Journal of the Korean Physical Society, Vol. 59, No. 2, August 2011, pp. 482∼484

Electrical and Photoelectrical Characteristics of the ZnO/Organic Hybrid Heterostructure

A. S. Zakirov* and Sh. U. Yuldashev

Quantum-functional Semiconductor Research Center, Dongguk University, Seoul 100-715, Korea and Department of Thermophysics, Academy of Sciences of Uzbekistan, Tashkent, Uzbekistan

H. D. Cho, J. C. Lee and T. W. Kang

Quantum-functional Semiconductor Research Center, Dongguk University, Seoul 100-715, Korea

(Received 28 April 2011, in final form 31 May 2011)

The characteristics of the p-n heterojunction between vertically aligned ZnO nanowires and a Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) thin film were investigated. The current-voltage characteristics of the structures had a very good rectifying diode-like behavior with a leakage current less than 5.39×10^{-7} A at -2 V, a breakdown voltage greater than 10 V, and a forward turn-on voltage of 1 V. In addition, the effects of ultraviolet (UV) illumination and temperature on the I-V characteristics of the ZnO/PEDOT:PSS configuration were also investigated. The photoelectric measurements demonstrated that the photodiode had a high sensitivity and selectivity to UV light.

PACS numbers: 72.40.+w, 72.80.Le, 73.30.+y
Keywords: ZnO nanowires, PEDOT:PSS, p-n- heterojunction, I-V characteristics
DOI: 10.3938/jkps.59.482

I. INTRODUCTION

Vertically aligned ZnO nanowires (NWs), as important functional oxide nanostructures, have received increasing attention over the past few years because of their exciting potential applications in optoelectronic devices, sensors, highly-efficient photonic devices, near-UV lasers, *etc.* [1,2]. Studies on ZnO-based optoelectronic thin-film devices were carried out by fabricating heterojunctions employing as-grown n-type ZnO with other p-type materials such as *p*-Si, *p*-NiO, and *p*-SiC. [3–6]. A few reports exist on the *n*-ZnO/*p*-Si heterojunction in which the a ZnO film is grown by using different techniques [7,8]. However, these deposition methods are relatively expensive. On the other hand, a considerable interest in the fabrication of ZnO/organic hybrid structure has developed for solar-cell, photodiode, photovoltaic, and photoelectrochemical applications [9,10]. Poly(3,4-ethylenedioxythiophene) doped with poly(4-styrenesulfonate) (PEDOT:PSS) is a potential *p*-type semiconducting polymer and has been proposed for use as a hole injection layer or an electrodes in organic solar cells and light-emitting diodes [11].

Although the p-n junction between vertically-aligned ZnO NWs and a p-type conductive polymer may play an important role in applications such as polymer-based solar cells, field emission transducers and sensors, the p-n junction formed between vertically-aligned ZnO NWs and conductive polymer thin films has not been systematically studied. In this work, the I-V characteristics of a sandwich-type structure constructed from ZnO NWs and PEDOT: PSS thin film was studied, and a p-n diode junction was reported. The I-V characteristics of the ZnO/PEDOT:PSS p-n junction as a function of UV illumination and temperature were also examined.

II. EXPERIMENTS AND DISCUSSION

Vertically-aligned ZnO NWs were grown on conducting glass (indium-doped tin oxide (ITO)-coated glass) and n-type silicon substrates through a vapor-phase transport process at temperatures of 800 – 1000 °C without using a catalyst. The typical length of the deposited nanowires was 70 μm and the average diameter was 250 nm. The ZnO NW surfaces were then spin coated with a PEDOT:PSS aqueous solution and dried in an air oven at 120 °C for 10 min. The active area of the devices was about 6 mm^2. To measure the I-V characteristics of pure ZnO or pure PEDOT:PSS thin films, we assembled the samples by directly putting one piece of ITO glass on top of the resulting ZnO NWs or the PEDOT:PSS

*E-mail: anvar_zakirov@yahoo.com; Fax: +82-2-2260-8823

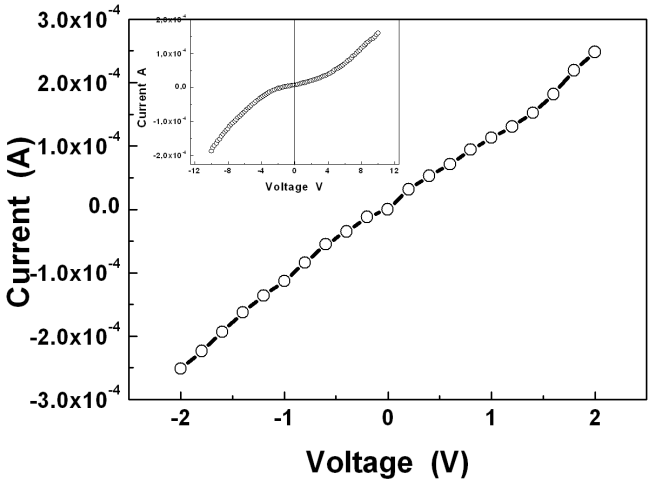

Fig. 1. I-V characteristics of the ZnO NWs and (inset) of pure PEDOT:PSS film sandwich-type devices.

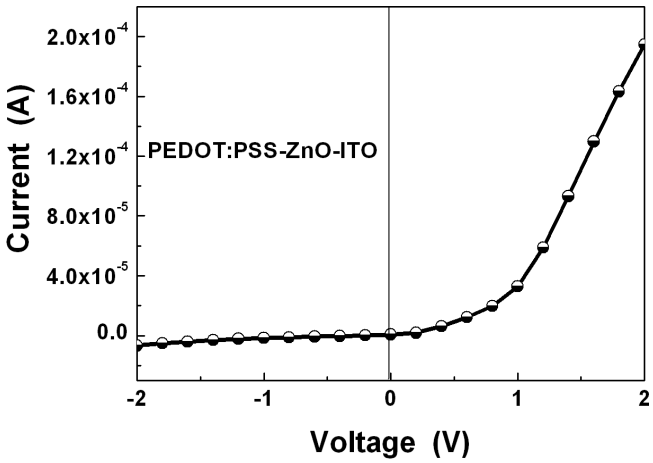

Fig. 2. Current-voltage characteristics of the PEDOT:PSS/ZnO -ITO structure.

thin film. The current-voltage characteristics of the fabricated devices were measured by using an Keithley 617 semiconductor parameter analyzer in laboratory atmosphere at room temperature and under dark condition. In the UV and the visible irradiation experiments, we used a 23 W mercury arc UV lamp (365 nm) and a red LED (635 nm).

Figure 1 shows the I-V characteristics of the sandwich-type devices. The I-V curve of the pure ZnO film is nearly linear, which represents an Ohmic contact. The PEDOT: PSS film shows a symmetric nonlinear I-V behavior (Fig. 1, inset), which demonstrates that the contact is not an ideal Ohmic contact though the work function of ITO (∼4.4 eV) is smaller than that of PEDOT: PSS (∼5.2 eV).

Studies of the I-V characteristics of the fabricated PEDOT:PSS/ZnO-ITO (or n-Si) structure revealed a good p-n heterojunction. From the curve in Fig. 2, the current rectification ratio (defined as the forward current

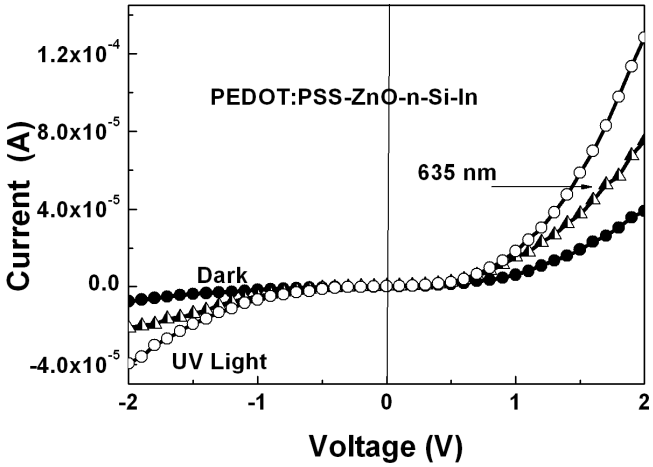

Fig. 3. (I-V) characteristics of the PEDOT:PSS/ZnO-n-Si-heterojunction measured in dark and under 365-nm and 635-nm light illuminations.

divided by the reverse current at a bias) can be seen to be about 10^3 at +2.0 V. The turn-on voltage and the reverse leakage current values are found to be 1 V and 5.39×10^{-7} A at -2 V, respectively. Therefore, the rectifying behavior mainly results from the formation of a p-n junction between the p-type PEDOT: PSS film and the n-type ZnO nanowires. A mathematical description of the current in the p-n junction is provided by the Shockley diode equation $I = I_s[\exp(eV/nk_bT) - 1]$. The calculated ideality factor (n) and saturation current density (I_s) for the device are found to be 4.8 and 2.2×10^{-7} A, respectively. Although the value of I_s is quite small, a value greater than 2 for n indicates that the diode is not an ideal one. This is probably due to the presence of surface states and/or presence the of an insulating layer of SiO_2 at the ZnO/Si interface.

The photo I-V characteristics, measured by illuminating the PEDOT:PSS/ZnO-n-Si heterojunction at wavelengths of 365 nm (UV) and 635 nm (visible), are shown in Fig. 3. Upon irradiating UV light with a wavelength of 365 nm both the forward and the reverse currents were increased. Compared to the 635-nm light source, a higher reverse photocurrent was produced with the 365-nm energy. The photocurrents for 635 nm and 365 nm are 21.1 μA and 40.2 μA, respectively, while the dark leakage current for the ZnO photodiodes is weak with the same 2 V reversed bias. In the dark, the reference turn-on current was reached at 1.1 V. Under UV illumination, the turn-on voltage was reduced to 0.76 V. This is attributed to the reduction of the UV-light-induced potential barrier, resulting in current enhancement at a fixed voltage value. This behavior indicates that the ZnO photodiodes can sensitively detect UV light to produce the measurable photocurrent response.

The I-V characteristics show thermally-activated diode like rectifying behavior and demonstrates that the small reverse current is slightly temperature dependent.

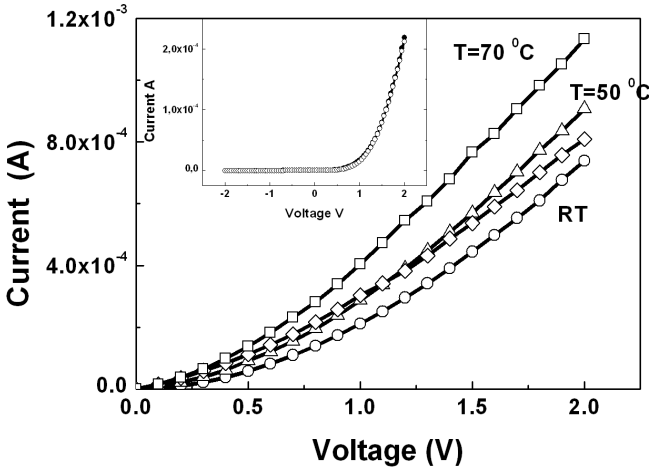

Fig. 4. Temperature-dependent I-V characteristics for a PEDOT:PSS/ZnO-n-Si -photodiode recorded at RT, 30 °C, 50 °C, and 70 °C.The inset shows no significant degradation of the devices.

However, the magnitude of the forward current at a given voltage increases significantly with increasing temperature (Fig. 4). This behavior is consistent with tunneling through a barrier out of occupied levels whose populations are slightly modified by a nonzero temperature and with a potential barrier that allows decreased penetration with increasing forward voltage [12]. The I-V characteristics measured after one month of storage showed no significant degradation of the devices, which demonstrated the excellent stability of those ZnO/organic hybrid heterostructures (Fig. 4, inset).

III. CONCLUSION

In summary, we have demonstrated the electrical performances of a hybrid photodiode based on a heterojunction of n-ZnO NWs with a PEDOT:PSS film. While pure ZnO and PEDOT:PSS sandwich devices show symmetric I-V curves, the ZnO/PEDOT:PSS configuration demonstrates an asymmetric I-V characteristic. The formation of a p-n junction between the p-type PEDOT:PSS and the n-type ZnO is verified by the rectifying behavior, with a cut-in voltage of about 1 V and a reverse breakdown voltage of >10 V. The temperature-dependent transport has also been investigated. The photoelectrical measurements demonstrate that the heterojunction based on ZnO NWs has a high sensitivity and selectivity with UV light. The results not only present a clear picture about the photoresponse properties, but also demonstrate the potential of using a low-cost heterojunction for detecting both UV and visible photons in the same structure.

ACKNOWLEDGMENTS

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korea government Ministry of Education, Science and Technology (MEST), (No. 2011-0000016) and by the Leading Foreign Research Institute Recruitment Program through the National Research Foundation of Korea (NRF) funded by the MEST (No. 2010-00218).

REFERENCES

[1] A. P. Ramirez, Science **9**, 1377 (2007).
[2] G. T. Du, W. F. Liu, J. M. Bian, L. Z. Hu, H. W. Liang, X. S. Wang, A. M. Liu and T. P. Yang, Appl. Phys. Lett. **89**, 052113 (2006).
[3] S. Mridha and D. Basak, J. Appl. Phys. **101**, 083102 (2007).
[4] Y. I. Alivov, U. Ozgur, S. Dogan, D. Johnstone, V. Avrutin, N. Onojima, C. Liu, J. Xie, Q. Fan and H. Morkoc, Appl. Phys. Lett. **86**, 241108 (2005).
[5] I.-S. Jeong, J. H. Kim and S. Im, Appl. Phys. Lett. **83**, 2946 (2003).
[6] Y. Vygraninko, K. Wang and A. Nathan, Appl. Phys. Lett. **89**, 172105 (2006).
[7] J. Y. Lee, Y. S. Choi, J. H. Kim, M. O. Park and S. Im, Thin Solid Films **403**, 553 (2002).
[8] K. Haga, T. Suzukia, Y. Kashiwabaa, H. Watanabea, B. P. Zhang and Y. Segawa, Thin Solid Films **433**, 131 (2003).
[9] A. M. Peiro, P. Ravirajan, K. Govender, D. S. Boyle, P. O'Brien, D. D. C.Bradley, J. Nelson and J. R. Durrant, J. Mater. Chem. **16**, 2088 (2006).
[10] J. P. Liu, S. C. Qu, X. B. Zeng, Y. Xu, X. F. Gou, Z. J. Wang, H. Y. Zhou and Z. G. Wang, Appl. Surf. Sci. **253**, 7506 (2007).
[11] L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik and J. R. Reynolds, Adv. Mater. **12**, 481 (2000).
[12] H. He, Sh. T. Ho, T. B. Wu, L. J. Chen and Z. L. Wang, Chem. Phys. Lett. **435**, 119 (2007).