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UV photo-detector based on p-NiO thin film/n-ZnO nanorods heterojunction prepared by a simple process

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Abstract

A UV photo-detector based on p-NiO thin film/n-ZnO nanorods heterojunction was fabricated using a simple two-step fabrication process. The aqueous chemical hydrothermal and thermal evaporation methods were combined to grow the ZnO nanorods and the NiO thin film, respectively. Structural investigation indicated that well aligned ZnO nanorods with hexagonal face having a preferential orientation along the c-axis (002) have been achieved and that the NiO thin film is covering all the ZnO nanorods. X-ray photoelectron spectroscopy (XPS) was used to investigate the band alignment of the heterojunction and the valence and the conduction band offsets were determined to be 1.50 eV and 1.83 eV, respectively. The current-voltage characteristics of the p-NiO thin film/ZnO nanorods heterojunction showed a clear rectifying behavior under both dark and UV illumination conditions. The response of the heterojunction diode was excellent regarding the photocurrent generation. Although other similar heterojunction diodes demonstrated lower threshold voltage, the rectification ratio and the sensitivity of the fabricated diode were superior in comparison to other similar heterojunctions reported recently, implying the vitality of the presented two-step process.

Keywords: ZnO nanorods, NiO thin film, UV photo-detector, Heterojunction.

1. Introduction

Zinc oxide (ZnO) heterojunctions based ultraviolet (UV) detectors have attracted considerable attention in comparison to those made from other semiconductors such as Si, SiC and AlGaIn [1-4]. Due to its wide direct band gap energy (3.37 eV), relatively large exciton binding energy (60 meV at room temperature) and excellent optical and electrical properties, ZnO has been recognized as a promising material for UV detector [5-7]. Ultra violet detection by ZnO is based on strong oxygen chemisorptions and photodesorption mechanism on the surface and for efficient UV detection high quality ZnO heterojunctions are needed [8]. So far ZnO based UV photo-detectors with high performance have been reported using different methods such as molecular beam epitaxy [9] and sol-gel [10]. Recently, it has been reported that hybrid structures of ZnO with other semiconductors could increase the performance of UV detectors [11-14]. On the other hand, nickel oxide (NiO) has been under investigation for different technological applications due to its wide direct band gap (3.6 – 4.0 eV) and it is intrinsically p type semiconductor. These properties make NiO a suitable candidate for the fabrication of p-NiO/n-ZnO heterojunction based UV photo-detectors [15-18]. Alternative inexpensive fabrication techniques are usually needed to realize large scale, mass production and low cost UV photo-detectors with high performance. Until now there are only few reports about using the thermal evaporation method for the synthesis of NiO thin film [19]. Moreover, there has been no detailed investigation reported about using this method to fabricate p-NiO thin film/n-ZnO nanorods heterojunction based UV photo-detector with high quality.

In the present study, we have synthesized the NiO thin film using thermal evaporation method to fabricate p-NiO thin film/n-ZnO nanorods heterojunction. The materials were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and photoluminescence (PL). The current-voltage characteristics were investigated under UV illumination via semiconductor parameter analyzer and potentiostat. Further, the obtained results were compared to those achieved from other UV photodetectors based on the similar heterojunction grown by other methods.

2. Experimental

2.1. *Growth of ZnO nanorods*

Commercially available fluorine doped tin oxide (FTO) glass substrate was used in this study and all the chemicals were of analytical grade and were purchased from Sigma Aldrich. The FTO glass substrate was cleaned by sonication in acetone, deionized water, and isopropanol, respectively. Part of the substrate at the edge was covered with scotch tape in order to have a metal contact area. Then the substrate preparation technique developed by Green et al. [20] was used to improve the quality of the grown ZnO nanorods. To grow the ZnO nanorods, an equimolar concentration of hexamethylenetetramine (HMT) and zinc nitrate hexahydrate solutions (0.075 M) were separately prepared and mixed together. Then the final solution was poured into a beaker and the pretreated substrate was immersed in the solution with the growth side facing downward. Then the beaker was sealed and heated in a laboratory oven at 95 °C for 5 hours and then it was allowed to cool down at room temperature. After the growth process, the sample was rinsed with deionized water to remove the residual salts and dried with nitrogen blow.

2.2. *Synthesis of the NiO thin film/ZnO nanorods heterojunction*

To fabricate the p-NiO thin film/n-ZnO nanorods heterojunction, Ni film with 50 nm thickness was deposited by thermal evaporation in a vacuum chamber with a pressure of 2×10^{-6} mbar on the top of ZnO nanorods. Then to oxidize the Ni film, the sample was annealed in oxygen ambient at a temperature of 400 °C for 5 hours. To prepare the UV detector device, Ag circular contact with 80 nm thickness and 1 mm diameter was afterwards deposited on top of the NiO thin film using the thermal evaporation method.

2.3. *Characterization*

The structural and morphological properties of the p-NiO/n-ZnO heterojunction were examined by X-ray diffraction (XRD: Phillips PW 1729 powder diffractometer using $\text{CuK}\alpha$ radiation), field emission scanning electron microscope (FESEM: LEO 1550 Gemini) and X-ray photoelectron spectroscopy (XPS: ESCA200 spectrometer in ultrahigh vacuum with a base pressure of 10^{-10} mbar). The light emission features of the samples were studied by a micro-photoluminescence (μPL) setup at room temperature. The excitation was performed by a

frequency doubled Nd:YVO laser as a continuous wave excitation source, giving a wavelength of $\lambda=266$ nm. The UV detection characteristics were evaluated by semiconductor parameter analyzer and potentiostat (Autolab) under lamp illumination at $\lambda_{\text{max}}=365$ nm with a light power of 18 W.

3. Results and discussion

3.1. *Morphological and structural properties*

Typical top view and cross-section SEM images of the ZnO nanorods and the NiO thin film grown on the top of the ZnO nanorods are shown in Figure 1(a-d). It is clearly seen that a relatively well aligned ZnO nanorods having hexagonal faces with an average diameter and height of approximately 100 nm and 1 μm , respectively were achieved. Also, as it can be seen that the NiO thin film covers all the ZnO nanorods with relatively smooth surface. In order to verify the crystal structure of the materials forming the heterojunction, XRD analysis was performed. Figure 2 (a) shows the XRD patterns of the FTO glass substrate, NiO thin film/FTO and NiO thin film/ZnO nanorods/FTO heterojunction. It can be observed that the XRD pattern displays diffraction peaks that corresponds to ZnO wurtzite structure (JCPDS No. 36-1451) and that the ZnO has a preferential orientation along the c-axis since the (002) peak is clearly seen to be the highest in intensity. The lattice constants for the ZnO calculated from the XRD data were $a=3.25\text{\AA}$ and $c=5.20\text{\AA}$. Also, the XRD patterns show the characteristic peaks of NiO which correspond to the (111) and the (200) planes of cubic NiO structure consistent with diffraction file (JCPDS No. 01-1239). The lattice constant of the grown NiO is calculated to be $a=4.16\text{\AA}$. It should be mentioned that the (111) direction of the NiO thin film has the same angle with one of the peaks of the FTO glass substrate ($2\theta = 37.66^\circ$).

3.2. *Optical properties*

Photoluminescence (PL) study is a convenient analysis method to gain useful information about the optical properties of semiconductor materials such as bulk material, thin films or individual nanostructures [21-24]. The PL spectra of the ZnO nanorods and the NiO thin film/ZnO nanorods heterojunction are shown in Figure 2 (b). All the spectra were taken at the same excitation power and integration time and are therefore comparable. It can be seen that the

ultraviolet (UV) emission which is called near band edge emission (NBE) and the deep level emission (DLE) peaks are observed for ZnO nanorods centred approximately at 375 nm, 520 nm (DLE1, green emission) and 680 nm (DLE2, red emission), respectively. The UV emission is attributed to the recombination of free excitons and the green and red peaks are ascribed to the recombination between the conduction band and zinc interstitial (Zn_i) energy level to oxygen vacancy (V_O) and oxygen interstitial (O_i), respectively [25, 26]. The PL emission intensity of the NiO thin film/ZnO nanorods heterojunction sample is lower in intensity compared to that of the pure ZnO nanorods. This can be explained by possible absorption of the PL signal by the top NiO layer. This effect was particularly prominent for the defect luminescence range, namely DLE1 and DLE2.

3.3. *Band alignment of the NiO thin film/ZnO nanorods heterojunction*

Three samples have been prepared to measure the valence band offset in the NiO thin film/ZnO nanorods heterojunction using X-ray photoelectron spectroscopy (XPS). ZnO nanorods were grown on the bare FTO substrate (sample 1) and NiO with 50 nm thickness were deposited on the another bare FTO substrate (sample 2) then NiO with 10 nm thickness deposited on the grown ZnO nanorods (sample 3). The core levels (CLs) and valence band (VB) edge XPS spectra of ZnO (sample 1) and NiO (sample 2) are shown in Figure 3(a-d) and Figure 4(a, b), respectively. All the CL XPS peaks have been fitted using Tougaard background and Voigt profile. As shown in Figure 3(a), the binding energy peak at 1022.34 ± 0.05 eV which corresponds to the core level of the Zn $2p_{3/2}$ has a symmetric shape and is attributed to the Zn-O band. The CL XPS spectrum of the Ni $2p_{3/2}$ consists of three components located at 853.65 ± 0.05 eV, 855.38 ± 0.05 eV and 860.92 ± 0.05 eV which all ascribed to Ni-O band [27]. The O 1s peak of the ZnO and the NiO observed around 531.08 ± 0.05 eV and 529.32 ± 0.05 eV could be assigned to O^{2-} ions in the ZnO and the NiO lattice array and the shoulder peaks around 532.27 ± 0.05 eV and 530.92 ± 0.05 eV can be attributed to defect sites such as O_2 on the ZnO and on the NiO surfaces [28]. The valence band maximum (VBM) of the ZnO nanorods and the NiO thin film measured from the VB spectra using linear fitting were 3.04 ± 0.05 eV and 0.61 ± 0.05 eV, respectively. The core levels of the Zn $2p_{3/2}$ and Ni $2p_{3/2}$ in the NiO/ZnO heterojunction (sample 3) which are shown in Figure 5(a, b) are located at 1021.83 ± 0.05 eV, 854.07 ± 0.05 eV, 855.74

± 0.05 eV and 861.27 ± 0.05 eV, respectively. As it can be seen the Zn 2p_{3/2} and the Ni 2p_{3/2} peaks in the NiO/ZnO heterojunction have a little shift. The experimentally observed values of peak positions and the VBM are given in Table 1. The valence band offsets of the NiO thin film/ZnO nanorods heterojunction were measured using the following equation [27, 29]:

$$\Delta E_V = (E_{Ni\ 2p}^{NiO} - E_{VBM}^{NiO}) - (E_{Zn\ 2p}^{ZnO} - E_{VBM}^{ZnO}) + \Delta E_{CL} \quad (1)$$

where $(E_{Ni\ 2p}^{NiO} - E_{VBM}^{NiO})$ is the energy difference between the Ni 2p_{3/2} and the VBM in the NiO thin film (sample 2), $(E_{Zn\ 2p}^{ZnO} - E_{VBM}^{ZnO})$ is the energy difference between the Zn 2p_{3/2} and the VBM in the ZnO nanorods (sample 1), $\Delta E_{CL} = (E_{Zn\ 2p}^{ZnO} - E_{Ni\ 2p}^{NiO})$ is the energy difference between the Zn 2p_{3/2} and the Ni 2p_{3/2} core levels in the NiO thin film/ZnO nanorods heterojunction (sample 3). Also, the conduction band offset of the heterojunction can be measured using following equation [27, 29]:

$$\Delta E_C = E_g^{NiO} - E_g^{ZnO} + \Delta E_V \quad (2)$$

The band gaps of ZnO and NiO are 3.37 eV and 3.70 eV at room temperature, respectively. Therefore, the measured ΔE_V and ΔE_C are found to be 1.50 eV and 1.83 eV, respectively, which are very close to the values reported by Zhi Guo Yang et al. [29]. The schematic band alignment of the NiO thin film/ZnO nanorods heterojunction is shown in Figure 6. It can be seen that a type-II band alignment is formed at the interface of the heterojunction.

3.4. Electrical properties

Figure 7 (a) shows the schematic diagram of the p-NiO thin film/n-ZnO nanorods heterojunction. Figure 7 (b) displays the typical observed current density – voltage (J-V) and the semilog J-V characteristics of the p-NiO/n-ZnO heterojunction in the dark and under UV illumination at room temperature. As it can be seen the diode shows an obvious rectifying behavior under both dark and UV illuminated condition. The electrical parameters of the p-NiO thin film/n-ZnO nanorods heterojunction in dark and under UV illumination conditions are listed in Table 2. The turn-on voltage of the diode exhibits a relatively low value indicating that the diode has fairly low power consumption. The high value of the I_F/I_R ratio in dark condition

displays the high quality of the heterojunction, where I_F and I_R is the current under forward bias and reverse bias (7 V), respectively. To evaluate the ideality factor of the diode, the dark current – voltage (I-V) response of the diode in low bias region can be modeled using the ideal diode equation [14]:

$$I = I_{\text{sat}} [\exp (V/nkT) - 1] \quad (3)$$

where I_{sat} is the reverse bias saturation current, V is the applied voltage, n is the ideality factor, k is the Boltzmann's constant and T is the temperature. The ideality factor (n) and the reverse bias saturation current (I_{sat}) can be calculated from the slope and intercept of the straight line region of the forward bias in $\ln(I)$ - V plot, as shown in the Figure 7 (c). These parameters are listed in Table 2. The ideality factor of the diode is much larger than the value of an ideal diode ($n=1$). Such a high value of n suggests that the transport mechanism is not dominated by the thermionic emission, but consisting of other mechanisms like defect assisted tunnelling with conventional electron-hole recombination [30]. A potentiostat was used to check the decay time response of the diode. The UV illumination was applied for 13 s and the gap between the UV illuminations to bring the diode at stable position was about 40 s as shown in Figure 7(d). It can be seen that the average decay time response of the diode is about 25 s. To understand the origin of the photocurrent probing the adsorption and desorption of oxygen from the ZnO surface under UV illumination is to be understood. In the present work, the NiO is prepared by annealing the Ni in oxygen ambient, therefore oxygen molecules are adsorbed onto the ZnO nanorods surface (Figure 3c) by capturing free electrons from the n-ZnO nanorods [$\text{O}_2 (\text{g}) + \text{e}^- \rightarrow \text{O}_2^-$] where a depletion layer will be formed near the interface of the p-NiO/n-ZnO heterojunction [13, 31-34]. Under UV illumination, more electron-hole pairs will be generated in the p-NiO thin film and due to the lower valence band offset compared to the conduction band offset; holes will be transferred from the NiO towards the ZnO. Then this will be followed by holes migration to the surface of the ZnO nanorods along the potential gradient, produced by band bending, discharging the negatively charged adsorbed oxygen ions [$\text{O}_2^- + \text{h}^+ \rightarrow \text{O}_2 (\text{g})$]. Then, oxygen is desorbed from the surface, resulting in an increase in the free carrier concentration and a decrease in the width of the depletion layer [13, 31-33]. This leads to an increase in the carrier injection, producing a persistent photocurrent.

As can be seen from Table 2, under UV illumination a relatively high I_F/I_R contrast ratio was observed. The enhancement of I_F/I_R ratio compared to the dark ratio is about 57% and it is revealing that the response of the present heterojunction diode is excellent in generating photocurrent in comparison to previous reports on similar heterojunctions prepared by different methods [8, 13, 18]. Much Lower current contrast ratio, i.e. low sensitivity to UV, was observed from similar thin film heterojunction prepared by r.f. sputtering [18]. The low sensitivity was attributed to the high density of interface traps. Using the low temperature chemical growth for decorating ZnO nanorods with NiO coral-reef like forming a heterojunction that was tested for UV detection was performed recently in our group [13]. Again, the present approach indicated that it provides a better diode performance and hence a better UV sensitivity.

Conclusion

In summary, p-NiO thin film/n-ZnO nanorods heterojunction was fabricated. The p-NiO/n-ZnO heterojunction showed an obvious rectifying behavior and the response of the diode was excellent in generating photocurrent upon UV illumination. X-ray photoelectron spectroscopy results show that the heterojunction has type-II band alignment with a valence band offsets of 1.50 eV and conduction band offset of 1.83 eV. The average decay time response of the diode was about 25 s. The PL emission intensity of the NiO thin film/ZnO nanorods heterojunction sample was lower than those of pure ZnO nanorods which can be explained by possible absorption of the PL signal by the top NiO layer. The sensitivity and the diode electrical rectification ratio presented here were superior to those achieved from similar heterojunctions prepared by different methods. The demonstrated two step process represents an alternative inexpensive fabrication technique suitable to realize large scale mass production with low cost of p-NiO thin film/n-ZnO nanorods UV photo-detectors with high performance. Moreover, with more optimization the present two-step process can yield more efficient heterojunction with improved characteristics.

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Table 1. XPS CL spectra fitting results and VBM positions in ZnO nanorods, NiO thin film and p-NiO/n-ZnO heterojunction.

Sample	State	Binding energy
ZnO nanorods	Zn 2p _{3/2}	1022.34 ± 0.05 eV
	O 1s	531.08 ± 0.05 eV
	VBM	3.04 ± 0.05 eV
NiO thin film	Ni 2p _{3/2}	853.65 ± 0.05 eV
	O1s	529.32 ± 0.05 eV
	VBM	0.61 ± 0.05 eV
p-NiO/n-ZnO heterojunction	Zn 2p _{3/2}	1021.83 ± 0.05 eV
	Ni 2p _{3/2}	854.07 ± 0.05 eV

Table 2: The turn-on voltage (V_T), current under forward bias (I_F), under reverse bias (I_R), ideality factor (n) and reverse bias saturation current (I_{sat}).

	V_T (V)	I_F (A)	I_R (A)	I_F/I_R	n	I_{sat} (A)
Dark	4.5	8.85×10^{-5}	1.47×10^{-6}	60.11	6.9	1.24×10^{-9}
UV light	4.1	5.28×10^{-4}	5.59×10^{-6}	94.47	-	-

Figure 1: Top view and cross section SEM images of ZnO nanorods (a, b) and NiO thin film/ZnO nanorods heterojunction (c, d).

Figure 2: (a) XRD pattern of NiO thin film/ZnO nanorods heterojunction and (b) room temperature PL spectra of ZnO nanorods and NiO thin film/ZnO nanorods heterojunction.

Figure 3. CL spectra of (a) Zn 2p_{3/2}, (c) O 1s in ZnO nanorods and (b) Ni 2p_{3/2},
(d) O 1s in NiO thin film.

Figure 4. Valence band edge spectra of (a) ZnO nanorods, and (b) NiO thin film.

Figure 5. CLs of (a) Zn 2p_{3/2} and (b) Ni 2p_{3/2} in NiO thin film/ZnO nanorods heterojunction.

Figure 6. Schematic diagram of the band alignment of the p-NiO/n-ZnO heterojunction.

Figure 7: (a) Schematic diagram of the p-NiO thin film/n-ZnO nanorods heterojunction, (b) Semilog Current density – voltage characteristics of p-NiO/n-ZnO heterojunction, (Inset shows the Current density-voltage characteristic of heterojunction), (c) the plot of $\ln(I)$ versus V to extraction ideality factor, and (d) the diode photo response of the p-NiO/n-ZnO heterojunction.