickel Oxide	
Nanostructures and its synthesis1	4
2.4 Problem Definition and Objectives1	6
2.4.1 Problem Definition1	6
2.4.2 Objectives:	6

Chapter 3 Synthesis Procedures 19
3.1 Different types of Synthesis Procedures
3.1.1 Physical Approach19
3.1.2 Chemical Approach19
3.2 HFMOVD Method and its Advantages and
Disadvantages
3.3 Hydrothermal Method and its advantages and
disad vantages
3.4 Materials, Preparation, and Synthesis Procedure
3.4.1 HFMOVD:
3.4.2 Hydrothermal Method
Chapter 4 Results and Discussions
4.1 FESEM Images
4.1.1 Chemically Synthesised Samples
4.2.2 Physically synthesized Samples:
4.2 XRD Analysis 32
4.2.2 Chemically Synthesised Samples
4.2.2 Physically Synthesised Samples
4.3 Cyclic Voltammetry (CV)
4.3.1 Understanding a simple CV graph
4.3.2 Introduction to the Electrochemical Cell
4.3.3 Recording the Cyclic Voltammogram
4.4 Cyclic Voltammograms of synthesized samples
4.4.1 Chemically synthesized samples
4.5 CV traces
4.6 Colored vs. Bleached Cycles
4.7 Chronocoulometry
4.8 The Electrochromism Mechanism
4.9 Electrochromic Properties

Chapter 5 Summary and Future Scope	57
5.1 Summary	57
5.2Future Scope	58
References	

LIST OF FIGURES

Figure 1.1 The Comparison of different window fenestration
technologies4
Figure 1.2 A view from the Smart Window
Figure 1.3 Types of ECD
Figure 1.4 Electrochromic device design, showing the movement of
ions under an externally applied electric field7
Figure 2.1 Research Work Plan17
Figure 3.1 HFMOVD Reactor 23
Figure 4.1 FESEM Images for the chemically synthesized samples28
Figure 4.2 FESEM Images for the physically synthesized
Sample G4 (top view images-low magnification 5k to 100k)30
Figure 4.3 FESEM Images for the physically synthesized sample G4
(side view images of 30k, 50k and 100k)
Figure 4.4 X-Ray Diffraction Patterns for the chemically synthesized
samples
Figure 4.5 X-Ray Diffraction Patterns for the physically synthesized
samples
Figure 4.6 Voltammograms of a electrode 35
Figure 4.7 Conventions used to report CV data
Figure 4.8 a schematic representation of an electrochemical cell37
Figure 4.9 Representation of an electrochemical cell as a potentiostat
Figure 4.10 Voltammograms recorded in 0.5 M KOH solution at 20
mV/s with NiO coated ITO glass as a working electrode, Pt foil as a
counter electrode, and Ag/AgCl as a pseudo-reference electrode .40
Figure 4.11 Transparency in bleach and coloured cycle measured
between 200 nm to 1000 nm for samples (a), (b), (c), (d) and (e) -6
hrs, 12 hrs, 18 hrs, 24 hrs, and 48 hrs respectively
Figure 4.12 CV traces of Nanobelts and Thin films measured at 20 mV/s

Figure	4.13 Colored	vs. E	Bleached	cycles	for	Nanobelts	and	Thin	films
									44
Figure	4.14 Colored	and	bleached	cycles	s of	Nanobelts	and	thin	films
(sa	mple D and sat	mple	G4)		••••		•••••		46

LIST OF TABLES

Table 1.1 The five groupings of the causes of the colour .	2
Table 1.2 A view from the Smart Window	3
Table 4.1 Electrochromic properties of Nanostructures	

List of Abbreviations

EC Electrochromic ECD Electrochromic Device TC Transparent Conductor NiO Nickel Oxide **1D** One Dimensional **CR** Contrast Ratio **CRT** Cathode Ray Tube LCD Liquid Crystal Display Q_i Charge Intercalation \mathbf{Q}_{di} Charge De-Intercalation NIR Near Infrared Region **XRD** X-Ray Diffraction HFMOVD Hot Filament Metal Oxide Vapour Deposition VS Vapour Solid CV Cyclic Voltametry CC Cyclic Chronocoulometry FESEM Field Electron Scanning Electron Microscope t_c Coloration Time t_b Bleaching Time JCPDS Joint Committee on Powder Diffraction Standards

Chapter 1 Introduction

1.1 Overview

"It's not about me. It's not about you, either. It's about the legacy, the legacy left behind for future generations. It's not about us."

Colour plays an extremely important role in our everyday lives. The questions regarding the colour, i.e. what is colour, what role does it play in nature, and our intellectual and social environment? [1, 2] In the late 17th century, Newton recognized the relationship between the colour and light. Since then, the science behind the colour and its many applications have been growing steadily. [3, 4]

Chemical and physical forces cause the colour change; these can be classified in five different basic mechanisms, as shown in table 1.1. Nassau divided these types further and derived "fifteen causes of colour." The group I, IV and V are considered as a physical phenomenon, group II is both chemistry and physics and group III includes only a chemical phenomenon. [3, 5]

Group	Causes	Examples
I	Vibrations and simple excitations (External heat or energy transfer	Incandescence, vapour lamps, some lasers
	within molecules)	
Π	Ligand field effects (from unpaired electrons in transition metal ions and complexes)	Phosphorescence, lasers
Ш	Transition between molecular orbitals	Absorbing dyes and pigments, both organic and inorganic, fluorescence
IV	Transition between energy bands	Metals, pure and doped semi- conductors
v	Geometrical and physical optics	Interference phenomena, iridescence, diffraction, liquid crystals

 Table 1.1 The five groupings of the causes of the colour[5]

The human eye or the simple spectrophotometric instruments can detect any color change of an object, even if it is from colorless to coloured, or from one colour to another, or from white to black. These colour changes give very useful visual signals which can be used to convey important information to an absorber. Furthermore, by choosing particular transmission or absorption of the light by a material, the restriction of the light energy is possible, e.g. the darkened glass in sunglasses. There is a third parameter as an external stimulus; it can be chemical or physical, it can change the colour, or the restriction of the light is possible. Based on the external stimulus, these colour change phenomena are named and classified.[5]

The process of changing a colour when an external stimulus is applied is called the chromism phenomena. It can be reversible. It can happen in different ways; Photochromism; Thermochromism, Electrochromism, Piezochromsim, Solvatochromism, etc. Table 1.2 shows the list of it.

It is used in various application as Smart Windows and Display devices. The smart window is a window which has two functions; they can impart energy efficiency as well as human comfort by varying transmittance levels depending upon the requirements, and they are also able to control visible throughput of light into the buildings. For Smart windows, various types of practical technologies are Thermochromic, Photochromic, and Electrochromic Technologies. Electrochromic technology is the most energy efficient technology than other types of window fenestrations.

Phenomena	Stimulus	Applications
Photochromism	Light	Ophthalmic lenses, novelty printing, security printing, cosmetics, optical data storage, memo- ries and switches, sensors
Thermochromism	Heat (intrinsic and indirect)	Thermochromic pigments, temperature indicators and thermometers, security and novelty printing
Electrochromism	Electrical current	Windows, mirrors, displays
Solvatochromism	Solvent polarity	Analysis, sensors, monitoring of polymers and polymerisation
Ionochromism	Ions	Colour formers, thermal fax papers, indicators, metal ion detection
(Halochromism)	(pH change)	(ditto)
Tribochromism	Mechanical friction	and a start of the second
Piezochromism	Mechanical pressure	

 Table 1.2 Colour change phenomena and their applications[5]

There are p-type, and n-type electrochromic oxides are used in an Electrochromic device. The Nickel oxide is a well-known p-type electrochromic oxide. For this research work, we have demonstrated the study of two types of samples synthesized by a physical and a chemical method. The standard characterization techniques were used to study their electrochromic properties. The cyclic voltammetry and chronocoulombomery were used to understand the different nature of their properties.

1.2 Comparison between the Existing and New Technologies

Fig. 1.1 shows a comparison of cooling energy and Electrical lighting energy with various Existing and New Technologies. Reflective glass gives a comparatively small need for cooling energy, but it requires relatively higher electric lighting energy as less amount of light rays enters into a room via fenestration.

Clear glass and tinted glasses need relatively higher cooling energy than reflective glasses. They are advantageous in terms of less demand for the electric lighting energy.



Figure 1.1 The Comparison of different window fenestration technologies[6]

Electrochromism based on fenestration has Electric lighting energy requirement up to 20 kWh/m² and cooling requirement up to 11 kWh/m². Thus, it has both advantages over other types of fenestrations.

There is a new concept of "light balancing," in which both types of fenestrations, i.e. chromogenic and light-guiding, can be used for energy efficiency. As well as a combination of more than one chromogenic technology can also be used. [7]

1.3 Electrochromism and Electrochromic Device

When a voltage is applied across it, an electrochromic material can change its optical properties. The original condition should be achieved on the application of reverse applied voltage. Thus, these optical properties should be reversible. Due to these electrochromic properties, there are different types of optical devices, e.g. smart windows, information display, light shutters, variable-emittance thermal radiators, and variable-reflectance minors.



Figure 1.2 A view from the Smart Window [6]

The optical modulation in the electrochromic oxides is related to differences in their electron density. Thus, the electrical contacts are required for the voltage should allow current extraction and injection. These layers or contacts must be transparent or at least set in a way that it does not significantly dim the optically functional electrochromic material. [8]

A colour can form in one or both of the electrodes or the electrolyte adjacent to the electrodes during the process of colouration in electrochromic cells by passing a charge in one direction. When the colour is formed by reduction at the anode, it is anodic coloration at a negative electrode and, on the other hand, it is called cathodic coloration. These types of cells are shown in Figure 1.3.[9]



Figure 1.3 Types of ECD [5]

The first type is the coloured electrode type in which the transparent electrodes are coated with organic or inorganic materials. The electrochromic material becomes coloured on passing a charge through the cell. If both electrodes change their colour, they must display complementary electrochromism; the colour change occurs by reduction at the first electrode must be the same as that occurring at the second electrode. The amount of charge passing through the cell controls the degree of the coloration. The electrochromic cell is bistable; i.e., it remains in its coloured state even in the absence of applied voltage, until an equal amount of charge is passed in the opposite direction. Therefore the coloration of the electrochromic cell is switchable and controllable on demand.

In the second type of the *coloured electrolyte type*, the electrolyte between the transparent electrodes has two complementary electrochromes. One becomes coloured by reduction and the other by oxidation, and accordingly, the electrolyte becomes coloured. The electrolyte remains coloured until a current is passed. It achieves a bleached condition on the removal of charge.[5]

1.4 Principle of Operation

There are many stable electrochromic device constructions available. The shown representation in figure 1.4 is the preferred in almost all work aimed at practical utilization of electrochromism. This set-up is suitable also as a prototype for discussing electrochromic systems in general. It has many layers supported by a substrate, in many cases is glass substrates. The glass has a conductor, which is transparent and electrically conductive. On that, the film of the electrochromic oxide is layered. [8]



Figure 1.4 Electrochromic device design, showing the movement of ions under an externally applied electric field [8]

This electrochromic oxide has mixed conduction for electrons and ions. If ions are inserted from an adjoining electrolyte or via an adjoining ion conductor, there is a corresponding charge-balancing counter-flow of electrons from the transparent electron conductor. These electrons will remain in the film. As long as the ions reside there, the electrons will induce a constant change of the optical properties.

The electron injection can increase or decrease the transparency based on the used electrochromic oxide. The ion conductor can be a bulk or thin film type material; for practical devices, solid inorganic or organic materials are preferred, whereas liquid electrolytes are suitable for research work.

The ion storage film can be with or without electrochromic properties. If the full device is for modulating light throughput, another electrical conductor must be a transparent film. In some devices, there is a second glass plate. Thus, the system has two substrates; each with a two-layer coating; and an ion conductor that can serve as a lamination material.

A disturbed electric field is generated and ions uniformly move into and out of the EC film. The electrons through the external circuit flow as a balancing counter-flow. This results in a variation of the electron density in EC film and modulates the optical properties.

The optical properties remain stable for long periods. Because the ion conductor has insignificant electronic conductivity so that the device will exhibit open circuit memory. The applied voltage between the TC should be of the order of a few volts. Higher voltages will result in rapid degradation of the device.

The large optical modulation and sufficient charge conductivity are the main requirements of the EC film. The ion storage film has the requirements on electronic and ionic conductivity as the EC film. They should have complementary electrochromism compared to the primary EC film. If the primary electrochromic film darkens upon ion deintercalation, the ion storage should darken upon ion intercalation (and vice versa). Darkening under ion deintercalation is called *anodic colouration*, and darkening under ion intercalation is termed as *anodic colouration*. The ion conductor should have low enough electron conductivity and sufficient ion conductivity. The TC must have low resistivity values. [8]

1.5 Performance Parameters

1.5.1 Contrast Ratio (CR)

In order to study an ECD, the quantitative measure of intensity change of the colour is required. It is described by Contrast ratio:

$$CR = \frac{Io}{Ix} \tag{1.1}$$

; Where I_o and I_x are intensities of diffuse reflected light in the bleached and coloured state respectively.

It should denote to a specific wavelength or relate to an integral value of white light. [10]

1.5.2 Cycle Life and Write-Erase Efficiency

The number of possible, stable cycles performed by an ECD before its failure is called its cycle life. A failure of an ECD can occur due to change of physical phases into solid or formation of chemical side reactions when the ECD is continually switching between two states, i.e. coloured state and bleached state.

As this parameter is a measure of the stability of a device, it is also an important factor in device design. The percentage of originally formed coloration when subsequently electro-bleached is the Write-Erase Efficiency. Conveniently, it can also be defined as the ratio of absorbance change of subsequent cycles. [10]

1.5.3 Response Time (τ)

It is required time for an ECD to bleach from its coloured state (or vice-versa). It is denoted by τ .

It is in the order of a few seconds for most devices.

Due to the diffusion of charged species through the electrode film or diffusion of the electrochrome to the electrode for all-solution systems, Response time is slower than CRTs and LCDs.

Response time of minutes (seconds for the case of mirrors) can be allowed in the application of electrochromic windows or mirrors. The very fast response times will be necessary if such devices are used in television screen optical switches or optical switches.

There are no formal conditions for determining τ . Change in optical density or time required for partial or all charge to be injected in the film or electrolyte is used in calculating the Response time. [10]

1.5.4 Coloration Efficiency

It is associated with an optical absorbance change (ΔA), an injected charge per unit area (Q), a linear coefficient (α) and a film thickness d.

$$\eta = \frac{\Delta A}{Q} = \frac{(\alpha d)}{Q} \tag{1.2}$$

There is an assumption that all optical effects are absorptive. A single absorbing element is effective at the wavelength chosen for the study. At this wavelength, the Beer-Lambert law has complied. (We have selected four different wavelengths for colouration efficiency calculation as 354, 420, 480 and 590 nm). [10]

Chapter 2 Review of Past Work and Problem Formulation

2.1 Smart Windows Review Papers

Yang Wang, Evan L. Runnerstrom, and Delia J. Milliron1, Switchable Materials for Smart Windows Annual Review of Chemical and Biomolecular Engineering, (2016) 7,283-304

In this research paper, the fundamental principles and recent developments in thermochromic, photochromic, and electrochromic materials used in Smart windows were discussed. The Smart window modulates the transmittance of solar radiation dynamically based on atmospheric conditions and human needs, whereas static window cannot do that. They can improve indoor human comfort as well as building energy efficiency. It was observed that widespread application of smart windows has not yet been recognized although they are commercially available.

Recent advances in nanostructured materials have been made which offer new opportunities for future-generation smart window technologies. These nanostructured materials can enhance coloration efficiency, faster switching kinetics, and longer lifetime.

This technology has a low-cost and high-throughput fabrication output. It was also discussed that the dual-band modulation of visible and near-infrared (NIR) light was important, as nearly 50% of solar energy lies in the NIR region. Some recent results show that nanostructured systems modulate the selective region of the NIR light without affecting the visible transmittance. Hence, these systems reduce energy consumption by a heating, air conditioning, and artificial lighting. [11]

Marco Casini, Active dynamic windows for buildings: A review Renewable Energy 119 (2018), 923-934

In this review paper, future generation window solutions were discussed. There is a rising demand for environmental comfort and the urgent need to improve the energy efficiency of buildings. In this review, technological solutions were discussed and compared. These solutions can guarantee maximum thermal insulation, as well as the regulation of the incident solar radiation, is also possible. In some cases, electrical energy can also be converted from solar radiation using solar cell devices along with these systems. Due to this progress in material science, a new type of highly innovative glazing systems is introduced to the market. These systems use smart or nanomaterials, which are produced by the new age technologies.

Active dynamic glazing, along with these new technologies, allows significant energy savings. It can be done by modulating the amount of NIR and visible region light with considering visual and thermal comfort.

Gasochromics, Electrochromics, and other further emerging technologies (e.g., glass-composites, windows with elastomers, etc.) were compared in terms of performances, operation, and materials. For understanding the impact the energy-efficiency and comfort, the relevant data were provided.[12]

12

Claes G. Granqvist, Recent progress in thermochromics and electrochromics: Thin Solid Films 614 (2016), 90-96

Contemporary architecture is characterized by large glazing, which can accomplish good indoors-outdoors contact and daylighting. However, glazing, encompassing windows and glass facades, is challenging about energy efficiency and often lead to excessive solar energy ingress and to large thermal losses, which must be balanced by energy-demanding cooling or heating. Cooling, especially, has grown strongly in importance during recent years. Emerging technologies utilizing thermochromics and electrochromics allow control of the inflow of visible light and solar energy and thereby produce better energy efficiency than traditional glazing employing static solutions. Thermochromic thin films, based on vanadium dioxide, let through less solar energy at high temperature than at low temperature, whereas electrochromic devices include thin films-usually based on tungsten oxide and nickel oxide-that can change their transmittance of solar energy and visible light upon the application of a voltage. It is important that electrochromics, and to some degree, thermochromics, can enhance indoor comfort and lead to better living and working conditions. This article represents a brief review of several recent advances in thermochromics and electrochromics with a view to applications in energy-efficient buildings. [13]

2.2 Review papers on Electrochromism

Gunnar A. Niklasson and Claes G. Granqvist, Electrochromics for smart windows: thin films of tungsten oxide and nickel oxide, and devices based on these Journal of Materials Chemistry, 2007, 17, 127– 156

Electrochromic devices based on tungsten oxide and nickel oxide thin films were discussed in this paper. EC materials can change their optical properties are persistent and reversible when the external voltage is applied. These materials, along with multilayer devices, can modulate the transmittance. The recent research work on tungsten oxide and nickel oxide is described in this article. The ion diffusion, electronic band structure, thin film deposition, structural properties were also included for both materials.

The conduction band density of the states can be achieved from simple electrochemical chrono-potentiometry. The counter-charge flow of electrons enters localized states due to ion insertion. It implies that the optical absorption of the electrochromism is due to transitions between occupied and empty localized conduction bands.

There is a superposition of transitions between different charge states of tungsten ions (+4, +5, and +6). The nickel oxide films are made up of small grains and are porous. The electrochromism is observed in Nickel oxide films is consistent with reversible changes between Nickel oxy-hydroxide and nickel hydroxide phase according to Bode reaction scheme. It was verified that electrochromism is linked exclusively with proton transfer.

The following part of this paper is of a more application and technological oriented. There are methods to improve the bleached-state transmittance by mixing the Ni oxide with other oxides having wide bandgaps.

Also, the novel flexible polyester-foil-based devices were discussed. The last part deals with the architectural smart windows which are capable of improving the indoor comfort as well as energy efficiency in the buildings.[14]

2.3 Research papers on ECD based on Nickel Oxide Nanostructures and its synthesis

Ranjit A.Patil, Rupesh S. Devan, Jin-Han Lin et al., One-Dimensional Metal-Oxide Nanostructures: Recent Developments in Synthesis, Characterization, and Applications, Advanced Functional Materials 22 (2012), 3326-3370

This review paper discusses the one-dimensional metal-oxide nanostructures basics, mechanisms, synthesis processes,

characterization techniques, and their applications. 1D metal-oxide nanostructures have attracted much attention because metal oxides are fascinating functional materials. These unidirectional morphologies can easily enhance the properties of the metal-oxides. It makes them suitable for widespread applications, including smart windows, sensing LEDs. supercapacitors, applications, nanogenerators, and nanoelectronics. There are different types of structures synthesized by various methods, i.e. nanowires, nanorods, nanobelts, and nanotubes, etc. Different chemical and physical deposition methods, and growth mechanisms are developed to manage the defects, homogeneous stoichiometry, perfect crystalline structure, uniform size, shape, and size of the nanostructures. The complete review of current developments in synthesis, properties, and well-known applications of transition metal oxides WO₃, Ta₂O₅, V₂O₅, Nb₂O₅, NiO, ZnO, and IO is provided. [15]

Ranjit A.Patil, Rupesh S. Devan, Jin-Han Lin et. al, Efficient electrochromic properties of high-density and large-area arrays of onedimensional NiO Nanorods, Solar Energy Materials & Solar Cells 112 (2013), 91–96

In this paper, the electorchromic properties of transparent largearea and high-density 1D Nanorods were reported. The physical synthesis process HFMOVD was used to synthesize the NiO film. The film contains the 100 nm wide and 500 nm long nanorods array. The phase of the nanorods was observed to be cubic crystalline with Fm3m space group.

The overview of the EC oxide properties can be studied in this article. The step by step procedure was explained along with the electrochromic mechanism involved. The CV, as well as CC traces, were recorded. Based on that the exceptional electrochromic properties were obtained from 1D-NiO nanorods. Large values of diffusion coefficient (6.33 x 10^{-8} cm²/s), reversible and stable bleaching-coloration cycles, very high transmittance difference as 60%, very fast bleaching and colouration times (1.22 and 1.55 s) at 630 nm wavelength,

and high OD were recorded. Thus, it suggests that 1D NiO nanomaterials can be useful for smart window applications. [16]

2.4 Problem Definition and Objectives

2.4.1 Problem Definition

It is clear that from various chromogenic technologies, Electrochromic Technology is suitable for practical window fenestrations. It is more user-friendly and dynamic. Furthermore, it can be linked with the Solar cell devices to minimize the operating cost. Thus, the need for comfort as well as visibility in the room can be served with no running cost.

As discussed in the previous chapter, an EC can be made up of many layers. An electrochromic oxide layer on a conducting layer can be of an anode or a cathode type material.

Tungsten Oxide and Nickel Oxide are very well-known anodic and cathodic electrochromic oxide materials.

We have chosen the basic primary type device for this research work, which includes following layers: glass as a substrate, ITO as a conducting layer, NiO as an anodic electrohromic oxide layer, and KOH as an electrolyte.

2.4.2 Objectives:

There are two main objectives for this research work:

a. To prepare samples from the chemical and physical synthesis process

b. To study the electrochromic properties of synthesized samples

In the first phase of the research work, the literature survey of the previous work on the Smart Windows. The optimization of parameters for both physical and chemical methods was done in the following step.


Figure 2.1 Research Work Plan

In the next phase, the samples were prepared using the HFMOVD and the Hydrothermal technique. The different characterization techniques were used to obtain the nature of the properties and structures of the prepared samples. In the last step, the obtained data were analysed by using standard calculation procedures used for the Electrochromic Smart Windows.

(This page is intentionally kept blank.)

Chapter 3 Synthesis Procedures

3.1 Different types of Synthesis Procedures

3.1.1 Physical Approach

There are different physical techniques for thin film deposition, which involves Thermal Evaporation, Sputtering, HFMOVD, etc.

The Evaporation technique includes Vacuum, Reactive (O_2, N_2, H_2O) , and Ion Assisted technique. The Sputtering technique includes Non-reactive (Ar), Reactive (Ar+O₂), and Chemical technique (O₂ + CF₄). [8]

3.1.2 Chemical Approach

Various chemical techniques, i.e. Hydrothermal method, Vapour Deposition, Sol-gel, Spray Pyrolysis, Decomposition reaction, and Thermal Oxidation, etc. can be used for preparing thin films.

The Vapour Deposition technique includes atmospheric pressure, low pressure, and plasma enhanced technique. The Sol-gel technique includes Dip-coating, Spin-coating, and Spraying technique. [8]

3.2 HFMOVD Method and its Advantages and Disadvantages

HFMOVD (Hot Filament Metal Oxide Vapour Deposition) is a technique in which metal filament is used for heating. This filament is kept in between two electrodes (copper electrodes). Its distance from the substrates is set after some improvisations. The air is sucked from the reactor, and vacuum pressure up to 10⁻² mbar is created. At this vacuum pressure, there is some residual oxygen present inside the chamber, which helps oxides the metal atoms. Due to heating, on the surface of the metal filament, the metal atoms sublimates into vapours.

Furthermore, Graphite crucibles can be used to concentrate the metal vapours from the metal source to the substrate surface. The filament completes the circuits, so heating can be regulated by changing the current. Thus, deposition thickness can be optimized by controlling current flows in the metal filament.

There are three main parameters affecting deposition quality:

- a. Deposition Time
- b. The Temperature of the filament and
- c. Distance between the metal filament and substrate

There are three steps in the deposition process:

- a. Thermal Sublimation
- b. A reaction between the metal atoms and residual oxygen atoms
- c. Adhesion of metal oxide atoms on the substrate surface

The three growth processes allow the HFMOVD technique to provide the catalyst-free vapour-solid (VS) growth for the synthesis of nanostructures. [15] Advantages:

a. Adhesion of the film on the substrate surface is good.

b. Deposition thickness can be controlled.

c. No need for a catalyst for reaction inside the chamber.

d. A very thin film and transparent films can be deposited by this method.

Disadvantages:

a. Uniformity of the film is undesirable; it needs to be optimized.

b. As the process is done in the vacuum, the vacuum system adds the cost of an instrument. It will increase the overall cost of the deposition.

- c. Reproducibility of the substrates is a little difficult.
- d. No control over the rate of deposition.

3.3 Hydrothermal Method and its advantages and disadvantages

"The heterogeneous chemical reaction with the presence of an aqueous or non-aqueous solvent higher than room temperature and a pressure greater than 1 atm in a closed system is called the Hydrothermal reaction." [17]

Based on the specific physical properties, mostly the compressibility, solvation power, and the mass transport of these solvents. There are different types of chemical reactions take place:

- 1. Stabilization of new complexes or synthesis of new phases.
- 2. Crystal growth of different inorganic compounds.
- 3. For a particular application, preparation of micro-crystallites with pre-defined morphology and size.
- 4. The leakage of ores in metal extraction.
- 5. Etching, corrosion, alteration, and Decomposition.[17]

Advantages:

- a. With this method, it is possible to grow crystals of compounds with high melting points at lower temperatures
- b. Materials which have a high vapour pressure near their melting points can be grown by the hydrothermal method.

c. The method is also particularly suitable for the growth of large good-quality crystals while maintaining control over their composition.

Disadvantages:

- a. The autoclaves are expensive.
- b. The impossibility of observing the crystal as it grows

3.4 Materials, Preparation, and Synthesis Procedure 3.4.1 HFMOVD:

• Materials:

Ni wire (Alfa Aesar, 1.0 mm diameter X 6.5 cm length), ITO coated glass substrate (Sigma Aldrich), Graphite crucibles (Thermo Forg Company), Ethanol (SRL Company), and DI water.

• Preparation and Synthesis Procedure:

Nickel wire was used as a filament for the synthesis of NiO thin film on ITO coated glass substrate in HFMOVD (Hot Filament Metal Oxide Vapour Deposition) chamber. Graphite crucible was used to confine metal vapours on the substrate so that more amount of metal vapour particles can adhere to the substrate. Copper Electrodes were used inside the reactor chamber for providing sufficient heating.

ITO coated glass substrates were cut into dimensions of $1.5 \times 3 \text{ cm}^2$ and were cleaned by Ultra-sonication with DI water and Ethanol several times. Nickel wire was carefully kept in between the copper electrodes.



Figure 3.1 HFMOVD Reactor

The distance between the ITO substrate and metal filament was optimized by various experimental trails. The vacuum pressure up to 3.0×10^{-2} mbar was created inside the reactor chamber. Deposition thickness was controlled by varying current. Deposition time and Temperature of the filament were observed. The filament temperature was measured by the pyrometer. After NiO deposited on ITO substrate, keep the substrate in the reactor as it is for 10 mins so that the substrate will come to room temperature.

3.4.2 Hydrothermal Method

• Materials:

1 M Ni(NO₃)_{2.6 H₂O (Sigma-Aldrich, 99.9%), Urea (0.05–0.2 g), ITO coated glass substrate (Sigma Aldrich), Ethanol (SRL Company), and DI water.}

• Preparation and Synthesis Procedure:

The NiO Nanobelts were synthesized by a simple hydrothermal method. All the chemicals are of analytical grade and used as received without further purification. In a typical synthesis, 1 M Ni(NO₃)₂.6 H₂O was dissolved in 10 ml of ethanol. After stirring for about 10 min, a transparent solution was obtained, and then a certain amount of Urea (0.05-0.2 g) was added into the above solution. After stirring for another 30 min, the obtained solution was transferred into a 25 ml Teflon-lined stainless steel autoclave. Keep the ITO substrate (1 cm x 1 cm) inside the autoclave by facing conducting side up, followed by heating at 180° C for a period of 6,12,18,24 & 48 in an electric oven. After that, the autoclave was cooled naturally to room temperature. Take it out the ITO substrate from autoclave and clean with DI water several times and dry it for some time at room temperature. [18]

Chapter 4 Results and Discussions

There are various types of characterization techniques performed for Nickel Oxide deposited on ITO coated thin films on glass substrates. The primary investigation of samples was done by X-Ray Diffraction technique. The morphology of the Samples was analyzed by Field Electron Scanning Electron Microscope. Cyclic voltammograms indicate the current density upon charge insertion and extraction as a function of the applied voltage. Chronocoulometry (CC) graphs were extracted to calculate reversibility and coloration efficiency.

The samples prepared by Hydrothermal Method were denoted by sample A, B, C, D, and E for the reaction time of 6, 12, 18, 24, and 48 hrs, respectively. The samples G and H were prepared by HFMOVD Method.

4.1 FESEM Images

FESEM is the abbreviation of Field Emission Scanning Electron Microscope. A FESEM is a microscope that works with electrons instead of light. These electrons are liberated by a field emission source. The object is scanned by electrons according to a zig-zag pattern.

FESEM is used to visualize very small topographic details on the surface or entire or fractioned objects. Researchers in biology, chemistry, and physics apply this technique to observe structures that may be as small as 1 nanometer.

4.1.1 Chemically Synthesised Samples

Initially, the thin film is grown on the ITO film as it can be seen from the image (a). In sample (b), (c), (d) and (e), the growth of the nanobelts take place. The width of the belts increases with the increasing annealing temperature.









Figure 4.1 FESEM Images for the chemically synthesized samples

4.2.2 Physically synthesized Samples:





Figure 4.2 FESEM Images for the physically synthesized Sample G4 (top view images-low magnification 5k to 100k)

As seen from the images, the physically synthesized samples have grown the nanoparticle layer on the surface. These nanoparticles have sizes in order of 10 nm and they were scattered uniformly over the sample surface.

Whether the nanorod shaped structures were grown, we checked the side view of the samples. Although it was observed to be the thin film structure on the surface.



Figure 4.3 FESEM Images for the physically synthesized sample G4 (side view images of 30k, 50k and 100k)

The energy required crystals to grow in one direction is very less, that can be the reason for thin film growth instead of nanorods on the surface. From side view images, thin films nanostructures can be observed.

4.2 XRD Analysis

X-ray diffraction is a technique for the study of the fine structure of the material. This technique is used in different purposes as chemical analysis, the study of phase equilibria, stress measurements, determination of crystal structure, particle size, and orientation of one crystal or the assembly of orientations in a polycrystalline aggregate.

4.2.2 Chemically Synthesised Samples

These patterns are called fingerprints of crystalline materials. The NiO and ITO phases' presence was identified by the obtained patterns. Figure 4.1 shows X-Ray Diffraction patterns for the different samples prepared by the chemical method. The reference pattern for the ITO film is JCPDS 89-4598, and reference pattern for the chemically deposited Nickel Oxide film is JCPDS 89-3080 and JCPDS 73-1519.





Figure 4.4 X-Ray Diffraction Patterns for the chemically synthesized samples

Thus, Nickel Oxide deposition was confirmed by this initial characterization. The NiO Nanobelts are of Rhombohedral phase, with lattice constants a = b = 0.59108 nm and c = 0.72259 nm; lattice angles are $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$. The diffraction peaks at 21.2°, 30.2° and 37.2° respectively to (101), (110) and (021) planes.

4.2.2 Physically Synthesised Samples



Figure 4.5 X-Ray Diffraction Patterns for the physically synthesized samples

The reference pattern for the ITO film is JCPDS 89-4598, and reference pattern for the physically deposited Nickel Oxide film is JCPDS 89-3080. The crystal structure of ITO is Cubic, and space group is Ia-3. The crystal structure of Nickel Oxide is Rhombohedral, and space group is R3-m. As the structure is Rhombohedral and the obtained XRD pattern is matched with the same JCPDS card as previous samples, the lattice constants are the same as above.

4.3 Cyclic Voltammetry (CV)

The CV is an electrochemical technique used to identify the oxidation and reduction processes of molecular species. It is also important to study electron-transfer-initiated chemical reactions, which includes catalysis. [19]

tiential (V vs Fc⁺/Fc)

4.3.1 Understanding a simple CV graph

Figure 4.6 Voltammograms of a electrode [19]

The traces in figure 4.6 are called cyclic voltammograms or cyclic voltammograms. The x-axis represents an applied potential (E), while the y-axis represents the resulting current (i) passed. Two conventions are commonly used to report CV data.

Each CV graph includes an indication arrow direction in which the potential was applied to record the data. The arrow specifies the beginning and sweeps direction of the first segment (or forward scan), and the caption suggests the condition of the experiment. The crucial parameter is the scan rate (v). It indicates at which rate the potential was linearly applied. We have used the IUPAC convention for CV graphs. [19]



Figure 4.7 Conventions used to report CV data

The scan rate of the experiment controls how fast the applied potential is scanned. The decrease in the size of the diffusion layer is due to the faster scan rates. Higher currents are observed as an effect of the faster scan rate.

$$ip = 0.446 \, n \, FA \, C^{\circ} \, \frac{n \, F \, \upsilon \, D_{\circ}}{R \, T}$$
 (4.1)

The Randles–Sevcik equation (4.1) describes for electrochemically reversible electron transfer processes;

Where i_p = peak current (A), v = scan rate (V s-1), n = the number of electrons transferred in the redox event, A = the electrode surface area (usually treated as the geometric surface area in cm²), Do = the diffusion coefficient of the oxidized analyte (cm2 s-1), and C₀ = the bulk concentration of the analyte (mol cm-3).

4.3.2 Introduction to the Electrochemical Cell

The vessel used for CV experiment is called an electrochemical cell. A schematic representation of this cell is shown in figure 4.8.



Figure 4.8 A schematic representation of an electrochemical cell [19]

For our experiments, we have used 0.5 M KOH solution at 20 mV/s with NiO coated ITO glass as a working electrode, Pt foil as a counter electrode, and Ag/AgCl as a pseudo-reference electrode.



Figure 4.9 Representation of an electrochemical cell as a potentiostat [20]

Electrolytic solutions have an intrinsic resistance Rsol in the electrochemical cell (Figure 4.9). While some potentiostats can compensate for most of this solution resistance (Rc), there remains a portion of uncompensated resistance (Ru) between the WE and the RE. During electrochemical measurements, the potential that the instrument records may not be the potential experienced by the analyte in solution due to Ru. This phenomenon is called ohmic drop.

4.3.3 Recording the Cyclic Voltammogram

The electrodes are connected to the potentiostat, and the experimental parameters are selected through the potentiostat software.

While different software will require different parameters, fundamental ones are the potential window that will be scanned (defined by the initial, switching, and final potentials), the scan rate, and the number of segments/scans.

4.4 Cyclic Voltammograms of synthesized samples

4.4.1 Chemically synthesized samples

Figure 4.10 shows the CV graphs of samples (a), (b), (c), (d) and (e). The potential window is 0.2 to 0.6 V. The oxidation and reduction cycles are measured and it was observed to be increase in high currents with faster scan rates. The values of scan rates were to be 20 to 100 mV/s. The linear potential sweep between -0.3 V to 0.60 V is set up for Sample D with a fixed scan rate of 20 mV/s for the forward and the reverse scans for comparison with physically synthesized samples.







Figure 4.10 Voltammograms recorded in 0.5 M KOH solution at 20 mV/s with NiO coated ITO glass as a working electrode, Pt foil as a counter electrode, and Ag/AgCl as a pseudo-reference electrode

The coloration and bleaching cycles were recorded after CV traces were obtained. Figure 4.11 represents the colored and bleached cycles. There is very less difference in the transmittance between colored and bleached cycles.







Figure 4.11 Transparency in bleach and coloured cycle measured between 200 nm to 1000 nm for samples (a), (b), (c), (d) and (e) - 6 hrs, 12 hrs, 18 hrs, 24 hrs, and 48 hrs respectively.

4.5 CV traces

The CV traces of chemically and physically synthesized samples were as shown in figure 4.12. We concluded that there is a significant amount of difference in Optical Transmittance in colored and bleached state of Nanobelts and Thin Films. The potential linear sweep is between -0.4 V to 0.65 V for Sample G4 (a physically synthesized sample) and -0.3 V to 0.60 V for Sample D (a chemically synthesized sample); with a fixed scan rate of 20 mV/s for the forward and the reverse scans.

OH⁻ ions were inserted in the Electrochromic oxide layer at applied positive potential during the forward scan because the Nickel Oxide Nanorods are p-type semiconductors. The transparent Nickel Oxide Nanorods/ITO thin film becomes somewhat brownish near 0.4 V but converts to a dark brown colour at 0.4 V. This is due to the concentration of OH^(-ve) ions generates a chemical potential. During reverse scan sample again becomes transparent.



Figure 4.12 CV traces of Nanobelts and Thin films measured at 20 mV/s

The peak current density is the maximum current density during the forward scan i.e. during the oxidation process. Their values were measured to be 2.2 mA/cm^2 and 3.3 mA/cm^2 for Nanobelts and Thin films respectively.

4.6 Colored vs. Bleached Cycles

The colored vs. bleached cycles were shown in figure 4.13 for Nanobelts and Thin Films. There was a large difference in the transmittance for thin films. Whereas there was a little difference in the transmittance for Nanobelts were observed.



Figure 4.13 Colored vs. Bleached cycles for Nanobelts and Thin films

4.7 Chronocoulometry

The reversibility, Charge intercalation and Charge Deintercalation values were calculated from the Charge Density vs. Time graph. These values were associated with the number of OH^(-ve) ions in the electrolyte. It is used to study the change in the charge density of the negative ions of the electrolyte. Due to this, the transparency of the material changes.

Figure 4.14 represents the charge density (C/cm²) as a function of time from the experiment. On the application of the positive voltage, there was a rise in the charge density, which was exactly the value of the charge insertion value. The transparent NiO nanostructures change their colour to brown. The fall in the charge density was observed when a negative voltage applied. The coloured NiO nanostructures were bleached, i.e. become transparent. Thin films have higher Charge Insertion and Charge De-intercalation values than Nanobelts. The charge intercalation (i.e. insertion) and deintercalation (i.e. disinsertion) values were 0.005660 and 0.005659 C/cm² for Nanobelts. Charge insertion and disinsertion values were 0.01459 C/cm² and 0.01242 C/cm² for thin films.

The ratio of charge disinsertion and insertion is called reversibility of an electrochromic oxide. It was observed to be 85.05 % and 99.98 % for thin films and Nanobelts respectively. Although the transmittance difference of the Nanobelts for the chemically synthesised sample D was observed to be 0.55 %. For calculation of the Coloration efficiency, charge insertion and difference in the transmittance is required. Thus, due to less value of ΔT the coloration efficiency of Nanobelts was low.



Figure 4.14 Colored and bleached cycles of Nanobelts and thin films (sample D and sample G4)

The optical transmittance measurements are useful to study the reversibility, stability, persistence, and switching response times for the device. As the Charge density values were low for the chemically synthesized samples, we have done the optical transmittance measurements only for the physically synthesised samples. The figure 4.15 represents the optical transmittance measurements at 354 nm, 420 nm, 480 nm, and 590 nm for sample G4.

4.8 The Electrochromism Mechanism

The chemical processes which represents the electrochromic mechanism can be expressed with two reactions (4.2) and (4.3). In the first reaction, the hydroxide layer of Ni(OH)₂ formed at the surface of the NiO nanostructures in KOH (an aqueous electrolyte solution). In the following reaction the Ni(OH)₂ reacts with OH⁻ ions to form the oxy-hydrogen layer. [21, 22] Nickel Oxy-hydroxide is a p-type semiconductor with a bandgap of ~1.7 to ~1.8 eV, whereas Nickel hydroxide phase is an n-type semiconductor. [23] The electronic structure of the hydroxide displays the similar nature of the charge transfer between Ni 3d and O 2p states. [24]

$$NiO (transparent) + H_2O \rightarrow Ni(OH)_2$$

$$Ni(OH)_2 + OH^- \rightarrow NiOOH (Dark Brown) + H_2O + e^-$$
(4.2)

The NiOOH and Ni₂O₃ are also oxygen-rich compounds. They absorb light to a large extent. Therefore, electrochromic Nickel Oxide films are only used in devices where an optical modulation is due to proton/electron transport. [25]

4.9 Electrochromic Properties

Table 4.1 represents the electrochromic properties of Nanostructures calculated from CC and CV traces at 354 nm. The value of the diffusion coefficient was calculated with Randles-Servick equation (4.1). The coloration efficiency was calculated as the ratio of the Optical density and the charge intercalation, i.e. $\frac{\Delta OD}{Qi}$. Its values were 74.08 % and 13.182 % for Thin films and Nanobelts structures respectively. The coloration times were in the range of 2-6 second and the bleaching times were in the range of 0.39-0.45 second.

Electrochromic Properties	Thin Film (Physical Method)	Nanobelts (Chemical Method)
Charge Insertion (C/cm ²)	0.01459	0.005660
Charge De-intercalation (C/cm ²)	0.01241	0.005659
Reversibility (Q_{di}/Q i, in %)	85.05	99.98
Difference In Optical Transmittance (ΔT = T(bleach)-T(colour), in %)	44.65	0.55
Optical Density (ΔΟD = In T(bleach)-In T(Colour), in %)	1.080	0.074
Coloration Time (s)	2.32558	~
Bleaching Time (s)	0.453	~
Diffusion Co-efficient (cm ² /s)	8.01e-11	3.32e-22
Coloration efficiency ($\eta = \Delta OD / Qi$, C/cm ²)	74.080	13.182

Table 4.1 Electrochromic properties of Nanostructures







(i) Optical transmittance spectra of colored and bleached state@ 354 nm, which is 44.65 %.

(ii) One single coloration-bleaching cycle displays the switching response characteristics; the coloration time is 2.32 second and the bleaching time is 0.45 second.

(iii) & (iv) $T_{colored/354 nm}$ and $T_{bleached/354 nm}$ for first 200 and 50 cycles.

(v) Bleaching and Colored state transmittance difference @354 nm





(i) Optical transmittance spectra of colored and bleached state@ 420 nm, which is 54.61 %.

(ii) One single coloration-bleaching cycle displays the switching response characteristics; the coloration time is 5.20 second, and the bleaching time is 0.43 second.

(iii) & (iv) $T_{colored/420 nm}$ and $T_{bleached/420 nm}$ for first 200 and 50 cycles

(v) Bleaching and Colored state transmittance difference @ 420 nm




(i) Optical transmittance spectra of colored and bleached state@ 480 nm, which is 49 %.

(ii) One single coloration-bleaching cycle displays the switching response characteristics; the coloration time is 5.20 second and the bleaching time is 0.39 second.

(iii) & (iv) $T_{colored/480 nm}$ and $T_{bleached/480 nm}$ for first 200 and 50 cycles

(v) Bleaching and Colored state transmittance difference @ 480 nm





(i) Optical transmittance spectra of colored and bleached state@ 590 nm, which is 41.85 %.

(ii) One single coloration-bleaching cycle displays the switching response characteristics; the coloration time is 6.04 second, and the bleaching time is 0.39 second.

(iii) & (iv) $T_{colored/590 nm}$ and $T_{bleached/590 nm}$ for first 200 and 50 cycles

(v) Bleaching and Colored state transmittance difference @ 590 nm

Chapter 5

Summary and Future Scope

5.1 Summary

In this research, there were two different types of Nickel Oxide Nanostructures synthesized by a chemical and a physical method. The nanostructures observed were thin films and Nanobelts for the Physical and the Chemical Method, respectively. Both of these structures were grown on the ITO thin film coated glass substrates, and Electrochromic properties of these prepared samples were checked.

FESEM images give the surface morphology. The width and length of the Nanobelts were in the micrometer and nanometer range. The thickness of deposition for samples prepared by the chemical and the physical method were in micrometre and nanometer range respectively.

Nickel oxide presence was confirmed by the EDS. The Intensity counts (a.u.) vs. Energy (keV) graph obtained from EDS analysis, have the Nickel, Oxygen, Indium, Tin and Silicon peaks.

Nickel Oxide plane direction was identified by XRD pattern analysis. The (101), (110) and (021) planes have 2θ angles at 21.2°, 30.2 ° and 37.2° respectively.

The electrochromic properties were calculated from the Cyclic voltammetry and Chronocoulometry analysis. The diffusion coefficient values at 354 nm were ~ $8.01e-11 \text{ cm}^2$ /s and $3.32e-22 \text{ cm}^2$ /s for thin film and Nanobelts respectively. The reversibility of the Nanobelts and Thin films are observed to be 99.98% and 85.05% respectively. The optical transmittance measurements were done for 354, 420, 480, and 590 nm for physically synthesized samples G4 and H1. The bleaching times for physically synthesized thin films are in the range of 0.39-0.45 s and the coloration times are in the range of 2.32-6.04 s for sample G4. The optical transmittance difference at 354 nm is 44.65%. The optical density is 1.08% at 354 nm.

5.2Future Scope

Physical Methods of deposition can be very helpful for Electrochromic Oxides Synthesis; It can be used for Practical Electrochromic Device Production.

Optimization can be done to improve coloration time, the difference in Transmittance and Diffusion Co-efficient values, and switching response time.

References

- 1. Gage, J., Color, and culture: Practice and meaning from antiquity to abstraction. 1999: Univ of California Press.
- 2. Riley, C.A., Color codes: Modern theories of color in philosophy, painting and architecture, literature, music, and psychology. 1995: UPNE.
- Nassau, K., The physics and chemistry of color: the fifteen causes of color. The Physics and Chemistry of Color: The Fifteen Causes of Color, 2nd Edition, by Kurt Nassau, pp. 496. ISBN 0-471-39106-9. Wiley-VCH, July 2001., 2001: p. 496.
- 4. McDonald, R., Colour physics for the industry. 1997.
- 5. Bamfield, P., *Chromic phenomena: technological applications of colour chemistry*. 2010: Royal Society of Chemistry.
- 6. https://www.mge.com/business/saving/madison/PA_6.html.
- Granqvist, C.-G., et al., Progress in chromogenics: new results for electrochromic and thermochromic materials and devices. Solar Energy Materials and Solar Cells, 2009. 93(12): p. 2032-2039.
- 8. Granqvist, C.G., *Handbook of inorganic electrochromic materials*. 1995: Elsevier.
- Tessler, N., Lasers based on semiconducting organic materials. Advanced Materials, 1999. 11(5): p. 363-370.

- Monk, P.M., R.J. Mortimer, and D.R. Rosseinsky, *Electrochromism: fundamentals and applications*. 2008: John Wiley & Sons.
- 11. Wang, Y., E.L. Runnerstrom, and D.J. Milliron, *Switchable materials for smart windows*. Annual review of chemical and biomolecular engineering, 2016. 7: p. 283-304.
- Casini, M., Active dynamic windows for buildings: A review. Renewable Energy, 2018. 119: p. 923-934.
- Granqvist, C.G., Recent progress in thermochromics and electrochromics: A brief survey. Thin Solid Films, 2016. 614: p. 90-96.
- 14. Niklasson, G.A. and C.G. Granqvist, *Electrochromics for smart windows: thin films of tungsten oxide and nickel oxide, and devices based on these.* Journal of Materials Chemistry, 2007. 17(2): p. 127-156.
- 15. R.S., al., One - dimensional metal- oxide Devan, et nanostructures: recent developments in synthesis, characterization, and applications. Advanced **Functional** Materials, 2012. 22(16): p. 3326-3370.
- Patil, R.A., et al., Efficient electrochromic properties of highdensity and large-area arrays of one-dimensional NiO nanorods. Solar Energy Materials and Solar Cells, 2013. 112: p. 91-96.
- 17. Byrappa, K. and M. Yoshimura, *Handbook of hydrothermal technology*. 2012: William Andrew.

- Meng, G., et al., *Hierarchical mesoporous NiO nanoarrays with ultrahigh capacitance for aqueous hybrid supercapacitor*. Nano Energy, 2016. 30: p. 831-839.
- Elgrishi, N., et al., A practical beginner's guide to cyclic voltammetry. Journal of Chemical Education, 2017. 95(2): p. 197-206.
- 20. Zoski, C.G., Handbook of electrochemistry. 2006: Elsevier.
- Bouessay, I., A. Rougier, and J.-M. Tarascon, *Electrochemically* inactive nickel oxide as electrochromic material. Journal of the Electrochemical Society, 2004. 151(6): p. H145-H152.
- Bouessay, I., et al., *Electrochromic degradation in nickel oxide thin film: A self-discharge and dissolution phenomenon*. Electrochimica Acta, 2005. 50(18): p. 3737-3745.
- Corrigan, D.A. and S.L. Knight, Electrochemical and spectroscopic evidence on the participation of quadrivalent nickel in the nickel hydroxide redox reaction. Journal of The Electrochemical Society, 1989. 136(3): p. 613-619.
- 24. Shen, Z.-x., et al., Anderson Hamiltonian description of the experimental electronic structure and magnetic interactions of copper oxide superconductors. Physical Review B, 1987.
 36(16): p. 8414.
- Chiu, K.-F., C. Chang, and C. Lin, *The electrochemical performance of bias-sputter-deposited nanocrystalline nickel oxide thin films toward lithium*. Journal of the Electrochemical Society, 2005. **152**(6): p. A1188-A1192.