Extended Abstracts of the 2015 International Conference on Solid State Devices and Materials, Sapporo, 2015, pp262-263

Preparation of porous p-ZnO films by hydrothermal method and its application on ultraviolet sensors

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

[1]Institute of Microelectronics, Department of Electrical Engineering, National Cheng Kung University, Tainan 701, Taiwan
[2]Advanced Optoelectronic Technology Center, National Cheng Kung University, Tainan, Taiwan
[3] Department of Electrical Engineering, WuFeng University, Chiayi 621, Taiwan

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

Abstract

The growth of porous p-ZnO films on n-GaN epilayer by hydrothermal growth (HTG) method is proposed and the fabrication and characterization of ultraviolet sensors based on p-ZnO/n-GaN heterojunction (HJ) is demonstrated. The evolution of porous p-ZnO during HTG process and effect of the ammonium phosphate ($NH_4H_2PO_4$) concentration used in HTG process on the morphology, optical, and electrical properties of the grown p-ZnO films are investigated. With good rectifying characteristics, the fabricated HJ ultraviolet sensors exhibit a superior response to UV light illumination (365 nm, 1 mW/cm^2), typical UV sensitivity (I_{UV}/I_{dark}) as high as 80.

1. Introduction

Ultraviolet sensors offer wide applications in space engineering, and electro-optical missile plume detection [1-3]. In general, the wide-bandgap materials are the familiar candidate for improving the sensitivity and stability of UV sensor. Meanwhile, ZnO is a well-known direct wide band-gap (3.37 eV at room temperature) thermally stable n-type hexagonal wurtzite structure semiconductor with large exciton binding energy (about 60 meV) but it's hampered by the lack of stable p-type doping due to self-compensation by donor-like native defects, low solubility of p-type dopants, and formation of deep acceptor levels [4].

For p-type doping, either group I cations or group V anions are possible candidates. However, it has been reported that compensation effect by interstitial defects or self-compensation limits the use of Group I elements as effective acceptors [5]. The present study proposes a low-temperature, simple, and low-cost hydrothermal growth (HTG) method for the growth of p-type ZnO porous layer on n-GaN with phosphorous from group V as the p-type dopant. Effect of the ammonium phosphate ($NH_4H_2PO_4$) concentration used in HTG process on the morphology, optical, and electrical properties of the grown p-ZnO films are investigated. Ultraviolet light sensors based on porous p-ZnO/n-GaN heterojunction (HJ) with much improved performance is also demonstrated.

2. Experiments

Figure 1-(a) schematically shows the device structures of p-ZnO/n-GaN. For the HTG of porous p-ZnO film on n-GaN (2.5 μm)/sapphire wafer, the samples were placed in a mix solution of zinc nitrate hexahydrate, hexamethylenetetramine, ammonium hydroxide, and $NH_4H_2PO_4$ at 70 ˚C for 6 hr. For UV sensing fabrication, an Ohmic-contact electrode with 200-nm-thick Ni/Pt film and Ti/Au film electrodes were deposited on the surface of the p-ZnO layer and the n-GaN layer through e-gun evaporation, respectively. All UV sensing reported in the work have a die size of 1000 μm ×1000 μm and a working area of 800 μm ×800 μm (Fig. 1(b)).

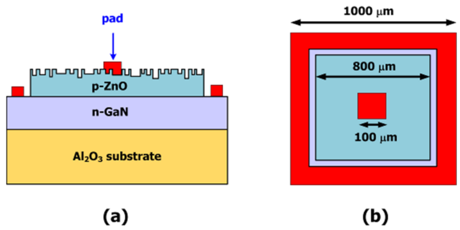

Fig. 1 Schematics showing the device structure and the device size.

3. Results and discussion

Figure 2(a)-(h) shows both tilted- and top- view SEM images of the surface morphologies under different growth processes and the p-ZnO surface morphologies with quite different nanostructures is clearly observed. Figure 2(a)-(b) show that many nanoballs-like structures on the n-GaN surface after growth 70°C for 20 min. After HTG for 2 hr, the surface morphology becomes anemones-like structures, which is due to the nanoballs quickly created nuclei aggregates by capturing nuclei from the solution, as shown in Figs. 2(c)-(d). Figures 2(e)-(f) show that the p-ZnO/n-GaN structure is composed of fully coalesced anemone structures, a continuous film is formed with a smooth surface morphology after growth 70 ºC for 4 hr. Furthermore, as shown in Figs. 2(g)-(h), p-ZnO layer with porous structure was obtained after growth 70°C for 6 hr. The formation of porous p-ZnO film is attributed to the occurrence of an etching reaction caused by the balance of the HTG solution during a lengthy HTG process.

The influence of the mole concentration of $NH_4H_2PO_4$ varied from 24 to 8 mM was also examined and the surface morphologies are shown in the Fig.3 (a)-(f). For the 24 mM case (sample-A, Fig. 3(a)-(b)), the grown p-ZnO film is about 1.5 μm in thickness with a pores size of 600~300 nm, which is larger that of the 16 mM case (sample-B, Fig. 3(c)-(d)). When the concentration of $NH_4H_2PO_4$ was further decreased to 8 mM (sample-C, Figs. 3(e)-(f)), the amount of pores is considerably decreased with a reduced film thickness of about 0.5 μm, which could be attributed to $NH_4H_2PO_4$ is insufficient in the mixed solution. To confirm the p-type property of the grown p-ZnO porous film, the samples were further analyzed by energy dispersive spectrometers (EDS) and Hall measurement (Table 1). The content of phosphorus atoms in the grown films are found ranging from 13.76%~19.04% for the three samples. The corresponding hole concentration obtained from Hall measurement is in the range of 7×10^{13}~5×10^{14} cm^{-3}.

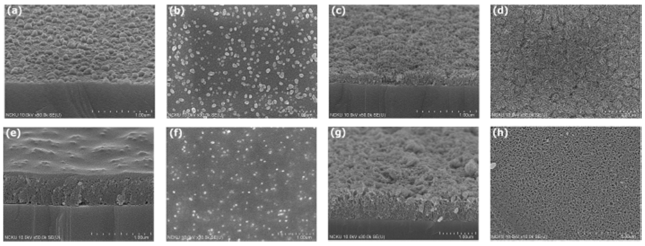

Fig. 2 SEM images of surface morphology of the prepared p-ZnO/n-GaN structures with different HTG times. (a)-(b) 20 min, (c)-(d) 2 hr, (e)-(f) 4 hr, and (g)-(h) 6 hr. Both the tilted and top views are shown.

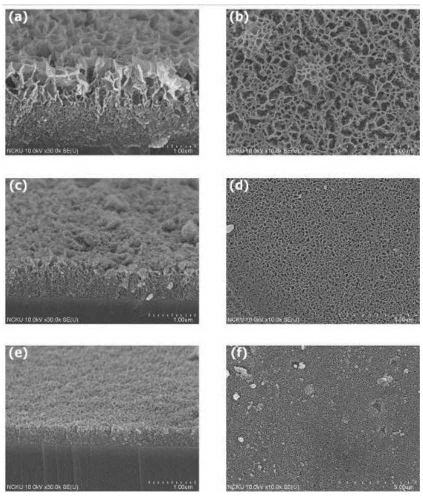

Fig. 3 SEM images of surface morphology of the prepared p-ZnO/n-GaN structures. (a)-(b) images of sample-A, (c)-(d) images of sample-B, and (e)-(f) images of sample-C. Both the tilted and top views are shown.

Table 1. The element components of the p-ZnO with variant concentrations of ammonium phosphate.

Element(%) / Sample	Zn	O	P	Concentration(cm^{-3})	Type
A	56.12	24.84	19.04	~5×10^{14}	P
B	57.44	28.81	13.76	~10^{14}	P
C	56.31	30.73	12.96	~7×10^{13}	P

The fabricated p-ZnO/n-GaN HJs with different phosphorus doping concentrations all exhibit a well-defined rectifying behavior in darkness as shown in Fig. 4. Note that sample-C exhibits the highest forward current. It could be attributed to the thickness of the p-ZnO layer is too thin (~500 nm) to have reduced build-in voltage and depletion region. Similarly, the forward current of the sample-A is significantly suppressed because of the large series resistance of the thicker p-ZnO layer (~1.5 μm). Among these three samples, the sample-B seems most suitable for ultraviolet sensors for having compromised depletion region width and series resistance. The possible band diagram of p-ZnO/n-GaN HJ under thermal equilibrium condition is shown in the inset of Fig. 4. The dynamic photoresponse of the sample-B under UV light (365 nm, 1 mW/cm^2) irradiation and 1V reverse bias is shown in Fig. 5. The superior performance with fast response time (rise time ~6 sec and the recovery time ~7 sec) and the UV sensitivity (I_{UV}/I_{dark}) as high as 80 of the sample B indicates the effectiveness of the proposed p-ZnO/n-GaN HJs.

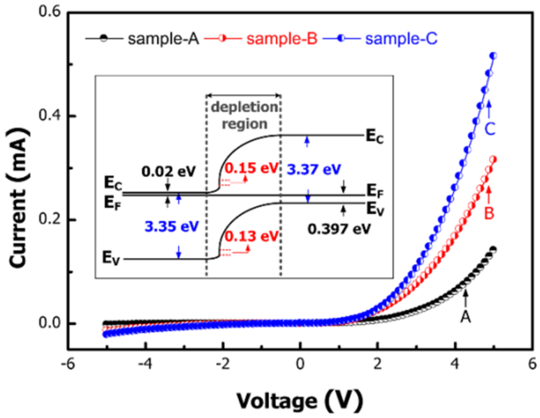

Fig. 4 The I-V charaqcteristics of the p-ZnO/GaN HJs in dark. The inset shows the possible energy band diagram of the p-ZnO/n-GaN HJ under thermal equilibrium.

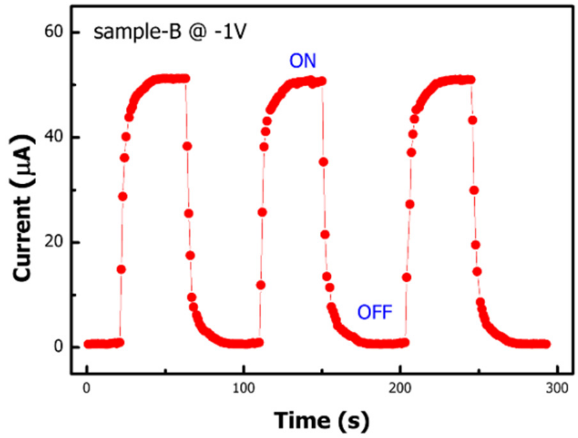

Fig. 5 The dynamic photoresponse of sample-B under UV light (365 nm, 1mW/cm^2) illumination.

4. Conclusion

In summary, the evolution of porous p-ZnO during HTG process has been investigated. Effects of the mole concentration of $NH_4H_2PO_4$ in HTG aqueous solution on the pores size, surface morphology, and hole concentration of the grown porous p-ZnO layer have also been elucidated. Experimental results reveal that the p-ZnO/GaN HJs have good response to UV light (365 nm) with an increase in the photocurrent of about 80 times. It is expected that the present HJs could provide a simple and effective mean for future optoelectronic applications.

Acknowledgement:
This work was supported by the National Science Council (NSC) of Taiwan, under Contract No. NSC 102-2221-E-006-217-MY2 and the Ministry of Science and Technology (MOST) of Taiwan, under Grant MOST 103-2221-E-006-132.

References

[1] *L. Luo et al, Sensor. Actuat. A-Phys.,* **127** (2006) 201.
[2] *E. Monroy et al, Semicond. Sci. Tech.,* **18** (2003) R33.
[3] *Z.-Q. Xu et al, Appl. Surf. Sci.,* **253** (2009) 476.
[4] *C. B. Tay et al, J. Phys. Chem. C,* **114** (2006) 9981.
[5] *S.-H. Hwang et al, Mater. Chem. Phys.,* **143** (2014) 600.