# Hydrothermal growth of single-crystalline ZnO thin films and theirs application on UV photodetectors

Cheng-Han Wu<sup>1</sup>, Shui-Jinn Wang<sup>\*1,2</sup>, Tseng-Hsing Lin<sup>1</sup>, Yung-Chun Tu<sup>1</sup>, Chien-Hsiung Hung<sup>1</sup>, Pang-Yi Liu<sup>1</sup>, Yu-Hsueh Chin<sup>1</sup>, Kai-Ming Uang<sup>3</sup>, and Tron-Min Chen<sup>3</sup>.

<sup>1</sup>Institute of Microelectronics, Department of Electrical Engineering, National Cheng Kung University, Tainan 701, Taiwan <sup>2</sup>Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan, Taiwan

<sup>3</sup> Department of Electrical Engineering, WuFeng University, Chiayi 621, Taiwan

\*Phone: +886-6-2757575-62351, Fax: +886-6-2763882, E-mail: <u>sjwang@mail.ncku.edu.tw</u>

## Abstract

The use of a single-crystalline ZnO film grown by hydrothermal growth (HTG) method on sapphire substrate for the fabrication of NiO/ZnO heterojunction (HJ) UV photodetectors is demonstrated. The HJ were formed via the sputtering deposition of a p-type NiO layer onto the HTG ZnO film. The optoelectronic properties of NiO/ZnO film with different NiO thicknesses (300-900 nm) under ultraviolet (UV) light (365 nm, 1 mW/cm<sup>2</sup>) were investigated and discussed. Owing to the much improved optoelectronic properties of the single crystalline HTG ZnO film, a UV sensitivity (I<sub>UV</sub>/I<sub>dark</sub>) as high as 40 has been obtained from the prepared HJ sensors.

# 1. Introduction

Zinc oxide (ZnO) is a well-known semiconductor material with a direct wide band gap of 3.37 eV and a large exciton binding energy of about 60 meV at room temperature, which make it suitable for UV-PDs application [1-2]. ZnO-based UV-PDs with nanowires (NWs) have attract a lot of attentional due to their ease of fabrication, low-temperature processing, and unique properties, such as higher aspect ratio, surface-to-volume ratio and carrier confinement in two dimensions that could improve device performance[3].

However, UV-PDs based on ZnO NWs suffer from reduced junction area for photo detection and weak mechanical strength. Integration of ZnO-NWs into working device still remains a complicated, time-consume and uneconomic method to avoid possible short-circuit and fragile issues for ZnO-NWs-based UV-PDs [4]. To solve these problems, ZnO film with a single crystalline structure fabricated by hydrothermal growth (HTG) method is reported in this work and the optoelectrical properties of UV-PDs with different NiO film thicknesses are compared and discussed.

## 2. Experiments

The key fabrication processes for the HTG of ZnO film and p-NiO/film-ZnO heterojunction (HJ) UV light sensor are shown in Fig. 1. At first, a 100-nm-thick zinc oxide film was sputtered on sapphire substrates to serve as a seed layer for the growth of ZnO film by HTG (Fig. 1(a)) [5, 6]. Then the samples were placed in a solution of 0.04 M zinc nitrate hexahydrate and hexamethylenetetramine at 70°C for 8 hr (Fig. 1(b)). After HTG, a p-NiO film was sputtered onto the ZnO film and the p-NiO/n-ZnO film HJ were formed (Fig. 1(c)). For comparison, the thickness of p-NiO film in p-NiO/n-ZnO HJ was varied from 300 to 900 nm. Finally, an Ohmic-contact electrode with 200-nm-thick Pt film and Ti film electrodes were deposited on the surface of the p-NiO layer and n-ZnO layer through e-gun evaporation, respectively (Fig. 1(d)). All the UV light sensors prepared in this study have a size of 1000  $\mu m {\times} 1000 \ \mu m.$ 



Fig. 1 Schematics of the fabrication process of the p-NiO/film-ZnO HJ.

#### 3. Results and discussion

The surface morphologies of the grown ZnO film and p-NiO/n-ZnO film were characterized by scanning electron microscopy (SEM). Figures 2(a) and 2(b) show that the single-crystalline ZnO films with a controllable thickness (900 nm) by hydrothermal and the tops of the ZnO films were covered with NiO films (300 nm), respectively. The material properties were further analyzed by XRD (Fig. 3). Based on the diffraction peak of (002) plane, ZnO films were indexed to the hexagonal wurtzite structure according to the standard JCPDS card. It indicates that ZnO films were mainly composed of crystalline ZnO film (002), with c-axis vertical to the substrate surface. The TEM image is shown in Fig. 4, which reveals that the ZnO film obtained from the HTG process is essentially single crystalline with a growth direction along the (001) basal plane [2]. The interlattice plane distance of the d-space was determined to be 0.26 nm from the TEM image, indicating that the main crystalline phase has a wurtzite single-crystalline structure with the c-axis direction of single-crystalline ZnO film [0001].



Fig. 2 SEM images of (a) HTG-ZnO film (900 nm) and (b) after NiO layer (300 nm) deposition.



Fig. 3 XRD pattern of the ZnO film prepared by HTG.



Fig. 4 TEM image and the corresponding SAED patterns of single-crystalline ZnO film.

The fabricated p-NiO/n-ZnO (HTG) HJs with different NiO thicknesses exhibit well-defined rectifying behaviors in dark and are shown in Fig. 5. Note that the sample with 300-nm-thick NiO film exhibits the highest forward current. It could be attributed to the thickness of the NiO layer is thin enough (300 nm) that the build-in voltage and depletion region are significantly reduced. Similarly, the decrease in the forward current of the 900-nm-thick NiO device might be due to a high series resistance from the thicker NiO layer. Among them, the sample with 600-nm-thick NiO film seems most suitable for UV-PDs with a comparably wider depletion region and the lower series resistance as compared with other samples. The possible band diagram of p-NiO/n-ZnO film HJ under thermal equilibrium condition is shown in the inset of Fig. 5.

Figure 6 shows the dynamic photoresponse of the photodetector based on p-NiO (600 nm)/film-ZnO (900 nm) HJ. The response times of the p-NiO/n-ZnO film HJ device were about 9 sec and the recovery times were about 33 sec, respectively, and the measured responsivities were about 40 times, respectively. The enhanced photoresponse of the p-NiO/n-ZnO film HJ device should be attributed to the superiority of the optoelectronic properties of the single-crystalline ZnO film prepared by HTG.



Fig. 5 The J-V curves of the p-NiO/HTG-ZnO films HJs in dark. The inset shows the energy band diagram of the p-NiO/n-ZnO HJ under thermal equilibrium.



Fig. 6 Transient response of photocurrent density.

## 4. Conclusion

In summary, p-NiO/film ZnO HJs with good UV sensitivity as high as 40 under UV light (365 nm, 1 mW/cm<sup>2</sup>) have been demonstrated. The improved performance of the prepared UV sensors should be attributed to the superiority of the optoelectronic properties of the single-crystalline HTG ZnO film and suitable thickness used for the p-NiO layer. It is expected that the present HJs could provide a simple and effective mean for optoelectronic applications.

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