Tuning of operation mode of ZnO nanowire field effect transistors by solvent-driven surface treatment

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Abstract
We report on the adjustment of the operation voltage in ZnO nanowire field effect transistors (FETs) by a simple solvent treatment. We have observed that by submerging ZnO nanowires in isopropyl alcohol (IPA), the surface of the ZnO nanowires is etched, generating surface roughness, and their defect emission peak becomes stronger. In particular, ZnO nanowire FETs before IPA treatment operate in the depletion-mode, but are converted to the enhancement-mode with a positive shift of threshold voltage after submersion in IPA. This solvent treatment can be a useful method for controlling the operation mode of ZnO nanowire FETs for wide applications of nanowire-based electronic devices and circuits.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

One-dimensional ZnO nanowires with a wide direct band gap ($\sim$3.4 eV) and a large exciton binding energy (60 meV) have been extensively studied for various applications, such as light emitting diodes (LEDs), electronic devices, sensors, logic circuits, and photovoltaic devices [1–6]. Of these, the ZnO nanowire has been widely investigated as a field effect transistor (FET) element. In particular, most of the ZnO nanowire FET devices have shown n-channel depletion-mode (D-mode) behaviour, which exhibits nonzero current at zero gate bias and negative threshold voltages [7–9]. However, n-channel enhancement-mode (E-mode) FETs may be preferable in comparison with D-mode nanowire FETs, because the E-mode FETs have off-current at zero gate bias, generating low power consumption [9]. In addition, by combining D-mode and E-mode nanowire FETs, it is possible to realize more practical applications, such as logic circuits [6]. Because of these advantages, E-mode ZnO nanowire FETs have become attractive, although E-mode operation for nanowire-based FETs is rather difficult to achieve. We have been researching

methods of creating E-mode ZnO nanowire FETs and recently demonstrated that E-mode ZnO nanowire FETs are possible by the adjustment of the surface morphology of ZnO nanowires grown on different substrates [10]. Furthermore, we have also demonstrated nanowire logic circuits made from combining D-mode and E-mode ZnO nanowire FETs [6].

In this study, we demonstrate a simple method of tuning the operational mode of ZnO nanowire FETs. A chemical treatment with isopropyl alcohol (IPA) allows the adjustment of the threshold voltage in ZnO nanowire FETs. To this end, ZnO nanowires grown by the thermal vapour transport method were submerged in IPA solvent for three different periods: as-grown, 15 days, and 30 days. We observed that IPA treatment can generate a surface roughness on the ZnO nanowires. The surface roughness of the nanowires can induce more trapping of carrier electrons, causing electron depletion in ZnO nanowire channel [10]. As a result, the threshold voltage of nanowire FET devices shifts toward the positive gate bias direction and the operation mode conversion from D-mode to E-mode is achieved.
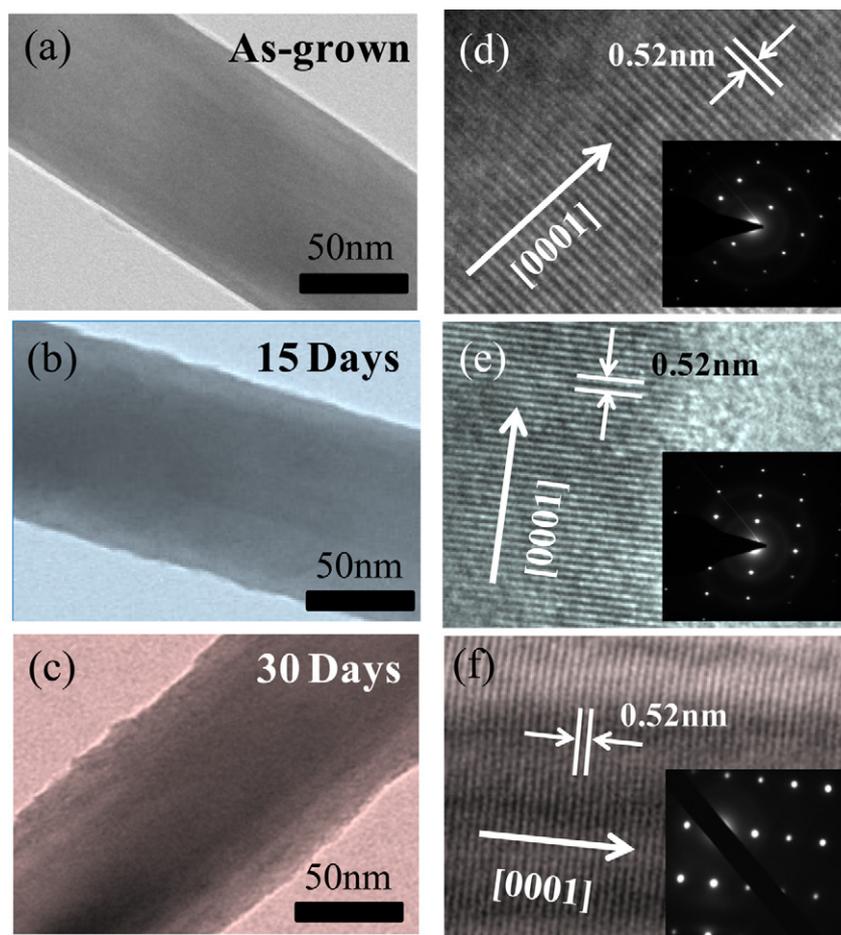
Figure 1. (a)–(c) TEM images and (d)–(f) HRTEM images of ((a), (d)) an as-grown ZnO nanowire and ZnO nanowires submerged in IPA for ((b), (e)) 15 days and ((c), (f)) 30 days. The scale bars are 50 nm. The electron diffraction patterns are shown in the insets of (d)–(f).

2. Experimental details

The ZnO nanowires were grown on Au-coated *c*-plane sapphire substrates by a vapour transport method in a horizontal quartz tube furnace [10]. Zn vapour was generated and deposited on the sapphire substrate by evaporation of a mixed source of ZnO and carbon powder at 920 °C under the flow of a mixed gas source of Ar and oxygen. During the reaction, the tube pressure was maintained at 700 Torr. After growth of ZnO nanowires, a nanowire suspension was made by sonicating the substrates with nanowires for about 20 s in IPA. To observe the effects of submersion time on ZnO nanowires in IPA solvent, three experimental conditions were employed: as-grown, 15 days submersion time in IPA and 30 days submersion time in IPA. Note that 20 s should be added to the submersion time for each condition. The transmission electron microscopy (TEM) images were used to examine the surface morphology of the ZnO nanowires, and photoluminescence (PL) measurements were carried out to compare the optical properties of the ZnO nanowires under these three submersion conditions. In order to study the electrical properties of ZnO nanowires with IPA treatment, nanowire FETs were fabricated in a conventional back-gate configuration by a method reported in detail elsewhere [10].

and tested after submersion in IPA. A semiconductor parameter analyzer (Agilent B1500A) was used to measure the transport characteristics of the ZnO nanowire FETs at room temperature.

3. Results and discussion

3.1. Surface morphology and optical properties of ZnO nanowires

Figures 1(a)–(c) show the low magnification TEM images of the surface morphologies of typical ZnO nanowires treated with different submersion times in IPA. The surface morphologies of these three sets of ZnO nanowires were compared. The as-grown nanowires have a smooth surface (figure 1(a)), whereas the ZnO nanowires with longer submersion times exhibit a rougher surface morphology (figures 1(b) and (c)), suggesting the surface etching of the nanowires by IPA solvent. The high-resolution TEM (HRTEM) images of ZnO nanowires for each condition and corresponding electron diffraction patterns (lower insets) in figures 1(d)–(f) show that even these etched nanowires remain as single crystalline with a preferred growth direction of [0001].

Figure 2(a) shows the PL spectra of ZnO nanowires with different submersion times. ZnO nanowires grown on the Au-
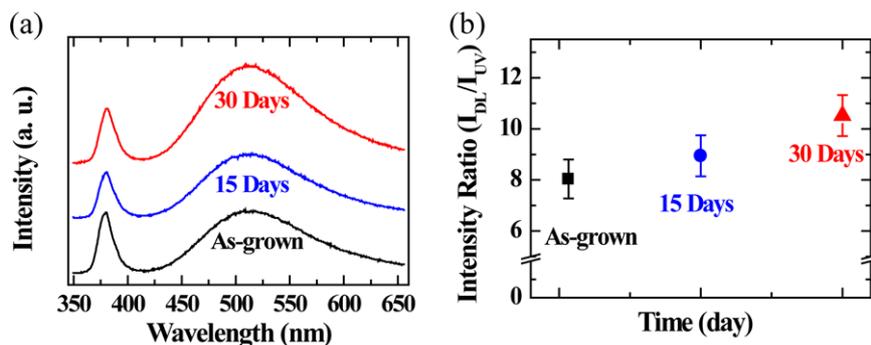
Figure 2. (a) PL spectra of ZnO nanowires with three submersion time conditions. (b) PL intensity ratios of I_{DL}/I_{UV} as a function of the submersion time.
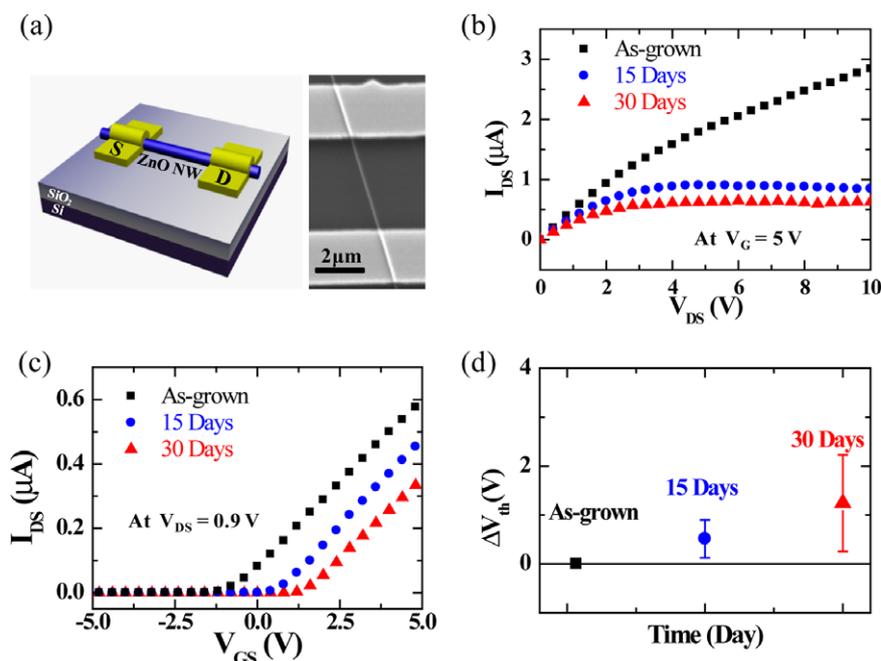

Figure 3. (a) Schematic diagram and SEM image of a ZnO nanowire FET. (b) $I_{DS}-V_{DS}$ curves measured at a fixed gate voltage of 5 V and (c) $I_{DS}-V_{GS}$ curves measured at a fixed drain voltage of 0.9 V for a FET of an as-grown ZnO nanowire (black symbols) and for ZnO nanowire FETs submerged in IPA for 15 days and 30 days (blue and red symbols, respectively). (d) Statistical distribution of the threshold voltage shift as a function of the submersion time.

coated *c*-plane sapphire substrate were transferred to Si wafers for PL measurements. In figure 2(a), the PL emission of the ZnO nanowires consisted of the ultraviolet (UV) emission band (left side, narrow band) and the defect level (DL)-related emission band (right side, broad band) associated with the surface defects of the nanowires. For the as-grown ZnO nanowires, the intensity of the DL emission is relatively weak in comparison with that of the UV emission. In contrast, for the ZnO nanowires with submersion times of 15 days or 30 days, the intensity of DL emission is relatively strong as compared with that of the UV emission. Figure 2(b) shows the DL-to-UV intensity ratios (I_{DL}/I_{UV}) of ZnO nanowires as a function of different submersion time. Since the DL emission peak is associated with a surface-related process, the large I_{DL}/I_{UV} ratio means that the ZnO nanowires have a large density of surface defects, whereas those with small I_{DL}/I_{UV} ratios have a small density of surface defects [11].

Therefore, the observation of the increase in the intensity of the DL emission peak of the ZnO nanowires with increasing solvent submersion time indicates that the surface defects of ZnO nanowires are also increased with submersion time.

3.2. Electrical properties of ZnO nanowire transistors

We investigated the electrical properties of the ZnO nanowires with solvent-driven surface treatment in IPA. For this study, we fabricated ZnO nanowires FET devices and examined their transport properties. The schematic diagram and SEM image of a ZnO nanowire FET are shown in figure 3(a). Figures 3(b) and (c) show the electrical characteristics of the representative nanowire FETs with and without submersion in IPA for 15 days and 30 days. Figure 3(b) displays the output characteristics ($I_{DS}-V_{DS}$, source–drain current versus source–drain voltage, at $V_G = 5$ V) and figure 3(c) displays the transfer characteristics
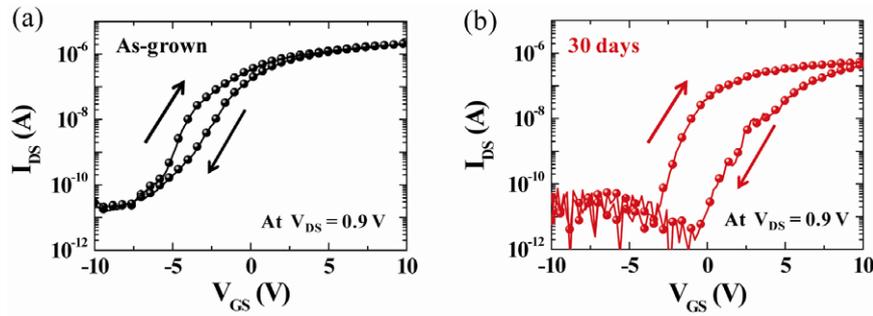
Figure 4. Hysteretic behaviours for FET devices made from (a) as-grown and (b) IPA-treated ZnO nanowires (at $V_{DS} = 0.9$ V). The arrows show the direction of the gate voltage sweep.

(I_{DS}−V_{GS}, source–drain current versus gate voltage, at $V_{DS} = 0.9$ V) of the representative FETs. From the I_{DS}−V_{DS} curves in figure 3(b), the drain current is reduced with submersion time of ZnO nanowire FETs in IPA. In figure 3(c), the three curves indicate that the electrical transport properties of ZnO nanowires are strongly influenced by IPA treatment. The FET made from the as-grown ZnO nanowires showed the n-channel D-mode (black symbols in figure 3(c)), which exhibits nonzero current at zero gate bias and a negative threshold voltage, indicating that carriers can only be depleted in the conducting channel by applying a greater negative gate bias. On the other hand, the nanowire FETs treated with a submersion time of 15 days and 30 days showed the normally-off type, n-channel E-mode (blue and red symbols in figure 3(c), respectively), which exhibits zero current at zero gate bias and positive threshold voltages, indicating that carriers can only be generated in the conducting channel by applying a greater positive gate bias. For the data shown in figure 3(c), the threshold voltage for the ZnO nanowire FET without IPA treatment was −0.64 V, and the threshold voltages for nanowire FETs with submersion times of 15 days and 30 days were found as 0.87 V and 1.56 V, respectively. This result clearly demonstrates the conversion of ZnO nanowire FETs from D-mode to E-mode operation with a simple chemical treatment. Note that the threshold voltage was obtained by extrapolating the linear portion of the transfer characteristics I_{DS}−V_{GS} to zero drain current curves from the point of maximum slope where the transconductance ($g_m = dI_{DS}/dV_{GS}$) is maximal [11]. From the transfer characteristics, the mobility can be calculated from the equation $\mu = g_m L^2 / V_{DS} C_G$, where $C_G = 2\pi \varepsilon_r \varepsilon_0 L / \cosh^{-1}((r+h)/r)$ is the gate capacitance. Here r is the nanowire radius ($\sim$50 nm), L is the nanowire channel length ($\sim$4 μm), h is the gate dielectric thickness (100 nm), ε_0 is the permittivity of free space, and ε_r is the dielectric constant of SiO$_2$ (3.9). Then, we calculated and compared the mobility values of ZnO nanowire FETs at an equal carrier concentration condition ($\sim$2.0 $\times$ 10^{17} cm^{-3}). The mobility was found to be 34.6, 33.0, and 31.3 cm^2 V^{-1} s^{-1} for ZnO nanowire FETs for different conditions; as-grown, 15 days submersion time, and 30 days submersion time, respectively.

Figure 3(d) summarizes the statistical distribution of the threshold voltage shift of the ZnO nanowire FETs relative to the threshold voltages for the nanowire FETs without IPA treatment. The error bars in this figure were obtained from measurements of several nanowire FET devices (5 nanowire FET devices for each submersion condition, for a total of 15 devices). Note that the error bar becomes larger with increasing submersion time in IPA solvent. However, it was clearly observed that the threshold voltage shifted toward the positive gate bias direction with increasing submersion time in IPA solvent. With more defects on the nanowire surface, there are fewer conduction electrons in the nanowire channel due to the electron trapping at the surface defect sites, resulting in the reduction of conductivity and thus a shift of the threshold voltage of nanowire FET devices to the positive gate bias direction, which is consistent with the optical data in figure 2.

In figures 4(a) and (b), the hysteric behaviours for as-grown nanowire FET and 30 days IPA-treated nanowire FET are presented. The result shows that the hysteresis is more severe for the device of 30 days submersion condition. This difference of hysteresis can be explained by chemical environments. It has been reported that the presence of adsorbed species plays a significant important role in the hysteresis of nanowire or nanotube FETs [11–13]. The adsorption of molecules can occur on the surface defect sites, causing the conduction electron trapping. As previously discussed, the surface defects are generated by the surface etching effect with IPA solvent treatment. Therefore, the hysteresis of the IPA-treated ZnO nanowire FET is larger than that for the as-grown ZnO nanowire FET. Note that the hysteresis of both as-grown (smooth) and IPA-treated (rough) nanowire FETs was mitigated after a passivation treatment, similarly to our previous report [11]. Particularly, the width of the hysteresis of the IPA-treated nanowire FET was dramatically reduced after the passivation.

The observed results of the IPA treatment on the physical properties of ZnO nanowires can be explained in figure 5. Figure 5 shows the cross-sectional schematics of nanowire FETs and energy band diagrams for as-grown nanowires (figure 5(a)) and ZnO nanowires submerged in IPA for 15 days or 30 days (figure 5(b)) at $V_G = 0$ V. In figure 5(a), for the as-grown ZnO nanowires, fewer defects were generated, showing less band bending and a smaller depletion region. On the other hand, in figure 5(b), for the ZnO nanowires submerged in solvent, more defects were generated, exhibiting more band bending and a larger depletion region. The difference between the as-grown nanowires and nanowires submerged in solvent can be explained by the surface etching effect caused by the
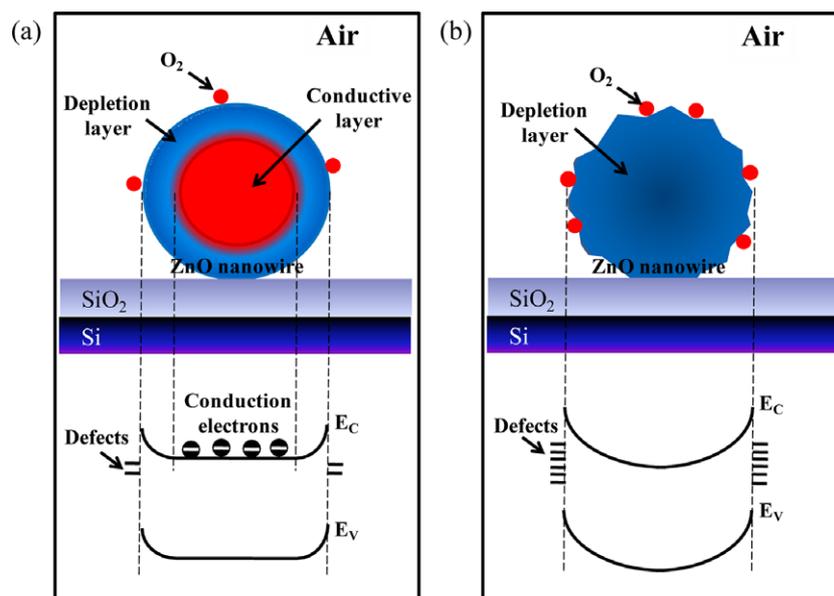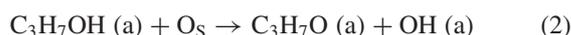
Figure 5. (Top) cross-sectional schematics of ZnO nanowire FETs and (bottom) the corresponding energy band diagrams at $V_{\rm G} = 0$ V for (a) as-grown nanowires and (b) solvent-etched ZnO nanowires after submersion in IPA for 15 days or 30 days. $E_{\rm C}$ is the conduction band and $E_{\rm V}$ is the valence band of the ZnO nanowires.

chemical reaction of solvents (such as IPA or acetone) on the ZnO nanowires [14–17]. We also observed a similar solvent effect of submerging ZnO nanowires in acetone (data not shown here). In particular, the reaction of these solvents is more active on the surface of ZnO nanowires due to the large surface to volume ratio [17]. The chemical reaction between the surface of a ZnO nanowire and solvents etches the surface and generates surface defects. For example, in the chemical processes between ZnO and IPA, oxygen vacancies can be generated as follows [16]

$$C_3H_7OH\ (l) \rightarrow C_3H_7OH\ (a) \tag{1}$$

$$C_3H_7OH\ (a) + O_S \rightarrow C_3H_7O\ (a) + OH\ (a) \tag{2}$$

$$C_3H_7OH\ (a) + OH\ (a) \rightarrow C_3H_7O\ (a) + H_2O\ (l) + V_O \tag{3}$$

where (a) and (l) refer to adsorbed and liquid-phase species, respectively: S in O_S refers to the lattice site, and V_O indicates an oxygen vacancy.

Since the electrical characterization was performed in ambient air, O_2 molecules can be adsorbed on the surface of ZnO nanowires. Surface defects on ZnO nanowires, such as oxygen vacancies, can serve as adsorption sites [18]. Then, O_2 molecules adsorbed at these defect sites form O_2^- and act as electron acceptors [19]. Thus, the conduction electrons are depleted from the conducting channel by the chemisorption of O_2^-, reducing the channel conductivity and shifting the threshold voltages of the nanowire FETs towards the positive gate bias direction. As shown in figure 5(b), for the ZnO nanowires treated in solvent, the depletion layer is extended by the high concentration of chemisorbed O_2^- on the ZnO nanowires. Moreover, the conduction electron trapping at the interface states between the SiO_2 dielectric layer and ZnO nanowires can partially contribute to the change of the electrical characteristics of ZnO nanowire FETs.

4. Conclusions

In summary, we investigated the structural, optical, and electrical properties of ZnO nanowires by IPA solvent treatment. We observed that with the submersion of ZnO nanowires in IPA, the intensity ratio of the defect-related PL peaks increased and the threshold voltages of the nanowire FETs shifted to the positive gate bias direction, and as a result, operation mode conversion from D-mode to E-mode was achieved. This solvent treatment can be explained by the surface defects generated in the chemical reactions between IPA and ZnO nanowires. Our study is intended to demonstrate that a simple chemical treatment can be a useful method to control threshold voltages and the operation mode of ZnO nanowire FET devices.

Acknowledgments

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