Supporting Information

Development of Ohmic Nanocontacts Via Surface Modification For Nanowire-Based Electronic and Optoelectronic Devices: ZnO Nanowires As An Example

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Electrical and microstructure analyses of the FIB-Pt contacts with unmodified ZnO nanowires (N₀)

The specific contact resistance for the condition of N₀ measured by four-probe method at room temperature is 9.4×10⁻⁶ Ωcm². To further characterize the contact between the FIB-Pt with unmodified ZnO nanowires, energy dispersive X-ray spectroscopy (EDS) mapping is employed to investigate the distribution of the chemical compositions. The scanning transmission electron microscopy (scanning TEM) image in Fig. S1(a) shows the unmodified nanowire covered by the FIB-Pt on the SiO₂/Si substrate. ZnO is composed of Zn and O, as shown in Fig. S1(b) and S1(c). The EDS mapping of Pt shows that the FIB-deposited contact contains Pt (Fig. S1(d)). Figure S1(e) shows that a certain amount of Ga exhibits in the FIB-Pt contact and at the junction of FIB-Pt/ZnO. There are two possible Ga sources accounting for this distribution. First, Ga-ion scanning is inevitable to be utilized for imaging microscope prior to Pt deposition in FIB. The surfaces of the ZnO would be modified under the Ga ion irradiation. The dose value of Ga ion beam is estimated by the scanning frame (42μm×48μm) of the Ga ion beam at 512×442 pixels at 50 pA current. The duration time at every pixel is 3 μs. The substantial dose on the area of a frame is:

\[
\frac{(512 \times 442 \times 50 \text{pA} \times 3 \mu s)}{1.6 \times 10^{-19}} \times 42 \mu m \times 48 \mu m = 0.9 \times 10^{13} \text{ (1/cm}^2\text{)}
\]

Secondly, due to the characteristics of FIB-induced deposition mechanism (i.e., Ga ion beam induced deposition), it is impossible to avoid the influence of the Ga ion, which was inevitably incorporated into the FIB-Pt contact during the Pt deposition process. Ga ion existing in the FIB-Pt contact and at the junction of FIB-Pt/ZnO might be responsible for the unusual low contact resistance of FIB-Pt to ZnO nanowires. The electrical characterization will be performed to confirm this speculation further.
The electron affinity of ZnO is 4.5 eV, and the work function of Pt metal is 5.65~6.1 eV,\(^1\) thus there exists a Schottky barrier at the Pt and ZnO interface ideally.\(^2,3\)
The current flowing through in a Schottky barrier junction is dominated by the transport of the carriers from semiconducting ZnO to Pt metal. The transport can occur by different possible mechanisms, such as (1) thermionic emission (TE) over the barrier, (2) thermal field emission (TFE) assisted by interface states existing in the metal-semiconductor junction, and (3) field emission (FE). While FE is a pure tunneling process, TFE is tunneling of thermally excited carriers which meet a thinner barrier than FE. The specific contact resistance is a function of barrier height, carrier concentration (in TFE and FE mechanisms), and temperature (in TE and TFE mechanisms).\(^4\) Since FIB-Pt metal forms low-resistance contacts with the unmodified ZnO nanowires, we deduce that the transport mechanism for contact of the FIB-Pt to unmodified ZnO nanowires could be the TFE or FE mechanism instead of TE (Schottky contact).

For further investigating the transport mechanism between the FIB-Pt and unmodified ZnO interface, the measurement of the temperature-dependent specific contact resistance were performed, as shown in Fig. S2. It is found that the specific contact resistance of FIB-Pt to unmodified ZnO nanowire decreased with temperature. Accordingly, we conclude that the electrical transport of the Pt contacts on the ZnO nanowire is the TFE mechanism since FE mechanism is independent of temperature. As the TFE mechanism dominates the transport of contact, the specific contact resistance when \(V \to 0\) is given by\(^4\)

\[
\rho_c = \frac{k \sqrt{E_{00} \cosh \left(\frac{E_{00}}{kT}\right) \coth \left(\frac{E_{00}}{kT}\right)}}{A^* T q \sqrt{\pi q \left(\phi_{bs} - \phi_n\right)}} \exp \left[ \frac{q \left(\phi_{bs} - \phi_n\right)}{E_{00} \coth \left(\frac{E_{00}/kT}{q}\right)} + \frac{q \phi_n}{kT} \right]
\]

\[
E_{00} = \frac{q h}{4 \pi \sqrt{N_d \varepsilon_0 \varepsilon_r m^*}}
\]

(S1)
TFE occurs at the energy above the conduction band, where $A^{**}$ is the effective Richardson constant, $h$ is the Planck constant, $k$ is the Boltzmann constant, $q$ is the electronic charge, $q\phi_n$ is the energy difference between conduction band edge and Fermi level, $q\phi_{bn}$ is barrier height, $E_{\infty}$ is the Padovani-Stratton parameter that depends on the semiconductor type and the carrier concentration at the interface ($N_d$), $m^*$ is the electron effective mass of the ZnO, $\varepsilon_0$ is the vacuum dielectric constant, $\varepsilon_r$ is the relative dielectric constant of the ZnO semiconductor. According to equations (S1), the specific contact resistance is a function of barrier height, $E_{\infty}$, and temperature. For the fitting of $\rho_c$-temperature curves, several material properties are assumed to be independent of temperature for simple but accurate fitting, although they actually vary somewhat with temperature. They are the barrier height, carrier concentration, the energy difference between conduction band edge and Fermi level of ZnO, the dielectric constant of the ZnO, the electron effective mass of the ZnO, and $E_{\infty}$. The fitting curve according to equation (S1) is consistent with the data we measured, as shown in Fig. S2. By the fitting constants of the curve, $E_{\infty}$ is calculated to be 0.35 meV. Substituting the constants of $m^*$, $\varepsilon_0$ and $\varepsilon_r$ into equation (S1), the carrier concentration at the interface is estimated to be $\sim 1.0 \times 10^{15}$ (1/cm$^3$).

The distributions of Ga atoms are calculated for unmodified ZnO nanowires by the TRIM (transport of ion in matter) code, which predicts a mean projected range of the Ga ions of $\sim 15$ nm. Thus most implanted Ga ions should be contained at the surface of the nanowires. To compare the implanted dose with the volume density of implanted Ga ions, we assume a penetration depth of 200 nm is equal to the diameter of the nanowire as a rough estimate, which corresponds to an implanted Ga concentration of $4.5 \times 10^{17}$ cm$^{-3}$ for a dose of $0.9 \times 10^{13}$ cm$^{-2}$. Ga doping concentration resulting from Ga ion
imaging is two orders higher than the estimated carrier concentration ($1.0 \times 10^{15}$ cm$^{-3}$), which is reasonable since it has been known that not all ions are electrically active as expected for as-implanted samples without any heat treatments.$^7$ It concludes that the TFE transport in unmodified ZnO nanowires is contributed from the slight introduction of Ga ions. Our characterizations provide the explanation as to why FIB-Pt exhibits abnormal low-resistance contacts to ZnO nanowires. The presence of Ga in the ZnO makes the corresponding width of the barrier decreases and the thermally excited carriers tunnel through rather than over the potential barrier. Moreover, it has been known that metal screening lengths are negligible (Angstrom scale) compared to semiconductors (tens to hundreds of nanometers). The barrier width is modulated by the doping within the semiconductor instead of metal.$^8$ The varied barrier width in the Pt due to the addition of Ga can be neglected.
Reference


Fig. S1 (a) Cross-sectional STEM image of unmodified ZnO nanowire, and the corresponding EDS mapping of (b) Zn, (c) O, (d) Pt, and (e) Ga.
Fig. S2 Temperature dependence of specific contact resistance by using four-probe Kelvin measurement. The squares are the data acquired from measurement. The solid line is the fitting curve according to equation (S1).
Fig. S3 Schottky behavior of FIB-deposited Pt contacts to ZnO nanowires with the Ga surface modification to the dose of N$_i$. 