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A new organic-inorganic MgZnO/Au/PEDOT:PSS hybrid heterojunction photodetector fabrication

Siyuan Weng^{1,a}, Dayong Jiang^{1,2,b*}, Xiaolan Zhang^{1,c}, Meijiao Wang^{1,3,d}, Jiamei Sun^{1,e}, Hongping Zhao^{1,f}, HaoDa Li^{1,g}, Yue Zhao^{1,h}, Meijiao Xing^{1,i}

¹School of Materials Science and Engineering, Changchun University of Science and Technology, Changchun, Jilin Province, China

²Engineering Research Center of Optoelectronic Functional Materials, Ministry of Education, Changchun Jilin Province, China

³Changchun College of Electronic Technology, Changchun, Jilin Province, China

^aemail:wwennuan2021@163.com, ^cemail: zxl17853687928@163.com, ^demail: youxian fengzhengmj@163.com, ^eemail: nanji2008@126.com, ^femail:13039290037@163.com
^gemail: lihaoda1994@163.com, ^hemail: suixineryue1995@163.com, ⁱemail: 15754315723@163.com

*Corresponding author: ^bemail: 2006800026@cust.edu.cn

Abstract. This research reports oxygen zinc magnesium (MgZnO)/gold (Au) photodetectors (PD) and organic-inorganic semiconductors MgZnO/Au/poly(3,4-ethylenedioxythio-phenylene): poly(4-styrenesulfonate) (PEDOT:PSS) PD research. At room temperature, spin-coating and radio frequency (RF) magnetron sputtering were used to deposit PEDOT:PSS layer and MgZnO thin film on the substrate, respectively. The properties of the heterojunction formed on the MgZnO/PEDOT:PSS inorganic/organic contact interface were studied. In order to manufacture ultraviolet (UV) heterojunction PDs, PEDOT:PSS is used as the hole transport layer (HTL), and MgZnO is used as the electron transport layer (ETL). This heterojunction shows excellent ultraviolet light detection capability. Under 40 V bias, the responsivity of MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD are 0.0473 A W⁻¹ and 0.134 A W⁻¹ under ultraviolet irradiation, respectively. The device shows good Schottky contact between metal semiconductor junctions. The excellent UV detector performance is due to the strong UV absorption of PEDOT:PSS.

1. Introduction

MgZnO heterogeneous interface structure is superior to a single junction structure composed of a single type of semiconductor, for example, it has higher sensitivity, faster response speed and better rectification characteristics. In addition, due to its physical and chemical properties, large energy band gap (approximately 3.37 eV at room temperature), high excitation binding energy (60 meV), chemical stability, transparency and electron mobility, MgZnO is a photodetector application Good choice[1-5]. zinc oxide is a composite material of group II-VI. Due to the natural donor defects, hydrogen defects, oxygen vacancies and/or zinc gaps in its structure, it acts as an n-type semiconductor.

MgZnO-based metal semiconductor metal (MSM) photodetector for detection in the ultraviolet region. In order to improve the performance of the MSM structure to increase the photocurrent and reduce the dark current, a polymer can be inserted between the electrode and the active layer to form a high-quality heterojunction. Since the physical/chemical stress at the heterojunction is small, it is



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expected that a solution-based process will be used to deposit p-type polymer on the n-type semiconductor layer to make an inorganic/organic heterojunction, which will reduce surface traps at the interface energy level. The solution can use hole transport polymer (p-type) and MgZnO (n-type) layers to achieve inorganic/organic heterojunctions[6]. PEDOT:PSS has good electrical conductivity, high transparency and durability, a large work function of 5.2 eV and low resistivity, so it has become one of the most studied polymers[7-8]. PEDOT:PSS is widely used as an electrode or hole transport layer[9]. Today, the application of PEDOT:PSS is not limited to organic devices, but also extends to hybrid semiconductor devices.

Recently, we have demonstrated a high-performance PD with the structure SiO₂/ZnO/Au/PEDOT:PSS. Our results prove that the product has good performance compared with previously reported properties of similar device structures and thin film materials. Therefore, this article aims to study the influence of the structure and optical properties of MgZnO/PEDOT:PSS heterojunction contacts[10].

2. Materials and Methods

2.1. Materials

All the reagents used in the experiments were in analytic grade and used without further purification. The conjugated polymer PEDOT:PSS was purchased from Aladdin. The chemical structures of the PEDOT:PSS used are displayed in Figure 1.

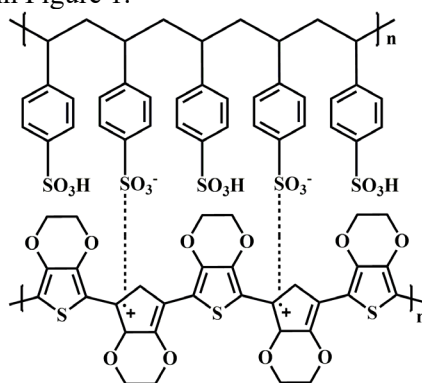


Figure 1. Chemical structures of PEDOT:PSS.

2.2. Synthesis of MgZnO thin film

The MgZnO thin film were prepared on quartz substrates. The substrate was cleaned in acetone, alcohol and deionizer water for 10 min by ultrasonic. First, the MgZnO thin film was deposited on quartz substrates by RF magnetron sputtering technique. Before deposition, the vacuum chamber was evacuated to a base pressure of 5×10^{-4} Pa. The pressure during growth was 0.6 Pa, at 10 sccm O₂ flow and 40 sccm Ar flow with RF power of 150 W during the 1h sputtering process. Then, thin Au layer were deposited upon the MgZnO thin film layer by the same method only changing the growth parameters. The interdigital electrodes were produced via photolithography and wet etching process to obtain MgZnO/Au PD.

2.3. Synthesis of PEDOT:PSS on MgZnO thin film

PEDOT:PSS was used for the fabrication of a p-n heterojunction with MgZnO thin film. PEDOT:PSS dispersed in water was deposited on the MgZnO layer using the spin coating technique. Afterwards, 50 μ L of the diluted polymer was poured on the rotating zinc oxide layer. The p-type polymer PEDOT:PSS was spin coated onto the interdigital electrodes on the MgZnO/Au PD. For spin coating, the rate of the spin was 500 rpm for first 10s. Then, the rate of spin was increased linearly for 1 min to achieve 3000 rpm and kept for next 1 min. The film was annealed on a hotplate at 120 °C for an hour and then left to cool down slowly, to prevent cracking the layer. All RF and spin-coating process were carried out at room temperature in air.

2.4. Characterization and measurement

All characterizations were conducted at room temperature in the ambient air. The phase identification of the MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD were measured by using a Rigaku Ultima VI X-ray diffractometer (XRD) with Cu K α radiation ($\lambda = 1.543 \text{ \AA}$) at 40 kV and 20 mA. The scanning electron micrographs (SEM) measurements were performed on a JEOL Field Emission Scanning Electron Microscope. Absorption spectra was measured in the wavelength range from 300 to 500 nm by using a PerkinElmer Lambda 950 UV/vis Spectrometer. The band gap of the films has been calculated from the absorption edge of the spectrum. The current-voltage (I-V) characteristics under dark and photo of MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD were measured by using an Agilent 16,442 A Test Fixture. The spectral responses of the MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD were measured by using a Zolix DR800-CUST testing system with bias voltages varying from 5 to 40 V at room temperature.

3. Results and discussion

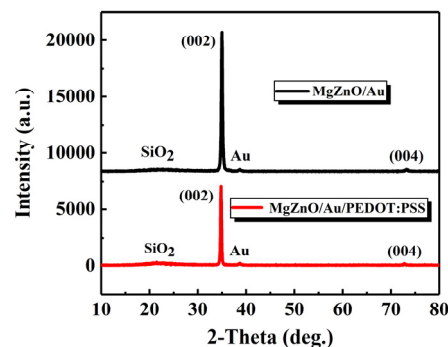


Figure 2. XRD spectrum of the MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD prepared on SiO₂ substrate.

Figure 2 shows the XRD patterns of MgZnO/Au PD and MZnO/Au/PEDOT:PSS heterojunction PD grown on SiO₂ substrate. The two diffraction peaks (002; $2\theta = 34.2^\circ$) and (004; $2\theta = 72.4^\circ$) indicate the hexagonal wurtzite structure of MgZnO crystals. The diffraction peaks observed at 21.3° and 38.6° are attributed to the amorphous SiO₂ and Au crystal phases, respectively. After spin-coating with the polymer PEDOT:PSS, there is almost no change in the XRD spectrum. The peak position and diffraction angle of MgZnO/Au/PEDOT:PSS heterojunction PD are very similar to those of MgZnO/Au PD. Compared with the MgZnO XRD pattern, the strength of the MgZnO/Au/PEDOT:PSS heterojunction PD is almost reduced by half. This is because the PEDOT:PSS thin film does not show XRD characteristic peaks due to its amorphous nature.

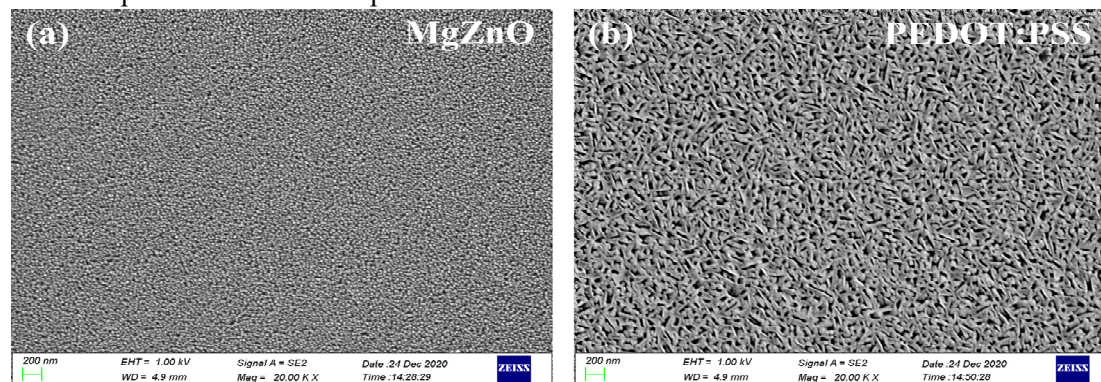


Figure 3. SEM micrographs of (a) MgZnO thin film and (b) PEDOT: PSS thin film.

Figure 3 shows the SEM spectra of (a) MgZnO thin film and (b) PEDOT:PSS thin film. Observed from the SEM micrograph, Figure 3(c) shows the image showing the microstructure of MgZnO

composed of many spherical crystalline particles, and the film presents a smooth surface. The inset of Figure 3(a) is observed to have nano-scale dimensions. The microstructure formed by the small grains. The SEM micrograph of PEDOT: PSS thin film is shown in Figure 3(b). However, the PEDOT:PSS thin film showed streak-like particles, and the microstructure was found to be uniform, with densely interconnected crystals.

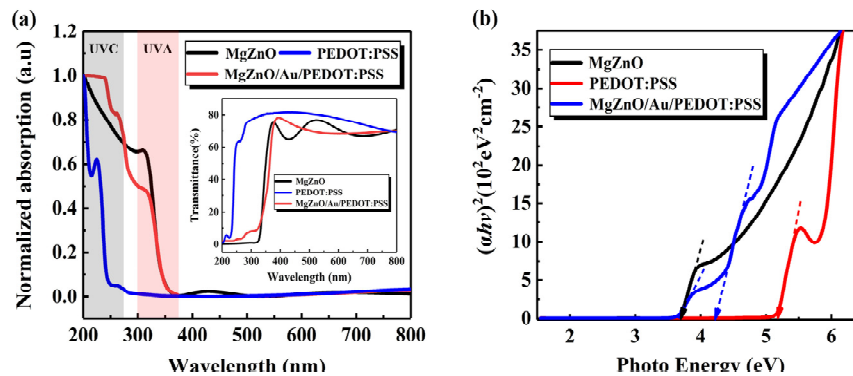


Figure 4. (a) Normalized absorption spectra of MgZnO thin film, PEDOT:PSS thin film and MgZnO/Au/ PEDOT:PSS heterojunction PD and inset shows transmission spectra of MgZnO thin film, PEDOT:PSS thin film and MgZnO/Au/PEDOT:PSS heterojunction PD. (b) The graph of $(\alpha h\nu)^2$ versus $h\nu$ plots for MgZnO thin film, PEDOT:PSS thin film and MgZnO/Au/PEDOT:PSS heterojunction PD.

MgZnO thin film, MgZnO/Au/PEDOT:PSS heterojunction PD and PEDOT:PSS thin film in the range of 200-800 nm showed normalized absorption spectrum characteristics, as shown in Figure 4. The absorption edges of PEDOT:PSS thin film and MgZnO thin film appear at 248nm and 356nm, respectively. For the ZnO/PEDOT:PSS heterojunction, there are two obvious absorption bands, which can be attributed to the characteristic absorption of PEDOT:PSS at 224 nm and MgZnO at 308 nm, Corresponding to the black and red areas in Figure 4a. It is observed that the MgZnO thin film absorbs in the wavelength range of 200 to 400 nm and has a high absorptivity in the visible light region of the spectrum. It can also be seen that the PEDOT:PSS thin film shows strong absorption in the visible wavelength range of 200 to 280 nm. It can be seen that all samples show an optical transmittance greater than 60% in the visible light range.

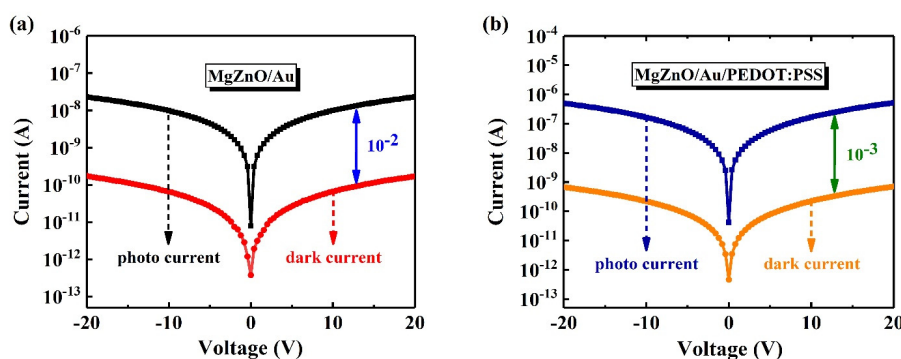


Figure 5. I - V characteristics of (a) MgZnO/Au PD and (b) MgZnO/Au/PEDOT:PSS heterojunction PD measured in darkness(dark current) and illumination (photocurrent).

The I - V characteristic curves of MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD in darkness and illumination are shown in Figure 5. Under ultraviolet light, the photocurrent (I_{photo}) of MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD are 9.87×10^{-9} A and 1.65×10^{-7} A, and the dark current (I_{dark}) are 6.60×10^{-11} A and 2.23×10^{-10} A, respectively, when the biased as 10 V. After applying a 10 V bias, it was found that the photocurrent and dark current contrast ($I_{\text{photo}}/I_{\text{dark}}$) of MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD were 149.5 and 741.5, respectively. The net photocurrent is obtained by subtracting the dark current ($I_{\text{ph}} = I_{\text{light}} - I_{\text{dark}}$) from the obtained

photocurrent because the dark current is relatively low compared to the photocurrent. Therefore, the rectification behavior is mainly caused by the formation of a heterojunction between the p-type PEDOT:PSS thin film and the n-type MgZnO thin film.

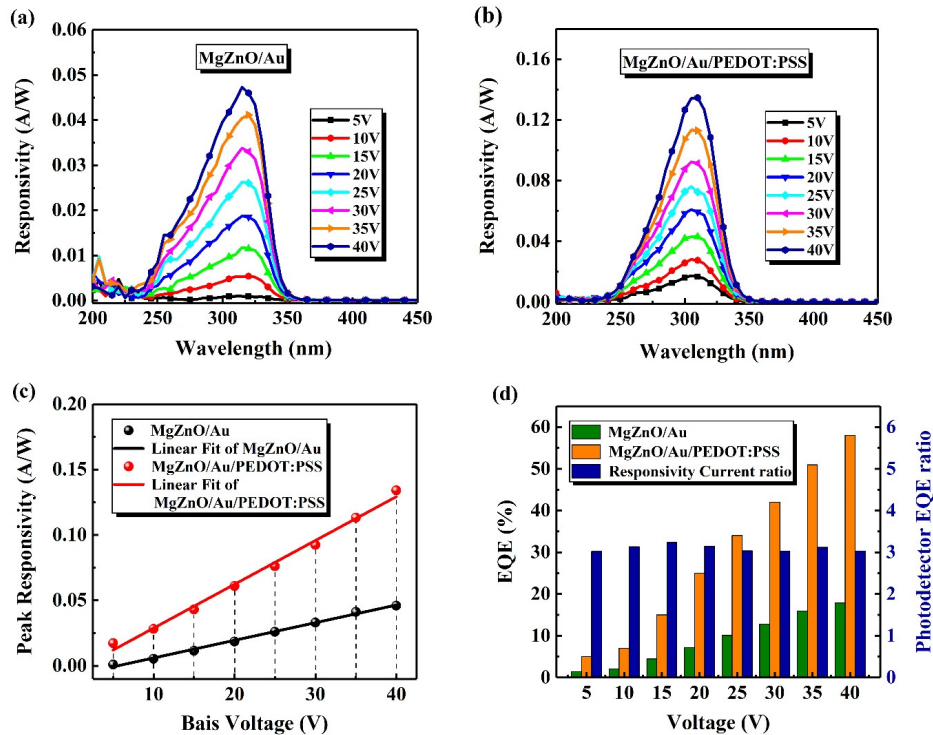


Figure 6. The responsivity of the (a) MgZnO/Au PD and (b) ZnO/Au/PEDOT:PSS heterojunction PD measured at different bias voltages. (c) Variation tendency of two peak responsivities in ZnO/Au PD and ZnO/Au/PEDOT:PSS heterojunction PD with different bias voltage. (d) The EQE values of the ZnO/Au PD and ZnO/Au/PEDOT:PSS heterojunction PD and PD EQE ratio measured at different bias voltages.

Figure 6(a) and Figure 6(b) show the responsivity graphs of MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD recorded under various bias conditions, respectively. With 40 V bias applied, the measured maximum responsivity for MgZnO/Au PD and MgZnO/Au/PEDOT:PSS heterojunction PD is 0.047 A/W and 0.134 A/W, respectively. The greater responsivity observed from MgZnO/Au/PEDOT:PSS PD can again be attributed to the insertion of high resistance PEDOT:PSS. After PEDOT:PSS spin coating, traps caused by MgZnO structural defects are filled. Figure 6(c) is a function of peak responsivity and bias voltage. A linear relationship is obtained between 5 and 40 V, indicating that there is no carrier mobility saturation or sweep-out effect until the bias is applied. In order to further evaluate the responsivity of the PD, we performed a spectrum analysis calculation on the EQE.

$$EQE(\lambda) = (R \times h \times c) / (q \times \lambda) \quad (1)$$

Where R is responsivity, h is Planck's constant, c is the speed of light, q is the charge of electrons, and λ is the wavelength of light. It is found that the EQE of MgZnO/Au PD is also smaller than the EQE measured from MgZnO/Au/PEDOT:PSS heterojunction PD. This is in good agreement with the smaller dark current of MgZnO/Au PD.

4. Conclusions

In short, we used RF magnetron sputtering MgZnO thin film on a quartz substrate, as well as the preparation and characterization of MgZnO/Au PD. Select gold metal as the planar interdigital electrode. The maximum responsivity of the MgZnO PD is measured to be 0.047 A/W at 315 nm under a bias 40V. The MgZnO/Au/PEDOT:PSS heterojunction PD was successfully prepared by spin-coating at room temperature, and a good heterojunction was formed. MgZnO/Au/PEDOT:PSS heterojunction PD shows

high wavelength selectivity at a wavelength of 305 nm, with a spectral response of approximately 0.134 A/W. After spin-coating, MgZnO/Au/PEDOT:PSS heterojunction PD parameters EQE, D_λ and R_λ have been further enhanced.

Acknowledgements

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