FABRICATION AND OPTIMIZATION OF N-Cu_2O THIN FILM USING ELECTRODEPOSITION METHOD FOR HOMOJUNCTION SOLAR CELL

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This thesis is dedicated to my parents,
family and friends.

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ABSTRACT

Cuprous oxide (Cu_2O) is a promising semiconductor that has been getting attention as the alternative material for solar cell application. It is abundant, low cost and non-toxic to the environment. A homojunction Cu_2O is said to provide high conversion efficiency for solar cell. However, as Cu_2O is a natural p-type semiconductor, it is a challenge to make an n-type Cu_2O. In this study, n-Cu_2O was prepared by using electrochemical deposition. The structural, morphological, optical and electrical properties of the electrodeposited Cu_2O were evaluated after optimizing the parameters for Cu_2O fabrication. Structural characterization of the deposited thin film was also done via X-Ray Diffractions (XRD) to confirm the existence of Cu_2O particles on fluorine-doped tin oxide (FTO) substrate and to determine the crystalline phases of Cu_2O in the sample. The surface morphology of Cu_2O thin films were characterized by Field Emission-Scanning Electron Microscopy (FE-SEM) in order to examine the changes in the surface morphology of the film as the parameter varied. Ultra violet-visible (UV-Vis) spectrophotometer was used to study the optical absorption of Cu_2O and to determine the band gap of the deposited thin film with further calculation including the thickness values of the thin film measured by surface profiler. The resistivity and sheet resistance of Cu_2O thin film were determined via four-point probe measurement test. Lastly, the deposited Cu_2O thin film was confirmed as n-type by using the photoelectrochemical cell (PEC) test. The parameters for electrodeposition of Cu_2O such as the deposition potential, pH solution, solution temperature, and deposition time were optimized at -0.10 V vs. Ag/AgCl, pH 6.5, 60 °C, and 60 minutes, respectively. The band gap obtained from UV-Vis spectrophotometer was 2.45 eV. The successful fabrication of n-Cu_2O will open a new door of Cu_2O-based homojunction development for thin film solar cell application.

ABSTRAK

Kuprum (I) oksida (Cu_2O) merupakan semikonduktor yang telah mendapat perhatian sebagai bahan alternatif bagi aplikasi sel solar. Bahan ini boleh didapati dengan banyak, dalam kos yang rendah dan tidak toksik kepada alam sekitar. Homosimpang Cu_2O dikatakan mempunyai kecekapan penukaran yang tinggi untuk sel solar. Walau bagaimanapun, secara semulajadinya, Cu_2O adalah semikonduktor jenis-p dan untuk membuat jenis-n adalah satu cabaran. Dalam kajian ini, n-Cu_2O telah disediakan dengan menggunakan pengendapan elektrokimia. Sifat-sifat struktur, morfologi, optikal dan elektrikal Cu_2O yang telah dimendapkan dinilai selepas parameter untuk fabrikasi Cu_2O dioptimumkan. Pencirian struktur filem nipis yang telah dimendapkan melalui difraksi sinar-x (XRD) untuk mengesahkan kewujudan partikel Cu_2O pada substrat *'fluorine-doped tin oxide'* (FTO) dan untuk menentukan fasa kristal Cu_2O dalam sampel. Morfologi permukaan filem nipis Cu_2O telah dicirikan oleh pancaran medan-mikroskopi imbasan elektron (FE-SEM) untuk meneliti perubahan morfologi permukaan filem apabila parameter diubah-ubah. Spektrofotometer *'ultra violet-visible'* (UV-Vis) telah digunakan untuk mengkaji penyerapan optik Cu_2O dan untuk menentukan jurang jalur filem nipis yang telah dimendapkan termasuk pengiraan membabitkan nilai ketebalan filem nipis yang diukur menggunakan pembukah permukaan. Kerintangan dan rintangan keping filem nipis Cu_2O telah ditentukan melalui ujian '*four-point probe*'. Akhir sekali, filem nipis Cu_2O yang telah dimendapkan disahkan sebagai jenis-n dengan menggunakan ujian sel fotoelektrokimia (PEC). Parameter untuk pemendapan Cu_2O seperti voltan pemendapan, pH larutan, suhu larutan, dan masa pemendapan telah dioptimumkan masing-masing pada -0.10 V vs. Ag/AgCl, pH 6.5, 60 °C, dan 60 minit. Jurang jalur yang diperoleh dari spektrofotometer UV-Vis adalah 2.45 eV. Kejayaan memfabrikasi Cu_2O jenis-n akan membuka ruang baru kepada industri homosimpang berasaskan Cu_2O untuk aplikasi sel solar.

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LIST OF SYMBOLS AND ABBREVIATIONS

AD	-	anno Domini
AgBr	-	silver bromide
AgCl	-	silver chloride
AM	-	air mass
a-Si	-	amorphous silicon
Au	-	aurum (gold)
bcc	-	body-centered cubic
CdO	-	cadmium oxide
CdTe	-	cadmium telluride
CIGS	-	copper indium gallium selenide
Cu	-	copper
CV	-	cyclic voltammetry
fcc	-	face-centered cubic
FE-SEM	-	field emission – scanning electron microscopy
FTO	-	fluorine doped tin oxide
GaAs	-	gallium arsenide
InP	-	indium phosphide
ITO	-	indium tin oxide
I-V	-	current-voltage
JCPDS	-	Joint Committee on Powder Diffraction Standard
Mg	-	magnesium
MiNT-SRC	-	Microelectronics and Nanotechnology – Shamsuddin Research Centre
MW	-	Mega watt
NaOH	-	sodium hydroxide
PEC	-	photoelectrochemical

rf	-	radio frequency
TCO	-	transparent conducting oxide
TFSC	-	thin film solar cell
UV-Vis	-	ultra violet – visible spectrophotometer
XRD	-	x-ray diffractions
ZnO	-	zinc oxide
Ω	-	ohm
°	-	degree
α	-	absorption spectra
h	-	Planck constant
Cu_2O	-	cuprous oxide
$CuSO_4$	-	copper (II) sulphate
Ga_2O_3	-	gallium (III) oxide
I_{SC}	-	short-circuit current
TiO_2	-	titanium dioxide
V_{OC}	-	open-circuit voltage

CHAPTER 1

INTRODUCTION

Introduction covers the overview, history and development of solar cell technology. Problem statement, objectives, scope, and thesis organization of this study are also stated.

1.1 Overview

Solar cell has become the most attractive future source of energy due to the depletion of current energy sources such as fossil fuels and nuclear energy. Over the past three decades, more fossil fuels and nuclear energy were consumed rather than new reserves were found. Thus a new energy source is needed and a renewable energy is a better option as it is naturally replenished, energy secured, climate change mitigated and economically benefited. Solar energy shows a promising outcome as an energy source because the radiation power that it provides to the earth is 1.8 x 10^{11} MW which is multiple times larger than the current energy demanded by the planet [1-2]. So, harvesting even a small amount of it gives a great source of energy.

Solar cells are devices used to convert sunlight into electricity by the photovoltaic effect. Photovoltaic effect is defined as the creation of voltage or electric current in a material upon exposure of light. This happens because when the light is incident upon a material surface, the electrons in the valence band absorbs energy and become excited, making them jump to the conduction band and become free electrons [3]. There are three basic attributes required in the operation of photovoltaic cell as listed below:

i. the light absorption which generates either electron-hole pairs or excitons,
ii. the charge carriers of opposite type being separated,
iii. the separated carriers being extracted to an external circuit.

Basically, a solar cell structure consists of antireflective coating, p-type semiconductor, n-type semiconductor, a depletion zone between the two semiconductors, an external circuit and front-back electrical contacts. Antireflective coating is used to minimize light from being reflected and guide the light through the photovoltaic cell. While front-back electrical contacts serve as conductors to collect electrons and usually is made out of metal. Electric current is generated inside the depletion zone of the p-n junction. When a photon of light is absorbed by one of the atoms, an electron will be dislodged, creating a free electron and a hole. They have sufficient energy to jump out of the depletion zone and if a wire is connected from cathode to anode, electrons will flow through the wire. This happens due to the attraction between electron and the positive charge of the p-type material. An electric current will be supplied if an external load (e.g. light bulb) is placed on the wire. While the free hole created by the dislodged electron will be attracted to the negative charge of electron and migrates to the back electrical contact and electron-hole recombination happens to restore the electrical neutrality [4-5].

1.2 Background of study

Solar technology is not new as it has long been used as early as the 7th Century when magnifying glass was used to make fire and burn ants by concentrating sun's rays. During this period also, in Alexandria, Egypt, solar energy was used to fire alembics for herbal extractions or for concentrating dilute alcoholic solutions to produce wine and various perfume oils [6]. Until 1200s AD, the applications of solar technology have widen including burning mirrors to light torches for religious purposes, setting fire to wooden ships, providing warmth into houses by building south-facing windows, and etc. This technology advanced into a more complex phase in 1767 when a Swiss scientist, Horace de Saussure built the world's first solar collector which later was used to cook food by Sir John Herschel during his South Africa expedition [7]. On September 27, 1816, a minister in the Church of Scotland, Robert Stirling patented his economiser, a heat engine. One of the working models was used by Lord Kevin during his university classes, and later was used in the Stirling system that concentrates the sun's thermal energy to produce power [8-9].

However, the technology of solar cell truly started only in 1839 when a French physicist, Alexandre-Edmond Becquerel discovered the photovoltaic effect [3, 10]. In his experiment, two electrodes were coated by light sensitive materials, silver chloride (AgCl) or silver bromide (AgBr), and were illuminated with different types of light in a black box that covered an acid solution. The result showed that when the light intensity increased, the electricity increased. Later, after 34 years of the discovery, an English electrical engineer, Willoughby Smith, discovered that selenium is photoconductive, followed with the discovery by William Grylls Adams and Richard Evans Day in 1876, that selenium produces electricity when exposed to light. Even though the power conversion was not enough to run any electrical equipment, the duo scientists proved that a solid material could directly convert light into electricity without heat or moving parts [10]. Over 100 years, researchers worked on the theoretical parts of solar technology such as the discovery of outer photoelectric effect and quantum mechanics, the recognition of the importance of single-crystal semiconductors and the explanation of p/n junction behaviour. Besides that, elements such as copper, cuprous oxide and cadmium sulphide, were discovered to be photoconductive. By 1954, the invention of the first modern silicon solar cell by Daryl Chapin, Gerald Pearson and Calvin Fuller, was announced by Bell Labs with 4% efficiency, and later was increased to 11% [11]. Towards the present time, the efficiencies of solar cell have been improved and material studies for solar cell application have been widened.

All the while, silicon-based cells have been the dominant material for solar cell because of its high conversion efficiency. However, it is difficult and expensive to be produced as it consumes more electricity rather than producing electricity when it is being manufactured [12]. So, researchers were trying to find other materials as alternatives and found out that cuprous oxide (Cu_2O) was one of them. With the material come in abundance, non-toxic and having low cost in production, Cu_2O has been receiving attention as p-type active layer. This is also due to its direct band gap of 2 eV (appropriate range for photovoltaic cells), and its high absorption coefficient [13-14]. In earlier work, Cu_2O has been used as p-type because, even though it is not intentionally doped, the presence of Cu^{2+} ions instead of Cu^{+} ions at some lattice cites cause Cu^{+} vacancies. This happens in order to maintain the charge neutrality and consequently result in formation of p-type conductivity [15]. Due to that, over the past three decades have shown the fabrication of p-Cu_2O solar cell with metal/Cu_2O Schottky junctions [16], and p-n heterojunctions such as n^+-ZnO/n-Ga_2O_3/p-Cu_2O [17], n-$Mg_xZn_{1-x}O$/p-Cu_2O [18], n-TiO_2/p-Cu_2O [19], n-TCO/p-Cu_2O [20], and CdO/Cu_2O [21].

In terms of Cu_2O thin film fabrication, there are several methods such as electrodeposition [15, 22], thermal oxidation [23], chemical vapor deposition [24], sol-gel process [25], sputtering [26], and activated reactive evaporation [27]. In this study, the method that will be used to fabricate n-Cu_2O thin film is electrodeposition method. The process of deposition from aqueous solution is simple, inexpensive, producing controllable film thickness, producing large scale deposition, and it can also be done at low temperature. Moreover, the parameters such as pH solution, bath temperature, electrode potential, and deposition time can be manipulated and controlled in order to determine the effects that they will have on the structural, optical, morphological, and electrical properties of the thin film [28]. Thus, by using electrodeposition method, the optimal conditions for better n-Cu_2O thin film can be chosen. The structures of n-Cu_2O are expected to be compact and homogenous with preferential plane of (111) in order to get smooth and good electron transfer, and further to reduce lattice mismatch when coupled with p-Cu_2O for thin film solar cell.

1.3 Problem statement

Latest studies focus on increasing the conversion efficiency of solar cell for other materials in order to replace silicon due to reasons mentioned before. Nevertheless, to this date, Cu_2O as the active layer in a p-n heterojunction structure achieved the highest conversion efficiency of around 5%, even though theoretically, the efficiency of Cu_2O solar cells should be around 20%. Generally, researchers have proposed that the best way to increase the efficiency of Cu_2O-based solar cells is to produce a p-n homojunction that has a large built-in potential of 1.7 eV [14]. Homojunction also performs better compared to heterojunction due to lack of interface strain between n- and p-type [29]. Problems faced by heterojunction solar cell such as finding proper energy level alignment between p- and n-type, and lattice mismatch between semiconductors, can be disregarded in homojunction solar cell [30]. However, Cu_2O is naturally p-type, so to fabricate an n-type is difficult and rarely reported. Thus, this work on improving the properties of n-Cu_2O thin films as a part of homojunction thin film solar cell is much needed and indispensable.

Another factor affecting the overall performance of thin film solar cell fabricated by electrodeposition is the substrate. Different substrates have been used in previous studies including metals such as copper, titanium, platinum, gold, etc. and transparent conducting oxide glass such as indium-doped tin oxide (ITO) and fluorine-doped tin oxide (FTO). There were not many studies using FTO compared to ITO even though it serves many advantages. It is more transparent which allows more lights to be absorbed, has larger conductivity, more stable against heating and environment and less expensive. Moreover, indium can diffuse to adjacent layers which will alter the characteristics of p-n materials. In this study, the chosen substrate was FTO as it offers many benefits towards performance of thin film solar cell where other substrate which the previous studies used were lack of.

1.4 Objective

This study aims on fulfilling several objectives which are:

i. To fabricate n-type Cu_2O thin film by using electrodeposition method.
ii. To characterize the surface morphology, structural, optical and electrical properties of the deposited n-Cu_2O thin films.
iii. To determine the optimal condition of n-Cu_2O thin film for homojunction solar cell application by manipulating deposition potential, pH solution, solution temperature, and deposition time.

1.5 Project scope

The scopes of this study are as follows:

i. Fabrication of n-type Cu_2O thin film via electrodeposition method.
ii. Optimization of deposition potential range via cyclic voltammetry when solution temperature and pH solution are manipulated. (40 – 60 °C, pH 5.0 – 6.5) [57-61]

iii. Deposition of n-type Cu_2O thin film when the deposition parameters: deposition potential, pH solution, solution temperature, and deposition time are manipulated. (-0.05 to – 0.2 V vs. Ag/AgCl, pH 5 – 6.5, 30 – 70 °C, 5 – 70 minutes) [57-61]

iv. Investigation of the parameters manipulation effects on the structural, morphological and optical properties via X-Ray Diffractometer (XRD), Field Emission Scanning Electron Microscopy (FE-SEM) and Ultraviolet-Visible Spectrophotometer (UV-Vis), respectively. Determination of polarization of Cu_2O deposit using Photoelectrochemical Cell (PEC), the four-point probe measurement test and determining the thickness of Cu_2O deposit using surface profiler.

1.6 Thesis organization

Chapter 1 covers the overview of solar cell history, background of study, problem statement, objectives and project scope. Chapter 2 includes literature review such as solar cell development, details on cuprous oxide and photoelectrochemical cell. Chapter 3 describes the methodology of this study consisting of fluorine-doped tin oxide substrate preparation, cuprous oxide solution preparation, electrodeposition process and characterization tests. Chapter 4 discusses the findings of this study which include the deposition potential range of cuprous oxide and the effect of deposition parameters on fabricated cuprous oxide. Chapter 5 concludes the results of this study and offers recommendation on improvements for future study.

CHAPTER 2

LITERATURE REVIEW

The literature review covers the theoretical explanation, historical, development and problem discussions of the subjects related to this study. Fabrication of n-Cu_2O thin film and homojunction solar cell will be discussed in detail in order to realize this project.

2.1 Solar cell

Generally, the development of solar cell has gone through three generations which are crystalline silicon (first generation), thin film solar cell (second generation) and emerging photovoltaic (third generation).

The first generation cells, also called conventional wafer-based cells were made up of materials such as monocrystalline silicon and polysilicon. Monocrystalline or single crystalline solar cells are the most unique among other solar cells. They are not only easily recognizable by their color, they are also considered to be made from a very pure type of silicon. The solar cell is more efficient at converting sunlight into electricity when the alignment of the silicon molecules are purer. This type of solar cell is the most efficient among solar cells with the recorded efficiencies of almost 20% [31]. Monocrystalline solar cells are made of a cylindrical-shaped design called 'silicon ingots' that increase the performance. To make up the solar panel, the cylindrical ingots are cut on four sides making them having rounded edges rather than being square like other types of solar cells. In addition to being the most efficient, monocrystalline solar cells are also the most space-efficient. This being said as fewer cells are needed per unit of electrical output. They also last the longest among all types of solar cells with the warranties being offered by manufacturers up to 25 years. However, with many advantages, monocrystalline cells comes with a price tag [32].

This type of solar cells is the most expensive and the manufacturing process is complex. This is because, the material being cut on four sides waste a lot of silicon which sometimes take up more than half. On investors and consumers point of view, this disadvantage discredits all the advantages that monocrystalline cells offer.

Another first generation cell, polycrystalline solar cells were first introduced to the industry in 1981. Instead of going through cutting process like monocrystalline, the silicon for polycrystalline is melted and poured into a square mold. By using this way, less silicon is wasted during the manufacturing process, making it more affordable on costing [31]. However, due to lower purity, polycrystalline is less efficient with the efficiency of around 13-16%. Consequently, more space are needed in polycrystalline cells for a similar amount of power output generated by monocrystalline cells. Compared to monocrystalline, polycrystalline has lower heat tolerance that makes it less efficient in high temperatures.

The second generation solar cells is called thin film solar cell. From 2002 to 2007, the growth rates were around 60% and by 2011, the thin film solar cell industry covered 5% of all cells on the market. One major advantage that this solar cell offers is the use of small amount of active material compared to silicon solar cell [33]. The active material is sandwiched between two panes of glass. Even though the weight is doubled compared to silicon cells that use single glass pane, the ecological impact is lesser, which was determined from life cycle analysis. In thin film solar cells generation, various type of semiconducting material are used such as cadmium telluride (CdTe), copper indium gallium selenide (CIGS), gallium arsenide (GaAs) and amorphous silicon (a-Si). By December 2013, the installation of CdTe per watt costed at $0.59 and the CIGS technology achieved 20.4% conversion efficiency in laboratory demonstrations while GaAs technology reached 28%. The production cost is their another advantage where the mass production is a lot easier compared to crystalline-based modules, consequently needed relatively lower cost. Besides that, thin film technologies are less impacted by high heat and shading which lead to the continuous grow of the research and development [34].

The third generation solar cell is called the emerging photovoltaic or organic photovoltaic cell. Like its name, this generation uses organic materials, often organometallic compounds which most of them are still in the development process and not yet been commercially applied. Some electronic conductive polymers, small molecules and inorganic substances are also included in this generation. Despite being low in efficiency, stability and strength compared to traditional solar cells, researchers are positive towards this generation as it promises a low cost, high efficiency solar cells with a flexible large scale production capability [35]. For now, emerging photovoltaic technology is still being developed aggressively and not ready for mass commercialization. Table 2.1 summarizes the different types of solar cells and the challenges occur in each type.

Table 2.1: Types of solar cells and their challenges [36]

<table>
<tr><th colspan="2">Generation</th><th>Type</th><th>Challenges</th></tr>
<tr><td colspan="2" rowspan="2">First (Silicon)</td><td>Single crystalline</td><td rowspan="2">i) Device structure development
ii) Crystal quality improvement</td></tr>
<tr><td>Polycrystalline</td></tr>
<tr><td rowspan="4">Second (Compound/Thin Film)</td><td>Silicon</td><td>Amorphous</td><td>i) Junctions multiplication</td></tr>
<tr><td>III-V Semiconductor</td><td>GaAs/InP</td><td rowspan="3">i) Band gap control
ii) Junctions multiplication</td></tr>
<tr><td>II-VI Semiconductor</td><td>CdTe/Cds – Cu_2S/Cds</td></tr>
<tr><td>Chalcopyrite Semiconductor</td><td>CIGS</td></tr>
<tr><td rowspan="2">Third (Emerging)</td><td>Organic</td><td>Pentancene</td><td rowspan="2">i) Materials development
ii) Device development</td></tr>
<tr><td>Photochemical</td><td>Dye sensitized</td></tr>
</table>

2.1.1 Thin film solar cells

Thin film solar cells (TFSC) are the second generation solar cells which consist of multiple thin film layers of photovoltaic materials, deposited on a substrate such as metal, glass or plastic. Unlike the conventional solar cells, the film thickness of TFSC is much thinner which varies from a few nanometres (nm) to tens of micrometres (µm) [37]. This enables TFSC to be flexible, lighter and lesser in friction or drag which give benefit in terms of solar panels implementation. More areas can be covered such as forests, solar fields, remote government sites, street and traffic lights, etc.

REFERENCES

1. Parida, B., Iniyan, S. and Goic, R. A review of solar photovoltaic technologies. *Renew. Sustain. energy Rev.* 2011. 15(3): 1625–1636.

2. Jones, S. *Solar power of the future: New ways of turning sunlight into energy*. The Librar. Rosen Publishing Group. 2003.

3. Goetzberger, A., Hebling, C. and Schock, H. W. Photovoltaic materials, history, status and outlook. *Mater. Sci. Eng. R Reports*. 2003. 40(1): 1–46.

4. Würfel, P. Basic structure of solar cells. In: Würfel, P. (Ed). *Physics of solar cells: From principles to new concepts*, Germany: Wiley-VCH Verlag GmbH. pp. 109–136; 2007.

5. Green, M. A. Photovoltaics: Technology overview. *Energy Policy*. 2000. 28(14): 989–998.

6. Delyannis, E. Historic background of desalination and renewable energies. *Sol. Energy*. 2003. 75: 357–366.

7. Petrova-Koch, V. Milestones of solar conversion and photovoltaics. In: Petrova-Koch, V., Hezel, R. and Goetzberger, A. (Eds). *High Efficient Low Cost Photovoltaics*. Springer-Verlag Berlin Heidelberg. pp. 1–5; 2009.

8. Tomar, A., Jain, L. and Batra, P. Solar energy- Finding new ways. *Int. J. Res. Advent Technol.* 2013.1(4): 1–6.

9. Goetzberger, A., Luther, J. and Willeke, G. Solar cells: Past, present, future. *Sol. Energy Mater. Sol. Cells*. 2002. 74: 1–11.

10. Fraas, L. M. and Partain, L. D. Solar cells: A brief history and introduction. In: Chang, K. (Ed). *Solar cells and their applications*. 2nd Ed. Wiley. pp. 1–15; 2010.

11. Chapin, D. M., Fuller, C. S. and Pearson, G. L. A new silicon pn junction photocell for converting solar radiation into electrical power. *J. Appl. Phys.* 1954. 25(5): 676–677.

12. Wöhrle, D. and Meissner, D. Organic solar cells. *Adv. Mater*. 1991. 3: 129–138.

13. Fernando, C. A. N. and Wetthasinghe, S. K. Investigation of photoelectrochemical characteristics of n-type Cu_2O films. *Sol. Energy Mater. Sol. Cells*. 2000. 63: 299–308.

14. Han, K. and Tao, M. Electrochemically deposited p-n homojunction cuprous oxide solar cells. *Sol. Energy Mater. Sol. Cells*. 2009. 93: 153–157.

15. Jayewardena, C., Hewaparakrama, K. P., Wijewardena, D. L. A. and Guruge, H. Fabrication of n-Cu_2O electrodes with higher energy conversion efficiency in a photoelectrochemical cell. *Sol. Energy Mater. Sol. Cells*. 1998. 56: 29–33.

16. Iwanowski, R. J. and Trivich, D. Enhancement of the photovoltaic conversion efficiency in Cu/Cu_2O Schottky barrier solar cells by H^+ ion irradiation. *Phys. Status Solidi*. 1986. 95: 735–741.

17. Minami, T., Nishi, Y. and Miyata, T. Effect of the thin Ga_2O_3 layer in n^+-ZnO/n-Ga_2O_3/p-Cu_2O heterojunction solar cells. *Thin Solid Films*. 2013. 549: 65–69.

18. Duan, Z., Du Pasquier, A., Lu, Y., Xu, Y. and Garfunkel, E. Effects of Mg composition on open circuit voltage of Cu_2O–$Mg_xZn_{1-x}O$ heterojunction solar cells. *Sol. Energy Mater. Sol. Cells*. 2012. 96: 292–297.

19. Ichimura, M. and Kato, Y. Fabrication of TiO_2/Cu_2O heterojunction solar cells by electrophoretic deposition and electrodeposition. *Mater. Sci. Semicond. Process*. 2013. 16: 1538–1541.

20. Tanaka, H., Shimakawa, T., Miyata, T., Sato, H. and Minami, T. Electrical and optical properties of TCO – Cu_2O heterojunction devices. *Thin Solid Films*. 2004. 469–470: 80–85.

21. Hameş, Y. and San, S. E. CdO/Cu_2O solar cells by chemical deposition. *Sol. Energy*. 2004. 77: 291–294.

22. Xue, J. B., Shen, Q. Q., Liang, W., Liu, X. G., Bian, L. P. and Xu, B. S. Preparation and formation mechanism of smooth and uniform Cu_2O thin films by electrodeposition method. *Surf. Coat. Technol*. 2013. 216: 166–171.

23. Musa, A. O., Akomolafe, T. and Carter, M. J. Production of cuprous oxide, a solar cell material, by thermal oxidation and a study of its physical and electrical properties. *Sol. Energy Mater. Sol. Cells*. 1998. 51: 305–316.

24. Jeong, S. H. and Aydil, E. S. Heteroepitaxial growth of Cu_2O thin film on ZnO by metal organic chemical vapor deposition. *J. Cryst. Growth*. 2009. 311: 4188–4192.

25. Akhavan, O., Tohidi, H. and Moshfegh, A. Z. Synthesis and electrochromic study of sol–gel cuprous oxide nanoparticles accumulated on silica thin film. *Thin Solid Films*. 2009. 517: 6700–6706.

26. Akimoto, K., Ishizuka, S., Yanagita, M., Nawa, Y., Paul, G. K. and Sakurai, T. Thin film deposition of Cu_2O and application for solar cells. *Sol. Energy*. 2006. 80: 715–722.

27. Balamurugan, B. and Mehta, B. R. Optical and structural properties of nanocrystalline copper oxide thin films prepared by activated reactive evaporation. *Thin Solid Films*. 2001. 396: 90–96.

28. Chen, L. C. Review of preparation and optoelectronic characteristics BN of Cu_2O-based solar cells with nanostructure. *Mater. Sci. Semicond. Process.* 2013. 16: 1172–1185.

29. Xiong, L., Huang, S., Yang, X., Qiu, M., Chen, Z. and Yu, Y. p-Type and n-type Cu_2O semiconductor thin films: Controllable preparation by simple solvothermal method and photoelectrochemical properties. *Electrochim. Acta*. 2011. 56: 2735–2739.

30. Yu, L., Xiong, L. and Yu, Y. Cu_2O homojunction solar cells: F-doped n-type thin film and highly improved efficiency. *J. Phys. Chem. C*. 2015. 119(40): 22803–22811.

31. Kumar Moluguri, N, Rama Murthy, C. and Harshavardhan, V. Solar energy system and design - Review. *Mater. Today Proc.* 2016. 3(10 Part B): 3637–3645.

32. Guha, S., Yang, J. and Yan, B. Amorphous and nanocrystalline silicon solar cells and modules. *Ref. Modul. Mater. Sci. Mater. Eng.* 2016. 6: 308–352.

33. Lee, T. D. and Ebong, A. U. A review of thin film solar cell technologies and challenges. *Renew. Sustain. Energy Rev.* 2017. 70(C): 1286-1297.

34. Khan, J. and Arsalan, M. H. Solar power technologies for sustainable electricity generation – A review. *Renew. Sustain. Energy Rev.* 2016. 55: 414–425.

35. Mohanty, P. and Tyagi, A. Introduction to solar photovoltaic technology. In: Ahuja, S. (Ed). *Food, Energy, and Water*. Boston: Elsevier. pp. 309–348; 2015.

36. Pandey, A. K., Tyagi, V. V., Selvaraj, J., Rahim, N. A. and Tyagi, S. K. Recent advances in solar photovoltaic systems for emerging trends and advanced applications. *Renew. Sustain. Energy Rev.* 2016. 53: 859–884.

37. Hosenuzzaman, M., Rahim, N. A., Selvaraj, J., Hasanuzzaman, M., Malek, A. B. M. A. and Nahar, A. Global prospects, progress, policies, and environmental impact of solar photovoltaic power generation. *Renew. Sustain. Energy Rev.* 2015. 41: 284–297.

38. Chopra, K. L., Paulson, P. D. and Dutta, V. Thin-film solar cells: An overview. *Prog. Photovoltaics Res. Appl.* 2004. 12(2–3): 69–92.

39. Hamakawa, Y. *Thin-film solar cells: Next generation photovoltaics and its applications*. Volume 13. Springer Science & Business Media. 2003.

40. Korzhavyi, P. A. and Johansson, B. Literature review on the properties of cuprous oxide Cu_2O and the process of copper oxidation. *Swedish Nucl. Fuel Waste Manag. Co*. 2011. Technical: 1-41.

41. Abdu, Y. and Musa, A. O. Copper (I) oxide (Cu_2O) based solar cell - A review. *Bayero J. Pure Appl. Sci.* 2011. 2: 8–12.

42. Olsen, L. C., Addis, F. W. and Miller, W. Experimental and theoretical studies of Cu_2O solar cells. *Sol. Cells*. 1982. 7(3): 247–279.

43. Rakhshani, A. E. Preparation, characteristics and photovoltaic properties of cuprous oxide-A review. *Solid. State. Electron.* 1986. 29(1): 7–17.

44. Nishi, Y., Miyata, T. and Minami, T. Electrochemically deposited Cu_2O thin films on thermally oxidized Cu_2O sheets for solar cell applications. *Sol. Energy Mater. Sol. Cells*. 2016. 155: 405–410.

45. Ottosson, M. and Carlsson, J. O. Chemical vapour deposition of Cu_2O and CuO from CuI and O_2 or N_2O. *Surf. Coatings Technol.* 1996. 78: 263–273.

46. Drobny, V. F. and Pulfrey, L. Properties of reactively-sputtered copper oxide thin films. *Thin Solid Films*. 1979. 61: 89–98.

47. Fortunato, E., Barquinha, P. and Martins, R. Oxide semiconductor thin-film transistors: A review of recent advances. *Adv. Mater*. 2012. 24: 2945–2986.

48. Mittiga, A., Salza, E., Sarto, F., Tucci, M. and Vasanthi, R. Heterojunction solar cell with 2% efficiency based on a Cu_2O substrate. *Appl. Phys. Lett.* 2006. 88(16): 163502.

49. Ievskaya, Y., Hoye, R. L. Z., Sadhanala, Musselman, A. K. P. and MacManus-Driscoll, J. L. Improved heterojunction quality in Cu_2O-based solar cells through the optimization of atmospheric pressure spatial atomic layer deposited $Zn_{1-x}Mg_xO$. *J. Vis. Exp*. 2016. 113: 53501.

50. Siripala, W. and Jayakody, J. R. P. Observation of n-type photoconductivity in electrodeposited copper oxide film electrodes in a photoelectrochemical cell. *Sol. Energy Mater*. 1986. 14: 23–27.

51. Mukhopadhyay, A. K., Chakraborty, A. K., Chatterjee, A. P. and Lahiri, S. K. Galvanostatic deposition and electrical characterization of cuprous oxide thin films. *Thin Solid Films*. 1992. 209: 92–96.

52. Golden, T. D., Shumsky, M. G., Zhou, Y., VanderWerf, R. A., Van Leeuwen, R. A. and Switzer, J. A. Electrochemical deposition of copper (I) oxide films. *Chem. Mater.* 1996. 8: 2499–2504.

53. Zhou, Y. and Switzer, J. A. Electrochemical deposition and microstructure of copper (I) oxide films. *Scr. Mater.* 1998. 38: 1731–1738.

54. Georgieva, V. and Ristov, M. Electrodeposited cuprous oxide on indium tin oxide for solar applications. *Sol. Energy Mater. Sol. Cells*. 2002. 73: 67–73.

55. Jayathileke, K. M. D. C., Siripala, W. and Jayanetti, J. K. D. S. Electrodeposition of p-type, n-type and p-n homojunction cuprous oxide thin films. *Sri Lankan J. Phys.* 2008. 9: 35–46.

56. Tang, Y., Chen, Z., Jia, Z., Zhang, L. and Li, J. Electrodeposition and characterization of nanocrystalline cuprous oxide thin films on TiO_2 films. *Mater. Lett.* 2005. 59(4): 434–438.

57. Wijesundera, R. P., Hidaka, M., Koga, K., Sakai, M. and Siripala, W. Growth and characterisation of potentiostatically electrodeposited Cu_2O and Cu thin films. *Thin Solid Films*. 2006. 500: 241–246.

58. McShane, C. M., Siripala, W. P. and Choi, K. S. Effect of junction morphology on the performance of polycrystalline Cu_2O homojunction solar cells. *J. Phys. Chem. Lett.* 2010. 1: 2666–2670.

59. Hsu, Y. K., Wu, J. R., Chen, M. H., Chen, Y. C. and Lin, Y. G. Fabrication of homojunction Cu_2O solar cells by electrochemical deposition. *Appl. Surf. Sci.* 2015. 1–6.

60. Wijesundera, R. P., Gunawardhana, L. K. A. D. D. S. and Siripala, W. Electrodeposited Cu_2O homojunction solar cells: Fabrication of a cell of high short circuit photocurrent. *Sol. Energy Mater. Sol. Cells*. 2016. 157: 881–886.

61. Siripala, W., Perera, L. D. R. D., De Silva, K. T. L., Jayanetti, J. K. D. S. and Dharmadasa, I. M. Study of annealing effects of cuprous oxide grown by electrodeposition technique. *Sol. Energy Mater. Sol. Cells*. 1996. 44: 251–260.

62. Han, X., Han, K. and Tao, M. Characterization of Cl-doped n-type Cu_2O prepared by electrodeposition. *Thin Solid Films*. 2010. 518(19): 5363–5367.

63. Han, K., Kang, F., Han, X. and Tao, M. Enhanced crystal grain size by bromine doping in electrodeposited Cu_2O. *Thin Solid Films*. 2012. 520: 5239–5244.

64. Fultz, B. and Howe, J. M. Diffraction and the X-ray powder diffractometer. In: *Transmission Electron Microscopy and Diffractometry of Materials*. 4th Ed. Springer Berlin Heidelberg. pp. 1–57; 2013.

65. Seiler, H. Secondary electron emission in the scanning electron microscope. *J. Appl. Phys.* 1983. 54: R1.

66. Tissue, B. M. Ultraviolet and visible absorption spectroscopy. In: *Characterization of Materials*. John Wiley & Sons, Inc. 2002.

67. Smith, A. M. and Nie, S. Semiconductor nanocrystals: Structure, properties, and band gap engineering. *Acc. Chem. Res.* 2010. 43: 190–200.

68. Cardona, M. and Yu, P. Y. Optical properties of semiconductors. In: Bhattacharya, P., Fornari, R. and Kamimura, T. (Eds). *Comprehensive*

Semiconductor Science and Technology. Amsterdam: Elsevier. pp. 125–195; 2011.

69. Wei, D. and Amaratunga, G. Photoelectrochemical cell and its applications in optoelectronics. *Int. J. Electrochem. Sci*. 2007. 2: 897–912.

70. Zhang, B., Li, F., Yu, F., Wang, X., Zhou, X., Li, H., Jiang, Y. and Sun, L. Electrochemical and photoelectrochemical water oxidation by supported cobalt-oxo cubanes. *ACS Catal.* 2014. 4: 804–809.

71. Poon, C. Y. and Bhushan, B. Comparison of surface roughness measurements by stylus profiler, AFM and non-contact optical profiler. *Wear*. 1995. 190(1): 76–88.

72. Zheng, J. Y., Jadhav, A. P., Song, G., Kim, C. W. and Kang, Y. S. Cu and Cu_2O films with semi-spherical particles grown by electrochemical deposition. *Thin Solid Films*. 2012. 524: 50–56.

73. Laidoudi, S., Bioud, A. Y., Azizi, A., Schmerber, G., Bartringer, J., Barre, S. and Dinia, A. Growth and characterization of electrodeposited Cu_2O thin films. *Semicond. Sci. Technol.* 2013. 28(11): 115005.

74. El-Shaer, A., Tadros, M. T. Y. and Khalifa, M. A. Fabrication of homojunction cuprous oxide solar cell by electrodeposition method. *Nat. Sci.* 2015. 13(5): 14–22.

75. Poizot, P., Hung, C. J., Nikiforov, M. P., Bohannan, E. W. and Switzer, J. A. An electrochemical method for CuO thin film deposition from aqueous solution. *Electrochem. Solid-State Lett.* 2003. 6(2): C21–C25.

76. Wu, H., Zhang, N., Wang, H. and Hong, S. First principle study of oxygen-vacancy Cu_2O (111) surface. *J. Theor. Comput. Chem.* 2012. 11(6): 1261–1280.

77. Ying, Y., Juan, H., Xiaohui, N. and Hongsheng, T. Effect of potential on the conductivity of electrodeposited Cu_2O film. *SPIE 9560, Solar Hydrogen and Nanotechnology X, 95600W*, 2015, pp. 6.

78. Zhao, W., Fu, W., Yang, H., Tian, C., Li, M., Li, Y., Zhang, L., Sui,Y., Zhou, X., Chen, H. and Zou, G. Electrodeposition of Cu_2O films and their photoelectrochemical properties. *CrystEngComm*. 2011. 13(8): 2871–2877.

79. Jiang, X., Zhang, M., Shi, S., He, G., Song, X. and Sun, Z. Microstructure and optical properties of nanocrystalline Cu_2O thin films prepared by electrodeposition. *Nanoscale Res. Lett.* 2014. 9(1): 1–5.

80. Arun, P., Tyagi, P. and Vedeshwar, A. G. Large grain size dependence of resistance of polycrystalline films. *Phys. B*. 2002. 322: 289–296.

81. Wang, L. and Tao, M. Fabrication and characterization of p-n homojunctions in cuprous oxide by electrochemical deposition. *Electrochem. Solid-State Lett.* 2007. 10: H248.

82. Paracchino, A., Brauer, J. C., Moser, J. E., Thimsen, E. and Graetzel, M. Synthesis and characterization of high-photoactivity electrodeposited Cu_2O solar absorber by photoelectrochemistry and ultrafast spectroscopy. *J Phys Chem C*. 2012. 116(13): 7341-7350.

83. Li, G., Huang, Y., Fan, Q., Zhang, M., Lan, Q., Fan, X., Zhou, Z. and Zhang, C. Effects of bath pH on structural and electrochemical performance of Cu_2O. *Ionics (Kiel).* 2016. 22(11): 2213–2223.

84. Wang, L. *Preparation and characterization of properties of electrodeposited copper oxide films*. PhD Thesis. University of Texas at Arlington; 2006.

85. Wang, C., Xu, J., Shi, S., Zhang, Y., Liu, Z., Zhang, X., Yin, S. and Li, L. Structural, optical and photoelectrical properties of Cu_2O films electrodeposited at different pH. *RSC Adv*. 2016. 6(6): 4422–4428.

86. Messaoudi, O., Assaker, I. B., Gannouni, M., Souissi, A., Makhlouf, H., Bardaoui, A. and Chtourou, R. Structural, morphological and electrical characteristics of electrodeposited Cu_2O: Effect of deposition time. *Appl. Surf. Sci.* 2016. 366: 383–388.

87. Rumbles, G., Lian, T. and Murakoshi, K. Electron transfer in nanomaterials: *Proceedings (The Electrochemical Society)*. May 9th - 14th 2004. San Antonio, Texas. 2006. pp. 1-458.

88. Jiang, T. F., Xie, T. F., Yang, W. S., Chen, L. P., Fan, H. M. and Wang, D. J. Photoelectrochemical and photovoltaic properties of p-n Cu_2O homojunction films and their photocatalytic performance. *J Phys Chem C*. 2013. 117(9): 4619-4624.