A Self-powered UV-visible Photodetector Based on p-Se/Al₂O₃/n-ZnO Nanorod Array Heterojunction

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Abstract: Self-powered photodetector is capable of transforming radiation signals to electronic signals without assistance of external power supply, which is widely utilized in industry and military. Herein, p-Se/n-ZnO nanorod array heterojunction was successfully synthesized and its application as UV-visible photodetector was explored. Due to the proper built-in electric field at the interface of ZnO and Se, the photogenerated electrons and holes are separated and transported in opposite directions, giving rise to high photocurrent at zero bias. Thus, this heterojunction can work as an independent and wireless self-powered photodetector. Introduction of Al₂O₃ interlayer between Se and ZnO efficiently reduces the dark current. The resulting device achieves high responsivity of 55 μA∙W⁻¹ and specific detectivity of 5×10¹⁰ Jones at 500 nm, as well as fast response speed (rise time of 0.9 ms and decay time of 0.3 ms).

Key words: ZnO; heterojunction; self-powered; photodetector
posite structure of single Se microtube and conducting polymers. The optimum device exhibited high on/off ratio of $1.1 \times 10^3$, large detectivity ($3.78 \times 10^{11}$ Jones) and high response speed (rise time of 4.5 μs and fall time of 2.84 ms) at zero bias voltage and 610 nm. Hu, et al. fabricated a photodetector by depositing plasmonic metallic nanoparticles on the Se microtube by utilizing both the heterojunction and surface plasmon coupling effect. The device demonstrates broadband photoresponse from 300 to 700 nm with peak responsivity of about 19 mA/W at 610 nm and response time of 0.32 ms. Despite these achievements, many associated problems, including interface defects caused by lattice mismatch between hetero-materials, low mobility of organic semiconductor and complex fabrication process, not only bring about obstacles to the fabrication of composite structures but also degrade the photodetecting performances.

In this work, we report the fabrication of p-Se/n-ZnO nanorod array heterojunction, and its integration into a self-powered and rapid-response UV-visible photodetector. The resulting device exhibits fast response with a rise time of 0.9 ms and decay time of 0.3 ms. Meanwhile, the device achieves the peak responsivity and specific detectivity of about 55 μA/W and $5 \times 10^{10}$ Jones at 500 nm, respectively.

1 Experimental

The fabrication process of p-Se film/n-ZnO nanorod array heterojunction is illustrated in Fig. 1. Firstly, the fluorine doped tin oxide (FTO) glass was cut into 1 cm × 1.5 cm small pieces, cleaned with acetone, ethanol and deionized water in sequence for 10 min each step, and dried with nitrogen. Then the prepared FTO was subjected to UV radiation for 20 min to improve its hydrophilic property. Afterward, 40 nm ZnO seed layer was deposited on FTO by atomic layer deposition (ALD) and then annealed at 500 °C for 60 min. For the growth of ZnO nanorods, zinc nitrate hexahydrate (Zn(NO$_3$)$_2$) (25 mmol/L) and hexamethylene tetramine (HMTA) (25 mmol/L) were dissolved in deionized water, and followed by stirring for 2 h. After that, the substrates were immersed into the solution with the conductive side facing down. Then the beaker was heated to 90 °C and maintained for 6 h in a thermostatic water bath. After the reaction completed, the sample was cleaned by deionized water several times, and then dried in a vacuum oven. To get crystallized ZnO nanorods, the sample was annealed at 500 °C for 60 min in a muffle furnace. Then, 2 nm Al$_2$O$_3$ film was deposited on the ZnO nanorod array by ALD. For the growth of Se film, a vapor transport and deposition process performed in a horizontal tube furnace. A ceramic boat containing 3 g Se powder was placed in the middle of the quartz tube. ZnO and Al$_2$O$_3$ coated FTO substrate was put 30 cm away from the Se source. To eliminate air in the furnace, pure nitrogen was aerated for 2 h with the speed of 300 sccm. Then the speed was changed to 200 sccm for deposition. During the deposition, the furnace was heated to 380 °C and maintained for 4 h. Finally, 100 nm Ag was thermal-evaporated on the surface of Se film as top electrode. The active area of device is 15 mm$^2$.

The morphology of the ZnO nanorod array and Se film was characterized using a field emission scanning electron microscope (FE-SEM, Hitachi, SU8010). The crystalline and structural properties of the layers were investigated by X-ray diffraction (XRD, D/MAX–III–B-40 KV, Cu Kα radiation, λ=0.15418 nm). The absorption spectra of the ZnO and ZnO/Se were measured using a UV-visible spectrometer (Shimadzu, UV-3600). The photoelectric properties of the obtained photodetectors, including current-voltage (I-V) curves, spectra responsivity, and time-dependent photoresponse (I-t), were characterized using a semiconductor characterization system (Keithley 4200) under 100 mW·cm$^{-2}$ simulated solar light (Newport, 94043A) and monochromatic light produced with monochromator (Zolix, Omni-λ 3009) using order sorting filters. The light intensity was measured by a power meter (Newport, 1936-R). The response speed was recorded by an oscilloscope (Tektronix, MSO 58). The lasers (FU405 AL200-GD16 and FU650AD5-GC12) were used as light sources during measurement of the relationship between photocurrent and light intensity. The power intensity of laser can be tuned by changing the DC current.

2 Results and discussion

Fig. 2 shows the top-view and cross-sectional SEM
images of the p-Se/n-ZnO nanorod array. As shown in Fig. 2(a), the ZnO nanorod array vertically align on FTO substrate with diameter of 50–150 nm. The length of ZnO nanorod array is about 2.5 μm (Fig. 2(b)). Fig. 2(c) reveals that Se film is composed of large crystals. The cross-sectional image in Fig. 2(d) reveals that the deposited Se film is around 3 μm thick and an intimate contact is formed at the interface between Se film and ZnO nanorod.

XRD pattern of the p-Se/n-ZnO nanorod array is plotted in Fig. 3(a). All peaks attained are in well agreement with the characteristic peaks of wurtzite ZnO (JCPDS 36-1451) and Se (JCPDS 06-0362). The sharp and strong peaks demonstrate that both ZnO and Se own high crystallinity. The relative intensity of ZnO (002) peak is much stronger than those of other peaks, indicating ZnO nanorods possess a preferred orientation with c-axis perpendicular to the substrate. The comparative UV-visible absorption spectra of pure ZnO and Se/ZnO are shown in Fig. 3(b). The pure ZnO nanorod array exhibits absorption when the light wavelength is below 368 nm, which corresponds to the bandgap of ZnO (3.37 eV)\(^{28,29}\). Upon deposition of Se film, there is an apparent absorption enhancement in visible light region. And the absorption edge is red-shifted to 730 nm, which is in consistence with the bandgap of Se (1.7 eV)\(^{30}\).

Fig. 4(a) and (b) represent the typical \(I-V\) characteristics of the device under dark, white light and monochromatic light. The significantly enhanced current under light illumination at zero bias voltage can be obviously detected. And the photocurrent curve does not pass the zero point, which means the device can work in self-powered mode. In comparison, \(I-V\) curve of the device without Al\(_2\)O\(_3\) interlayer shows a great dark current under white light illumination in the inset of Fig. 4(a). Fig. 4(c) and (d) represent the \(I-t\) curves of the device under periodic light on-off cycles at zero bias voltage. As shown in Fig. 4(c), the current obviously shows two distinct states when the white light irradiation is on and off, respectively. The dark current is only 2.2 pA; nevertheless, the photocurrent is remarkably boosted to a stable value of 435 pA, delivering a high on-off ratio (photocurrent to dark current ratio) of about 200. Fig. 4(d) shows the photoresponse of the device under 405 nm (1.664 \(\mu\text{W}\cdot\text{cm}^{-2}\)), 532 nm (1.543 \(\mu\text{W}\cdot\text{cm}^{-2}\)) and 650 nm (1.093 \(\mu\text{W}\cdot\text{cm}^{-2}\)) monochromatic light illumination. Reproducible and stable photoresponse is observed for the device. Environmental stability is a key parameter of photodetector, which is crucial to its practical application. \(I-t\) curve of the device under 500 nm illumination for 10 min is shown in Fig. 4(e). Noted that the device is exposed to air in ambient conditions without any encapsulation.

There is no obvious degradation for photocurrent after 10 min measurement, indicating its superior stability. Responsivity and detectivity are two important parameters to characterize the capability of a photodetector. Fig. 4(f) shows the spectral responsivity and detectivity from 300 to 800 nm for the device at zero bias voltage. It is revealed that the device exhibits obvious response to UV-visible light with a decrease at about 730 nm, which corresponds to the band gap of Se. Defects existed in Se film can introduce energy levels in the forbidden band,

![Fig. 2 SEM images of (a–b) ZnO and (c–d) p-Se/n-ZnO heterojunction](image)

(a, c) Top view; (b, d) Cross-sectional view

![Fig. 3 (a) XRD pattern of p-Se film and n-ZnO nanorod array, and (b) absorption spectra of pure ZnO and Se/ZnO hybrid structure](image)
which allows Se to absorb photon with energy less than its bandgap. Thus, there is still response between 730–800 nm. The heterojunction device has the peak responsivity and specific detectivity of 55 μA∙W−1 and 5×1010 Jones at 500 nm illumination, respectively. In comparison to the high responsivity in visible light region, the responsivity in UV region is relatively low. The responsivity at 320, 340 and 360 nm is 1.54, 1.15 and 1.57 nA∙W−1, respectively. The low responsivity in UV region is possibly because the light illuminates on the device from ZnO side. Due to the wide bandgap of ZnO, UV light is mainly absorbed by ZnO, generating electron-hole pairs. However, the holes cannot transit to the top electrode (Ag) to be collected because of the thick Se film, thus giving rise to low photocurrent and responsivity in UV region.

Fig. 5(a) and (c) show the I-t curves of the Se/Al2O3/ZnO heterojunction device under illumination of 405 and 650 nm lasers with varying intensities. The photocurrent increases gradually with the light power intensity increasing. The corresponding photocurrents as functions of light intensities are shown in Fig. 5(b) and (d). The photocurrents strongly depend on the light power densities, and the dependence can be described by the power law[10]:

\[ I_p \sim P^{\theta} \]  

where \( I_p \) represents the photocurrent, \( P \) is the power density of the incident light, and \( \theta \) is an exponent[9]. The fitting curves show that \( \theta=0.57 \) and 0.50 for the wavelength of 405 and 650 nm, respectively. The non-unity exponents suggest a complex process of electron-hole generation, recombination, and trapping within the Se/ZnO nanorod array.

A designed circuit diagram for characterizing the response speed is shown in Fig. 6(a). Fig. 6(b) presents the response speed testing, where the device was illuminated
Fig. 5  $I$-$t$ curves of the Se/Al$_2$O$_3$/ZnO heterojunction device under illumination of (a) 405 nm and (c) 650 nm lasers with varying light intensities (The unit of the light power is mW·cm$^{-2}$); Relationships between the photocurrent and the light intensity at 0 bias voltage under illumination of (b) 405 and (d) 650 nm lasers.

Fig. 6  (a) Diagram of electric circuit to characterize the response speed; (b) Time-dependent voltage curves at different chopper frequency; (c) Normalized voltage-frequency curve; (d) Enlarged one response cycle with rise and decay time with the chopped laser of 100, 200, 300, 400 Hz. A decreased response is shown with increasing frequency of the chopped laser in Fig. 6(c). To characterize the real response speed, one response cycle is enlarged. The rise time ($t_r$) and decay time ($t_d$) are defined as the values needed for the dark current to reach 90% of the maximum
photocurrent and down to 10% vice versa, respectively. It is found that $t_i$ and $t_d$ of the device are 0.9 and 0.3 ms, respectively, as shown in Fig. 6(d).

To disclose the work mechanism of the photodetector, an energy band diagram of the Se-Al2O3-ZnO is plotted in Figure 7. Before contact, Fermi level of ZnO is higher than that of Se (Fig. 7(a)). Once contact takes place, electrons would drift from ZnO to Se until Fermi levels line up. Upon illumination, well-aligned energy-band structure could separate the photogenerated electron-hole pairs in ZnO and Se at the heterojunction interface and help the charge carriers transport to electrodes, giving rise to large photocurrent.

As shown in Fig. 7(b), due to its particular band structure, Al2O3 interlayer prevents electron-hole recombination, which could efficiently decrease the dark current. Thus, the introduction of Al2O3 interlayer contributes to higher photo-dark current ratio, responsivity and detectivity.

3 Conclusions

In summary, a self-powered p-Se/Al2O3/n-ZnO UV-visible detector was prepared in this study. The self-powered functionality of the device is attributed to the proper built-in electric field between ZnO and Se arising from the well-aligned energy-band structure at the interface, which enables the photogenerated electrons and hole to separate and transport in opposite directions. Superior optoelectronic performances, including high responsivity (55 $\mu$A/W) and detectivity ($5 \times 10^{10}$ Jones), fast response speed (rise/decay time of 0.9/0.3 ms) are achieved for this device, which promise its potential application in light communication and image sensors.

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基于 p-Se/Al₂O₃/n-ZnO 纳米棒阵列异质结的自驱动紫外–可见光探测器

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摘 要: 自驱动光探测器能够在无外加偏压的情况下将光信号转化为电信号，从而广泛应用于工业和军事领域。本研究报道了 p 型 Se 薄膜和 n 型 ZnO 纳米棒阵列异质结的可控合成以及它们作为自驱动紫外–可见光探测器的应用。由于在 ZnO 和 Se 的界面处形成的内建电场将光生电子–空穴对分离，促使它们向相反方向传输，最终被电极收集，在 0 偏压下获得了较高的光电流 (435 pA)，从而实现无偏压自驱动光电探测。并且，在 Se 和 ZnO 界面处沉积的 Al₂O₃ 层有效降低了暗电流。最终，此器件在 500 nm 的单色光下显示了高响应率 55 μA·W⁻¹ 和大比探测率 5×10¹⁰ Jones，并表现出极快的响应速度（上升时间 0.9 ms，衰减时间 0.3 ms）。

关 键 词: 氧化锌; 异质结; 自驱动; 光探测器

中图分类号: O472 文献标识码: A