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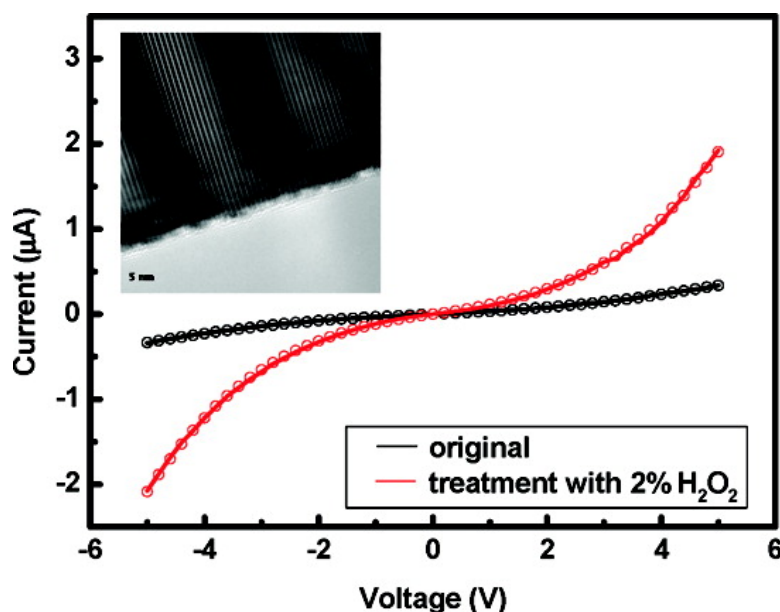
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Quantitative Study on the Effect of Surface Treatments on the Electric Characteristics of ZnO Nanowires

Youfan Hu,[†] Yang Liu,[†] Huilong Xu,[†] Xuelei Liang,[†] Lian-Mao Peng,^{*,†} Ngaisze Lam,[‡] Kawai Wong,[‡] and Quan Li^{*,‡}

Key Laboratory for the Physics and Chemistry of Nanodevices and Department of Electronics, Peking University, Beijing 100871, China, and Department of Physics, The Chinese University of Hong Kong, Shatin, New Territory, Hong Kong, China

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Treatment of ZnO nanowires (NWs) using hydrogen peroxide with increasing concentration results in a continuous increase in the amount of –OH group at the surfaces of the NWs, which demonstrates different characteristics in the transport behaviors of the NWs. Combined with results from theoretical simulation and microphotoluminescence, the variation in the nanowire transport property is explained by the change of carrier density and mobility as induced by the surface treatment.

Introduction

The large surface area associated with nanomaterials makes them promising candidates for chemical and biological sensors with greatly improved sensitivity.^{1–4} In order to improve the detecting specialty as well as to increase the density of docking sites for the targeted species, surface linker molecules are usually introduced at the surface of the nanomaterials.^{5,6} In this regard, nanostructured oxides such as ZnO and SiO₂ are attractive material systems as a small amount of self-formed –OH groups are readily available on their surfaces.^{1,6–8} These –OH groups are very suitable linkers between inorganic and organic molecules and have great biocompatibility. Nevertheless, the amount of the natural surface hydroxide and thus the surface –OH groups could be small without any intentional surface treatment, but can be increased using hydrogen peroxide.

On the other hand, when the size of the material comes into nanometer scale, the much higher surface-to-volume ratio also makes the surface effect more remarkable on the electrical characteristics of the nanomaterials,^{9–11} as compared to their bulk counterparts. In some cases, the surface effect can be dominant in their overall transport behavior,^{12,13} making it possible for the detection of very small change in the transport behaviors as induced by the incident molecules arriving at the surfaces. This is, in fact, the basic working principle of nanomaterial-based sensors. As any surface difference may cause change in their electrical behavior, the generation of surface linkers could also make contributions even before the targeted species arrive. Understanding the effect of surface linker molecule on the nanomaterial transport behavior would then be crucial for reliable device fabrication and further data interpretation of the sensing behavior.

In this letter, we investigate the effects of surface treatment on the electric characteristics of ZnO NWs. We demonstrate

that the surface of ZnO NWs can be modified by a simple hydrogen peroxide solution treatment in terms of both the amount of surface –OH group and the surface roughness, which would further modify the electrical properties of the NWs. All experimental current–voltage (*I*–*V*) curves are quantitatively analyzed using a metal–semiconductor–metal (MSM) model,^{14,15} and the results are correlated to the changes in the NW surface conditions.

Experimental Section

The ZnO NWs used in this study were synthesized by thermal evaporation of pure ZnO powder (99.99%) at 1200 °C. Microstructure and composition characterization were carried out using a FEI XL30 field-emission gun scanning electron microscope (SEM), a Tecnai F20 ST and Philip CM120 transmission electron microscope (TEM). The chemical states of the surface and compositional elements are determined by X-ray photoelectron spectroscopy (XPS). Micro-photoluminescence (PL) measurements were conducted using a He–Cd laser (with $\lambda = 325$ nm) at room temperature. The ZnO NW based devices were fabricated as follows. The as-grown ZnO NWs were first dissolved in ethanol by ultrasonic, and then dropped on a degenerately n-doped Si wafer covered with a 200 nm thick thermal SiO₂. Electron beam lithography, metal deposition and lift-off were then used to form contacts on individual ZnO NWs. Figure 1 shows a typical top view SEM image of a ZnO NW based device. Electrical measurements were carried out by using a Keithley 4200 semiconductor characterization system. The as grown ZnO NWs are n-type, which is confirmed by the transfer characteristics of the ZnO NW based field-effect transistors (FETs).

Results and Discussion

The –OH group is a very useful linker for the covalent bond formation between the oxide semiconductors and the biomolecules. The amount of the naturally existing surface hydroxide is small for ZnO, but can be increased via hydrogen peroxide

* To whom correspondence should be addressed. E-mail: (L.M.P.) lmpeng@pku.edu.cn; (Q.L.) liquan@phy.cuhk.edu.hk.

[†] Peking University.

[‡] The Chinese University of Hong Kong.

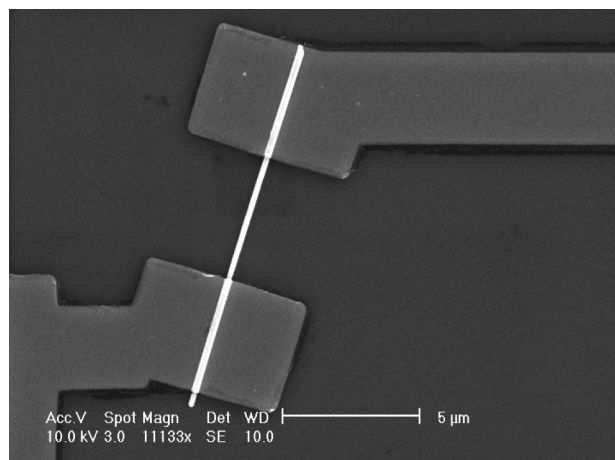


Figure 1. SEM image showing a top view of a typical ZnO nanowire based device

treatment. From the XPS data and the fitting results showed in Figure 2, we found that immersing the ZnO NW sample into H_2O_2 solution indeed results in increased $-\text{OH}$ group on the NW surface. Three samples were examined with sample 1 taken as a reference, which was only washed with deionisation (DI) water. Samples 2 and 3 were immersed in a 2 and 10% H_2O_2 solution for 30 min, respectively. All of the samples were then washed with DI water. The atomic percentage of OH or O can be estimated using XPS spectrum using the formula

$$\text{Atomic \%} = \frac{\frac{I_A}{S_A}}{\sum_i \frac{I_i}{S_i}} \times 100\%$$

where I is the integrated intensity under the corresponding peak (after the background being subtracted) and S is the sensitivity factor which depends in general on such factors as the photoionization cross-section, the inelastic mean free path of the photoelectrons, and the transmission function for the electron analyzer. In our case, since the sensitivity factors for oxygen at different chemical states are the same, the OH/O ratios can therefore be obtained directly from the XPS O 1s core level spectrum. Figure 2 shows that the OH/O ratio increases from 0.4 for sample 1 (Figure 2a) to 1.0 for sample 2 (Figure 2b), and eventually reaches 1.6 for sample 3 (Figure 2c), disclosing a general trend of increasing amount of $-\text{OH}$ group on the ZnO NW surface, when the NWs are treated with more concentrated H_2O_2 solution. An increasing trend in O/Zn ratio is also observed in these samples, but quantification of these results is less reliable and these results are therefore not shown here. Nevertheless, it is found that the ZnO NW surface roughness increases with increasing H_2O_2 concentration. As shown in the insets (high-resolution TEM images) of Figure 2, a similar surface morphology is found for sample 1 and 2 (2% H_2O_2 treated), which has a fluctuation less than 2 nm, but it becomes much rougher for sample 3 (10% H_2O_2) with surface roughness increased to ~ 5 nm. Quantitatively we may use the contour arithmetic mean deviation R_a (defined as $R_a = [\int_0^l |f(x)| dx] / l$, with $f(x)$ being the contour deviation, and l being the length of the NW) to describe the surface roughness. Using the HRTEM images shown in Figure 2 we have $R_a = 0.15$ nm for sample 1, $R_a = 0.29$ nm for sample 2, and $R_a = 1$ nm for sample 3.

It is well known that the presence of an $-\text{OH}$ group at the surface of ZnO will affect its surface carrier density,¹⁶ and the

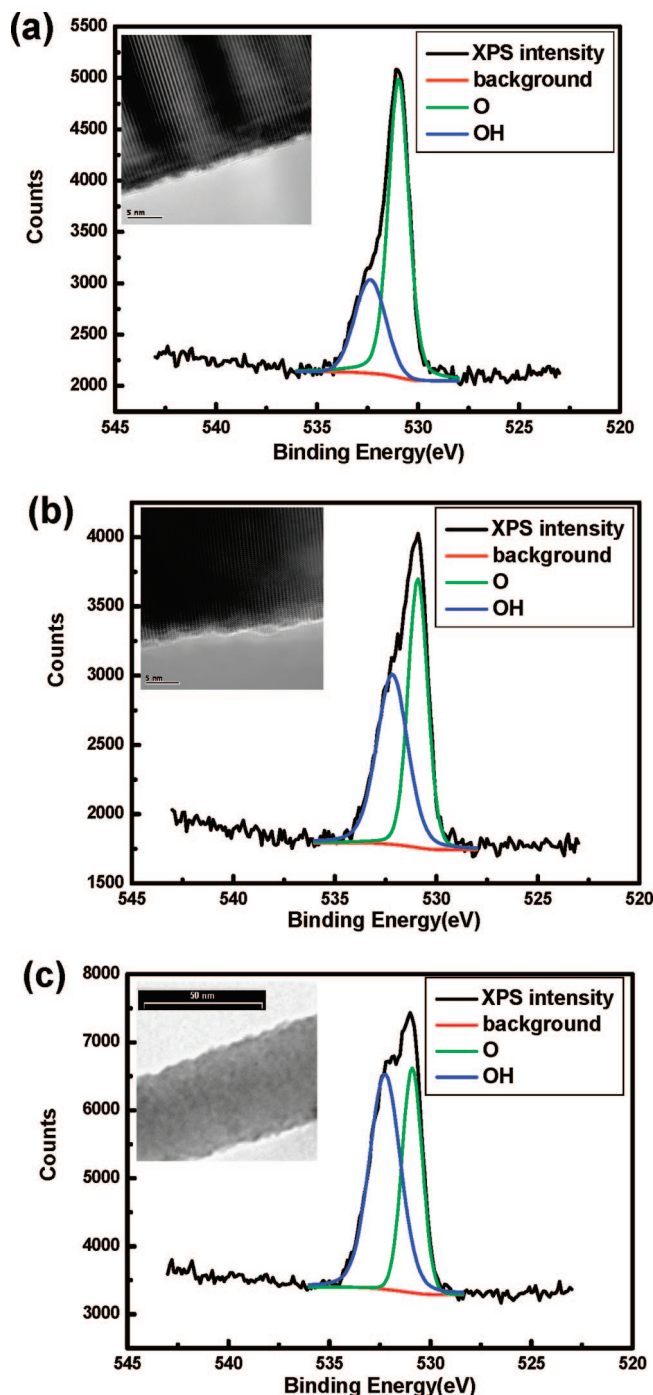


Figure 2. XPS results on ZnO NWs treated with (a) DI water, (b) 2% H_2O_2 , and (c) 10% H_2O_2 . Insets: corresponding TEM images showing the treated ZnO NWs. The scale bar in the inset denotes 5 nm in (a) and (b), and 50 nm in (c).

increased surface roughness will introduce more scattering centers which in turn will result in a reduced carrier mobility. Therefore, ZnO NW based devices were fabricated to investigate these effects. Micro-PL spectra were recorded from corresponding nanowire device to evaluate surface defects before and after the H_2O_2 treatment. In a typical procedure, 2 and 10% H_2O_2 solution were separately dropped on two nanowire devices and held for 10 s before the devices were washed with DI water and dried before the electrical measurements. The micro-PL measurements were carried out before and after the H_2O_2 treatment for individual devices. As shown in Figure 3, the current is increased for the device treated with 2% H_2O_2 (Figure

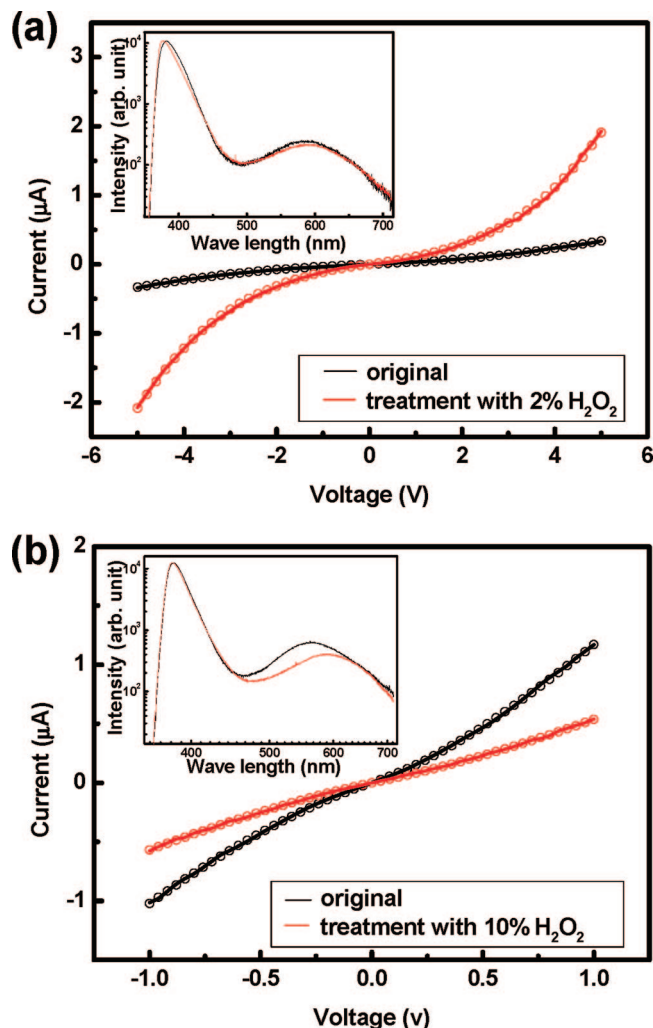


Figure 3. I - V curves of two ZnO NW based devices measured before (black curve) and after (red curve) treated with (a) 2% H_2O_2 and (b) 10% H_2O_2 . Circles: fitted data. Inset: corresponding PL spectrum recorded before and after H_2O_2 treatment.

3a), but decreased for that treated with 10% H_2O_2 (Figure 3b). To a good approximation, this type of long channel semiconductor devices may be described using the MSM model we recently developed.^{14,15} Experimental I - V curves can be analyzed quantitatively using the program described in ref 17 and shown in Figure 3 together with the best fitted curves (plotted as circles in Figure 3) with the device parameters given in Table 1.

Table 1 shows that the as-prepared ZnO NW has a carrier density or doping concentration N_d on the order of 10^{+17} to 10^{+18} cm^{-3} , which is typical for unintentionally doped ZnO.^{18,19} The electron mobility μ_e varies from 3.3 to 91 $\text{cm}^2/(\text{Vs})$, which is also similar to that obtained from the as-fabricated ZnO NWs based field-effect transistors (FETs) [with $\mu_e \sim 20$ –80 $\text{cm}^2/(\text{Vs})$].⁹ The carrier density is found to reduce after both H_2O_2

treatments. On the other hand, the electron mobility increased after the sample being treated with 2% H_2O_2 , but decreased when 10% H_2O_2 was employed. In the inserts of Figure 3, the micro-PL spectra recorded from the corresponding devices show that the PL intensity of the broad green emission band (commonly attribute to the existence of native defects such as oxygen vacancies,^{20,21}) was reduced slightly with moderate surface treatment by 2% H_2O_2 (Figure 3a). Such reduction becomes much more significant for the sample treated by 10% H_2O_2 (Figure 3b).

H_2O_2 contributes to the surface modification of ZnO NW in several distinct ways. First, the strong oxidizing property of H_2O_2 can annihilate oxygen vacancies at the ZnO surface. Since the doping concentration in native ZnO is related to the density of oxygen vacancies, we attribute the reduction in the carrier density after surface treatment with H_2O_2 to the reduced surface defects as evidenced in the PL-spectra shown in Figure 3. Second, both theoretical and experimental work indicate that H serves as a good donor to ZnO and may bond with the surface oxygen of ZnO to form hydroxide,¹⁶ i.e., $\text{H} + \text{O}^{2-} \rightarrow \text{OH}^- + \text{e}^-$. Therefore, the annihilation of oxygen vacancies on the surface of the ZnO NW will offer more sites for the H atoms in the environment to bond with, and thus result in increased $-\text{OH}$ group concentration on the surface. In an ideal situation, every annihilated oxygen vacancy (via surface treatment with H_2O_2) will contribute to a new site for the $-\text{OH}$ group. Therefore, higher H_2O_2 concentration would lead to an increased concentration of $-\text{OH}$ group on the ZnO surface, and this agrees with our XPS results (Figure 2). On the one hand, H atoms (via forming $-\text{OH}$ groups) act as donors on the surface of ZnO, which results in an increased carrier concentration in the NW. On the other hand, the reduced or annihilated surface oxygen vacancies would cause a decrease in the carrier concentration. Even in the ideal situation, there is a net annihilation of one carrier at every new site of the $-\text{OH}$ group, leading to a reduced carrier concentration of the ZnO NW as evidenced in Table 1. Third, the H_2O_2 etching also modifies the surface morphology of the ZnO NWs. In the case of diluted H_2O_2 solution (e.g., 2%), the surface remains smooth with no noticeable increase in surface roughness (Figure 2b). With the number of surface oxygen vacancies being reduced, charge carrier scattering in the surface region is suppressed leading to an increased carrier mobility (see device 1 of Table 1). At higher H_2O_2 concentration, (e.g., with 10%), the increased surface roughness (Figure 2c) will largely increase the surface scattering, which eventually outweigh the opposite effect of the reduced surface oxygen vacancies, leading to a reduced carrier mobility (see device 2 of Table 1). The conductivity of the ZnO-based device depends on both the carrier density and mobility and would be affected by every aspect of the surface change.

We now consider the effects of different surface treatments on the same device. Figure 4 shows three I - V curves that correspond to the as-fabricated ZnO NW device (black curve), the device treated by 2% H_2O_2 solution for 10 s (red curve), and the one with additional treatment by 10% H_2O_2 solution

TABLE 1: Retrieved Device Parameters for Two ZnO NW Based Devices before and after the Treatment with 2 and 10% H_2O_2 Solution

	device 1		device 2	
	as prepared	treatment with 2% solution	as prepared	treatment with 10% solution
$N_d (\text{cm}^{-3})$	3.4E+017	2.0E+017	1.0E+018	6.6E+017
mobility [$\text{cm}^2/(\text{Vs})$]	3.3E+000	9.9E+001	9.1E+000	6.9E+000
conductivity (s/m)	1.8E+001	3.2E+002	1.5E+002	7.3E+001

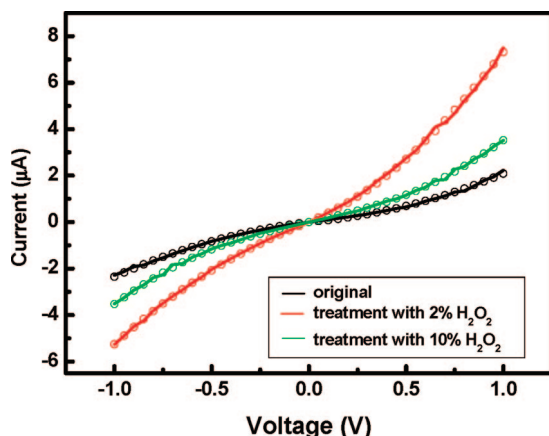


Figure 4. I – V curves of a device measured before and after treated with 2% H_2O_2 and 10% H_2O_2 step by step. Circles: fitted data.

TABLE 2: Retrieved Device Parameters of a ZnO NW Device before and after the Treatment with 2 and 10% H_2O_2 Solution Step by Step

	as prepared	treatment with 2% solution	treatment with 10% solution
N_d (cm^{-3})	1.6E+018	9.5E+017	3.1E+017
mobility [$\text{cm}^2/(\text{V}\cdot\text{s})$]	1.5E+001	7.3E+001	1.1E+001
conductivity (s/m)	3.9E+002	1.1E+003	5.7E+002

for 10 s (green curve). The experimental I – V curves are quantitatively fitted using the MSM model as discussed before, and the retrieved device parameters are given in Table 2. For this device, the carrier density is found to reduce after each of the H_2O_2 treatments. Nevertheless, the electron mobility is found to first increase (after being treated with 2% H_2O_2) and then decrease (after being treated again with 10% H_2O_2). All these results are consistent with the earlier results obtained on different devices being surface treated separately (Figure 3 and Table 1). We therefore conclude that surface treatment with suitable H_2O_2 solution (e.g., less than 2%) could increase the conductivity of ZnO NW and the quantity of $-\text{OH}$ group at the ZnO surface while not damage the surface morphology. This information will be important to guide further device fabrication for chemical/biological sensors.

Conclusions

In summary, the higher surface-to-volume ratio makes the transport properties of NWs very sensitive to their surfaces. The

treatment with hydrogen peroxide would remarkably increase the quantity of the $-\text{OH}$ group at the ZnO surface. By altering the density of carrier and scattering centers at the surface, hydrogen peroxide treatment plays important roles in affecting the electrical transport characteristics of ZnO nanowires.

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