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Synthesis of high-quality Cl-doped CdSe nanobelts and their application in nanodevices

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ABSTRACT

High-quality Chlorine (Cl) doped CdSe nanobelts (NBs) with single-crystal wurtzite structure were synthesized by using $CdCl_2$ as the dopant via a thermal co-evaporation method. The *n*-type conductivity of CdSe NBs was confirmed by field-effect transistors (FETs) based on single NBs. The electron concentration and mobility of these CdSe NBs are about 6.67×10^{18} cm^{-3} and 17.4 cm^2/Vs, respectively. High-performance nano-Schottky diodes on single CdSe NBs with Au Schottky contact electrodes have been fabricated and studied. The CdSe NB/Au Schottky diode show an excellent rectification characteristic with a rectification ratio up to 10^7 within ± 1 V and small ideality factor of ~1.2, which can also function as photodetectors with an ultrafast response speed of 26/50 μs, representing the best value obtained for the CdSe based nano-photodectecors. These results reveal that such CdSe NBs and their nanodevices have great potential for nano-electronic and optoelectronic applications.

1. Introduction

II–VI group one-dimensional (1D) nanostructures such as nanowires (NWs), nanobelts (NBs), and nanotubes (NTs) have attracted much attention in the past decade owing to their unique optical and electrical properties, and they are good candidates for the building blocks of functional nanodevices such as field-effect transistors (FETs) [1–4], photodetectors (PDs)[5–7], light-emitting diodes (LEDs) [8–10], and photovoltaic (PV) devices[11,12]. They are expected to play important roles as the key units of next-generation nanoscale electronic and optoelectronic devices. As one of the most important II–VI nanostructure semiconductors, CdSe with a direct band-gap of 1.7 eV have attracted much attention in the past decade owing to their unique optical and electrical properties. They are good candidates for the building blocks of functional nano-devices such as FETs, PDs, PV devices and so on [13–15]. However, the unintentionally doped CdSe nanostructures usually have high resistivity, which limits their performance both in electronic and optoelectronic devices. Therefore, finding effective doping ways to tune the transport properties of the CdSe nanostructures is very urgent in exploring their application in nanodevices. So far, In and Ga doping have been utilized to enhance the *n*-type conductivity of the CdSe nanostructures. [13,16]

Herein, we reported in situ Cl doping of single-crystal CdSe NBs by using $CdCl_2$ as the *n*-type dopant via the thermal co-evaporation method. Nano-FETs and Schottky diodes (SDs) based on single CdSe:Cl NBs were constructed and studied. It's worth pointing out that such SDs can function as PDs with fast response speed. Our results demonstrated that the *n*-type Cl-doped CdSe NBs may have great important applications in nano-electronics and optoelectronic applications.

2. Experimental

Synthesis of CdSe:Cl NBs: The undoped CdSe nanomaterials are highly insulative semiconductors with very low conduction current of ~10^{-11} A, which cannot function as elementary components for nanodevices. Hence, the Cl-doped CdSe NBs were synthesized via co-thermal evaporation in an alumina tube furnace. High-purity CdSe powder (99.999%) was loaded into an alumina boat and placed at the center of the tube furnace. $CdCl_2 \cdot 2.5H_2O$ powder was used as the Cl dopant and pre-heated at 200 °C for 2 h in nitrogen atmosphere to eliminate the crystalline water. Then the dry $CdCl_2$ powder was loaded in another alumina boat and located in the first heating zone, which is in the upstream position of the CdSe source. Si substrates coated with a layer of 10 nm gold catalyst were placed in the downstream ~10 cm away from the CdSe source. Before heating, the system was evacuated to a base pressure of 10^{-5} Torr and back filled with Ar/H_2 gas mixture at a constant flow rate of 90/10 sccm to a stable pressure of 150 Torr. Afterwards, the $CdCl_2$ and CdSe source were heated up to 450 °C and 890 °C, respectively and maintained at that temperature for 2 h. The system was cooled down to room temperature, and the Si

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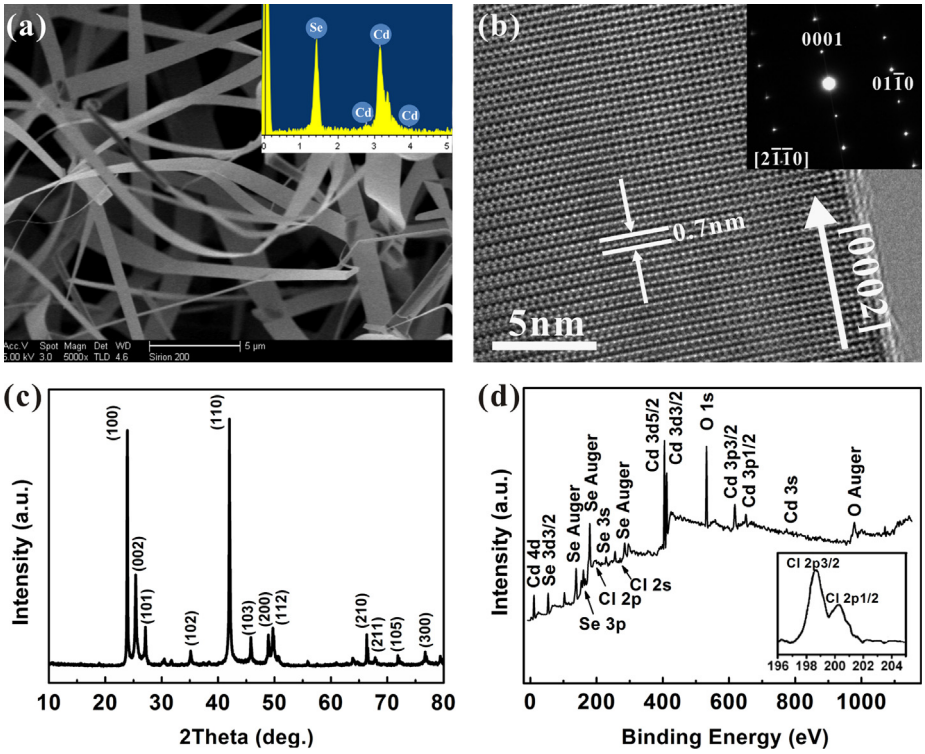

Fig. 1. (a) FESEM image, (b) HRTEM image, (c) XRD patterns and (d) XPS spectrum of the as-synthesized CdSe:Cl NBs. Insets in (a), (b) and (d) show the EDS spectrum, SAED pattern and the enlarged Cl peaks, respectively.

substrates were taken out of the furnace. A layer of black wool-like product could be observed on the substrates surface.

Morphologies and structures of the as-synthesized CdSe:Cl 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), high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010, at 200 kV) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250), as shown in Fig. 1.

Device construction: To construct nano-FETs, the as-synthesized CdSe:Cl NBs were dispersed on SiO_2 (300 nm)/*p*-Si substrates. Then, photolithography, and electron beam evaporation were used to fabricate the source and drain In (100 nm) Ohmic contact electrodes on the NRs. The *p*-Si substrates and SiO_2 served as the back-gate and dielectric, respectively. In order to construct SDs, the Au (50 nm) Schottky electrodes were defined by additional photolithography and electron beam evaporation. The electrical transport measurements were conducted 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 the Cl-doped CdSe NBs: Fig. 1a shows the typical FESEM image of the CdSe:Cl NBs. It is seen that the product is clean and free of evident impurities and particles. The width and length of the NBs are in the range of 2–3 μm and tens of micrometers, respectively. The inset of Fig. 1a shows the EDX spectrum taken from the CdSe NBs. It consists of Cd and Se signals with an atomic ratio ~53:47. HRTEM image and the corresponding selected-area electron diffraction (SAED) pattern recorded from a single NB are shown in Fig. 1b, indicating that the NB is hexagonal wurtzite structure with [0002] growth orientation. In the XRD patterns of the CdSe:Cl NBs (Fig. 1c), all the diffraction peaks can be assigned to hexagonal wurtzite CdSe (JCPDS 88-2346) and no obvious impurity phases and peak shift are observed, suggesting a single phase of the product.[13] XPS was used to detect the compositions of the CdSe:Cl NBs, as shown in Fig. 1d. In addition to the Cd and Se peaks, two weak peaks at 200 eV and 271 eV corresponding to Cl 2p and Cl 2s core level emission, implying that Cl might be successfully doped into the CdSe NBs.

Electrical characterization of CdSe:Cl NB nano-FETs: Fig. 2 shows the electrical transfer characteristics of the CdSe:Cl NB nano-FET. From the inset in Fig. 2a, it is found that the undoped CdSe NB exhibits an extremely low conduction current (~10^{-11} A). From the typical gate-dependent source–drain current (I_{DS}) versus source–drain voltage (V_{DS}) curves of the CdSe:Cl NBs (Fig. 2a), it is seen that the conductance of the NB increases (decreases) consistently with the increasing (decreasing) gate voltage (V_G), revealing the *n*-type conductivity of the CdSe:Cl NBs. The field-effect electron mobility (μ_e) and carrier concentration (n) of the CdSe:Cl NB can be estimated to be 17.4 $cm^2\ V^{-1}\ s^{-1}$ and 6.67×10^{18} cm^{-3} based on the following equation: $\mu_e = g_m L/ZC_0V_{DS}$ and $n = 1/\rho\mu_e$, where $g_m = dI_{DS}/dV_G = 0.16$ μS represents the transconductance of the nanoFET and deduced from the linear part of the I_{DS}–V_G curve (Fig. 2b), Z/L is the width-to-length ratio of the NB channel. The capacitance per unit area is given by $C_0 = \varepsilon\varepsilon_0/h$, where ε_0 is the dielectric constant (3.9 for SiO_2) and h (300 nm) is the thickness of the SiO_2 dielectric layer. The current on-off ratio of ~1.9 is obtained when V_G changes from −30 V to 30 V. We note that the CdSe:Cl NB nanoFETs have exhibited relative low device performance, which can be attributed to the weak gate–channel couple caused by the back-gate device structure.[13]

Performances characterization of CdSe:Cl NB/Au Schottky diodes: Fig. 3a and inset of Fig. 3b show the schematic illustration and SEM of SDs based on an individual CdSe:Cl NB, respectively. Fig. 3b depicts the typical *I–V* characteristics of the CdSe:Cl NB/Au SD measured in the dark, revealing an excellent rectification characteristic of the Schottky junction with a rectification ratio up to