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MODELING AND SIMULATION OF NANOSTRUCTURED COPPER OXIDES SOLAR CELLS FOR PHOTOVOLTAIC APPLICATION

by

George Chukwuebuka Enebe

(201100840)

Thesis submitted to the Faculty of Engineering and the Built Environment in partial fulfilment of the requirements for

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in

MECHANICAL ENGINEERING SCIENCE

AT THE

UNIVERSITY OF JOHANNESBURG

SUPERVISOR: Prof. Tien Chien-Jen

CO-SUPERVISOR: Dr. Kingsley Ukoba

2019
As the candidate’s supervisors, we have approved this thesis for submission.

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Name: Prof. T-C Jen

Signed: ..........................  Date:
Name: Dr. O.K. Ukoba
DECLARATION 1 – PLAGIARISM

1. George Chukwuebuka Enebe, declare that:

   1. The research reported in this dissertation, except where otherwise indicated is my original research.
      a. This dissertation has not been submitted for any degree or examination at any other University.
      b. This dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons.

   2. This dissertation does not contain other persons' writing, unless specifically acknowledged as being sourced from other researchers. Where other written sources have been quoted, then: Their words have been re-written but the general information attributed to them has been referenced.
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Signed: ___________________________ Date: 15/10/2019
DECLARATION 2 - PUBLICATIONS

This section presents the articles that form part and/or include the research presented in this dissertation. The following papers have been accepted and published, or are under review:

ISI/SCOPUS/DoHET Accredited Journals


International and DHET accredited conferences


This candidate is the main and corresponding author for all the publications and Prof. Tien Chien Jen and Dr. Kingsley Ukoba are the supervisors.
DEDICATION

This thesis is dedicated to every young person, especially the African child, who is struggling to make it in life. Never give up on your dreams. Also, to my family members and friends for sharing in my pain and joy all of the time.
ACKNOWLEDGEMENTS

I sincerely appreciate the opportunity afforded me by my supervisor Prof. Tien-Chien Jen for granting me the privilege to undertake my M-Eng. program under his direct supervision and furnishing me with the necessary resources, as well as his unstinting impact towards the success of my research. For that, I am most grateful. Prof Jen was always accommodating, kind, and ready with phenomenal encouragement. I am awed by the knowledge he imparted to me thus far.

I want to extend my genuine and unadulterated gratitude to my co-supervisor, Dr. Kingsley Ukoba for his patience, encouragement and relentless guidance and support during the course of my program. I am deeply appreciative of his swift and thoughtful responses to my challenges, his support through pushing me beyond my perceived limits, his guidance and the amazing role he played towards the success of my study.

I am grateful and thankful to my parents Chief and Lolo. G.O Enebe, without whom, it would not have been possible for me to go in pursuit of academic development for excellence. Special thanks and gratitude to Mr. George Onatu and family for granting me this rare privilege and his remarkable role in the success of my study. I am appreciative of his ever-supportive approach, invaluable guidance and pushing my limits for this study.

I would also like to recognize Mr. Donald Ugwuokafor and Mr. Ogochukwu Chijioke and their various family members for their immense support and encouragement from the start of my program to its completion. I also highly appreciate their unlimited assistance and insightful advice. I will be forever grateful.

I take this opportunity to give thanks to Solar Cell Capacitance Simulator (SCAPS) for the computing resources availed to me.

Finally, how can I forget to appreciate and thank my wonderful and supportive friends and colleagues of the JENano research group for their perceptive contributions and solidarity towards the successful completion of this work? Thank you.
ABSTRACT

The increasing global population and demand for clean and sustainable energy has led to increased research on affordable and efficient energy materials. Solar energy materials are one of those promising options. There is increased research on nanostructured metal oxide solar cell as an option for inexpensive, clean and efficient solar cells material. Copper oxide based solar cells are among those attracting interest although the efficiency is still low. This study investigates the numerical modeling and simulation of nanostructured copper oxide (cuprous and cupric oxide) heterojunction solar cells for photovoltaic applications. This is with a view to providing an optimized cell efficiency to aid experimentation and the development of high-efficiency metal oxide solar cells. The inspiration for this investigation is to give premise for experimental design for affordable, non-harmful and efficient alternative material for silicon-based solar cells. This was performed using Solar cells capacitance simulator (SCAPS). The optimization was performed by varying the effect of film thickness and by varying the effect of annealing temperature on properties of the copper oxide solar cells using SCAPS for the numerical analysis.

The simulation and optimization was modeled firstly by varying the thickness of both the absorber layer and the buffer layers of Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn nanostructured heterojunction solar cells. The input parameter for SCAPS, obtained from literatures includes; temperature of 300K for the film thickness, input power of 1000W/m$^2$ using illumination of AM1.5 lamp, under varying thickness of 0.5 µm to 10.0 µm for the absorber layers (Cu$_2$O and CuO) and 0.05 µm to 6.0 µm for the buffer layer (TiO$_2$) respectively. The simulated solar cell displayed a short-circuit current ($J_{sc}$) of 24.0764 A and 26.0516 A, open-circuit voltage ($V_{oc}$) of 1.0486 V and 0.0435 V, fill factor (FF) of 63.20 % and 71 % with an efficiency ($\eta$) of 1.6 % and 8.05 % respectively, at an absorber layer thickness of 500 nm and buffer layer thickness of 50nm. Furthermore, the defect density was obtained for each solar cell.

Secondly, the Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn nanostructured heterojunction solar cells was numerically analysed under varied annealing condition. Three annealing conditions were considered i.e. the as-deposited (300K), air and nitrogen annealed (423.15 K). Other working conditions include; an illumination of AM 1.5G with a 500 W Xenon lamp representing the sunlight. For this simulation, silver was used as the electrode/contact. The absorber layer thickness was 2000 nm and buffer layer thickness was 200 nm. The simulation report showed that nitrogen
annealed samples had best efficiency. The as-deposited efficiency for Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn heterojunction was 1.25 % and 0.21 % respectively. The fill factor of air annealed was 49.5 % and 53.50 % and efficiency was 3.23 % and 0.37 % for Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn heterojunction respectively. Nitrogen annealed was 53.50 % and 64.01 % for fill factor and efficiency was 3.85 % and 0.47 % for Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn heterojunction respectively.

These reports will open new platforms for optimization and fabrication of nanostructured Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn heterojunction solar cells in pursuit of developing an affordable, efficient, sustainable and environmentally friendly solar cell device from metal oxides mostly in developing countries.
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## NOMENCLATURE

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<thead>
<tr>
<th>Symbol</th>
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<th>Unit</th>
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<tr>
<td>I-V</td>
<td>Current-voltage</td>
<td>Ampere-volts</td>
</tr>
<tr>
<td>J-V</td>
<td>Current density-voltage</td>
<td>Amperes/m²-volts</td>
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<tr>
<td>J_{sc}</td>
<td>Short-circuit current density</td>
<td>Amperes</td>
</tr>
<tr>
<td>P_{in}</td>
<td>Power in</td>
<td>Watts</td>
</tr>
<tr>
<td>P_{max}</td>
<td>Maximum power</td>
<td>Watts</td>
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<tr>
<td>V_{oc}</td>
<td>Open-circuit voltage</td>
<td>Volts</td>
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<td>Cu_{2}O</td>
<td>Copper I Oxide</td>
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<td>CuO</td>
<td>Copper II oxide</td>
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<td>FF</td>
<td>Fill factor</td>
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<td>ITO</td>
<td>Indium tin oxide</td>
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<td>O</td>
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<td>Ti</td>
<td>Titanium</td>
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<tr>
<td>TiO_{2}</td>
<td>Titanium oxide</td>
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**ACRONYMS/ABBREVIATIONS**

<table>
<thead>
<tr>
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<tr>
<td>Cu₂O</td>
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<td>Fill Factor</td>
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<td>Gross Domestic Product</td>
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<td>Indium Tin Oxide</td>
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<td>National Renewable Energy Laboratory</td>
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<td>O</td>
<td>Oxygen</td>
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<td>P&lt;sub&gt;in&lt;/sub&gt;</td>
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<td>Photovoltaic</td>
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<tr>
<td>SCAPS</td>
<td>Solar Cell Capacitance Simulator</td>
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<td>Ti</td>
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CHAPTER 1: INTRODUCTION

1.1 Introduction

The growing human population and challenges of fossil-based fuels has necessitated investment and research for improved and sustainable energy supply using renewable energy. The international renewable energy agency reported that renewable energy now supplies one third of global capacity (IRENA, 2019). Renewable energy continues to advance especially in the past five years with additional 7.9% added in 2018. Solar energy and wind energy contributed 84% of the total growth in 2018. Solar energy contributed 94 GW representing 24% of the global renewable energy addition in 2018. Despite this increment in solar energy, Africa seems to be lagging behind. Asia contributed 64 GW representing 70%, Germany 3.6 GW, Australia 3.8 GW and USA 8.4 GW. Egypt is the only African country that contributed to the global solar energy increase in 2018. This has necessitated calls for the domestication of solar energy in Africa since the continent is endowed with the solar irradiance needed to make it thrive. Solar cells modeling is one of the tools used to improve the properties of solar cells, especially the cell efficiency. This study will model a nanostructured metal oxide (copper oxides) solar cell using Solar Cell Capacitance Simulator (SCAPS).

The rays from the sun is an endowment from nature to mankind capable of powering and meeting all of mankind’s energy needs. The energy from the sun supplies about 3.846 ×1026 watts (Sawant, Bondre, Joshi, Tambavekar & Deshmukh, 2018 and Johnson, 2018). This shows that the energy from the sun in an hour is capable of powering the earth for a year. It is a clean, renewable source although it needs to be adequately stored for it to be reliable (Ni, Leung, Sumathy, & Leung, 2006 and Ukoba, Inambao and Eloka-Eboka, 2018). However, some factors continue to hinder the full potential of sunlight as an energy source. These limiting factors include land requirement/space, efficiency, public perception and cultural acceptability (Hyder, Sudhakar, & Mamat, 2018).

Different methods exist for harnessing the sun’s energy, but photovoltaic application is the popular and commonly used technique to generate electricity from the sun. Solar cells are electrical gadgets that produce electricity from sunlight using photovoltaic method and it comprises of both physical
and chemical phenomenon (Kurokawa, Nguyen, & Taguchi, 2018). Solar cells have been subject to different generations and materials with silicon solar cells being the most popular with higher efficiency (Green, 2009). Nanostructured metal oxide continues to gain interest due to the low cost, ease of tuneability and promising efficiency. Modeling and simulation is a cost effective tool for improving solar cell efficiency using the Solar Cell Analysis Program SCAPS which is basically used for opto-electrical simulations of the 1-Dimentional(SCAP-1D) or 2-Dimentional(SCAP-2D) structures of semiconductor layers to simulate the different parameters of the selected metal oxide (Copper oxide) for optimization.

Copper oxides are among the cost effective solar energy materials (Rakhshani, 1986). It is very affordable, readily available with promising potential for photovoltaic applications (Mitiga, Salza, Sarto, Tucci and Vasanthe 2006). Copper oxide as a semiconductor dates back to 1920 when the Cu2O rectifier was discovered (Grondhal, 1926) and in the 1930s when the photosensitive device using CuO was studied (Lange, 1939). The environmentally friendly nature, abundance and easy and low-cost deposition technique makes copper oxide based thin films sought after in the quest for affordable, clean and efficient solar cells development. Copper oxides band gaps are close to the ideal band gap (between 1eV and 2 eV) of solar energy with Cu2O having 2.0eV and CuO having 1.5eV (Kidowaki, Oku, & Akiyama, 2012 and Rai, 1988).

SCAPS modeling tool gained prominence in 1996 to 2000. It is capable of simulating the effect of the properties of materials to understand the cell characteristics (Decock et al., 2012).

1.2 Research Motivation

Although, most developed and emerging countries are going green using solar and wind energy to provide inexpensive, clean and efficient energy to her citizens, other countries are yet to be fully domesticated with this green energy called solar. Although, most of the countries possess the potential for full domestication of the technology, many are hindered by factors including adequate home-grown research. The Council for Scientific and Industrial Research (CSIR) South Africa Annual Report (2018) shows the potency of solar cells to produce about 250KW at a level energy cost of 0.87 R/kWh. This is shown through the solar system installed on the rooftop of one of the buildings on its Pretoria campus. The motivation for this study is to encourage domestication of
solar energy in Africa through more study on solar cells in Africa’s laboratories that will result in an affordable, clean and efficient power supply using solar energy.

1.3 Problem Statement

Clean, efficient, affordable and sustainable energy resulting in a cleaner environment, tops global human challenges. Numerous research studies and investment is being undertaken to provide cleaner air, which is affordable and provides sustainable energy. Emerging economies and developed countries are switching from fossil-based fuels to renewable energy. According to International Renewable Energy Agency (IRENA) capacity statistics (2019), emergence and developed economies led to the over two-thirds power generation capacity global addition of 171 gigawatts (GW) in 2018. However, Africa only contributed 8.4 % behind Asia of 11.4 % and Oceania of 17.7 %. However, the report also suggested the need for a speedy deployment of renewable energy globally. Solar energy contributed 94 GW representing 24 % of the 171 GW of the renewable energy added in 2018. Unfortunately, Egypt was the only African country to experience this addition in solar energy with Asia contributing 64 GW representing 70 % of the global solar energy growth. Africa’s geographical positioning and average solar irradiance of 220 W/m² favours solar technology (Tinner, Conedera, Ammann & Lotter, 2005). However, several factors have been observed to slow the domestication of solar technology with cost and lack of uninterrupted power supply to perform research being the major factors (UNDP, 2018; Kaygusuz, 2011 and Ukoba, Eloka-Eboka, & Inambao, 2017).

Researchers in Africa are currently focusing on solar cells development with emphasis on affordability and efficiency. This has encouraged low equipment cost related to solar cell deposition technique and theoretical modeling to reduce manpower and logistic costs. Among the numerous modeling tools, SCAPS has gained prominence owing to the free and open access and in-depth understanding on solar cells modeling (Chelvanathan, Hossain, & Amin, 2010 and Verschraegen, & Burgelman, 2007). Hence, this study will attempt to give a theoretical framework for development of cheap, clean and efficient solar cells using SCAPS modeling software.

It would be quite beneficial both economically and environmentally for domestication of electricity generated using solar power in South Africa and the rest of Africa. These benefits include cost saving and health benefits due to reduction in air and water pollution hitherto emitted
by these coal and natural gas plants. In addition, the benefit of solar cells modeling includes the cost saving associated with experimental, chemicals and equipment, better efficiency compared to experiments, and gaining of an in-depth insight and to break down barriers between experimental studies (Moebius & Laan, 2015).

1.4 Background of Study

Solar cells being the bedrock of solar energy, are classified into three broad categories i.e, organic solar cells, inorganic solar cells (semiconductor) and silicon based solar cells (Song and Ichimura, 2013). Crystalline Silicon solar cells are at present domestically and commercially viable and have the highest conversion efficiency although with a high cost of production (De Wolf, Descoeudres, Holman, & Ballif, 2012 and Shah, Platz, & Keppner, 1995). Although, amorphous silicon solar cells have reduced production costs with a lower efficiency (14-15 %). The research focus on organic solar cells is aimed at solving the poor stability problem associated with the solar cells. However, the huge interest in solar cells semiconductors is attributed to the low production costs and potential for high solar cell efficiency. Solar cells of CdTe and CuInSe2 (CIS) are the commonest semiconductor solar cells. The major merit of CdTe and CIS over silicon solar cells is the absorption coefficient, which is large allowing for small film thickness. Similarly, the deposition technique is simple leading to a reduced production cost. Unfortunately, Te and In are rare earth elements and Cd and Se are hazardous. On the other hand, copper oxides are non-toxic, low cost, and abundant in nature. They are semiconductor metal oxides.

Modeling and simulation is used to optimize the solar cells variables to improve the efficiency and at same time minimize cost. SCAPS was initially used to model and simulate CuInSe2 and CdTe solar cells family (Chadel, Chadel, Bouzaki, Aillerie, Benyoucef, & Charles, 2017). However, the flexibility of the software has made it easier to be deployed in modeling of other types of solar cells. Limited work exists for the simulation of metal oxides using SCAPS. Hence, the need for this research and investigation is to simulate a nanostructured copper oxide (CuO and Cu2O) thin film solar cells with the intent of optimizing the efficiency to satisfy the need for cheap substitute solar cells for photovoltaic applications.
1.5 Solar Cells Development

According to “History of solar cell” by the U.S Department of Energy, Solar technology has been around for a long time. Its development started as at the 7th century BC (Malanima, 2011). Mankind started experimenting with the sun by focusing the sunlight with glass and mirrors to light fires and burning of animals (Perlin, 2013). Today, this has evolved into more advanced technologies like solar powered vehicles and solar powered airplanes.

The super powers in the 3rd century; Greeks and Romans used the sunlight burning mirrors to light torches for religious purposes and this was done by the Chinese in 20A.D (Maruga, N.K., 2014). The 1st to 4th Century A.D. saw sunlight being used in making warm water in the famous Roman Bathhouses through the use of large windows that were designed to face the south in order to allow the sun’s rays in. The Anasazi who live in North America lived in houses that faced the south, which captured the winter sun to demonstrate passive solar design in the 1200s A.D (History of Solar cell by U.S Department of Energy).

Horace de Saussure fabricated the world’s first solar harvester in 1767, which Sir John Herschel took to South Africa in his voyage in the 1830s for his cooking (Ruskin, 2017). A preacher in the Church of Scotland by name Robert Stirling applied for a patent in September 27, 1816 for his heat engine identified as an economizer at the Chancery in Edinburgh, Scotland (Kongtragool and Wongwises, 2003; Sufian, Ullah, Mazumder, & Baidya, 2014). This heat engine was used in a solar thermal electric technology to generate power. It concentrates the sun’s thermal energy in its operation to produce power (Kolin, 1992).

It was not until 1839 that photovoltaic effect was discovered. Edmond Becquerel, a French researcher, found it while testing with an electrolytic cell (Grätzel, 2001). The electrolytic cell comprises of two metal electrodes positioned in an electricity-conducting solution. This photovoltaic effect improved when visible to light. French mathematician August Mouchet and his assistant constructed the predecessor of modern parabolic dish collector known as the solar-powered engine which was used for various applications in the 1860s (Timilsina, 2017).

In 1873, Willoughby Smith learnt about the photoconductivity ability of Selenium while Williams Grylls Adams and Richard Evans Day found the ability of selenium to generate current when visible to sunlight in 1876, thus proving that a hard material could convert light into electricity.
without heat or locomotive parts. Though, selenium solar cells could not absorb sufficient sunshine to power electrical equipment, a paper was later published on a selenium cell known as 'The action of light on selenium. Charles Fritts was able to define the earliest solar cells produced from selenium wafers in 1883. In 1887, Heinrich Hertz learnt that ultraviolet light improves the lowest voltage enough to trigger a spark to jump amid two metal electrodes (History of Solar cell by U.S Department of Energy).

In 1904, Wilhelm Hallwachs learnt that certain metals and metal oxides are photosensitive, Copper and cuprous oxide. He made a semiconductor-junction solar cell out of it. A year later, Albert Einstein published his paper on photoelectric effect on a quantum basis. About a decade after Albert Einstein’s publication, the actualization of a barrier layer in photovoltaic devices was discovered. In 1916, Robert Millikan was able to experimentally prove the photoelectric effect and Jan Czochralski established a method of growing single-crystal silicon (Czolchraski, 1885 – 1953).

In 1932, Audobert and Stora discovered the effect of photovoltaics in Cadmium selenide (CdSe), which is the photovoltaic material in used today. 1948 - Gordon Teal and John Little adapted the Czochralski technique of crystal progress to yield single-crystalline germanium and further advanced to silicon (David, 2006). On April 25, 1954, Bell Labs declared the development of the first functional silicon solar cell (American Physical Society News, 2009 and Chapin et al, 1954). The result of the cells recorded a 6% efficiency. This was the first Western Electric licensed commercial solar cell technologies in 1955. That same year, Hoffman Electronics-Semiconductor Division developed a 2% efficient marketable solar cell, selling for $25/cell or $1,785/watt. Mandelkorn T., U.S. Signal Corps Laboratories, developed n-on-p silicon solar cells in 1958. This was more resistant to radiation effect and was suitable for space. Hoffman Electronics developed 9% efficient solar cells. This gave rise to the development of Vanguard I, the earliest solar powered satellite and was propelled with a 0.1W, 100 cm² solar panel.

The first amorphous silicon PV cells was developed in 1976 by David Carlson and Christopher Wronski of RCA Laboratories, with an efficiency of 1.1%. In 1980, the Institute of Energy Conversion at University of Delaware developed the first thin film solar cell above 10% efficiency using Cu2S/CdS technology. In 1985, a 20% efficient silicon cell was achieved by the Centre for Photovoltaic Engineering at the University of New South Wales.
In 1988, the Dye-sensitized solar cell was manufactured by Michael Grätzel and Brian O'Regan (chemist). The photo-electrochemical cells work as an organic dye compound within the cell and costs half as much as silicon solar cells. A novel record was set in Solar Cell Technology in 2006, thereby breaking the “40 Percent Efficient” Sunlight-to-Electricity Barrier (Brown, 2011). In the year 2008, another novelty in solar cell efficiency was envisaged. NREL Scientists achieved 40.8% conversion rate of a photovoltaic device of sunlight converted to electricity. However, it was below the concentrated energy of 326 sun that it was realized. The inverted metamorphic triple-junction solar cell was invented and independently measured at NREL (NREL Public Relations, 2008). In 2011, the fast-growing factories in China curbed the cost of manufacturing to about $1.25 per watt for silicon photovoltaic modules leading to more installations worldwide (Koshmr and Masia, 2010).

Photovoltaics examination and progress will intensify its importance in recent materials, cell models, along with new methods to develop solar materials. Leading to a time where our fabrics and our transportation networks are able to generate clean and safe power. With recent trends at the rate at which photovoltaic application is advancing, the cost of power generation will be challenging regarding alternative sources of electricity in years to come. The history of solar cells efficiency is presented in Figure 1.1 since 1975 to date and projected efficiency for the various classes of solar cells. The figure acts as a guide towards the next big things in solar cells efficiency and potentials promising materials.
Figure 1.1: Distribution of the best research-cell efficiencies (Girtan M, 2018)
1.5.1 History and Origin of Solar Cells

Photo is the Greek word for light while voltaic refers to electricity (from Alessandro Volta, an Italian Physicist who invented the electric battery). Photovoltaic is commonly used as the process of transformation of light energy (or solar energy) into electric energy. The fundamental science governing the effect of photovoltaics originated in 1839 through a nineteen-year-old Alexandre Edmond Becquerel, a French physicist. Becquerel discovered this conversion phenomenon of sunlight to electricity as he was conducting a study with metal electrodes and electrolytes. In 1883, an American scientist Charles Fritts, developed the earlier selenium wafers solar cell. Edward Weston received the US patent for the first "solar cell" in 1888. In 1901 Nikola Tesla was awarded a US patent for a "method of utilizing an apparatus for the generation of radiant energy" (Tesla., 1901). The pace of advancement really increased after the publication of the impressive Einstein's paper entitled “On a Heuristic Viewpoint Concerning the Production and Transformation of Light”. The publishing of this paper in 1905, proposed a theoretical explanation for the photoelectric effect (Einstein, 1905). An experiment validating the claim of Einstein's theory of the photoelectric effect was achieved by Robert Millikan a few years later. This lead to awarding the 1922 Physics Nobel Prize to Einstein for the success of his work on the photoelectric effect. Approximately three decades later, a Bell laboratories team unveiled the photoelectric abilities of silicon and hurriedly produced a Si solar cell realizing an efficiency of 6%. The initial satellites were basically the era this solar cell was first used in. By then, the commercial solar age had begun. During the following years, the advancements concentrated on special applications. By the 1970's oil crisis, also referred to as the ‘oil shock’, when the price of the oil quadrupled in less than half a year (Hegedus and Lugue., 2003), alternative sources of energy gained a more reputation.

More recently, global warming and climate change have become issues of ever-growing concern. Renewable energy source utilization has become even more encouraged. In fact, the rising attention that global warming has increased, has forced the world leaders to embrace some goals in order to minimize this effect. The Kyoto Protocol is an example of how the leaders decided to face the problem. On the Kyoto Protocol the goal was the reduction, by 2012, of at least 5.2% on the emissions of greenhouse gases by developed countries regarding levels recorded in 1990. These conditions, together with considerable subsidy programs have provided the means for an extraordinary growth of the photovoltaic industry for a relatively long period.
of time. Nowadays the photovoltaic sector is rapidly advancing and exists largely without subsidies (Hegedus and Lugue., 2003).

**Characteristics of nanostructured solar cells**

- The semiconductor junction is effectively controlled owing to the thinner structure of the films, causing a reduced recombination effect and energy loss forming a quicker light path generation for electrons and holes to pass through.
- Energy band gap of the layers can be fabricated to preferred values by changing the size of the nano-particles making the absorber and buffer layers very flexible.
- Ability to create multiple reflection of light in films leading to long lasting active optical channels for absorption.

### 1.5.2 The simulation program SCAPS

Different tools exist for simulating thin films solar cells (Decock, Khelifi, Burgelman, 2011). Simulation tools such as AMPS (Hernandez-Como & Morales-Acevedo 2010), ASPIN (Smole, Topiç, & Furlan, 1994), SCAPS (Burgelman, Nollet and Degrave, 2000), AFORS-HET (Stangl, Leendertz, & Haschke, 2010) possess the ability to simulate solar cell. However, there is more interest in SCAPS owing to its versatility, being freely available and is easy to understand the window based environment. SCAPS was developed as a window application program at Gent University using LabWindows/CVI of National Instruments. SCAPS was introduced to the photovoltaic community in 1998 (Burgelman et al., 2000). SCAPS allows users to input parameters such as voltage, temperature, illumination and frequency (Burgelman et al., 2000). In SCAPS environment, the device to be simulated and can be characterized as a pile of up to seven (7) layers of semiconductor, with different properties. It also allows entries for interface restrictions and two layers for back and front contacts. The layers are analysed by describing the numerical parameters. The output is calculated using I-V, C-f, C-V, Q(λ), band diagrams, electric field, partial recombination currents, carrier densities, characteristics.

### 1.6 Copper Oxides

Copper oxide comprises of two stable oxides namely cuprous oxide (Cu₂O) and cupric oxide (CuO). These two metal oxides have diverse physical properties, crystal structures, different colours, electrical properties (Serin et al., 2005 and Amin, 2012) although they have p-type conductivity (Johan et al., 2011). Cu₂O has an electron affinity of 3.2eV (Jeong et al., 2008) while
CuO is 4.07eV (Wang, Zhao and Li, 2011). Cu₂O has high hole mobility (Li, Akimoto and Shen, 2009) and is used for possible material for hole transport in heterojunction solar cells (Lee et al., 2013). CuO is the most stable state of oxidized copper and a rare earth metal (Filipic and Cvelbar, 2012). However, Cu₂O has a better potential of producing low cost solar cells. It is abundant in nature, low cost and simple in preparation and deposition technique. However, studies have opined that the low efficiency recorded for Cu₂O so far maybe due to the high temperature of preparation and deposition and suggested a low temperature may give a better efficiency (Weichman and Reyes, 1980). Cu₂O has the largest thermal expansion of 4.3 when compared to other metal oxide (Tylecote, 1960 and Tylecote, 2017). Also, CuO can be used for solar cells application based on the bandgap (Koffyberg and Benko, 1982).

Limited literature exists for Copper oxides solar cells despite the photovoltaic potentials. The National Science Foundation and Joint centre attempted the first Cu₂O for photovoltaic application in 1978 (Hossain, Alharbi & Tabet, 2015). Attempts were made to develop n-type Cu₂O and heterojunction Cu₂O solar cells, which resulted in low efficiency (Hossain and Albarbi, 2013). Akimoto et al., (2006) deposited Cu₂O thin film for solar cells application. Also, Song and Ichimura (2013) deposited Cu₂O electrochemically on ITO substrate and obtained a decrease in the bandgap after dipping in 30 % hydrogen peroxide. The AlₓGa₁−ₓO pulsed laser deposition technique on a thermal Cu₂O doped Na gave the highest copper oxide efficiency of 6.1% (Wong et al., 2016). The closest is 2.88 % efficiency obtained by incorporating a mixture of CuO and Cu₂O nanopowder. In Electrochemical doping and electrodeposition technique, the highest efficiency of copper oxide is 0.64 % after annealing treatment and surface defect passivation. Lastly, the deposition of Cu₄O₅/GaN using a sapphire substrate gave an efficiency of ~10⁻² %. Figure 1.2 gives the detail of power efficiency and reported year of cupric and cuprous solar cells.
Figure 1.2 Shows the power conversion efficiency for Cu$_2$O and CuO heterojunction solar cells vs. year of publication (Wong et al., 2016)

1.7 Research questions

The quest to obtain a better efficiency has led to several experiments and use of simulation and modeling tools. This led to the following questions being formulated to direct the study.

i. What are the needs for affordable, abundant and efficient nanostructured copper oxide solar cells?

ii. Can nanostructured copper oxide solar cell be simulated and optimized for a better efficiency?

iii. What is the annealing effect on the optimization of nanostructured copper oxide solar cell?

iv. What is the effect of thickness towards the optimization of a nanostructured copper oxide solar cell?

v. Which simulation tool should be used and why?

1.8 Aim of the Study:

This study aims to numerically model and optimize through the simulation of nanostructured copper Oxide Thin film based solar cell system for photovoltaic applications using SCAPS
1.9 Objectives

The general objective of this study is to optimize the efficiency of nanostructured copper oxide solar cell for PV application using Solar Cell Analysis Program in 1Dimension (SCAP1D).

1.9.1 Specific Objective:

- The task of this study includes;
  - i Evaluating the need for affordable, abundant and efficient nanostructured copper oxide solar cell and simulation tools used for solar cell simulations.
  - ii Explore through thorough reviews the operational potentials of nanostructured copper oxide (CuO & Cu$_2$O) based solar cells as alternative affordable material domestication.
  - iii Identifying the parameters and values to effectively optimize the nanostructured copper oxide solar cell.
  - iv Identifying the effect of annealing and thickness on nanostructured copper oxide solar cell.
  - v Using SCAPS as a modeling tool to simulate copper oxide for parametric optimization.
  - vi Suggesting the simulation and nanostructured copper oxide (CuO or Cu$_2$O) solar cell with better efficiency potentials.

1.10 Significance of the Study

The rate at which the modern world is advancing towards a sustainable energy generation, coupled with the necessity of the fourth industrial revolution, it is imperative to state that for efficient execution and proper dissemination of the discoveries in this effect, sustainable power generation is of the utmost importance. Due to the limited literature/studies on the modeling of copper oxide despite its potential properties of being abundant on the earth’s crust, processing ease with low processing energy, together with its toxic free nature (Wadia et al., 2009), prompted the use of SCAPS simulation tool to model nanostructured copper oxide solar cells. Its semiconducting potentials necessitates the modeling of this metal oxide for desired efficiency combined with being a cheap alternative solar cell device. With the recent issues of load shedding in South Africa, the CSIR (South Africa) reported through ‘The Creamers Media Engineering news’ in February, 2019 that solar cells PV and the concentrated solar power helped to reduce the effects of the system imbalance which estimates 10.8 TWh or 4.6% of South Africa’s system load observed to be higher than the imported electricity into South Africa.
1.11 Scope of the Study:

The study will be limited to the modeling of nanostructured CuO and Cu$_2$O solar cells using SCAPS for photovoltaic application with focus on annealing and film thickness. This will serve as a guide towards the fabrication of low-income solar cells in developing countries.

1.12 Thesis layout

Chapter 1: is the introductory part of this study and provides the rationale, problem statement, and background study, along with the aim, overall objectives, significance, scope and thesis layout. The thesis produced a total of two (2) publications; one (1) journal and one (1) conference paper along with two (2) prepared manuscripts.

Chapter 2: Provides a comprehensive review of modeling and simulation of nanostructured copper oxides solar cells for photovoltaic applications and previous research studies related to this investigation.

Chapter 3: Gives the modeling and optimization of the nanostructured Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ thin films through annealing (heat treatment).

Chapter 4: Gives the modeling and optimization of the nanostructured Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ thin films by varying film thickness.

Chapter 5: Presents the conclusions and future work recommendations.

Chapter 6: Shows the appendices associated with this study
CHAPTER TWO

2 LITERATURE REVIEW

2.1 Introduction

The trend at which the technological advancement in solar cell technology towards a sustainable energy distribution has been significant in recent times. The expensive nature of silicon as a semiconducting material necessitates the need for cheaper solar cells. Currently, silicon is mostly used for traditional and commercial solar cells semiconducting material (Ukoba, Inambao and Eloka-Eboka, 2017). Studies have shown that thinner solar cells possess the potentials of an ideal performance at a much-reduced cost, which gave rise to the nano-structuring of metal oxide thin fills (Ukoba, Inambao and Adeoye, 2018). Regardless of the rate at which the metal oxide solar cells are being fabricated (Ty and Yanagi, 2015; Ukoba, Inambao and Eloka-eboka, 2018; Liyanage et al., 2015), there is a need to investigate and adopt a modeling approach for indepth interpretation of the device principles.

This quest for cheaper and efficient solar cell material singled Copper oxide semiconducting potentials out as an intriguing material for photoelectric study (MT Kibria et al., 2016). Cu$_2$O and CuO as a solar cell material possess the characteristics of being cheap and abundantly accessible.

The semiconducting abilities of Cu$_2$O was recognised in 1920. Cu$_2$O brought about a big boost to the photovoltaic community in the seventies (Suleiman et al., 2013). This is due to the fact that electricity is the pioneer of the basic amenities necessary for human existence be it; good health, agricultural production and clean water treatment and distribution (Huynh and Stringer, 2018).

These methods of electricity generation have been adopted and practiced in many countries for its potency as a renewable source of energy to non-hydro alternatives (Blaschke et al., 2013). Recent advancements in solar cells production involves the use of metal oxides with lower production costs than the silicon-based wafers and possesses a significant amount of optical absorption and chemical stability (Dumitru et al., 2018).

Simulation of solar cell is an emerging technology that will ensure increased efficiency and productivity of PV production. It involves the development of a model that utilizes numerals for analyses and the interpretation of components of solar cells for efficient absorption and power
generation. The complex nature of the phenomenon under review is that it is beyond elementary calculations due to its realistic prediction of characteristics, or its principles (Ukoba, Inambao and Eloka-eboka, 2018). There is no doubt that, a numerical approach will play a vital role in solar cells fabrication for desired efficiency and domestication. Research shows that the numerical approach has contributed immensely towards recent advancements in cell production.

A better result for solar cell modeling for optimal performance can be attained if the entire solar cell parameters are inculcated in the optimization process (Ukoba, Inambao and Adeoye, 2018). This study reviews copper oxide solar cells’ existing models and simulations. It highlights the steps for device modeling and simulation, classification of the modeling and simulation tools, and examples of modeled and simulated metal oxides

2.2 PRINCIPLE OF METAL OXIDE SOLAR CELLS SIMULATIONS

Metal oxide thin film solar cells are basically P-N heterojunctions best described by the equivalent circuit model of the cells.

2.2.1 Equivalent circuit of a solar cell

Solar cells are generally current generators able to model current under a diode. The potentials amid the (+) and (–) terminals causes dark current to flow in an alternate direction. An ideal solar cell comprises of series resistance (R_s) and parallel resistance (R_p). The series resistance is caused owing to solar cell conduction inadequacy, while the parallel is triggered by an outflow of current from one point to the other owing to insulation defect (on the edge of the cell) as shown in Fig. 2.1 (Anwar and Ullah, 2012).

![Figure 2.1. Solar cells model equivalent circuit](image)
They exhibit nonlinear characteristics of I-V that vary with temperature of solar cells and the radiant intensity. Under ideal conditions, a solar cell can be theoretically simulated by way of current source under a diode. Solar cell I-V characteristic equation can be expressed in (1):

\[ I = I_{ph} - I_s \left[ e^{\left( \frac{q(V + R_s I_{PV})}{AKT_c} \right)} - 1 \right] - \frac{V + R_s I_{PV}}{R_{sh}} \]  \hspace{1cm} (1.1)

where; \( I_{ph} \) is photocurrent,

\( I_s \) is a current saturation reverse,

\( R_s \) and \( R_{sh} \) are the inherent resistances related to the cell in series and parallel,

\( q \) is electron charge,

\( K \) is Boltzmann’s constant,

\( A \) is the modified ideality factor.

The performance of solar cell is influenced through; short circuit current, open-circuit voltage and the fill factor. Short circuit current and open circuit voltage are the major determinant factors of solar cell efficiency, because the fill factor is a function of both parameters. Electron flow in the external circuit once the energy of incident photons is more than the band gap of cells.

**Figure 2.2** demonstrates the typical characteristics of solar cells. It shows the current, irradiation
temperature and the behaviour of the voltage.

Figure 2. Characteristics of a typical solar cells

Most solar cells comprise different layers of semiconductor materials stacked to form a one-dimensional sequence. Most metal oxide thin film solar cells can be modeled as one-dimensional cells because of the one direction flow of the electron/hole current (Stangl and Leendertz, 2012). Most silicon wafer solar cells can also be modeled in a similar manner. This is feasible provided the series connection is not clearly modeled. Two-dimensional modeling is applied in solar cells which have metal contacts embedded in a passivation layer that helps reduce recombination. In such two-dimensional modeling, the internal electron and hole current flows in two dimensions, or three dimensions in some cases.

2.3 Steps for device modeling

The phases for modeling and simulating metal oxide solar cells involve derivation of the basic equations. This is followed by normalization of the derived equations. Thereafter, the equations are linearized. Finally, a solution of the linearized equation is obtained. A partial understanding of device input parameters is needed for successful device modeling and simulation. A starting baseline is needed for all types of metal oxide solar cell modeling.

2.4 History of solar cell modeling

A lot of materials and methods have been studied with the intent of developing improved solar cells with regard to cost and efficiency. Experimental and modeling/simulation have also been employed for the purpose of device fabrication and tuning. Numerical analysis gives a better conception of the operation of metal oxide solar cell devices. The pioneer solar cell modeling tool
was developed in 1980 by a PhD student named Mark S. Lundstrom (M. S. Lundstrom, 1980). Gray (Cells, 1989) in 1989 developed the Thin-Film Semiconductor Simulation Program (TFSSP). Lundstrom also worked on the Solar Cell Capacitance Simulator (SCAP) in 1985 (Schwartz, Gray and Lundstrom, 1985). SCAPS is said to have been developed at Ghent University, Belgium (Niemegeers et al., 1996; Niemegeers et al., 1998). In 1989 a PhD student used the SCAPS in one-dimension and two-dimensions for a doctoral dissertation in an engineering faculty (Banghart, 1989). Purdue University also developed one- and two-dimensional modeling tools called PUSH (Demoulin and Lundstrom, 1989; Demoulin, Lundstrom and Schwartz, 1987).

3.5 Classifications of Solar Cell Device Modeling

Solar cell device modeling/simulation can be used to calculate current densities and the carrier. This is achieved through Poisson’s and the transport equation derivation (Singh, 2017). An overall solution to the current densities and carrier is derived via activating the essential boundary conditions at the junctions (P-N). However, the non-linear recombination makes it difficult to solve the current densities and carrier with ease. Device modeling of metal oxide solar cells are categorized into three broad categories, established on: the solver approach; the modeling tool used; and the dimension (one-dimensional, two-dimensional or three-dimensional).

3.5.1 The solver approach

This is divided into the analytical and numerical solver approach as shown in Fig. 3.

![Solver Approach Diagram](image)

**Figure 2.** 3. Presents schematic representation of the analytical and numerical approach to solar cell modeling
3.5.1.1 Analytical solver approach

This involves analytical modeling of the solar cell device. It is sub-grouped into analytical and semi-analytical.

The Analytical Approach

This approach solves the semiconductor equations. The equations include the diffusion-drift current, equation of carriers’ Poisson's and continuity equations. This approach is able to calculate key parameters of a solar cell efficiency. It is not sufficient to give the cells detailed parameters but it can give the fill factor, open circuit voltage and short circuit current. It is capable of simulating the effects of diameter and length on the optical absorption of the cell. It allows for comparison of the planar cell geometry and the solar cell performance in relation to the material properties. A good example is the work of Kayes and Atwater (Kayes, Atwater and Lewis, 2005). That study was able to achieve 11% efficiency from an initial efficiency of 1.5 %. It employed the analytical model to solve a continuity, Poisson and diffusion-drift equations for minority carriers. Analytically, the performance of (c-Si) and gallium arsenide (GaAs) were compared in this study, using a 100 mW/cm² Air Mass 1.5 spectrum. Petrosyan and his team (Petrosyan et al., 2012), solved the semiconductor equations using the analytical approach. Ali (et al., 2014) used the analytical model but employed the Green’s function technique. This technique eliminates the uniform generation assumption made by other models. This method gained prominence in 2014. Conversion efficiency, current density, fill factor and open circuit are calculated in this way.

The Semi-Analytical Approach

This approach is used to optimize the device absorption. It does not involve massive calculations yet is efficient. This method permits the assessment of the ideal design parameters for optimum charge generation over a shorter time and material thickness (Sturmberg et al., 2014). This approach relies on the refractive indices of the device parent material. The theoretical framework links the transmission, absorption and reflection of solar cells to parameters of the geometry. It focuses on abridged parameters that enable the device to achieve optimum short circuit currents. This reduces the time and resources associated with the comprehensive study of the geometry yet gives a better and faster optimized device.
Although analytical models are not voluminous in simulation, the results are easier to implement compared to numerical models. They also give a better view of the variables that influence the model.

### 3.5.2 Numerical Solver Approach

This involves numerical simulation techniques of modeling solar cell devices. Poisson’s equation connects the hole density and the electron. The complex nature of Poisson’s equation makes it difficult for mathematical tools to be used to solve the problem, but it can be solved with the numerical approach. The merit of this approach is that it permits inclusion of key physical effects which are not initially considered. These include parameters like; band-gaps, lifetime, doping, among others. This helps to prevent closed form solutions. The key numerical tools involved in deriving the differential equations are the finite element (Strang and Fix, 1973), finite difference (Smith, 1985), and finite volume methods (Kabir et al., 2018). Others include a transfer matrix method, finite difference time domain and rigorous couple wave analysis. The finite element is most flexible of the three methods in solving convoluted geometry involving complex working conditions. This is because it makes room for arbitrary geometries and consists of several physical parameters of the solar cells. It is more effective when the incident light is absorbed along the axis. This method has attracted several studies that employ Technology Computer-Aided Design (TCAD) (Wen et al., 2011) and COMSOL multi-physics (LaPierre, 2011). The Transfer Matrix Method is the most effective in devices involving small diameters and periodic structures (Born and Wolf, 2013). In such a case, one side of the unit cell is represented by the end of a transfer matrix.

### 3.6 The Modeling Tool Used

The second solar cell classification modeling is dependent on the modeling tool used, mainly software tools. Almost all modeling tools base their design on basic solar cell equations (continuity and Poisson equations for holes and electrons) (Burgelman et al., 2004). Any modeling tool that is able to solve basic semiconductor equations can equally model/simulate metal oxide solar cells. The continuity equation is non-linear owing to the existence of the recombination expressions. According to Ukoba et al., (2018), an extension metal oxide standard thin film solar cell modeling tool, ought to satisfy the conditions enumerated in Table 2.1 for it to be considered for usage.
Table 2.1. Criteria for metal oxide modeling and simulation tools

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layers</td>
<td>Multiple layers (5 layers minimum)</td>
</tr>
<tr>
<td>Band Gap $E_g$</td>
<td>$E_g &gt; 2 - 3.7$ eV</td>
</tr>
<tr>
<td>Band Discontinuity</td>
<td>$E_C$ &amp; $E_V$: $\Delta E_C$ &amp; $\Delta E_V$</td>
</tr>
<tr>
<td>Interface (GUI)</td>
<td>Simple, fast and friendly</td>
</tr>
<tr>
<td>Non-routine measurements</td>
<td>Able to simulate: J-V, C-V, C-f, QE(λ), as a function of ambient Temperature (T)</td>
</tr>
<tr>
<td>(current-density, capacitance, surface photo voltage, kelvin probe, transient measurement of current, voltage and)</td>
<td></td>
</tr>
<tr>
<td>Graded band Gaps</td>
<td>$E_g(x)$, $N_c(X)$, $N_v(X)$, $\alpha(x)$, Recombination even in deep interface states</td>
</tr>
<tr>
<td>Recombination Ability</td>
<td>Recombination even in bulk state</td>
</tr>
<tr>
<td>Recombination in bulk state</td>
<td></td>
</tr>
</tbody>
</table>

3.6.1 Solar Cell Capacitance Simulator (SCAPS)

Solar Cells Capacitance Simulator in one and 2-dimensions (SCAP1D and SCAP2D) was developed at Ghent University. This solar cell simulation program is used for opto-electrical simulations of 1-D or 2-D structures of semiconductor layers (Burgelman et al., 2008; Burgelman et al., 2000; Decock et al., 2011; Verschraegen et al., 2007). This program was firstly utilized for CuInSe2 and CdTe families. Nonetheless, there have been improvements on the software thereby creating room for other types of solar cells. SCAPS adopts finite difference methods to derive the differential equations, along with other relatives of the physics of semiconductors, defines mathematically the dynamics of a solar cell. SCAPS performs a complete numerical simultaneous resolution of the Poisson and continuity equation conditional on the working conditions suitable to one and two-dimensional cells (Schwartz, Gray and Lundstrom, 1985). The equations are expressed as shown in (2) to (4).
\[ \nabla^2 v = -\frac{q}{e} (p - n + N_D - N_A) \] (1.2)

\[ \nabla J_p = q(G - R) \] (1.3)

\[ \nabla J_n = q(R - G) \] (1.4)

The general terms of (3) and (4) can be represented as:

\[ G(x) = \int_0^\infty \phi a e^{-ax} d\lambda \] (1.5)

The hole and electron current densities which appear in (3) and (4) are expressed as:

\[ J_p = -q\mu_p p \nabla V_p - kT\mu_p \nabla p \] (1.6)

\[ J_n = -q\mu_n n \nabla V_n + kT\mu_n \nabla n \] (1.7)

\[ V_p = V - (1 - \gamma) \frac{\Delta_G}{q} \] (1.8)

\[ V_n = V + \gamma \frac{\Delta_G}{q} \] (1.9)

where \( v_p \) and \( v_n \) represent the effective potentials expressed in (8) and (9). \( \Delta_G \) and \( \gamma \) describes the variations in band structure; density states and band gap, and for Fermi-Dirac statistics.

**Figure 2.4** depicts the structure of the SCAPS program, summarizing its work. The operator inputs the set-up of materials properties, an account of the device to be examined, type of analysis to be performed and spectrum (optional). The results are printed in summary arrangement and the complete results of the calculation are stored. A plotting routine is activated to represent the data and demonstrate the proper parameters. The plotting activation is a vital feature of the system because it grants access to effectively have a distinctive view of most areas of the structure and
concentration in the inner layers of the cell under working conditions.

**Figure 2.4** Block diagram of the schematics of SCAP1D and SCAP2D

**Figure 2.5** shows the SCAP interface with the major input parameters used for solar cell modeling. Some studies have successfully used it for modeling thin film solar cells (Lin et al., 2014; Simya et al., 2015; Khoshsirat and Yunus, 2013; Sibiński et al., 2011; Zerfaoui et al., 2016; Pogrebnyak et al., 2011)
3.7 Copper Oxide (Cu$_2$O and CuO) and TiO$_2$ properties

Copper is a renowned metal oxide having the ability to form two metal oxides; cupric oxide (CuO) and cuprous oxide (Cu$_2$O) (Nayan et al., 2016). Cu$_2$O being brownish-red hard with a cubic crystal arrangement and CuO in the form of black-brown powder, with a monoclinic crystal structure. Semiconductors like metal oxides (copper oxide) have the potency to be substituted for silicon solar cells. CuO and Cu$_2$O are examples of such metal oxide materials.

The semiconducting properties of copper oxide are perceived to be advanced optical absorption, toxic-free and cheap materials (Kidowaki et al., 2012). Copper (II) oxide is affiliated to the
monoclinic crystal organization. The copper atom is harmonized by four oxygen atoms in almost square planar conformation. CuO and Cu$_2$O are both p-type semiconductors with band gap of 1.5 eV and 2.0 eV, respectively. They are both in close proximity to the ideal energy gap of 1.4 eV for solar cells and good for solar absorption. With an electron affinity of 3.2eV, density of 6.31gcm$^{-3}$, thermal expansion coefficient of 3.5x10$^{-6}$C$^{-1}$. Copper (I) oxide is a reddish cuprite material.

Copper oxide compound are made up of two elements known as copper and oxygen, from block d and block p elements in the periodic table respectively. It contains two elements, Copper (Cu) and copper oxide (Cu$_2$O) nanoparticles (Singh et al., 2016). Copper being one of the essential materials in current technologies and are readily obtainable, these elements have been found to be viable (Tranquada et al., 1995). Copper nanoparticle has intriguing qualities like mechanical, electrical, optical, and catalytic properties which triggers the rate at which it is being scrutinized. Four oxygen ions coordinate the crystal copper ion (Schwartz et al., 1985). Copper nanoparticles is attracting a lot of attention owing to their optical, catalytic, mechanical and electrical properties.

Titanium dioxide (TiO$_2$) being one of the best studies transition metal oxides (Rivera et al., 2013) have good electronic and optical properties. Titanium dioxide has a high refractive index and durability, which makes it a fit for photovoltaic applications; optical wave-guides and multilayer optical coating (Kars I. et al., 2010). The crystal structure of copper (II) oxide and copper (I) oxide is shown in Figure 2.6 and Table 2.2 shows the parameters of the properties for Cu$_2$O, CuO and TiO$_2$ which is also the parameters used for this simulation. While Table 2.3 illustrates the merits of the Cu$_2$O, CuO and TiO$_2$ materials.

![Figure 2.6. Crystal structure of: (a) Copper (II) oxide (b) Copper (I) oxide](image)
Table 2. Illustrates the parameters for the various properties of Cu$_2$O, CuO and TiO$_2$ at (Hossain, Alharbi, & Tabet, 2015; Li, et al., 2009; Ichimura, & Kato, 2013)

<table>
<thead>
<tr>
<th>Material properties</th>
<th>n-TiO$_2$</th>
<th>p-Cu$_2$O</th>
<th>p-CuO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap [eV]</td>
<td>2.26</td>
<td>2.17</td>
<td>1.51</td>
</tr>
<tr>
<td>Electron affinity [eV]</td>
<td>4.20</td>
<td>3.20</td>
<td>4.07</td>
</tr>
<tr>
<td>Dielectric permittivity (relative)</td>
<td>10.00</td>
<td>7.11</td>
<td>18.10</td>
</tr>
<tr>
<td>CB (conductive band) effective density of states [1/cm$^3$]</td>
<td>2.0E+17</td>
<td>2.0E+17</td>
<td>2.2E+19</td>
</tr>
<tr>
<td>VB (valence band) effective density of states [1/cm$^2$/Vs]</td>
<td>6.0E+17</td>
<td>1.1E+19</td>
<td>5.5E+20</td>
</tr>
<tr>
<td>Electron mobility [cm$^2$/Vs]</td>
<td>1.0E+2</td>
<td>2.0E+2</td>
<td>10.0E+1</td>
</tr>
<tr>
<td>Hole mobility [cm$^2$/Vs]</td>
<td>25.0</td>
<td>8.0E+1</td>
<td>1.0E-1</td>
</tr>
<tr>
<td>Shallow uniform donor density [1/cm$^3$]</td>
<td>1.0E+17</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 2.3 Advantages of Cu$_2$O and CuO (p-type) and TiO$_2$ (n-type)

<table>
<thead>
<tr>
<th>Material</th>
<th>Advantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_2$O</td>
<td>It has good absorption coefficient.</td>
</tr>
<tr>
<td></td>
<td>It is earth abundant.</td>
</tr>
<tr>
<td></td>
<td>Environmentally friendly (Non-toxicity).</td>
</tr>
<tr>
<td></td>
<td>Affordable fabrication.</td>
</tr>
<tr>
<td>CuO</td>
<td>Its earth abundant.</td>
</tr>
<tr>
<td></td>
<td>Environmentally friendly (non-hazardous).</td>
</tr>
<tr>
<td></td>
<td>The preparation method is affordable.</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>It has high transmission under illumination and near infrared regions.</td>
</tr>
<tr>
<td></td>
<td>Has good stability</td>
</tr>
<tr>
<td></td>
<td>To counter chemical attack, mechanical abrasion, and high temperature.</td>
</tr>
<tr>
<td></td>
<td>Has good adhesion.</td>
</tr>
</tbody>
</table>

3.8 Copper Oxide Solar Cells Modeling

Different steps are involved towards a successful simulation of copper oxide solar cells. This includes the derivation of the governing equations coupled with balancing the derived equations. The equation is linearized afterwards. Lastly, a solution of the linearized equation is acquired. The modeling and simulation of the device is run successfully using the fragments of the device parameters. This solar cell modeling approach requires a start baseline.
3.9 Dimension Basics

The dimensions of solar cells are distributed into: 1, 2, and 3-Dimensional. One (1)-dimensional modeling tool can be used to model the conservative geometric solar cells and small solar concentrations. While the 2-Dimensional effect can be adopted in some conservative geometry devices, 2-Dimensional or 3-Dimensional is usually necessary for high efficiency solar cell design. 2D Geometry is a model of the interlinked solar cell back contact, while the 3Dimensional geometry is ideal for point contact solar cells. An exclusive algorithm is developed for every class of solar cell though the basic modeling approach remains unchanged for all solar cell devices. SCAP1D, SCAP2D, PUSH1D, PUSH2D, among others, are the examples of the modeling tools and are discriminated with 1D, 2D and 3D.

Amin et al., (2007), used a 1Dimensional simulation program NSSP (Numerical Solar Cell Simulation Program) for CdTe solar cell structures from diverse viewpoints focusing on decreasing of CdTe absorber thickness using theoretical analysis. Other modeling tools which have extended usage are; Silvaco (Levinshtein et al., 2002; Kotov et al., 2006; Kersys et al., 2008; Jr, 2007), AFORS-HET (Automat for Simulation of Hetero-structures) (Zeman et al., 2011; Jeong et al., 2008; Stangl et al., 2007; Froitzheim et al., 2003), Crosslight (Piprek, 2013; Sheng et al., 2013), Sunshine (Krč et al., 2003), Synopsis (Padmanabhan, Vasileska and Schroder, 2008), and Advanced Semiconductor Analysis (ASA) (Zeman et al., 1997) and so on.

AFORS-HET occurs as 1D and 2D. TFT technology is a major technology used in Silvaco, using both the numerical method and physical models for thin film solar cell and transistor simulations. The Advanced Physical Model of Semiconductor devices (APSYS) is used by Crosslight. The finite element technique for modeling optoelectronic properties of 2Dimensional solar cells thin film devices were adopted. The nano-textured interface effects on solar cell performance is investigated using ASA (Zeman et al., 2011).

3.10 History and previous work on Modeling of Copper Oxide Solar cells

2.10.1 Background

For centuries, transition of metal oxide towards nanostructure technology has attracted a lot of researchers due to its potentials compared to other nanomaterials and has also proven to possess the necessary prospects to be applied in different technological advancements such as solar cells
applications. The study of cuprous oxide, CuO, as a semiconductor started in the twenties as at the time CuO rectifier was invented by Grondhal (Grondahl, 1933). This gave rise to a substantial amount of research conducted towards characterization of CuO from the thirties to date. In the thirties, Grondhal, (1933) conducted the study of CuO based Photosensitive devices which was later reviewed by Lange (Lange and John, 1938) before the successive change in interest from selenium to germanium, then to silicon. In the early seventies, the photovoltaic researchers (Trivich et al., 1976) commenced another investigation into the Cu₂O as an alternative low-cost material for solar cell production. However, for the duration of this research the output of this research was limited. Though an efficiency of 3.83% was reported by improving the procedure of ZnO layer (Chenet al., 2013; Minami et al., 2011), another efficiency of 5.38% was also recounted by Minami et al. (2013). In their study they placed a β-gallium oxide (Ga₂O₃) layer amid p-type Cu₂O and n-type aluminium-doped ZnO (ZnO:Al). Though significant, this was not up to the theoretical prediction of electrical conversion efficiency of 20% (Kardarian et al., 2016). Other studies obtained an efficiency of 2 % using Schottky and heterojunction solar cells (Mittiga et al., 2006b; Loferski, 1956; Olsen et al., 1982; Herion et al., 1980; Papadimitriou et al., 1981). For the study of Mittiga et al., (2006), the annealing method was used at high temperatures to derive Cu₂O highest efficiency of ~2 %.

2.10.2 Numerical modeling
Numerical simulation of solar cell is an emerging technology that will ensure increased efficiency and productivity of PV devices. It involves the development of a model that utilizes numerals to analyse and interpret the components of solar cells for optimum, efficient absorption and productivity. It is no doubt that this numerical approach will play a vital role in design and manufacturing of solar cells with desired efficiency (Zeman et al., 1997; Miyajima et al., 2011; Gloeckler et al., 2005). Research shows the numerical approach has contributed immensely towards recent advancements in cell production.

Solar cell simulation was started by Lee and Gray (2002) who conducted a simulation using a 1Dimentional solar cell simulation program ADEPT, which was developed in Purdue (Gray and Young Jung Lee, 2002). They investigated the influence of grain boundaries and determined the collection of parameters that is dependent on specific cell performance as well as the effect of non-ideal back contact.
2.10.3 Previous Works Based on Modeling Tools

A number of programs for solar cell simulation are in existence such as; Thin-Film Semiconductor Simulation Program (TFSSP), PUPHS, and PUPHS2D. All these simulation programs were already used to simulate solar cells –Si:H Thin-film, Cds/CIS, CdS/CdTe, Si, Ge and GaAs in 1-Dimension and high efficiency Si and GaAs in 2-dimensions (Ganvir, 2016).

While cuprous oxide (Cu₂O) possesses promising potentials, its low efficiency has been due to experimental deposition. Using the electrochemical deposition technique, an efficiency of 0.21% was obtained by (Pagare and Torane, 2018; Saehana and Muslimin 2013). The Electrochemical deposition method was used by employing polymer electrolytes to obtain an efficiency of 1.05 %. Many numerical modeling tools have been used towards improving the thin film solar cells efficiency such as; WxAMPS (Liu, Sun and Rockett, 2012; Liu, Sun and Rockett, 2012), PCID (Banerjee, 2017), MatLab Simulink (Ghosh and Kundu, 2017).

2.10.3.1 AMPS-1Dimention (Analysis of Microelectronic and Photonic Structures)

This simulation model was established at the Pennsylvania State University by Fonash and his colleagues to better understand solar cell device along with its physics and fabrication (Fonash et al., 1997). It is a 1-dimensional simulation tool, which uses finite differences and Newton-Raphson method to solve the poisson and continuity equations of solar cells. It has the ability to model p-n, single or heterojunction p-i-n, Schottky barrier devices and its likes. With its ability to function under illumination and dark, it simulates several opto-electronic devices including solar cells and diodes. Its parameters are temperature independent. Fahrenbruch conducted a simulation using AMPS software, His simulation was done with the intent of finding J-V curves through describing the effect of a thin layer of CdS amid TCO and CdTe area. Despite all these abilities, AMPS among other simulation programs is the slowest (Muthuswamy, 2005).

Nowshad and his team (Amin, Tang, et al., 2007), reported the optimization of CIS and CIGS parameters through numerical simulation using AMPS1-Dimension. His results prove that the increase in the absorber layer (3000 nm) could result in increased efficiency of solar cells, and thickness of the CdS buffer layer being ideal value of 50nm to limit photon loss.

wxAAMPS is a more stable simulation tool for solar cells with better computation regarding the initial AMPS simulation program (Liu, Sun and Rockett, 2012). It incorporates tunnelling the
current into the model by using the main physical principle of AMPS. Newton and Gummel’s approach are joined to solve the advanced algorithm, having better speed and stability. There exists a similarity of performance between SCAPS and wxAMPS with great potentials to simulate materials with band tails, exacts features of metal oxide, thin film photovoltaics and high defect densities. It is comparable to the performance of other simulation tools like SCAPS though with better capability to model materials with high band tails, defect densities and other structures distinctive of photovoltaics thin film. In tandem and graded, solar cells modeling, wxAMPS offers the complete competence required to attain steady and speedy simulations. The accompanying WIKI for device parameter distribution permits the users to make better use of the modeling tool (Liu et al., 2012).

Yuki Takiguchi and Shinsuke Miyajima (2015) developed a model to simulate cuprous oxide (Cu$_2$O)-based heterojunction solar cells. Their study validated already existing experimental current density–voltage features and the results of external quantum efficiency. This study was geared towards high-efficiency generation using Cu$_2$O-based heterojunction solar cells. They discovered that Cu$_2$O suggestively alters the solar cell performance. Surface recombination on the reverse side of the device can be curbed by engaging a highly doped back surface layer. Their simulation result shows an efficiency of 16% minus any optical confinement arrangement.

2.10.3.2 PCID

This simulation program was developed for personal computers to solve non-linear equations of one-dimensional electron and hole transport in semiconductor devices of photovoltaic devices. This program was written by Basore and his team at the Sandia National laboratory and later upgraded at the University of New South Wales, Australia (Basore, 1990). It is mainly used to interpret experimental data for device structure specification and determine different device parameters through aligning the experimental curve to simulated Internal Quantum Efficiency. PCID can simulate spectral response measurements, transient and J-V properties of solar cells (Patra et al., 2012). The result of this simulation can be manipulated in other programs (spreadsheets). Despite the fact that it has been used intensively in modeling and simulation of traditional solar cells (Li et al., 2013), it is also used in metal oxide solar cells modeling (Basore, 1990; Fonash., 1997; Haug et al., 2014; Kurtz et al., 2002; Swatowska et al., 2010; Mehta et al., 2008; Yeon et al., 2015). Sudipta Banerjee (2017) developed a numerical model to express the
supposedly feasible efficiency of CdS/CdTe thin film solar cells through numerous assumptions. Their simulation shows the enormous dilapidation of device parameters coupled with a decrease in absorber layer thickness. The Performance is not restricted merely by optical concerns, but the boundaries and back contact are essential roles as well. This result supports that, for an efficiency of 30% to be recorded, the thickness of the CdTe absorber layer needs to be increased to more than 20-30μm (Banerjee, 2017).

2.10.3.3 MAtlab/Simulink

Simulink has been used in many modeling and simulation studies. This simulation model permits the simulation, analysis and optimization of dynamic photovoltaic power system. The universal photovoltaic model was developed using Simulink by Tsai, Tu and Su (Tsai et al., 2008). This simulation tool has often been used in a variety of simulation of photovoltaic systems, including solar cells.

However, this research is based on one-dimensional simulation using SCAPS-1D as the simulating tool for the nanostructured copper oxide (Cu$_2$O and CuO) solar cell.

2.10.3.4 Introduction to SCAPS-1D

Solar cell capacitance simulator program 1 and 2-dimension (SCAPS-1D and 2D), was introduced at Gent University, department of Electronics and Information Systems (ELIS), Belgium. This program (SCAPS1& 2D) for structures of semiconductor layers was initially established for structures of CdTe and CuInSe2 families. Upgrades have been done to advance its proficiencies to be applicable to crystalline, amorphous and micro-morphous solar cells (Si, GaAs, a-Si and Si) respectively (Burgleman et al., 2016).

Due to the unique nature of SCAPS-1D, more than seven (7) semiconductor layers can be computed and nearly all the parameters can be categorized; Eg, ND, vthp, μn, ε, NC, vthn, NV, μp, χ, NA, all traps (errors) Nt. monovalent (acceptor, single donor), divalent (double donor, double acceptor, amphoteric), multivalent (user define) and No charge (idealization) are the four charge types. It also comprises of two parameters that are temperature dependent; band gaps and mobility (Anwar and Ullah, 2012). Three deep level for each layer can be specified and the three boundary states can be positioned between these three layers. The deep levels are dynamically circulated in the prohibited zones (uniform, single level, gauss or exponential tail). The various
deep levels vary dimensionally inside the layers (linear or exponentially, uniform and step). The dimensions of the other parameters are same for every layer. Several layers are used while introducing the graded junctions into the device and the various contact points can be identified (back and front). This program possesses different standards and various spectra for illumination which includes; AM0, AM1.5D, AM1.5G, AM1.5G edition 2, monochromatic, white etc. The illumination maybe from p-side or the n-side. Temperature, voltage and frequency are the respective calculation points. The program calculates various parameters like the energy bands, concentrations and current at a specified working condition, J-V-characteristics, ac-properties (C and G, as functions of V and/or f), shadow response (with light or voltage) (Burgleman et al., 2016; Anwar and Ullah, 2012). Though, results can be presented through batch calculations. Another vital point to note is that the loading and saving of the project setup can be done in SCAPS-1D. This domain of this program is arranged in panels, granting the user access to set the parameters or the result in display format. The program starts with an ‘action panel’, providing user access to set the operating conditions (illumination, temperature, voltage, and frequency), along with an action list containing the computation to execute (I-V, C-V, C-f, QE). The computing parameters (V, f or 1) are diverse in defined scope, while the supplementary boundary values are defined in the operating condition. This program allows the user to view the initial computational results of I-V, C-V, C-f, QE. The computation can be as a result of the illumination or dark condition and temperature dependent (Burgleman et al., 2016). The charge, current and energy band diagram within a device is displayed on the screen for every wavelength or intermediate bias voltage during the course of the simulation. The project can be saved to a file for each of the intermediate solution. At the end of the simulation, the features can be analyzed and compared with previous existing simulation and saved in a file. SCAPS simulation tool is unique with these interactive attributes.

The user function provides a good user interface along with a script language. SCAPS-1D is run from a “script file” which is incorporated into the program and the script can access and plot the various internal variables. Furthermore, SCAPS-1D has a console for the definition of admitting scales along with in-built curve installed provision (Burgleman et al., 2016).

**Governing Equation for SCAPS-1D (numerical model):**

Basically, since this program can solve the primary semiconductor equations, it also has the potential to model/simulate nanostructured solar cells. These governing equations are: Current-
density equations, poisson equations—connecting continuity equation for the electrons, holes and charge to the electrostatic potential.

**Current-Density Equation:**

There are two basic components contained in this current conduction; the drift component originated by electric field and diffusion component, originated by the concentration gradient.

They are known as the constitutive equation. (S.M. Sze, 2007);

\[ J_n = q\mu_n n\varepsilon + qD_n \frac{dn}{dx} q\mu_n \left(n\varepsilon + \frac{kT}{q} \frac{dn}{dx}\right) = \mu_n n \frac{dE_{Fn}}{dx} \]  
(2.1)

\[ J_p = q\mu_p p\varepsilon + qD_p \frac{dp}{dx} = q\mu_p \left(p\varepsilon + \frac{kT}{q} \frac{dp}{dx}\right) = \mu_p p \frac{dE_{Fp}}{dx} \]  
(2.2)

where, \(\varepsilon\) - Electric field

\(\mu_n, \mu_p\) — Mobility of electron and hole respectively

\(J_n, J_p\) — Electron and hole current density respectively

\(D_n, D_p\) — Diffusion coefficient for electrons and holes respectively

\(E_{Fn}, E_{Fp}\) — Quasi-Fermi level for electron and hole respectively

**Continuity Equations:**

There are different carrier transport mechanisms for semiconductors. Generation, recombination and low-level injection are time dependent occurrence which are contained in the continuity equation. The variation in transport concentration with respect to time are caused by the effect of drift, diffusion, indirect or direct thermal generation or combination. The difference between the generation and recombination is the resultant effect of net charge carrier concentration, along with the net current flowing in and out of the defined region.

The continuity equation is expressed as follows (Ganvir, 2016):

\[-\frac{\partial J_n}{\partial x} - U_n + G = \frac{\partial n}{\partial t}\]  
(2.3)
\[-\frac{\partial f_p}{\partial x} - U_p + G = \frac{\partial p}{\partial t}\]  \hspace{1cm} (2.4)

Where,

\(G\)- Generation rate

\(U_n, U_p\)- Net recombination/generation rate

**Poisson Equation:**

In order to derive the qualitative solution for electrostatic variables in a semiconductor, poisson equation is the starting point. It is expressed as follows (Ganvir, 2016)

\[\frac{\partial}{\partial x} \left( \varepsilon_0 \varepsilon \frac{\partial \psi}{\partial x} \right) = -q (p - n + N_D - N_A)\]  \hspace{1cm} (2.5)

Where, \(q (p - n + N_D - N_A) = \rho\) (charge density), with fully ionized dopants  \hspace{1cm} (2.6)

\(N_D, N_A\) - Donor and acceptor impurity concentration respectively.

**Physical Model**

**Deep Bulk Levels:**

The different types (donor and acceptor) along with the density of the shallow level in each layer can be described, being completely ionized without adding to recombination. An estimation of three (3) deep levels can be specified. Schockley-Read-Hall (SRH) formalism defined the recombination of different levels and their various positions, the various function of the various levels and its types (‘neutral’, donor or acceptor i.e theoretical center with no charge) defines the charge. Among the prohibited zones (level, single, uniform band, exponential tail or Gau beta) are the various levels that can be actively distributed. The deep or shallow states concentration can differ in structure/dimension (uniform, step, linear or exponential) (Ganvir, 2016)

**Band Discontinuities and Interface States**

Discontinuity at the interfaces are allowed by the quasi-fermi level. An additional node at every boundary is introduced into the discretization in order to compute it mathematically. Pauwells Vanhoutte model is used in the SCAPS-1D interface recombination. Four (4) bands for interface
states are examined in this model i.e. the valence bands and conduction of individual semiconductors at the interface. An electron bearing semiconductor having the hole of secondary semiconductor are hypothetically considered together with standard recombination of the electrons with holes inside the same semiconductor (Anwar and Ullah, 2012). The recombination of window electrons through the absorber holes is known as the vital recombination path. The discontinuity in dielectric displacement at the interface is equivalent to the total charge in the interface state (Burgelman et al., 2000). Figure 2.7 below shows the Paulwells Vanhoutte model.

![Paulwells Vanhoutte model for interface recombination](image)

In this case, the Pauwells Vanhoutte Model for interface recombination appropriate for CdS/ CdTe cell, and which is applicable to TiO$_2$/CuO and TiO$_2$/Cu$_2$O solar cell and the dominant recombination path is amid holes and electrons (Burgelman, Nollet and Degrave, 2000).

The interface conditions are distributed in energy, same as the bulk states in SCAPS program. Thermionic emission (Bethe theory) describes the passage of major carriers at the metal-semiconductor interface (contact).

Thermionic emission current for electrons for two direct band gap semiconductors with identical effective masses, have the following expression

\[
J_{th} n = v_{th} n \left( n^{(1)} \exp \left( - \frac{\Delta E_c}{kT} \right) - n^{(2)} \right) \quad (2.7)
\]

Where, \(j_{th} n\)=particle current from semiconductor 1 to 2

\(v_{th} n\) = thermal velocity of electrons
(\textsuperscript{1}), \(n^{(2)}\) = electron concentrations

\(\Delta E_c\) = conduction band discontinuity

Thermionic emission current for holes can also be calculated in the same way. The boundary equations are imposed on the continuity equation for the electron at the metal semiconductor contact with an expression [97];

\[ j_n = S_n (n - n_{eq}) \] \hspace{1cm} (2.8)

Where,

\(n_{eq}\) is the number electrons at the contact in equilibrium (Ganvir, 2016).

Sawicka-Chudy, et al (2017) used SCAPS to simulate Cu\textsubscript{2}O/TiO\textsubscript{2} and CuO/TiO\textsubscript{2} heterojunction solar cells and shows that different layer parameters such as defect density and thickness has an effect on cell performance. Their investigation ascertained that the thickness of the absorber layer (CuO and Cu\textsubscript{2}O) and the buffer layer (TiO\textsubscript{2}) influences the solar cells efficiency, short-circuit current and current density (J\textsubscript{sc}).

However, studies have shown that Nanostructured Cu\textsubscript{2}O and CuO solar cells has the potential of increasing the effectiveness, performance and limits the resistance series of solar cells at a reduced cost (Chen et al., 2013).

\textbf{2.10 Conclusion}

This study gave a review of modeling and simulation of nanostructured copper oxides solar cells for photovoltaic application. A mathematical modeling and theoretical validation of solar cells can markedly encourage research and development of solar technology in developing countries. There are numerous solar cell modeling tools, which have been developed and are used commercially and at laboratory scale, worldwide today. The study looked at the classification of the major modeling tools and did a review of previous modeling of copper oxides oxide.
CHAPTER 3


Chapter 3 looks at the modeling and optimization of the nanostructured CuO/TiO2 and Cu2O/TiO2 metal oxides heterojunctions. This chapter focused on effect of annealing temperature on the metal oxides heterojunctions. It is divided into two parts, viz;


3.1 Modeling parameters

3.1.1 Solar Cell Structure

An ideal solar cell structure is a device that can electronically convert sunlight to electricity. The rays from the sun absorbed by the solar cell generates electricity produced from the association amid the voltage and current. This process requires a series of actions and materials which involves an increase in electrons to an advanced energy state through the absorption of sunlight and this increased electron energy moves from the solar cell to the external circuit. At the end of this process, the electron returns to the solar cell after discharging the energy to the external circuit. In theory, many materials can be used in photovoltaic applications. However, photovoltaic energy conversion only comprises of p-n junction semiconductor materials.

3.1.2 Photovoltaic Effect

Photovoltaic cell involves two layers of semiconducting materials fitted together. The layer known as the n-layer is configured to absorb excessive free electrons, while the p-layer is configured to have excessive holes and vacancies. The electron holes are filled when electrons in n-layer moves into the p-layers. This is caused when two different semiconducting materials are connected at a common boundary. A barrier is formed when holes and electrons connect at a p-n junction making it very hard for more electrons to cross. A fixed electric field is caused when electrical imbalance is at an equilibrium state across the boundary, demarcating the two sides. Electrons are emitted when sunlight of a specific energy is absorbed by layer cell. The fixed field crosses the electron near to the p-n junction across the junction, owing to the fact that electrons cannot return to the opposite direction (contrary to the field gradient) but can easily cross the junction. The result is to charge the imbalance between the two semiconducting regions. Electrons move to n-layer through the fixed field leaving the layer to balance the charge. At this point, the electron will follow any available path. The flow of current continues so far electrons can return to the other layer through an external circuit as sunlight is absorbed through the solar cell (Anwar and Ullah., 2012). The essence of the metal contact layer at the outer face of two semiconductor layers is to create a path connecting the two layers to the external circuit. The resultant effect is to produce electricity through solar energy.
The voltage produced by a solar cell relies on the wavelength of incident light. The cells are designed to adopt a broad spectrum of daylight. Figure 1.6 below, illustrates a typical photovoltaic structure (Anwar and Ullah., 2012).

![Diagram of a solar cell]

**Figure 3.1 Structure of a Common Photovoltaic Device** (Anwar and Ullah., 2012).

### 3.1.3 Quantum Efficiency

Quantum efficiency is at unity when the photons of a particular wavelength are absorbed, while minority carriers are collected. Quantum efficiency (Q.E.) can be defined as the ratio of several carriers absorbed by a solar cell to the quantity of photons of a specified energy incident on a solar cell. Photons having an energy below the band gap results in zero quantum efficiency. The function of a wavelength or energy might be as a result of a given quantum efficiency. Though the recombination effects of quantum efficiency of solar cells are reduced, and the quantum efficiency ideally is observed to be square shaped. The power from the AM1.5 contained in such low wavelengths is low because the quantum efficiency is not regularly measured below 350nm (Anwar and Ullah., 2012).

#### 3.1.3.1 External Quantum Efficiency (EQE)

EQE is the ratio of the amount of transported charge absorbed by the solar cell to the quantity of photons of a specified energy shining on an external solar cell outside (incident photons).

\[
EQE = \frac{\text{electrons/sec}}{\text{photons/sec}} = \frac{\text{current/(charge of one electron)}}{\text{(total power of photons)/(energy of one photon)}}
\]  

(3.1)
3.1.4 Voltage and Current

Two parameters are essential for solar cell characterization;

3.1.4.1 Open Circuit Voltage (Voc):
Open circuit voltage can be defined as the highest voltage available in a solar cell. This usually occurs when the current through the junction is zero, and is expressed as (Hongmei Dang, 2015),

\[ V_{oc} = \frac{n kT}{q} \ln \left( \frac{I_s}{I_o} + 1 \right) \]  

(3.2)

3.1.4.2 Short Circuit Current (Isc):
Isc is the current generated at a point where the voltage across a solar cell is at zero. ISC of solar cells is the current density that flows across a junction under illumination at an applied bias of zero. Short-circuit current is the highest current absorbed from a solar cell. Short-circuit current is the same as the photo-generated current density (JL). There is a relationship between short-circuit current and the open-circuit voltage based on the fact that they are both the highest current and voltage of a solar cell at zero operating point respectively.
The maximum power point is a point on a J-V curve that produces the highest power, being the point of corresponding current density and voltage are at maximum current $J_{mp}$ and maximum voltage $V_{mp}$ (Hongmei Dang, 2015).

### 3.1.5 Fill Factor (FF) Of A Solar Cell

The FF is defined as the ratio of the highest power obtained from the solar cell to the product of Isc and Voc. The fill factor is the parameter which determines the highest power obtained from a solar cell. This is an amount of the square of the J–V curve and the area of the major rectangle which will fit in the IV curve. Fill factor (FF) is given by (Hongmei Dang, 2015),

$$FF = \frac{V_{mp}J_{mp}}{V_{oc}I_{sc}}$$  \hspace{1cm} (3.3)

### 3.1.6 Efficiency of Solar Cell

Solar cell efficiency refers to the amount of solar energy the solar cell can convert to electricity through photovoltaic application. The solar cell efficiency is a vital parameter for solar cell performance evaluation. Temperature, intensity of the incident sunlight and spectrum of a solar cell are some of the various parameters that influence the efficiency of a solar cell. It is necessary that the conditions needed for efficiency measurement be cautiously regulated. Solar cells are generally measured at a temperature of 25°C under AM1.5 conditions, and AM0 condition for space applications. The efficiency of a solar cell is the ratio of the highest output $P_{max}$ to the amount of sunlight (incident power) $P_{incident}$ and is given as (Hongmei Dang, 2015),

$$\eta = \frac{V_{oc}I_{sc}FF}{P_{in}}$$  \hspace{1cm} (3.4)

### 3.1.7 Current–Voltage curves

When the cell operates in the fourth quadrant of the graph, power is generated at a point when the current is on negative (-) and voltage is positive (+). A cell under illumination contributes to usually “dark” currents in the diode. The light moves an IV curve down to the fourth quadrant for power to be absorbed from the diode. The photo-generated current density ($J_L$) moves the dark curve when exposed to illumination. An IV curve of a solar cell diode in the dark along with light-produced current is the super-position of the IV curve of a solar cell.

$$I = I_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] - I_L$$  \hspace{1cm} (3.5)

Where; $I_0$ is the reverse saturation current,
n is the diode ideality factor and $I_L$ is light generated current.

**Figure 3.3** A typical solar cell current–voltage characteristic under and dark illumination (Hongmei Dang, 2015)

### 3.1.8 Effect of Series and Shunt Resistance

A solar cell comprises of a shunt resistance ($R_{sh}$) and parasitic series ($R_s$), these resistances are governed by different physical mechanisms. The front and back contacts and bulk resistance of a semiconductor materials makes up the series resistance $R_s$, while the leakage across the p-n junctions of the cells results in the shunt resistance $R_{sh}$. A typical solar cell has low series resistance ($R_s = 0$) and increased shunt resistance ($R_{sh} = \infty$). These resistances can significantly decrease the fill factor likewise low $R_{sh}$ and high $R_s$ can reduce the $V_{oc}$ and $J_{sc}$. The open-circuit voltage is not affected by Low $R_s$ as a result of lack of current flow at the $V_{oc}$, this is shown in **figure 3.4** (Hongmei Dang, 2015).
3.1.9 Effect of Temperature

The optimum performance of solar cell in certain weather conditions, like weather variance regarding areas and geographical locations, installed solar panels optimum performance might not be attained. Due to its output current which increases exponentially, (temperature range of 15°C (288K) to 50°C (323K) it is vital to investigate and understand the effect of temperature (T) on solar cells to which they are always exposed to. Existing literatures shows that semiconductors are usually modeled at 300K being room temperature. However, a typical solar cell is measured at 2 degrees lower at 25°C (298K). Though the difference is 4 mV of $V_{oc}$, both are regarded as room temperature. Solar cells are responsive to temperature just as other semiconducting devices. The Semiconductor band gap is reduced due to the increase in temperature which is a result of the increase in energy of electrons in a material. In a semiconductor bond model, the energy required to break the bond is lower due to the fact that the reduced bond energy leads to a reduced band gap. This is to conclude that increased temperature reduces the band gap. However, the effect of temperature increase in a solar cells open-circuit voltage is reflected on figure 3.5.
The influential parameters that serve as the deciding factors for optimum performance of solar cells are; short-circuit voltage, open-circuit voltage, current density, efficiency and fill factor. Decrease in open-circuit voltage is caused by a decrease in temperature, as a result of reverse saturation current density ($I_o$) is temperature dependent as. The p-n junction one side equation for $I_o$ is expressed by Hongmei Dang, (2015). It is a vital diode parameter such that it controls the change in performance parameters with temperature.

$$I_o = qA \frac{Dn_{i}^2}{LN_D}$$  \hspace{1cm} (3.6)

### 3.1.10 Impact of defect density in Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ solar cell thin film

Solar cells performance can be influenced by the semiconductor junctions and interface layer quality which can reduce the value and trigger much recombination. The interface defects are studied by two inserted hypothetical defect layers owing to the struggle in evaluating the recombination initiated by interface defects (Kai et al., 2016). The magnetic, optical, electronic and structural properties could be affected by these defects (Rivera & Stashans, 2013). In a simulation, the defects densities of n-TiO$_2$ and for p-CuO and p-Cu$_2$O were controlled in the range 1E+12 to 1E+22 cm$^{-3}$.

### 3.1.11 Thickness effects on photovoltaic parameters

Thickness is very important with relation to solar cells and contributes to the performance of the solar cell. A solar cell is completely dependent on an absorber layer (p) being the point of absorbed photons, the excess carriers are produced and the buffer layer (n) forms the p-n junction alongside
the absorber layer (p). The buffer layer thickness ought to be made very thin to limit the PV device resistance (Zhao et al., 2012).

For this current work, the effect of the absorber layer and buffer layer thickness on the solar cell was investigated. The various absorber layers (CuO and Cu₂O) and buffer layer (TiO₂) were simulated by varying the thickness from 0.5 to 10.0 for the absorber layer (CuO and Cu₂O) and 0.05 to 6.0 for the buffer layers (TiO₂). No additional defect was introduced to this simulation.
3.2 Effect of Annealing on Nanostructured Heterojunction Solar Cells (CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn) using SCAPS.

3.2.1 INTRODUCTION
Simulations have been adopted to offer a theoretical guide for speedy experimental optimization of processes. Different sectors have employed modeling and simulation for parameter optimization, such sectors include; energy (Ukoba and Freddie, 2018), transportation (Covill et al., 2015 and Ukoba, Imoisili and Adgidzi, 2015), production planning (Marchal, Ortega, & García, 2019), water and food production (Biemans et al, 2013). In photovoltaic applications, simulations are being adopted towards improving the properties of solar cells (Younas et al., 2019 and Fantacci, & De Angelis, 2019). Among the advancements in the photovoltaic applications is the nano-structuring of solar cells. The interest due to the simplicity and ease of manipulation of the Modeling tool for nanostructured metal oxide has increased significantly in recent years (Verma and Asthana, 2019 and Tyagi et al., 2019).

Photovoltaic continues to gain prominence in Europe and other parts of the world (D’Alpaos, & Moretto, 2019). However, Africa and other developing countries have limited or no access to it due to affordability and other factors hindering its usage and domestication (Asumadu-Sarkodie & Owusu, 2016, Ludin et al., 2016 and Ukoba, Eloka-Eboka, & Inambao, 2018). Although, nanostructured metal oxides solar cells show promise of low cost, clean and efficient photovoltaic usage in Africa is minimal (Ukoba, Inambao, & Eloka-Eboka, 2018). Nanostructured metal oxides (NMO) continue to attract interest due to the versatility in energy applications (Diab et al., 2011; Ge et al., 2016; Wick and Tilley, 2015 and Minami, et al., 2015). However, most of them still exhibit weak conversion efficiencies resulting in several experiments in the laboratory in an attempt to obtain the optimum power conversion efficiency. Although, metal oxide efficiency is low compared to other solar cells, but exhibits prospects attaining an efficiency of 20 % previously recorded by CIGS-based solar cells (Liu et al., 2010) but the laboratory experiments/trials are quite expensive. The numerous attempts and progress through physical and chemical fabrication techniques for PV applications have witnessed countless challenges (Maeda et al., 2011; Katagiri et al., 2008 and Ahmed et al., 2012). The simulation approach is aimed at curtailing the numerous
queries relating to expenses of experimental studies which includes; several mechanical losses owed to absorber layer structures, flaws, thermal or electrical properties conflicts.

Cupric oxide also known as copper (II) oxide is a black solid stable oxide of copper. CuO has a band gap of 1.2 eV. The metal oxide has a p-type semiconductor property, monoclinic structure with adsorption coefficient 105 cm\(^{-1}\), electrical resistivity of about 10 to 105 \(\Omega\).cm and high thermal conductivity (Liu, Lin, & Wang, 2011; Ooi et al, 2013; Shabu et al., 2015; Valladares et al., 2012). The first attempt to use copper (1) oxide (Cu\(_2\)O) for solar application was in 1978 (Abdu and Musa. 2009). Cuprous oxide has low electron affinity (3.2 eV) (Sawicka-Chudy et al, 2018) and very high hole mobility (Hossain, Alharbi and Tabet, 2015). Thus, it is recommended for possible hole transport material in heterojunction based solar cells (Lee et al, 2013). Several designs have been made to construct n-type Cu\(_2\)O and homo-junction Cu\(_2\)O cells, but the attained efficiency is quite low.

Solar cells produce about 0.5 volts to 0.6 volts of open circuit voltage and 1 to 8 amps DC current depending on a range of factors but mainly related to the semiconductor used (Cutter, 2012). About 36 to 72 solar cells are stacked together in series to form a module which can produce meaningful output. A solar panel is an arrangement of solar modules either in series or parallel. When the solar panel is connected in parallel and currents added, the voltage remains constant, while for series current produced remains constant (Singla and Garg, 2013).

This study was able to model the effect of annealing on the efficiency of a nanostructured CuO/TiO\(_2\) pn and Cu\(_2\)O/TiO\(_2\) pn heterojunction using SCAPS. The sunlight beam was simulated using AM 1.5G with a 500 W Xenon lamp using working temperature of 300 K and 423.15 K. The simulation recorded an optimized result for nanostructured Cu\(_2\)O/TiO\(_2\) pn heterojunction solar cell having the efficiency of 3.85 % and a fill factor of 53.50 % obtained for nitrogen annealed.

### 3.3 Numerical Modeling Overview

The first solar cells simulation work was reported by Lee using ADEPT 1dimension program developed at Purdue (Gauery et al., 2018). Lee and Gray investigated the effects of grain boundaries, non-ideal back contact, and specified the various necessary parameters for measuring cell performance. Gloeckler, Fahrenbruch, & Sites (2003) defined the initial simulating parameters by setting a CdTe baseline. The study defined the influence of thin layer of CdS amid the regions
of TCO and CdTe. J-V curves was defined in the simulation using an AMPS simulation tool. Various parameters in this simulation software are temperature independent. The simulation of graded junction is conceivable. J-V in spectral response measurement, dark and light can be simulated when the device definition is completed. Nonetheless, AMPS compared to supplementary simulating tools is slow in solving problems (Muthuswamy, 2005).

Numerous simulating tools are currently accessible. The earliest simulating program was developed as a PhD thesis by Mark S. Lundstrom (Ukoba et al., 2018). Additional programs include; TFSSP (Thin-Film Semiconductor Simulation Program), Solar Cell Analysis Program in 1dimension (SCAPS 1D), Solar Cell Analysis Program in 2Dimension, PUPHS and PUPHS 2D. A number of solar cell models has been used in thin-film Si: H, Si, Ge, CdS/CIS, GaAs and CdS/CdTe cells in one spatial dimension along with high efficiency Si and GaAs solar cells in 2Dimension (Ganvir, 2016).

For this current work, SCAPS is adopted for the simulation of nanostructured CuO/TiO₂ and Cu₂O/TiO₂ pn thin film solar cells. The nanostructured CuO/TiO₂ and Cu₂O/TiO₂ pn heterojunction solar cells were simulated at different working points and subjected to different annealing samples for thermal investigation using SCAPS.

3.3.1 Solar Cells Capacitance Simulator (SCAPS)

This simulation package is for solar cells structures used initially at Gent University for solar cells of CdTe and CuInSe₂ family (Burgelmna et al., 2013). It has since been used for other members of the family of solar cells (Ukoba and Inambao, 2018). It describes mathematically the performance of a solar cell using finite difference methods and solves differential equations, together with several physics of semiconductors. SCAPS performs a complete simultaneous numerical solution of Poisson's and continuity equations with conditions on the working points suitable to one and two-dimensional cells (Schwartz, et al., 1985). The equations are expressed as shown in the following equations (1) - (3).

\[ \nabla^2 v = - \frac{q}{\varepsilon} (p - n + N_D - N_A) \]  
\[ \nabla \cdot J_p = q(G - R) \]  
\[ \nabla \cdot J_n = q(R - G) \]
The general terms of equations 2 and 3 can be represented as:

\[ G(x) = \int_{0}^{\infty} \phi a e^{-\alpha x} d\lambda \]  

(3.10)

The hole and electron current densities are identified in equations 2 and 3 are expressed by

\[ J_p = -q\mu_p p \nabla V_p - kT \mu_p \nabla p \]  

(3.11)

\[ J_n = -q\mu_n n \nabla V_n + kT \mu_n \nabla n \]  

(3.12)

\[ V_p = V - (1 - \gamma) \Delta G / g \]  

(3.13)

\[ V_n = V + \gamma \Delta G / g \]  

(3.14)

where \( V_p \) and \( V_n \) represent the effective potentials expressed in equations 7 and 8. \( \Delta G \) and \( \gamma \) interprets the variations in band structure, such as the density of band gap and states, and describes the Fermi-Dirac statistics. Expression \( J_n \) and \( J_p \) represent the current density of the electron and holes individually. Similarly, \( \mu_n \) and \( \mu_p \) denote the mobility of the electron and hole separately.

3.3.2 Absorber (CuO) and Buffer (TiO₂) layer Properties

The absorber layer is the p-type semiconductor copper (II) oxide known as cupric oxide (CuO). The CuO and Cu₂O has an electron affinity of 4.07 eV and 3.20 eV and a large hole mobility (Hossain, et al., 2015 and Li, et al., 2009) respectively. However, the buffer layer is made of a widely studied material TiO₂, a transition metal oxide (Tripathi et al., 2013). TiO₂ has unique optoelectronic properties, durable with great refractive index making it the ideal material for several applications including solar cells (Kirbiyik et al., 2019).

3.4 Simulation Model and Result

3.4.1 SCAPS simulation of the CuO/TiO₂ and Cu₂O/TiO₂ pn heterojunction

The input parameters used for the SCAPS simulation are presented in Table 1 below as mentioned in figure 2.2 in chapter two (2).

<p>| Table 1. Parameters used for the metal oxide SCAPS modeling |</p>
<table>
<thead>
<tr>
<th>Material properties</th>
<th>Buffer (TiO$_2$)</th>
<th>Absorber (CuO)</th>
<th>Absorber (Cu$_2$O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band Gap (eV)</td>
<td>2.26</td>
<td>1.5</td>
<td>2.17</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>4.20</td>
<td>4.07</td>
<td>3.20</td>
</tr>
<tr>
<td>Dielectric permittivity (relative)</td>
<td>10.00</td>
<td>18.10</td>
<td>7.11</td>
</tr>
<tr>
<td>Conduction band (1/cm$^3$)</td>
<td>2.0E+17</td>
<td>2.2E+19</td>
<td>2.0E+17</td>
</tr>
<tr>
<td>Valence band (1/cm$^3$)</td>
<td>6.0E+17</td>
<td>5.5E+20</td>
<td>1.1E+19</td>
</tr>
<tr>
<td>Electron mobility (cm$^2$/Vs)</td>
<td>1.0E+2</td>
<td>10.0E+1</td>
<td>2.0E+2</td>
</tr>
<tr>
<td>Hole mobility (cm$^2$/Vs)</td>
<td>25.0</td>
<td>1.0E-1</td>
<td>8.0E+1</td>
</tr>
<tr>
<td>Shallow uniform donor density (1/cm$^3$)</td>
<td>1.0E+17</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Shallow uniform acceptor density (1/cm$^3$)</td>
<td>0</td>
<td>1.0E+16</td>
<td>1.0E+18</td>
</tr>
</tbody>
</table>
Table 3. 1. Summary of input parameters for the back and front contact used for the metal oxide SCAPS simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Front contact</th>
<th>Back Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holes</td>
<td>1.00E+5</td>
<td>1.00E+5</td>
</tr>
<tr>
<td>Electron</td>
<td>1.00E+5</td>
<td>1.00E+5</td>
</tr>
<tr>
<td>Metal Work function (eV)</td>
<td>5.0216</td>
<td>5</td>
</tr>
<tr>
<td>Majority Carrier Barrier height (eV) relative to E(f)</td>
<td>0.2216</td>
<td>0.4</td>
</tr>
<tr>
<td>Majority Carrier Barrier height (eV) relative to E(v)</td>
<td>0</td>
<td>0.2271</td>
</tr>
</tbody>
</table>

3.4.2 Annealing effect on a nanostructured CuO/TiO\(_2\) and Cu\(_2\)O/TiO\(_2\) heterojunction solar cells

Sunlight passes through a conducting substrate onto the absorber layer and buffer layer in a typical p-n heterojunction. Incident photons from the sun are absorbed by the absorber layer being a p-type semiconductor. The unabsorbed photons are dissipated in the form of heat. However, the buffer layer completes the p-n heterojunction with the absorber layer.

In this study, CuO and Cu\(_2\)O are used as the different absorber layer, TiO\(_2\) as the buffer layer and the effect of annealing on the efficiency and I-V characteristics is observed. The simulation mimicked as deposited for CuO and Cu\(_2\)O at room temperature and compared it with air and nitrogen annealed at 423.15 K and the absorber and buffer layer thickness is 2000 nm and 200 nm individually. Also, the thickness of the buffer layers was made thin to minimize resistance series in a solar cell device (Zhao, et al., 2012). A schematic representation of the nanostructured solar cells layer simulated using SCAPS is shown in Figure 3.6 and Figure 3.7
Figure 3. 6 SCAPS panel showing the CuO/TiO$_2$ Solar cells definition

Figure 3. 7 SCAPS panel showing the Cu$_2$O/TiO$_2$ Solar cells definition
3.4.3 The Simulated J-V result

The efficiency is obtained using Equation 9 as shown:

\[
\eta = \frac{FF \times (V_{oc} \times J_{sc})}{P_{in}}
\]  

(3.15)

3.5 RESULTS AND DISCUSSION

The parameters of solar cells analysed from J-V curve are presented in Table 3.2 and 3.3. The nitrogen annealed nanostructured CuO/TiO₂ had a fill factor of 64.01% with an efficiency of 0.47 % and the as-deposited with a FF of 41 % and efficiency of 0.21. However, nitrogen annealed nanostructured Cu₂O/TiO₂ pn heterojunction solar cell, a fill factor of 53.50 % with an efficiency of 3.85 % was recorded and the as-deposited with a FF of 41 % and efficiency of 0.21 %. The increase in the annealed samples validate the fact that annealing has effect on relieving strain caused by lattice mismatch and adjust the surface morphology, improve formation of CuO/TiO₂ and Cu₂O/TiO₂ films (Dussan, Bohórquez, & Quiroz, 2017).

Table 3.2. The parameters of the CuO/TiO₂ pn heterojunction solar cells.

<table>
<thead>
<tr>
<th>Model</th>
<th>J_{sc}</th>
<th>V_{oc} (mV)</th>
<th>J_m (mA/cm²)</th>
<th>V_m (mV)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>0.80</td>
<td>323</td>
<td>0.51</td>
<td>208</td>
<td>41</td>
<td>0.21</td>
</tr>
<tr>
<td>Air annealed</td>
<td>0.98</td>
<td>350</td>
<td>0.57</td>
<td>215</td>
<td>53.50</td>
<td>0.37</td>
</tr>
<tr>
<td>Nitrogen annealed</td>
<td>1.04</td>
<td>354</td>
<td>0.67</td>
<td>233</td>
<td>64.01</td>
<td>0.47</td>
</tr>
</tbody>
</table>

Table 3.3. The parameters of Cu₂O/TiO₂ pn heterojunction solar cells

<table>
<thead>
<tr>
<th>Model</th>
<th>J_{sc}</th>
<th>V_{oc} (mV)</th>
<th>J_m (mA/cm²)</th>
<th>V_m (mV)</th>
<th>FF (%)</th>
<th>η (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>0.80</td>
<td>323</td>
<td>0.51</td>
<td>208</td>
<td>41</td>
<td>0.21</td>
</tr>
<tr>
<td>Air annealed</td>
<td>0.93</td>
<td>323</td>
<td>0.57</td>
<td>215</td>
<td>49.50</td>
<td>3.23</td>
</tr>
<tr>
<td>Nitrogen annealed</td>
<td>1.02</td>
<td>354</td>
<td>0.67</td>
<td>233</td>
<td>53.50</td>
<td>3.85</td>
</tr>
</tbody>
</table>

### 3.5.1 Solar Cell Efficiency

**Figure 3.8.** shows the different annealing variables plotted against the solar cell efficiency for nanostructured CuO/TiO$_2$ pn heterojunction. This shows the effect of annealed sample and how it influences the rate of change in efficiency. The result shows the effect of annealing sample on solar cells efficiency as it increased from 0.21 % efficiency at 300K of annealed sample to 0.47 % at an annealed sample of 423.15K. This is an increase compared to the as-deposited efficiency of 0.21 % annealed at 300k and 0.36 % reported by Saeid M., *et al.*, (2014).

**Figure 3.9** denotes the effect of annealing sample on Cu$_2$O/TiO$_2$ pn heterojunction solar cells efficiency as it increased from 0.21 % efficiency at 300K to annealed sample to 3.85% being for annealed sample at 423.15K. This is an increase compared to the as-deposited TiO$_2$/Cu$_2$O pn heterojunction efficiency of ~0.01% TiO$_2$/Cu$_2$O reported by Li *et al.*, (2011).

**Figure 3.8** Plot of solar cells efficiency versus as-deposited and air and nitrogen annealed samples for Cu$_2$O/TiO$_2$ pn solar cells
Figure 3.9. Plot of solar cells efficiency versus as-deposited and air and nitrogen annealed samples for CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn solar cells.

Figure 3.10 and 3.11 (below) reflects the distribution of annealed temperature at different fill factor of the nanostructured CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ solar cells. From the figure, it was observed that for CuO/TiO$_2$ solar cell, the fill factor was 41% at 300 K annealing temperature, and at 423.15 K it was seen to be 53.5% and when the temperature was maintained at 423.15 K after a period of time, the fill factor increased to 64.01%. While Cu$_2$O/TiO$_2$ solar cells recorded a fill factor of 41% at 300 K as-deposited. At annealing temperature of 423.15 K it was seen to be 49.5% and when the temperature was maintained at 423.15 K after a period of time, the fill factor increased to 53.50%. This increment in the fill factor when the sample was annealed validates the fact that annealing has impact on the structural, optical and electrical properties of solar cells (Mahato, & Kar, 2017). This illustrates that the solar cell fill factor (FF) increases as annealing temperature increased from 300 K and continued to increase when an annealing temperature of 423.15 K was maintained.
Figure 3. 10 Plot of filled factor versus as-deposited and annealed samples (air and nitrogen) for CuO/TiO$_2$ pn solar cells.

Figure 3. 11 Plot of filled factor versus as-deposited and annealed samples (air and nitrogen) for CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn solar cells.

Figures 3.12 gives the J-V curve of as-deposited CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ heterojunction solar cells from 0 to 1.50 volts. Both CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ heterojunction solar cells exhibited the same value for the short-circuit current ($J_{sc}$) at 0.81 A, open-circuit voltage ($V_{oc}$) of 323 V, fill factor of 41% and an efficiency of 0.21%. The resultant J-V curve is in alignment to the standard J-V curve of solar cell under illumination.
Figure 3. 12 The J-V curve for as-deposited CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn heterojunction solar cells.

Figure 3.13 gives the $J$-$V$ curve for the air annealed CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn heterojunction solar cells. This plot reports that for CuO/TiO$_2$ pn heterojunction solar cell, a short circuit current ($J_{sc}$) of 0.98 A was exhibited, open-circuit voltage ($V_{oc}$) of 350 V, fill factor (FF) of 53.50 % and an efficiency of 0.37 %. While, Cu$_2$O/TiO$_2$ pn heterojunction solar cell shows a short circuit current ($J_{sc}$) of 0.93 A was exhibited, open-circuit voltage ($V_{oc}$) of 350 V, fill factor (FF) of 49.5 % and an efficiency of 3.23 %.

Figure 3. 13 The J-V curve for air annealed CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn heterojunction solar cells.
Figure 3.14 displays the result of the $J$-$V$ curve for the nitrogen annealed CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn heterojunction solar cells. From the curve, CuO/TiO$_2$ pn heterojunction solar cell shows 1.04 A short-circuit current ($J_{sc}$), open-circuit voltage ($V_{oc}$) of 354, a fill factor (FF) of 64.01 % with an efficiency of 0.47 %. The fill factor (FF) obtained was 0.21 %, at a working point of 300 K. At this point the Cu$_2$O/TiO$_2$ pn heterojunction solar cell displays a short-circuit current ($J_{sc}$) of 1.02 A, open-circuit voltage ($V_{oc}$) of 354, fill factor (FF) of 53.50% and an efficiency 3.85% at a working point of 423.15 K. This curve is in accordance with standard J-V curve of a solar cell experiencing illumination (Shi et al., 2012 and Anton Sundqvist et al., 2016).

![Figure 3.14. J-V curve for nitrogen annealed CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn heterojunction solar cells](image)

3.5.2 Effect of defect density

The defect in density of the absorber layers (CuO or Cu$_2$O) influences the solar cells performance. Decrease in densities effect yield limited recombination and trap cores and extends the performance of solar cells (Tan et al., 2016). Figure 7 shows that the total charge remains steady at 0.0E+0mA/cm$^2$ at an absorber thickness of 2000 nm and buffer of 200 nm, with annealed sample at 423.15K. The red-line signifies the hole, the blue signifies the electron and green is total (charge).
3.6 Conclusion

This simulation result shows the annealing effect on nanostructured CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ heterojunction solar cells by means of SCAPS:

- The different annealed samples were observed to have influenced the solar cells efficiency. This shows that, with an annealed sample within the range of 423.15 K to 500K the change in the solar cells efficiency is quite significant and this agrees with the data of Iqbal et al., (2018).

- The performance of CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ cells is influenced by the defect density. A lesser defect density mainly at absorber layer (CuO or Cu$_2$O) increases the photovoltaic effect.

- The annealed result shows the cell efficiency of 0.47 % at an annealed sample of 423.15 K, which is an increase compared to the as-deposited CuO/TiO$_2$ pn heterojunction efficiency of 0.21 % at working point of 300 K, and 0.36 % efficiency reported by S. Masudy et al., (2015).

- A fill factor of 53.50 % and efficiency of 3.85 % was obtained from Nitrogen annealed nanostructured Cu$_2$O/TiO$_2$ pn heterojunction solar cell. This is an improvement on 1.25 % obtained by Luo et al (2011) Cu$_2$O/TiO$_2$ solar cells.

- This simulation shows that for annealing optimization of CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn heterojunction solar cell, Cu$_2$O/TiO$_2$ the solar cell reached a better efficiency of 3.85 % which is higher than the efficiency of 0.47 % recorded by CuO/TiO$_2$ solar cell.
The values of this simulation model will provide a guide in experimental, fabrication and optimization of TiO₂/CuO and TiO/Cu₂O solar cells.
CHAPTER 4

4 THE EFFECT OF THICKNESS ON THE SIMULATION AND OPTIMIZATION OF NANOSTRUCTURED Cu$_2$O/TiO$_2$ AND CuO/TiO$_2$ PN HETEROJUNCTION SOLAR CELL

Chapter 4 looks at the effect of thickness in the modeling and optimization of the nanostructured Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ metal oxides heterojunctions. It is divided into two parts.


4.1 Introduction

Nanostructured metal oxides (NMO) continue to attract interest due to the versatility in energy applications (Diab et al., 2011; Ge et al., 2016; Wick and Tilley, 2015 and Minami, et al., 2015). NMO have good band gaps, affordable, tuneability, is abundant and environmentally friendly (Djinkwi Wanda et al, 2016). However, laboratory experiments are yet to rival conventional silicon solar cells for better efficiency and performance. The simulation of solar cells acts as a guidepost for faster and better experimental results.

Copper Oxide is the first semiconductor studied in relation to photovoltaic (Brattain, 1951). However, ZnO has since gained more interest despite the promising potential of Cu₂O. The metal oxide (Cu₂O) has a band gap of 2.17 eV, electron affinity of 3.2, and it is easily available (Wang et al., 2018).

Despite the promising potential of cuprous oxide (Cu₂O), experimental deposition has resulted in low efficiency. Pagare and Torane, (2018) obtained an efficiency of 0.21% using the electrochemical deposition technique. An improved efficiency of 1.05% was obtained by Saehana and Muslimin, (2013) by employing polymer electrolyte using electrochemical deposition. Efforts have been made towards improving thin film solar cells efficiency through numerical modeling tools such as PC1D (Banerjee, 2017), MatLab Simulink (Ghosh and Kundu, 2017), and wxAMPS (Liu, Sun and Rockett, 2012). SCAPS-1D is exceptional and possess the capacity to compute seven (7) semiconductor layers and at the same time characterize the parameters (Anwar et al., 2017). Essentially, this program can solve the primary semiconductor equations; it also has the potential to model/simulate nanostructured solar cells.

Copper (II) oxide (CuO) is among the few p-type NMO having semiconducting properties with potentials (Brattain, 1951) for affordable photovoltaic applications. Copper (II) oxide efficiency is low compared to efficiency of 20% recorded by copper indium gallium selenide (CIGS) solar cells at the laboratory experiment (Liu et al., 2010). CuO are environmentally friendly, socially acceptable, earthly abundant and economically viable with good band gap (Sibiński & Znajdek, 2011; Boudaoud L et al., 2015; Ukoba et al., 2018).

In this study, Cu₂O/TiO₂ and CuO/TiO₂ pn heterojunction solar cells were simulated using Solar cells capacitance simulator (SCAPS). The paper reported simulation results of the various heterojunction solar cells owing to the numerous uncertainty such as defect, thermal or electrical properties mismatches associated with an experiment.
This study showed the effect of thickness in the optimization process of nanostructured heterojunction solar cells. For Cu$_2$O/TiO$_2$ pn heterojunction solar cells, it showed an increased efficiency of 1.6% while CuO/TiO$_2$ pn heterojunction solar cell recorded an optimized efficiency of 8.05%. The various nanostructured solar cells were simulated at the same working conditions, at room temperature of 300K at a thickness of up to 400 nm before remaining constant. An improved, input power of 1000W/m$^2$, illumination of AM1.5 lamp, and under varied thickness of 500 nm to 10,000 nm for the absorber layer (Cu$_2$O and CuO) and 50 nm to 6000 nm for the buffer layer (TiO$_2$). This is with a view of providing a platform for the design and fabrication of cheap and efficient metal oxide solar cells.

4.2 Model background

4.2.1 Solar cells modeling governing equation

Solar cells are basically pn heterojunction. Photovoltaic systems exhibit nonlinear I–V features that differ with temperature of the solar cells and the radiant intensity. Under ideal conditions, a solar cell can be theoretically simulated as a current source under a diode. A direct current is produced when a solar cell is exposed to light and this current varies linearly with the solar radiation. This is represented in Figure 4.1. Solar cell model equivalent circuit

From the aforementioned, the characteristic equations are given as:

\[ I_{ph} = \frac{I_r \times I_{sc}}{I_{r0}} \]  
(4.1)

Equation (1) shows that the photocurrent relies on temperature and solar insolation.

\[ V_t = \frac{kT}{q} \]  
(4.2)

\[ I_s = I_{sc} \times \left( e^{\frac{V_{oc}}{nV_t}} - 1 \right) \]  
(4.3)
It can be seen from equation (3) that the cell’s saturation current varies with the cell temperature,

\[ I_d = I_s \times \left( e^{\left( \frac{V + I_R}{nV_t N_s} \right)} - 1 \right) \]  

Equation (4) gives the Shockley equation.

\[ I = I_{ph} - I_d - I_{sh} \]  

The output current of a solar cells is represented in equation (5) and gives the electrical behaviour and relationship between the current supplied and voltage. Where; \( I_{ph} \) is the photocurrent, \( I_{sc} \) is the reverse saturation current, \( R_S \) and \( R_{sh} \) are the inherent resistances in series and parallel connected to the cell, \( N_s \) is a number of cells in series, \( q \) is electron charge, \( K \) is the Boltzmann’s constant and \( A \) is ideality factor.

### 4.2.2 Solar cells capacitance simulator (SCAPS)

This is a simulation package for solar cells structures used initially at Gent University for solar cells of CdTe and CuInSe2 family (Burgelmna et al., 2013). Solar cells have since been used for other family of solar cells (Ukoba and Inambao, 2018). It mathematically describes the performance of a solar cell using finite difference methods. SCAPS performs a complete numerical solution of Poisson and continuity equation with condition to the working conditions applicable to one and two-dimensional cells (Schwartz, et al., 1985). The equations are expressed as shown in equations (6) - (8).

\[ \nabla^2 v = - \frac{q}{\varepsilon} (p - n + N_D - N_A) \]  

\[ \nabla . J_p = q (G - R) \]  

\[ \nabla . J_n = q (R - G) \]  

The general terms of equations 7 and 8 can be represented as:

\[ G(x) = \int_0^\infty \phi a e^{-ax} d\lambda \]  

The hole and electron current densities are represented in equations 7 and 8 are expressed as

\[ J_p = -q \mu_p p \nabla V_p - kT \mu_p \nabla p \]  

\[ J_n = -q \mu_n n \nabla V_n + kT \mu_n \nabla n \]  

\[ V_p = V - (1 - \gamma) \Delta G / g \]  

\[ V_n = V + \gamma \Delta G / g \]
Where $v_p$ and $v_n$ represent the effective potentials expressed in equations 12 and 13. $\Delta G$ and $\gamma$ represents the variations in band structure; the band gap and density of states, together with Fermi-Dirac statistics. Expression $J_n$ and $J_p$ denote the current density of the electron and holes individually. Similarly, $\mu_n$ and $\mu_p$ signifies mobility of the electron and hole.

### 4.2.3 Absorber (Cu$_2$O) and Buffer (TiO$_2$) layer Properties

The absorber layer is made of a p-type oldest semiconductor material known as Cuprous oxide (Cu$_2$O) and cupric oxide (CuO) (Brattain, 1951). The National Science Foundation were the first to use it for photovoltaic application in 1978 (Olsen, et al., 1982). Cu$_2$O has electron affinity of 3.2 eV and a large hole mobility and CuO with an electron affinity of 4.07 eV and a good hole mobility (Hossain, et al., 2015 and Li, et al., 2009). However, the buffer layer is made of a widely studied material, TiO$_2$, a transition metal oxide (Tripathi et al., 2013). TiO$_2$ has unique optoelectronic properties, durable with great refractive index making it the ideal material for several applications including solar cells (Kirbiyik et al., 2019).

### 4.3 Simulation model and result

#### 4.3.1 SCAPS simulation of the Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn heterojunction

The input parameters used for the SCAPS simulation are presented in the Table below as in the table 2.3 in chapter two (2) and Table 2.

The Table below shows a Summary of input parameters used for the metal oxide SCAPS modeling (Hossain, Alharbi, & Tabet, 2015; Li, et al., 2009; Ichimura, & Kato, 2013).

<table>
<thead>
<tr>
<th>Material properties</th>
<th>Buffer (TiO$_2$)</th>
<th>Absorber (Cu$_2$O)</th>
<th>Absorber (CuO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band Gap (eV)</td>
<td>2.26</td>
<td>2.17</td>
<td>1.5</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>4.20</td>
<td>3.20</td>
<td>4.07</td>
</tr>
<tr>
<td>Dielectric permittivity (relative)</td>
<td>10.00</td>
<td>7.11</td>
<td>18.10</td>
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### Conduction band (1/cm^3)

<table>
<thead>
<tr>
<th></th>
<th>Front</th>
<th>Back</th>
</tr>
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<tbody>
<tr>
<td>2.0E+17</td>
<td>2.0E+17</td>
<td>2.2E+19</td>
</tr>
</tbody>
</table>

### Valence band (1/cm^3)

<table>
<thead>
<tr>
<th></th>
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<th>Back</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.0E+17</td>
<td>1.1E+19</td>
<td>5.5E+20</td>
</tr>
</tbody>
</table>

### Electron mobility (cm^2/Vs)

<table>
<thead>
<tr>
<th></th>
<th>Front</th>
<th>Back</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0E+2</td>
<td>2.0E+2</td>
<td>10.0E+1</td>
</tr>
</tbody>
</table>

### Hole mobility (cm^2/Vs)

<table>
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<th></th>
<th>Front</th>
<th>Back</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.0</td>
<td>8.0E+1</td>
<td>1.0E-1</td>
</tr>
</tbody>
</table>

### Shallow uniform donor density (1/cm^3)

<table>
<thead>
<tr>
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<th>Front</th>
<th>Back</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0E+17</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### Shallow uniform acceptor density (1/cm^3)

<table>
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<th></th>
<th>Front</th>
<th>Back</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0E+18</td>
<td>1.0E+16</td>
</tr>
</tbody>
</table>

The table below shows Summary of input parameters for the front and back contact used for the metal oxide SCAPS simulation as in table 3.1 in chapter Three (3)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Front contact</th>
<th>Back Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holes</td>
<td>1.00E+5</td>
<td>1.00E+5</td>
</tr>
<tr>
<td>Electron</td>
<td>1.00E+5</td>
<td>1.00E+5</td>
</tr>
<tr>
<td>Metal Work function (eV)</td>
<td>5.0216</td>
<td>5</td>
</tr>
<tr>
<td>Majority Carrier Barrier height (eV) relative to E_f</td>
<td>0.2216</td>
<td>0.4</td>
</tr>
<tr>
<td>Majority Carrier Barrier height (eV) relative to E_v</td>
<td>0</td>
<td>0.2271</td>
</tr>
</tbody>
</table>
4.4 Effect of Thickness on the nanostructured Cu$_2$O/TiO$_2$ heterojunction solar cells

Sunlight passes through a conducting substrate onto the absorber layer and buffer layer in a typical p-n heterojunction. Incident photons from the sun light is absorbed by the absorber layer being a p-type semiconductor. The unabsorbed photons are dissipated in a form of heat. However, the buffer layer being n-type completes a p-n heterojunction together with an absorber layer.

In this study, Cu$_2$O is used as the absorber layer, TiO$_2$ as the buffer layer and the influence of different thickness on the efficiency, and I-V characteristics may be observed. The absorber layer thickness is varied from 500 nm to 10,000 nm and the buffer layer thickness is varied from 50 nm to 600 nm. These thicknesses were chosen because it was found that an improved Cu$_2$O solar cells efficiency is achieved in the range of this layer thickness (Pavan et al., 2015). However, the thickness of the buffer layer is to be thin to minimize resistance series in a solar cell device (Zhao, et al., 2012). A schematic representation of a nanostructured solar cells layer simulated using SCAPS is shown in Figure 4.1 and 4.2.
Figure 4.1. SCAPS panel showing the Cu$_2$O/TiO$_2$ Solar cells definition

Figure 4.2. SCAPS panel showing the CuO/TiO$_2$ Solar cells definition

4.5 RESULTS AND DISCUSSION

4.5.1 Effect of Thickness on the Solar Cells Efficiency

Figure 4.4 and 4.5 show a plot of the varied absorber and buffer layer thickness versus the solar cells efficiency for CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn heterojunction solar cells. It is observed that solar cells efficiency decreases with an increment in the buffer layer (TiO$_2$) up to 400 nm before
maintaining a constant value. An increase in the absorber layer (CuO and Cu₂O) results in more photons being absorbed, culminating in photo-generated current increment (Liao et al., 2009). The optimized result for CuO/TiO₂ pn heterojunction solar cell gave a cell efficiency of 8.05%. While the optimized result for Cu₂O/TiO₂ pn heterojunction solar cell gave a cell efficiency of 1.6% at 500 nm absorber layer thickness and 50 nm buffer layer thickness. This is an increment on existing result of 1.05% using electrochemical deposition of Cu₂O/TiO₂ heterojunction solar cells recorded by Saehana and Muslimin (2013).

**Figure 4.3** shows the plot of absorbers CuO and buffer layer (TiO₂) thickness with the solar cells efficiency.
Figure 4.4 shows the plot of absorbers Cu$_2$O and buffer layer (TiO$_2$) thickness with the solar cells efficiency.

The efficiency was obtained using Equation 14 as shown below

$$\eta = \frac{FF \times (V_{oc} \times J_{sc})}{P_{in}}$$

(4.14)

Figure 4.6 and 4.7 illustrates the plot of the varied absorber and buffer layer thickness versus the solar cells Fill Factor for CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn heterojunction solar cells. The plot shows that for CuO/TiO$_2$ pn heterojunction solar cells, the highest fill factor of 71% was obtained at 0.40 nm thickness. While Cu$_2$O/TiO$_2$ pn heterojunction solar cell indicates a high fill factor of 63.20% at 0.05 nm thickness. The Fill factor decreased as the thickness increased until an increment was observed. Thereafter, the FF maintained further decrease. This agrees with the solar cells efficiency which also experienced a fluctuation at the same thickness.
Figure 4.5 plot of absorber and buffer layer thickness with the solar cells filled factor for Cu$_2$O/TiO$_2$ pn heterojunction solar cells.

Figure 4.6 plot of absorber and buffer layer thickness with the solar cells filled factor for CuO/TiO$_2$ pn heterojunction solar cells.
4.6 J-V Parameters

The simulated optimized J-V curve is revealed in Figure 4.8 for the optimized Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn heterojunction solar cells. This is in harmony with the standard solar cell J-V curve under illumination (Shi et al., 2012).

![Figure 4.7](image)

Figure 4.7 Fig 5 J-V curve for the optimized CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ pn heterojunction

From the solar cell evaluated parameters of the J-V curve presented in Table 4.1. The modeled solar cell displays 26.0516 A short-circuit current ($J_{sc}$), an open-circuit voltage ($V_{oc}$) of 0.0435 V, the fill factor (FF) of 71 %, and an efficiency ($\eta$) of 8.05 % at absorber layer thickness of 500 nm and buffer layer thickness of 50 nm. This is a marked improvement in the efficiency of 1.05% obtained from the electrochemical deposition of CuO/TiO$_2$ pn heterojunction solar cells recorded by Saehana, and Muslimin (2013). While the Cu$_2$O/TiO$_2$ exhibits a short-circuit current ($J_{sc}$) of 24.0764 A, the open-circuit voltage ($V_{oc}$) of 1.0486 V, the fill factor (FF) of 63.20 %, and an efficiency ($\eta$) of 1.6% at absorber layer thickness of 500 nm and buffer layer thickness of 50 nm.

Table 4.1 The parameters of the Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn heterojunction solar cells.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$J_{sc}$ (A)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>24.0764</td>
<td>1.0486</td>
<td>63.20</td>
<td>1.6</td>
</tr>
<tr>
<td>(Cu$_2$O)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Value</td>
<td>26.0516</td>
<td>0.0435</td>
<td>71</td>
<td>8.05</td>
</tr>
<tr>
<td>(CuO)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Figure 4.9** illustrates the current density of the optimized Cu$_2$O/TiO$_2$ solar cell. The red curve shows the current density of the holes and the blue curves depict that of the electron current density. The total current density, the green curve, was observed to have a constant at a value of 2 mA/cm$^2$ at an absorber layer thickness of 500 nm and buffer layer thickness of 50 nm.

![Figure 4.8 The Current density of the optimized Cu$_2$O/TiO$_2$](image)

**Figure 4.10** illustrates the current density of the optimized CuO/TiO$_2$ pn heterojunction solar cell. The red curve shows the current density of the holes and the blue curves depict that of the electron current density. The total current density, the green curve, was observed to have a constant at a value of 1.5 mA/cm$^2$ at an absorber layer thickness of 500 nm and buffer layer thickness of 50 nm. In contrast, **Figure 4.11** shows the simulated band diagram of the optimized CuO/TiO$_2$ heterojunction solar cells.

![Figure 4.9 Simulated Current Density of the optimized CuO/TiO2 heterojunction solar cells.](image)
4.7 Effect of defect density

Lower defect densities produce less traps and recombination centers leading to prolonged performance of solar cells (Tan et al., 2016). The defect density of the absorber layers (Cu$_2$O and CuO) has impact on the solar cells performance. The occupational probability of deep defect is presented in Figure 4.12. The red line denotes the hole, the blue represents the electron and the black is for the total. A constant value is recorded for the hole at 1E+18 per cm$^3$, for the electron it is lower at 1E+12 per cm$^3$ and the total is at 1E+5 per cm$^3$

It is therefore recommended that the defect density be reduced to improve the interface quality of the Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ solar cells. This is in concordance with the study by Sawicka-Chudy., et al. (2018).
4.8 Conclusion

This study was able to simulate and optimize nanostructured CuO/TiO$_2$ and Cu$_2$O/TiO$_2$ heterojunction solar cells using SCAPS. The defect density and thickness effect on the solar cell efficiency and performance was demonstrated. It was found that:

- The absorber and buffer layer thickness variation affects the solar cells’ efficiency. The optimized solar cells parameter was found at an absorber layers (Cu$_2$O and CuO) thickness of 500 nm, buffer layer (TiO$_2$) thickness of 50 nm. This translates to a cost reduction as compared to large thickness.

- Defect density has impact on the performance of Cu$_2$O/TiO$_2$ cells. An increased photovoltaic effect is experienced by a lower defect density especially at the absorber layers (Cu$_2$O and CuO).

- This study obtained an improved efficiency of 1.6 % for Cu$_2$O/TiO$_2$ pn heterojunction solar cell and 8.05 % efficiency for CuO/TiO$_2$ pn heterojunction solar cell when compared to lower value recorded experimentally in previous studies.

- This shows that CuO/TiO$_2$ pn heterojunction solar cell has a better efficiency of 8.05 % for thickness optimization.

- This numerical simulation value will provide a guideline in experimental deposition of Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ pn heterojunction solar cells.

This simulation result contributes to the pursuit to develop affordable and sustainable energy and provides guide for more research towards affordable solar cells technologies.
CHAPTER 5

5 CONCLUSION AND RECOMMENDATION

The final chapter presents a summary of the findings and recommendations for future work about similar studies.

5.1 Summary of the study

The aims and objectives of this study is to explore through modeling and simulation, characterization and optimization of nanostructured copper oxide based solar cell on Cu$_2$O/TiO$_2$ and CuO/TiO$_2$ p-n heterojunction. The intent is to provide a framework for efficient design, using an experimental approach, of efficient, clean and affordable solar energy using a nanostructured metal oxide solar cells. This numerical study was done with the intent to providing sustainable and affordable energy to developing and low-income countries.

Chapter 1 summarized the background of the study coupled with an overview in the history of solar cell investigations. This chapter also brought to light the problem statements as one of the major challenges faced in South Africa and Africa in general, regarding the issue of cheap and sustainable power generation. It also presented the research questions, scope and objective of the study along with its significance. The author was able to answer research question (i) and achieved the study objective (i).

This study focused on numerical optimization of nanostructured copper oxide (CuO and Cu$_2$O) solar cells, through characterizing and optimizing the parameters and improving the performance of the nanostructured copper oxide solar cells being an affordable alternative to silicon wafers. The optimization examined the effect of thickness and effect of annealing on the two oxides of copper i.e. CuO and Cu$_2$O.

Chapter 2 presented a comprehensive literature review on the trends of solar cell simulations, developments of simulation programs and the progress so far. This set the basis for the need to use the SCAPS simulation program. It also gave an overview including the basics and its potentials as an affordable, simple and reliable simulation tool for thin films modeling. However, emphasis was placed on the modeling and simulation of nanostructured metal oxide solar cells towards a more
sustainable and affordable energy development and distribution. It also displays the potency of solar energy to satisfy the energy demand of the developing countries. However, further investigation is needed to reduce the current cost, increase the efficiency and sustainability of current solar technology in the market. This chapter was able to answer research questions (i and v) and achieved the study objective (ii and iii).

Chapter 3 Summarizes the performance improvement through numerical simulation of annealed nanostructured CuO/TiO₂ and Cu₂O/TiO₂ pn heterojunction solar cells and the effect of annealing on the modeled nanostructured heterojunction solar cells device. This chapter was able to establish that for CuO/TiO₂ pn heterojunction solar cell, the efficiency of 0.47 % and a fill factor of 64 % being for nitrogen annealed at 423.15 K. Also, for Cu₂O/TiO₂ pn heterojunction solar cell, an efficiency of 3.85 % and a fill factor of 53.50 % being for nitrogen annealed at 423.15 K was recorded. This shows that Cu₂O/TiO₂ heterojunction solar cell recorded a better efficiency of 3.85 % with a fill factor of 53.50 % for annealing optimization at 423.15 K. From this chapter, the author was able to answer the research question (iii) and achieve objective (iv and v).

Chapter 4 presented the simulation and optimization of nanostructured Cu₂O/TiO₂ and CuO/TiO₂ pn heterojunction solar cells. It studied the effects of film thickness variation and its effect on nanostructured heterojunction solar cell device. A conversion efficiency of 8.05 % was obtained for CuO/TiO₂ pn heterojunction solar cell under an absorber layer thickness of 500 nm and buffer layer thickness of 50 nm. For Cu₂O/TiO₂ pn heterojunction solar cell, an efficiency of 1.6 %, fill factor of 63.20 % at an absorber layer thickness of 500 nm and buffer layer thickness of 50 nm was recorded. This shows that for thickness optimization, CuO/TiO₂ pn heterojunction solar cell recorded a better efficiency of 8.05 % with a fill factor of 71 % at an absorber layer thickness of 500 nm and a buffer layer thickness of 50 nm. This chapter was able to answer research question (iv) and achieve objective (iv and v).

These simulation results shows that nanostructured CuO/TiO₂ and Cu₂O/TiO₂ pn heterojunction solar cells can be optimized through thickness and annealing methods. Also, this study was able to acknowledge the fact that SCAPS simulation tool has the potentials of a good simulation tool for solar cell simulation.
In conclusion, from this simulation, nanostructured CuO/TiO$_2$ pn heterojunction solar cell possess a better efficiency through thickness optimization with an efficiency of 8.05% at an absorber layer thickness of 500 nm and buffer layer thickness of 50 nm.

5.2 Future work

The potential and opportunities in solar cells photovoltaic applications are huge and limitless with its broad evolving areas. However, due to resources and the scope of this study, some areas could not be covered. The following can be investigated further to help obtain an improved efficiency and performance:

**Theoretical/Simulation:**

- Other modeling tools and software can also be explored for formulating and validating results.
- Further optimization can be done on the concentration by combining with other low-cost deposition techniques. Ageing and other substrates can also be explored.
- There are other parameters which can be explored during the course of the modeling and then validated via experimental results.
- Additional cheap metal oxides with good semiconducting abilities can also be investigated using different but cheap techniques for possible optimization and fabrication.
- Tuning can be done by varying simulation parameters and a possibility of doping with other materials.
LIST OF REFERENCES


APPENDICES

APPENDICE A: SCHEMATIC OF THE DESSERTATION

SCHEMATIC OF THE MODELING AND SIMULATION OF NANOSTRUCTURED COPPER OXIDE SOLAR CELLS FOR PHOTOVOLTAIC APPLICATIONS

NANO+COPPER OXIDE+SOLAR CELLS+MODELING

REVIEW

ANNEALING OPTIMIZATION
Aims energy Journal (published)

THICKNESS OPTIMIZATION
JOURNAL OF ENERGY STORAGE (UNDER REVIEW)
ICAE CONFERENCE (PRESENTED TO BE PUBLISHED BY YEAR END)
JOURNAL OF MATERIAL SCIENCE (UNDER REVIEWS)
Numerical modeling of effect of annealing on nanostructured CuO/TiO₂ pn heterojunction solar cells using SCAPS

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Abstract: The problem of global warming has led to increased research on solar energy and other renewable energy. Solar cells are a building block of solar energy. Different materials for solar cells fabrication exist with silicon-based being commercially viable and common. The bulk of the alternate materials aimed at providing cheap, efficient and sustainable solar cells. Nanostructured Metal oxides solar cells goes a step further to providing a clean, affordable, sustainable solar cells although the efficiency is still low. This study examined the numerical modelling of the annealing effect on the efficiency of nanostructured CuO/TiO₂ pn heterojunction using SCAPS. The motivation for the study is to provide a basis for experimental design of affordable, non-toxic and efficient alternate material for silicon solar cells. The modelling was performed using Solar cells capacitance simulator (SCAPS). The input parameters, obtained from literature, include a working point of 300 K for the as-deposited CuO/TiO₂ which was compared with air and nitrogen annealed (423.15 K) nanostructured CuO/TiO₂ pn heterojunction. Other working condition included simulated sunlight using illumination of AM 1.5G with a 500 W Xenon lamp, silver was used as the electrode/contact. Film thickness of 2000 nm and 200 nm for absorber and buffer respectively. The results gave an optimum efficiency of 0.47 obtained from Nitrogen annealed CuO/TiO₂ pn heterojunction. Also, the optimum Fill Factor was obtained to be 64.01% from Nitrogen annealed. The annealed samples performed better than the as-deposited CuO/TiO₂ pn heterojunction. This result will help in the experimental fabrication of improved efficiency metal oxide-based solar cells.

Keywords: annealing; CuO/TiO₂; modeling; SCAPS; solar cells; pn heterojunction
Abbreviations: CuO: Cupric Oxide; FF: Filled Factor; I–V: Current-voltage; J–V: Current density-voltage; Jsc: Short-circuit current; NMO: Nanostructured Metal Oxide; PN: p-type (excess hole), n-type (excess electron) heterojunction; SCAPS: Solar cells capacitance simulator; TiO₂: Titanium dioxide; Voc: Open circuit voltage; ZnO: Zinc Oxide; η: Efficiency

1. Introduction

Numerical modeling has been employed to offer a theoretical road map for speedy experimental optimization of processes. Simulation have been used for optimization of parameters in energy [1], transportation [2,3], production planning [4], water and food production [5]. Numerical simulation has also been employed in improving the properties of solar cells [6,7]. Nanostructured metal oxide is among the emerging solar cells. Modeling of nanostructured metal oxide interest has increased significantly for decades due to the simplicity and ease of manipulation of the tool [8,9].

Photovoltaic continue to gain prominence in Europe and other part of the world [10]. However, affordability and other factor continue to hinder the usage in Africa and other developing countries [11–13]. Although, nanostructured metal oxides solar cells show promise of low cost, clean and efficient photovoltaic usage in Africa [14,15]. Nanostructured metal oxides (NMO) continue to attract interest due to the versatility in energy applications [16–19]. However, most of them still exhibit weak conversion efficiencies resulting in several experiments in the laboratory in an attempt to obtain the optimum power conversion efficiency. Although, metal oxide efficiency is still low compared to other solar cells, similar efficiency of 20% recorded by CIGS-based solar cells [20]. Though the progress of numerous physical and chemical fabrication techniques for PV [21–23]. While, different explanations could describe this condition, such as several loss mechanisms owed to absorber structures.

Cupric oxide also known as copper (II) oxide is a black solid stable oxide of copper. CuO has a band gap of 1.2 eV [24]. The metal oxide has a p-type semiconductor property, monoclinic structure with adsorption coefficient 105 cm⁻¹, electrical resistivity of about 10 to 105 Ω cm and high thermal conductivity [25–27].

Solar cells produce about 0.1 volts to 0.6 volts of open circuit voltage and 1 to 8 amps DC current depending on a range of factors but mainly related to the semiconductor used [28]. About 36 to 72 solar cells are stacked together in series to form a module which can produce meaningful output. A solar panel is an arrangement of solar modules either in series or parallel. When the solar modules are connected in parallel the currents are added and voltage is the same, while for series the voltages are added and current produced remains the same [29].

The first solar cells simulation work was reported by Lee using ADEPT 1dimension program developed at Purdue [30]. Lee and Gray [31] investigated the effect of grain boundaries, non-ideal back contact, and specified the various necessary parameters for measuring cell performance. Gloeckler, et al. [32] defined the initial simulating parameters by setting CdTe baseline. The study defined the influence of thin layer of CdS amid the regions of TCO and CdTe. J–V curves was defined in the simulation. The study used AMPS Simulation software developed at Pennsylvania university by S. Fonash and coworkers. Various parameters in this simulation software are temperature independent. The simulation of graded junction is conceivable. J–V in spectral response measurement, dark and light can be simulated when the device definition is completed. Nonetheless, AMPS compared to supplementary simulating tools is slow in solving problem [33].
This study was able to model the annealing effect on efficiency of nanostructured CuO/TiO$_2$ pn heterojunction using SCAPS. The annealing temperatures were varied between 300 K and 423.15 K. The sunlight beam was simulated using AM 1.5G with a 500 W Xenon lamp. The highest fill factor and efficiency of 64.01 and 0.47 was obtained for nitrogen annealed nanostructured CuO/TiO$_2$ heterojunction.

2. Numerical modeling overview

Numerous simulating tools are currently accessible. The earliest simulating program was developed as a PhD thesis by Mark S. Lundstrom. Additional programs include; TFSSP (Thin-Film Semiconductor Simulation Program), Solar Cell Analysis Program in 1dimension (SCAPS 1D), Solar Cell Analysis Program in 2Dimension, PUPHS and PUPHS 2D. A number of solar cell models has been used in thin-film Si: H, Si, Ge, CdS/CIS, CdS/CdTe and GaAs cells in one spatial dimension and high efficiency Si and GaAs solar cells in 2Dimension [34].

For this current work, SCAPS is adopted for the simulation of nanostructured CuO/TiO$_2$ thin film solar cells. The nanostructured CuO/TiO$_2$ pn heterojunction solar cells was simulated at different working point and subjected to different annealing samples for thermal investigation using SCAPS.

2.1. Solar cells capacitance simulator (SCAPS)

It is a solar cells simulation package for solar cells structures used initially at Gent University for solar cells of CdTe and CulnSe$_2$ family [35]. It has since been used for other family of solar cells [36]. It describes mathematically the performance of a solar cell using finite difference methods and solves differential equations which, along with several relations from physics of semiconductors. SCAPS performs a complete simultaneous numerical solution of the two continuity equations and Poisson's equation conditional on the boundary conditions appropriate to one and two-dimensional cells [37]. The equations are expressed as shown in Eqs 1–3.

\[ \nabla^2 v = -\frac{q}{\varepsilon (p - n + N_D - N_A)} \]

\[ \nabla J_P = q(G - R) \]

\[ \nabla J_n = q(R - G) \]

The general terms of Eqs 2 and 3 can be represented as:

\[ G(x) = \int_0^x \phi ae^{-ax} d\lambda \]

The hole and electron current densities which appear in Eqs 2 and 3 are given by

\[ J_p = -q\mu_p p\nabla p - kT\mu_p \nabla p \]

\[ J_n = -q\mu_n n\nabla n + kT\mu_n \nabla n \]

\[ V_p = V - (1 - \gamma) \Delta G / g \]

\[ V_n = V + \gamma \Delta G / g \]
where $v_n$ and $v_s$ represent the effective potentials expressed in Eqs 7 and 8. $\Delta G$ and $\gamma$ account for variations in the band structure, such as the density of band gap and states, and account for Fermi-Dirac statistics. Expression $J_n$ and $J_p$ represent the current density of the electron and holes respectively. Similarly, $\mu_n$ and $\mu_p$ represent the mobility of electron and hole respectively.

2.2. Absorber (CuO) and Buffer (TiO$_2$) layer properties

The absorber layer is made of a p-type semiconductor copper(II) oxide known as cupric oxide (CuO). The CuO has electron affinity of 4.07 eV and a large hole mobility [38,39]. However, the buffer layer is made of a widely studied material TiO$_2$, a transition metal oxide [40]. TiO$_2$ has unique optoelectronic properties, durable with great refractive index making it ideal material for several applications including solar cells [41].

3. Simulation model and results

3.1. SCAPS simulation of the CuO/TiO$_2$ pn heterojunction

The input parameters used for the SCAPS simulation were adapted from literature using properties and values of TiO$_2$ and CuO and are presented in Table 1 [39,42,43].

Table 1. Summary of input parameters used for the metal oxide SCAPS modelling [39, 42,43].

<table>
<thead>
<tr>
<th>Material properties</th>
<th>Buffer (TiO$_2$)</th>
<th>Absorber (CuO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band Gap (eV)</td>
<td>2.26</td>
<td>1.5</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>4.20</td>
<td>4.07</td>
</tr>
<tr>
<td>Dielectric permittivity (relative)</td>
<td>10.00</td>
<td>18.10</td>
</tr>
<tr>
<td>Conduction band (1/cm$^3$)</td>
<td>2.0E + 17</td>
<td>2.2E + 19</td>
</tr>
<tr>
<td>Valence band (1/cm$^3$)</td>
<td>6.0E + 17</td>
<td>5.5E + 20</td>
</tr>
<tr>
<td>Electron mobility (cm$^2$/Vs)</td>
<td>1.0E + 2</td>
<td>10.0E + 1</td>
</tr>
<tr>
<td>Hole mobility (cm$^2$/Vs)</td>
<td>25.0</td>
<td>1.0E - 1</td>
</tr>
<tr>
<td>Shallow uniform donor density (1/cm$^3$)</td>
<td>1.0E + 17</td>
<td>0</td>
</tr>
<tr>
<td>Shallow uniform acceptor density (1/cm$^3$)</td>
<td>0</td>
<td>1.0E + 16</td>
</tr>
</tbody>
</table>

The input parameters for the back and front contact were optimized values using the SCAPS software and is shown in Table 2.
Table 2. Summary of input parameters for the back and front contact used for the metal oxide SCAPS simulation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Front contact</th>
<th>Back Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holes</td>
<td>1.00E + 5</td>
<td>1.00E + 5</td>
</tr>
<tr>
<td>Electron</td>
<td>1.00E + 5</td>
<td>1.00E + 5</td>
</tr>
<tr>
<td>Metal Work function (eV)</td>
<td>5.0216</td>
<td>5</td>
</tr>
<tr>
<td>Majority Carrier Barrier height (eV) relative to E_F</td>
<td>0.2216</td>
<td>0.4</td>
</tr>
<tr>
<td>Majority Carrier Barrier height (eV) relative to E_F</td>
<td>0</td>
<td>0.2271</td>
</tr>
</tbody>
</table>

3.2. Effect of Annealing on the nanostructured CuO/TiO_2 heterojunction solar cells

Sunlight passes through a conducting substrate onto the absorber layer and buffer layer in a typical p-n heterojunction. Incident photons from the sunlight are absorbed by the absorber layer which is a p-type semiconductor. The unabsorbed photons are dissipated in the form of heat. However, the buffer layer completes the p-n heterojunction with the absorber layer.

In this study, CuO is used as the absorber layer, TiO_2 as the buffer layer and the effect of annealing on the efficiency, and I-V characteristics is observed. The simulation mimicked as-deposited CuO at room temperature and compared it with air and nitrogen annealed at 423.15 K. Researches have shown that titanium dioxide is a top n-type for CuO pn heterojunction solar cells with a great efficiency [44]. In this study, 2000 nm and 200 nm was used for the absorber and buffer layer thickness respectively. These values are within the optimize thickness range and also thickness of the buffer layer should be made thin to minimize resistance series in solar cell device [45]. A schematic representation of the nanostructured solar cells layer simulated using SCAPS is shown in Figure 1. The main panel showing layer definition and numerical setting is shown in Figure 1a. Schematic of the nanostructured CuO/TiO_2 pn Heterojunction Solar Cells is shown in Figure 1b.

![SCAPS panel showing the CuO/TiO_2 pn heterojunction solar cells definition.](image_url)

Figure 1. SCAPS panel showing the CuO/TiO_2 pn heterojunction solar cells definition.
3.2.1. The Simulated J-V result

The efficiency is obtained using Eq 9 as shown.

\[
\eta = \frac{FF \times (V_{oc} \times J_{sc})}{P_{in}}
\]  

(9)

The parameters of solar cells analysed from J-V curve are presented in Table 3. The nitrogen annealed nanostructured CuO/TiO_2 had the highest fill factor of 64.01% with an efficiency of 0.47%. The as-deposited/nanostructured CuO/TiO_2 had the lowest with a FF of 41% and efficiency of 0.21. The increase in the annealed samples validate the fact that annealing has consequence on relieving strain caused by lattice mismatch and adjust the surface morphology, improve formation of CuO/TiO_2 films [46].

Table 3. The parameters of the CuO/TiO_2 pn heterojunction solar cells.

<table>
<thead>
<tr>
<th>Model</th>
<th>J_ab (mA/cm^2)</th>
<th>V_ab (mV)</th>
<th>J_sc (mA/cm^2)</th>
<th>V_sc (mV)</th>
<th>FF (%)</th>
<th>( \eta ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>0.80</td>
<td>323</td>
<td>0.51</td>
<td>208</td>
<td>41</td>
<td>0.21</td>
</tr>
<tr>
<td>Air annealed</td>
<td>0.98</td>
<td>350</td>
<td>0.57</td>
<td>215</td>
<td>53.50</td>
<td>0.37</td>
</tr>
<tr>
<td>Nitrogen annealed</td>
<td>1.04</td>
<td>354</td>
<td>0.67</td>
<td>233</td>
<td>64.01</td>
<td>0.47</td>
</tr>
</tbody>
</table>

3.3. Solar cell efficiency

Figure 2, shows the different annealing variables plotted against the solar cell efficiency. This shows the effect of annealed sample and how it influences the rate of change in efficiency. The result shows the effect of annealing sample on solar cells efficiency as it increased from 0.21% efficiency at 300 K of annealed sample to 0.47% at an annealed sample of 423.15 K. This is an increase compared to the as-deposited CuO/TiO_2 pn heterojunction efficiency of 0.21% annealed at 300 K and 0.36% reported by Sachana M., et al., [47].

Figure 2. Plot of solar cells efficiency versus as-deposited and air and nitrogen annealed samples.
Figure 3 below shows the distribution of annealed temperature at different fill factor of the nanostructured CuO/TiO$_2$ solar cells. From the figure 3, it was observed that the fill factor was 41% at 300 K annealing temperature, and at 423.15 K it was seen to be 53.5%. However, when the temperature was maintained at 423.15 in Nitrogen environment after a period of time, the fill factor increased to 64.01%. This increment in the fill factor when the sample was annealed validates the fact that annealing has impact on the structural, electrical and optical properties of solar cells [48]. This shows that the solar cell FF increases as annealing temperature increased from 300 K and continued to increase when an annealing temperature of 423.15 K was maintained.

![Figure 3](image-url)  
**Figure 3.** Plot of filled factor versus as-deposited and annealed samples (air and nitrogen).

Figure 4 gives the J-V curve of as deposited CuO/TiO$_2$ heterojunction solar cells. It shows a short-circuit current ($J_{sc}$) of 0.81A, open-circuit voltage ($V_{oc}$) of 323 mV, fill factor of 41% and an efficiency of 0.21%. The resultant $J-V$ curve is in alignment with the standard $J-V$ curve of solar cell under illumination.

![Figure 4](image-url)  
**Figure 4.** The J-V curve for as deposited CuO/TiO$_2$ pn heterojunction solar cells.
Figure 5 gives the $J-V$ curve for the air annealed CuO/TiO$_2$ pn heterojunction solar cells. This plot reports that a short circuit current ($J_{sc}$) of 0.98A was exhibited, open-circuit voltage ($V_{oc}$) of 350 mV, fill factor (FF) of 53.50% and an efficiency of 0.37%.

![J-V curve for air annealed CuO/TiO$_2$ pn heterojunction solar cells.](image1)

**Figure 5.** The $J-V$ curve for air annealed CuO/TiO$_2$ pn heterojunction solar cells.

Figure 6 displays the result of the $J-V$ curve for the nitrogen annealed CuO/TiO$_2$ pn heterojunction solar cells. The curve shows a short-circuit current ($J_{sc}$) of 1.04A, open-circuit voltage ($V_{oc}$) of 354 mV, fill factor (FF) of 64.01% and an efficiency of 0.47%. The fill factor (FF) obtained was 0.21%, at a working point of 300 K. This curve is in accordance with standard J-V curve of a solar cell experiencing illumination [49].

![J-V curve for nitrogen annealed CuO/TiO$_2$ pn heterojunction solar cells.](image2)

**Figure 6.** J-V curve for nitrogen annealed CuO/TiO$_2$ pn heterojunction solar cells.
3.3.1. Effect of defect density

Defect in density of the absorber layer (CuO) influence the solar cells performance. Decrease in densities effect yield limited recombination and trap cores and extend the performance of solar cells [50]. Figure 7 shows that the total charge remains steady at 0.0E + 0 mA/cm² at an absorber thickness of 2000 nm and buffer of 200 nm, with annealed sample at 423.15 K. The red-line signifies the hole, the blue signifies the electron and green is total (charge).

![Image](image.png)

**Figure 7.** Current density of annealed CuO/TiO₂ heterojunction solar cells.

4. Conclusions

This simulation result shows the effect of annealing of nanostructured CuO/TiO₂ heterojunction solar cells by means of SCAPS.

- The different annealed samples were observed to have influenced the solar cells efficiency. This interprets that, with an annealed sample within the range of 300 K to 423.15 K the change in the solar cells efficiency is quite significant and this agrees with [51].
- The performance of CuO/TiO₂ cells is influenced by defect density. A lesser defect density mainly at absorber layer (CuO) increases the photovoltaic effect.
- The annealed result shows the cell efficiency of 0.47% at an annealed sample of 423.15 K, which is an increase compared to the as-deposited CuO/TiO₂ pn heterojunction efficiency of 0.21% at working point of 300K, and 0.36% efficiency reported by Masudy S, et al., [52].
- The values of this simulation model will offer a guide in experimental, fabrication and optimization of CuO/TiO₂ solar cells.

Acknowledgments

The authors acknowledge the SCAPS software team for the computational resources. Professor Jen and Dr. Ukoba acknowledges financial support of NRF and URC University of Johannesburg.

Conflict of Interest

The authors declare that there is no conflict of interest.
References


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APPENDICE C: PRESENTED CONFERENCE PAPER

SIMULATION AND OPTIMIZATION OF NANOSTRUCTURED Cu₂O/TiO₂ PN HETEROJUNCTION SOLAR CELLS USING SCAPS

International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 0081

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ABSTRACT
This paper reported numerical simulation and optimization of nanostructured Cu₂O/TiO₂ pn heterojunction solar cells. This is with a view to providing an optimized cell efficiency to aid experiment and development of high-efficiency metal oxide solar cells. The solar cells equations were modelled and thereafter theoretically validated on the nanostructured metal oxides. The model working points include a room temperature of 300K, input power of 1000W/m² using illumination of AM1.5 lamp, and under varied thickness of 0.5 μm to 10.0 μm for the absorber layer (Cu₂O) and 0.05 μm to 6.0 μm for the buffer layer (TiO₂). The modelled solar cell exhibits a short-circuit current (Isc) of 24.0764 A, the open-circuit voltage (Voc) of 1.0486 V, the fill factor (FF) of 63.20 %, and the efficiency (η) of 1.6% at absorber layer thickness of 500 nm and buffer layer thickness of 50 nm. Also, the defect density was obtained for the solar cells. This will serve as a theoretical guide for laboratory research on the improvement of efficiency of Cu₂O metal oxide solar cells. This will open a new frontier for modelling of metal oxide based thin film solar cells especially Cu₂O thin films solar cells. This is a booster in the quest to develop affordable and sustainable energy by encouraging more research in solar cells technologies in low-income countries.

Keywords: Cu₂O/TiO₂, Optimization, Metal Oxide, Nanostructured, Thin films solar cells, SCAPS

NOMENCLATURE

Abbreviations

Cu₂O Cuprous Oxide
FF Filled Factor
J-V Current density - voltage
I-V Current-voltage
Jsc Short-circuit current

| NMO | Nanostructured Metal Oxide |
| SCAPS | Solar cells capacitance simulator |
| TiO₂ | Titanium dioxide |
| Voc | Open circuit voltage |
| ZnO | Zinc Oxide |

Symbols

η Efficiency

1. INTRODUCTION
Nanostructured metal oxides (NMO) continue to attract interest due to their versatility in energy applications (Diab et al., 2011; Ge et al., 2016; Wick and Tilley, 2015 and Minami et al., 2015). NMO have good band gaps, affordable, tuneable, abundance and environmentally friendly (Djinkwi et al., 2016). However, laboratory experimental results are yet to rival conventional silicon solar cells in terms of efficiency and performance. The simulation of solar cells acts as a guidepost for faster and better experimental results.

Copper Oxide is the first semiconductor studied in relation to photovoltaic application (Brattain, 1951). However, ZnO has since gained more interest despite its promising potential of Cu₂O. The metal oxide (Cu₂O) has a band gap of 2.17 eV, electron affinity of 3.2, and it is easily available (Wang et al., 2018).

Despite the promising potential of cuprous oxide (Cu₂O), experimental deposition has resulted in low efficiency. Pagare and Torane, (2018) obtained an efficiency of 0.21% using electrochemical deposition technique. Improved efficiency of 1.05% was obtained by Saehana and Muslimin, (2013) by employing polymer electrolyte using electrochemical deposition. Attempts have been made to improve the thin film solar cells efficiency using numerical modelling tools such as PC1D (Banerjee, 2017), MatLab Simulink (Ghosh and Kundu, 2017), and wxAMPS (Liu et al., 2012). SCAPS-1D is exceptional and possess the capacity to compute seven (7)
semiconductor layers and at the same time characterize the parameters (Anwar et al., 2017). Essentially, this program can solve the primary semiconductor equations, it also has the potential to model/simulate nanostructured solar cells. In this study, Cu2O/TiO2 pn heterojunction solar cells was simulated using solar cells capacitance simulator (SCAPS). The paper reported simulation result of Cu2O/TiO2 pn heterojunction solar cells owing to the numerous uncertainty such as defect, thermal or electrical properties mismatches associated with an experiment. This is with the aim of providing a useful guideline for the experimental design of high-performance metal oxide-based solar cells.

In this study, the efficiency of the Cu2O/TiO2 pn heterojunction solar cells increased up to 400 nm before remaining constant. Improved efficiency of 1.6% was recorded at a room temperature of 300K, input power of 1000 W/m², illumination of AM1.5 lamp, and under varied thickness of 500 nm to 10,000 nm for the absorber layer (Cu2O) and 50 nm to 6000 nm for the buffer layer (TiO2).

2. MODEL BACKGROUND

2.1 Solar cells modelling governing equation

Solar cells are basically pn heterojunction. Photovoltaic systems exhibit a nonlinear I-V characteristics that vary with the temperature of the solar cells and the radiant intensity. Under ideal conditions, a solar cell can be theoretically modelled as a current source under a diode. A direct current is produced when the solar cells are exposed to light and this current varies linearly with the solar radiation. This is represented in Figure 1.

![Solar cells model equivalent circuit](image)

Fig 1 Solar cells model equivalent circuit

From the aforementioned, the characteristic equations are given as:

\[ I_{ph} = I_t \times \frac{I_{sc}}{I_{tn}} \]  

Equation (1) shows that the photocurrent depends on the temperature of the solar cells and solar insolation.

\[ V_T = \frac{kT}{q} \]  

\[ I_s = I_{sc} \times \left( e^{\frac{V_{oc}}{kT}} - 1 \right) \]  

It can be seen from equation (3) that the cell’s saturation current varies with the cell temperature,

\[ I_s = I_t \times \left( e^{\frac{V_{oc}}{nV_T}} - 1 \right) \]  

Equation (4) gives the Shockley equation.

\[ I = I_{ph} - I_t - I_s \]  

The output current of the solar cells is represented in equation (5) and gives the electrical behaviour and relationship between the current supplied and voltage. Where; \( I_{ph} \) is the photocurrent, \( I_t \) is the reverse saturation current, \( R_s \) and \( R_a \) are the inherent resistances in series and parallel associated with the cell, \( N_s \) is a number of cells in series, \( q \) is the electron charge, \( K \) is the Boltzmann’s constant and \( A \) is the ideality factor.

2.2 Solar cells capacitance simulator (SCAPS)

SCAPS is a solar cells simulation package for solar cells structures used initially at Gent University for solar cells of CdTe and CuInSe2 family (Burglemann et al., 2013). It has since been used for other families of solar cells (Ukoba and Inambao, 2018). It solves the differential equations which, along with several relations from the physics of semiconductors, describe mathematically the performance of a solar cell using finite difference methods. SCAPS performs a complete simultaneous numerical solution of the two continuity equations and Poisson’s equation conditional on the boundary conditions appropriate to one and two-dimensional cells (Schwartz et al., 1985). The equations are expressed as shown in equations (6)-(8).

\[ \nabla^2 \psi = - \frac{q}{\varepsilon} (p - n + N_D - N_A) \]  

\[ \nabla \cdot J_p = q (V - R) \]  

\[ \nabla \cdot J_n = q (R - G) \]  

The general terms of equations 7 and 8 can be represented as:

\[ G(x) = \int_0^x \phi e^{-ax} d\lambda \]  

The hole and electron current densities which appear in equations 7 and 8 are given by

\[ J_p = -q \mu_p \nabla \psi - kT \mu_p \mu_p \nabla \psi \]  

\[ J_n = -q \mu_n \nabla \psi + kT \mu_n \nabla \psi \]  

\[ V_p = V - (1 - \gamma) \Delta G / g \]  

\[ V_n = V + \gamma \Delta G / g \]  

where \( \psi_p \) and \( \psi_n \) represent the effective potentials expressed in equations 12 and 13. \( \Delta G \) and \( \gamma \) account for variations in the band structure, such as the density of states and band gap, and account for Fermi-Dirac statistics. Expression \( J_s \) is the current density of the electron and holes respectively. Similarly, \( \mu_n \) and \( \mu_p \) represent the mobility of electron and hole respectively.
2.3 Absorber (Cu₂O) and Buffer (TiO₂) layer Properties

The absorber layer is made of a p-type, known as Cuprous oxide (Cu₂O) oldest semiconductor material (Brattain, 1951). The National Science Foundation was the first to use it for photovoltaic application in 1978 (Olsen et al., 1982). Cu₂O has electron affinity of 3.2 eV and large hole mobility (Hossain et al., 2015 and Li et al., 2009). However, the buffer layer is made of a widely studied material TiO₂, a transition metal oxide (Tripathi et al., 2013). TiO₂ has unique optoelectronic properties, durable with great refractive index making it the ideal material for several applications including solar cells (Kirbiyik et al., 2019).

3. SIMULATION MODEL AND RESULT

3.1 SCAPS simulation of the Cu₂O/TiO₂ p-n heterojunction

The input parameters used for the SCAPS simulation are presented in Table 1 and Table 2.

Table 1. Summary of input parameters used for the metal oxide SCAPS modelling

<table>
<thead>
<tr>
<th>Material properties</th>
<th>Buffer (TiO₂)</th>
<th>Absorber (Cu₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band Gap (eV)</td>
<td>2.26</td>
<td>2.17</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>4.20</td>
<td>3.20</td>
</tr>
<tr>
<td>Dielectric permittivity (relative)</td>
<td>10.00</td>
<td>7.11</td>
</tr>
<tr>
<td>Conduction band (1/cm²)</td>
<td>2.0E+17</td>
<td>2.0E+17</td>
</tr>
<tr>
<td>Valence band (1/cm²)</td>
<td>6.0E+17</td>
<td>1.1E+19</td>
</tr>
<tr>
<td>Electron mobility (cm³/Vs)</td>
<td>1.0E+2</td>
<td>2.0E+2</td>
</tr>
<tr>
<td>Hole mobility (cm³/Vs)</td>
<td>25.0</td>
<td>8.0E+1</td>
</tr>
<tr>
<td>Shallow uniform donor density (1/cm³)</td>
<td>1.0E+17</td>
<td>0</td>
</tr>
<tr>
<td>Shallow uniform acceptor density (1/cm³)</td>
<td>0</td>
<td>1.0E+18</td>
</tr>
</tbody>
</table>

Table 2. Summary of input parameters for the back and front contact used for the metal oxide SCAPS simulation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Front contact</th>
<th>Back Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Holes</td>
<td>1.00E+5</td>
<td>1.00E+5</td>
</tr>
<tr>
<td>Electron</td>
<td>1.00E+5</td>
<td>1.00E+5</td>
</tr>
</tbody>
</table>

3.2 Effect of Thickness on the nanostructured Cu₂O/TiO₂ heterojunction solar cells

Sunlight passes through a conducting substrate onto the absorber layer and buffer layer in a typical p-n heterojunction. Incident photons from the sunlight is absorbed by the absorber layer which is a p-type semiconductor. The unabsorbed photons are dissipated in the form of heat. However, the buffer layer completes the p-n heterojunction with the absorber layer.

In this study, Cu₂O is used as the absorber layer, TiO₂ as the buffer layer and the effect of varying the thickness on the efficiency, and I-V characteristics are observed. The thickness of the absorber layer is varied from 500 nm to 10,000 nm and the buffer layer thickness is varied from 50 nm to 600 nm. These thicknesses were chosen because it was found that an improved Cu₂O solar cells efficiency is achieved in the range of this layer thickness (Pavan et al., 2015). Also, the buffer layer should be made thin to minimize series resistance in the solar cell device (Zhao et al., 2012). A schematic representation of nanostructured solar cells layer simulated using SCAPS is shown in Figure 2.

3.3 Solar cells efficiency

Figure 3 shows the plot of the varied absorber and buffer layer thickness with the solar cells Fill Factor and Figure 4 depicts the plot of the varied absorber and buffer layer thickness with the efficiency of the solar cells.

The efficiency of solar cells decreases with an increment in the buffer layer (TiO₂) up to 400 nm before maintaining a constant value. An increase in the absorber
layer (Cu$_2$O) results in more photons being absorbed culminating in a photo-generated current increment (Liao et al., 2009).

![Image of a graph showing Cu2O/TiO2 solar cells filled factor as a function of thickness.](Image)

**Fig 3** A plot of absorber and buffer layer thickness with the solar cells filled factor.

The optimized result gave a cell efficiency of 1.6% at absorber layer thickness of 500 nm and buffer layer thickness of 50 nm which is an incremental improvement on the existing result of 1.05% obtained using electrochemical deposition of Cu$_2$O/TiO$_2$ heterojunction solar cells recorded by Sachana and Muslimin (2013).

![Image of a graph showing Cu2O/TiO2 efficiency as a function of solar cells thickness.](Image)

**Fig 4** A plot of absorber and buffer layer thickness with the efficiency of the solar cells.

3.4 J-V Parameters

The simulated optimized J-V curve is shown in Figure 5. This is in concordance with the standard J-V curve of solar cells under illumination (Shi et al., 2012).

Similarly, Figure 6 shows the current density of the optimized result. The red curve shows the current density of the holes and the blue curves depict that of the electron current density. The total current density, the green curve, was observed to have a constant at a value of 2 mA/cm$^2$ at an absorber layer thickness of 500 nm and buffer layer thickness of 50 nm.

![Image of a graph showing current density as a function of distance.](Image)

**Fig 5** The J-V curve for the optimized Cu$_2$O/TiO$_2$ pn heterojunction

The efficiency is obtained using Equation 14:

$$\eta = \frac{FF \times (V_{oc} \times J_{sc})}{P_{in}}$$  \hspace{1cm} (14)

![Image of a graph showing current density.](Image)

**Fig 6** Current density of the optimized Cu$_2$O/TiO$_2$ heterojunction solar cells.

The solar cell parameters evaluated from the J-V curve are presented in Table 3.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$J_{sc}$ (A)</th>
<th>$V_{oc}$ (V)</th>
<th>FF (%)</th>
<th>$\eta$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value</td>
<td>24.0764</td>
<td>1.0486</td>
<td>63.20</td>
<td>1.6</td>
</tr>
</tbody>
</table>

The modelled solar cell exhibits a short-circuit current ($J_{sc}$) of 24.0764 A, the open-circuit voltage ($V_{oc}$) of 1.0486 V, the fill factor (FF) of 63.20 %, and the efficiency ($\eta$) of 1.6% at absorber layer thickness of 500 nm and buffer layer thickness of 50 nm. This is a marked improvement in the efficiency of 1.05% obtained from the electrochemical deposition of Cu$_2$O/TiO$_2$ heterojunction solar cells recorded by Sachana, and Muslimin (2013).

3.5 Effect of defect density
Lower defect densities produce fewer traps and recombination centres and prolong the performance of the solar cells (Tan et al., 2016). The defect density of the absorber layer (Cu2O) has an impact on the performance of the solar cells performance. The occupational probability of deep defect is shown in Figure 7. The red line represents the hole, the blue represents the electron and the black is for the total. A constant value is recorded for the hole at 1E+18 per cm³, for electron, it is lower at 1E+12 per cm³ and the total is at 1E+5 per cm³.

It is therefore recommended that the defect density be reduced to improve the interface quality of the Cu2O/TiO2 solar cells. This is in concordance with the study by Sawicka-Chudy et al. (2018).

![Fig 7 Occupational Probability of deep defect for electron](image)

**CONCLUSION**

This study was able to simulate and optimize nanostructured Cu2O/TiO2 heterojunction solar cells using SCAPS. The effect of layer thickness, defect density on the solar cell’s efficiency was demonstrated. It was found that:

- The absorber and buffer layer thickness variation affects the efficiency of the solar cells. The optimized solar cells parameter was found at an absorber layer (Cu2O) thickness of 500 nm, buffer layer (TiO2) thickness of 50 nm. This translates to cost reduction as compared to large thickness.

- Defect density has an impact on the performance of Cu2O/TiO2 cells. An increased photovoltaic effect is experienced by a lower defect density especially at the absorber layer (Cu2O).

- This study obtained an improved efficiency of 1.6% when compared to the lower value recorded experimentally in previous studies.

- This numerical simulation value will provide a guideline in the experimental deposition of Cu2O/TiO2 solar cells.

This simulation result contributes to the pursuit to develop affordable and sustainable energy and provides guide for more research in solar cells technologies in low-income countries.

**ACKNOWLEDGEMENT**

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**REFERENCE**


APPENDICE D: EDITING CERTIFICATE

CERTIFICATE of EDITING
the following thesis
MODELING AND SIMULATION OF NANOSTRUCTURED COPPER OXIDES SOLAR CELLS FOR PHOTOVOLTAIC APPLICATION

By
George Chukwuebuka Enebe
(201100840)

Thesis is submitted to the Faculty of Engineering and the Built Environment in partial fulfilment of the requirements for
Master’s degree (MEng)
IN
MECHANICAL ENGINEERING SCIENCE
AT THE
UNIVERSITY OF JOHANNESBURG
JOHANNESBURG, SOUTH AFRICA

This document certifies that the above manuscript was proofread and edited by
DELICIA ROSELINE LANGENHOVEN (510603062087)

It certifies that the document was edited for proper English language (UK) grammar, punctuation, spelling and overall style.

All amendments were tracked with the Microsoft Word 'Track Changes feature 'which allowed the author to accept or reject each change individually.

The editor endeavoured to ensure that the author’s intended meaning was not altered during the review.

Dated : 1 October 2019

Best wishes

DRLangenhoven