Characterization of Cu_2O-ZnO Interface for Photosensitive Devices

by

Muyar Htun

B.E., Yangon Technological University, 2006

Project Submitted in Partial Fulfillment of the
Requirements for the Degree of
Master of Engineering

in the
School of Engineering Science
Faculty of Applied Sciences

SIMON FRASER UNIVERSITY

Summer 2015

Approval

Name:	**Muyar Htun**
Degree:	**Master of Engineering**
Title:	***Characterization of Cu_2O-ZnO Interface for Photosensitive Devices***
Examining Committee:	**Chair:** Steve Whitemore Senior Lecturer

Dr. Ash M. Parameswaran, P.Eng
Senior Supervisor
Professor

Dr. Andrew Rawicz,**P.Eng**
Internal Examiner
Professor
School of Engineering Science

Date Defended/Approved: July 17, 2015

Abstract

This project investigates the photo sensitive characteristics of Cu_2O-ZnO interface from painted cuprous oxide on copper. Existing methods of producing Cu_2O-ZnO photosensitive layers are complex, costly and require high temperature conditions. The paintable medium developed in our approach was a simple mixture of cuprous chloride, adhered hydrate cuprous oxide, de-ionised water and acetone. The prepared medium was painted on a clean copper sheet. The device was then heated at 75^oC for 30 minutes. The ZnO layer was electroplated in zinc nitrate solution at 72^oC. The surfaces of Cu_2O and ZnO were analyzed by SEM and the results showed homogenous surface morphology. The photosensitivity of the manufactured Cu_2O-ZnO was also characterized using a semiconductor parameter analyser (SPA) and a light source. The manufactured devices exhibited ohmic (I-V) characteristics in the dark. Upon illumination, the current density increased by 40 %. Samples that were annealed for two-hours at 75°C before ZnO electrodeposition, exhibited a solar-cell type (I-V) response.

Keywords: Cu_2O-ZnO; photosensitivity; paintable medium; homogenous surface morphology; solar cell type (I-V) behavior

Dedication

To my supervisor Dr. Ash Parameswaran, my beloved family and raped victims who are struggling to get their normal lives back.

Acknowledgements

First of all I'm deeply thankful to my supervisor, Dr. Ash Parameswaran, for his guidance, support, patience and giving me a second chance. Working under him was a very pleasant experience and I was able to gain a lot of knowledge and experience. Without his support, this research would never have been completed.

I would like to thank to Dr. Mahendra Prasad for sharing me his time to helping me finish my project and guiding me through every step of my work.

Sincere thanks to Dr. Andrew Rawicz for agreeing to be the examiner for my project presentation.

I would like to thank to associate dean of graduate studies, Dr. Mary-Ellen Kelm, for helping me in pursuing my dream. I would also like to thank to Dr. Mitchell Stoddard - director, Centre for Students with Disabilities.

Special thanks to Shruti and Sae-Won for all the help and support they have provided.

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List of Acronyms

CAD	Chemical vapor deposition
CdTe	Cadmium telluride
CdO	Cadmium oxide
Cu_2O	Cuprous oxide
DC	Direct current
FF	Fill factor
GaAs	Gallium arsenide
KOH	Potassium hydroxide
LDR	Light dependant resistor
LiOH	Lithium hydroxide
M-MOS	Metal metal-oxide semiconductor
NaOH	Sodium hydroxide
NiO	Nickel oxide
PbS	Lead sulfide
PbSe	Lead selenide
RF	Radio frequency
SEM	Scanning electron microscope
TEM	Transmission electron microscopy
TiO_2	Titanium dioxide
XPS	X-ray photoelectron spectroscopy
ZnO	Zinc oxide

Chapter 1.

Introduction

1.1. Cuprous Oxide (Cu_2O) and Zinc Oxide (ZnO) Semiconductors

Metal Metal-oxide interfaces (M-MOS) take part a major role in electronic and optical applications. Due to their electrical properties, the M-MOS can be used as insulators, conductors and superconductors [1]. Moreover, they can also be used as optical and photo sensitive devices such as light emitting diodes, photoconductors and solar cells [1, 2]. Cu_2O and ZnO are the most popular among the various types of M-MOS since they are non-toxic, abundant, inexpensive and simple to produce. Furthermore, they have a relatively high light absorption coefficient [3]. Common techniques used to develop Cu_2O include thermal oxidation, electrochemical deposition, sol-gel spray and sputtering. Existing techniques used to develop Cu_2O require complicated procedures and some require high temperature conditions of at least 200° Celsius [4]. Therefore, we have investigated a simple and unique painting method to develop Cu_2O on the surface of copper. This painting method does not require a complicated instrumental set up and can be performed at a far lower temperature than those required in existing methods [4].

A hetero-junction is an active interface for many semiconductor devices [5]. Typically a hetero-junction will comprise of n-type and p-type semiconductor with different bandgaps [5]. An n-type semiconductor is one which has a majority of electron carriers and a p-type semiconductor is one which has a majority of holes. Thus, an n-type semiconductor, zinc oxide (ZnO), and p-type semiconductor, Cu_2O were used to achieve the hetero-junction and this combination of hetero-junction has been the most notably investigated semiconductor [6-8]. The most commonly used method to produce

Cu_2O-ZnO is electrochemical deposition of both materials [6-8]. While Cu_2O has typically been created using electrochemical deposition, however research has been done investigating sputtering and annealing of ZnO instead of electrochemical deposition [9,10].

Although in the past research has been conducted on the electrical properties of Cu_2O and ZnO, nowadays most research primarily focuses on the photosensitive properties of Cu_2O and ZnO, which proves to be useful for photo-detectors, photodiodes and solar cell applications [10-12].

1.2. Motivation

Cu_2O is one of the most attractive materials for various applications such as photo-sensitive and photovoltaic applications. Moreover, literature reports a theoretical energy conversion efficiency of Cu_2O is approximately 20%, while the maximum energy conversion efficiency that was observed was only a 3.8% [13, 14]. There are various preparation techniques to develop Cu_2O: thermal oxidation, electrochemical deposition, sputtering, anodic oxidation and sol-gel chemistry methods. However, no prior research has been done on developing M-MOS photosensitive Cu_2O devices by a simple painting method. Therefore, this research explored a simple and unique process of depositing Cu_2O by painting a colloidal solution mixture of cuprous-cupric chloride on cleaned copper sheet. The painting method provided a homogenous Cu_2O layer on top of copper sheet and that allowed the investigation of its photosensitivity. The painting technique is economical, simple and can also be performed under lower temperature conditions which are attractive for low cost manufacturing process.

1.3. Thesis Organization

Chapter 2 presents photosensitive materials and their role as semiconductors.

Chapter 3 presents copper oxide and ZnO as economical photosensitive materials and a literature review on existing methods of producing both materials.

Chapter 4 presents device processing technique of Cu-Cu_2O-ZnO device.

Chapter 5 presents photo-sensitivity of the device.

Chapter 6 and Chapter 7 present conclusion and future work.

Chapter 2.

Photosensitive devices and photosensitive materials

2.1. Photosensitive devices

Photosensitive devices are used to convert optical energy into electrical energy. There are several types of photosensitive devices such as photo-resistors, photodiodes and solar cells.

2.1.1. Photo-resistor or light dependent resistor (LDR)

A photo resistor is a semiconductor device whose resistance alters when it is illuminated by light source. Depending on the materials used for photoresistor production, there are two types of photoresistors: intrinsic and extrinsic. In an intrinsic photoresistor, light stimulates the electrons from the valance band and makes those electrons jump to the conduction band. As a result, there are more free electrons present in the device to increase current flow and decrease the resistance of the device. Extrinsic photoresistors can be produced by doping impurities to the semiconductor material. In this way a new band is generated above the valance band. The electrons from the new band need lesser energy to transfer to the conduction band and when the surface is illuminated, the electrons movement increases, and thus allows current flow [15.

During the 1930s, silicon, germanium and selenium were used to produce photoresistors. Nowadays most commercial photoresistors are made from cadmium sulfate which is highly toxic and banned in many countries [16]. Therefore, in those countries, alternative devices such as photodiodes have to be used instead of

photoresistors. Therefore, there is a commercial need for photoresistors manufactured from non-toxic and low cost materials.

2.1.2. Photodiode and solar cell

The exposure of light generates electron-hole pairs in a photodiode and those carriers contribute to the photosensitivity of the material. A photodiode can be p-n photodiode or p-i-n photodiode [17]. Semiconductor materials such as Cu_2O, ZnO, Silicon(Si), gallium arsenide (GaAs), lead selenide (PbSe) and lead sulfide (PbS) are used for photodiodes [17,18]. Photodiodes are used in blood spectrum analysers, X-ray detection for CAT scanners, smoke detectors and various biomedical, safety and communication applications. Figure 2 shows V-I characteristics of a typical photodiode [18].

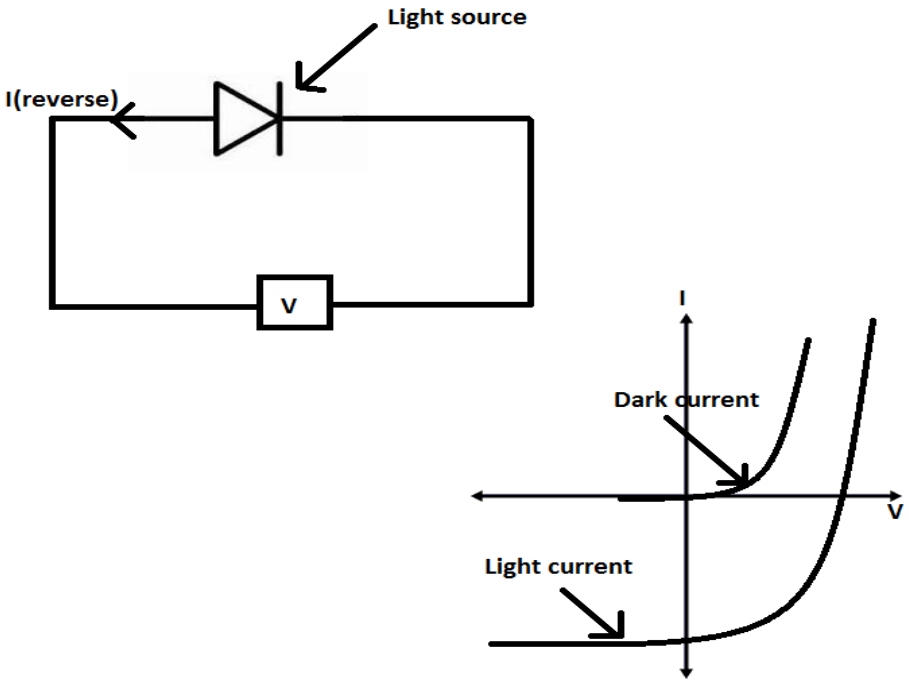

Figure 2.1. V-I Characteristics of a photodiode
Note: Adapted from [18]

Although the basic principles of photodiodes and solar cells are almost the same, photodiodes require a faster response time and are designed to detect light. On the

other hand solar cells are designed to generate more electrical carriers than photodiodes and also have higher energy conversion efficiency.

The standard V-I characteristics of a solar cell is shown in Figure 2.2 .There are important parameters that can be derived from the V-I characteristics such as the open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor (FF) and the conversion efficiency (η). I_{sc} is current through the solar cell when the voltage across the solar cell is zero and V_{oc} is voltage through the solar cell when the current is zero. Moreover, V_{oc} is maximum voltage achieved by the solar cell. Fill factor and η in following equations 2 and 3 describe the performance characteristics of the solar cell [19].

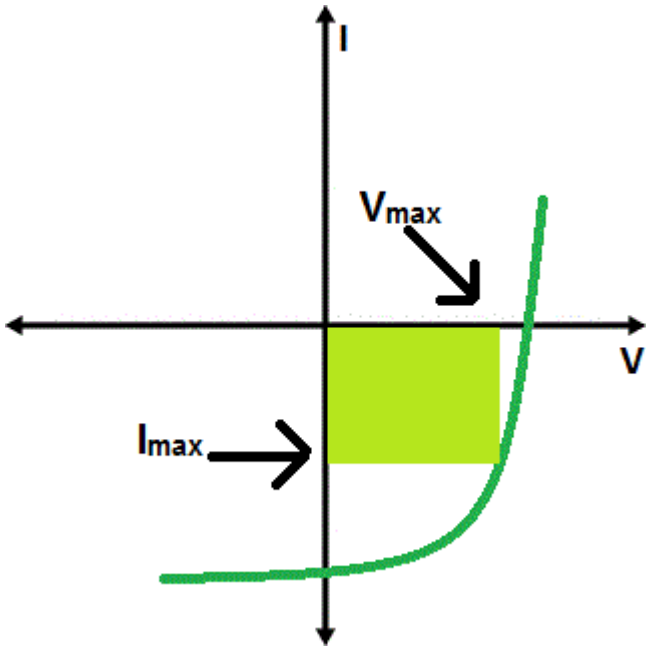

Figure 2.2. V-I characteristics of solar cell

The maximum power can be calculated from the values of voltage and current (V_{max} and I_{max}) and the maximum power point is also known as the optimal working point. Therefore,

$$P_{max} = V_{max} \times I_{max} \quad \text{.....(1)}$$

The fill factor can be expressed as the ratio of the P_{max} divided by the product of V_{oc} and I_{sc} as given in Equation 2.

$$FF = \frac{P_{\max}}{V_{oc} I_{sc}}$$

(or)

$$FF = \frac{V_{oc} - \ln(V_{oc} + 0.72)}{V_{oc} + 1} \quad \text{..... (2)}$$

The conversion efficiency η can be calculated from power of input light provided from external light source P_{in}, V_{oc}, I_{sc} and FF

$$\eta = \frac{V_{oc} I_{sc} FF}{P_{in}} \quad \text{..... (3)}$$

2.2. Photosensitive semiconductor materials

Photosensitivity or photoconductivity of a material explains that when sufficient energy of light is exposed to the surface of certain material, the electrical conductivity of the materials increases. There are two groups of photosensitive materials: organic (polymer) and inorganic, for example, Metal Metal-Oxide (M-MOS) materials.

Organic photosensitive materials are manufactured from conductive organic polymers or small organic molecules [20]. Research on organic photosensitive materials has been going on for more than 3 decades. These materials are flexible, light weight and low-cost to manufacture although their maximum efficiency is approximately 10% which is quite low compared to the 20% theoretical energy efficiency value of Cu_2O [13,21] . There are two methods used to prepare organic photosensitive materials: thermal evaporation method and wet processing method. In the thermal evaporation method, a polymer film is deposited on the substrate within a vacuum chamber which helps remove contaminants such as water and oxygen [20]. There are four categories of wet processing methods and they are spin coating, doctor blading, screen printing and ink printing [20]. Common to all these methods is that organic materials are dissolved in an appropriate solvent such as water or any other polar or non-polar organic solvent

before forming an insoluble film on the substrate [20]. The main disadvantage of organic photosensitive materials is that polymers and organic photosensitive materials can degrade when exposed to light and the stability of real life application is still questionable although there have been tremendous efforts to reduce degradation as well as to increase life time of the materials [21].

Inorganic photosensitive materials are metalloids or M-MOS materials such as Cu_2O, cadmium telluride (CdTe), nickel oxide (NiO), Titanium oxide (TiO_2), ZnO and amorphous silicon (a:Si) [21,22]. Most of the materials in these groups provide high efficiency and stability of the photosensitive device. A wide variety of preparation methods such as thermal oxidation, sputtering, chemical vapour deposition and electrochemical deposition are used to develop metalloids or M-MOS depending on the required materials.

2.2.1. Silicon as photosensitive material

There are three types of silicon solar cells: mono-crystalline silicon (c:Si), poly-crystalline silicon (p:Si) and amorphous silicon (a:Si). The very first silicon solar cell was introduced by Bell Laboratories in 1941. In 1954 silicon solar cells which provided 6% energy conversion efficiency was developed and used in satellites. Nowadays, the efficiency of silicon solar cells has reached 23%. Although silicon solar cells provide high energy conversion efficiency, there are several disadvantages. The developing process of c:Si is complex and needs to be done at high temperature conditions. The fabrication process of a:Si costs more than c:Si Therefore, oxide-based photosensitive materials are becoming popular in photovoltaic research [24].

2.3. Common oxide photosensitive materials

Some M-MOS play a major role in photosensitivity and photovoltaic research due to their sensitivity to light. Many M-MOS are easy to produce, low cost, abundant, chemically stable and environmental friendly. Although commercial success has been demonstrated, their popularity is growing and based on the research being done at

present, it is clear that the future of M-MOS holds great promise. M-MOS can be used as photodiodes, photo-resistors, photo-sensors and solar cells [25 - 27].

Oxide semiconductors such as cadmium oxide (CdO), nickel oxide (NiO), Titanium oxide (TiO_2), Cu_2O and ZnO provide photosensitivity. They have been investigated as photodiodes, photo-resistors, photo-sensors and solar cells. While TiO_2 and ZnO work as transporting electrons, NiO provides hole transportation [22]. The following sub sections discuss the photosensitive properties of CdO, NiO and TiO_2. Cu_2O and ZnO will be discussed in greater depth in chapter 3.

2.3.1. Cadmium oxide (CdO)

CdO is an n-type semiconductor that has a band gap energy between 2.2 to 2.5 eV. Due to this narrow band gap, CdO is not as attractive as other M-MOS [28].There are several methods used to prepare CdO including, mechano-chemical, hydrothermal, solvo-thermal, chemical precipitation and micro-emulsion methods. Literature reports mechnochemical method is the most efficient, convenient as well as cost effective for CdO. CdO can be used in solar cells, gas sensors, photocatalysis, photodiodes and transparent electrodes [29]. Although CdO as a photosensitive material provides higher efficiency among oxide semiconductors, it is highly carcinogenic and toxic [30]. Therefore, cadmium oxide is not a favorable photosensitive material for commercial use.

2.3.2. Nickel oxide (NiO)

NiO is a p-type semiconductor as well as a non-stoichiometric semiconductor with a wide band gap from 3.6 to 4.0 eV. It is also an anti-ferromagnetic material. The preparation methods of NiO include electron beam evaporation, vacuum evaporation, anodic oxidation, chemical deposition, rf-magnetron sputtering, sol-gel, spray pyrolysis technique and atomic layer epitaxy [31]. NiO can be used in solar thermal absorbers, photocatalysts, electrochromic devices and positive electrodes in batteries [32]. NiO has been used for hole transport as well as to enhance the charged carrier in organic solar cells [33] .Although it doesn't provide reasonable efficiency as a solar cell, it enhances the efficiency and conductivity of organic solar cells. The nature of NiO allows it to be

used as hole transport materials in organic polymer solar cells. However, NiO by itself is not an efficient photosensitive device [22].

2.3.3. Titanium dioxide (TiO_2)

TiO_2 is an n-type semiconductor and it can be prepared using chemical vapor deposition (CVD), sol-gel, electrochemical deposition, sputtering and plasma vapor deposition (PVD) techniques [34, 35]. Due to its light absorption properties, it can be used in solar cells, solar hydrogen production, solar water purification, photo-oxidation in organic pollutants and photo-killing of bacteria such as E-Coli [36].

TiO_2 is mostly used as an electron conductor in organic solar cells which provides an energy conversion efficiency of approximately 12%. Although TiO_2 layered with organic solar cells provides high efficiency, the hetero-junction layers of Cu_2O/TiO_2 provide an energy conversion efficiency of only 0.1-1% [22].

Chapter 3.

Copper oxides and Zinc Oxide as economical photosensitive hetero-junction

3.1. Copper Oxides

Copper oxides are attractive among semiconductor materials because they are abundant, non-toxic and their preparation cost is inexpensive as well as simple. They also have favorable band-gaps and are physically and chemically stable. There are two stable types of copper oxides: cupric (CuO) and cuprous (Cu_2O).

The band gap of Cu_2O is approximately 2 eV and the color is reddish brown. CuO has black or dark gray color with band gap of 1.4 eV. The main property difference between Cu_2O and CuO is the copper valences. Copper valences for Cu_2O is Cu^+ and CuO is Cu^{2+} and Cu_2O is more promising material than CuO due to its high absorption coefficient. [37].

3.1.1. Cuprous oxide (Cu_2O)

Cu_2O is a p-type semiconductor material which results from the cation deficiencies mainly caused by copper vacancies rather than oxygen interstitials or any other defects [38]. Figure 3.1 shows a simple cubic structure of Cu_2O with a lattice parameter 4.2696 Å. A unit Cu_2O cell has four copper atoms and two oxygen atoms with each oxygen at the centre surrounded by a tetrahedron of copper atoms [39].

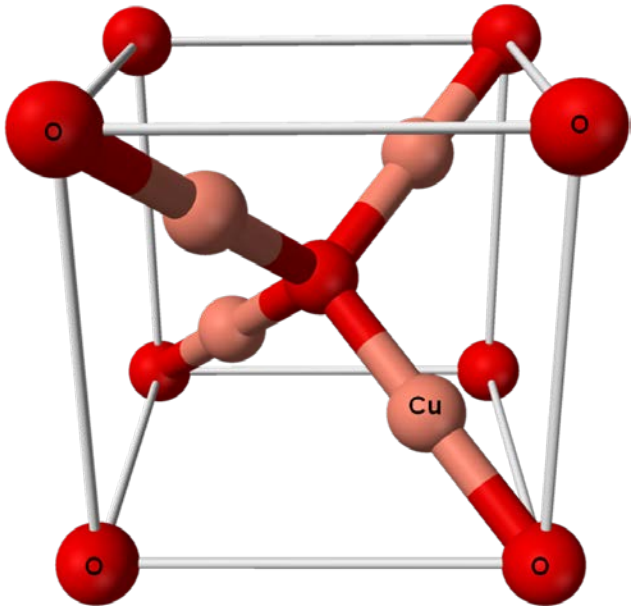

Figure 3.1. Crystal structure of Cu_2O [40]

3.1.2. Properties of Cu_2O

Table 3.1. Basic properties of Cu_2O [39]

Formula weight	143.14g
Density	5.749-6.140 g/cm^3
Melting point	1235 °C
Lattice constant	4.2696 Å
Thermal expansion coefficient	2.3 x 10^{-7} K^{-1}(283K)
Dielectric constant	$\varepsilon(0)=7.11$; $\varepsilon(\infty)=6.46$
Hole hall mobility	μ=70 cm^2/V sec

3.1.3. Cu_2O in semiconductor history

The very first Cu_2O device was a rectifier invented by Grondhal in the 1920s which established the future of Cu_2O in the semiconductor industry [41]. Since then, there has been a significant amount of research conducted on Cu_2O rectifier characterization. By the 1940s, Cu_2O rectifier research was one of the main semiconductor researches at Bell Telephone Laboratory [42]. Almost at the same time,

new semiconductor materials such as silicon and germanium became more prominent and the interest turned to these new materials.

The history of Cu_2O solar cells dates back between 1920 and 1933 although the very first solar cell was made by Charles Fritts in 1883 from selenium and gold [43]. It was reported that A.E. Becquerel discovered the photovoltaic effect in 1839 [44]. In 1888, a Russian scientist A.G. Stoletov made a solar cell which was better than the solar cell developed by Charles Fritts [45]. The fabrication of cuprous solar cells was initiated in 1930s. It was prepared by thermal oxidation on copper sheets to demonstrate the Cu/Cu_2O photovoltaic cell [46]. In 1935, E.D Wilson et al. made use of transparent Cu_2O to fabricate a photo-sensitive material [47]. However the device was limited to the visible spectrum of light of 700 to 800 nm. The real progress in solar cells fabrication was accomplished in 1940s. In 1954, Bell Laboratory successfully launched a silicon p-n junction solar cell with 6% efficiency [48]. Since then the era of solar cells began with different photosensitive materials in the world. Although the history of Cu_2O solar cells is quite primitive, research and development on Cu_2O solar cells was eventually stopped due to its low photovoltaic energy conversion efficiency (<1%). Simultaneously there had been a tremendous progress of silicon technology of photovoltaic cells which provided a higher conversion efficiency of approximately 23% [24]. However, realising the cost factor abundance of copper and easier methods of preparation of Cu_2O, researchers were encouraged to explore the application of Cu_2O for harvesting solar energy for mass consumption in different parts of the world.

Furthermore, a comprehensive review was done on Cu_2O solar cells by Nelson et.al., which emphasized the issues that need to be addressed in increasing the photovoltaic energy conversion efficiency of Cu_2O in order to make it feasible for commercial production of Cu_2O [49].

In order to get a deeper insight into these issues, fabrication and characterisation of Cu_2O solar cells was initiated under a research program during the late 1970s. This research addressed the three main areas that needed to be addressed in using Cu_2O which were: (1) complex preparation method of Cu_2O (2) increasing the photoconductivity of the materials (3) improving the p-n junction [50]. The theoretical

efficiency of Cu_2O solar cells is approximately 20% under solar illumination of AM1.5 (radiation power 100 mW/cm^2). Rakhshani et. al., reviewed the existing methods of preparation of Cu_2O for the fabrication of the Cu_2O solar cell. This research investigated preparation methods which needed temperatures less than 300°C as most preparation techniques required high temperature oxidation of copper of more than 1000°C [51]. Since then, there has been a great deal of research on low temperature preparation of Cu_2O [52].

3.1.4. Various methods of preparing Cu_2O

There are many existing methods used to prepare Cu_2O such as electro-deposition, chemical vapour deposition, sputtering, anodic oxidation and sol-gel chemistry. However, the most commonly used method is thermal oxidation. Thermal oxidation is one of the simplest methods to produce Cu_2O and the thinness of the Cu_2O film can easily be adjusted by the length of the thermal oxidation time. Oxidation can be performed under the temperatures between 200°C to 1500 °C and the oxidation time can vary from several hours to a couple days in order to achieve the desired thickness [4,51,53]. Moreover, thermal oxidation can be done not only in air but also water vapor and oxygen. During thermal oxidation CuO and Cu_2O can be formed depending on the thermal stability of the oxides [53]. In this method thermal stability is important if the desired copper oxide is Cu_2O. There are very few p-type semiconductors which can be electrochemically deposited and Cu_2O is one of them [54]. The quality and efficiency of Cu_2O depends on the type of aqueous solution and their pH level, deposition potential and temperature. Although n-type Cu_2O electrodeposition has been done, both p-type and n-type depositions result in low efficiency owing to the high resistivity. Doping is required in order to reduce this resistivity [55].

CVD is another method which provides high- purity and high-quality materials. Cu_2O produced by CVD can be polycrystalline or amorphous based on the materials and reactors used for the process. There are many factors that determine the quality of the deposited Cu_2O such as, the type of precursor, process temperature and pressure, gas flow rate and the design of the reactor used during CVD [55, 56].

Sputtering is a technique of emitting materials from a source to deposit on a desired substrate. Cu_2O can be deposited by using the sputtering method which needs a low pressure vacuum system. Depending on RF power and oxygen flow, Cu_2O and CuO rich deposited substrates can be produced. Moreover, the resistivity of the oxide depends on the RF power and oxygen flow. The lowest resistance of the Cu_2O substrate produced by sputtering is 10 Ohms [58, 59].

Anodic oxidation is a high speed electrochemical oxidation method which can provide natural oxide films on the metal. Anodic oxidation can produce Cu_2O on the copper surface although the purity of the Cu_2O produced by this method is still questionable. In this process, the oxide film is composed of two layers: the inner layer is Cu_2O with partly hydrated CuO and the outer layer is $CuO_x(OH)_{2-2x}$ [60, 61].

The sol-gel method is chemical transformation of liquid into gel state with post treatment and changing into solid state oxide materials. It is simple, low cost and it does not need a sophisticated work place. Moreover, its crystallization and distribution can be controlled by molecular precursors and annealing conditions used during the process. [62,63].

3.2. Zinc Oxide (ZnO)

ZnO is a semiconductor which belongs to II-VI semiconductor group. ZnO can be found in a mineral called zincite which is red or manganese in colour. Zincite can also be synthetically produced. Therefore it is low cost, nontoxic and abundant. Artificial ZnO is always an n-type semiconductor with a wide band-gap energy of 3.3 eV. Therefore ZnO is a popular semiconductor material and is widely used in photovoltaic applications [64].

3.2.1. Crystal Structure of ZnO

The crystalline structure of ZnO has three phases: wurtzite (hexagonal), zinc-blende (cubic) and rocksalt (cubic). The ZnO hexagonal unit cell has two molecules and the oxygen atoms surround the ZnO atoms in a tetrahedral structure [64]. In a cubic structure substrate zinc-blende can be made and rocksalt can be formed at high

pressures of 9.8 GPa at 300^{o}K [64]. Figure 3.2 shows the wurtzite structure of ZnO. ZnO is a powerful n-type material without deliberately doping. The major source of essential donors comes from the original defects which is oxygen vacancies or zinc interstitials [65].

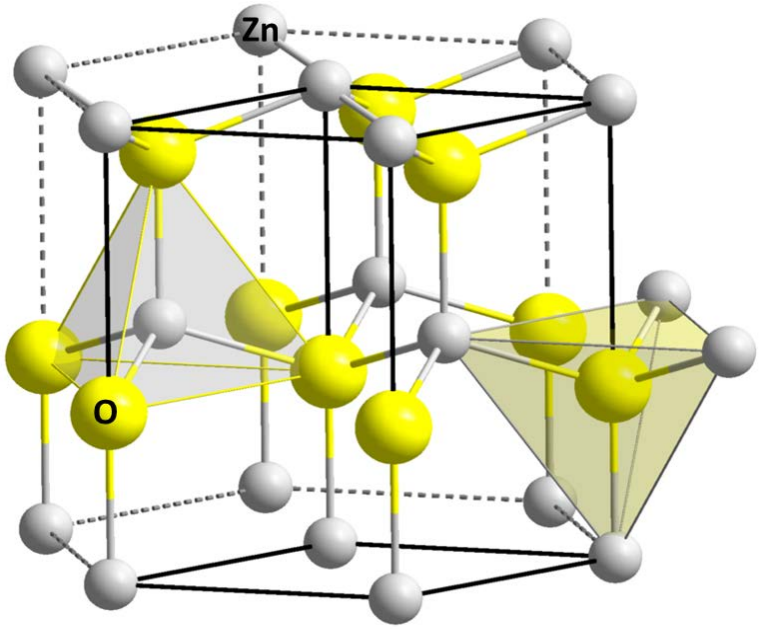

Figure 3.2. Wurzite structure of ZnO [66]

3.2.2. Properties of ZnO

Table 3.2. Fundamental properties of ZnO [64]

Formula weight	81.36g
Density	5.67g/cm^3
Melting point	2242 K
Lattice constants	a=3.24Å, c=5.2 Å
Thermal expansion coefficient (at 300K)	$\alpha^{\perp}$ =4.31, $\alpha^{\parallel}$ =2.49
Dielectric constant	$\varepsilon(o)_{\perp c}$ =7.8, $\varepsilon(\infty)_{\perp c}$= 3.7, $\varepsilon(o)_{\parallel c}$=8.75, $\varepsilon(\infty)_{\parallel c}$=3.75
Hall mobility	$\mu_{\perp c}$= 70, Thin film $\mu_{\parallel c}$=170, Bulk single crystal $\mu_{\perp c}$=150 (cm^2/V sec)

3.2.3. ZnO in semiconductor history

The first ZnO research was started in 1920. In 1960 piezoelectric properties of ZnO were investigated and later ZnO was used in acoustic wave devices. After that researchers have been investigating ZnO in areas such as optoelectronics, photovoltaic as well as ferromagnetic properties [67]. Moreover, ZnO is a popular semiconductor material in thin film metal oxide semiconductor field effect transistors (MOSFETs). Research has also been done on p- type doping of ZnO, however, the p-type properties of ZnO are transient and only last for six months. [68].

3.2.4. Various methods of depositing ZnO

ZnO semiconductor material can be prepared by various methods. The following sub chapter will discuss some of methods including, sputtering, CVD, sol-gel method, pulsed laser deposition and chemical bath deposition. Electrochemical deposition will be discussed in the following chapter.

Sputtering is one of most popular methods used to produce ZnO semiconductors. The quality of electrical conductivity highly depends on the crystal structure, chemical deposition and sputtering modes such as DC and RF. Moreover, the amount of bias voltage is responsible for the surface homogeneousness and the density of the deposited ZnO layer [69].

There are different types of CVD that can be used to deposit ZnO on the substrate. The surface roughness and thickness of the layer rely on the temperature used during the deposition. Although the deposition temperature affects the band gap energy, the exact correlation between temperature and the amount deposited is unknown [70, 71].

Although the sol-gel method is one of the simplest and cost effective methods, the substrate has to be heated at 300°C for 10 minutes every time it is coated with a solution. In some cases, the same procedure needs to be repeated up to 9 times. After that the substrate needs to be heated at 500°C for two hours to achieve compact ZnO deposition [72].

For pulsed laser deposition, a 248nm KrF excimer laser is used and the pulse frequency and duration are 10 Hz and 10 ns respectively. The deposition takes place for two hours in a 10^{-4} Pa vacuum chamber. The limit of the surface roughness of deposited ZnO is typically between 2-9 nm. An increase in the temperature of the chamber reduces the resistivity of the deposited ZnO [73].

In chemical bath deposition, the pretreated substrate is immersed into a pH controlled chemical solvent for 30 s to 90 s. After that the substrate is annealed for half an hour at 300°C to crystallize the ZnO. In this process, maintaining the pH is quite important [74].

3.3. Cu_2O - ZnO Hetero-junction

Cu_2O and ZnO make one of the most popular and effective p-n junctions. In order to get a hetero-junction, two different semiconductors with different band gap energy are needed. ZnO posses a 3.3eV band gap energy which is wider than the 2eV band gap of Cu_2O (Figure 3.3). The Cu_2O-ZnO photosensitive hetero-junction has received a great deal of attention due to its theoretical energy conversion efficiency of 18% and its higher light absorption coefficient than other silicon photosensitive devices [75].

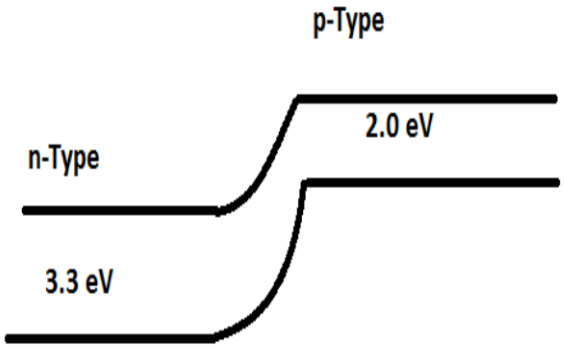

Figure 3.3. Band-structure of Cu_2O-ZnO hetero-junction
Note: Adapted from [76]

There are various existing methods used to produce the Cu_2O-ZnO junction. However, the two most popular methods are electrochemical deposition and sputtering of both Cu_2O and ZnO.

3.3.1. Efficiency of Cu_2O-ZnO produced by existing methods

Electrochemical deposition of Cu_2O for Cu_2O-ZnO photovoltaic devices can be achieved using three different pH reagents: LiOH, NaOH and KOH. Devices that use LiOH have an energy conversion efficiency of 1.43% while devices that use NaOH and KOH have efficiencies of 0.698 and 0.591% respectively [77]. Low temperature Cu_2O-ZnO electrodeposited photovoltaic devices have shown to achieve energy conversion efficiencies of 0.1% to maximum 1.28% [78]. Another type of photosensitive device has also been developed by electrodepositing ZnO and Cu_2O and superimposing this layer with sputtered ZnO. This device provided maximum energy conversion efficiency 1.02%. Whereas a simple electrodeposited layer of ZnO and Cu_2O only allowed 0.09% of energy conversion efficiency [79]. Another method involves RF sputtering of ZnO followed by electrodeposition of Cu_2O at different potentials. The energy conversion efficiency of devices developed at a -0.5 V electrodeposition potential was 0.023% and at -0.6 V was 0.24% which was the maximum energy conversion efficiency [80]. Electrodeposition of FTO/ZnO/Cu_2O resulted in 0.25% energy conversion efficiency

while ITO/ZnO/Cu_2O and ITO/ZnO/CuO provided 7.3 x 10^{-3}%and 1 x10^{-5}% respectively [81].

Although the theoretical energy conversion efficiency of Cu_2O-ZnO is 18%, in reality, the maximum energy conversion energy obtained for Cu_2O-ZnO solar cell, using a high temperature annealing and pulse laser deposition technique, is 3.83% [14]. Till date, the maximum efficiency achieved has been far lower than the theoretical efficiency. Therefore, further research is needed to fully understand the material properties of Cu_2O and thus, boost the maximum energy conversion efficiency.

Chapter 4.

Processing technique for paintable photosensitive devices

Cu_2O is one of the most attractive semiconductor materials because it is plentiful, low cost and easy to produce. Many researchers have been investigating a simpler alternative to the existing methods of preparation. This thesis presents a unique, cheaper and uncomplicated process technology of producing p-type Cu_2O on a copper sheet by a painting technique.

The second part of the process involves electrodepositing of ZnO on top of the painted Cu_2O. Since the Cu-Cu_2O layer represents a p-type, an n-type semiconductor is required to form a junction. ZnO is one of the most abundant n-type semiconductors and is simple to produce. Cu_2O and ZnO have been a good match for semiconductor research for decades and has been used in this research. Therefore, the device consists of three layers: copper, Cu_2O and ZnO. At the end, two electrode connections were made for device characterization.

4.1. Cu_2O process technology

4.1.1. Preparation of colloidal suspension paint for Cu_2O

The preparation of the colloidal suspension paint consists of three main steps: A mixture adhered hydrate Cu_2O, de-ionised water and acetone was prepared in a glass container of cuprous chloride. For this, 5 gm of cuprous chloride and adhered hydrate Cu_2O was added to 10 ml of de-ionised water and stirred thoroughly. 5 ml of acetone was added into the solution and mixed well. Finally, the colloidal suspension was ready for Cu_2O painting.

4.1.2. Painting process

A bare copper sheet which was made from 99.99% pure copper, of 0.18 mm thickness, 41.1 mm length and 30.4 mm width. First, the copper sheet was cleaned with a very fine sand paper and washed with acetone and de-ionised water thoroughly. The copper sheet was then left to dry. Next, the colloidal suspension paint was applied on the cleaned copper sheet with a small paintbrush evenly and homogenously. Approximately half of the copper sheet was painted and the rest was left to make electrical contact for the device. The paint was allowed to settle for 5 minutes and then it was washed with de-ionised water first and acetone later with the help of a clean cotton swab to remove any contamination of H_2O. Finally, a clean reddish brown or orange film of homogenous Cu_2O was formed on the sheet as shown in Figure 7 . After that the device was heated on the hot plate. The device which was heated for 30 minutes at 75 °C was denoted as device (1) and the device which was heated for two hours at 75 °C was denoted as device (2) . After this step both devices were ready for ZnO electrodeposition. Therefore, device (1) and device (2) after ZnO deposition provided different results and the results will be discussed in Chapter 5.

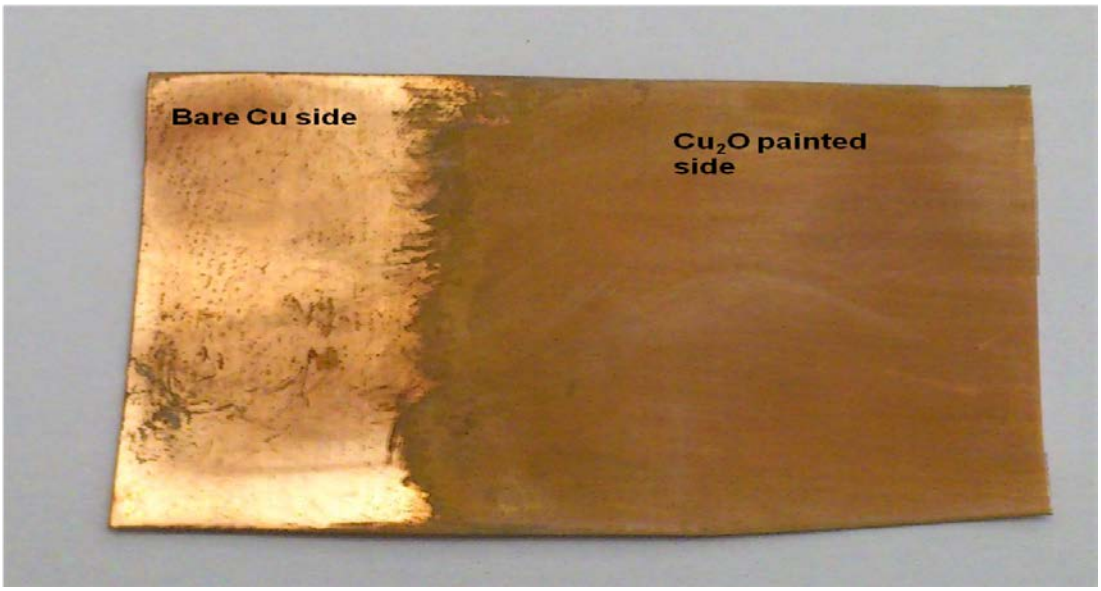

Figure 4.1. Photograph of the Cu_2O painted on bare Cu sample

When the painted Cu_2O was heated for longer time than two hours, the longer air exposure time transformed Cu_2O to CuO. Therefore, without proper equipment to prevent from air exposure, painted Cu_2O subsrtate was not able to be heated more than two hours in our experimentation.

4.2. ZnO deposition

There are many approaches to process ZnO such as sputtering, pulsed laser deposition, chemical bath deposition, sol-gel method, chemical vapor deposition and electrochemical deposition. Out of these techniques, electrochemical deposition has the benefits of having control over the area of deposition, being low cost, requiring low process temperatures and being easy to set up.

4.2.1. Electrochemical deposition

Electrochemical deposition has been one of the most popular methods among semiconductor research. Electrochemical deposition provides flexibility and control of variables so that desired product can be achieved. Figure 8 shows the basic electrochemical deposition diagram with the variables that can be controlled during

deposition. In the electrochemical deposition process, the current flow between two electrodes brings the ions from the desired electrode and deposits them on the surface of the other electrode.

There are two types of electrochemical deposition methods: the galvanic method and the potentiostatic method. The galvanic method has been used for electrochemical deposition since the 19th century [82]. The galvanic electrochemical deposition process includes two electrodes and a DC power source connected to those electrodes. The power source is a current source. The two electrodes immersed into the electrolytes are the anode (positive) and the cathode (negative) where oxidation and reduction take place. For the potentiostatic method, three electrodes are required along with a voltage source. These are the anode (positive), cathode (negative) and reference electrodes. The working electrode is an anode when anodic deposition is required.

Working electrode: The required reaction occurs at the working electrode and during electrochemical deposition; the working electrode is usually a substrate with a small surface area. Working electrode should not chemically react with the solution in which it is immersed and the surface of working should not be smooth [83]. In a cathodic deposition, the working electrode is a cathode and the counter electrode is an anode. In an anodic deposition, the working electrode is an anode.

Counter electrode: the counter electrode conveys current to the working electrode through the solution. Using the counter electrode, the electrolyte composition is kept constant during the deposition process [83].

Reference electrode: The reference electrode is only for potential measurement and is not a mandatory for electrochemical deposition. A quality reference electrode shows a constant potential independent of the amount of current during the process. For small amount of current, counter electrode works as reference electrode [83].

4.2.1.1. Electrode potentials during electrochemical deposition

If a metal named S is immersed into the solution containing metal S ions S^{z+}, there will be an interchange of S^{z+} ions between metal S and the solution it is in. The

crystal lattice of metal S will transfer some S^{z+} ions to the solution and the solution will transfer some ions S^{z+} to the metal S. One side of the reaction occurs more rapidly than the other side. If more S^{z+} ions depart from the metal than the reverse direction, there will be an excessive amount of electrons on the surface of the metal. Therefore the metal obtains a negative charge. After a certain period of time, the dynamic equilibrium in the process can be expressed as,

$$S^{z+} + ze \Leftrightarrow S$$

Where, z is the number of electrons participating in the process. From left to right, the reaction accepts electrons and so it is called reduction. On the contrary, in the reserve direction, the reaction releases electrons and so it is called oxidation. During the process, the number of electrons released from the metal is equal to number of electrons accepted by the metal [84].

4.2.1.2. Faraday's Law

Faraday's Law mentions that the weight of the deposited ions at an electrode during electrochemical deposition process is directly proportional to the amount of electricity flowing to that electrode [84]. Mathematically,

$$w = mIt/nF \quad \text{.....(4)}$$

where:

w = weight of the deposited substance

m = molecular weight of the substance

I = current

t=time

n = number electrons transferred

F = Faraday's constant (96,485.309 Coulombs/eqv)

4.2.1.3. Electrochemical deposition of ZnO

Figure 4.2 shows a photograph of the ZnO deposition set-up. It consists of two electrodes, a 250ml beaker and a DC power supply with a 2k-ohm resister. In this step of the process, device (1) and device (2) were processed in a similar manner.

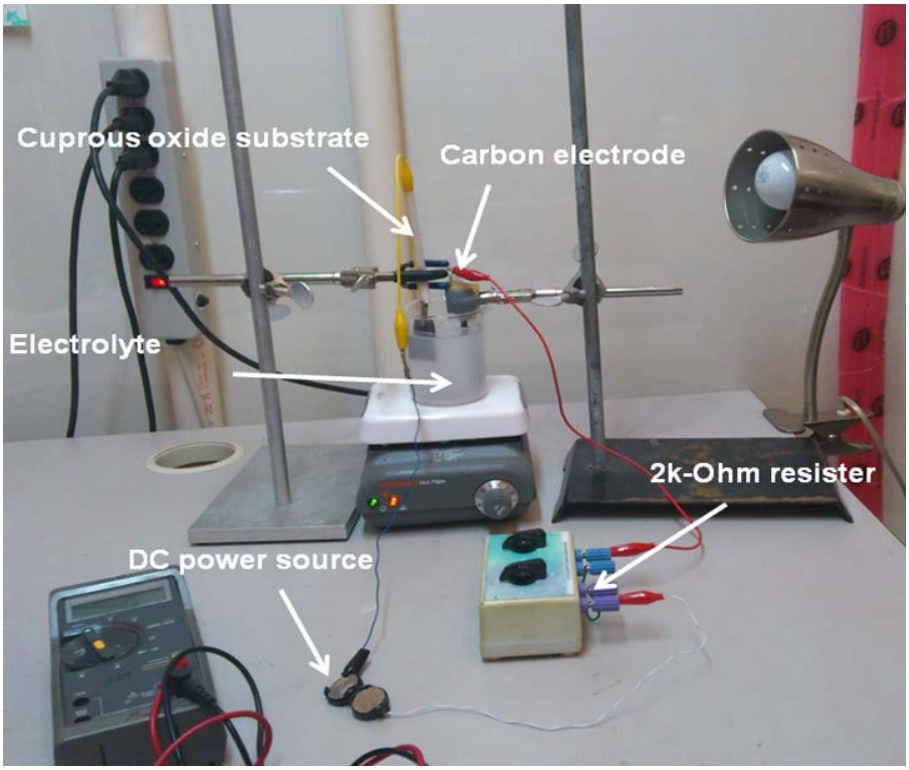

Figure 4.2. Detail set up of ZnO electrochemical deposition

Electrodepostion of ZnO was prepared with an ordinary galvanic electrochemical system using two electrodes. The deposition was a cathodic deposition process. The painted Cu_2O was used as the working electrode (cathode) and a carbon electrode was used as counter electrode (anode).

Three two-volt lithium batteries were used as a DC voltage source which was connected with 2 kΩ resistor to provide a 3mA constant current supply.

0.6g of zinc nitrate was diluted in 250ml of de-ionised water and the resulting pH of the electrolyte solution was 7. In order to reach the desired pH level of 12, NaOH was added into the electrolyte solution. When the desired pH level was reached, the solution was heated on the hot plate and the temperature of the solution was constantly monitored with a thermometer. When the temperature of the solution reached 70°C, the two electrodes were immersed into the solution and connected with a 3mA constant current source which had already been prepared. The deposition was conducted for 4 hours at the maintained temperature of 70°C. At the end of the process, the sample was washed with de-ionised water and dried to prepare for making contact electrodes for the experiment. The ZnO electrochemical deposition can be described as shown in Equations below [85],

$$Zn(NO_3)_2 \rightarrow Zn^{2+} + 2NO_3^- \quad \text{..... (5)}$$

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad \text{.....(6)}$$

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \quad \text{.....(7)}$$

$$Zn(OH)_2 \rightarrow ZnO + H_2O \quad \text{.....(8)}$$

During the electrochemical deposition, the reaction rate of equation (5) and (6) increased along with the amount of OH^- on the surface of the working electrode. Equation (8) shows that the, the extra amount of OH^- was counterbalanced by attraction of H^+ [81].

4.2.1.4. Results

Using Faraday's law, the weight of the deposited ZnO can be calculated from Equation (4) to be,

w=(81.4084x (4x3600)x 3m) / (2x 96485.309)= 0.018225 grams

In above equation, molecular weight of the ZnO (m) is 81.4084 g/mol. The time (t) was 4 hours, mentioned in seconds in calculation and the current I was 3 mA. The valance electron of ZnO was 2 and Faraday's constant was 96485.309 coulombs/mol. From these variables, the weight of the deposited substance (w) was calculated to be 18.225 mg .

With a known weight and area of the deposited substance, the thickness of the substance could be calculated easily as follows: Volume of the substrate = weight of the substrate / density of ZnO. Therefore, Volume of the substrate = 18.225mg (from calculations above) / 5.506gm/cm^{-3}

$$= 3.25 \times 10^{-3} \text{ cm}$$

Thus, the thickness of the substrate = Volume/surface area of the substrate (8)

$$= 3.25 \times 10^{-3} / 4.1174 = 7.89 \ \mu m$$

4.3. Contact electrode

For testing, two contact electrodes were connected to the prepared device. An insulated wire-wrap wire of approximately 5 cm length was used for these electrical connections. About 1 cm of the sleeve was removed from the wire ends, and the exposed wire tips were attached to the sample by Nickel Conductive Paint 840-20G manufactured by MG-Chemicals. One connection was made to the deposited ZnO layer and the other connection was made to the bare Cu. Figure 4.3 shows the device preparation steps and Figure 4.4 illustrates a completed prototype photosensitive device sample and.

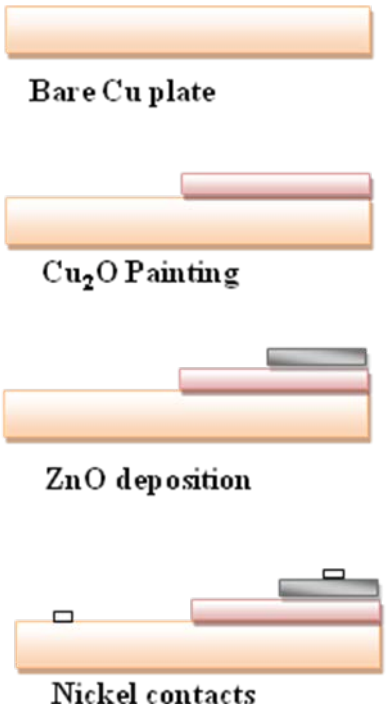

Figure 4.3. Cu-Cu_2O-ZnO device processing steps

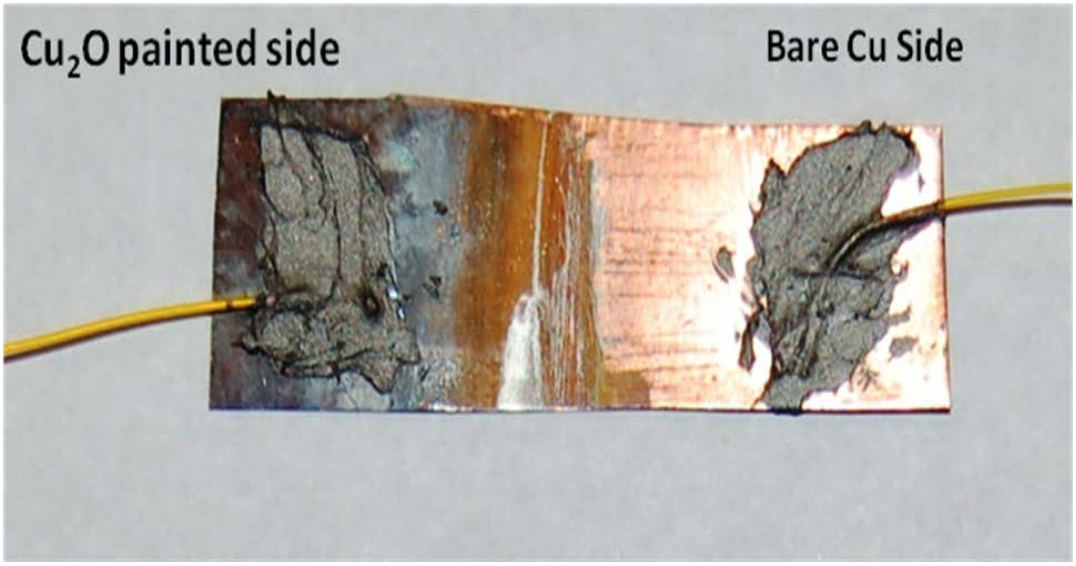

Figure 4.4. A complete Cu-Cu_2O-ZnO device with nickel painted electrodes

4.4. Surface Morphology

In order to investigate the surface of the device, we used FEI/Aspex Explorer variable pressure SEM (scanning electron microscope) with its oil-free pumping system and W filament. The variable pressure of the vacuum can range between 0.01-1.0 torr for the imaging mode. The range of voltage acceleration is 0.2-25 kV. Although the maximum image resolution of the device is theoretically approximately 20 nm, in reality the image begins to blur beyond 12 μm. The resolution of the electron detectors for FEI/Aspex explorer is 133 eV.

The surface morphology of the painted Cu_2O and deposited ZnO was observed using SEM operating at 20kV. Before ZnO deposition, the surface of the painted Cu_2O substrate was investigated by SEM. The texture of Cu_2O shown in SEM appeared homogenous and this result suggests that painting method of Cu_2O is effective. Figure 4.5(a) shows the painted Cu_2O surface texture. After ZnO deposition, on the surface of the electrodeposited substrate, the ZnO crystals were examined. Figure 4.5 (b) and (c) are the SEM images of ZnO in 12 μm and 20 μm respectively.

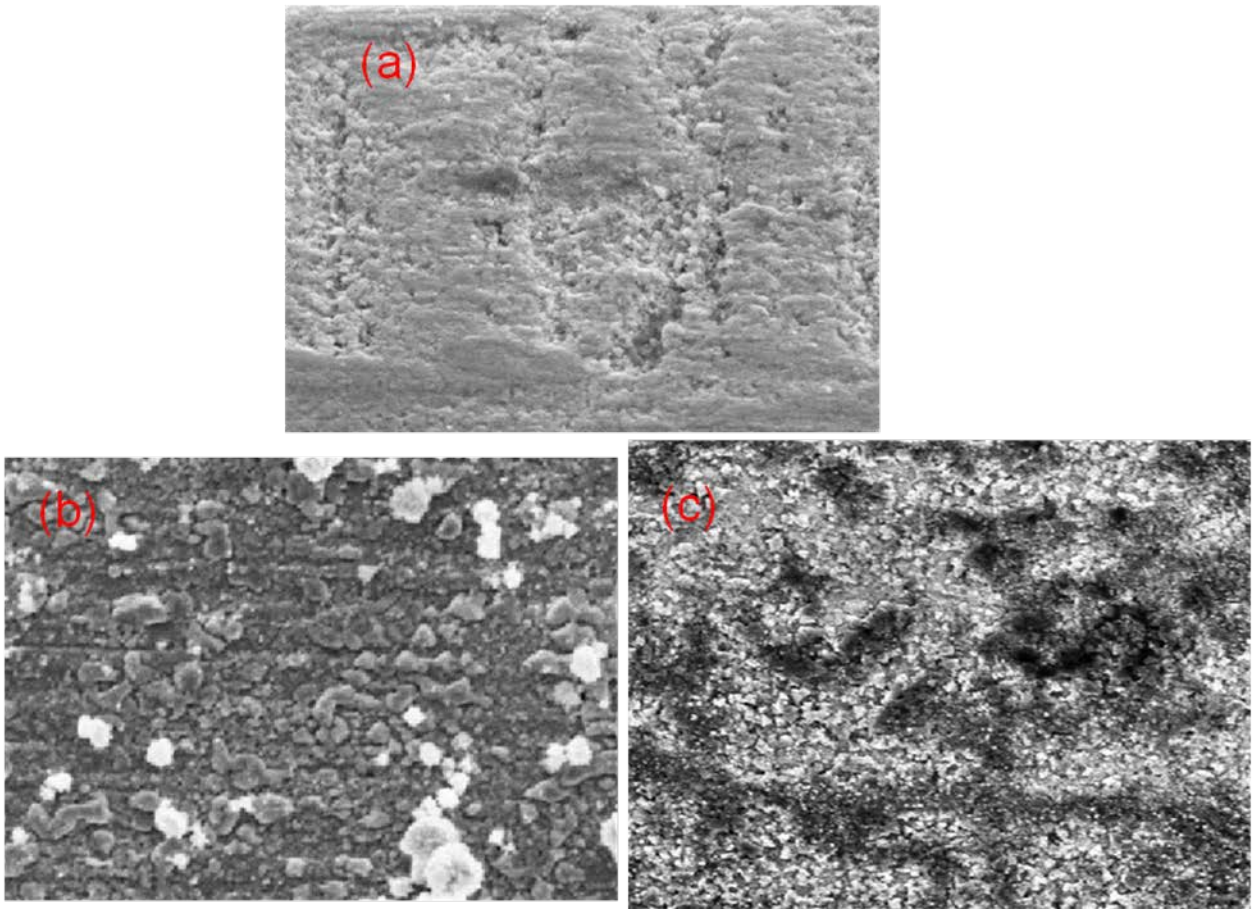

Figure 4.5. (a) SEM image of Cu_2O in 18μm, (b) SEM image of ZnO in 20 μm and (c) SEM image of ZnO in 12 μm

4.5. Electrical Characteristics

The electrical characteristics of cuprous oxide and zinc oxide were investigated by measuring the Hall Effect. The Hall Effect is used to investigate the behavior of charge transport in metal and semiconductor substrates when a combination of a magnetic field and an electric field called Lorenz force is applied to the substrate in a perpendicular direction. Additionally, Hall Effect measurement can be used to distinguish whether the type of semiconductor is n-type or p-type [86].

The magnetic field and the charge q provide the force on a particle which can be mentioned as the cross product of velocity and magnetic field those are perpendicular to the force vector as shown in equation 9[86].

$$\vec{F} = (q\vec{v})x(\vec{B}) \text{ ……..(9)}$$

Equation 1 shows that the Lorenz force F relies on the charge of the particle q, and the velocity of the particle v due to the presence of an Electric field E and a magnetic field B.

$$\vec{F} = q(\vec{E} + \vec{v}x\vec{B}) \text{ ……..(10)}$$

Where, $\vec{F}$ = Lorenz force,

q= electric charge of particle ($1.602x10^{-19}$ C)

$\vec{E}$ = electric field

$\vec{v}$ = velocity of the particle

$\vec{B}$ = magnetic field

When a magnetic field and a constant current source applied are known, Hall voltage can be calculated by using equation 11

$$V_H = \frac{IB}{qnd} \text{ ……..(11)}$$

Where, I = current

B= magnetic field

d = sample thickness

q= electric charge of a particle

On the other hand, the multiplication of n and d can be mentioned as n_L (layer density). Therefore,

$$n_L = \frac{IB}{q|V_H|} \quad \text{.....(12)}$$

From the above equation n_L layer density of charge carriers of a semiconductor can be calculated by using the measured Hall voltage V_H and given values of I, B and q.

Moreover, Hall mobility can be calculated using the sheet resistance value,

$$\mu = \frac{|V_H|}{R_s IB} \quad \text{.....(13)}$$

Where, μ = Hall mobility

R_s=sheet resistance

4.5.1. Hall voltage measurement for Cuprous Oxide

In order to investigate the semiconductive properties of cuprous oxide, the Hall effect was measured using an instrument which consists of two powerful magnetic coils with variable current supply to adjust the magnetic force acting on the cuprous oxide substrate. Two pairs of electrodes were set up on the surface of the cuprous oxide substrate in order to provide the current supply and measure the Hall voltage (V_H). The detailed electrodes setup is shown in figure 4.6.

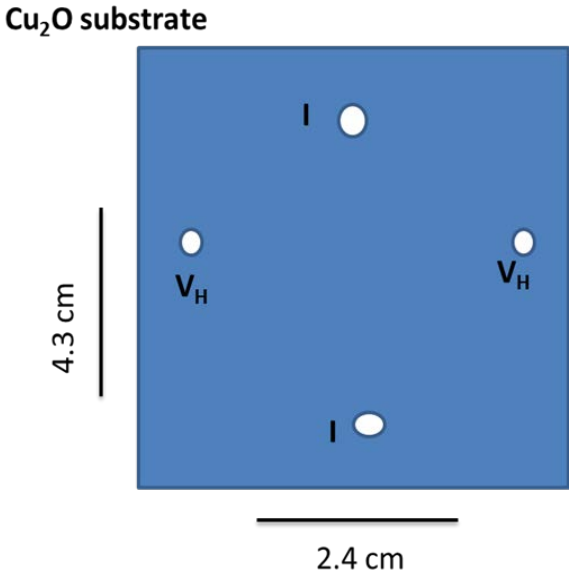

Figure 4.6. Electrode location details. I – Current electrodes and V – Hall voltage probing electrodes

The Hall voltage was measured while a supply current of 53.3 μA was being provided under different magnetic field strengths, at room temperature. At first, the current supply was connected between the two electrodes and the multi-meter was connected between the two V_H electrodes for Hall voltage measurement. After that the magnetic field was applied to the cuprous oxide substrate and the resulting voltage on the multi-meter was recorded. The multi-meter showed a voltage spike, right after the magnetic field was applied. This spike sustained for fraction of a second and then dropped to 0V (steady state). Moreover, there was a very small value of voltage spike approximately 0.2mV after the magnetic field was turned off. In our case, we used the value of the voltage spike after the magnetic field was applied as the Hall voltage and calculated the Hall layer density n_L and Hall mobility μ.

Table 4.1. Hall Voltage measurement of cuprous oxide

Magnetic field(Tesla)	Turn on spike (mV)	Turn off spike(mV)	Steady state(mV)	Layer density ($x10^{17}cm^{-3}$)	Hall Mobility ($cm^2\ V^{-1}sec^{-1}$)
0.2	0.29	0.02	0	2.3	13.56
0.4	0.53	0.02	0	2.5	12.38
0.555	0.59	0.06	0	3.17	9.85
0.74	0.99	0.06	0	2.4	12.5
0.875	1.13	0.06	0	2.6	12.07
1	1.26	0.08	0	2.65	11.78

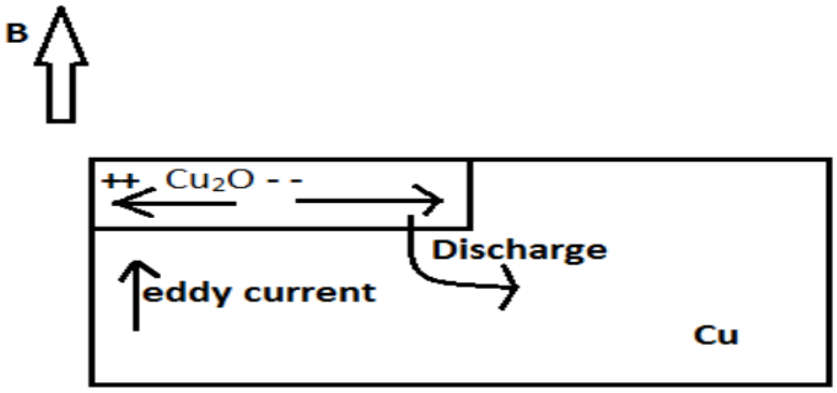

Figure 4.7. Voltage discharge through copper

Although there is no previous report of a similar result mentioned, we hypothesize that the voltage spike was due to eddy current ferromagnetic semiconductor cuprous oxide [86]. Furthermore, the conductive and ferromagnetic copper sheet beneath the cuprous oxide layer was causing the cuprous oxide to discharge through the copper sheet. Due to the discharge through the copper sheet, the constant voltage could not be measured before and after the magnetic field was applied. The main purpose of this project was to investigate a simple painting method in order to make cuprous oxide. To do so, the copper sheet had to be underlying a layer of cuprous oxide and the top

most layer of copper sheet was oxidized to a thin layer of cuprous oxide. Therefore, according to nature of the project, it was not possible to make cuprous oxide without the underlying copper sheet which is a conductor and ferromagnetic material. Therefore, according to Hall Voltage measurement, cuprous oxide can be mentioned as a semiconductor although there was a notable abnormality due to voltage discharge through the copper.

4.5.2. Hall voltage measurement for Zinc Oxide

The measurement of Hall voltage for zinc oxide was performed using the same procedure as that used for cuprous oxide. During the Hall Effect measurement for Zinc oxide, the multi-meter for Hall voltage showed a constant voltage of 23 mV. When the magnetic field was applied, the 23mV increased to the certain level depending on the strength of magnetic field for fraction of a second and settled to 23 mV again. The Hall voltage was denoted as the voltage spike just after the magnetic field was applied. We measured the Hall voltage in different magnetic fields and calculated the layer density n_L and Hall mobility μ. Although Eddy currents may have caused the voltage spike, the constant voltage of 23 mV voltage confirmed that the zinc oxide on the glass substrate behaved as a semiconductor.

Table 4.2. Hall Voltage measurement of zinc oxide

Magnetic field(Tesla)	Turn on spike (mV)	Turn off spike(mV)	Steady state(mV)	Layer density ($x10^{17}cm^{-3}$)	Hall Mobility ($cm^2\ V^{-1}sec^{-1}$)
0.2	0.52	0.02	0.23	1.28	26.99
0.4	0.76	0.02	0.23	1.76	19.73
0.555	0.94	0.06	0.23	1.99	17.43
0.74	1.17	0.06	0.23	2.1	16.42
0.875	1.42	0.06	0.23	2.06	16.83
1	1.57	0.08	0.23	2.13	16.30

Chapter 5.

Photosensitivity of Cu_2O-ZnO device

The manufactured device was tested by using an Aligent 4155C Semiconductor Parameter Analyzer (SPA) under the diode characterization settings.

The device was tested for dark current and illuminated current to study its photovoltaic and photo-conductive characteristics. It was also tested under different temperatures to study its temperature dependency. According to the results we have obtained, the device can be characterized under four categories: photo resistivity, photo diode behaviour, photovoltaic behaviour and temperature dependency.

5.1. Experiment and result of Cu_2O-ZnO device (1) (biased voltage mV)

The device was tested under diode characterization setting and the voltage sweep was set from -200mV and 200mV. Fiber-Lite high intensity illuminator series 180 manufactured by Dolan-Jenner Industries Inc was used as the illuminating light source. The light intensity was 36.3 mW. Figure 5.1 shows the increase in the current when the device was illuminated. Therefore, the resistance of the device decreased under the illumination of light source.

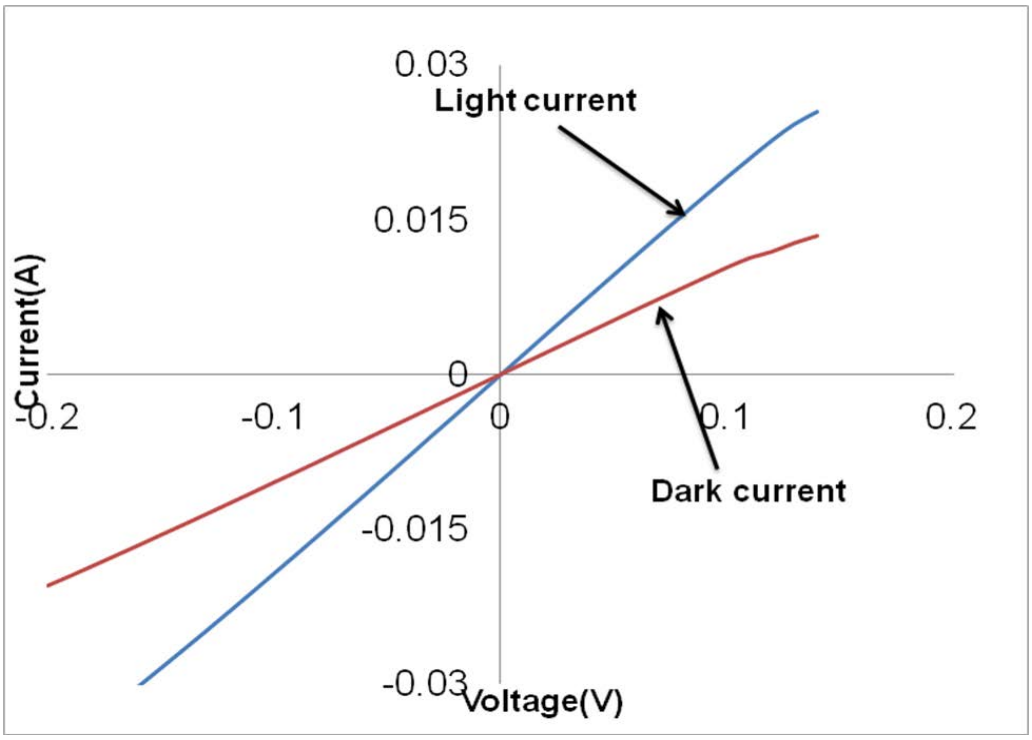

Figure 5.1. V-I response of the Cu-Cu_2O-ZnO device (biased voltage mV range)

According to th V-I response result, the device exhibited more than a 40% increase of current under illumination. On the other hand, the resistance decreased by more than 40% under illuminated current. Therefore, from the characterization result, there was a significant change of resistance when the device was illuminated with a light source. This beheavior can be categorized as photo-resistive beheavior of the device.

5.2. Experiment and result of Cu-Cu_2O-ZnO device (1) (biased voltage μV)

The same device was tested under the diode characterization setting and the voltage sweep set from -800 μV to 800 μV. It was tested for dark and illuminated current using the same light source to characterize the V-I characteristics of the device. According to the result, the device behaviour under dark current was ohmic while the behaviour under light current showed diode characteristics.

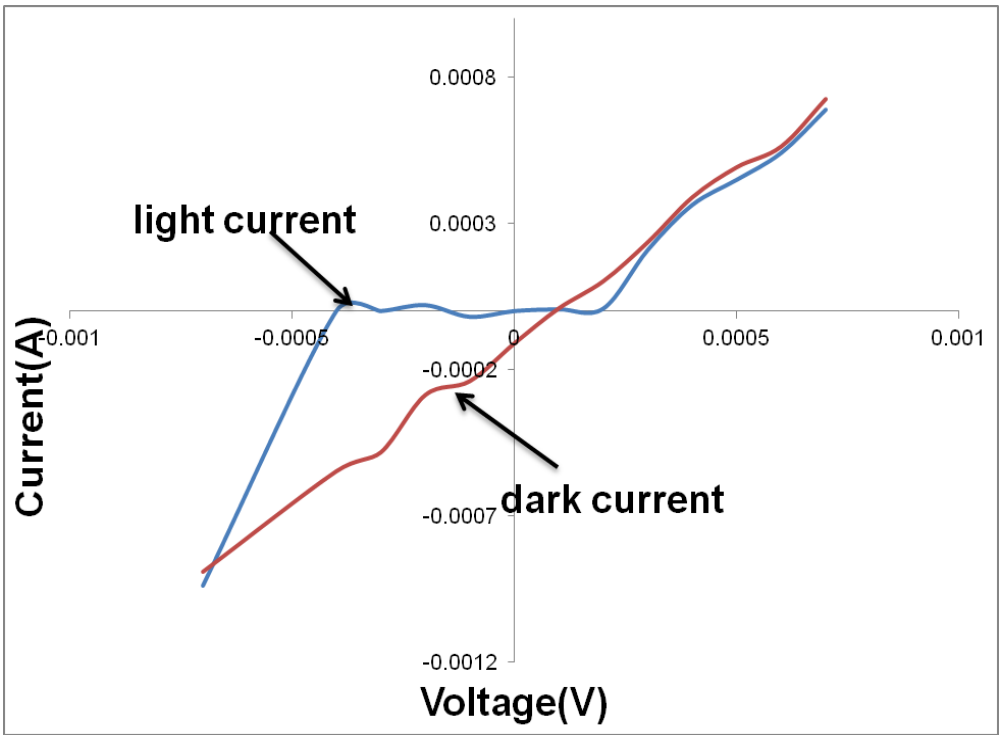

Figure 5.2. V-I response of the Cu-Cu_2O-ZnO device (biased voltage μV range)

5.3. Experiment and results of Cu-Cu_2O-ZnO Device (2)

Device (2), which was heated for 2 hours after the painting process, did not work at the milli-volt bias range. Therefore it was tested at the micro-volt biased voltage range under dark and illuminated current. The result for this device is shown in Figure 5.3 and behaved as a solar cell. The diode characteristic response under illumination showed the increasing amount of current flow which is a typical behavior of a solar cell.

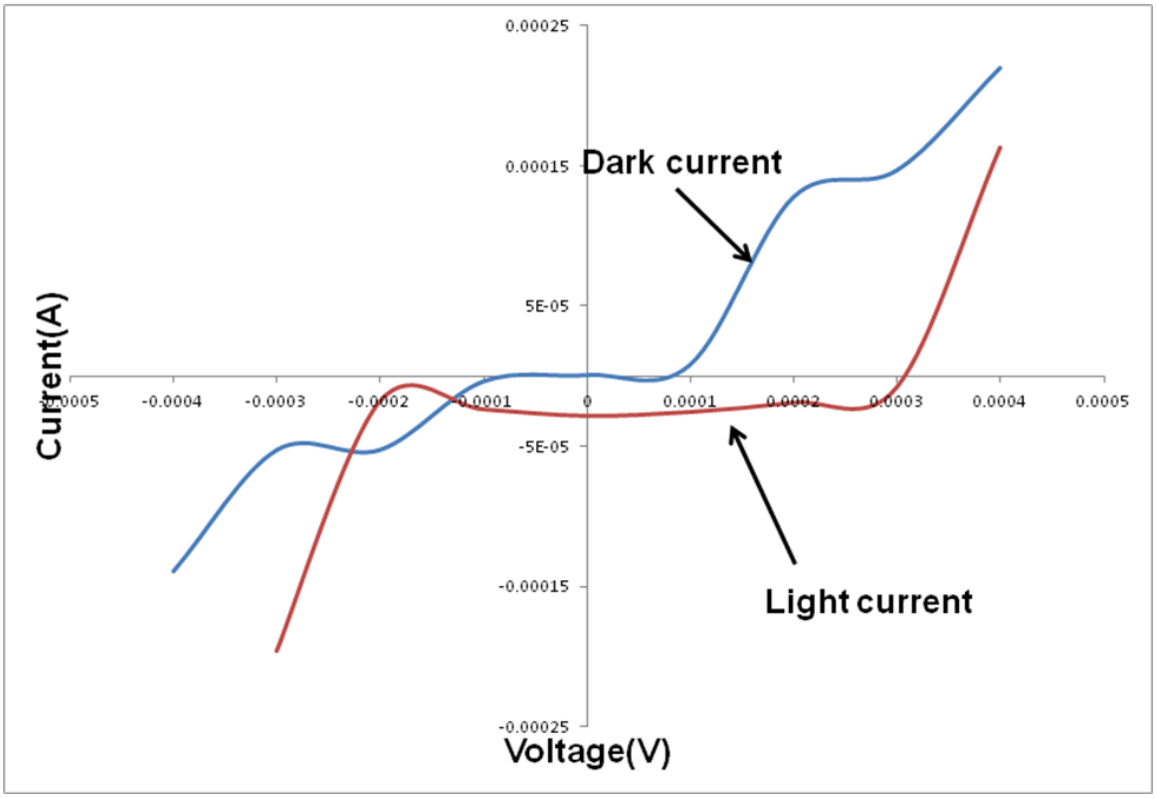

Figure 5.3. V-I response of the device observed as a solar cell

According to the graph, the data values were observed as V_{oc} = 0.3 μV, I_{sc} = 25 μA and Fill factor = 0.32 at the input light power 36.4 mW . From these values, energy conversion efficiency was calculated to be approximately 6.59 x 10^{-6}%. The theorical energy conversion was apporoximately 0.034% calculated from V_{oc} =0.3 μV, fill factor = 0.32 and Isc = 0.144 μA (calculated by dividing Voc by device resistance 2.077 Ω).

Chapter 6.

Conclusion

The goal of this research was to investigate the photosensitivity of Cu_2O-ZnO devices prepared by using a painting technique followed by a low temperature electrochemical deposition process. The surfaces of Cu_2O and ZnO that were examined by SEM showed homogeneousness of the surfaces.

The electrical properties of Cu_2O and ZnO were investigated by Hall Voltage measurement. Although the results from Cu_2O showed abnormality due to voltage discharge through copper substrate, it can be determined as a semiconductor. The results achieved from ZnO showed semi-conductive behaviour.

Two devices were prepared and heated for the different times. When tested, the device that was heated for 30 minutes showed V-I characteristics similar to a photo-resistor or LDR. When it was exposed to light, it showed approximately 40% of an increase in current flow in the milli-volt range biased voltage. The same device when tested with a micro-volt biased voltage showed a different result. Under dark current, the V-I characteristics showed ohmic behaviour whereas under a light source it showed diode characteristics. These results unequivocally demonstrate the photosensitive behavior of the Cu/Cu_2O-ZnO device that has been developed in this research. The second device which was heated for 2 hours showed V-I photovoltaic characteristics. Comparing to dark and light diode characteristics, light diode characteristics showed current increased. However, energy conversion efficiency was only 6.59×10^{-6}%.

Both shorter and longer heating procedures provided a Cu_2O-ZnO interface with low device resistances of approximately 2 Ω which is one of the most important requirements for photosensitive device. Thus, the preparation of Cu_2O using a simple

painting method followed by ZnO electrochemical deposition successfully showed device with photosensitive and photovoltaic properties with very low device resistance

Chapter 7.

Future work

There are a number of areas that need to be considered in further stages of this work to improve the photosensitivity and energy conversion efficiency of the device. In order to maintain the physiochemical conditions that help enhance the stability of Cu_2O, the device should be stored in vacuum desiccators. This would help yield high purity Cu_2O that is free of cupric oxide contaminants. One of the issues in the heating process was that the heating needed to be stopped promptly at two hours. This is because when the sample was heated for more than two hours, the air exposure made the sample contaminated with CuO. Therefore, an air tight oven should be used to heat the painted Cu_2O sample to avoid contamination from air exposure. Moreover, in order to investigate the composition of CuO in the Cu_2O substrate, XPS examination has to be performed and higher quality SEM, TEM and AFS should be used to determine its homogeneity, crystalline nature, cross section and the thickness. The device purity, thickness and crystalline nature could then be used to determine the diffusion length for the recombination of electrons and holes. This is an important property for improving energy conversation efficiency. Furthermore, prior to the electrochemical deposition of ZnO on the Cu_2O surface, bulk resistance should be characterized. In addition, a constant current density should be monitored with a power supply source during ZnO deposition. The electrical contacts for electrochemical deposition and V-I measurements should also be improved.

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