Study on Ultraviolet Photodetector modified by Au Nanoparticles on ZnO Nanowires

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Abstract. Zinc oxide (ZnO) is a direct wideband gap semiconductor material with a band gap of 3.37eV at room temperature. It can absorb ultraviolet light with a wavelength shorter than 385nm and is light blind to visible light. Using different growth methods or different growth conditions, the final prepared ZnO nanomaterials have different growth structures, which can be presented as nano dots, nanowires, nanoribbons, nano rings, nano tubes and other structures. In this paper, the ultraviolet (UV) photodetector (PD) of ZnO nanowires (NWs) was first prepared by wet etching and hydrothermal method. Then, gold (Au) nanoparticles (NPs) was used as metal nanoparticles with surface modification to characterize the performance of the PD, and the study of NPs modification on the performance of the detector was explored. After testing, the NPs modification improved the responsivity by about 12 times and the absorption was also improved to a certain extent. This paper provides a valuable reference for the material selection of UV PDs based on ZnO NWs surface modification.

1. Introduction

Ultraviolet radiation (UV) can be divided into three groups according to wavelength, including UV-A (315-400nm), UV-B (280-315nm) and UV-C (100-280nm). Compared with UV-C wavelength, most UV-A and a certain proportion of UV-B penetrate the upper atmosphere and reach the earth's surface. Excessive exposure to UV-A radiation can cause skin aging, skin cancer and cataract. Therefore, in recent decades, the monitoring of ultraviolet radiation in the environment has become a focus of attention. In addition to chemical and biological analysis, ultraviolet detection has a wide range of applications in optics, such as flame detection, solar astronomy, missile plume detection and combustion monitoring [1–4]. Therefore, it has been found that various semiconductor materials, such as SiC, AlN, ZnO, GaN and graphene, have been used to prepare visible blind UV PDs [5-7]. Among them, ZnO is widely used because of its excellent properties.

ZnO is the first generation of semiconductor material and is widely used because of its advantages
such as high electron mobility, small exciton binding energy, and wide direct optical band gap of about 3.37eV [8-10]. However, it is also limited by large device size, low photocurrent generation and high electron hole complex, which is due to the external bias as the photocurrent generator. People are constantly looking for ways to improve it. The preparation of nanowires combined with ZnO and introduced into the device is the most common and effective method.

ZnO nanomaterials have received extensive attention and research due to their excellent optical, electrical, gas sensitive and photocatalytic properties. At present, ZnO nanomaterials can be used in piezoelectric devices, gas sensors, solar cells, light-emitting diodes and other devices, as well as in environmental protection as an excellent metal oxide photocatalyst [11,12]. Combining nanomaterials with thin film PDs can improve the performance of PDs.

In this paper, ZnO NWs UV PD was prepared by magnetron sputtering, wet etching and hydrothermal method, and the device was modified with Au NPs. After testing, it was found that the responsivity was improved by 12 times, and the absorption was also significantly improved. It is proved that the NPs modification can improve the performance of the device effectively.

2. Materials and Methods
ZnO thin film has been grown on quartz substrate SiO2 by RF magnetron sputtering at a sputtering power of 120 W. The O2/Ar flow ratio is about 10:40. Subsequently, the Au finger electrode was prepared by lithography. Secondly, ZnO NWs were prepared by hydrothermal method and dissolved in deionized water with 0.002 mol·L⁻¹ Zn(CH3COO)2·2H2O and 0.002 mol·L⁻¹ hexamethylenetetramine (HMTA) as reaction materials. The prepared ZnO film UV PD was placed into the stainless steel autoclave lined with teflon of the obtained solution and kept at 90 °C for 10 h. Finally, a small amount of Au was sputtered to modify the sample by magnetron sputtering to make the Au NPs attached to the surface of ZnO NWs.

The morphologies of the products were characterized by HITACHI SU8010 Cold Field Emission SEM. The phase identification of photodetectors was characterized by the Rigaku Ultima VI x-ray diffractometer (XRD). The absorption spectra were collected using a Perkin Elmer Lambda 950UV/VIS spectrophotometer. The responsivity was measured on a Zolix DR800-CUST semiconductor parameter analyzer and the current–voltage (I-V) measurements under dark and light conditions were carried out on an Agilent16442A Test Fixture.

3. Results & Discussion
Figure 1 shows the SEM images of the ZnO NWs modified with Au. It can be seen that homogeneous and dense hexagonal ZnO NWs were successfully grown in the middle of the Au finger electrode by hydrothermal method. As can be seen from figure (b), the modified Au NPs were more obvious.

Figure 1. SEM images of the Au-ZnO NWs UV PD with different magnification.

Figure 2 shows the XRD comparison of ZnO film, ZnO NWs UV PD before and after modified with Au NPs. It can be seen that after the growth of NWs, the (002) crystal plane peak corresponding to ZnO
was significantly enhanced, and no obvious increase of Au peak was observed in the modified XRD pattern, possibly because the content of Au was too small.

![XRD comparison of ZnO film/ ZnO NWs UV PD/ Au-ZnO NWs UV PD.](image1)

Figure 2. XRD comparison of ZnO film/ ZnO NWs UV PD/ Au-ZnO NWs UV PD.

Figure 3 is the comparison of absorption curves of PDs before and after Au NPs modification. It can be seen that the absorption is significantly enhanced after modification. The increase in light absorption is due to the plasma effect, resulting in increased absorption.

![Absorption curves of ZnO NWs UV PD with and without Au NPs modification.](image2)

Figure 3. Absorption curves of ZnO NWs UV PD with and without Au NPs modification.

Figure 4 (a) and (b) are light dark current (I-V) curves before and after the modification, respectively. Under UV irradiation, the local field excites the electrons in the NPs, causing the electrons to transfer from Au NPs to ZnO conduction bands, resulting in the increase of photocurrent.

![I–V curves of ZnO NWs UV PD (a) with and (b) without Au NPs modification.](image3)

Figure 4. I–V curves of ZnO NWs UV PD (a) with and (b) without Au NPs modification.
Figure 5 (a) is a comparison of responsivity before and after Au NPs modification, and the figure 5 (b) is the responsivity curve before modification. It can be calculated that the modified responsivity is improved by about 12 times. It shows that Au NPs can effectively improve the responsivity of the device. Under UV irradiation, the surface plasmonic resonance of Au NPs was induced by UV light, which enhanced the electromagnetic field near the Au NPs. The enhanced electromagnetic field excites the electrons in Au NPs to cross the lower Schottky barrier height (SBH) and reach the ZnO conduction band. Thus, the separation rate of electron hole pairs in ZnO thin film is improved, and the response rate is improved. [13]

![Figure 5. (a) Responsivity of ZnO NWs UV PD with and without Au NPs modification ; (b) responsivity curve before modification .](image)

4. Conclusions
In this paper, the ZnO NWs UV PD was prepared by wet etching and hydrothermal method, and the Au NPs were used as metal nanoparticles with surface modification to characterize the performance of the PD, and the study of NPs modification on the performance of detector was explored. It is proved that the performance of the plasma modified detection equipment is improved, which provides an effective method to improve the performance for further exploration of NWs UV PD.

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References
[1] Razeghi, M. (2002) Short-Wavelength Solar-Blind Detectors—Status, Prospects, and Markets. Proc. IEEE, 90:1006-1014.
[2] Ohta, H., Hosono, H. (2004) Transparent oxide optoelectronics. Mater. Today, 7:42-51.
[3] Rogalski, A. (2004) Optical detectors for focal plane arrays. Opto-Electron. Rev., 12:221-245.
[4] Pearton, S. J., Ren, F., Wang, Y. L., Chu, B. H., Chen, K. H., Chang, C. Y., Lim, W., Lin, J., Norton, D. P. Prog. (2010) Recent advances in wide bandgap semiconductor biological and gas sensors. Mater. Sci., 55:1-59.
[5] Tian, C.G., Jiang, D.Y., Zhao, Y.J., Liu, Q.F., Hou, J.H., Zhao, J.X., Liang, Q.C., Gao, S., Qin, J.M. (2014) Effects of continuous annealing on the performance of ZnO based metal-semiconductor-metal ultraviolet photodetectors. Mat. Sci. Eng. B-Adv., 184:67-71.
[6] Zhao, Y.J., Jiang, D.Y., Zhao, M., Deng, R., Qin, J.M., Gao, S, Liang, Q.C., Zhao, J.X. (2013) Effects of power on properties of ZnO thin films grown by radio frequency magnetron sputtering. Appl. Surf. Sci., 266:440-444.
[7] Sun, M.X., Fang, Q.Y., Xie, D., Sun, Y.L., Qian, L., Xu, J.L., Xiao, P., Teng, C.J., Li, W.W., Ren, T.L., Zhang, Y.F. (2017) Heterostructured graphene quantum dot/WSe2/Si photodetector with suppressed dark current and improved detectivity. Nano. Res., 11:3233-3243.

[8] Mahanti, M., Basak, D. (2012) Highly enhanced UV emission due to surface plasmon resonance in Ag–ZnO nanorods. Chem. Phys. Lett., 542:110-116.

[9] Duan, Y.H., Zhang, S.Q., Cong, M.Y., Jiang, D.Y., Liang, Q.C., Zhao, X.J. (2020) Performance modulation of a MgZnO/ZnO heterojunction flexible UV photodetector by the piezophototronic effect. J. Mater. Chem. C, 8:12917-12926.

[10] Jiang, D.Y., Tian, C.G., Liu, Q.F., Zhao, M., Qin, J.M., Hou J.H., Gao, S., Liang, Q.C., Zhao, J.X. (2014) Young's modulus of individual ZnO nanowires. Mat. Sci. Eng. A-Struct.,610:1-4.

[11] Lee, C., Lim, K., Song, J. (1996) Highly textured ZnO thin films doped with indium prepared by the pyrosol method. Sol. Energy Mater. Sol. Cells, 43:37–45.

[12] Khranovskyy, V., Grossner, U., Lazarenko, V., Lashkarev, Svensson, B. G.,Yakimova, R. (2007) Conductivity increase of ZnO:Ga films by rapid thermal annealing. Superlattice. Microst., 42:379–386.

[13] Young, S.J., Liu, Y.H., Chien, J.T. (2018) Improving field Electron emission properties of ZnO nanosheets with Ag nanoparticles adsorbed by photochemical method. ACS Omega, 3:8135–8140.