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Piezoelectric effect enhancing decay time of p-NiO/n-ZnO ultraviolet photodetector



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ABSTRACT

An ultraviolet photodetector based on p-NiO/n-ZnO heterojunction was fabricated using thermal oxidation and hydrothermal growth processes. The properties of the UV photoresponse under various strains were investigated. The results showed that the magnitude and the sign of the strain (tension/compression) have a great influence on the decay time by coupling piezoelectric and surface oxygen adsorption/desorption effects. These results demonstrate an effective approach for designing and fabricating strain modulated fast reset UV photodetectors.

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1. Introduction

Ultraviolet (UV) photodetectors are important devices with applications such as solar-blind detectors, environmental monitoring, and chemical analysis [1–3]. For these applications, fast response time, fast reset time, high selectivity, high responsivity, and good signal-to-noise ratio are commonly desired characteristics. The same as the UV photodetectors made from the semiconductor materials, such as Si [4,5], SiC [6], GaN [7,8], AlGaN [9], ZnO based UV detectors have been studied more intensively. ZnO is considered a promising UV semiconductor material owing to its wide direct band-gap energy (3.37 eV), very large excition binding energy of 60 meV at room temperature, excellent optical and electrical properties, outstanding chemical and thermal stability, higher radiation hardness and low growth temperature, as well as rich raw materials.

The unique coupled piezoelectric and semiconducting properties of ZnO have been forming a new field of piezotronics. The piezo-phototronic effect has been demonstrated as an effective approach to enhance the performance of solar cells [10], light

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emission diodes [11], and photodetectors [12–18] by modulating the charge carrier transport, separation, or recombination across the local surface/interface through strain-induced piezoelectric polarization charges [19–21].

In this work, a p-NiO/n-ZnO heterojunction UV photodetector is synthesized by thermal oxidation and hydrothermal growth processes. The structural, morphological properties and photoelectric response properties of the devices were investigated in this study. Generally speaking, UV photodetectors based p-n junction or schottky contact have a fast rise time, and their decay time could be divided into two processes, a fast decay procedure and a very slow decay procedure. The slow decay is attributed to the oxygen molecules adsorption and desorption at the ZnO surface. We designed and fabricated a p-NiO/n-ZnO heterojunction UV photodetector by utilizing strain-induced piezo-polarization charges near the surface of piezoelectric n-ZnO side to optimize the performance of a photosensing device. Under a compressive strain of -4%, the decay time decreased from 8 s to 2.4 s (about 70%); conversely, under a tension strain of 4%, the decay time increased from 8 s to 31 s (about 287.5%). The performances of the UV photodetector are optimized and significantly enhanced after introducing a piezo-phototronics effect by externally applying strains to modify the depletion region and band structure of ZnO film surface. These results indicate that the piezo-phototronic effect can effectively influence the decay time of the UV photodetector.

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2. Experimental

Fig. 1(a) presents the schematic diagram of the p-NiO/n-ZnO film heterojunction UV photodetector. The Ni foil substrate was oxidized to form a thin film of NiO in a furnace at 800 °C for 1 h under an air atmosphere after being cleaned ultrasonically in acetone, ethanol and deionized water. Then a \sim 20 nm thick ZnO seed layer was deposited on the NiO film by room temperature radio frequency (RF) magnetron sputtering, using a high purity ZnO (99.99%) target source. The background pressure of the vacuum chamber was 1×10^{-4} Pa and argon was used as the sputtering gas with a pressure of 3.5 Pa. After that the ZnO thin film was grown from the ZnO seeds by a simple and low-cost hydrothermal process [22]. The nutrient solution used here was composed of a 50 mmol L⁻¹ 1:1 ratio of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) with sodium citrate dihydrate $(5 \text{ mmol } L^{-1})$ [Na₃C₆H₅O₇] as a crystal morphology-controlling agent. The solution was fully and evenly stirred and then transferred into a Teflon reaction kettle in which the ZnO seed coated substrate was suspended vertically. After the hydrothermal treatment for 4 h at 95 °C, the substrate with grown NiO/ZnO films was removed from the solution, rinsed in deionized water and then air-dried. At last, two small drops of silver (Ag) paste were deposited as the electrodes.

2.1. Characterization

The structural and morphological properties of the p-NiO/n-ZnO heterojunction were examined by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and Photoluminescence (PL) spectra. The photoelectric properties of the obtained UV photodetectors were characterized using a Semiconductor Characterization System (Keithley 4200) under UV (365 nm) illumination with a power density of 20 mW cm⁻².

3. Results and discussion

To investigate the morphological features of the NiO and ZnO films, their corresponding field-emission scanning electron microscope (FESEM) images are shown in Fig. 1(b) and (c). It can be observed in Fig. 1(b) that the surface of the NiO film was continuous and dense. It means that the NiO film could provide a smooth surface for the deposition of a thin ZnO seeding layer which can guarantee the growth of highly ordered and crystalline ZnO film. The ZnO film was dense and highly ordered due to adding Na-citrate [22] in the nutrient solution. The compact ZnO nanorods as shown in Fig. 1(c) will reduce the adsorption quantity of oxygen and other gases, which may improve the response speed and lead to reduced responsivity for ZnO based UV photodetectors [23,24]. The highly oriented ZnO film is beneficial to optimize performance of the p-NiO/n-ZnO heterojunction UV photodetectors by the piezoelectric effect. Fig. 1(d) shows the XRD patterns of the NiO film on Ni foil and the ZnO film grown on the NiO film. The as-prepared NiO film was well crystallized, and the peak positions at around 37.22, 43.28 and 62.86° could be easily assigned to the (111), (200) and (220) crystal planes of the cubic NiO structure. The dominant ZnO XRD peak for the (002) plane at 34.48° was clearly observed. This means that the ZnO NRs were mainly grown along the *c*-axis of the hexagonal wurtzite structure [24].

Fig. 2(a) shows the Pl spectra of ZnO film, The spectrum of ZnO film exhibits two emission peaks located at 383 nm and 560 nm, which are the typical near-band edge and defects related emissions of ZnO. We propose the green emissions located at 560 nm are attributed to oxygen vacancies and impurity involved. Fig. 2(b) displays the *I–V* characteristic of the p-NiO/n-ZnO heterojunction in the dark. As it can be seen the diode shows an obvious rectifying behavior in the dark, which indicates the p–n junction formation.

A schematic diagram of the measuring setup is shown in Fig. 3. The sample is fixed on a plastic board (PB) with a length of 10 cm, a



Fig. 1. (a) Schematic illustration of the ultraviolet (UV) photodetector. (b) SEM image of NiO film. (c) SEM image of ZnO film. (d) XRD patterns of the as-prepared NiO film and p-NiO/n-ZnO heterojunction.

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