

Preparation of NiO/ZnO nanoheterojunction arrays and their optoelectric characteristics under UV light illumination

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1. Introduction

Zinc oxide (ZnO) with a wide direct bandgap (3.4 eV) and a large excitation binding energy (60 meV) is a promising n-type semiconductor material for applications of light emitting diodes, sensors, and solar cells [1]. Recently, one-dimensional (1D) ZnO-nanowires (ZnO-NWs) have attracted considerable interests because of their unique physical properties and applications compared with bulk materials [2-3]. In addition, the surface active area of nanostructures based on ZnO-NWs is very large because of considerable quantities of NWs. It implies that the surface of ZnO-NWs can lead to a better efficiency of sensor and solar energy than thin films. Essentially, nickel oxide (NiO) is a p-type semiconductor with a bandgap of 3.7 eV [4] and widely used in sensors, fuel cells, and antiferromagnetic devices [5-6] due to their high stability and low material cost.

In this study, the use of a ZnO-NW-based heterojunction structure for applications of nano optoelectronic sensors was proposed. Nano heterojunctions (NHJs) were formed via e-beam deposition of p-type NiO onto the vertical-aligned ZnO-NWs grown by hydrothermal growth (HTG) method. The electrical properties of p-NiO/n-ZnO-NWs NHJs show a rectifying behavior of a p-n junction. The optoelectronic properties of the NiO/ZnO-NWs NHJs with different NiO thicknesses under UV light (366 nm, 6 mW/cm²) illumination, with good UV sensitivity were presented and discussed.

2. Experiments

The key fabrication processes were shown in Fig. 1. A 200-nm-thick aluminum-doped-zinc-oxide (AZO) film was sputtered on ITO-glass substrates to serve as a seed layer for the growth of ZnO-NWs by HTG (Fig. 1(a)). Then the samples were placed in a solution of 0.04 M zinc nitrate hexahydrate and Hexamethylenetetramine at 90°C for 1 hour (Fig. 1(b)). After HTG growth, NiO film was subsequently e-beam deposited onto the ZnO-NWs and then the p-NiO/n-ZnO-NWs NHJs were formed (Fig. 1(c)). Finally, an ohmic electrode with 100-nm-thick AZO film and 100-nm-thick grid Au electrodes were deposited on the surface of the p-NiO layer through e-gun evaporation (Fig. 1(d)).

3. Results and Discussion

The SEM images of the ZnO-NWs and p-NiO/n-ZnO-NWs prepared with different NiO thicknesses (50, 100, 200, and 300 nm) are shown in Fig. 2. According to Fig. 2(a), well-ordered and vertically-aligned ZnO-NWs

with controllable length (~1 μ m) were obtained. Figures 2(b)-(e) show the p-NiO/n-ZnO-NWs NHJs with different NiO thickness films which were e-beam deposited onto the ZnO-NWs. It can be observed that the tips of the ZnO-NWs were covered with NiO films and high-aspect-ratio p-NiO/n-ZnO-NWs NHJs with hemispheric-cap tips and matchstick-like were formed.

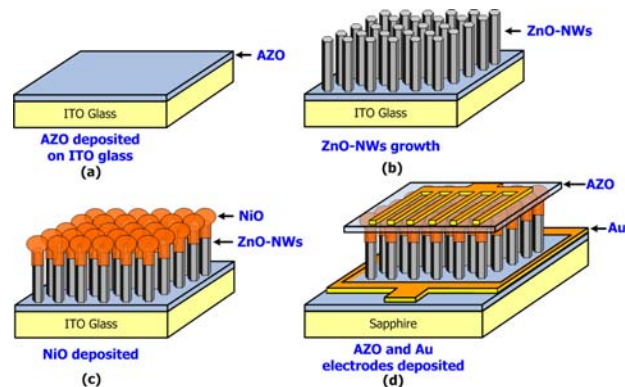


Fig. 1 The key fabrication processes of p-NiO/n-ZnO-NWs NHJs.

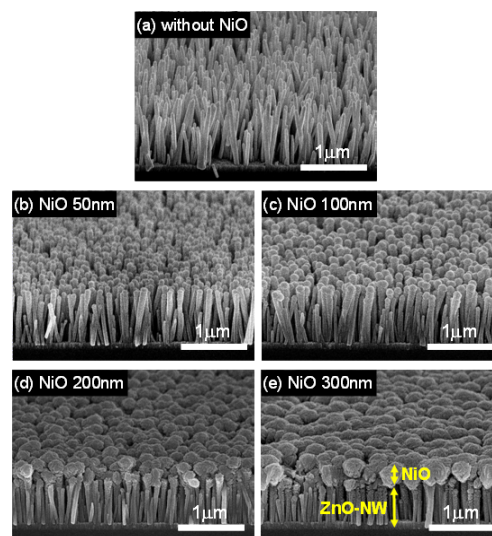


Fig. 2 The SEM images of the ZnO-NWs (a); the p-NiO/n-ZnO-NWs NHJs with different NiO thicknesses: (b) 50 nm, (c) 100 nm, (d) 200 nm, and (e) 300 nm.

Figure 3 shows the TEM image, the corresponding high-magnification TEM images and the SAED patterns of an individual p-NiO/n-ZnO-NW NHJ. The SAED patterns and the corresponding high-magnification TEM images show that the polycrystalline NiO and single crystalline ZnO-NW images were found from the left and the right region of the p-NiO/n-ZnO-NWs NHJ, respectively. The diameter of the ZnO-NWs was around 100 nm and clear stripes of lattice plane were observed at the

high-magnification TEM image. The inter plane distance of d-space was determined to be 0.26 Å, indicating the main crystalline phase of the wire should be ZnO [0001] phase, along the c-axis direction.

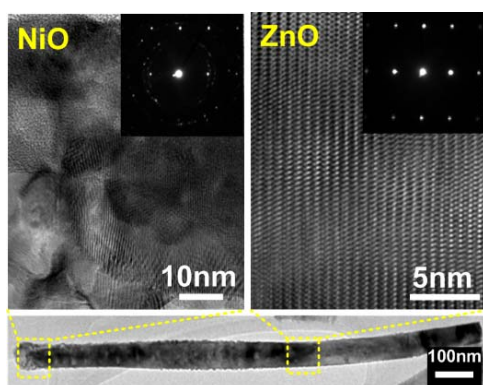


Fig. 3 The TEM image of an individual p-NiO/n-ZnO-NWs NHJ. The corresponding high-magnification TEM images and the SAED patterns of an individual p-NiO/n-ZnO-NW NHJ were shown in the top side figures.

The fabricated p-NiO/n-ZnO-NW NHJ arrays all exhibit a well-defined rectifying behavior in darkness as shown in figure 4. Note that the sample with 100-nm-thick NiO film exhibits the highest forward current. The dark J - V curve shows a diode-like behavior with a forward threshold voltage (V_{th}) of 5.9 V, a leakage current (J_r at -5V) of 0.64 $\mu\text{A}/\text{cm}^2$, and a good rectification ratio ($I_{forward}/I_{reverse}$ at 5 V) of 89, respectively. The measured J - V characteristics under UV light (366 nm) illumination and the corresponding photoresponse curve of the prepared NHJ arrays were shown in figures 5 and 6, respectively. The sample with 100 nm-thick NiO film still yields the best photocurrent characteristics (an obvious photocurrent of 6 $\mu\text{A}/\text{cm}^2$ at -5 V) among all the prepared samples, revealing an increase in the diode current of about 8 \times . Schematic energy band diagrams of the NiO/ZnO-NWs NHJ are also depicted in the inset of figure 4 and 5 showing the carrier transport processes under thermal equilibrium and reverse bias, respectively. As shown in Fig. 6, the fast photoresponse times (rise time \sim 4 s and fall time \sim 13 s) indicate that the optoelectronic properties of the p-NiO/n-ZnO-NW NHJ arrays are quite good. In addition, the reversible cycles of the photoresponse curve indicates a stable and repeatable operation of photo detecting and optical sensing.

4. Conclusion

In summary, preparation of p-NiO/n-Zn-NWs NHJs using HTG method for use in UV photodetectors has been demonstrated in this study. The 1D p-NiO/n-Zn-NWs NHJ arrays showed a rectifying behavior in dark and evident photonic sensitivity under UV light illumination. The optoelectronic characteristics demonstrate that the 1D NiO/Zn-NWs NHJs have fairly good sensitivities and fast responses to UV light with an increase in the photocurrent of about 8 \times . It is expected that the present NHJs based on ZnO-NWs would provide an effective and simple way for future developments of optoelectronic devices.

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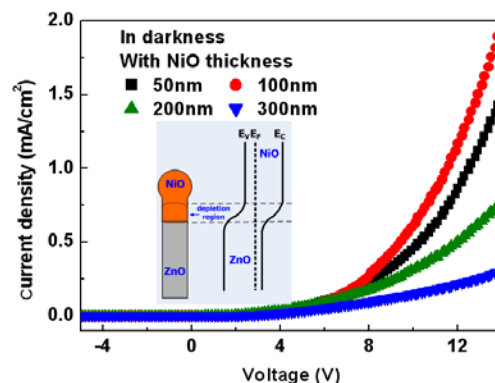


Fig. 4 The J - V curves of the p-NiO/n-ZnO-NW NHJ arrays with different thickness of NiO in darkness.

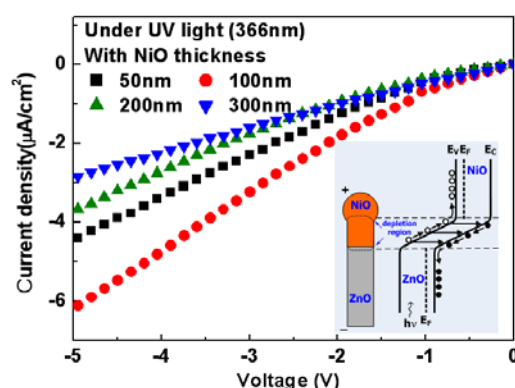


Fig. 5 The J - V curves of the p-NiO/n-ZnO-NW NHJ arrays with different thickness of NiO under UV light (366 nm).

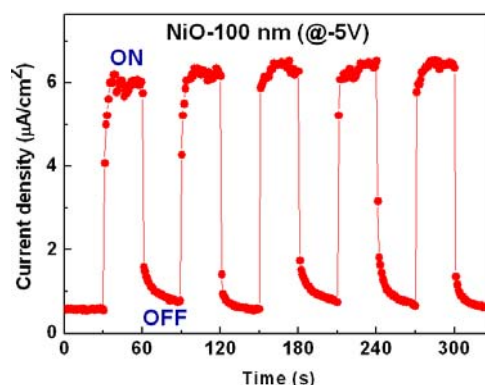


Fig. 6 The time dependence of photocurrent density of the p-NiO/n-ZnO-NW NHJ arrays under UV light (366 nm) with 100 nm-NiO film at -5V.

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