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Cathodoluminescent and electrical properties of an individual ZnO nanowire with oxygen vacancies*

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A single ZnO nanowire with intrinsic oxygen vacancies is utilized to fabricate four-contact device with focus ion beam lithography technique. Cathodoluminescent spectra indicate strong near-UV and green emission at both room temperature and low temperatures. Experimental measurement shows the temperature-dependent conductivity of the ZnO nanowire at low temperatures (below 100 K). The further theoretical analysis confirms that weak localization plays an important role in the electrical transport, which is attributed to the surface states induced by plenty of oxygen vacancies in ZnO nanowire.

Keywords: ZnO nanowire, electrical transport, oxygen vacancies, weak localization
PACC: 7280, 7210F, 7320F, 7860H

Low dimensional nanostructures with novel physical properties have extensive potential applications in constructing nanoscale electronic and optoelectronic devices.[1−4] In recent years, zinc oxide (ZnO) has been converted to one-dimensional nanowires by using vapour transport process.[5] ZnO is a direct and wide gap semiconductor with band gap energy of 3.37 eV and exciton binding energy of 60 meV at room temperature (RT).[6] ZnO nanowires are then suggested to be used to build blocks for bottom-up technique in functional nanoscale electronics,[7] such as electro-optical devices,[8] gas[9] and chemical sensors,[10] field-effect transistors,[11−13] and nano-generator etc.[14] In addition, ZnO has also been demonstrated as an ideal host doped by Mn,[15] Co[16] and Bi,[17] which will dramatically change the electrical characteristics of nanostructures. As a result, electrical transport properties of ZnO nanowires and nanostructures have been widely investigated.[18−20] However, the physical mechanism of the electrical transport in ZnO nanowires is still far from being well understood. Oxygen vacancies in ZnO are believed to play very important roles on its physical properties, while up to now the effect of intrinsic oxygen vacancies on the electrical transport in ZnO nanowires has not been reported.

In this paper we have made an effort to understand the electrical transport of ZnO nanowire with intrinsic oxygen vacancies. We proposed and fabricated a four-contact single ZnO nanowire device with focus ion beam (FIB) lithography technique. The cathodoluminescent (CL) spectra and temperature-dependent electrical resistance measurements of the single ZnO nanowire indicate that the electrical transport mechanism varies for different temperature ranges.

The ZnO nanowire used in our experiment was synthesized on quartz substrate via reduction and oxidation of ZnS powders.[21] Then the nanowire was dispersed on silicon substrate which was capped with a 500 nm silicon dioxide layer as insulator. The standard FIB technique was used to position the individual ZnO nanowire and to deposit Ti/Au (30 nm thickness Ti and 250 nm thickness Au) electrodes on it. The four-electrode configuration was made in order to eliminate the effect from contact resistance with four-terminal electrical measurement. After the ZnO device was completed, it was loaded into an ultra-high vacuum (UHV) chamber equipped with scanning electron microscope (SEM, FEI company, Model 2LE-Column)

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and sensitive spectrograph (Acton company, Model Inspectrum-300-122B) to collect CL spectra.[22] The SEM image of the final structure of this single ZnO nanowire with four electrodes is shown in Fig.1. The diameter of ZnO nanowire is about 300 nm. The distance between two inner electrodes is 5.2 μm. All electrical transport measurements were performed with Keithley SCS 4200 in dark environment and the electron beam of SEM has been shielded.

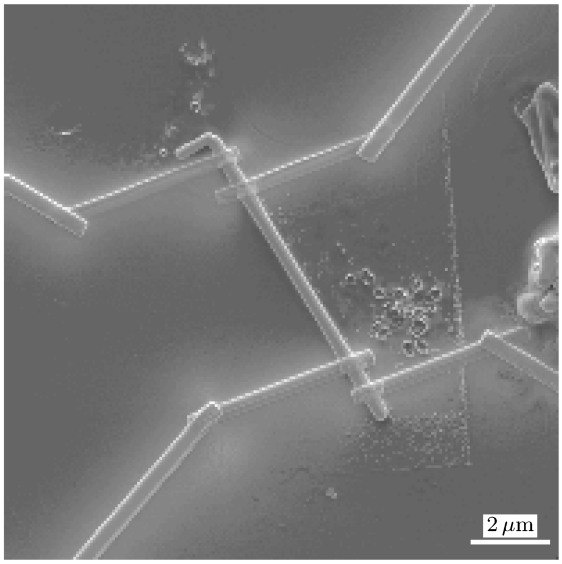


Fig.1. SEM image of four-contact ZnO nanowire device fabricated with FIB technique.

The CL spectra of single ZnO nanowire are shown in Fig.2. At both room temperature (300 K) and low temperature (30 K), it is seen clearly that the spectra consist of a sharp and strong near-UV emission and also a shallow green emission. In the CL spectra at room temperature, the peak of near-UV emission occurs at 389.3 nm. This peak is in agreement with the band gap of bulk ZnO (around 380 nm)[23−25] and its occurrence is due to the recombination of free excitons.[26] The green emission around 551.7 nm is due to single-ionized oxygen vacancy and arises from the recombination of a hole with a single ionized charge state of a specific defect. The appearance of green emission proves that there are plenty of intrinsic oxygen vacancies in the ZnO nanowire. When the temperature decreases to 30 K, the CL spectrum shows an obvious blue shift. In addition, due to the temperature effect, the near-UV emission at low temperatures becomes sharper and shows more details of band gap structure at 369.5, 372.1, 374.7 and 383.7 nm, respectively, as shown in the inset of Fig.2.

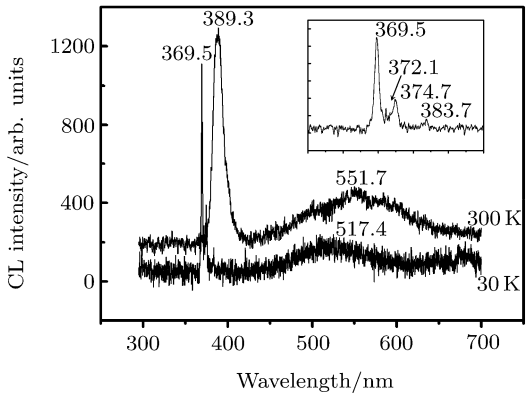


Fig.2. CL spectra of single ZnO nanowire at room temperature (the upper one) and 30 K (the lower one). These spectra indicate the existence of plenty of oxygen vacancies at the surface of ZnO nanowire. The inset shows the details of low temperature spectra around near-UV emission.

The CL spectra clearly manifest that there are plenty of ionized oxygen vacancies in the ZnO nanowire. It has been proved that these oxygen vacancies can increase the electrical conductivity remarkably by inducing defect states in the band gap.[27,28] Previous studies have shown that the ionized oxygen vacancies are mostly located in the surface of ZnO nanowire. In this case, oxygen vacancies can affect electrical transport of ZnO nanowire just as an n-type dopant in the surface. However, this intrinsic dopant is quite different from traditional ones. In order to understand the mechanism of electrical transport in ZnO nanowire with oxygen vacancies, we have carried out electrical measurements for the ZnO nanowire device at different temperatures.

Figure 3 shows typical $I-V$ curves of the ZnO nanowire at temperatures 460, 300 and 35 K. The linear characteristic indicates that ohmic contacts are formed and no obvious effect from contact resistance is involved in our electrical measurements. From 460 to 35 K, the resistance of ZnO nanowire has a small change from 6.87 to 8.63 kΩ. Compared with conventional undoped ZnO nanowire,[8] the relatively high metal-like conductivity (6.9 S/cm at room temperature) indicates that the electrical transport in ZnO nanowire with oxygen vacancies is distinctively different from that without oxygen vacancies.

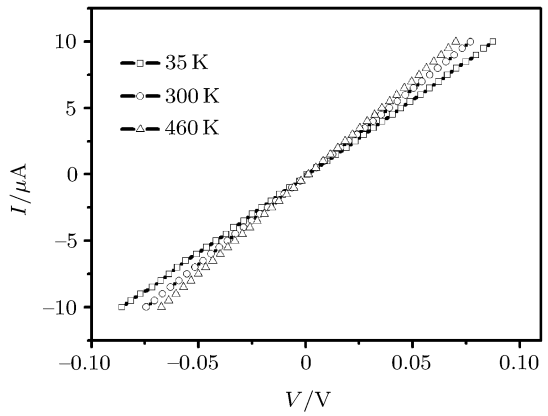


Fig.3. $I-V$ curves of the single ZnO nanowire at 35 K, 300 K and 460 K respectively.

The temperature dependence of conductivity from 35 to 460 K is measured and shown as circles in Fig.4. From these experimental data, we can arrive at conclusions as follows. First, the absolute values of conductivity of ZnO nanowire are very high compared to the results reported previously elsewhere. Secondly, the conductance change is very small (∼19%) in the large temperature range (35–460 K). Considering the surface states induced by plenty of oxygen vacancies in ZnO nanowire surface, the above two facts imply that the electron transport characteristic of the ZnO nanowire is similar to that of a two-dimensional noncrystalline metal rather than a semiconductor. However, as shown in Fig.4, the conductance of ZnO nanowire increases slightly with increasing temperature in the whole range, showing that the ZnO nanowire in our experiment appears like a semiconductor. But we also noticed that, at low temperatures (35–100 K), the conductance increases linearly with increasing temperature expressed logarithmically. Considering the facts mentioned above, if we

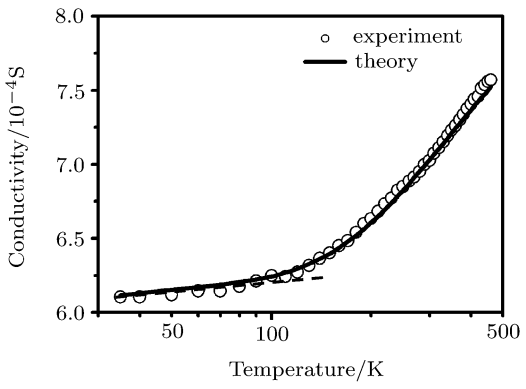


Fig.4. Temperature-dependent conductivity of the single ZnO nanowire. The horizontal axis is in logarithmic scale. The circle line comes from the experimental data, while the solid line denotes the fitted curve.

assume the ZnO nanowire to be a metal, weak localization of electrons or Coulomb interaction will cause similar resistance anomaly as a function of temperature.[29,30] The conductivity correction for weak localization[29,31] can be shown

$$\Delta\sigma = -\frac{e^2}{\pi h}\ln\left(\frac{\tau_{\rm i}}{\tau_0}\right), \tag{1}$$

where $\tau_{\rm i}$ and τ_0 are the lifetimes of the inelastic conduction electrons and the elastic electrons, respectively. This correction is temperature dependent because the inelastic electrons lifetime $\tau_{\rm i}$ depends on the temperature ($1/\tau_{\rm i} \propto T^p$) while elastic electrons lifetime τ_0 is a constant. Rewrite τ_0 as $1/\tau_0 = T_0^p$, where T_0 is a characteristic temperature, so we have

$$\Delta\sigma = \frac{e^2 p}{\pi h}\ln\left(\frac{T}{T_0}\right) + \text{const.} \tag{2}$$

Considering that the conduction electrons are excited by thermal energy from the new surface states to the conductive states at high temperatures, the conductivity of ZnO can be given as

$$\sigma = \alpha \ln T + \frac{\beta}{1+\exp\left(\Delta E/k_{\rm B}T\right)} + \gamma, \tag{3}$$

where

$$\alpha = \frac{e^2 p}{\pi h} = 1.2\times 10^{-5}\times p, \tag{4}$$

here α is in unit of S.

Generally, p is a constant (=1–3) for a two-dimensional metal. ΔE is the energy difference between surface state and the bottom of the conduction band in the ZnO nanowire, and β, γ are numerical factors. Fitting the experimental data with Eq.(3), we obtain the solid curve shown in Fig.4. Therefore, Eq.(3) can be written as

$$\sigma = 1.0\times 10^{-5}\ln T + \frac{0.00048}{1+{\rm e}^{530.2/T}} + 0.00056, \tag{5}$$

here σ is in unit of S.

Compared with the value in weak localization theory, α is very close to the theoretical value. The obtained ΔE is about 45.7 meV. Therefore, we can draw the conclusion that weak localization is the most possible reason for the temperature-dependent conductivity at low temperatures. While in high temperature range (above 100 K), thermally activated transport becomes more predominant than weak localization. It should also be noted that our temperature range is higher than the range in which $\ln T$ behaviour is typically seen in normal metals. As discussed above, the electron transport of the ZnO nanowire behaves like a weakly disordered metal rather than a semiconductor.

In summary, we have studied the CL spectra and temperature-dependent conductivity of a single ZnO nanowire with intrinsic oxygen vacancies. Both near-UV emission and green emission are observed. Due to the presence of plenty of oxygen vacancies in the surface of ZnO nanowire, the electrical transport properties in this ZnO nanowire show two-dimensional noncrystalline metal properties rather than conventional semiconductor. At temperatures below 100 K, weak localization contributes to electrical conductivity of ZnO nanowire, resulting in linearly-increasing conductivity with logarithmically-increasing temperature. While at temperatures above 100 K, thermal activation becomes the predominant factor that affects the electrical transport.

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