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P-ZnO/n-Si Photodiodes Prepared by Ultrasonic Spraying Pyrolysis Method

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Abstract: ZnO ultraviolet (UV)/visible photodiodes were fabricated. The N-In codoped p-type ZnO films were deposited on (111)-oriented silicon substrate by ultrasonic spraying pyrolysis method. It was found the photocurrent approximately 3.9×10^{-7} A at a bias of 1 V and a photocurrent to dark current contrast ratio higher than around two orders of magnitude. The photodiodes exhibited two higher responsive regions denoted as A and B, respectively. Region A at wavelength from 400 nm to 700 nm was owing to ZnO film absorption occurring through the band-to-deep level, and region B at wavelength from 700 nm to 1000 nm was owing to Si substrate absorption occurring through the band edge.

Keywords: Zinc oxide, spraying pyrolysis method, photodiodes.

1. INTRODUCTION

Zinc oxide (ZnO) has been regarded as promising materials for optical devices, due to its wide direct band gap energy of 3.37 eV and large exciton binding energy of 60 meV [1-3]. Therefore, ZnO has a potential for light-emitting diodes (LEDs), laser diodes (LDs) and ultraviolet (UV) detecting devices [3-6]. A variety of deposition techniques have been employed for the growth of ZnO layers, including metalorganic chemical vapor deposition (MOCVD) [7], plasma-assisted molecular beam epitaxy (PA-MBE) [8], pulsed laser deposition (PLD) [9], and spray pyrolysis method [10,11]. The synthesis of p-type ZnO films with acceptable stability and reproducibility by means of indium and nitrogen codoping has recently been demonstrated [12,13].

ZnO photoconductors, Schottky diodes, metal-semiconductor-metal (MSM) photodiodes, and phototransistors detecting in the UV region have also been demonstrated [14-19]. Si-based photodiodes was usually employed for the detecting in the UV/visible region. However, the responsibility of Si-based photodiodes is relatively week in the UV/blue region, such as less than 0.1 A/W at 400 nm [20].

This article reports a p-ZnO/n-Si heterostructure photodiode. An N-In codoped p-type was deposited on a (111)-oriented silicon substrate by ultrasonic spraying pyrolysis method. The growth and crystallinity of the ZnO films were studied. Finally, we report the fabrication and performance of the p-ZnO/n-Si heterostructure photodiode.

2. EXPERIMENTAL

In the study, N–In codoped ZnO films were deposited by ultrasonic spray pyrolysis method at atmosphere on (111)-oriented silicon substrate. Three kinds of aqueous solution, $Zn(CH_3COO)_2{\cdot}2H_2O$ (0.5 mol/l), CH_3COONH_4 (2.5 mol/l), and $In(NO_3)_3$ (0.5 mol/ l), were chosen as the source of zinc, nitrogen, and indium, respectively. The atomic ratio of Zn/N is 1:2 for N-doped film, and Zn/N/In is 1:2:0.15 for N–In codoped film [12]. The n-type Si (111) wafers (ρ = 0.005 Ω cm) were used as the substrates, which were etched with HCl for 5 min prior to the deposition. The aerosol of precursor solution was generated by the commercial ultrasonic nebulizer. P-type N-In codoped ZnO films were obtained during the substrate heated at 650 °C, and examined by Hall measurement (on sapphire substrate). The hole concentration and mobility of p-ZnO were around 1×10^{17} cm^{-3} and approximately 46 cm^2/V-s, respectively.

After there, fabrication of p-ZnO/n-Si heterostructures was accomplished. The films' crystallinities were studied by X-ray diffraction (XRD) using a rotating anode Rigacu x-ray diffractometer with Cu-Kα_1 radiation of 1.54 Å, radiation generated at 40 kV and 50 mA, and the films had a polycrystalline structure. The Ni/Au ohmic contact layer was evaporated onto the p-type ZnO film as the anode electrode, and a Ti/Pt/Au electrode was formed on the backside of the n-type Si substrate as the cathode electrode. Fig. (**1a**) shows the cross section of the completed structure. Fig. (**1b**) shows the current-voltage (*I-V*) for ohmic check of Au/Ni/p-ZnO and Au/Pt/Ti/n-Si structures, respectively. Subsequently, the photodiode chip was bonded on TO-18 can to measure the dark and illuminated current-voltage (*I-V*) characteristics. A 30 W deuterium lamp and 35 W halogen lamp were used as the light source for the spectral responsivity studies. All measurement was carried out at room temperature.

3. RESULTS AND DISCUSSION

Fig. (**2**) shows a cross-sectional SEM image of the layer of p-type ZnO film deposited on (111)-oriented Si substrate. The ZnO film with thickness of about 1.3 μm was formed on silicon substrate. The interface between the ZnO film and Si substrate is flat and free from inclusions. Fig. (**3**) shows a typical X-ray diffraction (XRD) pattern of ZnO film deposited on (111)-oriented Si substrate prepared by ultrasonic

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spraying pyrolysis method. Three dominant diffraction peaks, ZnO(100) ($2\theta = 32.04°$), ZnO(002) ($2\theta = 34.84°$), and ZnO(101) ($2\theta = 36.6°$), are observed. The lattice parameters are found to be a = 3.222 Å and c = 5.147 Å. The film demonstrated a polycrystalline structure.

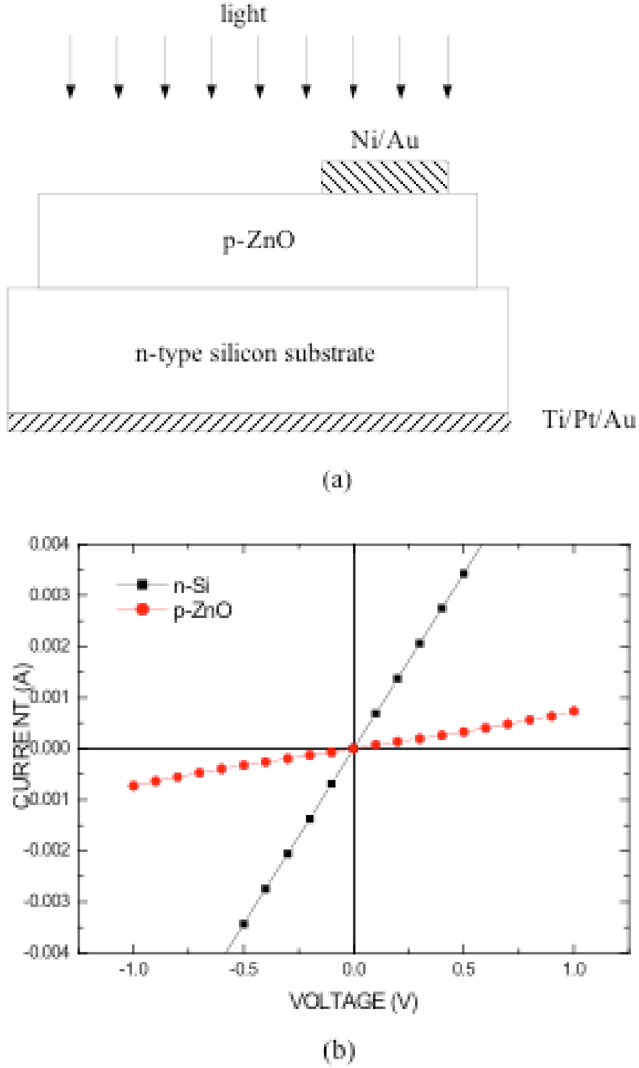

Fig. (1). (**a**) Schematic cross section of the completed structure. (**b**) The current-voltage (*I-V*) for ohmic check of Au/Ni/p-ZnO and Au/Pt/Ti/n-Si structures, respectively.

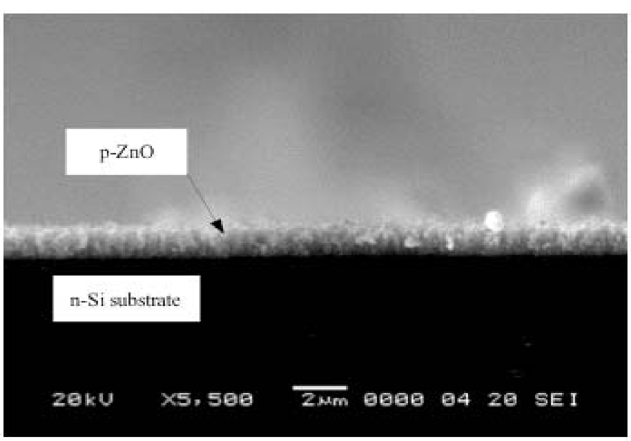

Fig. (2). Cross sectional SEM image of ZnO/Si heterostructure.

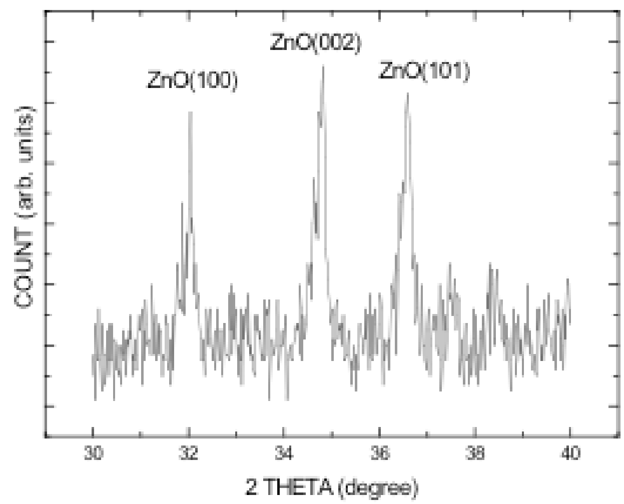

Fig. (3). X-ray diffraction (XRD) pattern of N-In codoped ZnO film deposited on (111)-oriented Si substrate.

Typical *I-V* characteristics of the ZnO/Si heterostructure photodiodes at room temperature are shown in Fig. (**4**). To avoid the degeneration of films, voltage was limited from -2 V to 1 V. The photodiode has a turn-on forward bias of ~ 0.3 V. In the reverse direction, the reverse leakage current prior to breakdown is around 10^{-9} A. Fig. (**5**) shows the plots of the *I-V* characteristics of the photodiodes measured in the dark (dark current) and under illumination (photocurrent, λ = 530 nm) at reverse biases from 0 to 1 V. As shown in Fig. (**5**), it was found the photocurrent approximately 3.9×10^{-7} A and the dark current was approximately 8.87×10^{-9} A at a bias of 1 V. Therefore, it was found that a photocurrent to dark current contrast ratio is around two orders of magnitude.

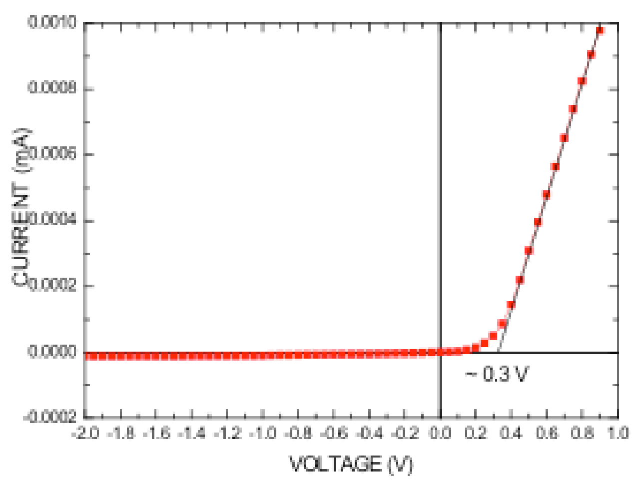

Fig. (4). Typical I-V characteristics of the ZnO/Si heterostructure photodiodes.

Fig. (**6**) shows the plot of responsivity as a function of the wavelength for a ZnO/Si heterostructure photodiode at a bias of 1 V. The photodiodes exhibited two higher responsive regions denoted as A and B, respectively. Region A at wavelength approximately from 400 nm to 700 nm was owing to ZnO film absorption occurring through the band-to-

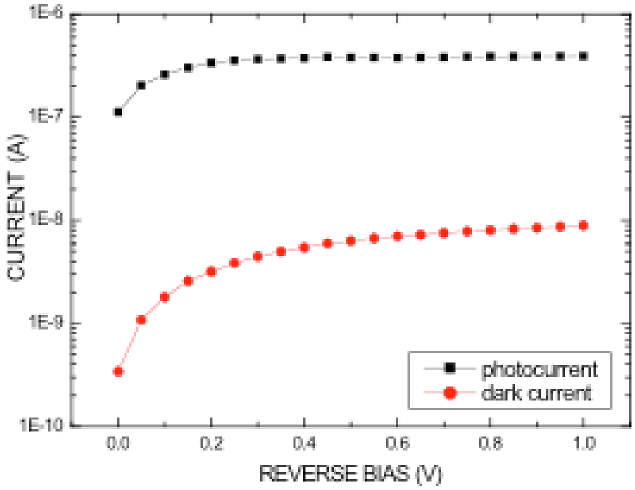

Fig. (5). The dark and illuminated (λ = 530nm) *I-V* characteristics of the ZnO/Si heterostructure photodiode.

deep level [18], and region B at wavelength approximately from 700 nm to 1000 nm was owing to Si substrate absorption occurring through the band edge. Responsivity *R* can be described as [21]:

$$R = I_{ph} / P_{inc} = \eta \frac{q}{h\nu} \qquad (A/W) \tag{1}$$

where I_{ph} is the photocurrent and P_{inc} is the incident power, and η, q, ν, and h are the quantum efficiency (QE), electron charge, frequency of incident light, and Planck constant, respectively. Using eq. (1), the values of responsivity and QE at 530 nm at biases of 1 V were 0.204 A/W and 47.73%, respectively. The values of responsivity and QE at 850 nm at biases of 1 V were 0.209 A/W and 30.49%, respectively. As shown in Fig. (**6**), in contrast to conventional Si-based photodetectors, the ZnO film has been improved the responsivity in UV/blue region. However, the responsivity was degraded in near infrared region (700 – 1100 nm). This result means that the portion of light with higher energy, such as 400 – 500 nm, was absorbed by ZnO film and the portion of light with lower energy, such as 800 – 1000 nm, can completely incident into Si substrate and was absorbed. However, the responsivity owing to the ZnO film absorption occurring through the band-to-band did not observe in this work.

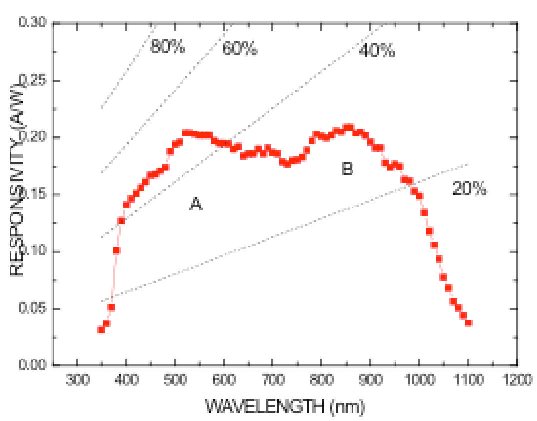

Fig. (6). The responsivity as a function of the wavelength for a ZnO/Si heterostructure photodiode at a bias of 1 V.

4. CONCLUSION

ZnO ultraviolet (UV)/visible photodiodes were fabricated. The N-In codoped p-type ZnO films were deposited on (111)-oriented silicon substrate by ultrasonic spraying pyrolysis method. The photodiodes exhibited two higher responsive regions denoted as A and B, respectively. Region A at wavelength from 400 nm to 700 nm was owing to ZnO film absorption occurring through the band-to-deep level, and region B at wavelength from 700 nm to 1000 nm was owing to Si substrate absorption occurring through the band edge. In the region A, the values of responsivity and QE at 530 nm at biases of 1 V were 0.204 A/W and 47.73%, respectively. In the region B, the values of responsivity and QE at 850 nm at biases of 1 V were 0.209 A/W and 30.49%, respectively.

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REFERENCES

[1] Zhang XH, Chua SJ, Yong AM, *et al*. Exciton radiative lifetime in ZnO nanorods fabricated by vapor phase transport method. Appl Phys Lett 2007; 90: 013107.

[2] Danhara Y, Hirai T, Harada Y, Ohno N. Exciton luminescence of ZnO fine particles. Phys Stat Sol (c) 2006; 3: 3565-8.

[3] Lim JH, Kang CK, Kim KK, *et al*. UV electroluminescence emission from ZnO light-emitting diodes grown by high-temperature radiofrequency sputtering. Adv Mater 2006; 18: 2720-4.

[4] Wei ZP, Lu YM, Shen DZ, *et al*. Room temperature *p-n* ZnO blue-violet light-emitting diodes. Appl Phys Lett 2007; 90: 042113.

[5] Leong ESP, Yu SF, Lau SP. Directional edge-emitting UV random laser diodes. Appl Phys Lett 2006; 89: 221109.

[6] Lee CW, Choi H, Oh MK, *et al.* ZnO-Based cyclodextrin sensor using immobilized polydiacetylene Vesicles. Electrochem Solid State Lett 2007; 10: J1-3.

[7] Abe T, Kashiwaba Y, Onodera S, *et al*. Homoepitaxial growth of non-polar ZnO $(11\bar{2}0)$ films on off-angle ZnO substrates by MOCVD. J Crystal Growth 2007; 298: 457-60.

[8] Wang X, Lu YM, Shen DZ, *et al*. Growth and photoluminescence for undoped and N-doped ZnO grown on 6H-SiC substrate. J Luminescence 2007; 122-123: 165-7.

[9] Park SM, Ikegami T, Ebihara K. Effects of substrate temperature on the properties of Ga-doped ZnO by pulsed laser deposition. Thin Solid Films 2006; 513: 90-4.

[10] Castañeda L, Maldonado A, Cheang-Wong JC, Terrones M, Olvera M de la L. Composition and morphological characteristics of chemically sprayed fluorine-doped zinc oxide thin films deposited on Si(1 0 0). Phys B 2007; 390: 10-6.

[11] Kaid MA, Ashour A. Preparation of ZnO-doped Al films by spray pyrolysis technique. Appl Sur Sci 2007; 253: 3029-33.

[12] Bian JM, Li XM, Gao XD, Yu WD, Chen LD. Deposition and electrical properties of N–In codoped *p*-type ZnO films by ultrasonic spray pyrolysis. Appl Phys Lett 2004; 84: 541-3.

[13] Chen LL, Ye ZZ, Lu JG, Chu PK. Control and improvement of *p*-type conductivity in indium and nitrogen codoped ZnO thin films. Appl Phys Lett 2006; 89: 252113.

[14] Zheng XG, Li QS, Zhao JP, *et al.* Photoconductive ultraviolet detectors based on ZnO films. Appl Sur Sci 2006; 253: 2264-7.

[15] Liang S, Sheng H, Lin Y, Huo Z, Lu Y, Shen H. ZnO Schottky ultraviolet photodetectors. J Crystal Growth 2001; 225: 110-3.

[16] Moon TH, Jeong MC, Lee W, Myoung JM. The fabrication and characterization of ZnO UV detector. Appl Sur Sci 2005; 240: 280-5.

[17] Young SJ, Ji LW, Fang TH, Chang SJ, Su YK, Du XL. ZnO ultraviolet photodiodes with Pd contact electrodes. Acta Mater 2007; 55: 329-33.

[18] Bae HS, Im S. Ultraviolet detecting properties of ZnO-based thin film transistors. Thin Solid Films 2004; 469-470: 75-9.
[19] Oh DC, Suzuki T, Makino H, Hanada T, Ko HJ, Yao T. Electrical properties of ZnO/GaN heterostructures and photoresponsivity of ZnO layers. Phys Stat Sol (c) 2006; 3: 946-51.
[20] Veerasamy VS, Amaratunga GAJ, Park JS, Milne WI, MacKenzie HS. Photoresponse characteristics of *n*-type tetrahedral amorphous carbon/*p*-type Si heterojunction diodes. Appl Phys Lett 1994; 64: 2297-9.
[21] Sze SM. Physics of Semiconductor Devices. 2nd ed. John Willey & Sons; 1981.

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