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The influence of surface chemical dynamics on electrical and optical properties of ZnO nanowire field effect transistors

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Abstract
We demonstrate the effect of surface chemical dynamics on carrier transport and recombination processes of electron–hole pairs in ZnO nanowire field effect transistors. We have found that the electrical conductance decreases and the threshold voltages shift in a positive gate voltage direction, as electrical characteristics are measured repeatedly. We associate this with the enhancement of oxygen adsorption by capturing electrons from the induced current during the probing. This results in an overall depletion of electrons and thus causes the positive shift in threshold voltages associated with the origin and width of characteristic hysteresis loops. In addition, the surface environment dependence of the photo-response related to a recombination process in ZnO nanowires is discussed in terms of the surface chemical reaction and band bending.

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

ZnO nanowires continue to be of considerable interest as one-dimensional (1D) building blocks for new functional nanoscale device applications in electronics, optics, optoelectronics, and sensors due to their unique electrical, optical, and piezoelectric properties as well as unique dimensionality [1–4]. In particular, until recently, remarkable progress in nanoelectronics has been made to achieve high performance devices and nanoscale interconnects through the considerable improvement of synthesis methods and nanofabrication techniques [5–10]. Nevertheless, there remains substantial difficulty in using ZnO nanowires for making predictable and controllable nanoscale devices since surface chemistry and structure of ZnO nanowires, playing an important role in determining their physical properties, give an influence on device properties such as conductance, mobility, threshold voltages, and light emission [11–13]. These are particularly relevant for 1D nanowires due to the large surface to volume ratio, which is large enough for surface effects to make the operation of nanoscale devices uncontrolled and unpredictable [14, 15]. To date, studies on ZnO nanowires, showing interesting features, have mainly focused on chemical sensors, field effect transistor (FET) device performance, and photodetectors. Thus, in order to extend the feasibility of practical nanoelectronics applications, requiring controllable and predictable ZnO nanowire FETs as useful components, the detailed dynamics of the interaction between the ZnO nanowire surface and chemical species in environments associated with their electrical and optical properties has to be understood. In addition, the understanding of the origin of hysteresis caused in ZnO nanowire FETs is still lacking, although the removal

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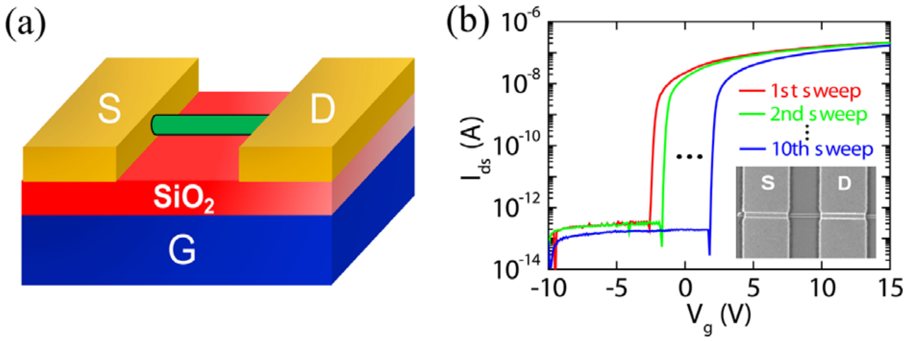

Figure 1. (a) A schematic view of a back gated ZnO nanowire FET. (b) Typical transfer characteristics at a drain bias of 0.1 V measured at room temperature in ambient air. The inset is a SEM top-view image of a ZnO nanowire between the source and drain electrodes.

or control of the hysteresis is particularly important for device applications such as logic circuits and memory storage. Also, little attention has been given to surface chemical dynamics that affects carrier transport and recombination processes of electron–hole pairs in ZnO nanowires. Here, we report that the transport phenomena across ZnO nanowires are strongly dependent on the electrical interaction between chemical species and ZnO nanowires near the surface. We demonstrate that the adsorption of oxygen on the ZnO nanowire surface is significantly mediated by capturing electrons during the electrical probing, inducing the positive shift in threshold voltages continuously as we measure electrical characteristics repeatedly. This causes hysteresis in ZnO nanowire FETs due to the depletion of electrons during the measurement. We also investigate the influence of the adsorbed oxygen on the photo-response of nanowires associated with a recombination process. It is found that negatively charged oxygen ions on the nanowire surface lead to band bending upwards and thus result in a separation of photo-generated electron–hole pairs, contributing to the slow decay of the conductivity due to the difficulty in the direct recombination of electron–hole pairs.

The ZnO nanowires employed in this study were grown on a-plane sapphire substrates with Au catalysts by the vapour phase transport process reported previously [10, 11, 16]. In order to fabricate ZnO nanowire FETs, ZnO nanowires were first dispersed by sonication in isopropyl alcohol and then transferred onto a silicon substrate by dropping a liquid suspension of ZnO nanowires from a pipette. A 100 nm-thick silicon oxide layer was employed as a gate oxide layer on a heavily doped p-type silicon substrate used as a global back gate, as shown schematically in figure 1(a). Source and drain electrode patterns were defined by conventional photolithography followed by electron-beam evaporation of Ti (80 nm)/Au (40 nm) electrodes on a ZnO nanowire and lift off processes. The separation of source and drain electrodes was $\sim 3\ \mu$m. The inset of figure 1(b) shows a SEM image of such a device. The electronic transport characteristics of ZnO nanowire FETs were measured using a semiconductor parameter analyzer (Keithley 4200 and HP 4155B) at room temperature.

Figure 1(b) shows typical transfer ($I_{\mathrm{ds}} - V_{\mathrm{g}}$) characteristics of n-channel ZnO nanowire FETs measured in ambient air. We observed a large modulation of the channel conductance, more than 6 orders of magnitude, by applied gate bias. These characteristics indicate clearly the electrical behaviour of n-type semiconducting FETs, showing the increase (decrease) in the channel conductance with increasingly positive (negative) gate bias. Here, an interesting finding is that the electrical conductance decreases and the threshold voltage shifts gradually to the positive gate voltage direction as the gate voltage is repeatedly swept from negative to positive values at a sweep rate of 0.2 V s^{-1}. These phenomena can be understood by oxygen effects observed similarly in previous work that reported the influence of the measurement parameters, such as the gate bias sweep rate and the gate bias sweep direction, on oxygen adsorption on the nanowire surface [17, 18]. It seems that as the repeated sweep of the gate voltage proceeds, the total amount of adsorbed oxygen on the nanowire surface increases by capturing electrons from the ZnO nanowire as a result of the increased availability of electrons at the surface when current flows through the nanowire and under the influence of the applied positive gate bias, promoting oxygen adsorption during the probing. This results in the depletion of more electrons and thus causes the positive shift in the threshold voltage and a decrease in conductance due to the extension of depletion regions.

In order to investigate the origin of changes in electrical properties associated with surface effects, we performed transfer measurements with gate voltages being cycled from -10 to $+15$ V and back to -10 V at a sweep rate of 0.2 V s^{-1} in various environments. Figures 2(a) and (b) show the hysteretic behaviour before and after the PMMA coating of FETs exposed to an ambient air environment. Regardless of PMMA passivation, we clearly observed hysteresis loops in all FETs exposed to ambient air where threshold voltages shift toward the positive gate voltage direction when the gate voltage is cycled to back to -10 V. Similar to device properties taken from the sweep of gate voltages shown in figure 1(b), threshold voltage values increase and carrier concentration[5] decreases with repeated measurements as shown in figures 2(a), (b)

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[5] The threshold voltage can be used to calculate the carrier concentration from the total charge, $Q_{\mathrm{tot}} = C_{\mathrm{g}}|V_{\mathrm{g}} - V_{\mathrm{th}}|$ in the nanowire, where C_{g} is the gate capacitance and V_{th} is the threshold voltage required to deplete carriers in the nanowire. The gate capacitance can also be estimated using a model of a cylinder on an infinite metal plate, $C_{\mathrm{g}}/L = 2\pi\varepsilon_0\varepsilon/\cosh^{-1}(r + h/r)$, where r is the nanowire radius (55 nm), L is the nanowire channel length (3 μm), h is the SiO thickness (100 nm), ε_0 is the permittivity of free space, and ε is the dielectric constant of SiO_2 (3.9). Thus, the carrier concentration can be determined from the equation, $n_e = Q_{\mathrm{tot}}/e\pi r^2 L$.

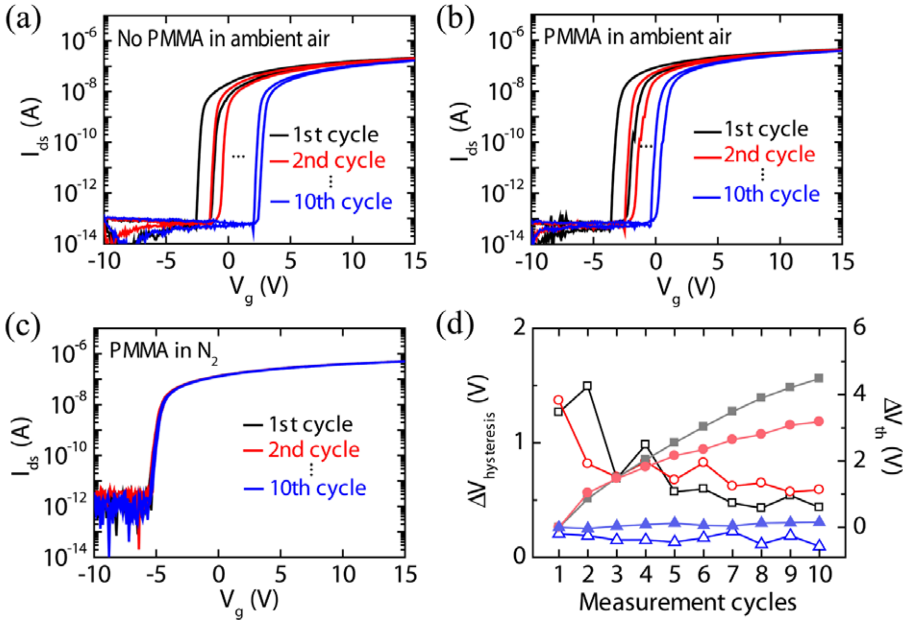

Figure 2. Transfer curves as a function of numbers of repeated measurements (a) for an uncoated ZnO nanowire FET in ambient air, (b) for a PMMA-coated ZnO nanowire FET in ambient air, and (c) for a PMMA-coated ZnO nanowire FET in N_2. (d) Hysteresis width (open symbols) and threshold voltage shift (filled symbols) as a function of measurement cycles in three different environments. Black, red, and blue curves indicate an uncoated FET in ambient air, a PMMA-coated FET in ambient air, a PMMA-coated FET in N_2, respectively.

and (d). It is also shown that electrical behaviours of a PMMA-coated device exposed to an air environment exhibit the same general trend of changes compared with those of an uncoated device, although the degree of changes in electrical properties such as threshold shifts and carrier concentration is slightly smaller. This may be a reason for less effective oxygen adsorption on the nanowire surface from oxygen contained in a PMMA layer or permeated oxygen. In addition, the amount of the shift in threshold voltages and the hysteresis width (the difference in threshold voltages) reduce with increasing numbers of measurements, i.e., a smaller shift of threshold voltages produces a smaller hysteresis loop, when the gate voltage is cycled repeatedly (figure 2). This implies that hysteresis is closely correlated to the threshold voltage shift occurring during the measurement, which has a significant dependence on the amount of adsorbed oxygen by capturing electrons creating a depletion region. In contrast to an air environment, the same device placed in an N_2 environment shows that hysteresis in FETs is completely absent and the threshold voltage values are nearly unchanged during repeated cycles of gate voltages shown in figure 2(c) (i.e. the coincidence of the first cycle (black curve, figure 2(c)) and the tenth cycle (blue curve, figure 2(c))). Also, we did not observe a change in carrier concentration (not shown here). This is because there is a negligible effect of oxygen on the threshold voltage shifts and hysteresis in an N_2 environment due to the suppression of oxygen adsorption on ZnO nanowire surface [17]. Kim *et al* reported that water molecules adsorbed on carbon nanotubes or In_2O_3 nanowires are an important cause of the hysteresis in devices exposed to ambient environments [14, 19]. However it is well known that water molecules bound to silanol groups on silicon oxide cannot be completely removed in N_2 or vacuum environments at room temperature and thus still cause the hysteresis [14, 19]. Thus, these findings suggest that the hysteresis and the continuous positive shifts in threshold voltages are mainly caused by the depletion of carriers by the adsorption of oxygen during the measurements because all devices were heated at 200 °C, which is a suitable temperature to remove water molecules [14], before measurements. It is important to note that as the repeated measurements proceed, the total amount of adsorbed oxygen increases and the probability of oxygen being adsorbed on nanowires during the probing tends to be reduced due to the small number of available sites and hence many fewer electrons are depleted, causing a relatively smaller threshold voltage shift. In other words, the amount of the depletion of electrons by adsorbed oxygen during each electrical characterization plays a significant role in determining the width of the hysteresis loops defined by threshold voltage shifts.

It is well known that ZnO nanowires are very sensitive to UV illumination [20–22]. Thus, for their potential applications in optoelectronic devices, we studied the effect of the UV light on the behaviour of ZnO nanowire FETs with and without a PMMA layer. Figures 3(a) and (b) show transfer curves of uncoated and PMMA-coated ZnO nanowire FETs, respectively, measured repeatedly in an air environment after turning off the UV light, which is exposed to samples placed at a distance of 8 cm away from a UV lamp with a wavelength of 254 nm. We found that more negative gate voltages are needed to deplete electrons in ZnO nanowire FETs than those of ZnO nanowire FETs measured in a dark environment, as shown in figures 1(b) and 2, due to the increase in carrier concentration, resulting from both photo-generated electrons and the desorption of oxygen by the discharge through the surface electron–hole recombination. Note that, generally, as

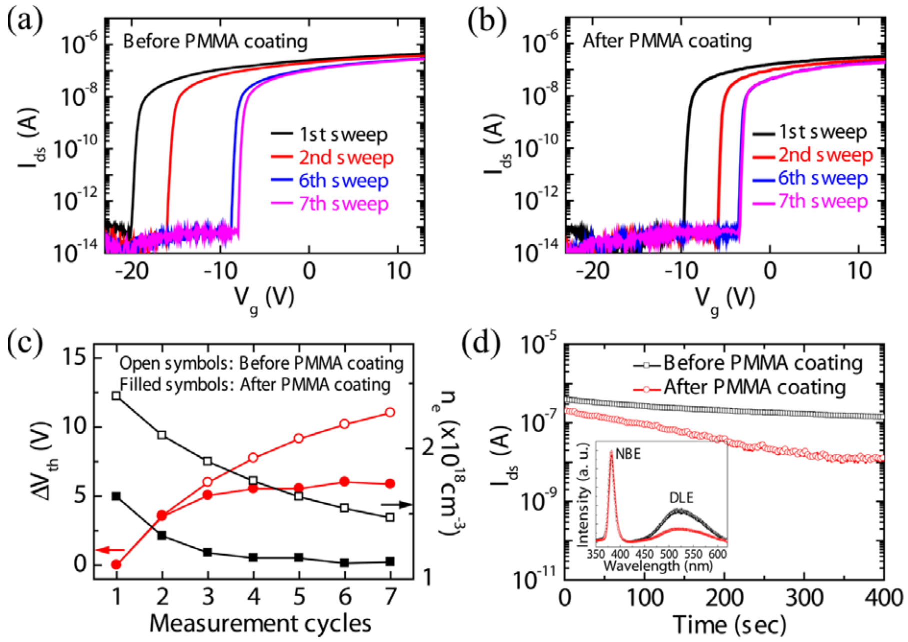

Figure 3. Transfer curves of ZnO nanowire FETs (a) without and (b) with a PMMA layer measured in an ambient air environment after turning off the UV light. (c) Threshold voltage shift and carrier concentration for uncoated and PMMA-coated ZnO nanowire FETs as a function of measurement cycles after turning off the UV light. (d) I_{ds} measured at a drain bias of 0.1 V as a function of time after the UV light is switched off. The inset shows normalized PL spectra of ZnO nanowires before and after PMMA coating.

soon as the UV light is turned off, the carrier concentration decreases with time because of the recombination of electron–hole pairs as well as the adsorption of oxygen [23], resulting in a decrease in current and a positive shift in threshold voltages. Interestingly, in opposition to the electrical properties shown in the dark (figure 2), carrier concentration in a FET before PMMA coating is higher than that of a FET with a PMMA layer, leading to a larger negative threshold shift to deplete electrons in the nanowire, as shown in figure 3(c). This indicates that the photo-response related to a recombination process is strongly dependent on surface environments of nanowires, being fast and slow in ZnO nanowire FETs with and without a PMMA layer, respectively.

A comparison of electrical properties of ZnO nanowire FETs measured in the dark and after the UV light exposure shows that the decay of conductivity in an uncoated nanowire FET is much slower than that in a PMMA-coated nanowire FET, as shown in figure 3(d). This behaviour can be explained in terms of the surface chemical reaction and band bending. For an uncoated ZnO nanowire, oxygen is adsorbed on the nanowire surface by capturing electrons from a nanowire and is formed as a negatively charged ion, thereby creating a depletion region near the surface [20]. This process leads to band bending upwards, resulting in a separation of photo-generated electron–hole pairs, as shown schematically in figure 4(a). Photo-generated holes migrate to the surface along the band bending and discharge negatively charged oxygen ions. As a result, photo-generated electrons increase the conductivity, but the current decreases slowly with time due to the separation of photo-generated electron–hole pairs making the recombination of electron–hole pairs difficult after the UV light is turned off [23]. Therefore, decay of conductivity progresses by the re-adsorption of oxygen on the nanowire surface. In case of a PMMA-coated ZnO nanowire, a PMMA layer surrounding the nanowire surface can act as a dielectric and induce a modification of the ZnO nanowire surface, causing a decrease in surface charge states and defect states due to screening effects [12, 23]. This is consistent with our PL results shown in the inset of figure 3(d). Compared with the uncoated sample, the relative intensity of the deep-level emission (DLE) to the near band-edge emission (NBL) is significantly reduced. DLE is related to surface defects such as oxygen vacancies. These results clearly reveal that there is a reduction of band bending (lowering surface potential barrier) after the PMMA coating, as shown in figure 4(b). Therefore, the decay process will at first be fast from the direct recombination of electron–hole pairs, immediately after turning off the UV light, and then become slower by a surface recombination process being dominantly induced by interaction between oxygen and the nanowire surface.

In summary, we have shown that adsorption of oxygen on the ZnO nanowire surface occurs significantly by capturing electrons creating a depletion region and thus induces continuously positive shifts in threshold voltages during the probing. This causes hysteresis in ZnO nanowire FETs due to the depletion of electrons from nanowires during the measurements, which has a strong dependence on the adsorbed oxygen. We also find that the photo-response related to the recombination process of electron–hole pairs is strongly dependent on the surface environment of the nanowires. For an uncoated ZnO nanowire, the slow decay of conductivity is correlated with the adsorption of oxygen on the surface due to a separation of photo-generated electron–hole pairs by band bending, while for a PMMA-coated ZnO nanowire, the decay process is at first fast from the direct recombination of electron–hole pairs due to the reduced band bending and then

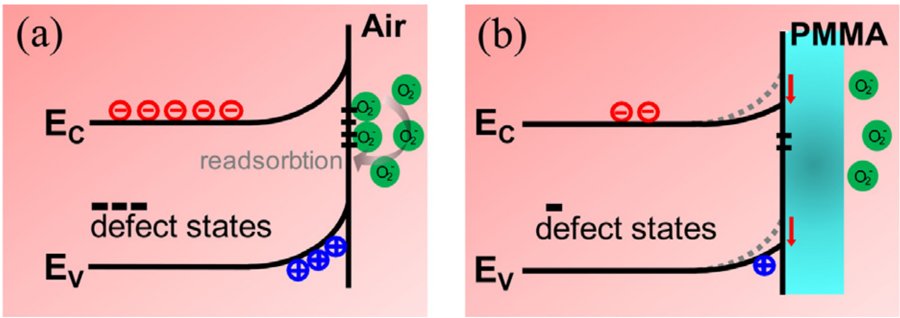

Figure 4. Energy band diagram of a ZnO nanowire with different interfaces. (a) A nanowire directly exposed to air. (b) A nanowire surrounded by a PMMA layer.

becomes slower by a surface recombination process becoming dominant through the oxygen adsorption.

Acknowledgments

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