Study of Optoelectronic Properties of Nanostructured TiO_2/NiO Heterojunction Solar Cells

Kingsley O. Ukoba, *Member, IAENG,* and Freddie L. Inambao

***ABSTRACT*— This study investigates the optoelectronic properties of nanostructured TiO_2/NiO heterojunction solar cells. The heterojunction was fabricated using spray pyrolysis technique at above 350 °C on Indium Tin Oxide substrate. The X-ray diffraction shows that the heterojunctions have a polycrystalline cubic structure with a preferred orientation along the (1 1 1) and (2 0 0) planes. The elemental properties show the presence of TiO_2 and NiO. The optical band gap, refractive index and other optoelectronic properties were also investigated. These findings will enhance the study of cheap, efficient and sustainable alternate materials for solar energy development and affordable energy in developing countries.**

***Index Terms*— Solar energy; TiO_2/NiO; Spray Pyrolysis Technique; optical properties; solar cells.**

I. Introduction

Electricity access has direct links to clean drinking water, good health and agricultural activities for rural dwellers [1]. Globally, about 20 % of the population lack access to electricity [2]. Several developing countries still struggle to deliver affordable and stable electricity [3], [4]. Africa is home to about 85 % of the 1.3 billion people in developing countries without access to electricity [5]. The estimated electrification rate of Africa is 32 % [6]. Renewable energy is a viable solution to ending the global electricity and environment problems caused by fossil fuels [7]. There is a vast amount of sunlight incidence in several developing countries to support solar technology [8]. Solar energy can be converted to use direct current electricity using solar cells [9].

A major breakthrough in solar cell fabrication would be large-scale production at an affordable cost [10]. The major obstacle in using silicon solar cells is the expensive nature of the material and the complexities involved in fabricating the solar cells [11]. Apart from the expensive and commercially available silicon-based solar cells, there is difficulty in scaling up existing methods of solar cell fabrication. Most of the available methods for deposition of solar cells requires a stable and steady supply of electricity. This has discouraged manufacturers in developing countries due to their erratic power supply [12].

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The solution to such electricity woes may be found in nanostructured metal oxides [13], due to the low cost of processing and the simplicity of deposition methods of nanostructured metal oxides. Nickel oxide (NiO) holds great promise being a p-type metal oxide with a vast range of applications [14], [15], [16].

Several methods have been used to deposit NiO with a view to optimizing it for various applications. The deposition methods include sputtering, hydrothermal growth, sol-gel, and laser ablation [17], [18], [19], [20]. However, the spray pyrolysis technique (SPT) is preferred for films because it allows coatings on large areas in thin layers with uniform thickness [21]. SPT's simplicity, affordability and the possibilities for mass production singled it out for this study [22]. It requires electricity only during deposition, which can be less than 4 hours per deposition.

This study investigated the optoelectronic properties of a nanostructured metal oxide for possible use in fabrication of affordable and efficient heterojunction solar cells. The optical properties of a metal oxide play a vital role in its usage in the fabrication of optoelectronic devices [23]. The optical properties reveal information relating to the microscopic behaviour of the material.

II. Methodology

A. Deposition

The chemicals used are of analytical reagent grade and were used without further purification. Distilled and deionized pure water was used during the course of the experiment.

The solar cell was fabricated using a modified SPT as reported by Ukoba, Inambao and Eloka-Eboka [24].

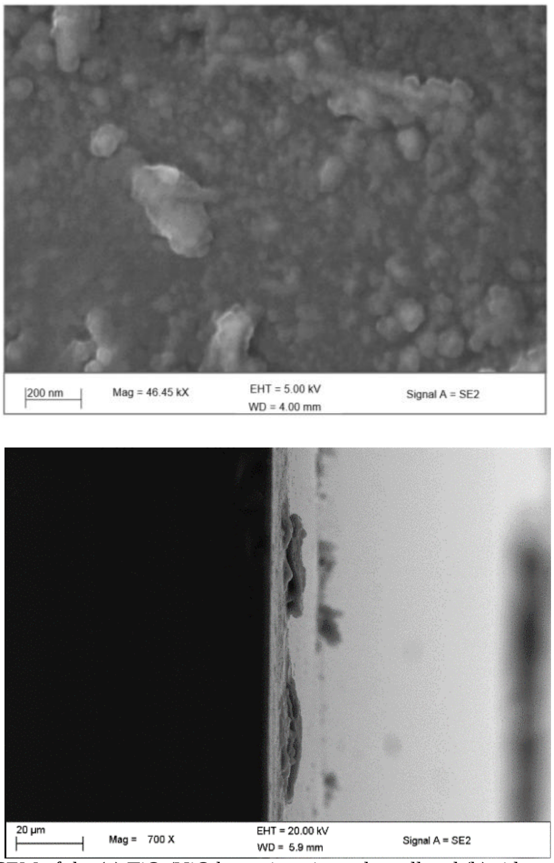
Figure 1 is a pictorial representation of the experimental set-up. Prior to sample preparation, the glass and the indium tin oxide (ITO) coated glass used as substrates were cleaned ultrasonically as reported by Adeoye Abiodun and Salau [25].

Fig. 1. Pictorial representation of the experiment set-up for depositing the TiO_2/NiO heterojunction solar cells

The titanium oxide (TiO_2) nanostructure thin film was prepared by mixing 3 ml of titanium ethoxide with 30 ml of distilled water and ethanol mixture, and three droplets of acetic acid. This was stirred for one hour before spraying on cleaned indium tin oxide (ITO) coated glass substrates maintained at about 350 ºC. Deposition parameters such as substrate temperature, carrier gas flow rate and pressure were optimized to obtain quality films.

The nanostructured Nickel oxide (NiO) was deposited on the prepared ITO/TiO_2 layers using SPT. The precursor for NiO was obtained by preparing 0.05 M nickel acetate tetrahydrate in double distilled water.

The precursors were thoroughly stirred for several minutes prior to spraying onto preheated substrates maintained at about 350 ºC. Other deposition parameters were maintained to obtain good quality thin films. The optimized parameters used in the deposition of the NiO films are tabulated in table 1.



(a)

(b)

Fig. 2. SEM of the (a) TiO_2/NiO heterojunction solar cell and (b) side view of the TiO_2/NiO heterojunction solar cell

B. *Testing*

The TiO_2 and NiO prepared on ITO were used to study the elemental, morphological, structural and other optoelectronic characteristics of TiO_2 and NiO using Energy Dispersive X-ray Spectrometer (EDS or EDX: "AZTEC OXFORD DETECTOR"), a ZEISS ULTRA PLUS Field Emission Gun Scanning Electron Microscope (FEGSEM). BRUKER AXS with D8 Advance diffractometer Cu-K α radiation X-ray Diffractometer (XRD) respectively. The weight difference method was also used. Optical properties were studied in the wavelength range of 300 nm to 1000 nm with a SHIMADZU UV-3600UV-VIS Spectrometer. The results of the characterized nanostructured TiO_2/NiO heterojunction solar cells are here reported.

III. RESULTS AND DISCUSSION

A. *Morphological studies*

Figures 2a and 2b show the scanning electron micrograph of the heterojunction of p-NiO/n-TiO_2 and the side view respectively. The micrograph reveals scattered distribution and broader flakes of the TiO_2/NiO particles across the surface of the film. The film has even distribution, is adherent to the film surface, and has no cracks. This represents a better surface morphology compared to that of NiO films reported by Sriram and Thayumanavan [26]. This micrograph was obtained by the SEM at the point of interaction between the TiO_2 and NiO. It shows a polycrystalline structure. The micrograph shows the P-type NiO and N-type TiO_2 of the thin film with their polycrystalline structures. It shows complete penetration at the heterojunction.

B. *Elemental composition*

Figure 3 shows the elemental composition of the TiO_2/NiO heterojunction solar cell deposited on the ITO coated glass substrate. The figure shows the presence of Ti, O, and Ni in the TiO_2 and NiO respectively and Indium (In) representing the ITO coated glass substrate. This confirms the presence of the metal oxides in the heterojunction.

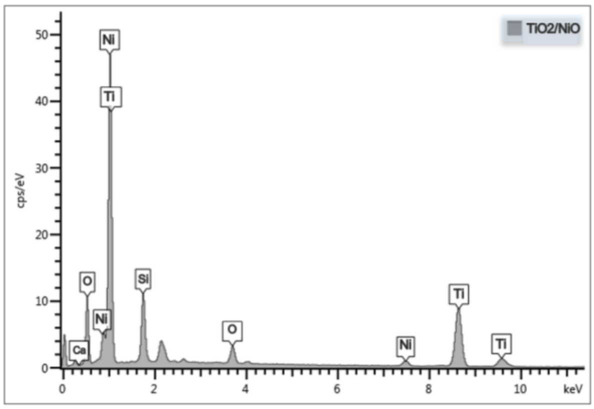


Fig. 3. Elemental composition of TiO_2/NiO

C. *Structural analysis*

Figure 4 shows the X-ray diffraction patterns of the fabricated TiO_2/NiO heterojunction solar cell on the ITO substrate. The peaks corresponding to NiO and TiO_2 were determined with JCPDS patterns.

The XRD spectrum indicates strong NiO peaks with (1 1 1), (2 0 0) and (2 2 0) preferential orientations. The patterns of the NiO thin film has peak diffractions at (2θ = 37º, 2θ = 43º and 2θ = 64º) for the (1 1 1), (2 0 0) and (2 2 0) planes. The XRD analysis confirms bunsenite which corresponds to the JCPDS card 04-0835 for nickel oxide [27] confirming it as a good absorber layer of solar cells [28]. The TiO_2 spectrum also shows strong spectrum and polycrystalline structures typical of N-type in heterojunction solar cells. The structure of the heterojunction indicates that the film is

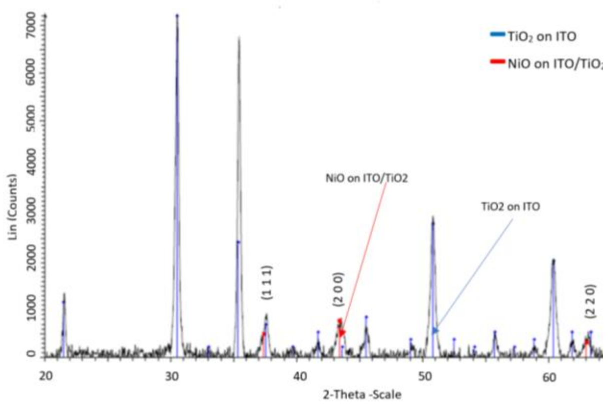


Fig. 4. Diffraction patterns of TiO_2/NiO heterojunction solar cell

polycrystalline and chemically pure.

D. *Optical properties*

The optical properties of a semiconducting material are vital for understanding the electrical properties [29]. Transmittance and reflectance are required for measuring the absorption coefficient. The absorption coefficient measurement gives information about the energy band gap. The energy band gap is a major determinant of the electrical properties of the semiconductor.

Film thickness

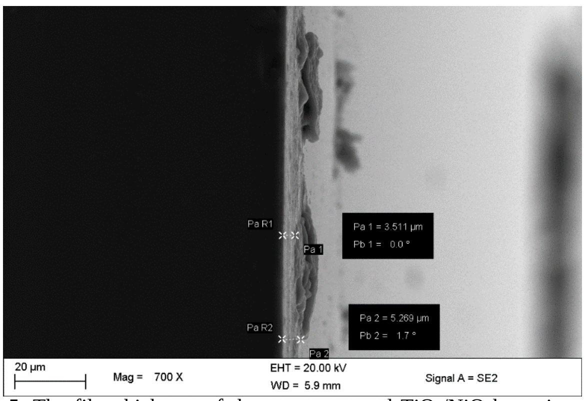


Fig. 5. The film thickness of the nanostructured TiO_2/NiO heterojunction solar cell

The measured data of the film thickness of the heterojunction is depicted in Fig. 5.

The measured film thickness was found to be 4.39 µm. This is due to the joint deposition of TiO_2 and NiO on the ITO.

Transmittance

Figure 6 represents the measurement of transmittance for deposited nanostructured TiO_2/NiO heterojunction solar cells.

The graph shows the nanostructured TiO_2/NiO deposited

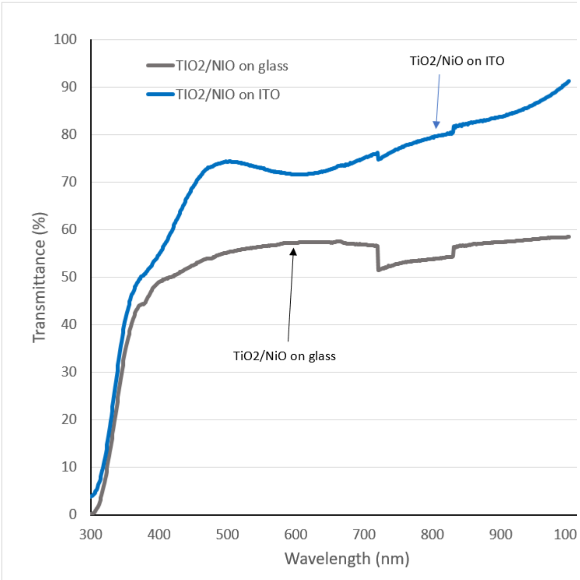


Fig. 6. The plot of transmittance of nanostructured TiO_2/NiO heterojunction solar cell

on ITO substrate and a control graph of TiO_2/NiO deposited on glass. The nanostructured TiO_2/NiO has a better transmittance of 91% when compared to that on a glass substrate of 58%. The nanostructured TiO_2/NiO deposited on a glass substrate is denser than the one on ITO substrate. The absorption peak is shifted to lower energies.

Absorbance

Figure 7 shows the absorbance of the TiO_2/NiO heterojunction on ITO and a glass substrate.

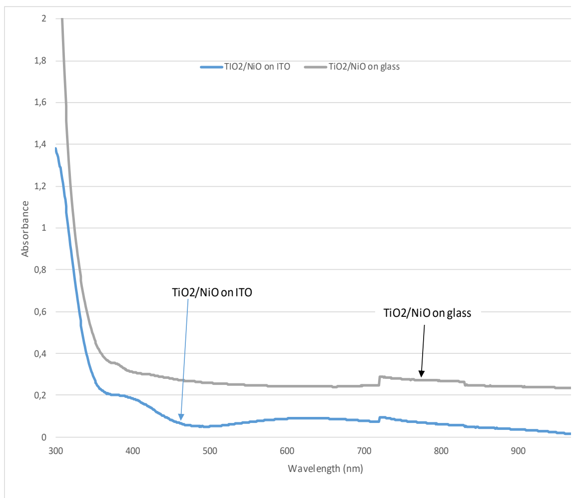


Fig. 7. The plot of absorbance of nanostructured TiO_2/NiO heterojunction solar cell

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TABLE I
THE OPTIMUM DEPOSITION PARAMETERS OF SPT

Deposition parameter	Value
The substrate to nozzle height	20 cm
Rate of spray	1 ml/min
Spray time	1 min
Sprays interval	30 sec
Carrier gas	1 bar filled compressed air

This shows marked resemblance to the standard absorbance characteristic of transition metals (to which Ti and Ni belong) [30]. The heterojunction on ITO substrates absorbs more compared to the heterojunction deposited on the glass substrate. This shows that the ITO will perform better. A strong absorbance is an indication of better performance and usage in solar cell fabrication [31].

Absorption coefficient (α)

Absorption coefficient, α was obtained using (1) [32]

$$\alpha = (2.303 \times A) / t \qquad (1)$$

Where t is film thickness and A is absorbance.

The absorption coefficient is a vital parameter in the determination of the optical band gap. The absorption coefficient of the nanostructured TiO_2/NiO heterojunction solar cell is shown in Fig. 8.

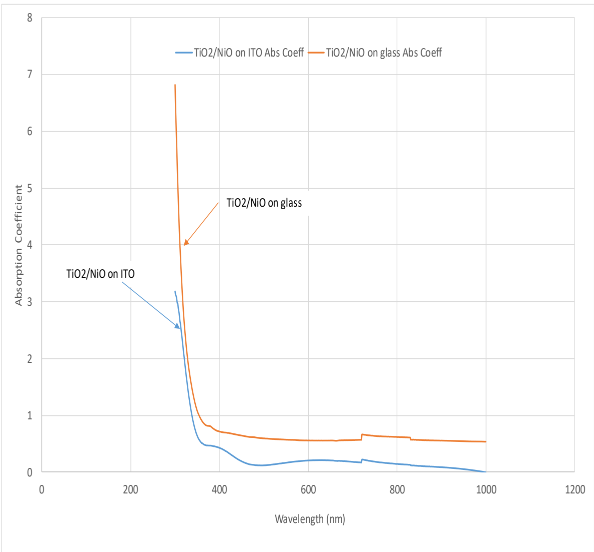

Fig. 8. The plot of the absorption coefficient of nanostructured

Optical band gap

The relationship between optical absorption and optical energy band gap is expressed in (2) [33], [34]

$$\alpha^2 = C\left(h\upsilon - E_g\right) \qquad (2)$$

Where C has a constant value, h denotes Planck's constant, υ represent incidence light frequency, and E_g denotes optical energy band gap.

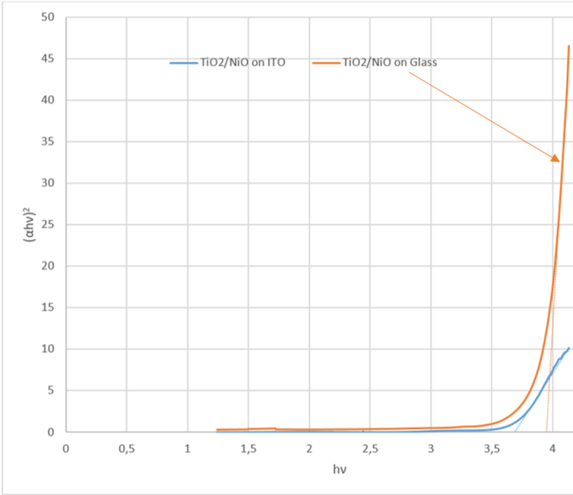

Fig. 9. Graph of (αhυ)2 against hυ for nanostructured TiO_2/NiO heterojunction solar cell

Figure 9 shows a graph of $(\alpha h\upsilon)^2$ against hυ for TiO_2/NiO heterojunction deposited on ITO and glass substrate. Extrapolation of Fig. 10 to the hυ axis for $(\alpha h\upsilon)^2 = 0$ gives the optical band gap. A shift towards lower energy is observed for optical band gap value. The reduction is attributed to the Moss-Burstein shift [35]. Optical energy band gaps are 3.67 eV and 3.875 eV for ITO and glass substrate respectively.

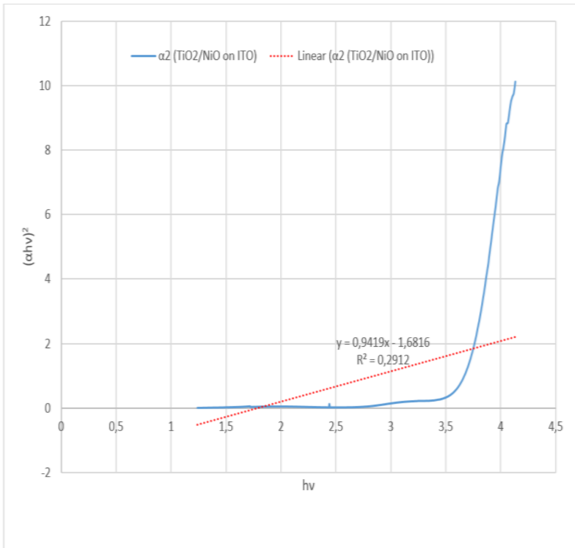

Fig. 10. The gradient of the nanostructured TiO_2/NiO heterojunction solar cell

The ITO substrates value compares favourably with optical band gap reported value of 3.5 eV [36].

The quantum size effect may be responsible for the large value of the band gap [37]. Careful and well-optimized deposition parameters also help in obtaining a better optical band gap.

Figure 10 shows the band gap of the TiO_2/NiO on ITO with the trend line and the equation generated. A positive

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gradient of 0.9419 was obtained as seen from the generated equation shown in (3) and (4).

$$y = 0.9419x - 1.6816 \quad (3)$$

$$R^2 = 0.2912 \quad (4)$$

IV. CONCLUSION

This study investigated the optoelectronic properties of nanostructured TiO_2/NiO heterojunction solar cells deposited on ITO substrates at 350 °C. The surface morphology shows the P-type NiO and N-type TiO_2 of the thin film with their polycrystalline structures. Both the TiO_2 and NiO had complete penetration at the heterojunction. The XRD spectrum indicates strong NiO peaks with (1 1 1), (2 0 0) and (2 2 0) at preferential orientation at 2θ = 37º, 2θ = 43º and 2θ = 64º respectively. Film thickness was found to be 4.39 µm. The nanostructured TiO_2/NiO have a better transmittance of 91 %. Optical energy band gap was 3.67 eV. A positive gradient of 0.9419 was obtained for the TiO_2/NiO heterojunction deposited on ITO substrate. This improved heterojunction is recommended for affordable and efficient solar cells fabrication especially in developing countries.

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