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## Nano-Schottky barrier diodes based on Sb-doped ZnS nanoribbons with controlled p-type conductivity

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ZnS nanoribbons (NRs) with controlled p-type doping were synthesized by using Sb as dopant. The p-type conductivity of the ZnS:Sb NRs could be tuned in a wide range of seven orders of magnitude by adjusting the Sb doping level. Nano-Schottky barrier diodes based on Al/p-ZnS NRs junctions exhibited excellent device performances with a high rectification ratio  $>10^7$  and a small ideality factor of  $\sim 1.22$ . The diodes also showed the potential as high-sensitive UV detectors. The p-ZnS NRs are expected to act as key building blocks in nano-optoelectronics. © 2011 American Institute of Physics. [doi:10.1063/1.3569590]

ZnS nanostructures have attracted much attention due to the unique optical and optoelectronic properties.<sup>1-4</sup> In order to extend their functions in devices, it is essential to tune the optical, electrical, and magnetic properties. This is typically done by introducing various dopants, as demonstrated, for instance, Mn- and Cu-doped ZnS nanocrystals have shown new luminescence with tunable colors.<sup>5,6</sup> Co doping in ZnS nanoparticles also resulted in a 35 times enhancement in the emission intensity.<sup>7</sup> Despite these progresses, controlling the transport properties of the ZnS nanostructures, particularly the p-type conductivity, remains a challenge and is seldom studied. The reliable p-type doping in II-VI films is often obstructed by the serious self-compensation effect. However, owing to the key merits such as high-crystal quality and size effect, more effective p-type doping is anticipated to be achieved in the II-VI nanostructures.

Recently, Yuan and co-workers have fabricated the nitrogen-doped p-type ZnS nanoribbons (NRs) by using ammonia (NH<sub>3</sub>) as the dopant.<sup>8</sup> Nevertheless, ZnS NRs with tunable p-type conductivity is not realized yet, and the capability of other V group elements as the p-type dopants is needed to be further exploited. In addition, practical applications of the p-type ZnS nanostructures in high-performance nanodevices are still lacking and much desired.

Herein, we report the efficient p-type doping in ZnS NRs by using antimony (Sb) as the acceptor dopant. Nano-Schottky barrier diodes (nanoSBDs) fabricated from Al/p-ZnS NR junctions exhibit excellent device performance as well as great potential as high-sensitive UV photodetectors.

Synthesis of the p-ZnS NRs were conducted in a horizontal tube furnace via thermal evaporation. Sb (purity 99.999%) and ZnS powers (purity 99.99%) were loaded on two alumina boats with separation of 8 cm and heated to 800 °C and 1060 °C, respectively, during the NR growth. Si substrates covered with Au catalyst were placed at the downstream position with ~10 cm away from the ZnS source. Ar and H<sub>2</sub> (5%) mixture gas was fed at a constant flow rate of 100 SCCM and the gas pressure was adjusted to 200 Torr. After a growth duration of 2 hours, the product was collected from the Si substrates. In this work, two samples with varied

doping levels were fabricated, which were marked as sample 2 and sample 3, corresponding to the different ZnS:Sb molar ratio of 2:1 and 1:1, respectively. Undoped ZnS NRs were also synthesized at the same condition except the use of Sb source, which was marked as sample 1. The as-synthesized ZnS:Sb NRs were characterized by x-ray diffraction (XRD, Rigaku D/Max-rB), field-emission scanning electron microscope (FESEM) (SIRION 200 FEG), high-resolution transmission electron microscope (HRTEM, JEOL JEM-2010), and x-ray photoelectron spectroscopy (XPS, Thermo ES-CALAB 250). Room-temperature photoluminescence (PL) spectra were measured under the excitation of 325 nm laser. To fabricate the field-effect transistors (FETs) based on single NR, the NRs were first dispersed on a SiO<sub>2</sub> (300nm)/p<sup>+</sup>-Si substrate and then Au (80 nm) source and drain electrodes were defined by photolithography and liftoff processes. The Si substrate served as the global back gate. As for the nanoSBDs, additional photolithography process was performed to fabricate the Al (80 nm) Schottky contact.

Figure 1(a) shows the typical SEM image of the ZnS:Sb NRs. It can be seen that the width of the NRs ranges from 200 to 400 nm and the length is from tens of micrometers up to hundreds of micrometers. Energy dispersive spectroscopy (EDS) measurement on the ZnS:Sb NRs reveals a near stoichiometric composition of ~49.4% Zn and ~50.6% S [Fig. 1(b)]. HRTEM image and the corresponding selected-area electron diffraction (SAED) pattern of the ZnS:Sb NR are shown in Fig. 1(c), indicating that the NRs are wurtzite single-crystal with [210] growth orientation. The smooth surface also confirms the high quality of the ZnS:Sb NRs. Fig. 1(d) depicts the XRD patterns of the samples, in which all the diffraction peaks could be assigned to wurtzite ZnS (Joint Committee for Powder Diffraction Standard No. 36-1450), and no obvious peak shift is observed for the ZnS:Sb NRs. In the XPS spectrum [Fig. 1(e)], two weak peaks located at 530.4 and 539.9 eV that correspond to Sb 3d core levels have appeared in addition to the Zn and S signals, indicating that Sb is indeed incorporated into the ZnS NRs with overall content of  $\sim 1.5$  at. %. The room-temperature PL spectra of the samples consist of two emission bands [Fig. 1(f)], i.e., the sharp near-band edge emission at  $\sim$ 336 nm and broad green emission at  $\sim$ 520 nm. The latter can be attributed to

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FIG. 1. (Color online) Characterizations of the ZnS:Sb NRs (a) SEM image. (b) EDS spectrum. (c) HRTEM image. Inset shows the corresponding SAED pattern. (d) XRD pattern. (e) XPS spectrum. Inset shows two peaks at 530.4 eV and 539.9 eV, corresponding to Sb  $3d_{5/2}$  and Sb  $3d_{3/2}$ , respectively.

the self-activated defect centers formed by the zinc vacancies.<sup>9</sup> In the Sb-doped ZnS NRs, the Sb dopants are presumed to occupy Zn sites and spontaneously induce Zn vacancies, forming  $Sb_{Zn}-2V_{Zn}$  complexes. Such acceptor complexes have already been investigated and are suggested to be responsible for the p-type conductivity of As or Sb doped ZnO and ZnSe materials.<sup>10–12</sup> Note that the greenband emissions become stronger from sample 1 to sample 3, implying that the concentration of the Zn vacancies in the ZnS NRs increases with the increasing of Sb doping level.

To assess the electrical properties of the ZnS:Sb NRs, back-gate nanoFETs were fabricated based on individual NRs (Fig. 2). Before the measurements, the acceptors in the NRs were activated by a fast-annealing process at 650 °C



FIG. 2. (Color online) (a) Schematic illustration of the back-gate nanoFET based on the ZnS:Sb NR. (b) Typical *I-V* curves of both the undoped and Sb-doped NRs. Inset shows the SEM image of the device. (c) and (d) are electrical transfer characteristics of sample 2 and sample 3, respectively.  $I_{ds}$ - $V_{ds}$  curves were plotted at varied  $V_g$ . Insets show the  $I_{ds}$ - $V_g$  curves at This a  $V_{ds}$ = $\tau$ 5 V/pyrighted as indicated in the article. Reuse of AIP content is subj conductivitys of the /NR at  $V_g$ =0 and q is the elementary to IP:



FIG. 3. (Color online) (a) Schematic illustration of the nanoSBD based on the ZnS:Sb NR. (b) SEM image of the nanoSBD with artificial colors. (c) *I-V* curve measured between two adjacent Au electrodes. (d) Rectifying characteristics of five different nanoSBDs, which are marked from SBD 1 to SBD 5. Inset shows the semilog plots of the rectifying curves. (e)  $I_a$ -a curve of SBD 1. The series resistance  $R_s$  is estimated by linearly fitting the data. (f) Semilog *I-V* curves of the SBD 1 with and without  $R_s$  correction at forward bias.

for 10 min via the dissociation of Sb–H bonds. Figure 2(b) depicts the typical *I-V* curves measured from the samples. The ideal linearity of the *I-V* curves confirms the good Ohmic contact between the ZnS NR and the Au electrode. Significantly, it is found that the conductivity of the ZnS NRs has been increased by ~seven orders of magnitude by Sb doping. The undoped ZnS NRs (sample 1) have the conductivity as low as  $\sim 6.5 \times 10^{-7}$  S cm<sup>-1</sup>, while the conductivity increases dramatically to  $\sim 3.0 \times 10^{-3}$  S cm<sup>-1</sup> and 9.1 S cm<sup>-1</sup> for sample 2 and 3, respectively.

Figure 2(c) shows the electrical characteristics of the representative ZnS:Sb NR FETs fabricated from sample 2. The source-drain current  $(I_{ds})$  versus source-drain voltage  $(V_{\rm ds})$  curves were measured under varied gate voltage  $(V_{\rm g})$ from +40 to -40 V with a step of -20 V. It is noted that the device exhibits an evident p-type gating effect, that is, when  $V_{\sigma}$  decreases (increases), the conductance increases (decreases) correspondingly. This gate dependence clearly proves the p-type nature of the ZnS:Sb NRs. The hole mobility  $(\mu_{\rm h})$  can be further estimated from the channel transconductance  $(g_m)$  of the nanoFET according to the equation  $g_{\rm m} = dI_{\rm ds}/dV_{\rm g} = \mu_{\rm h} C V_{\rm ds}/L^2 = \mu_{\rm h} \varepsilon_0 \varepsilon_{\rm SiO_2} W V_{\rm ds}/hL$  in the linear regime of the  $I_{ds}$ - $V_g$  curve [inset in Fig. 2(c)], where C is the channel capacitance, L the channel length (5.8  $\mu$ m),  $\varepsilon_{SiO_2}$ the dielectric constant of SiO<sub>2</sub> (3.9), W the channel width (250 nm), and h the SiO<sub>2</sub> thickness (300 nm). From the transfer characteristics,  $g_{\rm m}$  is ~0.4 nS at  $V_{\rm ds}$ =-5 V, resulting in a hole mobility of ~0.2 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>. Furthermore, the hole concentration  $(n_{\rm h})$  is deduced to be ~9.3  $\times 10^{16}$  cm<sup>-3</sup> through the relation  $n_{\rm h} = \sigma / q \mu_{\rm h}$ , where  $\sigma$  is the charge. Analogous analysis was performed to sample 3 [Fig. 2(d)], revealing the  $g_m$ ,  $\mu_h$  and  $n_h$  values of 86.4 nS, 22.3 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, and  $6.5 \times 10^{18}$  cm<sup>-3</sup>, respectively. The lager hole mobility for sample 3 is a result of improved electrical contact between the electrode and the NR at higher doping level. From the value of the hole concentration, we can judge that only a small fraction of Sb in the source contributes to the doping, which might be caused by the poor solubility of Sb in ZnS.

To further exploit the device applications of the p-type ZnS:Sb NRs, nanoSBDs were constructed by using Al as the Schottky contact, as shown in Fig. 3. The Ohmic contact of the Au electrode with the p-ZnS NR is first verified by the linear I-V curve measured from two adjacent Au electrodes [Fig. 3(c)]. In contrast, obvious rectifying behavior is observed between the Al and Au electrodes. Further analysis reveals a low turn-on voltage of  $\sim 0.35$  V and a high rectification ratio  $>10^7$  for the device [Fig. 3(d)]. Measurements on five different nanoSBDs exhibit the similar results, indicating the good reproducibility of the devices. It is known that the total current for a Schottky diode is composed of both the thermionic emission and the tunneling components. Assuming that the thermionic emission is the predominant mechanism, the I-V characteristics of the nanoSBD in the forward bias regime are given by the following relations:

$$I = I_0 \left[ \exp\left(\frac{qV}{nkT}\right) - 1 \right] \approx I_0 \exp\left(\frac{qV}{nkT}\right), \tag{1}$$

$$I_0 = AA^*T^2 \exp\left(-\frac{q\Phi_b}{kT}\right),\tag{2}$$

where  $I_0$  is the reverse saturation current, *n* the ideality factor, *A* the Schottky contact area,  $A^*$  the effective Richardson constant, and  $\Phi_b$  the Schottky barrier height. The ideality factor *n* can be written as  $n = (q/kT)(dV/d \ln I)$  based on Eq. (1). From the semilog *I-V* plots [inset in Fig. 3(d)], *n* is determined to be 1.31–1.39 for the nanoSBDs. And  $\Phi_b$  is deduced to be 0.62–0.66 eV from Eq. (2).

It is noted that the semi-log *I-V* curves of the nanoSBDs are linear at low forward bias voltage, but deviate considerably from linearity at large bias voltage. One of the possible reasons is the existence of series resistance  $(R_s)$ . The Eq. (1) could be modified to  $I = I_0 \{ \exp[q(V - IR_s)/nkT] - 1 \}$  $\approx I_0 \exp[q(V - IR_s)/nkT]$  by taking account of  $R_s$ . Here,  $R_s$  is evaluated by using Lien–So–Nicolet method.<sup>13</sup> This method is based on Norde-type function that defined by  $G_{a}(V,I)$ =(V/a)-(kT/q)In $(I/AA^*T^2)$ , where a is an arbitrary parameter larger than *n* and determined by (1/a) = (kT/q) $\times$ (d In *I*/d*V*) at *I*=*I*<sub>a</sub>. Setting d*G*<sub>a</sub>/d*V*=0 at *I*=*I*<sub>a</sub>, *I*<sub>a</sub>  $=(kT/qR_s)a-(nkT/qR_s)$  is deduced. Eventually, the  $R_s$  value is estimated to be ~99.4 k $\Omega$  by linearly fitting the  $I_a$ -a curve [Fig. 3(e)]. When the value of  $R_s$  is obtained, it could be used to accurately calculate n and  $\Phi_{\rm b}$ . Figure 3(f) shows the corrected semi-log I-V characteristics of the nanoSBD, and corrected n and  $\Phi_{\rm b}$  values of 1.22 eV and 0.71 eV, respectively, are obtained.

Upon the UV light illumination (254 nm, 300  $\mu$  W cm<sup>-2</sup>), the nanoSBD shows a remarkable increase in the photocurrent (Fig. 4). The  $I_{\text{light}}/I_{\text{dark}}$  ratio is about 3 at forward bias (+1 V), in contrast to the large value of >10<sup>2</sup> at reverse bias (-1 V). The enhancement of the photocurrent



FIG. 4. (Color online) Photoresponse of the nanoSBD. (a) Device characteristics measured in dark and under UV light illumination, respectively. (b) Photoresponse at reverse bias. Insets in (a) and (b) show the time response of the device at forward bias (+1 V) and reverse bias (-1 V), respectively.

at forward bias mainly comes from the reduction in the Schottky barrier, while the electron-hole pairs excited by the UV light at the junction region are responsible for the photocurrent at reverse bias. The low dark current at reverse bias results in the high  $I_{\text{light}}/I_{\text{dark}}$  ratio. We also note that the device shows higher response speed at reverse bias. The trap states in the p-ZnS NRs limit the response speed at the forward bias. At reverse bias, however, the electron-hole pairs could be separated quickly by the strong self-built in electric field at the junction, thus leading to a higher response speed.

In summary, p-type ZnS NRs were fabricated by using Sb as the dopant via thermal evaporation. NanoSBDs based on the Al/p-ZnS NR Schottky junctions exhibited excellent rectifying behaviors. The potential of nanoSBDs as high sensitive UV photodetectors was also investigated. Our results demonstrate that the p-type ZnS NRs are promising building blocks for future nano-optoelectronic applications.

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