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Construction of high-quality CdSe NB/graphene Schottky diodes for optoelectronic applications

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ABSTRACT

High-quality CdSe nanobelts (NBs) and monolayer graphene were synthesized *via* a chemical vapor deposition (CVD) method. Schottky diodes based on CdSe NBs/graphene have been fabricated and investigated. The as-fabricated Schottky diodes exhibit excellent rectification characteristic with rectification ratio up to 10^3 within ± 2 V in the dark and distinctive photoresponse to light switching between on and off. Further analysis reveals that the Schottky diodes were highly sensitive to light illumination with very good stability, reproducibility and fast response speeds of 47/122 μs. Our results suggest that CdSe NBs/graphene Schottky diodes have potential future application in integrated nano-optoelectronic systems.

1. Introduction

As one of the most important II–VI group semiconductor with a direct band-gap of 1.7 eV at 300 K, CdSe nanostructures have been intensively studied in the past decades due to its promising optical and electrical properties. They are good candidates for the building blocks of functional nano-devices such as field-effect transistors (FETs) [1,2], photodetectors (PDs) [3,4], light-emitting diodes (LEDs) [5,6], photovoltaic (PV) devices [7,8] and so on. Graphene, a single atomic layer of carbon, has become one of the most exciting topics of research interest since its discovery in 2004. Its important physical properties, such as high carrier mobility and conductivity, high transparency, mechanical flexibility and environmental stability, have made graphene a promising material for next-generation electronic and optoelectronic devices [9–11].

Herein, we report synthesis of single-crystal CdSe NBs and monolayer graphene *via* the chemical vapor deposition (CVD) method, and a simple method for constructing CdSe NB/graphene Schottky diodes. The devices exhibit excellent rectification characteristic in the dark and obvious photoresponse to light switching between on and off with good stability, reproducibility and fast response speeds.

2. Experimental

CdSe NBs and monolayer graphene synthesis and characterization: Both CdSe NBs and monolayer graphene used in this work were synthesized *via* the CVD method [8,12]. The undoped CdSe nanomaterials are highly insulative semiconductors with very low conduction. For increasing the conductance of CdSe NBs, CdSe (99.99%) and Cd (99.99%) mixture powders were used as the source, placing at the center region of the furnace and a Si substrate covered with 10 nm Au catalysts were used as the substrates which was placed at the downstream position to collect product. The source was heated up to 880 °C and kept for two hours under pressure of 150 Torr. The monolayer graphene was prepared at 1000 °C by using a mixed gas of CH_4 (40 SCCM) and H_2 (20 SCCM) in a tube furnace, and Cu foil was employed as the catalytic substrate. After growth, the graphene were spin-coated with polymethylmethacrylate (PMMA), and the underlying Cu foils were removed in $FeCl_3$ solution. To construct the devices, the PMMA-supported graphene was directly transferred onto the top of Si/SiO_2 substrate. After that, PMMA was removed by acetone.

Morphologies and structures of the as-synthesized CdSe NBs were characterized by X-ray diffraction with Cu Kα radiation (XRD, D/max-rB), field-emission scanning electron microscopy (FESEM, SIRION200, FEI, at 5 kV) equipped with an energy-dispersive X-ray (EDX) spectroscope and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010, at 200 kV), as shown in Fig. 1. Raman spectra of monolayer graphene were collected by microzone confocal Raman spectroscopy (Jobin Yvon, LABRAMHR).

Devices construction: To construct the CdSe NB/graphene Schottky diodes, photolithography and magnetron sputtering were performed to define Si_3N_4 (100 nm) insulating pads on graphene/SiO_2/Si substrate. CdSe NBs were dispersed on the substrates. Ohmic contacts electrodes (In, 100 nm) to CdSe NBs were fabricated on the Si_3N_4 pads by additional photolithography and lift-off

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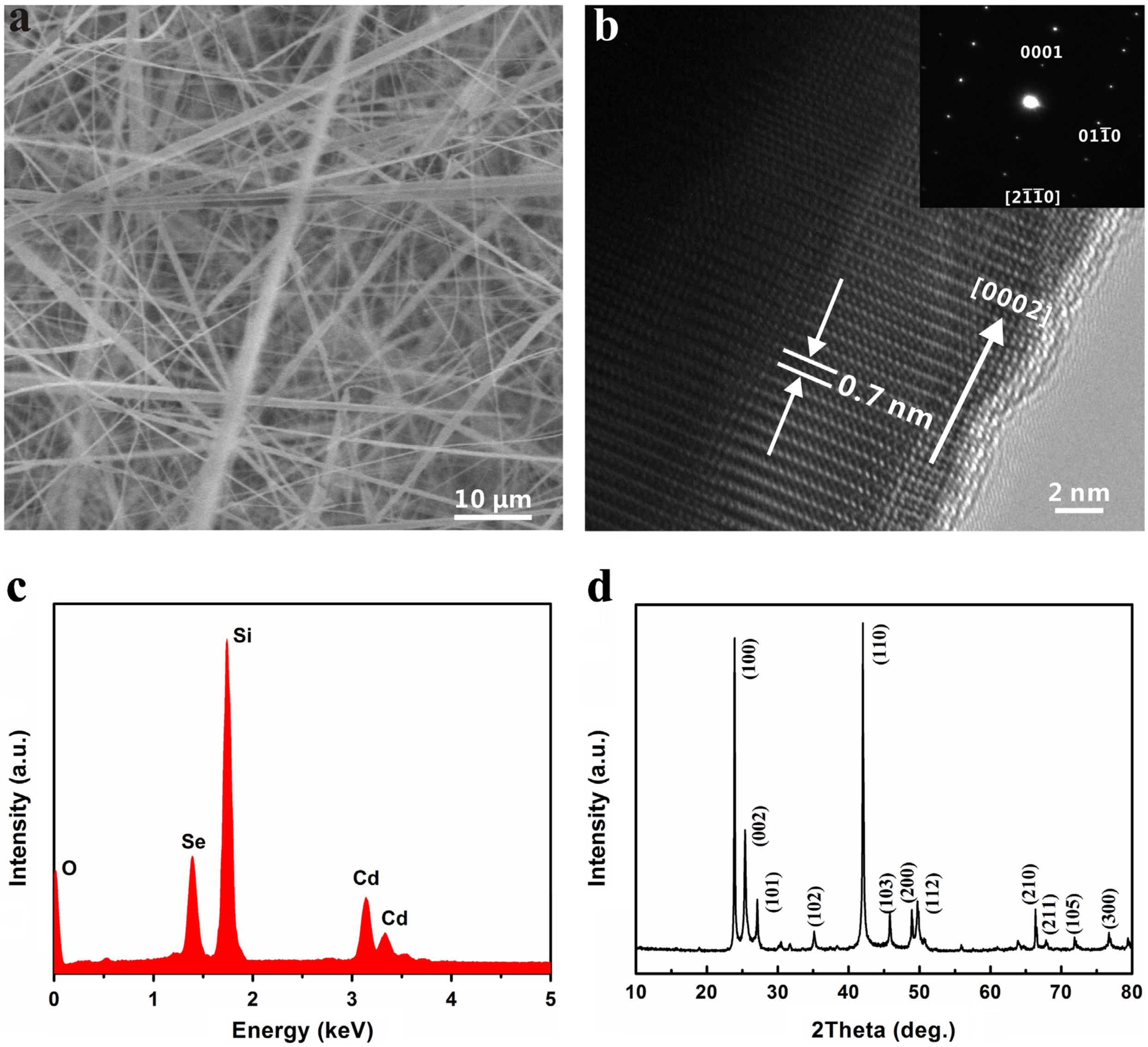

Fig. 1. (a) SEM image, (b) HRTEM image, (c) the EDX spectrum and (d) XRD patterns of CdSe NBs. Insets in (b) show the SAED pattern.

processes. Au electrodes on graphene film were fabricated at last. The SEM of a typical device is shown in inset of Fig. 3a. The electrical transport measurements were carried out with a semiconductor characterization system (Agilent 4155C). The photoresponse characteristics were analyzed by using a system that combines a xenon lamp source, an oscilloscope and a mechanical chopper.

3. Results and discussion

Characterization of CdSe NBs and graphene: Fig. 1a shows a typical SEM image of CdSe NBs. It is seen that the product is clean, uniform and free of evident impurities and particles. The NBs have width in the range of 0.5–2 μm and length of tens of micrometers. HRTEM image and the corresponding selected-area electron diffraction (SAED) pattern recorded from a single NB is shown in Fig. 1b, indicating that CdSe NB is hexagonal wurtzite structure with [0002] growth orientation. The EDX spectrum taken from the CdSe NBs is shown in Fig. 1c. It consists of Cd and Se signals with an atomic ratio ~52:48. In the XRD patterns of the CdSe NBs (Fig. 1d), all the diffraction peaks can be assigned to hexagonal wurtzite CdSe (JCPDS 77-2307) and no obvious impurity phases and peak shift are observed or detected suggesting a single phase of the product.

Fig. 2 shows the Raman spectrum of the monolayer graphene transferred onto a Si/SiO_2 substrate. Two peaks at 1582 cm^{-1} (G) and 2682 cm^{-1} (2D) can be observed clearly. The ratio of 2D to G peak intensity is ~2.1, indicating the formation of monolayer graphene. Besides, no defect-related D-band peak (~1350 cm^{-1}) was detected, indicating the high quality of the graphene film. The typical sheet resistance of the graphenes is about 350 Ω/□.

Performances characterization of CdSe NB/graphene Schottky diodes: Fig. 3a depicts the typical *I–V* characteristics of the CdSe NB/graphene Schottky diode measured in the dark, revealing an excellent rectification characteristic of the device with a rectification ratio up to 10^3 within ± 2 V. From the curve, a low turn-on voltage of ~1 V can be deduced at the forward bias direction. For an ideal diode, the rectification curve can be expressed as $I_{DS}=I_0[\exp(qV/nkT)-1]$. Hence, the ideality factor n can be described as $n=(q/kT)(dV/d\ln I)$, where I_0 is the reverse bias leakage current, k and T are the Boltzmann's constant and Kelvin temperature, respectively. The ideality factor is determined to be 1.24 at low voltage by fitting the measured *I–V* curve in above equation

[13,14]. It is close to the value of an ideal Schottky junction ($n=1$), indicating that a good Schottky contact has been formed between CdSe NB and graphene film.

Fig. 3b shows the *I–V* curves of the diode in dark and under light irradiation. The current became strong both at forward and reverse under light irradiation, indicating that the diode can function as a visible light photodetector. Photoresponse at positive bias (+1.5 V) and reverse bias (−1.5 V) are shown in Fig. 3c and d, respectively, both of them show the reversible switching between high and low conductance, when light illumination with intensity of ~0.6 mW/cm^2 was turned on and off. The I_{on}/I_{off} ratio can be obtained to be ~1.6 for positive bias (+1.5 V) and ~10^2 for reverse bias (−1.5 V). Responsivity (R) and photoconductivity gain (G) for a photodetector can be estimated according to the relation: $R=I_p/P_{opt}=\eta(q\lambda/hc)G$, where I_p is the photocurrent, P_{opt} the incident light power, η the quantum efficiency, h is Planck's constant, λ is the light wavelength and c is the light speed. Hence, R and G were estimated to be 6.67×10^3 A/W and 1.76×10^4 A/W at positive bias, and 9.17×10^2 A/W and 2.42×10^3 A/W at reverse bias, respectively.

The response speed of a photodetector determines its capability of following a fast-varying optical signal, which is particularly important in light-wave communication and optical-switch applications[15]. It is worth noting that the device has a fast response speed of less than one second at reverse bias, while a response speed of several seconds at positive bias has been illustrated in Fig. 3c and d. For further evaluating the natural response speed of the device, the photoresponse of the device at reverse bias was

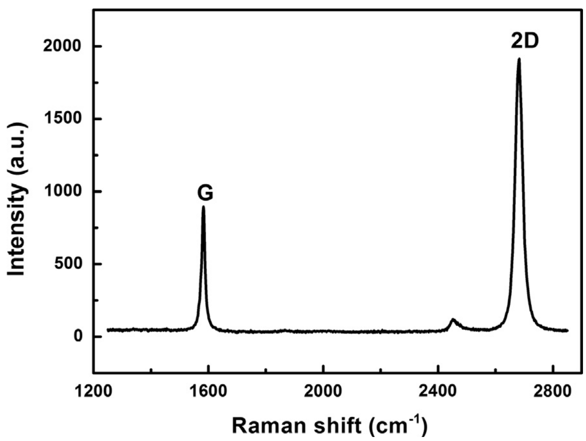

Fig. 2. Raman spectrum of monolayer graphene on Si/SiO$_2$ substrate.

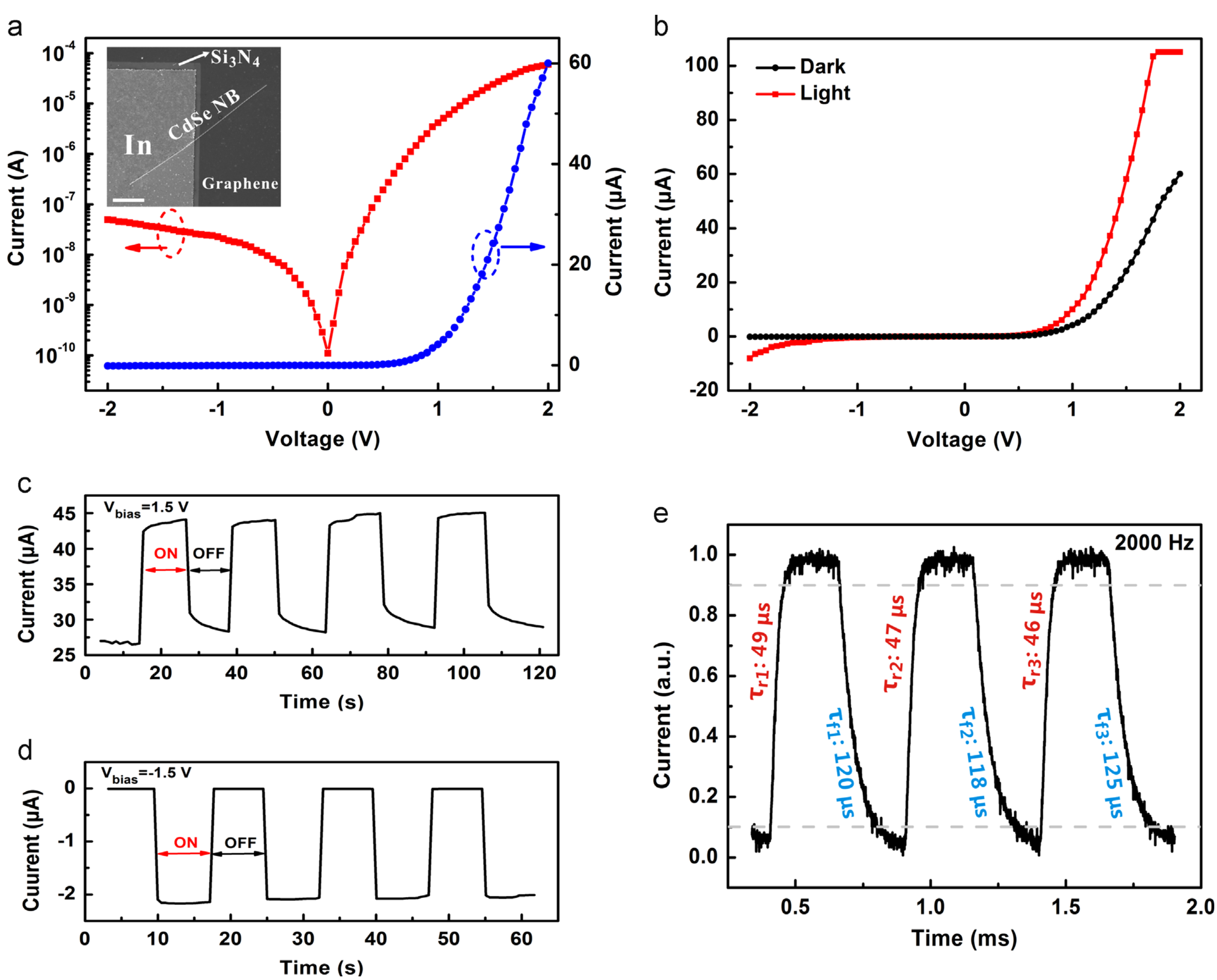

Fig. 3. (a) *I–V* curves of CdSe NB/graphene Schottky diode; inset shows a SEM image of the device. (b) *I–V* curves of Schottky diode in dark (black) and in light irradiation (red). Photoresponse at (c) positive bias and (d) reverse bias. (e) Photoresponse characteristics to pulsed light irradiation at a frequency of 2000 Hz with bias voltage of −1.5 V.

Table 1
Summary of the performances of CdSe NB/NW photodetectors.

Devices	Response speed	Responsivity(A/W)	Gain	Ref.
CdSe NB/graphene	47/122 μs	6.67×10^3	1.76×10^4	This work
CdSe NB	639/5680 μs	$\sim 3 \times 10^3$	$\sim 5.7 \times 10^3$	[15]
CdSe NW	~1/10 s	$\sim 10^5$	$\sim 10^6$	[17]
CdSe NB/Au	26/50 μs	5	13.2	[16]
CdSe NB/graphene	82/179 μs	10.2	28	[18]

studied by modulating the incident light with a mechanical chopper. Fig. 3e shows the photoresponse characteristics to pulsed light irradiation with intensity of ~50 mW/cm^2 at a frequency of 2000 Hz, which indicate a very fast speed to light switching. The speed is often characterized by the rise time (τ_r) and the fall time (τ_f) of its response to a pulse signal, which is defined as the time interval for the response to rise (or fall) from 10 to 90% (or 90 to 10%) of its peak value. The τ_r and τ_f were deduced to be 45–52 μs with an average value of 47 μs and 114–128 μs with an average value of 122 μs, respectively, according to more than 20 cycles statistics. The high-performance of the CdSe NB/graphene devices are believed to be associated with the high crystalline quality, appropriate doping concentration of the CdSe NBs, low surface-state density, and high-quality Schottky junction between the CdSe NB and graphene film [16]. Table 1 summarizes the performances of CdSe NW/NR photodetectors. It is worth noting that the devices in this work show robust performances close or superior to the previous results.

4. Conclusion

In summary, high-quality CdSe NBs and monolayer graphene film were synthesized *via* CVD method. Photodetectors based on CdSe NB/graphene film Schottky diodes were constructed and investigated. The Schottky diodes exhibit excellent rectification characteristic and such photodetectors exhibit high responsivity and gain, as well as a fast photoresponse speed. Our work demonstrates that the photodetector based on CdSe NB/graphene Schottky junctions have great potential opportunities for future flexible transparent nano-optoelectronic device applications.

Acknowledgments

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