Photoresponse properties of p-type ZnSe nanowire photodetectors

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Nanophotodetectors are constructed based on individual p-type ZnSe nanowires (NWs), and the photoresponse properties are investigated. The nanophotodetectors show high sensitivity and fast response speed to the incident light with a sharp cutoff at 470 nm. The light-to-dark currents ratio I_{light}/I_{dark} is approximately two orders of magnitude; photoconduction is 20.5 nS at incident light intensity of 5.11 mWcm^{-2}. The response characteristics reveal that different energy levels (shallow and deep) in the bandgap and defects on the NW surface play an important role in the recombination. The ZnSe NW photodetector with good reliability and reproducibility will have great potential application in optoelectronic nanodevices.

1. Introduction: One-dimensional (1D) ZnSe nanostructures have attracted considerable attention in new electric and optoelectronic device applications because of their specific geometries and excellent properties [1–9]. Enormous efforts have been made to synthesise and characterise 1D ZnSe nanostructures in recent years, such as nanowires (NWs) [1, 2, 10, 11], nanoribbons/nanobelts [3, 12], nanotubes [13, 14], nanorods [15, 16], nanoneedles etc. Shan *et al.* [6] investigated the growth mechanism, photoluminescence (PL) and Raman properties of ZnSe NWs. Saxena *et al.* [7] had established that deviations from stoichiometry during the growth of ZnSe crystals result in point defects, and studied their PL with excitonic emission at 2.794 eV related to the neutral donor at V_{Se}.

1D ZnSe nanophotodetectors with smaller size, higher conversion efficiency and lower power consumption have significant applications in imaging technology, lightwave communications, information storage and optoelectronic integrated circuits [2, 17]. Up to now, much progress has been made to fabricate the ZnSe nanophotodetectors. Salfi *et al.* fabricated ZnSe nanowires-based photodetectors and the spectral photocurrent responsivity of the nanowire reaches 22 A/W at 400 nm, and the shape of the spectral response strongly reflects the absorption coefficient of ZnSe [5]. Philipose *et al.* reported conductivity and photoconductivity in an undoped ZnSe nanowires array [4]. For the practical application of 1D nanophotodetectors, it is all-important to study its photoresponse properties, including spectral response, switch frequency response, light intensity response and so on; it is significant to investigate the optical mechanism and to enhance device performance. Nevertheless, there are few reports about p-type ZnSe NW photodetectors.

In our previous report, the p-type ZnSe NWs were synthesised by using the atmosphere compensating technique with an individual selenium source, and the electrical properties based on nanofield effect transistors were investigated [18]. Here, we fabricated the nanophotodetectors based on individual ZnSe NWs, and investigated the photoresponse properties. The nanophotodetectors present higher light sensitivity, higher light-to-dark currents ratio in the cutoff wavelength range, good reliability and reproducibility.

2. Experimental: ZnSe NWs with p-type conductivity were synthesised via a thermal evaporation process in our previous report [18]. To access the photoresponse properties of the p-type ZnSe NWs, nanophotodetectors based on individual p-type ZnSe NWs were constructed. The p-type ZnSe NWs were dispersed on a degenerately doped silicon wafer with 300 nm dielectric of silicon dioxide. A mesh-grid consisting of 5 μm tungsten wire was used as the shadow mask and gold electrodes (100 nm) were deposited in a high-vacuum electron-beam evaporation system. The photoresponse measurements were conducted by employing signal detection and a data processing system with a monochromatic light source at room temperature.

3. Results and discussion: The response characteristics of ZnSe NW photodetectors at incident light with different wavelengths are shown in Fig. 1. Five *I–V* curves measured at a scanning voltage from −2 to 2 V are shown in Fig. 1*a*, the incident light intensity is 5.11 mWcm^{-2}; the top inset is the scanning electron microscope (SEM) image and the bottom inset is the schematic diagram of the nanophotodetector. The curves shown in Fig. 1*a* with good linearity and symmetrical characteristic reveal that the contacts between NW and the electrodes are good ohmic contacts. Photoconduction is an important parameter which represents the sensitivity of the photodetector. From the data shown in Fig. 1*a*, the photoconduction of nanophotodetectors at incident light with different wavelengths can be estimated as follows: G_{330} = 8.7 nS (incident light wavelength λ = 330 nm), G_{380} = 14.3 nS (λ = 380 nm), G_{430} = 18.7 nS (λ = 430 nm), G_{470} = 20.5 nS (λ = 470 nm), G_{520} = 4.27 nS (λ = 520 nm) and G_{dark} = 0.09 nS (no incident light). The cutoff wavelength is 470 nm according to the measurements; this level is lower than that of the intrinsic ZnSe block materials [19]. The spectral response of the nanophotodetector shown in Fig. 1*b* illustrates the sensitivity of the nanophotodetector. The sensitivity strongly depends on the incident light wavelength, which increases with the increasing wavelength and reaches the maximum value at ∼470 nm, but shows a steep decline in the long wavelength direction. For the wavelength from 470 to 500 nm, the current decreases to <30% of the normalised value. On the other side, the current decreases to 80% when the wavelengths decrease from 470 to 400 nm of the normalised value. The photocurrent results from the photoelectric effect when the nanophotodetector is exposed to light (the wavelength should be lower than the cutoff wavelength), the photon whose energy is higher than the bandgap of ZnSe will transfer the energy to the ZnSe NW, and eject the electron–hole pair (exciton). Under the electric field, the electron–hole pair can be separated and produce a photocurrent. However, the photocurrent resulting from the metastable energy level of the ZnSe NW is lower than that of the interband transition. The performance of the nanophotodetector illustrates that photons with energy near the bandgap of ZnSe are preferentially adsorbed, whereas the photons with energy far away from the bandgap are less adsorbed.

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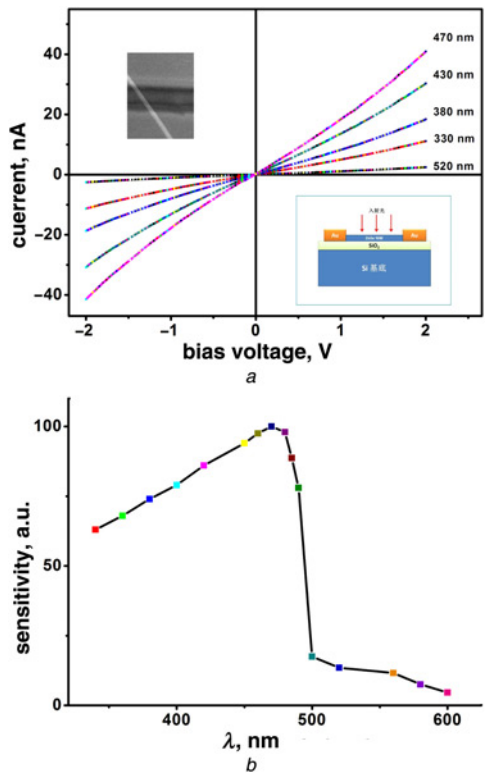

Figure 1 *Response characteristics of ZnSe NWs photodetectors at incident light with different wavelengths*
a *I–V* curves
Top inset is the SEM image; bottom inset is the schematic diagram of the nanophotodetector
b Spectral response of nanophotodetector

The response of the nanophotodetector to the switching frequency is particularly important in lightwave communication and optical switch applications. Fig. 2 shows the response characteristics of ZnSe NW photodetectors at different switching frequencies, the data are normalised to the highest current under light irradiation. For all the switching frequencies shown in Figs. 2*a–c*, the rise rate is always faster than the fall rate, and the ratio of light current to dark current I_{light}/I_{dark} is approximately two orders of magnitude. The rise time τ_r and fall time τ_f at different switching frequencies can be deduced as follows: $\tau_r = 0.52$ ms, $\tau_f = 7.5$ ms (frequency 50 Hz); $\tau_r = 0.36$ ms, $\tau_f = 4.06$ ms (frequency 100 Hz); and $\tau_r = 0.24$ ms, $\tau_f = 2.86$ ms (frequency 200 Hz). Moreover, the nanophotodetectors present excellent stability and reproducibility in a wide frequency range. As shown in Fig. 2*d*, the nanophotodetector functions well for frequency switching upto 200 Hz – the relative balance, 100 $(I_{max}-I_{min})/I_{max}$, is greater than 80%.

The photocurrent of the nanophotodetector also depends strongly on light intensity. Fig. 3 shows the *I–V* curves of the nanophotodetector irradiated with different light intensities. The incident light wavelength is 470 nm, light intensity is 5.11, 3.61, 1.48 $mWcm^{-2}$, respectively. The photoconduction is estimated to be $G_a = 20.5$ nS (5.11 $mWcm^{-2}$), $G_b = 11.7$ nS (3.61 $mWcm^{-2}$) and $G_c = 6.3$ nS (1.48 $mWcm^{-2}$), respectively. It is noted that the photoconduction increases with the increase of incident light intensity.

For the ZnSe compound semiconductors, the electron–hole recombination is a unimolecular process and the recombination rate is proportional to the excess carrier concentration:

$$\frac{d\Delta n}{dt} = g_n - \frac{\Delta n}{\tau_n}$$

where g_n is the growth rate of the photo-induced carrier, n is the concentration of the photo-induced carrier, τ_n is the time constant.

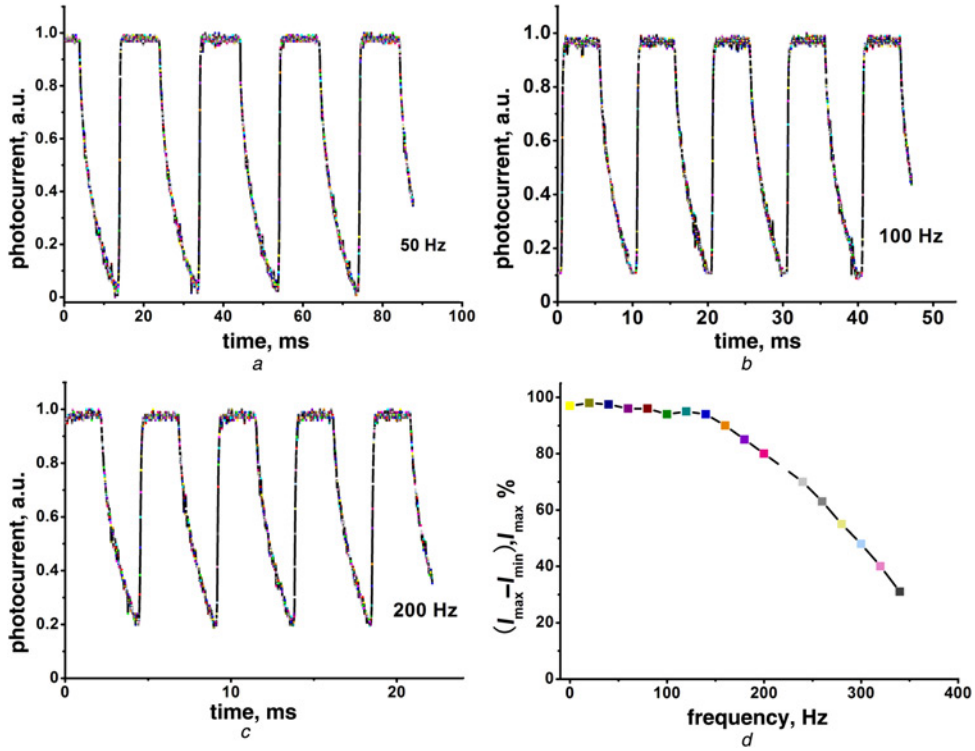

Figure 2 *Response characteristics of ZnSe NWs photodetectors at different switching frequencies*
a 50 Hz
b 100 Hz
c 200 HZ

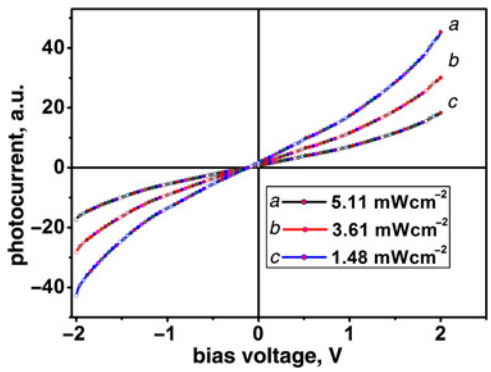

Figure 3 *I–V curves against light intensity of ZnSe NWs photodetectors*

The photocurrent has a certain functional relationship with the rise and fall time [20]

$$I = I_o\left(1 - e^{-t/\pi}\right)$$
$$I = I_o e^{-t/\tau_f}$$

where I is the photocurrent, τ_r is the rise time and τ_f is the fall time. Fig. 4 shows the natural logarithmic plot of the rising and falling edges of the time response spectrum, the wavelength of incident light is 470 nm, and the light intensity is 5.11 mW cm^{-2}. To fit the rising and falling edges by the above equation, respectively, the linear relationship between ln$I$ and t is obtained. It is remarkable that there is a single rise time $\tau_r = 0.6$ ms, but two different fall times $\tau_{f1} = 0.4$ ms, $\tau_{f2} = 8.9$ ms (a fast and a slow decay tail). It is interesting to note that the fall time is larger than the rise time; it is believed that traps and other defect states were also involved in this recombination process. The photogenerated carriers may first fill the traps and then reach the maximum after all the traps are saturated, which induces a delay in reaching the steady photocurrent [20, 21]. On the other hand, two different fall times imply the existence of various traps in the ZnSe NW.

The response characteristics reveal that the rise rate is always much larger than the fall rate at different incident light switching frequency and wavelength, this is attributed to the traps resulting from different energy levels (shallow and deep) in the bandgap which can capture the photocurrent carriers. When the nanophotodetector is exposed to the incident light, the p-type ZnSe NWs will produce non-equilibrium carriers (including non-equilibrium electron and hole). Meanwhile, two quasi-Fermi levels are formed, one is below the conduction band resulting from the electron, and the other is above the valence band resulting from the hole. Two quasi-Fermi levels move towards the conduction band and valence band with increasing light intensity, respectively, and then the amount of recombination centres will increase. In addition, the ZnSe NW has a high specific area; the defects on the NW surface also play an important role in the recombination. Moreover, the Zn vacancy of ZnSe NW resulting from the Se atmosphere compensating effect would become a recombination centre. Hence, in a ZnSe NW photodetector, the frequency response and light intensity response are the result of various factors.

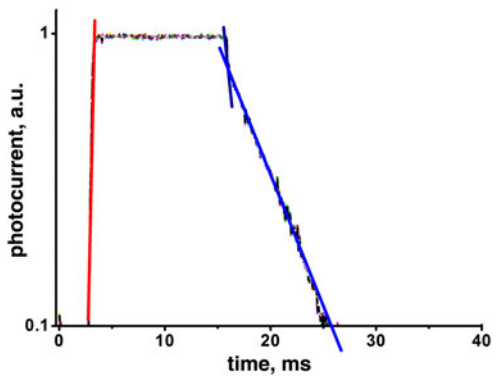

Figure 4 *Natural logarithmic plot of rising and falling edges of time response spectrum*
Straight lines show the fitting results

4. Conclusion: Nanophotodetectors are fabricated based on the p-type ZnSe NW and the photoresponse properties are investigated. The nanophotodetectors present high responsivity, a high light-to-dark current ratio I_{light}/I_{dark} of approximately two orders of magnitude in the cutoff wavelength range, photoconduction of 20.5 nS and fast response speed. The ZnSe NW photodetector with good reliability and reproducibility will have great potential application in electrical and optoelectronic nanodevices.

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