DEPARTMENT OF MECHANICAL ENGINEERING SCIENCE
FACULTY OF ENGINEERING AND THE BUILT ENVIRONMENT

Cover letter

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Dear Editor,

I write this letter with gratitude as I resubmit to you a revised version of manuscript paper ID 0081, *Simulation and Optimization of Nanostructured Cu_2O/TiO_2 pn Heterojunction Solar Cells Using SCAPS.* I appreciate the feedback provided by the reviewer and time you spent reviewing this manuscript.

The observed corrections have been incorporated into the manuscript to the best of my ability.

1. The grammatical mistakes have been carefully proof read and corrected.
2. The simulation results were used instead of the experimental result due to the fact that this manuscript reports a simulation result, which is under perfect conditions (e.g., no defects were presented).
3. The form style has been modified, and the pictures have been adjusted to be uniform.
4. Various advantages of this simulation program have been added to the introduction. These new additions are highlighted in red

The manuscript will certainly benefit from these insightful revision suggestions. Thank you for your kind consideration.

Thank you for your consideration.

With kind regards,

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SIMULATION AND OPTIMIZATION OF NANOSTRUCTURED CU_2O/TIO_2 PN HETEROJUNCTION SOLAR CELLS USING SCAPS

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ABSTRACT

This paper reported numerical simulation and optimization of nanostructured Cu_2O/TiO_2 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/m^2 using illumination of AM1.5 lamp, and under varied thickness of 0.5 µm to 10.0 µm for the absorber layer (Cu_2O) and 0.05 µm to 6.0 µm for the buffer layer (TiO_2). 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 (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 Cu_2O metal oxide solar cells. This will open a new frontier for modelling of metal oxide based thin film solar cells especially Cu_2O 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: Cu_2O/TiO_2, Optimization, Metal Oxide, Nanostructured, Thin films solar cells, SCAPS

NOMENCLATURE

Abbreviations	
Cu_2O	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 Cu_2O. The metal oxide (Cu_2O) 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 (Cu_2O), 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,

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2017), and wxAMPS (Liu *et al.*, 2012). SCAPS-1D is exceptional and possess the capacity to compute seven (7) semiconductor layers and at 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, Cu_2O/TiO_2 pn heterojunction solar cells was simulated using solar cells capacitance simulator (SCAPS). The paper reported simulation result of Cu_2O/TiO_2 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 Cu_2O/TiO_2 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/m^2, illumination of AM1.5 lamp, and under varied thickness of 500 nm to 10,000 nm for the absorber layer (Cu_2O) and 50 nm to 6000 nm for the buffer layer (TiO_2).

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.

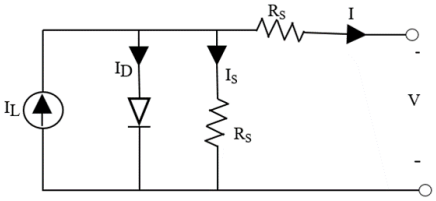

Fig 1 Solar cells model equivalent circuit

From the aforementioned, the characteristic equations are given as:

$$I_{ph} = \frac{I_r \times I_{sc}}{I_{ro}} \quad (1)$$

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

$$V_t = \frac{kT}{q} \quad (2)$$

$$I_s = I_{sc} \times \left(e^{\left(\frac{V_{oc}}{n.V_t}\right)} - 1\right) \quad (3)$$

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

$$I_d = I_s \times \left(e^{\left(\frac{V + I.R_S}{n.V_t.N_S}\right)} - 1\right) \quad (4)$$

Equation (4) gives the Shockley equation.

$$I = I_{ph} - I_d - I_{sh} \quad (5)$$

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_{sc} is the reverse saturation current, R_S and R_{sh} 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 $CuInSe_2$ family (Burgelmna *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).

$$\nabla^2 v = -\ q/\in (p - n + N_D - N_A) \quad (6)$$

$$\nabla . J_p = q(G - R) \quad (7)$$

$$\nabla . J_n = q(R - G) \quad (8)$$

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

$$G(x) = \int_0^\infty \phi a e^{-ax} d\lambda \quad (9)$$

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

$$J_p = -q\mu_p p \nabla V_p - kT\mu_p \nabla_p \quad (10)$$

$$J_n = -q\mu_n n \nabla V_n + kT\mu_n \nabla_n \quad (11)$$

$$V_p = V - (1 - \gamma)\,\Delta G/g \quad (12)$$

$$V_n = V + \gamma\,\Delta G/g \quad (13)$$

where v_p and v_n represent the effective potentials expressed in equations 12 and 13. ΔG and γ account for variations in the band structure, such as the density of states and band gap, and account for Fermi-Dirac statistics. Expression J_n and J_p represent the current density of the electron and holes respectively. Similarly,

μ_n and μ_p represent the mobility of electron and hole respectively.

2.3 Absorber (Cu_2O) and Buffer (TiO_2) layer Properties

The absorber layer is made of a p-type, known as Cuprous oxide (Cu_2O) oldest semiconductor material (Brattain, 1951). The National Science Foundation was the first to use it for photovoltaic application in 1978 (Olsen *et al.*, 1982). Cu_2O 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 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).

3. SIMULATION MODEL AND RESULT

3.1 SCAPS simulation of the Cu_2O/TiO_2 pn 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

Material properties	**Buffer (TiO_2)**	**Absorber (Cu_2O)**
Band Gap (eV)	2.26	2.17
Electron affinity	4.20	3.20
Dielectric permittivity (relative)	10.00	7.11
Conduction band ($1/cm^3$)	2.0E+17	2.0E+17
Valence band ($1/cm^3$)	6.0E+17	1.1E+19
Electron mobility (cm^2/Vs)	1.0E+2	2.0E+2
Hole mobility (cm^2/Vs)	25.0	8.0E+1
Shallow uniform donor density ($1/cm^3$)	1.0E+17	0
Shallow uniform acceptor density ($1/cm^3$)	0	1.0E+18

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

Parameter	**Front contact**	**Back Contact**
Holes	1.00E+5	1.00E+5
Electron	1.00E+5	1.00E+5
Metal Work function (eV)	5.0216	5
Majority Carrier Barrier height (eV) relative to E_f	0.2216	0.4
Majority Carrier Barrier height (eV) relative to E_v	0	0.2271

3.2 Effect of Thickness on the nanostructured Cu_2O/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 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, Cu_2O is used as the absorber layer, TiO_2 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 Cu_2O 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 the nanostructured solar cells layer simulated using SCAPS is shown in Figure 2.

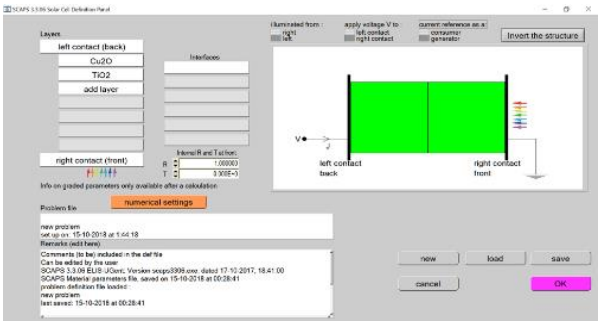

Fig 2 SCAPS panel showing the Cu_2O/TiO_2 Solar cells definition

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 (TiO_2) up to 400 nm before maintaining a constant value. An increase in the absorber layer (Cu_2O) results in more photons being absorbed culminating in a photo-generated current increment (Liao *et al.*, 2009).

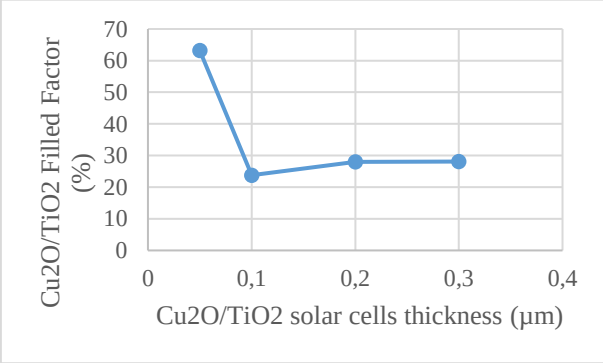

Fig 3 A plot of absorber and buffer layer thickness with the solar cells filled factor.

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_2O/TiO_2 heterojunction solar cells recorded by Saehana and Muslimin (2013).

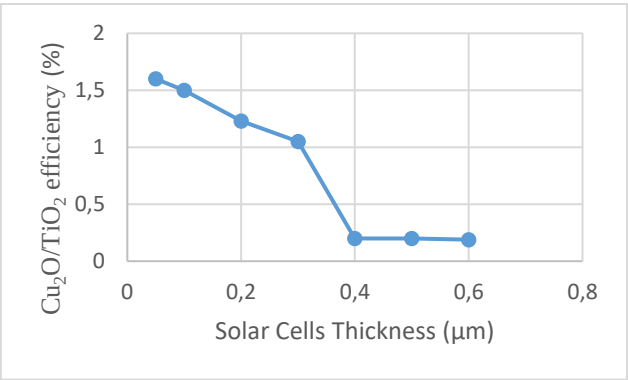

Fig 4 A plot of absorber and buffer layer thickness with the efficiency of the solar cells.

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.

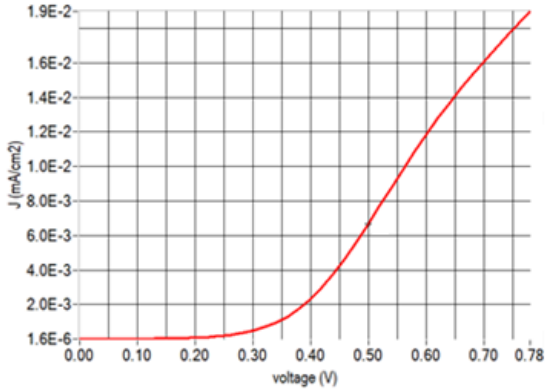

Fig 5 The J-V curve for the optimized Cu_2O/TiO_2 pn heterojunction

The efficiency is obtained using Equation 14:

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

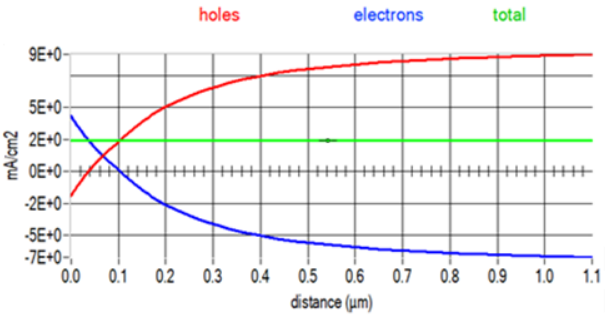

Fig 6 Current density of the optimized Cu_2O/TiO_2 heterojunction solar cells.

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

Table 3. The parameters of the Cu_2O/TiO_2 pn heterojunction solar cells.

Parameter	J_{sc} (A)	V_{oc} (V)	FF (%)	η (%)
Value	24.0764	1.0486	63.20	1.6

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 (η) 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_2O/TiO_2 heterojunction solar cells recorded by Saehana, 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 (Cu_2O) 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 cm^3, for 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_2O/TiO_2 solar cells. This is in concordance with the study by Sawicka-Chudy *et al.* (2018).

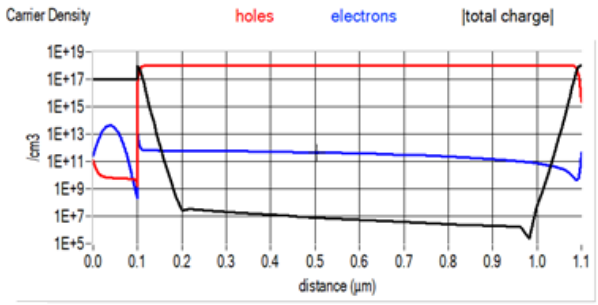

Fig 7 Occupational Probability of deep defect for electron

CONCLUSION

This study was able to simulate and optimize nanostructured Cu_2O/TiO_2 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 (Cu_2O) thickness of 500 nm, buffer layer (TiO_2) thickness of 50 nm. This translates to cost reduction as compared to large thickness.
- Defect density has an impact on the performance of Cu_2O/TiO_2 cells. An increased photovoltaic effect is experienced by a lower defect density especially at the absorber layer (Cu_2O).
- 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 Cu_2O/TiO_2 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.

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