

Performance of $\text{TiO}_2/\text{In}(\text{OH})_i\text{S}_j/\text{Pb}(\text{OH})_x\text{S}_y$ Composite ETA Solar Cell Fabricated from Nitrogen Doped TiO_2 Thin Film Window Layer

C. O. Ayieko^{1,*}, R. J. Musembi¹, S. M. Waita¹, B. O. Aduda¹, P. K. Jain²

¹Department of Physics, University of Nairobi, P.O. Box 00100-30197, Nairobi, Kenya

²Department of Physics, University of Botswana, P/ Bag 0022, Gaborone, Botswana

Abstract In this work, Titanium Dioxide (TiO_2) thin films were prepared by spray pyrolysis and thermally annealed at 400°C . The films were characterized as deposited (no annealing) as well as after annealing. Optical studies showed that the energy band gap of the films was lowered from 3.25 eV to 2.90 eV on Nitrogen (N_2) doping. The reduction in energy band gap was attributed to the introduction of N_2 impurity states on the bands (conduction band and or valence band). The effect of N_2 doping of Titanium Dioxide window layer on the efficiency of the ETA $\text{TiO}_2/\text{In}(\text{OH})_i\text{S}_j/\text{Pb}(\text{OH})_x\text{S}_y$ solar cell was investigated using a conventional current-voltage (I-V) technique. The photovoltaic conversion efficiency (η) increased from 1.06% for the solar cell with undoped films to 1.32% for the solar cell with N_2 -doped films. The increase in photovoltaic conversion efficiency on doping was attributed to increased light absorption due to the Nitrogen doping.

Keywords Titanium Dioxide, Conversion efficiency, Doping

1. Introduction

Meeting human energy requirements has been an elusive task even after the discovery of the immense energy from the atom when the phrase “*too cheap to meter*” was coined[1] and the energy cost has been soaring each passing day. The energy crisis in the 1970's which made the cost of petroleum almost quadruple necessitated intensive research and development on renewable energy sources[1].

Solar energy, one of the renewable sources, is environmentally friendly. It is also universal and versatile with the ability to be made available even to the remotest parts of the world. Solar energy systems do not involve heavy moving parts and hence present minimal wear and tear and therefore require very low maintenance once installed. The initial cost of installation for solar energy systems is high just as for other energy sources but due to low maintenance costs, it guarantees free energy after a short payback period. This makes solar energy systems viable[2].

Solar cells convert solar energy into electrical energy. Different technologies have been developed to fabricate solar cells, and the Extremely Thin Absorber (ETA) technique is one of the promising methods. The concept of ETA solar cells involves using an extremely thin absorber

layer of less than 50 nm. Some promising characteristics of ETA solar cells include: reduced charge carrier transport time through the solar cell due to thin absorber, enhanced photon absorption due to scattering resulting from the porous nature of the window layer[3]. A major challenge facing ETA solar cells is low photoelectric conversion efficiencies.

TiO_2 has been used as window layer for both all-solid state and dye sensitized solar cells. A porous TiO_2 deposited by spray pyrolysis was used as a window layer in the fabrication of $\text{TiO}_2/\text{In}(\text{OH})_i\text{S}_j/\text{Pb}(\text{OH})_x\text{S}_y/\text{PEDOT:PSS}$ ETA solar cell and it was observed that the highly porous TiO_2 ensured increased absorption of incident radiation through scattering[4].

Studies on N_2 -doped TiO_2 deposited by the pressing technique for dye sensitized solar cells (DSSC) application have been done[5]. However, the challenge encountered with the DSSC solar cell was leakages from the liquid electrolyte. Gartner *et. al*[6] have also done some studies on N_2 -doped TiO_2 thin films and reported an increase in light harvesting towards the visible range. However, they never used the doped films in any specific application.

Although some work has been done for N_2 -doped TiO_2 , to the best of our knowledge, N_2 doping of TiO_2 has not been done for spray pyrolysis deposited TiO_2 films and applied to the ETA solar cell. This work therefore investigates the performance of an all-solid state ETA solar cell with TiO_2 thin films deposited by spray pyrolysis followed by N_2 doping, that is, $\text{N}:\text{TiO}_2/\text{In}(\text{OH})_i\text{S}_j/\text{Pb}(\text{OH})_x\text{S}_y$ solar cell.

* Corresponding author:

opiyoc2006@yahoo.com (C. O. Ayieko)

Published online at <http://journal.sapub.org/ijme>

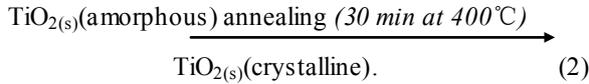
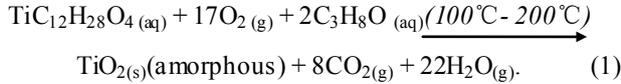
Copyright © 2013 Scientific & Academic Publishing. All Rights Reserved

2. Experimental

Fluorine-doped tin oxide coated glass substrates (FTO) were cleaned in an ultrasonic bath filled with distilled water for 2 minutes before deposition. The substrates were then rinsed in acetone and finally rinsed in distilled water.

Deposition of TiO_2 by spray pyrolysis was done by mixing 120 μl of commercially available Titanium (iv) Isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4$) (purity 99.7%) and 200 ml Isopropanol ($\text{C}_3\text{H}_8\text{O}$) (purity 99.7%) from Fluka Ltd. The mixture was heated to 50 $^\circ\text{C}$ using an electric hot plate and the temperature maintained constant while stirring with a magnetic stirrer for about 15 minutes. The mixture formed the precursor which was used for spray pyrolysis. Nitrogen gas was used as the carrier gas.

The spray nozzle-to-substrate distance was kept at about 15.0 cm. The substrate temperature (T_s) was varied from 100 $^\circ\text{C}$ to 200 $^\circ\text{C}$ for different samples. Coating was done by spraying in pulses. A pulse consisted of 5 seconds of spraying and 30 seconds of pause. Ten pulses were done for every sample at a precursor flow rate of 2.6 ml/min. The chemical reaction resulting in the formation of amorphous TiO_2 thin film was as follows:



The film thicknesses were determined using a computerized KLA-Tencor Alpha –Step IQ surface profiler.

Doping of the TiO_2 films was done using a pyrex glass tube placed in a programmable horizontal tube furnace (ThermoScientific Lindberg/Blue Mini-Mite) in Nitrogen gas atmosphere flowing at a controlled rate of 20 cm^3/sec . The tube furnace was fitted with a digital thermometer which was used to measure the temperature of the doping chamber. The films were heated gradually from room temperature to about 450 $^\circ\text{C}$ and the temperature maintained constant for about 30 minutes after which, the films were allowed to cool to room temperature without cutting off the Nitrogen flow.

The crystal structure of the films was determined using a computer controlled Phillips PW 3710 X-ray diffraction (XRD). Scanning Electron Microscope (SEM) images of the films were carried out using a Carl ZeissTM LEO 1530 SEM model while Energy Dispersive X-ray (EDX) studies were carried out using an EDX unit attached to the SEM.

Total transmittance and reflectance measurements were made at near normal incidence in the wavelength range of 300 -1200 nm using a UV-VIS-NEAR INFRA RED computerized double beam solid-spec 3700 DUV Shimadzu Spectrophotometer equipped with a Barium Sulphate (BaSO_4) integrating sphere. The reflectance and transmittance data were used for calculation of optical properties: energy band gap and absorption coefficient as in equation (3)[7] and (4)[8] respectively;

$$\alpha h\nu = a(h\nu - E_g)^r \quad (3)$$

$$k = \alpha\lambda / 4\pi \quad (4)$$

2.1. Deposition of Indium Hydroxy Sulphide ($\text{In}(\text{OH})_i\text{S}_j$) buffer Layer

Nitrogen-doped and undoped TiO_2 thin films were coated with Indium Hydroxy Sulphide buffer layer by chemical bath deposition (CBD) in a solution prepared using commercially obtained reagents from Sigma Aldrich Ltd and prepared as follows: 20000 \pm 1 μl of distilled water was mixed with 1250 \pm 1 μl of 0.005M of Hydrochloric acid (HCL) which was then mixed with 1250 \pm 1 μl of 0.005M Indium (III) Chloride (In_2Cl_3) and 2500 \pm 1 μl of 0.1M Thioacetamide (CH_3CSNH_2). The resulting solution was kept in a water bath that was maintained at a temperature of 70 \pm 1 $^\circ\text{C}$.

The TiO_2 films were dipped into the solution prepared above in turns, each dip lasting 30 minutes. The films were then rinsed in distilled water to clean off unwanted chemical remnants. The procedure was repeated three times for each film. Finally the films were annealed at a temperature of 300 $^\circ\text{C}$ in air.

2.2. Deposition of Lead Hydroxy Sulphide ($\text{Pb}(\text{OH})_x\text{S}_y$) Coating

Lead Hydroxy Sulphide ($\text{Pb}(\text{OH})_x\text{S}_y$) coating was deposited by successive ion layer adsorption and reaction (SILAR). In this process, saturated Lead Acetate ($\text{Pb}(\text{CH}_3\text{OOH})_2$) solution (97% pure) and Sodium Sulfide (Na_2S) solution (97% pure) both commercially obtained from Sigma Aldrich Ltd. were used. To deposit Lead Hydroxy Sulphide ($\text{Pb}(\text{OH})_x\text{S}_y$) coating, the following four-stage process was followed: First the films were submerged in lead acetate solution for 10 seconds for the metal ions to be adsorbed then rinsed in distilled water Secondly, they were submerged in Sodium Sulfide solution for 10 seconds to allow Sulphur ions to react with metal ions and finally were rinsed in distilled water. The procedure constituted one cycle giving a particular thickness.

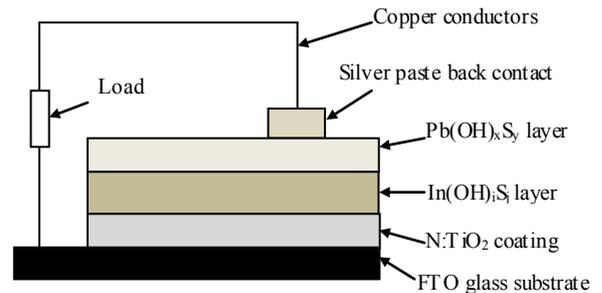


Figure 1. Schematic cross-section of the $\text{N}:\text{TiO}_2/\text{In}(\text{OH})_i\text{S}_j/\text{Pb}(\text{OH})_x\text{S}_y$ composite (ETA) solar cell

A thin silver coating was applied on the $\text{Pb}(\text{OH})_x\text{S}_y$ to make an electrical contact. Figure 1 below is a schematic

display of the assembled ETA solar cell.

2.3. I-V Characterization

Current-voltage (I-V) characterization was done using a solar simulator equipped with a 0.5kW Xenon arc lamp and a 1.5 AM Global Air Mass Filter. Illumination was maintained at 1 sun (1000 W/m^2). The solar cell area was 0.1256 cm^2 .

3. Results and Discussion

3.1. Structural Analysis

Figure 2 shows a SEM micrograph of Nitrogen-doped TiO_2 and Indium Hydroxy Sulphide ($\text{Pb}(\text{OH})_x\text{S}_y$) layer. The TiO_2 is porous with nano pore sizes of approximately 500 nm. This morphology is favourable for light scattering effect and increases the light optical path, thus enhancing light absorption which makes the films appropriate for solar cell applications.

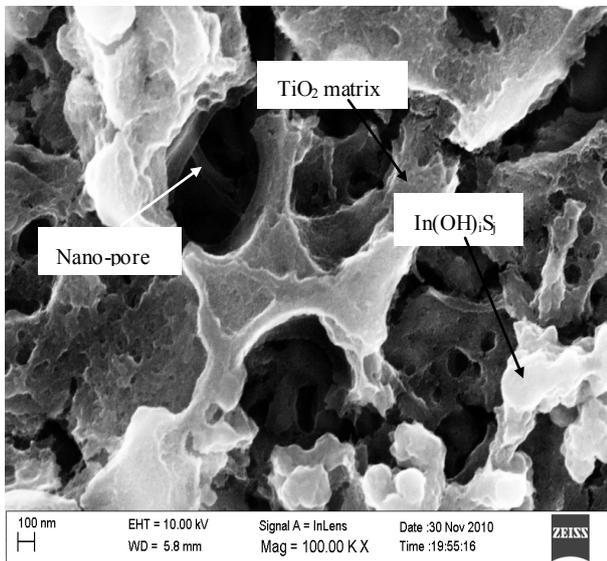


Figure 2. SEM micrograph of nitrogen-doped TiO_2 ($\text{N}:\text{TiO}_2$) coating on FTO glass substrates and annealed at 400°C with indium hydroxyl sulphide ($\text{In}(\text{OH})_3\text{S}$) deposited on top of porous nitrogen-doped TiO_2

3.2. Optical Characterization

3.2.1. Reflectance, Transmittance and Absorption

Figure 3 shows transmittance and reflectance characteristics for undoped and Nitrogen-doped TiO_2 films (both annealed and unannealed). Except the doped and annealed film (which is thicker compared to all other films), the other three films are of comparable thickness as seen from the transmittance and reflectance spectra. Generally, thicker films tend to have lower transmittance than thin films. The lower transmittance observed can therefore be attributed partly to the film's thickness. To find out whether doping plays any role, we compare the undoped and unannealed and the doped and unannealed films since they are of similar thickness. It is observed that the doped and unannealed has a lower transmittance (22-55%) compared to (34-60%) for the

undoped and unannealed in the visible range-400-800 nm and this can be attributed to the presence of the dopant in the film since all the other conditions are the same. It can therefore be concluded that doping also contributes to the low film transmittance (10-45% in the visible range-400-800 nm) in the doped and annealed film.

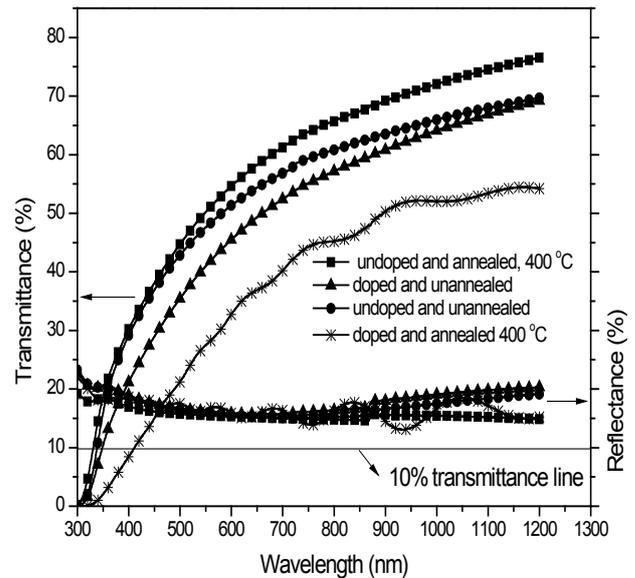


Figure 3. Dependence reflectance and transmittance on wavelength of nitrogen doped and undoped TiO_2 thin films of approximate thickness of 400 nm deposited on fluorine doped tin oxide (FTO) glass slides

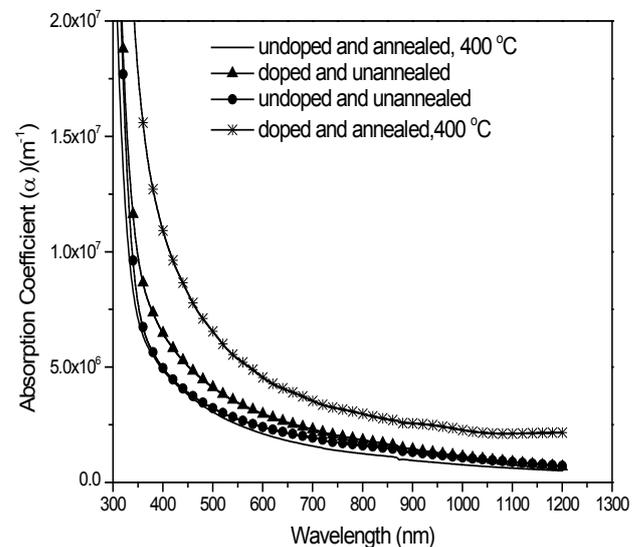


Figure 4. Dependence of absorption coefficient on wavelength of Nitrogen doped and undoped TiO_2 thin films deposited on fluorine doped tin oxide (FTO) glass slides

Figure 4 shows the graph of absorption coefficient, α , versus wavelength of the Nitrogen-doped and undoped TiO_2 for both annealed and unannealed thin films. Clearly, there is more absorption for the N_2 -doped film compared to both undoped films within the visible range 350-800 nm. The observed increase in doping can be explained in terms of the presence of the nitrogen dopant in the film. This is in agreement with the observation on transmittance. The doped

and annealed film stands out clearly with the highest absorption in all wavelengths. Doping as well as the film thickness both contribute to the high absorption observed.

3.2.2. Effect of Nitrogen-doping on the band gap of TiO_2 Coated on Fluorine Doped Tin Oxide (FTO) Glass Slides

Figure 5 shows the estimated band gap of the films coated on Fluorine doped Tin Oxide (FTO) substrate and annealed at 400°C . The band gap decreases from 3.25 eV for the undoped film to 2.90 eV for Nitrogen-doped. Our results are in agreement with those obtained by Baoshun[9] who also observed a decrease in the band gap TiO_2 prepared by sputtering from 3.2 eV to 2.7 eV upon Nitrogen doping. This reduction is as a result of nitrogen impurity states which

introduce tail energy levels either in the conduction band or valence.

3.3. $\text{TiO}_2/\text{In}(\text{OH})_3/\text{S}_y/\text{Pb}(\text{OH})_2/\text{S}_y$ ETA Solar Cell Performance

3.3.1. J-V characterization

The current density versus voltage graph for the fabricated solar cells is shown in Figure 6.

The ETA solar cell fabricated from the doped TiO_2 film shows superior performance. The current density increases by a factor of 1.65 while the efficiency increases by a factor of 1.24. The improved performance of the ETA solar cell on doping can be attributed to the increased light absorption due to Nitrogen doping.

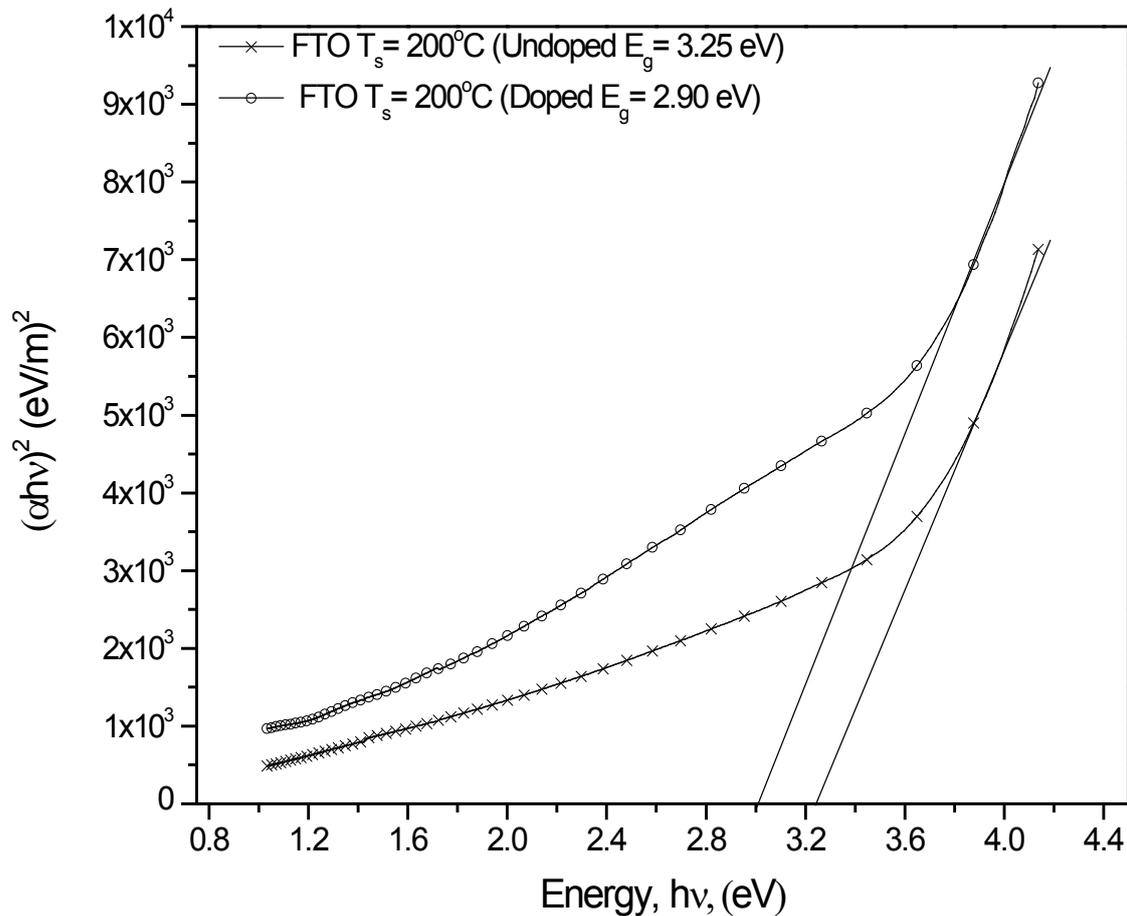


Figure 5. Graph showing the effect of doping TiO_2 thin film coated on conducting fluorine doped tin oxide (FTO) glass slides with Nitrogen (N_2) and annealed at 400°C

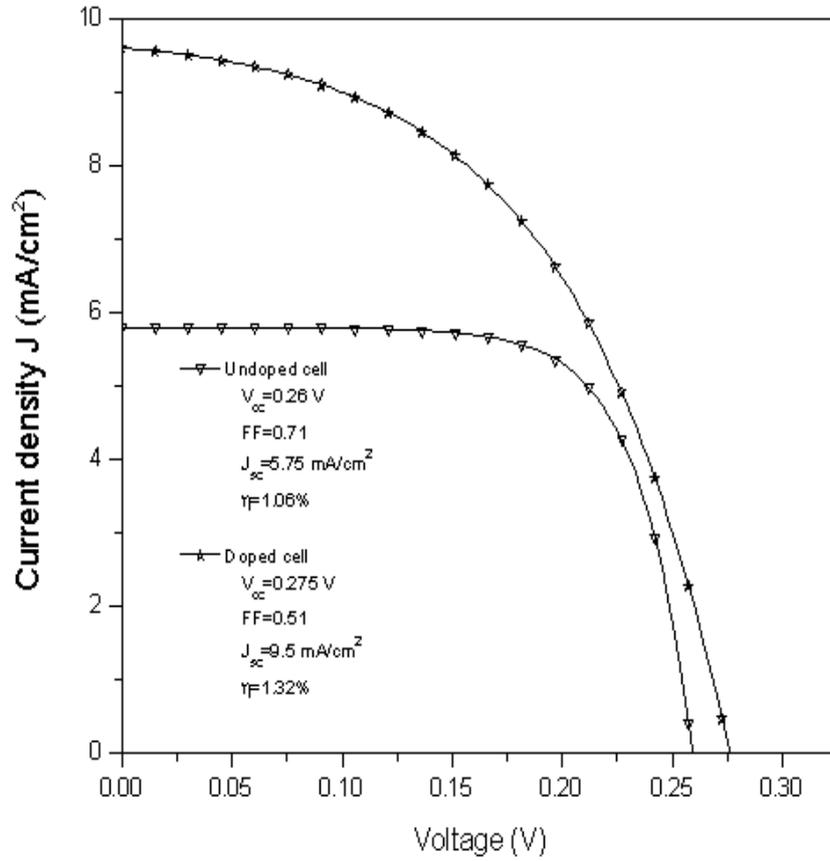


Figure 6. Current density–Voltage curves for Nitrogen-doped and undoped TiO_2 window layer in $\text{TiO}_2/\text{In}(\text{OH})_3\text{S}_3/\text{Pb}(\text{OH})_x\text{S}_3$ ETA solar cell taken under illumination of 1000 W/m^2 at 23°C with a cell area= 0.1256 cm^2

4. Conclusions

Doped and undoped TiO_2 thin films have been prepared by spray pyrolysis. X-ray diffraction studies shows that the as prepared films are transformed from amorphous to crystalline after annealing at 400°C . The films were confirmed to be porous through SEM images.

Optical studies showed that Nitrogen doping increases the light absorption of the films by lowering the energy band gap from 3.25 eV to 2.90 eV.

ETA solar cells fabricated from doped TiO_2 films had better photovoltaic performance than those from undoped films. The current density increases by a factor of 1.65 while the efficiency increases by a factor of 1.24. The improved performance of the ETA solar cell on doping can be attributed to the increased light absorption due to energy band gap lowering through Nitrogen doping.

It has been established that spray pyrolysis and the doping technique (heat treatment) used in this paper are viable options for the preparation of Nitrogen doped TiO_2 films.

ACKNOWLEDGEMENTS

The authors thank African Materials Science and Engineering Network (AMSEN) and International

Programme in the Physical Sciences (IPPS), Uppsala University (Sweden) for financial support.

REFERENCES

- [1] Quashing, V. (2005). Understanding renewable systems, Earthscan, London, 1-130.
- [2] Hankins, M. (1995), *Solar electric systems for Africa*, Motif Creative Arts, Ltd. Nairobi, Kenya.
- [3] Nanu, M., J. Schooman, A. Goosens (2004), Inorganic Nano-composite Semiconductors; a new type of 3D solar cell, *Advanced Materials* 16, (5) 453-455.
- [4] Musembi, R. (2009), Fabrication and characterization of $\text{In}(\text{OH})_3\text{S}_3$ modified highly structured $\text{TiO}_2/\text{Pb}(\text{OH})_x\text{S}_3/\text{PEDOT}:\text{PSS}$ eta Solar cell, and study of its transport mechanisms, *PhD Thesis*, Department of Physics, University of Nairobi, 88-91.
- [5] Wafula, B., J. Simiyu, S. Waita, B. Aduda, J. Mwabora (2007), Effect of nitration on pressed TiO_2 Photoelectrodes for Dye-Sensitized solar cells, *African Journal of Science and Technology (AJST)*, Science and Engineering Series 8, (2) 63-71.
- [6] Gartner, M., P. Osiceanu, M. Anastasescu, T. Stoica, T.F. Stoica, C. Trapalis, T. Giannakopoulou, N. Todorova, A. Lagoyannis (2008), Investigation on the nitrogen doping of

- multilayered, porous TiO_2 thin films, *Thin solid Films*, 516, 8184-8189.
- [7] Mardare, D., M. Tasca, M. Delibas, G. Sugu (2000), Structural Properties and Optical Transmittance of TiO_2 R.F Sputtered Thin Films, *Applied Surface Science*. 156 GL Asahi, Technical University, Iasi R-6600 Romania, 203-205.
- [8] Aksay, S. and B. Altiokka (2007), Effect of substrate temperature on some of the optical parameters of CuInS_2 films, *Phys. Sta. Sol. (c)* 4, (2) 585-588.
- [9] Baoshun, L., W. Liping, Z. Xiujuan (2007). The structure and photocatalytic studies of N-doped TiO_2 films prepared by radio frequency reactive magnetron sputtering. *Solar Energy Materials and Solar Cells*, 92, 1-10.