Development of Hole Transport Layer Based on NiO Nanoparticles for Perovskite Solar Cells

M.Tech Thesis

By HARIOM SHARMA



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2019

Development of Hole Transport Layer Based on NiO Nanoparticles for Perovskite Solar Cells

A THESIS

Submitted in partial fulfillment of the requirements for the award of the degree of Master of Technology

> *by* HARIOM SHARMA



DISCIPLINE OF METALLURGY ENGINEERING AND MATERIALS SCIENCE INDIAN INSTITUTE OF TECHNOLOGY INDORE JUNE 2019



INDIAN INSTITUTE OF TECHNOLOGY INDORE CANDIDATE'S DECLERATION

I hereby certify that the work which is being presented in the thesis entitled "Development of Hole Transport Layer Based on NiO Nanoparticles for Perovskite Solar Cells" in the partial fulfillment of the requirements for the award of the degree of MASTER OF TECHNOLOGY and submitted in the discipline of METALLURGY ENGINEERING AND MATERIALS SCIENCE, Indian Institute of Technology Indore, is an authentic record of my own work carried out during the time period from July 2017 to June 2019 under the supervision of Dr. Mrigendra Dubey and Dr. Ajay K. Kushwaha, Assistant professor, 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.

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ACKNOWLEDGEMENTS

I would like to express my sincere thanks of gratitude to my supervisor/s Dr. Mrigendra Dubey and Dr. Ajay K. Kushwaha for providing me this great opportunity to work under him. His timely advice, untiring guidance, and scientific approach have helped me in accomplishing my work. Without his constant inspiration and encouragement, it would not have been possible for me to complete this research work. I would like to thank the members of my PSPC committee, Dr. Vinod Kumar and Dr. Lalit Borana for their constant support and vital suggestions throughout this work. The insights provided by them helped me to understand theoretical as well as practical aspects of this work. I am grateful for FESEM and XRD facilities provided at the Sophisticated Instrument Centre (SIC), IIT Indore. I would further like to thank HOD (MEMS) for providing various facilities. I am very happy to attribute my sincere thanks to the Director of Indian Institute of Technology, Indore for providing me the necessary research facilities. I also thank my lab mates Mr. Mukurala Nagaraju, Aditya Bhardwaj and Harsh Vaid for their constant support and motivation. I would like to acknowledge my family for their affection, care and untiring support. Finally, I would like to express my sincere gratitude to the Almighty.

Hariom Sharma

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LIST OF ABBREVIATIONS

S.No.	Abbreviation	Meaning
1.	EHP	Electron Hole Pair
2.	DSSC	Dye Synthesized Solar cells
3.	HTM	Hole Transport Material
4.	HTL	Hole Transport Layer
5.	ETL	Electron Transport Layer
6.	FTO	Fluorine doped Tin Oxide
7.	PSC	Perovskite Solar Cell
8.	PCE	Power Conversion Efficiency
9.	XRD	X-ray Diffraction
10.	SEM	Scanning Electron Microscope
11.	FESEM	Field Emission Scanning Electron Microscope
12.	FES	Field Emission Source
13.	FTIR	Fourier Transform Infrared Spectroscopy
14.	CV	Cyclic Voltammetry
15.	NP's	Nanoparticles
16.	UV	Ultra Violet
17.	FF	Fill Factor
18.	CRT	Cathode Ray Tube
19.	EMF	Electromagnetic field
20.	CE	Counter Electrode
21.	OCV	Open Circuit Voltage
22.	SCC	Short Circuit Current

LIST OF SYMBOLS

Symbol	Meaning of symbol
σ	Conductivity
λ	Wavelength
L	Length
С	Concentration
Е	Absorption co-efficient
А	Area
Т	Transmittance
Т	Thickness
А	Absorbance
D	Crystalline size
К	Shape factor
β	Line width (FWHM)
θ	Bragg's angle
Ι	Intensity of transmitted light
Io	Intensity of incident light
L	Length of the light through sample
С	Sample concentration
Ipc	Photocurrent
I _{sc}	Short circuit current
V_{oc}	Open-circuit voltage
Le	Diffusion length of electron
L_{h}	Diffusion length of hole
Eg	Band gap
	Symbol $σ$ $λ$ L C E A T A T A T A T A T A D K $β$ $Π$ I_{0} L C I_{pc} I_{sc} V_{oc} L_{e} L_h

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ABSTRACT

Nickel oxide (NiO) based nanoparticles have been prepared by following conventional chemical precipitation method, by maintaining the pH ~10 with the help of NaOH of the aqueous solution of 0.1M Ni(NO₃)₂.6H₂O followed by centrifuged at 6000rpm. The obtained precipitate has been dried at 80°C for 6 hours and obtained green powder was annealed at 270°C for 2h. Powder X-ray diffraction data suggests the formation of cubic structure of nickel oxide. UV-Visible spectroscopy is used to determine optical properties of NiO including optical transmittance, optical absorbance and bandgap calculations (Band gap =3.5eV and Transmittance = 92%). Further, we prepared thin film of aqueous dispersed nickel oxide (NiO) by using spin coating method at 3000rpm for 60s and then annealed at temperature 400°C for 30 minutes to remove the moisture content, if present in sample. The effect of concentration of Ni(NO₃)₂.6H₂O solution on structural properties and optical properties was studied by using X-ray diffraction and UV-visible spectroscopy techniques, respectively. It is found that with sequential increment in concentrations of the NiO solution (0.1M, 0.2M and 0.4M) the transmittance decreases (92% to 81%) and band gap decreases (3.51eV to 3.49eV). In order to enhance the conductivity of hole transporting layer, we prepared the copper doped nickel oxide nanoparticles and thin films at the Cu percentage of 1, 2, 4 %, in turn, found to be the slight increment in absorbance but decrement in transparency (92% to 86%) of the thin film. In addition, with increment of the copper concentration (1-4%) the crystallinity of the Cu doped NiO also affects and it varies from 14 nm to 5 nm, conductivity was also found to increase. In order to fabricate the device, the all inorganic perovskite solar cell FTO/TiO₂/CsPbBr₃/NiO/Ag. The dark current profile of the device shows similar response as that of a p-n junction diode. However, device does not show proper photo-response in presence of light.

CHAPTER-1

1. INTRODUCTION

1.1 Solar Cell

Solar cell is an example of photovoltaic device. It is a semiconductor device that converts light energy into the electrical energy through the principle of photo-voltaic effect. The photovoltaic effect was first discovered by Alexander Edmund Becquerel, in 1839. Who observed a voltage when sun light strikes on the surface then the electrons absorb energy and jump from valance band to the conduction band. These electrons have ability to flow freely. In the absence of external load some potential developed across the electrode (Figure 1.1).



Figure 1.1: Schematic diagram of photovoltaic effect

1.2 Working principle of Solar cell:

Solar cell is a p-n junction diode, where the n-region is thin and highly doped so that the sunlight can easily pass through it. On the other hand, the p-region is lightly doped so that most of the depletion region lies in this side. When the solar radiation come from the sun have long, medium and shorter wavelength or in terms of the energy of shorter, medium and higher, respectively. The shorter wavelength usually absorbs by the nregion because the absorbance co-efficient is large, hence penetration depth is small. As the wavelength increases, penetration depth also



increases.



When the wavelength of light gets absorbed, it generates the electron as well as hole pairs (EHP's), for instance, the medium wavelength region generates an EHP's within the depletion region (Figure 1.2). The electrons accelerate towards the n-region and holes is accelerated towards p-region. This means now the potential developed between n and p region. In the absence of any external load this potential is called as open-circuit potential and denoted by V_{oc} . Instead of open circuit, we have a short circuit wherein current flows through the outer circuit because of the electrons and holes pair generated which can be termed as short circuit current.

In this particular case, solar radiation falls on the sample and EHP's generated the electrons accelerated towards n-side and holes towards p-side so the current flows through p-region to n-region. This current is called as photo current.

$I_{pc} = photo current$

EHP's are mostly generated within depletion region and some of them also in n and p regions. These electrons and holes act as minority carriers.

 L_e = Diffusion width/length of the electrons which are the minority carriers on p-side

 $L_h = Diffusion width/length of the holes which are the minority carriers on n-side$

Thus, the total region from which current is generated,

Total region = $L_h + W + L_e$.

When the load is connected to the circuit, the electron-hole pairs are generated in the n and p side of the semiconductor device. The higher frequency radiations are absorbed at the n-region and the low frequency radiations are absorbed by the p-region.

The flows of charge current through a semiconductor material are of two types namely

- (i) Drift current
- (ii) Diffusion current

(i) **Drift current:**

When an external electric field is applied, the flow of electric current takes place due to the motion of charge carriers. Drift current flows due to charge carriers.

(ii) Diffusion current:

It is a current in semiconductor caused by the diffusion of charge carriers. The direction of the diffusion current depends on the slope of the carrier concentration. Diffusion current can be in same or in opposite direction to that of drift current.

1.3 Different types of Solar cell:

It is based on the types of crystal used; solar cell is classified as,

1. Monocrystalline silicon cells:

The monocrystalline silicon cells are obtained from pure single crystal silicon. The monocrystalline silicon is in pure form and free of defects. The efficiency of the monocrystalline based silicon solar cell is highest as compared to its other forms.

2. Polycrystalline silicon cells:

In this type of solar cell, liquid silicon is used as raw material and it is obtained by solidification process. This type of material contains various crystalline sizes. Thus, the efficiency of the polycrystalline type solar cell is less than the monocrystalline cell.

3. Amorphous silicon cells:

It is obtained by depositing silicon film on thin substrate in layered form like glass plate and layer thickness is usually less than the 1 μ m. The efficiency of the amorphous silicon cell is much lower than the other two type of solar cell. Hence, they are commonly used in low power equipment like scientific calculators.

Materials	Efficiency (%)
Monocrystalline	18-22
Polycrystalline	15-17
Amorphous	6-10

Comparison of type of solar cell efficiencies:

Generation of solar cells:

1. First generation solar cells:

First generation types of solar cells include single crystal solar cells and multi crystal solar cells. These are the oldest and most commonly used technology due to higher efficiencies. In general, first generation solar cells are two types of solar cells which differ by their crystalline level. First generation solar cells produced on wafers. If whole wafer is only one crystal, then it is called as single crystal solar cells and if wafer consist of crystal grains then it is called multi crystal solar cells.

2. Second generation solar cells:

This generation type of solar cells is low cost and low efficiency solar cells which has been development during the 1990s and early 2000s. These are the most common solar cells, designs that use minimum materials and cheap manufacturing processes. The most popular materials used for this type are copper indium gallium selenide, cadmium telluride (CdTe) and amorphous silicon.

3. 3rd generation solar cells:

Third generation type of solar cells are mainly four types: (a) Nanocrystal based solar cells (b) Polymer based solar cells (c) Dye sensitized solar cells and (d) Concentrated solar cells. Among these third-generation solar cell types, the most advanced is dye sensitized and concentrated solar cell in terms of efficiency. Concentrated solar cell is also promising technology and it works on the principle is to concentrate large amount of solar radiations on to a solar cell. In this system, concentration levels start from 10 suns to thousands of suns. Thus, the total cost can be lower than the conventional system. Concentrated solar cells are considered as promising technology for near future.

1.4 Solar cell parameters:

Open Circuit Voltage:

Open circuit voltage (OCV) is the maximum voltage which can be generated by a solar cell when load is not connected between two electrodes. It is denoted by V_{oc} .

Short Circuit Current:

It is the maximum current that can be delivered by a solar cell is called as short circuit current (SCC). In a real solar cell, when load is connected then the short circuit current will be less than photo current because of finite shunt resistance (R_{sh}) and non-zero series resistance (R_{se}).

Fill Factor:

It is the figure of merit of a solar cell. It is the ratio of maximum power obtained to the maximum ideal power of the solar cell. i.e.

$$FF = \frac{Vmp.Imp}{Voc.Isc}$$

Efficiency of Solar Cell:

It is defined as the ratio of maximum electrical power output of the cell to the input solar energy radiation on the cell. The standard solar radiation on earth's surface is considered to be 1000 watt/square meter. Considering 'A' be the total area of the solar cell, the mathematical expression for the efficiency is given as:

$$\dot{\eta} = \frac{Vmp.Imp}{1000 A}$$

CHAPTER-2

2. LITERATURE SURVEY

2.1 Introduction of Perovskite solar cell:

Perovskite solar cells have mainly three types of layers; electron transport layer (ETL), perovskite layer and Hole transport layer (HTLs) (Figure 2.1). The active layer or active material is mainly absorb photons and then convert into the free charge carriers. In order to achieve good performance of the device the Electron Transport Layer (ETL) and Hole Transport Layer (HTL) are used. ETL and HTL are the charge transport layers, which transport the electrons and holes, respectively. Electrons will flow from higher energy level to lower energy level and holes will flow from lower energy level to higher energy level.



Figure 2.1: Schematic representation of perovskite solar cell

2.1.1 Introduction of Electron Transport Layer (ETL):

The electron transport layer helps in extraction and transportation of photo generated electrons, it also acts as a hole blocking layer to reduce charge recombination. The energy level of conduction band of electron transport material should be less than the perovskite material so as to provide the low energy path for the passage of electrons. The electron mobility of ETL is a key factor which determines photovoltaic performance of device (higher electron mobility is suitable so as to increase the electron extraction rate). The energy level of ETL must match with the perovskite layer to improve the fill factor values which significantly improve the device performance. Various types of ETLs are being used, such as ZnO, SnO₂ and TiO₂.

2.1.2 Introduction of Hole Transporting layer:

The Hole transport layer is helpful in extracting holes from the perovskite layer and rapidly transports them towards metal electrode to avoid charge recombination. The HTL must have high charge mobility, high thermal stability and moisture sensitivity. Spiro-OMeTAD, is commonly used HTL. The complex synthesis process and multi- step purification, poor charge mobility prevents in formation of a stable HTL. Other HTL materials such as CuI, CuSCN, PEDOT: PSS, PTAA, NiO, etc. are also used. Good device efficiency was reported in case of using NiO as HTL, Thus, our objective in the project was to utilize a low cost and facile synthesis procedure for making HTL.

2.2 Importance of Hole Transport layer [1]:

The HTL play a significant role in perovskite solar cells are:

- It prevents the direct connection between the active perovskite layer and the metal contact, which reduces charge recombination.
- It prevents degradation at the perovskite-metal boundary.
- It blocks electrons and improve the hole transfer efficiency.

- It extracts holes from perovskite and transports them towards the metal contact.
- It protects perovskite from moisture and oxygen.

Remarkable properties of Hole Transport Layer [2]:

- It should have suitable energy levels, facilitating the driving force required for the purpose of charge transfer.
- It should act as a restriction between perovskite layer and anode in order to block electrons without entering the anode.
- It should have a high hole transfer efficiency to avoid the charge recombination.
- It should favor V_{oc} by determining the fermi energy level of the perovskite.
- It should prevent the diffusion process to occur between the electrode and perovskite layer.
- It should be less expensive.
- It should have high thermal stability.
- It must be environmentally friendly.

2.3 Classification of hole transport materials for perovskite solar cells:

Hole transport materials are mainly classified in two major categories namely; organic hole transporting materials and inorganic hole transporting materials. Further, the organic materials are subdivided into two categories; long polymer based and small molecule based hole transporting materials. The inorganic based materials are divided into Nickel-based and copper based hole transport materials, p-type semiconductor-based materials and transition metal-based materials. Figure 2.2 shows the classification of solar cells discussed below in detail.



Figure 2.2: Classification of Hole Transport Materials

2.3.1 Inorganic based hole transporting materials:

Metals such as copper, nickel etc. and their derivatives can play the role as a hole transporting layer in perovskite solar cells.

i. Nickel based hole transporting materials [3-5]:

Nickel oxide is extensively used in organic solar cells, DSSCs and other optoelectronics devices because of high charge career mobility, good optical transmittance and excellent thermal stability.

ii. Copper based hole transporting materials:

Copper Iodide (CuI), Copper sulphide (CuS), Cuprous oxide (Cu₂O), and Copper oxide (CuO) are used as hole transporting materials in inorganic PSCs.

iii. Transition metal-based hole transporting materials:

Transition metal oxide-based materials such as MoO_3 , V_2O_5 , WO_3 etc. was successfully demonstrated as a dopant and as a material for the hole transporting layer due to enhanced stability in PSCs

and also due to high transparency, smooth surface, good conductivity and easy solution-based synthesis process.

Table	1:	Photovoltaic	Parameter	of	Representative	PSCs	Based	on
inorga	nic	e HTM.						

S.	HTM	Perovskite	Dopants	PCE	Reference
				(%)	
1.	CuI	MAPbI ₃	-	6.0	(6)
2.	NiO	MAPbI _{3-x} Cl _x	-	7.3	(7)
3.	NiO	MAPbI ₃	-	16.4	(8)
4.	$Li_{0.05}Mg_0$	MAPbI ₃	Li ₂ O	18.3	(9)
	.15Ni0.8O				
5.	NiO _x	MAPbI ₃	F ₆ -TCNNQ	19.8	(10)
6.	NiO _x	CsFA _{0.85} MA _{0.15} Pb	F ₆ -TCNNQ	20.9	(11)
		$I_{2.55}Br_{0.45}$			
7.	CuSCN	MAPbI ₃	NH ₃ (aq)	17.5	(12)
8.	CuSCN	CsFA0.83MA0.17Pb	-	20.4	(14)
		$I_{2.53}Br_{0.45}$			~ /
9.	CuO	MAPbI ₃	-	12.2	(15)
10.	Cu ₂ O	MAPbI ₃	-	13.4	(16)
11.	CuO _x	MAPbI _{3-x} Cl _x	-	19.0	(17)
12.	MoO ₂	MAPbI ₃	-	15.7	(18)

2.3.2 Organic based hole transporting materials [19]:

Generally organic materials are divided into two types of hole transporting materials; (i) long polymer based and (ii) small molecular based. In most cases, the long polymers based and small molecules based are obtained in such a way that they possess suitable photovoltaic properties such as charge mobility, luminescent property, or photo absorption property for photo voltaic device applications. The most commonly used organic long polymer based hole transporting materials is Spiro-OMeTAD (2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9-spirobifluorene) in PSCs because its favorable glass transition temperature, solubility, ionization potential, absorption spectrum and solid state morphology. Pyrene, Thiophene and Porphyrins are the organic small molecules-based hole

transporting materials. This small molecules-based material is easily synthesized with high purity and high yield.

S.No.	Organic hole transport	Inorganic hole transport	
	materials	materials	
1.	Organic materials-based hole	Inorganic materials-based hole	
	transport layer have poor	transport layer has good stability.	
	stability.		
2.	It has poor transparency.	It has good transparency.	
3.	It has not electron blocking	It has not electron blocking	
	capability.	capability.	
4.	It has lower energy	It has higher energy consumption	
	consumption in perovskite	in inorganic hole transport layer	
	solar cells.	based solar cells.	
5.	Organic materials based solar	Inorganic materials based solar	
	cells have higher efficiency.	cells have lower efficiency.	

2.4 Comparison between organic and inorganic HTMs:

2.5 Nickel Oxide (NiO) as Hole Transporting Materials [20]:

The drawbacks of the Organic semiconductor hole transport layers are poor stability and severe degradation. Most of the higher efficiency perovskite solar cells are based on the organic hole transporting materials such as molecular spiro-MeOTAD or polymeric PTAA. Moreover, relatively low-temperature degradation of organic HTMs is responsible for poor stability of perovskite solar cells. For improving the stability of the perovskite solar cells, various inorganic hole transporting materials developed and applied in perovskite solar cells. Recently, the device based on Cu:NiO HTMs have higher PCEs which is comparable to PCEs of devices based on organic HTMs. Most importantly, the stability of perovskite solar cells is much improved by the inorganic HTMs. This indicates that inorganic HTMs are promising alternative to organic HTMs. To overcome this limitation, these organic materials are replaced with inorganic materials because of their higher mobility and good stability. For HTMs, MoO₃, CuO, CuO_x, CuSCN, V₂O₅ and NiO_x nanoparticles which are synthesized at lower temperatures have commonly been used. NiO_x offers promising characteristics such as intrinsic semiconducting nature, good hole extraction properties, good optical transparency, low temperature deposition, and large bandgap. NiO_x is used for inorganic hole transport layer in PSCs, especially in inverted structure.

2.6 Objective:

- Synthesis of NiO NPs using chemical precipitation method and fabrication of thin film using spin coating method.
- Synthesis of Cu-doped NPs and fabrication of thin films.
- Effect of Cu-doping in NiO nanoparticles.
- Study of electrical and optical properties of NiO and Cu-doped NiO nanoparticles.
- Fabrication of perovskite solar cell device.

CHAPTER-3

3. EXPERIMENTAL DETAILS

3.1 Materials:

Nickel nitrate (II) hexahydrate, Cupric nitrate (II) hexahydrate, Sodium hydroxide (NaOH) was purchased from SRL and Sigma aldrich used as recieved.

3.1.1 Copper:

Copper is the d-block element. It is a ductile metal with high thermal and electrical conductivity. The physical properties is shown in table below:

S.No.	Properties	Metric
1.	Density	8.94 g/cm ³
2.	Molar mass	63.55 g/mol

The thermal properties of the copper as shown in table below:

S.No.	Properties	Metric
1.	Melting point	1083°C
2.	Boiling point	2567°C

3.1.2 Cupric nitrate (Cu(NO₃)₂):

Cupric nitrate is an inoroganic compound which is forms in a blue crystalline.

Properties of cupric nitrate:

S.No.	Properties	Metric
1.	Appearance	Blue
2.	Density	3.05 g/cm ³
3.	Melting point	256°C
4.	Molar mass	187.56 g/mol

3.2 Synthesis of pristine NiO nanoparticles:

Step-1:

To synthesize Nickel Oxide nanoparticles, 0.1M Ni(NO₃)₂.6H₂O was dissolved in 50 mL of DI water and obtained dark green solution.

Step-2

After obtaining the dark green solution, we continuously mixed sodium hydroxide drop by drop into it until the pH of the solution attained to 10. After attaining the required pH, the solution was stirred for additional 10 minutes.

Step-3

The green colloidal precipitate was obtained which was the centrifuged at 6000 rpm for 15 minutes. The sample was then washed by DI water for two times and the obtained precipitates ware dried at 80°C for 6 hours. The obtained green precipitate was turned into its powder form by mortar and pestle.

 $Ni(NO_3)_2 + 2NaOH \longrightarrow Ni(OH)_2 + 2NaNO_3$

Step-4

Then the green powder was annealed at 270°C for 2 h to get dark black powder as shown in figure 3.1.

Annealed at 270°C for 2h
Ni(OH)₂
$$\longrightarrow$$
 NiO + H₂O



Figure 3.1: Schematic representation of formation of nickel hydroxide and nickel oxide

3.3 Preparation of NiO based thin films:

FTO substrates or glass substrate were cleaned by detergent powder and then sonicated in water, then acetone and isopropyl alcohol (IPA) sequentially for 15 min. After being dried, the hole transport layer was obtained by using spin coated method corresponding nickel oxide (NiO) aqueous solutions (20 mg/ml) at 3000 rpm for 60 sec and then prepared thin film annealed at 450°C for 30 minutes to remove the residual water. Thin film was obtained as shown in figure 3.2 below.



Figure 3.2: Photograph of nickel oxide thin film on FTO substrate

3.4 Synthesis of copper doped NiO nanoparticles:

Step-1

 $Cu(NO_3)_2.6H_2O$ was mixed with $Ni(NO_3)_2.6H_2O$ solution at different molar ratios (1%, 2% and 4%) in 50 mL of DI water and obtained green solution.

Step-2

After obtaining the dark green solution, we continuously mixed NaOH drop by drop into it until the pH of the solution does not gets 10. After the required pH was achieved, the resulting solution was stirred for additional 10 minutes.

Step-3

The obtained green colloidal precipitate was centrifuged at 6000rpm for 15 minutes. The sample was then washed by DI water for two times and the resulting precipitate was dried at 80°C for 6 hours. The obtained green precipitate was converted into its fine powder by using the mortar and pestle.

Step-4

The obtained green powder was annealed at 270°C for 2 hours and obtained black powder.

3.5 Preparation of copper doped NiO based thin films:

FTO substrates or glass substrate were cleaned by detergent powder, acetone and isopropyl alcohol (IPA) and then sonicated in water sequentially for 10 min. After being dried, the hole transport layer was obtained by spin coating method corresponding copper doped NiO aqueous solutions (20 mg ml⁻¹) at 3000 rpm for 60 sec and then annealed at 450°C for 30 min to remove the residual water.
CHAPTER-4

4. CHARACTERIZATION TECHNIQUES

4.1 X-ray Diffraction Analysis:

X-ray diffraction (XRD) is a technique which is used for determining the crystalline structure of a material and it provides information on unit cell dimensions.

XRD analysis mainly used for the purpose of

- 1. Finding the crystalline structure of materials.
- 2. Determining the positioning of a single crystal or grain.
- 3. Measuring the crystalline size and shape of the nanoparticles.
- 4. Finding the average distance between the layers.

Fundamental principle of XRD:



Figure 4.1: Working principle of XRD spectrometer

It is widely used technique for the studying and analyzing crystal structures, also determines the atomic spacing between crystals. A sample and monochromatic X-rays create a constructive interference. X-rays which produced by a cathode ray tube (CRT), are categorized to generate a monochromatic radiation; they collimate to confine in an indented direction towards the sample.

The interaction between the incident rays and material atoms create a constructive interference when incident rays satisfies Bragg's law condition. A detector as shown in the figure 4.1 is used to record the signal and process it. The produced X-ray signal as the output is monitored on the computer screen.

Bragg's law:



When constructive interference between the sample and monochromatic X-rays occurs then,

 $AB + BC = m\lambda;$

Where m = 0, 1, 2, 3...

"m" is denoted as the order of diffraction

AB = BC

 $m\lambda = 2 AB$

 $\sin\theta = AB/d$

Hence, $m\lambda = 2dsin\theta$

This is the final equation of Bragg's law.

Unit cell:

Parameters of the unit cell are listed below:

The unit cell dimensions are a, b, c along the direction of x, y, z respectively.

The angles are α in between B and C, β in between C and A and γ in between A and B respectively.

Shape of the unit cell:

Based on the relationship of unit cell dimensions a, b, c and angles α , β , γ ; all the possible shapes of the unit cell are defined, which are listed in the below:

Crystal System	Crystal Parameters
Cubic system	$a = b = c; \ \alpha = \beta = \gamma = 90^{\circ}$
Tetragonal system	$a = b \neq c; \ \alpha = \beta = \gamma = 90^{\circ}$
Orthorhombic system	$a \neq b \neq c; \ \alpha = \beta = \gamma = 90^{\circ}$
Rhombohedral system	$a = b = c; \ \alpha = \beta = \gamma \neq 90^{\circ}$
Hexagonal system	$a = b \neq c; \ \alpha = \beta = 90^{\circ}; \ \gamma = 120^{\circ}$
Monoclinic system	$a \neq b \neq c; \alpha = \gamma = 90^{\circ} \neq 120^{\circ}$
Triclinic system	$a \neq b \neq c; \ \alpha \neq \beta \neq \gamma \neq 90^{\circ}$

Scherer equation:

From this equation we can find out the crystalline size or particle size,

$$D = \frac{K\lambda}{\beta cos\theta}$$

Where, D = crystalline size

K = shape factor

 $\lambda = X$ -ray wavelength

 β = line width (FWHM) in radians

 $\theta = Bragg's angle$

Applications of XRD:

- In determining lattice distortion, phase composition.
- Crystal shape and its size.

4.2 UV-visible spectroscopy:

The optical properties of a material can be determined by using UV-visible spectroscopy. These optical properties include transparency, optical conductivity, bandgap calculation etc. It measures the transmittance or absorption of light across the visible and UV light wavelengths through a thin film or a liquid solution.

Working Principle:

Samples (solution) are dispensed into cuvette and placed in between a UV-Visible light and a detector as shown in figure 4.2. According to Beer-Lambert's law, with a known absorption coefficient and constant path length of light radiation, the concentration of a sample can be determined from the quantity of light absorbed at particular wavelength.



Figure 4.2: Working principle of UV-visible spectrometer

Absorbance and beer-lambert law:

Absorbance:

Absorbance is defined as the "measure of quantity of light by the sample". It is a dimensionless quantity and is denoted by a.u. (Arbitrary Unit).

 $A = -\log T = \log (1/T)$

Where, T is the transmittance.

Transmittance:

It is the ratio of the intensity of the transmitted light (I) to the intensity of the incident light (I_0). It is denoted by "T".

 $T=I \; / \; I_o$

Transmittance is always less than 1 because the incident light intensity always greater than transmitted light intensity. If all light absorbed or no light passes through the sample, then we can say that the absorbance is infinite and percentage transmittance will be zero. If all light transmitted through the sample, then absorbance will be zero. It means no photons are absorbed by the sample.

Beer-lambert law:

The law states that the intensity of transmitted light exponentially decreases as the absorbance of substances increases or the light absorption is proportional to the thickness (t) of media through which transmitted light multiplied by the concentration of sample.

The Beer-lambert law is mainly used to the calculate absorbance:

$$\frac{dI}{I} = -\sigma c dl$$

$$\int_{I_o}^{I} \frac{dI}{I} = \int_{0}^{1} \sigma c dl$$

$$\ln \frac{I}{I_o} = -\sigma c l$$

$$\log \frac{I}{I_o} = -2.303\sigma c l = \log T$$

$$\boxed{A = \varepsilon c l}$$

Where,

A = absorbance (A =
$$\log \frac{I}{I_0} = \log T$$
)

- ε = Molar absorptivity (Lmol⁻¹cm⁻¹) = -2.303 σ
- c = Concentration of sample (molL⁻¹)
- 1 =light path length through the sample

Thus, absorbance is directly proportion to the all factors ε , *c* and 1.

4.3 Field Emission Scanning Electron Microscope:

Field Emission Scanning Electron Microscope (FESEM) is mainly used to determine the image of the surface of thin films at high magnifications. It can not only provide images of the surface but also by rotating the sample, one can obtain information about the thickness of various layers in the structure (cross-sectional SEM). The morphology, lengths, size and orientation of the NiO nanostructures used in the present study were investigated by FESEM. Characterization is performed at 5-15 kV acceleration voltage with a working distance of 1-12 mm. It is an electron microscope which produces images of a sample by scanning the surface. When the electrons interact with sample, then producing various signals which provides various information about the surface structure and also confers the information about elemental composition of sample. The FESEM image is shown in figure 4.3.



Figure 4.3: Field Emission Scanning Electron Microscope [21]

Working Principle:

Figure 4.4 shows a schematic representation of FESEM working principle. Firstly, an electron gun emits the electrons. These electrons pass through the condenser lens and then pass through objective lens and an electron beam condense into a few nanometers (nm) diameter. Further, when the electrons beam bombard on the sample surface, in turn, electron signals are generated as shown in figure 4.5 and detectors collect all these signals: X-rays, secondary electrons and backscattered electrons and convert them into a signal and this signal are sent to a screen and then produce the image.



Figure 4.4: Working principle of Field Emission Scanning Electron Microscope [22]





Advantages of FESEM:

- Bulk materials elemental analysis
- at low kV, Ultra-high resolution
- Fast elemental mapping
- Finding of small variations of element content
- Oil-free vacuum
- Compositional, Graphical and other information

Applications of FESEM:

- To determine the surface morphology
- Film thicknesses of the semiconductor device
- Determine the uniformity of structure and thickness of coating
- Elemental composition is also used to determine by FESEM.
- Fracture and failure analysis
- Defect analysis

4.4 Fourier Transform Infrared Spectroscopy (FTIR):

Fourier Transform Infrared Spectroscopy (FTIR) is an analytic technique which is used to identify the functional group containing organic materials, inorganic materials and polymeric materials. It is also used to obtain the IR spectrum of emission or absorption of a liquid, gas or solid. The mainly use IR (Infrared) light for FTIR analysis to scan samples and for observing chemical properties of the materials. Over a wide spectral range, FTIR collects high resolution data. FTIR image is as shown in figure 4.6.



Figure 4.6: Fourier Transform Infrared Spectroscopy

Working principle:

The FTIR instrument sends IR radiation in the range of 10,000 cm⁻¹ to 100 cm⁻¹, some of the IR radiation passed through the sample and some absorbed by the sample. The absorbed radiation is converted into vibrational or rotational energy by the sample molecules. The resulting signal presents as a spectrum, typically from 4,000 cm⁻¹ to 400 cm⁻¹, representing a molecular finger print of the sample. Each molecule or chemical structure will produce a unique spectral fingerprint. FTIR is a good technique for chemical identification. The functional group represents corresponding to wavenumber as shown in table 2.

 Table 2: FTIR functional groups represent corresponding to

 wavenumber range [23]

S.No.	Wavenumber range (cm ⁻¹)	Functional group
1.	3550-3450	Hydroxide group
2.	3400-3200	Hydroxide group
3.	2926-2854	Methyl group
4.	1745-1725	Carbonyl compound
5.	1150-911	C-O-C group
6.	858-773	C-H
7.	700-600	Ni-O compound

5.5 Current – Voltage Characteristics:

Current – Voltage characterization is a widely used and important method to measure the efficiency of perovskite solar cells. Photocurrent measurement setup is shown in figure 4.7. Electrical characteristics of the photo-detectors are measured by a KEITHLEY 2604B source meter. Source meter instrument are electronic test type equipment which measures Current and Voltage data. It collects information with high accuracy, Ideal for I-V characterization, semiconductor testing and testing devices with both negative and positive current source values.



Figure 4.7: Photograph of KEITHLEY instrument

The solar cell behaves as a diode circuit in dark and has similar I-V characteristic like a p-n junction diode as shown in figure 4.8. When illuminated, the charge careers gets separated and results in increased current in fordard bias.



Figure 4.8: I-V characteristics of perovskite solar cell

Where,

V_{oc} is the open circuit voltge

 I_{sc} is the short circuit current

 V_{mp} is the voltge at maximum power point

Imp is the current at maximum power point

The parameters I_{sc} and V_{oc} can be directly determined by from I-V curve and V_m , I_m , P_m , Fill Factor and efficiency are easily calculated.

CHAPTER-5

5. RESULT AND DISCUSSION

5.1 X-ray diffraction (XRD) pattern of NiO nanoparticles:

NiO powder was characterized by a X-ray diffractometer at a scanning rate of 4° per minute. Figure 5.1 (a) shows XRD patterns of the nanoparticles at different annealing temperatures (200°C, 270°C, 300°C and 400°C). After annealing at 200°C for 2h to 270°C for 2h, these peaks show low intensity and some new peaks were observed due to decomposition of nickel hydroxide (Ni(OH)₂) to nickel oxide (NiO). These peaks are 37.31°, 43.34°, 62.83°, 75.33° and 79.27° could be assigned to the plane (111), (200), (220), (311) and (222) of nickel oxide (NiO), respectively. If annealing temperature increases up to 270°C, all the peaks of Ni(OH)₂ were disappeared and the peak width was reduced with increasing annealing temperature may be due to the enhancement in the crystallinity, if peak width is reduced (Scherrer equation). The temperature doesn't affect the composition of the nickel oxide (NiO) powder. The optimization of experiment suggests that the better crystallinity of NiO can be obtain at 270°C heating for 2h. If annealing temperature increases upto 400°C, the peak width is reduced, it means that crystalline size is incresed.



Figure 5.1 (a) X-ray diffraction pattern of NiO nanoparticles at different annealing temperature.

Now we can calculate the crystallite size by using data from the XRD pattern shown in figure 5.1 (b). From the Scherrer equation, the crystallite size of the NiO nanoparticles calculated to be 14 nm.



(b) XRD pattern of pristine NiO nanoparticles annealed at 270°C

5.2 UV-visible spectroscopy of NiO nanoparticles:

UV-visible spectroscopy is used to determine the optical behavior of NiO nanoparticles. As shown in figure 5.2 (a), the low absorption was obtained in visible region of spectra and high value of transmittance in the visible region. The band gap of NiO nanoparticles was calculated and found to be 3.504 eV using the Tauc-plot as shown in figure 5.2 (b).



Figure 5.2 UV-visible spectra of NiO NP's (a) Absorption spectra and (b) Tauc-plot

The optical transmittance spectra of the NiO thin film is shown in figure 5.2 (c). The optical transmittance was observed approximately 92% in the visible region.



Figure 5.2 (c) Optical transmittance spectra of NiO on glass substrate

5.3 XRD analysis of NiO Nanoparticles at different Concentrations:

NiO nanoparticles of various molarities were prepared using chemical method. The structure of NiO nanoparticles was analyzed by X-ray diffraction for different molarities. Three Bragg peaks indicated formation of the polycrystalline nature having a cubic structure as shown in figure 5.3. The crystallite size of the nickel oxide nanoparticle was not affected with increased concentration of Ni(NO₃)₂.6H₂O in solution.



Figure 5.3 XRD pattern of nickel oxide at different concentration

5.4 UV-visible analysis of NiO nanoparticles at different concentration:

The optical absorption spectrums showed low absorbance in visible region as shown in figure 5.4 (a). The optical transmittance spectra (200 nm to 800 nm) of NiO nanoparticles as shown in figure 5.4 (c). A small decrease in transmittance was observed in the visible region with increase in molar concentration (0.1M, 0.2M and 0.4M). We also calculated band gap (E_g) using tauc-plot as shown in figure 5.4 (b). We observed that if the concentration of Ni(NO₃)₂.6H₂O increases then band gap decreases (3.51 to 3.49eV) as shown in table 3 below.



Figure 5.4 UV- visible analysis of Nickel oxide for different molarity (a) absorption spectra



(b) Tauc-plot



(c) Transmittance spectra

 Table 3: The effect of concentration on the band gap of NiO nanoparticles

S.No.	Concentration (NiO)	Band gap (eV)
1.	0.1M	3.51
2.	0.2M	3.5
3.	0.4M	3.49

5.5 X-ray diffraction pattern of NiO thin film:

The structural analysis of the NiO thin films was obtained by X-ray diffraction data analysis. The XRD pattern of NiO thin films deposited over glass substrate using spin coating method. Three Bragg peaks were observed as shown in figure 5.5, which can be assign at plane (111), (200) and (220) of NiO. The highest intensity peak was observed at plane (200) and pattern also indicates the cubic structure of the polycrystalline material.



Figure 5.5: X-ray diffraction (XRD) analysis of nickel oxide thin film on glass substrate

5.6 UV-visible spectroscopy of NiO thin films:

The optical absorption spectra and Tauc-plot of the NiO thin films are shown in figure 5.6 (a) and figure 5.6 (b), respectively. We observed low absorbance in the visible region and band gap of thin film is 3.38eV. By transmittance curve, we observe higher transmittance of around 92 % in visible region as shown in figure 5.6 (c).



Figure 5.6: UV-visible spectra of NiO thin film on glass substrate

(a) Absorption spectra



Figure 5.6: UV-visible spectra of NiO thin film on glass substrate



Figure 5.6: UV-visible spectra of NiO thin film on glass substrate

(c) Transmittance plot

5.7 FESEM image of NiO Thin film:

The surface analysis of NiO thin films were observed under field-emission scanning electron microscope (FESEM). The NiO thin film showed nano sized (small) crystalline grains and also observed the large particles of the NiO nanoparticles. It may be observed due to the fuse of the nanoparticles as shown in figure 5.7.



Figure 5.7 FESEM images of NiO thin film coated on glass substrate

5.8 XRD analysis of copper doped nickel oxide nanoparticles:

Figure 5.8 shows the three main peaks observed at angle 37.31°, 43.34°, and 62.83°, which could be assigned at the planes (111), (200) and (220) of nickel oxide (NiO), respectively. The highest intensity peak was observed at plane (200). If cupric nitrate was mixed with nickel nitrate solution then the diffraction peaks related to copper were not observed. But, it can observe that if the doping of the copper content increased, then peaks corresponding to the (111) and (200) planes are slightly shifted towards the lower angle. Further, we can calculate average crystalline size using Debye-Scherrer equation. The calculated crystalline size decreased when the content of copper doping increased shown in table 4. The crystallite size of the nanoparticles for different copper ratio (NiO, 1% Cu:NiO, 2% Cu:NiO and 4% Cu:NiO) was obtained the 14nm, 11nm, 9nm and 5nm, respectively.





 Table 4: Intensity peak and Particle size for different copper doping in NiO

	Maximum intensity peak at 2O	Particle size (D)
	(in degree)	
NiO	43. 47529	14 nm
1%Cu:NiO	43.34062	11 nm
2%Cu:NiO	43.27163	9 nm
4%Cu:NiO	43. 25348	5 nm

5.9 FTIR spectra of NiO nanoparticles:

Figure 5.9 represents the FTIR reflectance spectra for NiO and Cu:NiO nanoparticles over the entire range from 400 to 4000 cm⁻¹. Due to the vibrations of functional group, some bands around 3586 cm⁻¹, 1628 cm⁻¹, 1353 cm⁻¹, 1144cm⁻¹, 838cm⁻¹,751 cm⁻¹ are clearly observed. The peak around 3586 cm⁻¹ and 1628 cm⁻¹ on the FTIR spectrum related to O-H bond and carbonate bond, respectively. The absorption at 1353 cm⁻¹ and 1224cm⁻¹ indicates the existence of isopropyl group and the absorption bond at 651 cm⁻¹ is assigned to Ni-O stretching bond.



Figure 5.9: FTIR spectra of NiO and copper NiO nanoparticles

Table 5: FTIR results depicting functional groups corresponding to wavenumber (cm⁻¹)

S.No.	Wavenumber (cm ⁻¹)	Functional group
1.	3586	Hydroxide group
2.	1628	Carbonyl group
3.	1353	Isopropyl group
4.	1144	Isopropyl group
6.	651	Nickel Oxide group

5.10 UV-vis spectroscopy of NiO and copper doped NiO nanoparticles:

UV-visible spectroscopy was performed to determine the optical behavior of NiO nanoparticles and copper doped NiO nanoparticles. It was observed that the incorporation of Cu atoms slightly narrowed the band gap, when the doping of the copper concentration increased then the absorbance will be increased, and transparency will be decreased as shown in figure 5.10 (a) and figure 5.10 (c), respectively. We also noticed that when the doping of the copper concentration increased then band gap decreased (3.4eV to 3.3eV) using Tauc-plot (figure 5.10 (b)) as shown in table 6.



Figure 5.10: UV-visible analysis of NiO and Copper doped NiO NP's

(a) Absorption spectra



Figure 5.10: UV-visible analysis of NiO and Copper doped NiO NP's

(b) Tauc plot



Figure 5.10: (c) UV visible transmittance spectra of NiO and Copper NiO on glass substrates

 Table 6: The doping of copper concentration effect on transmittance

 and band gap

S.No.		Transmittance (%)	Bandgap (eV)
1.	pristine NiO	93	3.4
2.	1%Cu: NiO	91	3.38
3.	2%Cu: NiO	82	3.36
4.	4%Cu: NiO	80	3.3

Fabrication of Hole Transport Layer (HTL):

FTO or glass substrates cleaned with detergent water followed by ultrasonicated in deionized (DI) water for 15 minutes, acetone and isopropyl alcohol sequentially for 15 minutes. After dried FTO or glass, the HTL were obtained by spin-coating method of NiO or Copper doped nickel oxide (Cu:NiO) aqueous solutions (20 mg mL⁻¹) at 3000 rpm for 60 s and then annealed at 400 °C for 30 minutes for removing the moisture content, if present. All the procedures were carried out at ambient atmosphere.

5.11 X-ray Diffraction of NiO and copper doped NiO thin films:

We prepare a good quality nickel oxide (NiO) thin films on the glass substrates by using spin coating method. We observe major diffraction peaks at 35.31°, 42.27°, and 61.75° for NiO and copper doped nickel oxide (Cu: NiO) corresponding to the plane of (111), (200) and (220) as shown in Figure 5.11.





The optical behavior (transmittance and absorption) of NiO and Cu: NiO films were measured by UV-visible spectrometer. We observed that if doping of copper content increased then the absorbance increased (figure 5.12 (a)), and transparency decreased. The optical transmittance spectrum in figure 5.12 (c) shows the high transmittance (92% to 86%) in the visible region and the band gap varies from 3.48eV to 3.37eV using tauc-plot (figure 5.12 (b)) as shown in table 7.



Figure 5.12: UV-visible analysis of NiO and Cu:NiO nanoparticles on FTO substrate (a) Absorption spectra



Figure 5.12: UV-Visible analysis o of NiO and Cu:NiO nanoparticles on FTO substrate (b) Tauc plot



Figure 5.12: UV-Visible analysis o of NiO and Cu:NiO nanoparticles on FTO substrate (c) Transmittance spectra

S.No.		Transparency (in %)	Band gap (eV)
1.	NiO	92	3.48
2.	1% Cu:NiO	90	3.4
3.	2% Cu:NiO	87	3.43
4.	4% Cu:NiO	86	3.37

 Table 7: Transparency and band gap effect with copper doping in

 NiO thin films

5.13 FESEM analysis of thin films on FTO substrates:

FESEM images of the thin films on substrates for pristine NiO and for different molar ratio (1%Cu:NiO, 2%Cu:NiO and 4%Cu:NiO) of copper are shown in below figure 5.13, which revealed the surface morphology of NiO and Cu: NiO thin films. It suggests the randomly arranged almost circular grains. We also observed that with the increment of doping of the copper concentration particle size decreased.



Figure 5.13 FESEM images of NiO and Copper doped NiO thin films on FTO substrates (a) NiO (b) 1% Cu:NiO



Figure 5.13 FESEM images of NiO and Copper doped NiO thin films on FTO substrates (c) 2%Cu:NiO and (d) 4%Cu:NiO

5.14: Current - voltage characteristics of NiO and copper doped NiO thin films:

Figure 5.14 depicts the I-V characteristics of NiO film. The resistance of films was calculated from slope of graph. From the formula $\rho = \frac{RA}{L}$, we can calculate the value of resistivity, where R is the resistance, A is the contact area and L is the length of sample. As we know that resistivity is inversely proportional to conductivity, we can also obtain value of conductivity. The obtained values are shown in table 8.



Figure 5.14: Current – Voltage characteristic of NiO and Copper doped NiO thin films on FTO substrates

Table 8: Representation of electrical parameters of NiO and copperdoped NiO thin films on FTO substrates:

	R (kΩ)	ρ (Ω-cm)	σ (S/cm)
NiO	20.09	2 x 10 ⁴	5 x 10 ⁻⁵
1% Cu:NiO	18.61	1.86 x 10 ⁴	5.37 x 10 ⁻⁵
2% Cu:NiO	17.13	1.71 x 10 ⁴	5.83 x 10 ⁻⁵
4% Cu:NiO	15.6	$1.56 \ge 10^4$	6.41 x 10 ⁻⁵

5.15: Current-Voltage Characteristics of perovskite solar cell:

In order to explore the utility of NiO as hole transport layer in perovskite solar cell, we performed the detailed Current-Voltage (I-V) experiment as demonstrated in figure 5.15. In the first step, FTO substrate was cleaned by detergent powder followed by sonicated in water, acetone and isopropyl alcohol sequentially for 10 min. The TiO₂ layer obtained on FTO substrate by hydrothermal process was taken as bottom layer of device, subsequently layer of perovskite material CsPbBr₃, followed by hole transport layer of NiO was drop casted. Then silver paste was coated on top layer to complete the device fabrication. I-V characteristics of the device (FTO/TiO₂/CsPbBr₃/NiO) was studied in dark condition and found that the devices work properly, but in presence of light the device unable to perform effectively.



Figure 5.15: I-V characteristic of Perovskite solar cell device in dark light

CHAPTER-6

6. Conclusion

In conclusion of thesis, we have prepared NiO based nanoparticles by using chemical precipitation method. At first outmost, the effects of annealing temperature on structural properties of nanoparticles were studied using X-ray diffraction technique. The nanoparticles after annealed at different temperature (200°C, 270°C, 300°C and 400°C), the temperature 270°C for 2 hours was the most suitable temperature for prepare of NiO (Nickel Oxide) nanoparticles. After annealed at 270°C for 2h, these peaks (200°C for 2h) observe low intensity and new peaks generated due to decomposition of Ni(OH)₂ to NiO. These peaks are 37.31°, 43.34°, 62.83°, 75.33° and 79.27°C could be assigned at the planes (111), (200), (220), (311) and (222) of NiO, respectively. Then we prepare of NiO nanoparticles for different molar concentration (0.1M, 0.2M and 0.4M) at 270°C for 2hrs. We observed that increment in the molar concentration does not affect the crystalline size. Furthermore, for better conductivity the doping of copper was performed with NiO and characterized by using X-ray diffraction. With % increment of copper doping the peaks shifted towards lower angle. Optical spectroscopy data suggested the low-absorbance in visible region, a decrease in transparency (89% to 85%) and band gap (3.41eV to 3.17eV). A good quality NiO thin films was used for XRD analysis, only three major peaks were observed at 35.31°, 42.27°, and 61.75°, while the other two peaks were not observed clearly. FESEM of NiO thin film revealed randomly arranged particles on the surface. By doping of copper in 1% Cu, 2% Cu and 4% Cu into NiO, we observed that the doping of copper content decreases the transparency of the thin film and increases the absorbance. And by using surface analysis technique, we observed the crystalline size decreases as increasing the percentage of copper doping. From I-V characteristics of NiO and Cu doped NiO thin films, conductivity and resistivity was

obtained and it was observed that conductivity increased with increase in doping of copper. Finally, complete the device fabrication, the I-V characteristic of the device was studied in dark condition and found that the device was able to work properly.
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