Fabrication of transparent p-NiO/n-ZnO heterojunction diode for ultraviolet photodetector

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1. Introduction

The ZnO thin film has been the subject of much research in recent years due to its varied potential applications for optoelectronic devices. Due to the wide band gap (3.4 eV) and large exciton binding energy (60meV)[1-2].The p-n junction is widely-adopted structures for UV photodetectors [3-4]. However, since the growth of reproducible p-type ZnO films are still under development. A number of p-n heterojunctions have been reported by combining n-type ZnO such as Si, SiC, SrCu₂O₂, and ZnMgO. However, the high leakage current due to imperfection of the heterojunction interface is a major technical issue for these devices as UV detectors. The lowest level of leakage current reported is 2×10^{-4} A/cm² at -10 V for n-ZnO/p-SiC heterojunction diodes grown by plasma-assisted molecular-beam epitaxy [5].

NiO is a *p*-type semiconductor with a wide range of applications such as transparent conductive films [6],electrochromic devices[7]. NiO has a wide bandgap of 3.6–4.0eV at room temperature [8].It is known that nickel oxide (NiO) is an example of a material that is easily fabricated and is usually *p*-type semiconductor.

In this paper, we report the fabrication and the properties of an optically transparent p-n heterojunction photodiode consisting of p-NiO and n-ZnO thin films. The structural and optical properties of the p-NiO/n-ZnO heterojunction were characterized by X-ray diffraction (XRD), UV–visible spectroscopy, Hall measurement, and I-V photocurrent measurements.

2. Experimental details

The heterojunction having the structure of p-NiO/n-ZnO were fabricated by rf magnetron sputtering with a ZnO and NiO ceramics target of 99.99% purity. Ar(99.995%) and O₂ (99.99%) were controlled by the electronic mass flow controller was introduced as the sputtering gases at a total pressure of 1.33 Pa The r.f. power was set in the 200 Watts range, the ratio of oxygen to argon for the deposited ZnO and NiO films was set at 6% and 100%, respectively. Both all the thickness of films was controlled by sputtering time at approximate100nm. The XRD patterns of the films were determined with a Shimadzu XD-1 diffractometer using high-intensity radiation monochromatic CuKa $(\lambda = 1.51418 \text{\AA})$. The optical transmittance of the thin films was measured by using UV-Vis spectrophotometer measurements. The resistivity of the films was measured by Hall-effect measurements using the Van der Pauw configuration at room temperature. The current-voltage (I-V) characteristics of the devices were measured by a HP 4156 semiconductor parameter analyzer in both the darkness and illumination at 365 nm.

3. Results and Discussion

Fig. 1 shows the XRD spectra of ZnO and NiO thin films deposited on glass substrate by rf magnetron sputtering. The ZnO thin films corresponded to the wurtzite-type ZnO structure and only the (0 0 2) diffraction peak at about 34.41. The XRD spectrum of NiO films shows the film was polycrystalline with (111) and (222) orientations are observed in the pattern. Ryu et al. have observed that the development of preferred orientation in NiO film is primarily governed by surface energy [9].



Fig. 1 XRD pattern of ZnO and NiO films deposited on glass substrate by rf magnetron sputtering

Table 1 The resistivity (ρ), carrier concentration (n) and mobility (μ) of p-NiO and n-ZnO thin films.

layer	ρ(ohm-cm)	Carrier density $(1/cm^3)$	Mobility (cm ² /V-s)	Туре
NiO	0.19	7.52E+18	2.26	p-type
ZnO	2.35E-2	4.29E+19	6.02	n-type

The electrical parameters of p-NiO and n-ZnO were listed in Table 1. The nonstochiometric undoped ZnO films usually exhibit n-type conductivity due to the native donor such as oxygen vacancies and zinc interstitials. During n-ZnO deposition, the film was grown in an oxygen deficiency ambiance, which effectively increased the native donor, thus, resulting in high carrier concentration. The ZnO film has the lowest resistivity of 2.35x10⁻²ohm-cm, carrier concentration of 4.29×10¹⁹ cm⁻³ and Hall mobility of 6.02cm²/V-sec.The electrical conductivity of NiO has a strong dependence on the formation of point defects, such as nickel vacancy or interstitial oxygen. [10-11]. Wei-Luen et al. claimed that the (111) orientation of NiO films deposited in an oxygen rich environment and the (200) orientation deposited in an oxygen deficiency ambiance [12].Compared with our data, the (111) preferred orientation were observed for the NiO films deposited in an oxygen-rich ambiance. The p-type NiO film has the lowest resistivity of 0.19 ohm-cm, carrier concentration of 7.52×10^{18} cm⁻³ and Hall mobility of 2.26 cm²/V-sec.

Fig.2 shows the transmittance spectra of ZnO, NiO and p-NiO/n-ZnO heterojunction device, respectively. All the films show a high transmittance about 80%, indicating that these films can be used as transparent windows or UV photodetector. According to the transmission spectra, the optical band gaps of ZnO and NiO can be determined. The method based on the relation [13] is used

$$(\alpha h v)^2 = A(h v - E_g)$$

where α is the absorption coefficient and hv is the photon energy. The energy bandgap (Eg) is obtained by linear extrapolation to the hv-axis. From this result, it is found that the energy band gaps of ZnO and NiO are 3.24 and 3.51eV, respectively.



Fig.2. The visible optical transmittance of ZnO, NiO and n-ZnO/p-NiO heterojunction device

In order to evaluate the feasibility of p-NiO/n-ZnO heterojunction as a UV photodetector, I–V measurements for this heterojunction were performed under illumination with a wavelength of 365 nm and 0.3mW/cm², and the results shown in Fig. 3. The curve shows nonlinear and rectifying I-V characteristics, confirming the proper formation of the p-n junction. The lowest of leakage current is 4.35×10^{-8} A/cm² for p-NiO/n-ZnO heterojunction device. Moreover, the leakage current level was very low up to 2 V under the reverse bias. However, during I–V measurements, no luminescence was observed under the forward bias because of the high density of interface traps between n-ZnO and p-NiO film [14].



Fig.3. The current density–voltage (J–V) characteristics of the n-ZnO/p-NiO heterojunction measured both in the dark and under illumination with a wavelength of 365 nm and 0.3mW/cm².

Furthermore, photocurrent to dark current contrast ratios for p-NiO/n-ZnO heterojunction can be determined from the measured dark currents and photocurrents. With 1V applied reverse bias, it was found that photocurrent to dark current contrast ratios of the p-NiO/n-ZnO heterojunction device was 11.56. A low current contrast ratio is possibly due to imperfection of the heterojunction interface traps between ZnO and NiO films, which provide current tunneling paths under reverse current.

4. Conclusions

Transparent p–n heterojunction diodes consisting of n-type ZnO and p-type NiO thin film was successfully fabricated and characterized. The n-ZnO/p-NiO heterojunction device has an average transmittance of over 80% in the visible region. In-depth study on current density–voltage (J–V) shows that the n-ZnO/p-NiO heterojunction diode can detect ultraviolet light by the application of reverse bias. The lowest of leakage current is 4.35x10⁻⁸ A/cm² for n-ZnO/p-NiO heterojunction diode. However, the low current contrast ratio suggests that high density of interface traps between n-ZnO and p-NiO film.

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