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ARTICLE

High-Performance Blue-Light Photodetectors Based on Single-Crystal ZnSe Nanoribbons with Controlled Gallium Doping

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ABSTRACT

Nano-photodetectors were constructed from *n*-type ZnSe nanoribbons (NRs) with controlled gallium doping, and the device performances were systematically studied. The ZnSe:Ga NR photodetectors show spectral sensitivity in the blue-light range with high photo-to-dark current ratio ($>10^3$) and fast response speed (<0.1 s), which also function with excellent stability and reproducibility. The photoconductivity of the ZnSe NRs is greatly enhanced by Ga doping. The responsivity and photoconductive gain of the ZnSe:Ga NRs have substantially increased compared with the intrinsic ZnSe NRs. It is expected that the ZnSe:Ga NRs will have important applications in the future nano-optoelectronics as high-sensitive blue-light nano-photodetectors.

KEYWORDS: ZnSe Nanoribbons, Gallium Doping, *n*-Type, Blue-Light, Nano-Photodetectors.

1. INTRODUCTION

In the past decade, tremendous efforts have been made to fabricate the one-dimensional (1D) semiconductor nanostructures and study their applications in new-generation nanoelectronic and nano-optoelectronic devices. A variety of nanodevices, including field-effect transistors (FETs),[1] lasers,[2] sensors,[3] and photodetectors[4] have been successfully realized, revealing an exciting progress towards the "bottom-up" electronic and optoelectronic systems with reduced size, higher efficiency, and less energy consumption. As an important optoelectronic device, photodetectors have been widely used in optical switching, light-wave communications, imaging techniques, and memory storage. 1D semiconductor nanostructures are particular suitable for the photodetector applications due to the unique photoconductive characteristics. The main advantages include: (i) spatial resolution in nanoscale. (ii) large photocurrent owing to the single-crystal quality of the nanostructures. (iii) polarization-sensitive light response because of the 1D geometry. (iv) high photoconductive gain due to the surface effect. (v) large surface-to-volume ratio, allowing the enhancement of the photoconductive properties via appropriate surface modification.

ZnSe is an important II–VI compound semiconductor with a wide direct band-gap of ~2.70 eV (~460 nm) at room temperature, which has long been considered as a prospective material for optoelectronic devices.[5–7] It has important applications in light-emitting diodes (LEDs) and laser diodes (LDs) working in the blue-light region, and can also serve as high sensitive blue/UV photodetectors. Although the growth and optical properties of the 1D ZnSe nanostructures have been intensively investigated in the recent years, studies on their photoconductive properties are still very insufficient.[8–12] For the intrinsic ZnSe nanostructures, they may suffer from the poor electrical properties and show weak response to the incident light. In order to overcome this difficulty, doping to the ZnSe nanostructures has been demonstrated to be an efficient method.[13–15] Controlled doping also offers the capability to further modulate the photoconductive properties of the nanostructures. For instance, Cl-doped CdS nanowires (NWs) showed much enhanced photoconductivity,[16] and negative photoconductivity was observed in the Bi-doped *p*-type ZnSe NWs.[17]

Herein, we report the synthesis of *n*-type ZnSe nanoribbons (NRs) by using gallium (Ga) as the donor dopant. Nano-photodetectors based on the *n*-ZnSe NRs exhibit a

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fairly good device performance. They have spectral sensitivity in the blue-light range with large photocurrent, high $I_{\mathrm{light}}/I_{\mathrm{dark}}$ current ratio, as well as fast response speed. The photoconductive gain of the n-ZnSe NR is as high as 1.4×10^{5}, which is the best value obtained for ZnSe nano-photodetectors thus far. Our results demonstrate the great potential of the Ga-doped ZnSe NRs as high-performance blue-light photodetectors.

2. EXPERIMENTAL DETAILS

Synthesis of the Ga-doped ZnSe NRs was conducted in a horizontal tube furnace via chemical vapor deposition (CVD) method. First, ZnSe, Ga, and Ga_2O_3 powders with molar ratio of ZnSe:Ga:Ga_2O_3 = 125:4:1 were fully mixed and milled in an agate bowl, and then the mixture powder was loaded into an alumina boat and transferred to the center region of the tube furnace. Si substrates, which were ultrasonically cleaned and coated with 10 nm gold catalyst, were placed in the downstream position of the ZnSe source with 10 cm distance. The system was evacuated to a base pressure of 10^{-3} Pa, and backfilled with 30 sccm H_2 (5% in Ar) to a pressure of 10 Torr. Thereafter, the furnace was heated up to 1040 °C at a rate of 20 °C min^{-1}, and maintained at this temperature for 2 h. A layer of yellow wool-like product was observed on the silicon substrates after the growth. Undoped ZnSe NRs were also synthesized under the same conditions for comparison except that no Ga source was used. As-synthesized Ga-doped ZnSe NRs were characterized by X-ray diffraction (XRD, Rigaku D/Max-rB) with Cu Kα radiation ($\lambda = 1.54178$ Å), field-emission scanning electron microscopy (FE-SEM, Sirion 200 FEG) equipped with energy-dispersive X-ray spectroscopy (EDX), and high-resolution transmission electron microscopy (HRTEM, Philips CM200 FEG).

To fabricate the nano-FETs from individual ZnSe:Ga NRs, the as-synthesized ZnSe:Ga NRs were first dispersed on a SiO_2 (300 nm)/p^+–Si substrate with desired density, in which the SiO_2 insulator and the degenerated Si substrate serve as the gate dielectric and the global back-gate, respectively. Afterward, 50 nm indium tin oxide (ITO) transparent electrodes were deposited on the NRs by a pulsed laser deposition (PLD) system with KrF excimer laser (Lambda Physik COMPexPro 102, 248 nm, 120 mJ, 5 Hz) under the assistance of a shadow mask that consisted of 5 μm thick tungsten wires. The electrical transport characteristics of the ZnSe:Ga NRs were measured by using a Keithley 4200 semiconductor characterization system on a probe station. To assess the photoconductive properties of the ZnSe:Ga NRs, monochromatic light from a source that composed of a xenon lamp (150 W) and a monochrometer (Omni-λ300) was guided and focused onto the NRs perpendicularly. The light was turn ON/OFF manually to detect the time response of the ZnSe NRs nano-photodetectors.

3. RESULTS AND DISCUSSION

Figure 1(a) shows the typical SEM image of the as-synthesized ZnSe:Ga NRs, indicating that the NRs have smooth surfaces and uniform morphology. The width and thickness of the NRs are in the range of 0.8–1 μm and 60–80 nm, respectively. And the typical length of the NRs is about 80–100 μm. Besides the Zn and Se elements, EDX result also reveals the presence of trace Ga in the sample (Fig. 1(b)). In the XRD pattern (Fig. 1(c)), only the diffraction peaks come from cubic ZnSe (JCPDS 37-1463) are investigated. HRTEM image and the corresponding selected-area electron diffraction (SAED) pattern indicate that the ZnSe NRs are cubic single crystals with growth orientation along $[-11\ -1]$ (Fig. 1(d)). These results demonstrate that high-quality Ga-doped ZnSe NRs are obtained, and the crystalline quality and structural integrity of the ZnSe NRs are not seriously degraded by Ga incorporation.

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ZnSe:Ga NR FETs were measured to further evaluate their transport properties, as shown in Figure 2. To avoid the impact of the incident light, all the measurements were performed in dark. From the typical source-drain current (I_{DS}) versus source–drain voltage (V_{DS}) curves measured at varied gate voltages (V_G) from −5 to +20 V in a step of +5 V (Fig. 2(a)), it is found that the device shows evident gate effect, that is, I_{DS} increases monotonously with the increasing of V_G. Such a gate-dependent device characteristic is in well agreement with the feature of a typical n-channel metal-oxide-semiconductor FET (MOSFET),[18] indicating that the n-type ZnSe NRs were obtained due to Ga doping. Moreover, the electron mobility (μ_e) of the ZnSe:Ga NRs can be estimated from the channel transconductance (g_m) of the NR FET according to the equation $g_m = \partial I_{\mathrm{DS}}/\partial V_G = (Z/L)\mu_e C_o V_{\mathrm{DS}}$ in the linear regime of

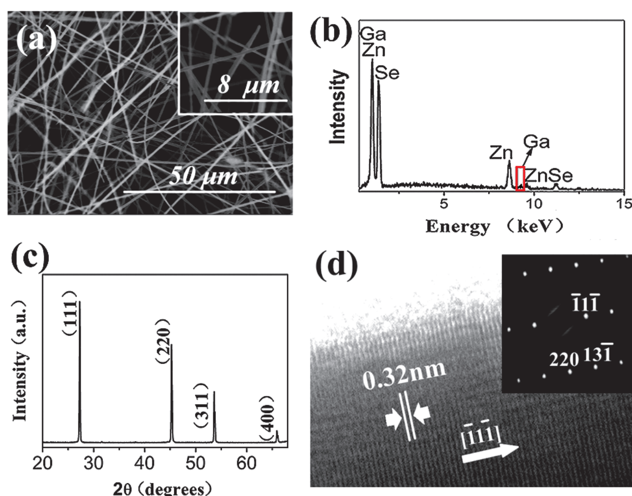

Fig. 1. Characterizations of the ZnSe:Ga NRs. (a) SEM image. Inset shows the enlarged SEM image. (b) EDS spectrum. (c) XRD pattern. (d) HRTEM image. Inset shows the corresponding SAED pattern.

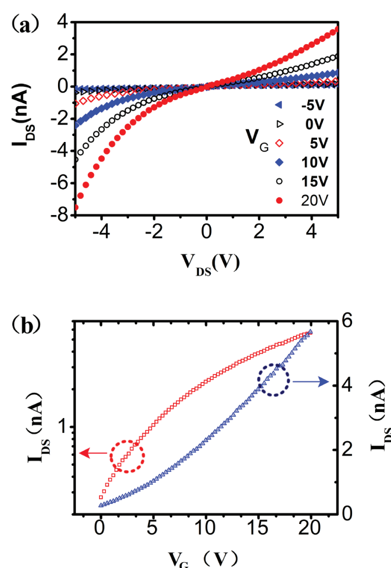

Fig. 2. Electrical transfer characteristics of the ZnSe:Ga NR FET. (a) I_{DS}–V_{DS} curves with varied V_G increased from −5 to +20 V in a step of +5 V. (b) I_{DS}–V_{GS} curve measured at V_{DS} = +5 V.

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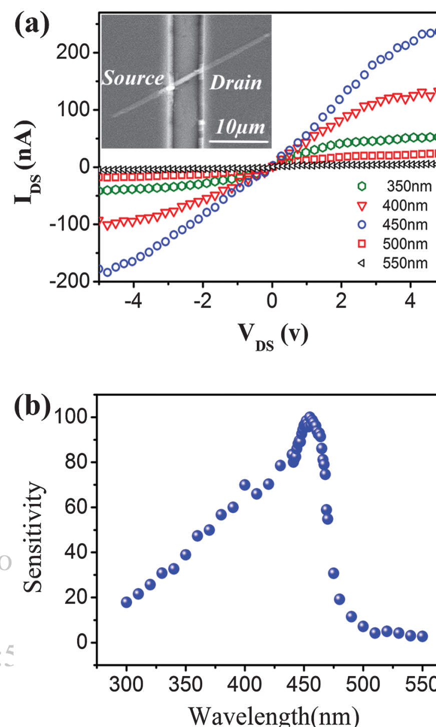

Fig. 3. Photoconductive characteristics of the ZnSe:Ga NRs. (a) I_{DS}–V_{DS} curves illuminated by monochromatic light with varied wavelength. (b) Spectral response of the NR measured at a constant light intensity of ~72 μW cm^{-2} at V_{DS} = +5 V.

the I_{DS}–V_G curves (Fig. 2(b)), where Z/L is the width-to-length ratio of the NR channel.[19] The capacitance per unit area is given by $C_o = \varepsilon\varepsilon_o/h$, where ε is the dielectric constant (~3.9 for SiO_2) and h is the thickness of the SiO_2 dielectric layer. Based on the above equations, $\mu_e \approx 0.12$ cm^{2}V^{-1}s^{-1} can be obtained. And the electron concentration n_e can be deduced to be $\sim 1.29 \times 10^{16}$ cm^{-3} via the relationship of $n_e = \sigma/(\mu_e q)$, where $\sigma = 1 \times 10^{-4}$ Scm^{-1} is the conductivity of the ZnSe:Ga NR at $V_G = 0$ V. It is noted that the conductivity of the ZnSe:Ga NRs has been dramatically enhanced as compared with the undoped ones, which only have the value lower than 4×10^{-8} Scm^{-1}.

Owing to the appropriate band-gap, ZnSe NRs are expected to function as high-performance nano-photodetectors for short wavelength light detection, particular for the blue-light detection. Figure 3(a) depicts the typical I–V curves obtained when the ZnSe:Ga NR was exposed to the monochromatic light with varied wavelength (λ) at a constant light intensity of ~72 μWcm^{-2}. The approximately linear shape of the curves reveals the good ohmic contact of the NR with the ITO electrodes. It is seen that the conductance of the ZnSe NR is very low upon the 550 nm light illumination, while it gradually increases with the decreasing of the light wavelength and reaches the maximum at 450 nm. However, the further shortening of the light wavelength results in the decrease of the NR conductance. This tendency could be clearly observed in the spectral response of the ZnSe:Ga NR (Fig. 3(b)). The sensitivity of the ZnSe NR photodetector is rather low ($<5\%$) for the wavelength longer than 500 nm. In contrast, when the wavelength is shorter than 500 nm, the sensitivity increases steeply and reaches a maximum at blue-light region (450–460 nm). A decline in the sensitivity is observed for the wavelength less than 450 nm. Nevertheless, the sensitivity at 300 nm is still near 20%, indicating that the ZnSe:Ga NR photodetector can function well with detection range spanning from blue to UV light. Based on the response spectrum of the ZnSe NR, we can conclude that the enhancement of the photoconductive sensitivity is due to the excess carriers (electron–hole pairs) generated by the incident light with energy larger than the band-gap of ZnSe.[20] Light with smaller energy can not excite the electrons to the conduction band thus contributes little to the photocurrent. For the light with shorter wavelength, the surface recombination will become more serious, leading to the reduction of the photocurrent.

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The photoconductance of the ZnSe:Ga NRs also depends on the light intensity as well. Figure 4(a) depicts the I–V curves of the ZnSe:Ga NR irradiated with the 460 nm light at varied light intensity. It is seen that the NR photoconductance increases with the increasing of the light intensity, revealing a near linear relationship between the photocurrent and the light intensity (inset in Fig. 4(a)). Time response spectra of the NR photodetector to pulsed light indicate the excellent stability and reproducibility of the device (Figs. 4(b and c)). The conductance of the ZnSe:Ga NR increases by about 3 orders of magnitude from 5×10^{-11} S in the dark to 4.2×10^{-8} S at the light intensity of 70 μW/cm^2 (Fig. 4(c)). In contrast, the undoped ZnSe NR has a much lower I_{light}/I_{dark}

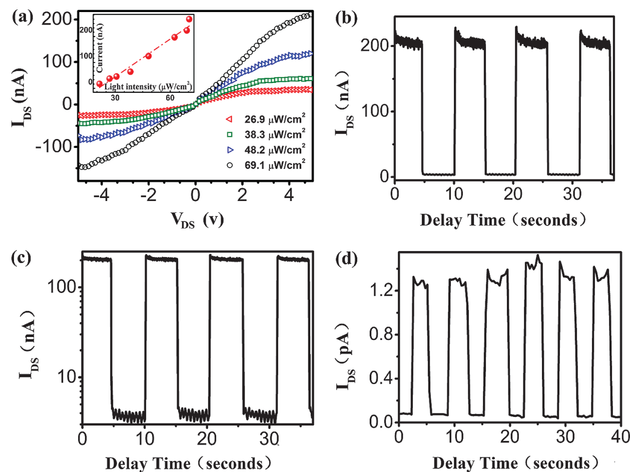

Fig. 4. Intensity and time response of the ZnSe:Ga NRs. (a) I_{DS}–V_{DS} curves measured at varied light intensity under the illumination of 460 nm light. Inset shows the photocurrent as a function of the light intensity. (b) Time response to the pulsed 460 nm light at $V_{DS} = +5$ V. (c) Logarithmic plot of the time response spectrum. (d) Time response spectrum of the undoped ZnSe NR for comparison.

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ratio of ~15. Also, the ZnSe:Ga NR exhibit a fast response to the pulsed light with both the rise time and the fall time less than 0.1 S. This value is comparable or even shorter than that of the undoped ZnSe NR (Fig. 4(d)).

Responsivity (R) is an important parameter that reflects the electrical output per optical input of a photodetector. R is defined as $R(AW^{-1}) = I_P/P_{\rm opt} = \eta(q\lambda/hc)G$, where I_P, $P_{\rm opt}$, η, λ, h, c and G are photocurrent, incident light power, quantum efficiency, light wavelength, Planck's constant, light speed, and photoconductive gain, respectively.[18] Based on this equation, R is estimated to be 5×10^4 AW^{-1} for the ZnSe:Ga NR at $V_{DS} = 5$ V by assuming $\eta = 1$ for simplify, while a much smaller value of ~1.3 AW^{-1} is obtained for the undoped ZnSe NR. In addition, G has also increased from ~3.4 for the undoped ZnSe NR to 1.4×10^5 for the ZnSe:Ga NR. Such a result suggests that an large internal gain exists in the ZnSe:Ga NR photodetectors.[21] We note that the R and G values of the ZnSe:Ga NRs in this work represent the best values obtained for the ZnSe nano-photodetectors thus far, and are also comparable with the previous reports on ZnO and GaN nano-photodetectors.

From above results, it is seen that the Ga doping plays an important role in determining the photoconductive properties of the ZnSe NRs. The high carrier concentration in the ZnSe:Ga NRs results in the improvement of the electrical contact and thus contributes to the large photocurrent. In addition, owing to the existence of the surface states, the energy band near the ZnSe NR surface will bend upwards, facilitating the separation of the photo-generated electron–hole pairs. As a result, the recombination of the electron–hole pairs is reduced. On the other hand, Ga donors in the ZnSe NR will serve as the trapping centers for the minority carriers, i.e., the holes, leading to the prolongation of the carrier (electron) lifetime. Above factors explain the large photocurrent as well as the high photoconducive gain observed for the ZnSe:Ga NRs. In previous work, it is found that the doping resulted surface/bulk defects might be an unfavorable fact that decreases the response speed through trapping (releasing) the photocarriers under light illumination (in dark).[22] However, we demonstrate here that a high response speed also could be achieved in the ZnSe:Ga NRs by carefully controlling the doping level. The modest Ga doping will be of benefit to the enhancement of the photoconductivity but not cause the degradation of the response speed.

4. CONCLUSION

In summary, we report the high-performance blue-light nano-photodetectors fabricated from the single-crystal ZnSe NRs with controlled Ga doping. The n-type ZnSe:Ga NRs have carrier concentration of $\sim1.29\times10^{16}$ cm^{-3}, and electron mobility ~0.12 cm^2 V^{-1} s^{-1}. The ZnSe:Ga NR photodetectors show spectral sensitivity in the blue-light range with high response speed (<0.1 s) and a high photo-to-dark current ratio ($>10^3$), as well as excellent stability and reproducibility. The photoconductivity of the ZnSe NRs is greatly enhanced by Ga doping. As a result, the responsivity and photoconductive gain of the ZnSe:Ga NRs are as high as 4.96×10^4 AW^{-1} and $1.34\times10,^5$ respectively. It is expected that the high-performance ZnSe:Ga NR blue-light photodetectors will have important applications in the nano-optoelectronic devices.

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