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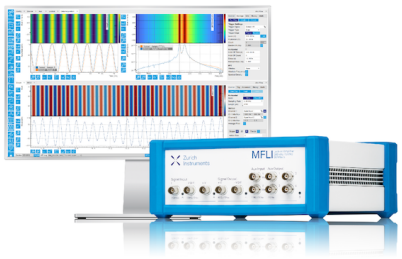

A method to identify shallow dopants in semiconductor nanowires

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In this paper, an electrical measurement method to identify shallow dopants in lowly doped semiconductor nanowires was suggested. Room temperature electrical measurement indicates that electron concentrations of the *n*-GaN nanowires are about 5.4×10^{17} cm^{-3}. Temperature-dependent measurement of conductivities of single nanowires in low temperature region gives activation energy of 13.3 meV, which is consistent with the reported activation energy of 14 meV for Si donor in *n*-GaN films with donor concentration of 7.4×10^{17} cm^{-3}. Our results confirm that the shallow donors in the as-synthesized GaN nanowires are silicon. We consider such a method may be applicable to other semiconductor nanowires. © *2007 American Institute of Physics*.
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Semiconductor nanowires (NWs) are good candidates of building blocks for functional nanodevices.[1–11] In order to improve their performances in both electronic and optoelectronic devices, usually, appropriate doping is necessary. Up to now, various doping methods have been tried and reported.[12,13] Because of the very small dimension of NWs, so far, the most powerful technique to detect the doping elements in NWs is energy-dispersive x-ray (EDX) spectroscopy. However, the sensitivity of EDX is only about 1 at. %. In this paper, we suggested a method to identify the shallow dopants in the semiconductor NWs by measuring their activation energy and comparing it with those of the bulk semiconductor. The activation energies are obtained by the temperature-dependent electrical transport measurements in low temperature region. In this paper, we use the GaN NWs, which is one of the most promising nanomaterials for the electronic/optoelectronic device applications,[14,15] as a representative to present this method.

The GaN NWs were synthesized via the chemical vapor deposition (CVD) method in a tube furnace. First, a drop of molten Ga (99.999%) was placed on a quartz boat as the source. Then the (100) Si substrates, which have 10 nm thick thermally evaporated Ni catalyst films, were loaded on the quartz boat 1–5 cm downstream away from the source. Later, the boat was inserted into the center of a quartz tube inside the tube furnace. After being pumped with a rotation pump and backfilled with NH_3 (99.999%) gas, the quartz tube was rapidly heated to 920 °C. The synthesis duration was 1 h with constant NH_3 flow rate of 80 SCCM (SCCM denotes cubic centimeter per minute at STP.) at the atmosphere pressure. After the synthesis, yellowish products were characterized by a field emission scanning electron microscope (FESEM) (Amray 1910 FE) and a high-resolution transmission electron microscope (HRTEM) (Tecnai F30) equipped with an EDX spectroscope.

A typical FESEM image of the GaN NWs is shown in Fig. 1(a). The inset is the magnified one. We can see that each GaN nanowire has smooth surface and uniform diameter along the growth direction. The average diameter of the NWs is about 80 nm, and the lengths of them are more than 10 μm. Figure 1(b) shows a HRTEM image of a single GaN NW, where the crystal planes with the spacing distance of about 0.27 nm are clearly seen along the growth direction. The HRTEM image together with the selected area electron diffraction (SAED) pattern (the inset in the upper-right corner) reveals that the GaN NW is a single crystal with the wurtzite structure, and its growth direction is $[\bar{1}010]$. The EDX spectrum (the inset in the upper-left corner) taken from the NW consists of only Ga and N signals within its sensitivity.

GaN single NW field-effect transistors (SNW-FETs) were fabricated. First, the GaN NWs ethanol suspension was dropped on oxidized *p*-Si substrates (the SiO_2 layer is 600 nm). Then, UV lithography, thermal evaporation, and lift-off processes were used to fabricate the source and drain ohmic contact In/Au (10/100 nm) electrodes. The underlying *p*-Si substrate was used as the back gate with an ohmic contact Al electrode. The electrical transport measurements were conducted with a semiconductor parameters characterization system (Keithley 4200). During the measurements, the source electrodes were grounded.

Figure 2(a) shows the source-drain current (I_{ds}) versus voltage (V_{ds}) curves under various gate biases (V_g) for a GaN SNW-FET. The inset is the FESEM image of the GaN SNW-FET. The I_{ds}-V_{ds} curves of this SNW-FET are linear and symmetric, indicating that the In/Au electrodes have formed good ohmic contacts with the GaN NW. For identical V_{ds}, the I_{ds} increases when V_g varies from −20 to +20 V.Figure 2(b) shows the I_{ds}-V_g curve measured at V_{ds}=1 V. The I_{ds} versus V_g relation shows that this GaN NW is *n* type. From the linear region of the curve, the threshold gate voltage (V_{th}) and the transconductance ($g_m=dI_{ds}/dV_g$) can be extrapolated to be −7 V and 20 nS, respectively. The channel mobility of the device μ_e can be estimated to be about 12.5 cm^2/V s with the equation $\mu_e=g_m(L^2/CV_{ds})$,[16] where *C* is the capacitance of the nanowire and the *L* is the channel length

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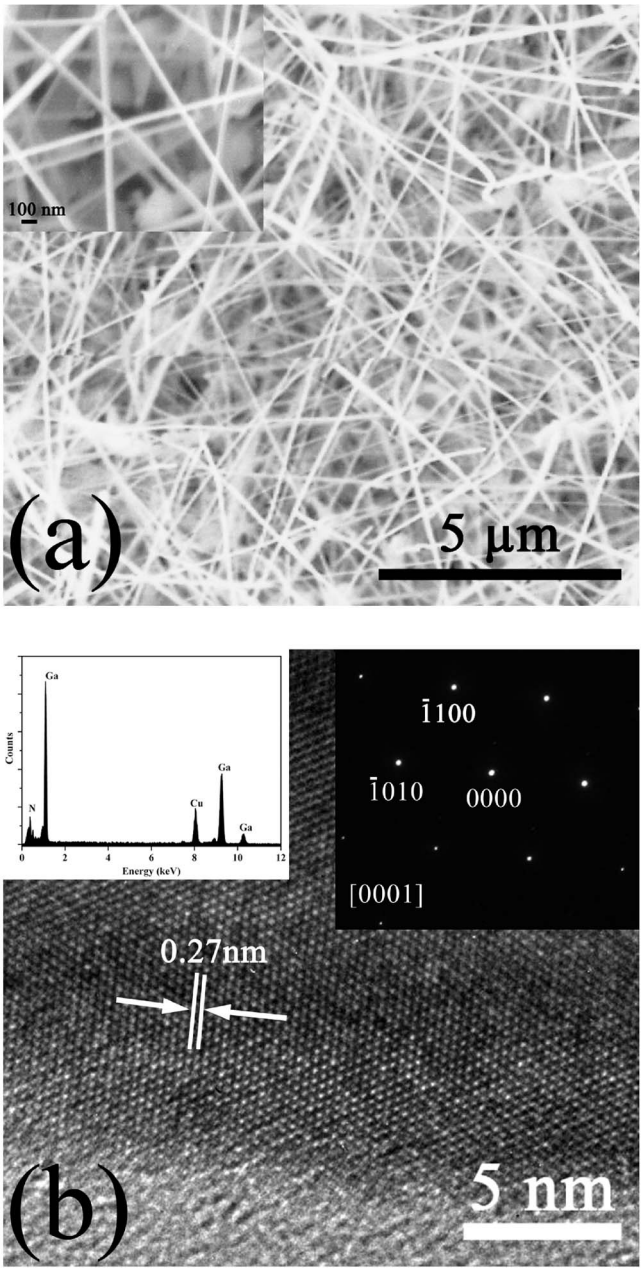

FIG. 1. (a) A FESEM image of as-synthesized GaN NWs. The inset is a magnified image which shows that the diameters of the NWs are about 80 nm. (b) A HRTEM image of an as-synthesized GaN NW. The inset shows the corresponding SAED pattern recorded along the [0001] zone axis and the EDX spectrum of the nanowire.

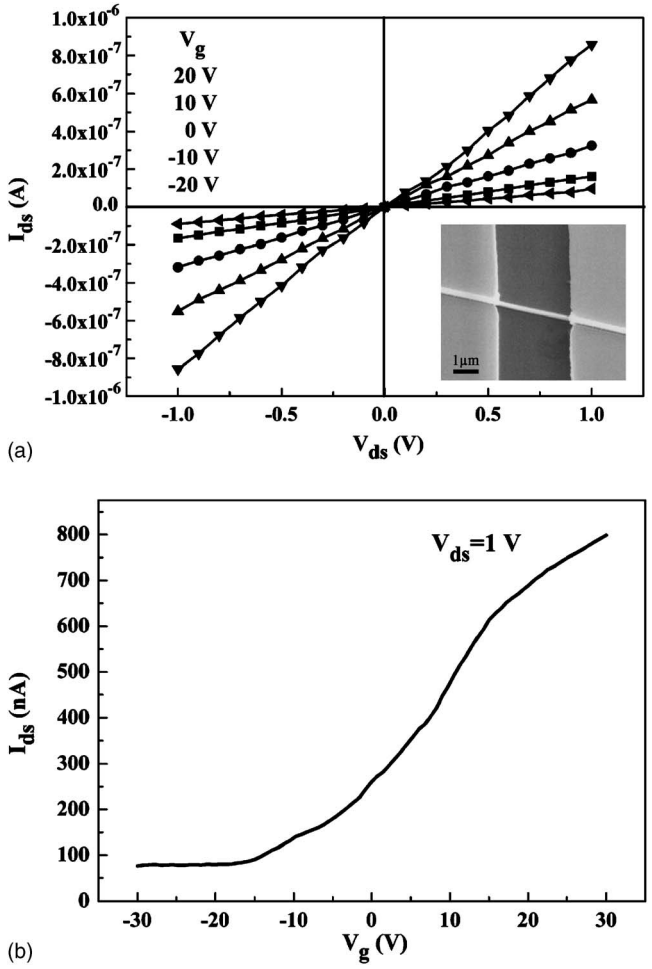

FIG. 2. (a) I_{ds}-V_{ds} characteristics of GaN SNW-FET measured at 300 K under gate bias ranging from −20 to +20 V with a step of 10 V. The inset is a FESEM image of the SNW-FET. (b) I_{ds}-V_g curves of the SNW-FET at V_{ds}=1 V.

(4 μm) of the SNW-FET. Here, C is given by $C=2\pi\varepsilon\varepsilon_0 L/\ln(2h/r)$,[16] where ε is the relative dielectric constant of SiO_2 (=3.9), h is the thickness of the silicon oxide layer, and r (40 nm) is the nanowire radius. The electron concentration (n) can be estimated to be about 5.4×10^{17} cm^{-3} from the equation $n=CV_{th}/e\pi r^2 L$.[16] Assuming the donors are all ionized at room temperature, the donor concentration is about 5.4×10^{17} cm^{-3}.

Because Si and Ga can form an alloy at a temperature as low as 29.774 °C, and the percentage of Si in the Ga–Si alloy at the growth temperature (920 °C) is about 10 mol %, we think during our synthesis process certain amount of Si atoms may evaporate from the Si substrate and diffuse into the GaN NWs.[14,15] However, in our case no Si element can be detected in the GaN NWs by the EDX spectroscope with a sensitivity of only about 1 at. %. Therefore, we employ the following activation energy measurement method to identify shallow dopants in lowly doped semiconductor nanowires.

The temperature-dependent electrical transport measurements on the n-GaN SNW-FETs were conducted at various temperatures from 50 to 100 K in a helium refrigeration system. Figure 3 shows the I_{ds}-V_{ds} curves of a GaN SNW-FET measured at temperatures of 100, 90, 80, 70, 60, and 50 K. The excellent linear characteristic of the I_{ds}-V_{ds} curves indicates a good ohmic contact behavior between the nanowire and the In/Au electrodes even at low temperature. The inset shows the calculated resistivity (ρ) versus temperature (T) . In weak ionization temperature region, the electron concentration n follows the relation $n\sim T^{3/4}\exp(-E_d/2k_BT)$,[17] where E_d is the donor activation energy. In low temperature region where the impurity scattering mechanism is dominant, the electron mobility μ follows the relation $\mu\sim T^{3/2}$.[18] Using the equation $\rho=1/ne\mu$, we obtained a relation $\rho\sim T^{-9/4}\exp(E_d/2k_BT)$. By fitting the experimental data with this relation, we obtained a value of E_d to be about 13.3 meV for GaN NWs. In our case, the quantum confinement effect is not evident because the dimensions of GaN NWs are much larger than the exciton Bohr radius of the bulk GaN (about 2.8 nm). Hence, the GaN NW conduction properties are similar to those of the bulk or film GaN. Comparing the activation energy here with those of some possible dopants

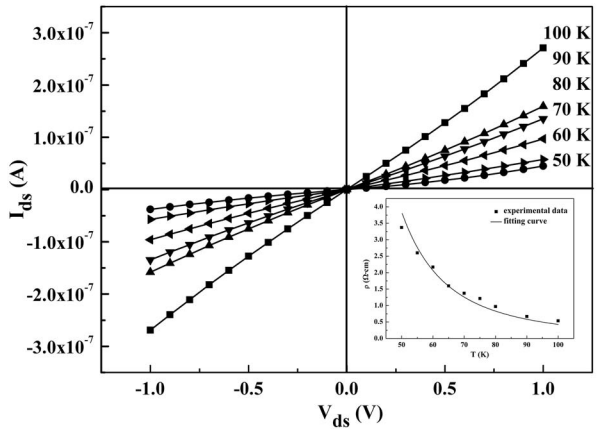

FIG. 3. The I_{ds}-V_{ds} curves of a GaN SNW-FET measured at temperature from 50 to 100 K. The inset is the calculated ρ vs T at the low temperature region (50–100 K), where the experimental data are fitted by a solid curve using the formula of ρ vs T.

in GaN, we can make a conclusion that the dopants in the GaN NWs are most probably to be the Si atoms, since the reported value of Si donor activation energy in GaN films is about 14 meV at donor concentrations of about 7.4×10^{17} cm^{-3}.[19]

It is worth to point out that we have also synthesized the heavily Si-doped *n*-GaN NWs (Si donor concentration $\sim 6.0 \times 10^{20}$ cm^{-3}) by directly placing a drop of molten Ga (99.999%) on a Si substrate with a 10 nm thick thermally evaporated Ni catalyst film. EDX data show that the GaN NWs contain about 1% Si atoms(Fig. 4). This confirms that certain amount of Si atoms had evaporated from the Si substrate and diffused into the GaN NWs during our synthesis process. The temperature-dependent electrical transport measurements conducted on the heavily Si-doped *n*-GaN SNW-FETs (Ref. 14) in low temperature region show no evident change of the conduction. The reason may be the well-known fact that when the donor concentration is high, the wave functions of the electrons will overlap and form an impurity band, and the conduction will behave like it is in metal.[17] According to this, the shallow dopant identification method presented above is only applicable to the lowly doped semiconductor NWs.

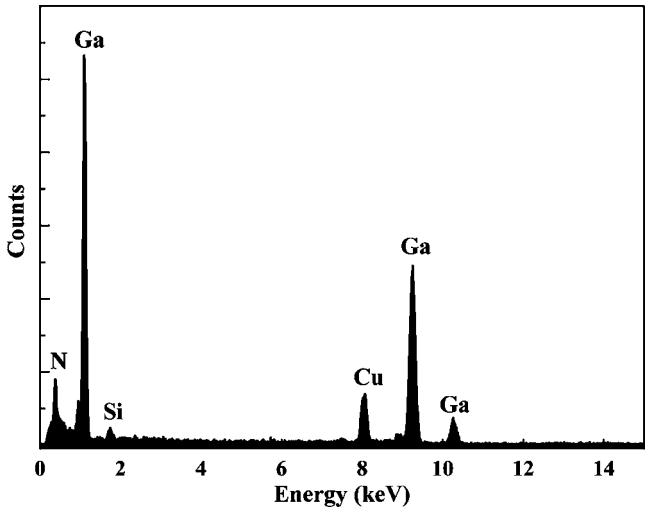

FIG. 4. EDX data obtained from the heavily Si-doped GaN NW.

In conclusion, we suggest a feasible method to identify the shallow dopants in the lowly doped semiconductor NWs. The activation energy of the donors in single GaN NW is estimated to be about 13.3 meV through temperature-dependent electrical transport measurements on single GaN NWs in low temperature region. Our experimental results reveal that the shallow donors in our GaN NWs are Si atoms. Such a method is significant for the study of semiconductor NWs.

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