Visible-Blind Ultraviolet Photodetectors Based on NiO/ZnO NRs with Poly-(N-vinylcarbazole) Intermediate Layer

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ABSTRACT

This study reports a hybrid visible-blind ultraviolet (UV) photodetectors (PDs) with a poly-(N-vinylcarbazole) (PVK) intermediate layer between the NiO thin film and ZnO nanorods (NRs). The insertion of a PVK buffer layer between the NiO thin film and ZnO NRs is able to effectively reduce leakage path and lower the recombination of photo-excited carriers at the interface. The best photo-responsivity of the n-ZnO/PVK/p-NiO PD was found to be as high as 57.31 A/W at a -3 V bias under UV illumination at 380 nm, which corresponded to an external quantum efficiency of 1.87×104%. The light-to-dark current ratios of the PD with and without the PVK intermediate layer at a reverse bias of 3 V are 3.32×102 and 12, respectively. The ZnO/PVK/NiO PD also exhibited UV-selective photo-response with an UV-to-visible rejection ratio (R_{380nm}/R_{450nm}) of more than 102. The proposed PD with a PVK intermediate layer has the potential for developing low-cost and high-performance UV PDs in sensing applications.

Keywords: UV photodetectors, ZnO nanorods, PVK, NiO

INTRODUCTION

Ultraviolet (UV) photodetectors (PDs) have useful applications including flame detection, UV environmental monitoring, early missile threat warning systems, etc.1 UV PDs based on wide-band-gap materials, such as GaN and ZnO have a visible-blind advantage over silicon-based PDs. ZnO is a potential absorber material with advantages of low-cost processing and simple synthesis, making it an alternative to GaN or SiC. It has thus attracted significant research interest. Generally, as-grown ZnO exhibits n-type conduction owing to the presence of native donor-type defects such as zinc interstitials or oxygen vacancies and the self-compensation process of impurities, making it difficult to realize reliable and repeatable p-n homojunction ZnO devices.2

Therefore, the development of ZnO-based heterojunctions with other mature p-type semiconductors, such as Cu2O,3 CuInAlSe2,4 and NiO, could be an alternative scheme. Among the above mentioned p-type semiconductors, NiO is a potential candidate as a transparent semiconducting oxide for p-n junction devices because of its direct optical band-gap of ~3.4-4.0 eV, high hole mobility, good chemical stability, and simple fabrication process.5,6 Recently, ZnO/NiO heterojunction has gained much interest for optoelectronic applications due to their good energy level alignment. A visible-blind UV PD based on p-NiO thin film /n-ZnO nanorod arrays (NRAs) heterojunction has been reported in the literature,7 but the performance of the PDs is not encourage for practical applications due to the
imperfection interface between ZnO and NiO. With this scheme, achieving high-performance UV PDs with both low dark current and high photo-current is still a challenge.

In this study, we propose a high-performance UV PD with a poly-(N-vinylcarbazole) (PVK) interfacial layer between NiO thin film and ZnO NRAs and demonstrate its high UV photo-responsivity and high UV-to-visible rejection ratio using a low light intensity and a low bias voltage. The UV PD employs a low-cost sol-gel-derived NiO thin film as the p-type material, a thin PVK layer as the interface modification layer which can significantly reduce defect states at the NiO/ZnO interface and can minimize the leakage current, and low-temperature chemical bath synthesized ZnO NRs as the UV light-detecting material. It exhibits a maximum photo-responsivity of 57.31 A/W at a -3 V bias under UV illumination at 380 nm and a high UV-to-visible rejection ratio of 330. We have thus demonstrated that the hybrid ZnO/PVK/NiO heterojunction PD is a great potential as a low-cost UV PD for optoelectronic applications.

**Experimental**

Schematic of the n-ZnO/PVK/p-NiO heterojunction PD is shown in Fig.1. Commercially available indium-tin-oxide (ITO)-coated glass substrates with a sample size of 1×3 cm² were first cleaned with acetone and isopropyl alcohol for 20 min using ultrasound agitation, followed by a deionized water rinse and N₂ gas blow drying. The deposition of NiO thin films on the ITO substrate was performed using a sol-gel process. In a typical procedure, the 0.1M precursor solution was prepared by dissolving the nickel acetate tetrahydrate (Ni(CH₃COO)₂ • 4H₂O) and monoethanolamine in ethanol with a mole ratio of 1:1. After stirring at 70°C for 4h, the solution was spin cast onto the ITO substrate at 3000 rpm for 30 sec. The NiO thin films were obtained by post-annealing at 350°C for 1h in air. Then,12mg/ml PVK solution (dissolved in chlorobenzene) was spin-coated onto the NiO thin film at 1000 rpm for 40s, followed by baking at 90 °C for 1h to evaporate the residual chlorobenzene. A 15 nm-thick ZnO seed layer was then deposited on top of the PVK layer by radio-frequency magnetron sputtering at room time through a shadow mask. Next, vertically aligned ZnO NRAs were grown on the as-deposited ZnO seed layer via chemical bath deposition process in an equimolar (45mM) aqueous solutions of Zn(CH₃COO)₂ • 2H₂O and C₆H₅N₄ at 88°C. Finally, a 350 nm-thick silver top electrode was deposited by magnetron sputtering using a shadow mask.

The cross-sectional view of the samples was observed using scanning electron microscopy (SEM, Hitachi SU-8000) with an accelerating voltage of 10 keV. The chemical composition of the sol-gel-derived NiO thin films was performed using X-ray photoelectron spectroscopy (XPS, PHI 500 VersaProbe). The current density-voltage (J-V) characteristics of the ZnO/PVK/NiO heterojunction PDs were measured using an Agilent B1500A semiconductor parameter analyzer, and a 300W xenon lamp dispersed by a monochromator was used as the light source to measure the photocurrent and the spectral response of the PDs. The optical power density used for the measurement at 380 nm is 29.6 µW/cm².

![Schematic of the ZnO/PVK/NiO UV PD](image)
Results and discussion

A top-view SEM image of the ZnO NRAs is shown in Fig. 2(a), which shows a well-defined hexagonal shape with an average diameter of ~150 nm. A cross-sectional SEM image of the device (Ag electrode is not included) is shown in Fig. 2(b). The individual layers of p-NiO/PVK/n-ZnO NRAs can be easily distinguished, and have thicknesses of 70, 150 and 2000 nm, respectively. The quality of the sol-gel-derived NiO thin film after annealing at 350°C can be analyzed by the Ni 2p3/2 XPS spectra of the NiO film as is shown in Fig. 3(a), which can be divided into three distinct peaks. First, the peak located at a binding energy of 853.55 eV corresponds to Ni2+ octahedral bonding of the cubic NiO rock salt. Second, the peak centered at 855.15 eV is attributed to the Ni2+ vacancy induced Ni3+ states in Ni2O3 or Ni(OH)2. Finally, the broad peak centered at 860.75 eV is ascribed to a shake-up process in the NiO structure. Fig. 3(b) presents XPS spectra of the O 1s peaks in NiO, which can be divided into two peaks. The peak centered at 529.05 eV confirms octahedral bonding of Ni-O. The peak at 530.65 eV may be considered in the presence of Ni2O3 or Ni(OH)2. Hence, this confirms the non-stoichiometric nature of the as-deposited NiO film.

Fig. 4(a) and (b) show the J-V curves of the p-NiO/n-ZnO heterojunction PDs with and without a PVK layer at dark and under 450nm and 380nm light illumination. With a -3V bias, the dark current density of the ZnO NRs/PVK/NiO PD is 5.11×10^-6 A/cm², whereas the light current density under 380nm UV illumination is 1.70×10^-4 A/cm². In contrast, for the ZnO/NiO PD, the dark current density is 8.17×10^-5 A/cm², and the light current density is 9.43×10^-4 A/cm² at same bias. From these results, it shows that the inserted PVK layer effectively reduced the dark current of the NiO/ZnO PD and also enhanced the UV photo-response. The inserted PVK layer is able to reduce leakage path (between the NiO film and the ZnO NRs) and lower the recombination of photo-generated carriers at the interface. As shown in Fig. 5, at a -3V bias, a responsivity (R) of 57.31 A/W is achieved for the ZnO/PVK/NiO PD under UV illumination at wavelength of 380 nm, indicating the near-band-edge absorption of the ZnO NRs. The extra-high UV responsivity is ascribed to the oxygen-related hole trapping states on the ZnO NRs surfaces, which results in an increase in photo-induced conductivity. The ZnO/PVK/NiO PD also exhibits UV-selective photo-response with an UV-to-visible rejection ratio (R380nm/R450nm) of more than 10².

Fig. 2. (a) SEM image of surface morphologies of ZnO NRAs and (b) cross-sectional image of the ZnO/PVK/NiO UV PD structure.

Fig. 3. (a) The Ni 2p3/2 and (b) O 1s XPS spectra of the NiO film after annealing at 350 °C.
high UV-to-visible rejection ratio, allowing it to achieve a higher signal-to-noise ratio; (c) the PD with high photoconductive gain can be attributed to the adsorption–desorption process of oxygen molecules on the surface of ZnO NRs. Hence, the proposed PD has the potential for developing low-cost and high-performance UV PDs for sensing applications.

References