Effect of thermal annealing on the characteristics of ZnO nanorods UV photodetector

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Abstract. This paper reported a ZnO UV photodetector synthesized by room temperature radio frequency (RF) magnetron sputtering and hydrothermal growth process. In addition, the effect of thermal annealing on the photoresponse properties of the ZnO photodetector was studied. This work may provide a potential approach to enhance the performance of ZnO UV photodetector.

1. Introduction

Ultraviolet (UV) photodetectors are important devices with applications such as solar-blind detection, biosensing, and ozone monitoring [1, 2]. Conventional UV photodetectors are based on wide-gap inorganic semiconductors such as SiC, GaN, ZnO and diamond. Among these materials, ZnO is considered as a promising semiconductor material for fabricating ultraviolet (UV) detector owing to its wide direct band-gap energy (3.37 eV), very large exciton 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 [3-5]. For practical application, the high sensitivity, fast response time and high stability for the UV photodetector is crucial.

Here, we have prepared an UV photodetector based on ZnO nanorods synthesized by room temperature radio frequency (RF) magnetron sputtering and hydrothermal growth process. And the structural properties, optical properties and photoelectric response properties of the device were investigated. Especially, the effect of thermal annealing on the performance of the device was discussed. The results showed that thermal annealing could influence the defect density of ZnO nanorods, thereby influencing the sensitivity of the ZnO photodetector.

2. Experiment

Figure 1 presented the schematic diagram of the ZnO UV photodetector. At first, the sapphire substrates were cleaned ultrasonically in acetone, ethanol and deionized water. Then, a seed layer of ZnO was prepared by room temperature radio frequency (RF) magnetron sputtering. 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 nanorods(NRs) were grown from the ZnO seeds by a simple and low-cost hydrothermal process. The nutrient solution used here was composed of a 50 mmol L⁻¹ 1 : 1 ratio of zinc acetate dehydrate and hexamethylenetetramine (HMTA). The solution was fully and evenly stirred and then transferred into a Teflon reaction kettle in which the samples were suspended.
vertically. The reaction was carried out at 95 °C for 4h. After the reaction, the samples were taken out of the solution, rinsed with deionized water and then air-dried. To study the effect of thermal annealing on the properties of the device, the samples were thermal annealed in a furnace at 550°C for 30min in air. At last, two small drops of silver (Ag) paste were separately deposited on the ZnO nanorods to act as the electrodes.

![Diagram](image)

**Figure 1.** Schematic diagram of the ZnO nanorods photodetector.

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

4. Results and discussions
Figure 2 (a) and (b) showed the SEM images of the ZnO nanorods, respectively, which showed the ZnO nanorods were hexagonal prismatic in shape with diameter of 100–300nm.

To confirm the structural property of the ZnO nanorods, X-ray diffraction (XRD) patterns were investigated. Figure 2(c) showed the XRD pattern before annealed. The result showed that the ZnO nanorods had a preferential orientation along the c-axis since the (002) peak was clearly seen. The normalized PL spectra of ZnO nanorods before/after annealing were shown in figure 2(d), which both showed a relatively sharp UV emission at 379 nm attributed to near-band-edge emission. A broad visible emission could be seen at 480-600 nm, which was attributed to defect-related transitions such as the surface oxygen vacancy defects. Furthermore, it could be seen that the ZnO nanorods after annealing exhibited much lower visible emission intensity than that before annealing, which may be due to the decreased defect density.
Figure 2. (a), (b) SEM images. (c) XRD pattern of ZnO nanorods. (d) PL spectra of ZnO nanorods before/after annealing.

Figure 3. (a) The I-V curves of the photodetector before/after annealing, without/with UV light. (b) and (c) The ultraviolet responses of the ZnO photodetector after/before annealing. (d) The sensitivity (S) of ZnO photodetector before/after annealing as a function of bias voltage.
Figure 3 (a) showed the I-V characteristics of the ZnO photodetector before/after annealing, without/with UV light. It could be seen that the device showed an obvious rectifying behavior under both dark and UV illuminated condition. The symmetric rectifying I-V curves indicate that there were two back-to-back junctions in the device. The ZnO nanorods photodetector is highly responsive to UV light. After annealing, the current decreases both at dark and under UV light. At 5V bias, I_{light} decreases from 35.3 µA to 27.2 µA, and I_{dark} decreases from 12.2 µA to 5.8 µA. In the dark, the surface of the ZnO nanorods is depleted by absorbed oxygen molecules which increase the bulk resistance of ZnO nanorods. Under UV illumination, electron-hole pairs are photo-generated and holes are readily trapped at the surface, leaving behind unpaired electrons, which increase the conductivity of the ZnO nanorods and increase the current. The photo-response properties of the UV photodetector before/after annealing were shown in figure 3(c) and (b). The current can fully recover and has no drift even after repeated cycles, which demonstrates that this photodetector has good stability and repeatability. It can be found that after annealing, the recovery time of the ZnO nanorods photodetector decreases from 82s to 60s, which demonstrates annealing can effectively decrease recovery time.

The sensitivity(S) defined as (I_{light}-I_{dark})/I_{dark} is shown in figure 3 (d). At different bias voltages, the sensitivity of the ZnO nanorods photodetector was enhanced after annealing. For example, at 5V bias, the sensitivity increases from 10.1 to 13.2, nearly 30%, indicating annealing can enhance performance of the ZnO nanorods UV photodetector.

5. Conclusions
In summary, we have demonstrated a simple and low-cost approach for the fabrication of ZnO UV photodetector by room temperature radio frequency (RF) magnetron sputtering and hydrothermal growth process. In particular, by comparing the photoresponse properties of the UV photodetector before/after annealing, we suggested that thermal annealing could increase sensitivity of the ZnO photodetector. This work could serve as a valuable guideline for designing and improving UV photodetectors in a low-cost and large-scale way.

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