



# ZnSe nanoribbon-Si nanowire crossed p-n nano-heterojunctions: Electrical characterizations and photovoltaic applications

Xiwei Zhang<sup>a,\*</sup>, Di Wu<sup>b</sup>, Dan Hu<sup>a</sup>, Zhenjie Tang<sup>a</sup>, Huijuan Geng<sup>a</sup>, Junlong Tian<sup>a</sup>, Jiansheng Jie<sup>c,\*</sup>

<sup>a</sup> College of physics and electrical engineering, Anyang Normal University, Anyang, Henan 455000, PR China

<sup>b</sup> Department of Physics and Engineering, and Key Laboratory of Material Physics, Zhengzhou University, Zhengzhou, Henan 450052, PR China

<sup>c</sup> Institute of Functional Nano & Soft Materials (FUNSOM) & Collaborative Innovation Center of Suzhou Nano Science and Technology, Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou, Jiangsu 215123, PR China

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## ABSTRACT

p-type ZnSe nanoribbon and n-type Si nanowire are used to prepare crossed p-n nano-heterojunction through a two step of contact sliding transfer method. Obvious diode characteristics with a large rectification ratio of  $\sim 20$  and a small ideality factor of  $\sim 2.1$  are presented due to the nano-heterojunction's half-surrounded structure and the appropriate energy band alignment between the two materials. Kelvin probe force microscopy measurement and temperature-dependent electrical characterization are devoted to demonstrate the energy barrier and investigate the transport mechanism of the nano-heterojunction. Moreover, under AM 1.5G light illumination, the crossed nano-heterojunction exhibits evident photovoltaic behavior, yielding a power conversion efficiency of  $\sim 3\%$ . Our results demonstrate the great potential of the prepared crossed nano-heterojunction in high-performance nano-device applications.

## 1. Introduction

P-n junction is considered as core element for modern electronic devices. For nanoscale p-n junction, superior electronic and optoelectronic properties are achieved due to their advantages in terms of less interface defects, atomic-sharp interface and higher carrier injection efficiency [1], thus opening the opportunities for the next-generation electronic and optoelectronic devices with high integration, high speed but low power consumption [2]. Therefore, designing and fabricating nanoscale p-n junction have excited a great deal of interests across the world and a host of nano-devices, such as solar cells, photodetectors and light emitting diodes (LEDs) have been realized based on nanoscale p-n junction [3–5]. For example, solar cells with excellent performances were realized in CdS–Cu<sub>2</sub>S NW radial p–n junction [6], p-ZnSe/n-CdS core–shell heterojunctions [7] and CdSe/ZnTe type II core–shell nanowires [8]; High-sensitivity and self-driven photodetectors with broadband light response from visible to infrared light were prepared by Ge–CdS core–shell heterojunction nanowires via atomic layer deposition [9]; High-performance ultraviolet photodetectors were prepared based on ZnO/GaN nanoscale p-n junctions [10]; High-efficiency color tunable light-emitting diodes were successfully fabricated by n-CdS<sub>x</sub>Se<sub>1-x</sub>/p<sup>+</sup>-Si parallel-nanobelts heterojunctions [11]. What's more, nonvolatile resistance switching memory devices with high resistance

on/off ratio, long retention time and low operating voltage were achieved by n-CdSe nanoribbon/p-Si heterojunctions [12]. In spite of this progress, the practical applications of the nanoscale p-n junctions are still hampered by the difficulty in their preparation because of complicated multistep preparation process [13,14]. Therefore, preparation strategies with facile method should be developed for their more extensive applications in the future.

As representative direct band-gap II-VI group semiconductor, ZnSe has attracted a great deal of attentions because it can offer extensive applications in optoelectronic devices [15,16]. Recently, ZnSe nanostructures have received many attentions and their synthesis and optical properties have been intensively studied [17,18]. At the same time, p-n nano-heterojunctions based on ZnSe nanostructures have shown the great promise for realizing high performance devices. For instance, high performance solar cells were fabricated by ZnSe nanoribbon/Si nanowire p–n heterojunction arrays and a kind of nanoscale p–n junction were constructed by directly transferring the p-ZnSe nanowires onto a SiO<sub>2</sub>/n-Si substrate with pre-defined Si patterns [19,20]; Photodetector with high sensitivity to ultraviolet light irradiation and fast response time was achieved by p-ZnSe:Sb nanowire/n-ZnO:Ga nanowire junction [21]. Although p-n nano-heterojunctions based on ZnSe nanostructures have achieved several promising applications, their electrical transport properties have not been adequately addressed, particularly their

\* Corresponding authors.

E-mail addresses: [xwezhang@outlook.com](mailto:xwezhang@outlook.com) (X. Zhang), [jsjie@suda.edu.cn](mailto:jsjie@suda.edu.cn) (J. Jie).

temperature-dependent behaviors which can investigate the transport mechanism of heterojunctions. Therefore, the electrical study is essential and will be helpful to further develop these nanoscale p-n junctions to be integrated into mainstream electronics.

Herein, p-type ZnSe nanoribbons (ZnSeNRs) and n-type silicon nanowires (SiNWs) are used to prepare crossed p-n nano-heterojunctions through a facile two step of contact sliding transfer method. Significantly, the prepared ZnSeNR-SiNW crossed p-n nano-heterojunctions present obvious diode characteristics due to their half-surrounded structures and the appropriate energy band alignment between the two materials. Kelvin probe force microscopy measurement is devoted to demonstrate the energy barrier between ZnSeNR and SiNW. Furthermore, temperature-dependent electrical characterization is used to investigate the transport mechanism of the heterojunction based on the thermionic emission (TE) model. It is found that the energy barrier height increases from 0.18 to 0.56 eV as the temperature rises from 90 K to 300 K. On the other hand, the crossed nano-heterojunction exhibits evident photovoltaic behavior under AM 1.5G light illumination, yielding a power conversion efficiency of ~3%.

## 2. Experimental details

### 2.1. Synthesis of p-type ZnSeNRs and n-type SiNWs

p-type ZnSeNRs were synthesized by using ZnSe powder (99.999%, Aldrich) and  $\text{NH}_3$  gas as the source material and N-dopant source in a horizontal alumina tube furnace through thermal evaporation method. In a typical experiment, ZnSe powder was loaded into an alumina boat and silicon substrates coated with 10 nm Au catalyst were placed at the downstream position with ~10 cm away from the ZnSe source. The reaction chamber was evacuated and then filled with  $\text{Ar}/\text{H}_2$  ( $\text{H}_2$ , 5% in volume), and  $\text{NH}_3$  gas mixture at a constant flow rate of 96 SCCM and 4 SCCM, respectively. The gas pressure in the tube was maintained at 200 Torr and the ZnSe powder was heated at 1040 °C during the whole growth process. After a growth duration of 1.5 h, a layer of yellow products as the synthesized ZnSeNRs could be observed on the Si substrates surfaces. Characterizations of N-doped p-type ZnSe nanostructures were shown in our previous paper and their p-type conduction was confirmed by a bottom-gate metal-oxide-semiconductor field effect transistor (MOSFET) based on single ZnSe nanostructure [2].

Phosphorus doped n-type SiNWs were synthesized by chemical vapor deposition (CVD) through vapor-liquid-solid (VLS) growth method [22]. Si substrates covered with 10 nm Au film were put into the tube chamber before it was evacuated to a base pressure of  $\sim 3 \times 10^{-3}$  Pa.  $\text{SiH}_4$  (10% in  $\text{H}_2$ , 60 sccm) and  $\text{H}_2$  (40 sccm) mixed gas was used as reaction gas and  $\text{PH}_3$  (1% in  $\text{H}_2$ , 10 sccm) was used dopant gas. During the growth process, the substrates were heated up to 580 °C and then maintained at the temperature for 1 h. A layer of yellowish-brown products of the as-synthesized SiNWs could be obtained on the substrate.

### 2.2. Preparation and characterization of ZnSeNR-SiNW crossed p-n nano-heterojunctions

In order to prepare ZnSeNR-SiNW crossed p-n nano-heterojunctions, the as-synthesized n-type SiNWs were first transferred from the growth substrate to  $\text{Si}/\text{SiO}_2$  substrate in a uniform direction by contact sliding transfer method, as shown in Fig. 1a. Then, Ti (50 nm) was deposited by photolithography and magnetron sputtering system (Kurt J Lesker Company, PVD 75) and served as the Ohmic contact to n-type SiNW (Fig. 1b). Secondly, ZnSeNRs were transferred in perpendicular direction by using the same transfer method and Au (50 nm) electrodes were deposited on the two ends of ZnSeNR for Ohmic contact (Fig. 1c and d). The electrical and optoelectronic characteristics of the heterojunction were measured by a semiconductor characterization system (Keithley 4200-SCS). Temperature-dependent electrical measurements were

carried out by using a low-temperature probe station (Lake Shore, CRX-4K/CRTTF6). To measure the photovoltaic properties of the nano-heterojunction, a solar simulator (Zolix-SolarIV-150) with a calibrated illumination power density of  $100 \text{ mW cm}^{-2}$  was used as the light source.

## 3. Results and discussion

The fabricated nano-heterojunction is presented in Fig. 2a. The SEM image shows that Si nanowire contacts with Ti electrodes at its ends while contacts with a perpendicular ZnSe nanoribbon in its middle. The inset in Fig. 2a shows the enlarged SEM image of the crossed nano-heterojunction. It should be noted that Si nanowire is covered by ZnSe nanoribbon in the contact area, which could be considered as a kind of half-surrounded structure. This structure could enlarge the heterojunction area and will be beneficial to its performance. Fig. 2b depicts the current versus voltage ( $I$ - $V$ ) curves of a typical ZnSeNR-SiNW crossed p-n nano-heterojunction in dark at room temperature. A obvious rectifying behavior (rectification ratio  $\sim 20$  at  $\pm 5$  V in dark) is observed, which indicates that a built-in electric field with the direction from n-type SiNW to p-type ZnSeNR, as well as an energy barrier is established at the interface of the nano-heterojunction. As a result, electrons could transport from p-type ZnSeNR to the n-type SiNW under the built-in electric field while the opposite direction of electrons flow is blocked by the barrier. Furthermore, an ideality factor ( $n$ ) of  $\sim 2.1$  is obtained based on the following equation:

$$n = \frac{q}{k_B T} \frac{dV}{d \ln I} \quad (1)$$

where  $k_B$  is Boltzmann constant,  $T$  is the absolute temperature,  $q$  is quantity of a positive charge. The above results demonstrate the obvious diode characteristic of the ZnSeNR-SiNW crossed p-n nano-heterojunction, even it is prepared by a simple physical contact method. However, this ideality factor is larger than unity, which can be ascribed to the surface defects of ZnSeNR and SiNW.

In order to directly visualize the potential profile of the ZnSeNR-SiNW crossed p-n nano-heterojunction, Kelvin probe force microscopy (KPFM) which measures the electrostatic force between the tip and the sample is used here. Because of the different work functions/Fermi levels of the tip and the sample material, a contact potential difference (CPD) appears, leading to an electrostatic force between the tip and sample. The CPD could be measured and compensated by applying an external control voltage  $V_{dc}$  to the tip until the electric field caused by the CPD and the electrostatic force vanish [23]. With the KPFM technique, the surface potential profile of the ZnSeNR-SiNW crossed p-n nano-heterojunction which reflects the energy barrier of the heterojunction could be measured. The measurement results of the topography and Kelvin voltage are depicted in Fig. 3. Topography of the nano-heterojunction (Fig. 3b) indicates that Si nanowire is covered by ZnSe nanoribbon in the contact area, which is agreement with the SEM image. Fig. 3c shows the KPFM measurement of the nano-heterojunction, which depicts the Kelvin voltage decreases along the direction from n-type SiNW to p-type ZnSeNR in the junction area, indicating that the Fermi level of n-type SiNW is smaller than that of p-type ZnSeNR. To analyze this contrast in more detail, a line scan has been extracted from the 2D Kelvin voltage image and plotted versus the position as shown in Fig. 3d. From which we can see that there is a potential drop of  $\sim 30$  mV between the n-type ZnSeNR and the n-type SiNW. It should be noted that this value is much lower than the barrier height value which is derived from the temperature-dependent  $I$ - $V$  curves in the following part. Similar result was obtained for axial GaAs nanowire junction sample [23] and this deviation is considered resulting from the change of surface potential of ZnSeNR and SiNW due to the following reasons: 1) surface contaminants such as water or oxygen because of the ambient atmosphere during the measurement. 2) Surface states or 3) Surface oxide thin film on ZnSeNRs and SiNWs. In any case, the KPFM

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