Photovoltaic Cell Based on n-ZnO Microrods and p-GaN Film

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A photovoltaic cell based on p-GaN film/n-ZnO microrods quasi-array heterojunction was fabricated and investigated for the first time for harvesting energy from a near-ultraviolet source (395–400 nm). The source was a commercially available indoor light-emitting diode. According to the scanning electron microscopy data, the ZnO array consisted of tightly packed vertical microrods with a diameter of approximately 2–3 μm. The turn-on voltage of the heterojunction of ZnO/GaN (rods/film) was around 0.6 V. The diode-ideality factor was estimated to be of around 4. The current–voltage characteristic of the photovoltaic cell under near-ultraviolet illumination showed an open-circuit voltage of 0.26 V, a short-circuit current of 0.124 nA, and a fill factor of 39%, resulting in an overall efficiency of 1.4×10^{-5}%. These results may be useful in the engineering of electronic devices based on the materials with optical transparency.

topics: zinc oxide, gallium nitride, microrods, heterojunction

1. Introduction

Power generation by fossil-fuel resources has peaked, whilst solar energy is predicted to be at the vanguard of energy generation in the near future. Moreover, it is predicted that by 2050, the generation of solar energy will increase to 48% due to economic and industrial growth [1]. Perovskite solar cells, due to their ability to produce high (more than 25%) power conversion efficiencies, have been recognized as one of the most promising technologies in contemporary photovoltaic research [2]. Photovoltaic cells are usually designed and fabricated to utilize visible light, which is the major part of the solar spectrum, to generate electricity. On the other hand, transparent photovoltaic cells transforming ultraviolet (UV) light into electric energy could be used as a window glass of buildings or cars. The transparency of the glass in this case will not be altered much but may reduce possible harm caused by UV irradiation to humans. The generated electricity may also be used to power household appliances [3].

Recently, a Britich research group in Glasgow has fabricated perovskite solar cells that can harvest energy from near-ultraviolet (UV-A) lights from an indoor light-emitting diode (LED) (395–400 nm, 9 W) [4, 5]. These near-UV lights, also called black lights, are commonly used for decoration (e.g., in bars, pubs, aquariums, parties, clubs, body art studios, neon lights, and Christmas and Halloween decorations) [4]. Their devices achieved an efficiency of 26.19%, an open-circuit voltage of 0.90 V, a short-circuit current of 1.42 mA/cm^2, and a fill factor of 77.56%, resulting in a maximum power output of 991.21 μW/cm^2 [4].

ZnO/GaN heterostructure-based light-emitting devices, photodetectors and lasers have already been demonstrated [3, 6, 7], but there are few reports on the photovoltaic cells based on such structures [3, 8]. The reported photovoltaic cells [3, 8] were made on the basis of p-GaN epitaxial films and ZnO films grown by the molecular beam epitaxy [3] or obtained by the radio-frequency magnetron sputtering [8]. The photovoltaic cell made by Yang et al. [3] showed, under simulated AM 1.5 illumination (100 mW/cm^2) without and with the ZWB2 filter, an open-circuit voltage of 0.28 V and 0.26 V, a short-circuit current density of 0.258 mA/cm^2 and 0.214 mA/cm^2, a fill factor of 34.6% and 36%, an efficiency of 0.025% and 0.46%, respectively. The device fabricated by Nam et al. [8] under 1-Sun illumination showed a conversion efficiency of about 0.001% and a small short-circuit current. Alwadai et al. [9] developed an electrically pumped UV n-ZnO nanotubes/p-GaN LED as a proof of concept, demonstrating its high internal quantum efficiency (> 65%). The demonstrated performance of this cost-effective UV LED suggests its potential application in large-scale device production [9]. Owing to the fundamental principles of thermodynamics, in particular the detailed balance between light absorption and emission, the performance of the photovoltaic cells and electroluminescent diodes is linked by reciprocity relations [10, 11]. Recently, we created LED devices based on n-ZnO nanostructures deposited on p-GaN films with a photopositive resist as an insulator that emits light in the near-UV spectral region [7]. The corresponding technology possesses some advantages, such as ease of manufacture and does not require expensive instrumentation.

In this paper, we report the fabrication and characterization of a photovoltaic cell based on p-GaN film/n-ZnO microrods array heterojunction for harvesting energy from a commercially available near-UV (UV-A) indoor LED light (395–400 nm).

2. Experimental part

The investigated heterojunctions were fabricated on the basis of p-type GaN templates purchased from UNIPRESS (Poland). Such templates consisted of 2 μm thick (0001)-oriented GaN:Mg layer grown by metalorganic vapor phase epitaxy (MOVPE) on a 430 μm thick sapphire substrate with a GaN non-conductive 1.5 μm thick buffer layer. According to the technical specification, the p-GaN film is characterized by: relatively low dislocation density — (3–5) $\times$ 10^8 cm^{-2}; concentration of the embedded magnesium impurity — 2×10^{19} cm^{-3}; concentration of the electrically active holes — (2–3) $\times$ 10^{17} cm^{-3}.

ZnO hexagonal microrods (Fig. 1) were grown by the method of gas-transport reactions on a p-GaN epitaxial film [7]. For seed-supported growth of ZnO nanorods, nanocrystalline ZnO seed particles were prepared in a solution of 0.005 mol/l zinc acetate [$Zn(CH_3CO_2)_2$] dissolved in ethanol at 90°C for 15 min. The seed solution was then spin-coated onto the p-type GaN templates. Then, the seed-coated p-type GaN substrates were thermally annealed at 300°C for 5 min to remove the residual solvent. The mixture of high-purity powdered zinc oxide, metallic zinc and graphite in the proportion of 1:1:1 was taken as an initial material for vaporization. This material and p-GaN templates were placed into a quartz tube. The mixture of the powders was placed in a sealed end of the tube whereas the substrates — near the open end. The quartz tube was placed into a horizontal oven. The powder mixture was heated to a temperature of about 1050°C and the substrates were located in the temperature zone of 700–750°C. These temperature distributions were maintained for 1 h. Afterwards the oven was shut off and cooled spontaneously to room temperature. This yielded a deposited white layer of zinc oxide on the substrates. Since the p-GaN substrates were placed with a partial overlap, the ZnO nanostructure did not grow on the entire surface of the substrate.

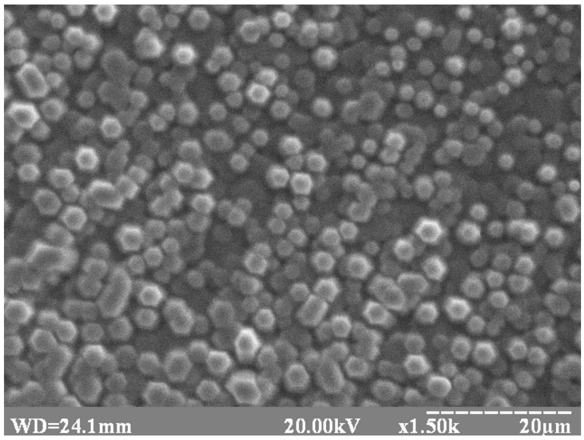

Fig. 1. Microphotographs of ZnO hexagonal microrods grown by the method of gas-transport reactions.

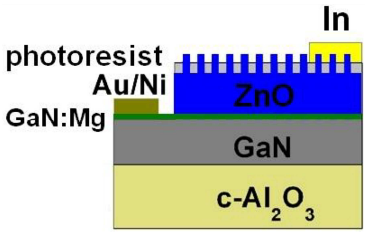

Fig. 2. Schematic diagram of the p-GaN film/ZnO microrods array heterojunction photovoltaic cell structure.

The contacts on the p-GaN template were deposited using thermal evaporation of Ni (30 nm) followed by Au (35 nm) [6, 7]. A quartz-crystal microbalance was used as a thin film deposition monitor. To produce the photovoltaic cell, an array of ZnO microrods was partially covered with an insulator layer of photoresist using spin coating. The thickness of the photoresist film was monitored by microinterferometer MI-4 and was found to be 450 $\pm$ 50 nm. This stage was followed by deposition of In thin film as the top electrode using the magnetron sputtering method [12]. The In contact was deposited through the shadow mask. The liquid photo-positive resist "Cramolin Positiv Resist" was used as a photoresist-insulator [7, 13]. A schematic image of the photovoltaic cell is shown in Fig. 2. The size of the sample was 1 $\times$ 1 cm^2. The area of the contact between ZnO and GaN was equal to 0.06 cm^2.

The morphology of the sample surface was examined using REMMA-102-02 Scanning Electron Microscope-Analyzer (JCS SELMI, Sumy, Ukraine).

Measurements of current–voltage (I–V) characteristics and photovoltaic properties were carried out using a Keithley Model 6514 System Programmable Electrometer (Keithley Instruments Inc., Ohio, USA).

LCR Meter IM3536-01 (HIOKI E.E. Corporation, Nagano, Japan) was used for capacitance–voltage (C–V) measurements. The C–V characteristics are measured at a frequency of 10 kHz at room temperature.

A UV-LED was used as a light source calibrated with a Thorlabs power meter (PM100USB) for UV illumination of a photovoltaic cell. It produced a non-polarized exciting radiation with a wavelength of 395 nm, a bandwidth (FWHM) of 13 nm and a power density of UV light of 2 mW/cm^2.

The absorption spectrum of the photoresist film in the ultraviolet and visible regions was investigated using a portable fiber optic spectrometer AvaSpec-ULS2048L-USB2-UA-RS (Avantes BV, Apeldoorn, Netherlands) with an input slit of 25 μm, diffraction grating of 300 lines/mm and resolution of 1.2 nm. A balanced, compact deuterium-halogen light source Avantes AvaLight-DHc (200–2500 nm) was used. Light detection in the spectrometer was carried out by a 2048 pixel CCD detector.

3. Results and discussion

According to scanning electron microscopy data, a ZnO layer with a thickness of around 6 μm grown on an epitaxial GaN film consists of tightly packed vertical microrods with a diameter of approximately 2–3 μm (Fig. 1).

Zinc oxide shows n-type conductivity without any intentional doping, and obtaining of reproducible p-doped ZnO is very challenging [14]. The concentration of electrons (N_d) in the ZnO microrods is obtained by plotting the inverse squared junction capacitance ($1/C^2$) against the applied reverse voltage (V). Concentrations were extracted from the slope of the linear segment of the curve shown in Fig. 3 using the equation [14–16]

$$N_d = \frac{2}{q\varepsilon\varepsilon_0} \frac{\mathrm{d}V}{\mathrm{d}\,(A^2/C^2)}, \qquad (1)$$

where ε is the relative permittivity of ZnO having a value of 8.47 [16], and $\varepsilon_0 = 8.84 \times 10^{-12}$ F/m. The value of contact area of A is found to be 0.06 cm^2. The extracted concentration is 4.3×10^{15} cm^{-3} for the microrods. This value is in good agreement with the data for undoped ZnO films (2.8×10^{15} cm^{-3}) and nanorods (5.9×10^{15} cm^{-3}) [14, 16].

The I–V characteristics of the created photovoltaic cell with the In/ZnO/GaN:Mg/Ni/Au structure are shown in Figs. 4 and 5. The I–V curve clearly shows the nonlinear increase of current under forward bias, indicating the reasonable p–n junction characteristics.

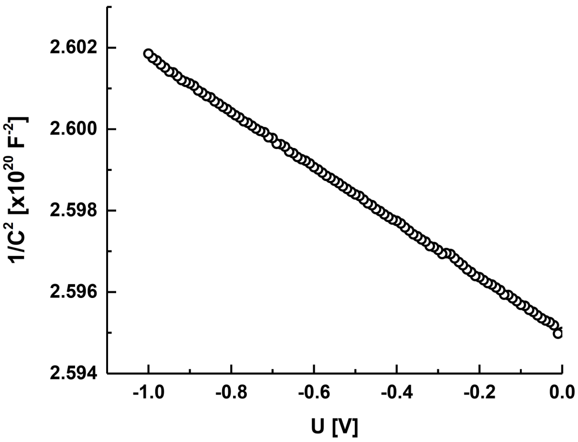

Fig. 3. Plot of $1/C^2$ versus voltage of ZnO/GaN heterojunction for 10000 kHz at room temperature.

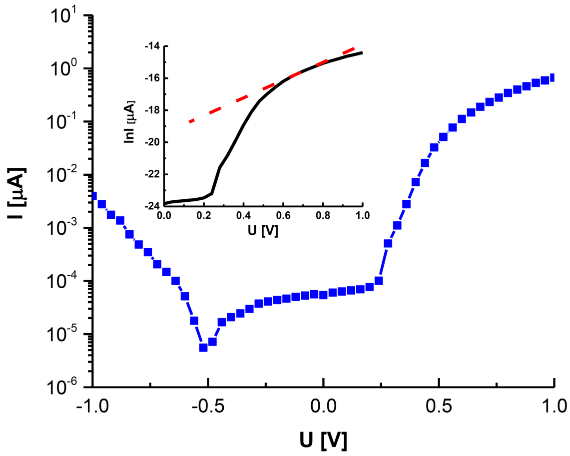

Fig. 4. The I–V characteristics of the created photovoltaic cell with the In/ZnO/GaN:Mg/Ni/Au structure measured in darkness. The inset shows the ln(I) versus V plot to acquire the diode-ideality factor from the slope of the fitting curve.

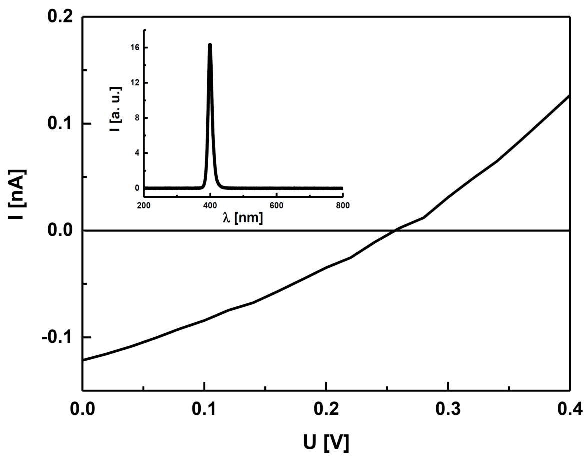

Fig. 5. The I–V characteristics of the created photovoltaic cell with the In/ZnO/GaN:Mg/Ni/Au structure under UV LED illumination. The inset shows the UV LED emission spectrum.

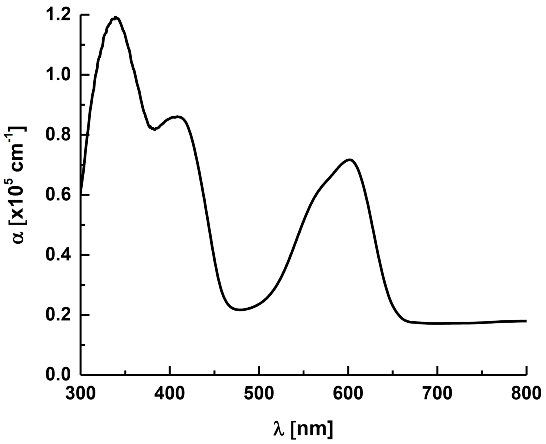

Fig. 6. The room temperature absorption spectrum of a 0.45 μm thick photoresist film.

The rectification coefficient, determined for a voltage of 1 V, was found to be 170. The turn-on voltage of the ZnO/GaN (rods/film) heterojunction is around 0.6 V. This parameter is important since it determines the power consumption of the device. The diode-ideality factor (η) was determined from the slope of the linear region of the plot of $\ln(I)$ versus V in the near turn-on voltage region from 0.6 to 0.8 V (inset to Fig. 4), using the equation

$$\eta = \frac{e}{k_{\mathrm{B}}T}\left[\frac{\delta(\ln(I))}{\delta V}\right]^{-1}, \qquad (2)$$

where k_{B} is the Boltzmann constant and T is the operating temperature.

In our case, the diode-ideality factor was calculated to be of around 4. This result is in agreement with the data on the current–voltage behavior of n-ZnO/p-GaN heterostructures presented in [17, 18]. In our previous works, devoted to LEDs based on n-ZnO micro- and nanostructures grown by various methods and p-GaN films, we obtained ideality factor values in the range of 30–45 [6, 7]. Typically, for wide bandgap semiconductors, the tunneling-recombination process is considered as the main transport mechanism for annealed p–n heterojunctions [18]. Large values of the ideality factor indicate a high density of trap states [19] and may be also connected with the quality of contacts to the p–n junction [20, 21].

Figure 5 shows the I–V curve of the p-GaN/n-ZnO microrods structure under UV LED illumination (2 mW/cm^2). The I–V characteristic of the p-GaN/n-ZnO structures exhibits an open-circuit voltage of 0.26 V, a short-circuit current of 0.124 nA, and a fill factor of 39%, which gives the overall efficiency of 1.4×10^{-5}%. It is necessary to note that the obtained value of efficiency is quite low. For comparison, as reported in papers [3, 8], the efficiency values of the photovoltaic cells on the basis of p-GaN epitaxial films and n-ZnO films measured under simulated AM 1.5 illumination with and without a ZWB2 filter (visible light blocking filter suitable for 365 nm UV flashlights) and under 1-Sun illumination were found to be 0.025%, 0.46% and 0.001%, respectively. However, contrary to the cases described in [3, 8], we used for the photovoltaic studies a source of UV light emitting in a much narrower spectral range.

Figure 6 presents the room temperature absorption spectrum of the photoresist film of 450 nm thickness. The spectrum reveals absorption bands with maxima at 339, 408 and 602 nm, which is consistent with the technical data sheet of "Cramolin Positiv Resist".

On the basis of the literature data [3, 8] and our experimental results, one can conclude that the performance of the produced device is limited mainly by defects at the ZnO/GaN interface and partial light absorption by the photoresist layer. Under such circumstances, device performance may be improved by reducing of interface defects and replacing of the chosen photoresist with an UV transparent insulator, such as a SiO_2 layer.

4. Conclusions

In summary, one can conclude that the n-ZnO microrods quasiarray/p-GaN film photovoltaic cell was created with hexagonal ZnO microrods prepared by the method of gas-transport reactions. Under the illumination of UV LED light, a clear photovoltaic effect was observed. The fabricated photovoltaic cell device shows a turn-on voltage of 0.6 V. The power conversion efficiency of the photovoltaic cell is 1.4×10^{-5}% under UV LED illumination. Although this parameter was found to be quite low, the proposed comparatively simple technology and scheme of the solar cell look as a very suitable basis for further improvements and application. The performed analysis shows ways to considerably enhance the cell's performance by reducing the interface defects and optimizing the photoresist layer parameters. Such an approach would be fruitful for the design of transparent ultraviolet photovoltaic cells with optimized parameters.

Acknowledgments

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