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# Enhancement in the photodetection of ZnO nanowires by introducing surface-roughness-induced traps

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**Abstract**
We investigated the enhanced photoresponse of ZnO nanowire transistors that was introduced with surface-roughness-induced traps by a simple chemical treatment with isopropyl alcohol (IPA). The enhanced photoresponse of IPA-treated ZnO nanowire devices is attributed to an increase in adsorbed oxygen on IPA-induced surface traps. The results of this study revealed that IPA-treated ZnO nanowire devices displayed higher photocurrent gains and faster photoswitching speed than transistors containing unmodified ZnO nanowires. Thus, chemical treatment with IPA can be a useful method for improving the photoresponse of ZnO nanowire devices.

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

## 1. Introduction

One-dimensional semiconducting ZnO nanowires (NWs) have many advantageous properties, including a wide direct bandgap (∼3.4 eV), large exciton binding energy (60 meV) and piezoelectricity [1–3]. ZnO NWs have been considered for various applications, such as field effect transistors (FETs), logic circuits, light-emitting diodes (LEDs), nanogenerators and photo-or chemical sensors [3–12]. In particular, ZnO NWs are suitable candidates for highly responsive photodetectors due to their large surface-to-volume ratio. In addition, deep-level surface trap states extend the lifetime of photocarriers in ZnO NW photodetectors [5, 13, 14].

In ZnO NW photodetectors, the generation of a photocurrent is attributed to a surface-related mechanism. Electron–hole pairs are photogenerated by UV illumination and negatively charged oxygen molecules are subsequently neutralized and desorbed by migration of photogenerated holes at the surface of the ZnO NW. Upon desorption of oxygen molecules, the electrons of the electron–hole pairs remain at the surface and contribute to the photoconductivity [5, 9, 15–17]. This theory implies that the photoresponsivity of ZnO NWs can be enhanced by increasing the amount of adsorbed oxygen on the surface of the NW; thus, surface characteristics play an important role in the photoresponsivity. We have previously reported several methods for introducing surface roughness-induced

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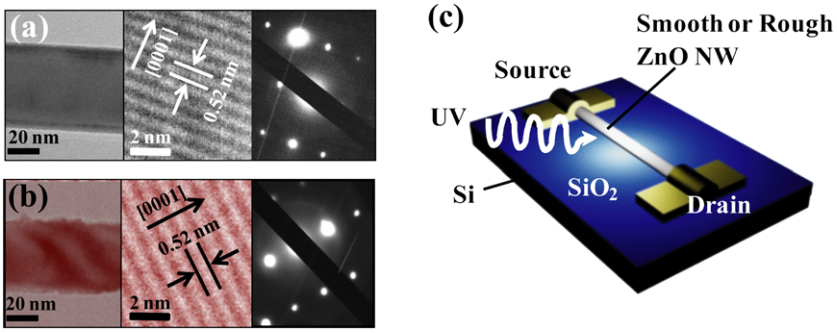


**Figure 1.** Low-magnification TEM images (left), HRTEM images (middle) and electron diffraction patterns (right) of (a) an unmodified ZnO NW and (b) a ZnO NW submerged in IPA for 30 days. (c) A schematic illustration of a ZnO NW FET under UV illumination.

traps onto ZnO NWs and determined the resultant changes in the electrical properties of the ZnO NWs due to adsorbed oxygen [7, 18]. The application of the techniques to modify the surface morphology of ZnO NWs is expected to improve the photoresponse of ZnO NW devices.

In this study, ZnO NW photodetectors with surface-roughness-induced traps were generated by submersion in isopropyl alcohol (IPA) [18] and the photoresponse of the resultant detectors was investigated. Increased photocurrent and enhanced photoswitching speed were observed in surface-roughened ZnO NW photodetectors. These results demonstrate that a simple chemical treatment can be an effective method for improving the photoresponsivity of ZnO NW devices.

## 2. Experimental details

ZnO NWs were synthesized by vapor transport in a horizontal quartz tube furnace on an Au-coated *c*-plane sapphire substrate at 920 °C under a flow of Ar and oxygen [1, 7]. After the growth process, the surfaces of the ZnO NWs were roughened by submerging the NWs in isopropyl alcohol (IPA) for 30 d [18], and the photoluminescence (PL) from both roughened and smooth ZnO NWs were tested using a mapping system (RPM2000 model, Accent Opt. Tech., UK) with a 325 nm He–Cd laser (4.6 mW) as an excitation source. Back-gated ZnO NW FETs were fabricated on a highly doped p-type Si substrate with a thermally grown $SiO_2$ layer according to a procedure described in the literature [1, 7] and the electrical properties of the resultant FETs were evaluated before and after treatment with IPA. A semiconductor parameter analyzer (Agilent B1500A) was used to measure the electrical properties of the ZnO NW FETs at room temperature. Furthermore, the photoresponse properties of the ZnO NW FETs were examined with a portable UV lamp. The optical power density was calibrated using a Karl Suss 1000 UV intensity meter.

## 3. Results and discussion

### *3.1. Surface morphology and electrical properties of ZnO NWs*

Low-magnification TEM images of unmodified and IPA-treated ZnO NWs are shown in the left images of figures 1(a) and (b), respectively. These images revealed the surface morphologies of unmodified and IPA-treated ZnO NWs. The surfaces of IPA-treated ZnO NWs were considerably rougher than those of unmodified NWs, suggesting that IPA etches the surfaces of ZnO NWs [18]. High-resolution TEM images (middle images of figures 1(a) and (b)) and the corresponding electron diffraction patterns (right images) show that, although the surfaces of the IPA-treated ZnO NWs were etched, the NWs remained single crystalline [18]. Figure 1(c) shows the schematic of a ZnO NW-based FET device under UV illumination.

Figure 2 shows the electrical characteristics of unmodified (smooth) and IPA-treated (rough) ZnO NW FETs in the absence of light and under UV illumination. Smooth and rough ZnO NW FETs are shown schematically in figure 2. The photocurrents were measured under UV illumination at an intensity of 0.7 mW $cm^{-2}$ and a wavelength of 365 nm. The results shown in figures 2(a) and (b) are the representative transfer characteristics ($I_D$–$V_G$, source–drain current versus gate voltage measured at a fixed drain voltage $V_D = 0.4$ V) of the smooth and rough ZnO NW FETs, respectively. We observed that *n*-channel depletion-mode behavior (i.e. threshold voltage is negative) was achieved in the smooth ZnO NW FET. On the other hand, the threshold voltage was not found (or was very large, over 20 V) for the rough ZnO NW FET in the gate bias sweep range, indicating that the rough ZnO NWs are more depleted due to the surface states, as discussed previously [18]. The smooth ZnO NW FET exhibited a higher dark current compared to that of the rough ZnO NW FET at the same gate voltage, again suggesting more charge depletion due to more surface states on the rough ZnO NWs [7, 18]. However, under UV illumination, the conductivity of the rough ZnO NW FET was higher than that of the smooth ZnO NW FET. In addition, a much higher photocurrent to dark current ($I_{photo}/I_{dark}$) ratio was observed from the rough ZnO NW FET. For the device shown in figure 2, the ratio $I_{photo}/I_{dark}$ was observed as ~5.3 and $3.0 \times 10^6$ at $V_D = 0.4$ V and $V_G = 0$ V for smooth and rough ZnO NW FETs, respectively.

Figures 2(c) and (d) show the output characteristics ($I_D$–$V_D$, source–drain current versus drain voltage measured at gate voltages of $V_G = 0$ V) of the smooth and rough ZnO NW FETs. The results indicated that the photoconductivity of the rough ZnO NW FETs is greater than

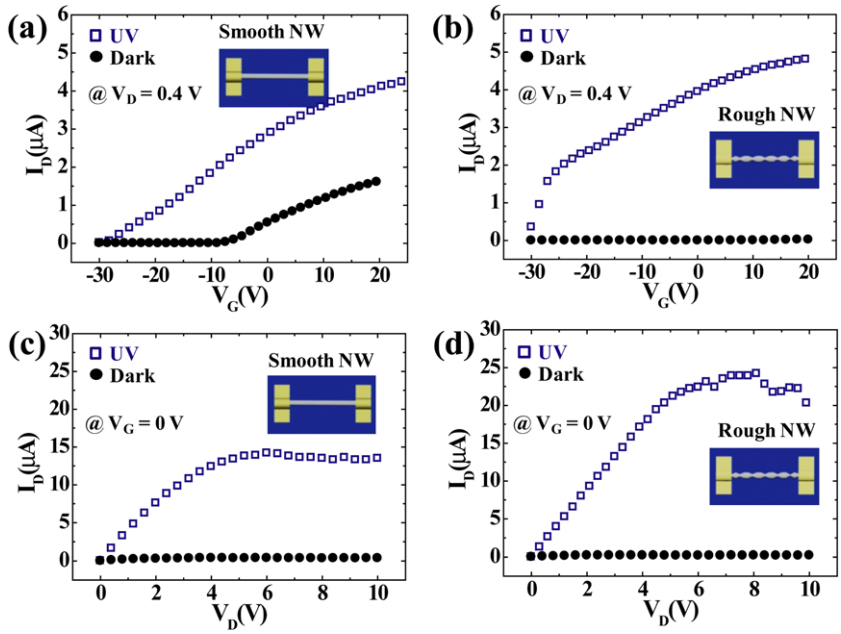


**Figure 2.** The electrical characteristics of ZnO NWs in the absence of light and under UV illumination. The insets display schematic images of smooth and rough ZnO NW FETs. $I_D$–$V_G$ (at $V_D = 0.4$ V) and $I_D$–$V_D$ (at $V_G = 0$ V) curves of smooth ((a), (c)) and rough ZnO NW FETs ((b), (d)), respectively.

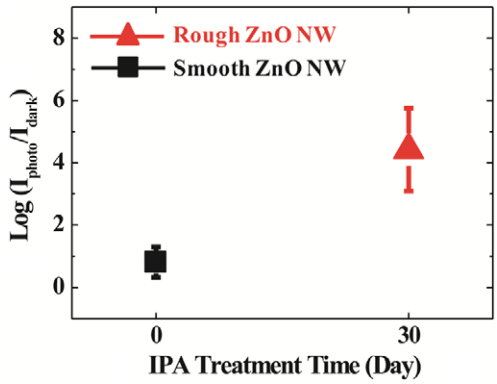


**Figure 3.** The statistical results of $\log(I_{photo}/I_{dark})$ versus IPA treatment time for unmodified (smooth) and IPA-treated (rough) ZnO nanowire FETs obtained from the transfer characteristics of a total of eight devices. The currents measured at $V_D = 0.4$ V and $V_G = 0$ V were used to determine the $I_{photo}/I_{dark}$ ratio.

the photoconductivity of the smooth ZnO NW FET. The results shown in figure 2 revealed enhanced photoconductivity in the IPA-treated roughened ZnO NW FET.

The phenomenon of the enhanced photoconductivity was confirmed by investigating more devices. Figure 3 displays the average of $\log(I_{photo}/I_{dark})$ versus IPA treatment time, obtained from the currents measured at $V_D = 0.4$ V and $V_G = 0$ V for a total of eight devices. In this figure, the ratio of the rough ZnO NWs was observed to be much higher than that for the smooth ZnO NWs by 2–3 orders of magnitude. The average $I_{photo}/I_{dark}$ value was found to be ~6.5 and $2.6 \times 10^4$ for the smooth and the rough ZnO NW FETs, respectively.

### *3.2. Photoresponsivity of ZnO NW FETs*

To compare the photoswitching speeds of the NW FETs, the time-dependent on/off photoconduction behavior of the FET was investigated. In these experiments, gate biases of −5 V and 3 V were applied to the smooth (black line) and rough (red line) ZnO NW FETs, respectively (figure 4(a)). Note that in this measurement the gate voltages were selected to compare different FETs with similar dark currents. Each measurement was conducted for 1600 s and sample illumination with UV light began after 420 s. Illumination was maintained for 180 s and the entire UV illumination sequence was repeated twice. As shown in figure 4(a), the rough ZnO NW device displayed a higher photocurrent than the smooth ZnO NW device under UV illumination. After turning on the UV light, both smooth and rough ZnO NW FETs show a quick increase of photocurrent, followed by a much slower increase. However, the rise time of the photocurrent from 10 to 90% of the maximum was 37 s in the rough ZnO NW device, shorter than the rise time (91 s) of the smooth ZnO NW device. Furthermore, after turning off the UV light, the rough ZnO NW FET exhibited a considerably sharper decay than the smooth ZnO NW FET which presented a gradually decaying photocurrent. Note that we also observed similar behaviors in the rough NW FET at the gate bias of −5 V that was applied to the smooth NW FET, as shown in the blue line in figure 4(a). It means that the enhanced photoresponsivity in the rough NW is not caused simply by a different gate bias.

To confirm the photoresponsive behavior of the devices, the rough ZnO NW FET was evaluated under UV light with intensities ranging from 70 nW cm$^{-2}$ to 0.7 mW cm$^{-2}$, as shown in figure 4(b). In these experiments, the

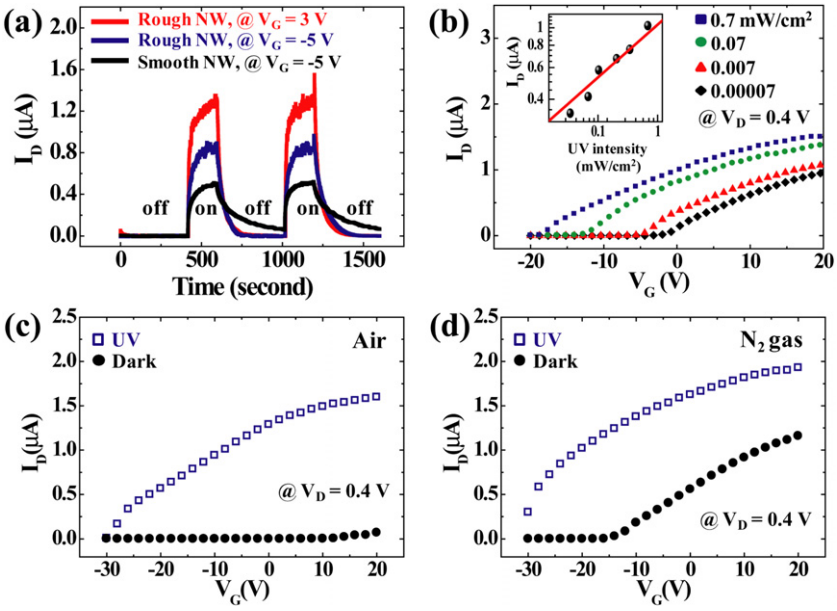


**Figure 4.** (a) Time-dependent on/off photocurrents of smooth ZnO NW FET measured at the gate bias ($V_G$) of −5 V (black line) and rough ZnO NW FET measured at $V_G$ of 3 V (red line) and −5 V (blue line) and (b) $I_D$–$V_G$ curves of the rough ZnO NW FET with various UV light intensities (from 70 nW cm$^{-2}$ to 0.7 mW cm$^{-2}$). The inset displays the photocurrent of the rough ZnO NW FETs as a function of the intensity of UV light at 365 nm. $I_D$–$V_G$ (at $V_D = 0.4$ V) curves of a rough ZnO NW FET with and without UV illumination measured under (c) air and (d) $N_2$ gas.

intensity of the light was adjusted with neutral density (ND) filters. The results showed that the drain current gradually increased as the illumination intensity increased, because the photocurrent depends on the brightness of light at the same wavelength [5, 11, 19, 20]. The inset in figure 4(b) shows the photocurrents of the rough NW FET as a function of the intensity of incident light. Similar to the results of Kind *et al*, a simple power-law relationship between the photocurrent and the power of the incident light was observed [9];

$$I_{pc} \propto P^{0.3} \tag{1}$$

where $I_{pc}$ is the photocurrent and $P$ is the power of the incident light.

The photoresponsivity for an IPA-treated ZnO NW FET was investigated under various environmental conditions to further understand the current transport mechanism. Figures 4(c) and (d) are the transfer characteristics of an IPA-treated ZnO NW FET device measured under air and $N_2$ gas at room temperature. Under $N_2$ gas, the $I_{photo}/I_{dark}$ ratio was much lower than the ambient air case, due to much higher dark current and slightly higher photocurrent under $N_2$ gas. The $I_{photo}/I_{dark}$ ratios for air and $N_2$ gas were $\sim 8.3 \times 10^3$ and 2.9, respectively.

### *3.3. Electrical transport mechanism of ZnO NWs under UV illumination*

The results of the present study provide information regarding the mechanism of photoresponse enhancement in rough ZnO NW FETs. Figures 5(a) and (b) show the schematic illustration of electron transport in smooth and rough ZnO NWs under UV illumination. The generation of photoelectrons in ZnO NWs is attributed to desorption of oxygen molecules from the surface of ZnO NWs [5, 9, 16, 17]. In the dark, oxygen molecules are adsorbed on the surface of ZnO NWs and capture free electrons from the NW conducting channels. As a result, a depletion layer with low conductivity forms near the surface of the NW [7, 18]:

$$O_2(g) + e^- \rightarrow O_2^-(ad). \tag{2}$$

Under UV illumination, electron–hole pairs are created in the NW and a portion of the photogenerated holes migrate to adsorbed oxygen molecules on the surface of ZnO NWs. The migrated holes neutralize the adsorbed oxygen molecules and allow them to desorb from the NW surface. As a result, the photogenerated electrons remain in the NW and contribute to the photoconductivity:

$$e^- + h^+ + O_2^-(ad) \rightarrow e^- + O_2(g). \tag{3}$$

When the smooth and rough ZnO NWs are illuminated with light of the same intensity, the number of photogenerated electron–hole pairs in both NWs is nearly identical. As reported previously, a greater number of oxygen molecules are adsorbed on the surfaces of rough ZnO NWs than smooth ZnO NWs [7, 18]; thus, more photogenerated holes are trapped by adsorbed oxygen on the surfaces of rough ZnO NWs, suppressing the recombination of excitons under UV illumination. After turning off the UV, the high density of oxygen molecules adsorb on the roughened surface of ZnO NWs more quickly, presumably due to increased binding energies for oxygen adsorption on the roughened surface. As a result, higher photoconductivity and faster photoswitching speeds were achieved for the roughened ZnO NW device, as

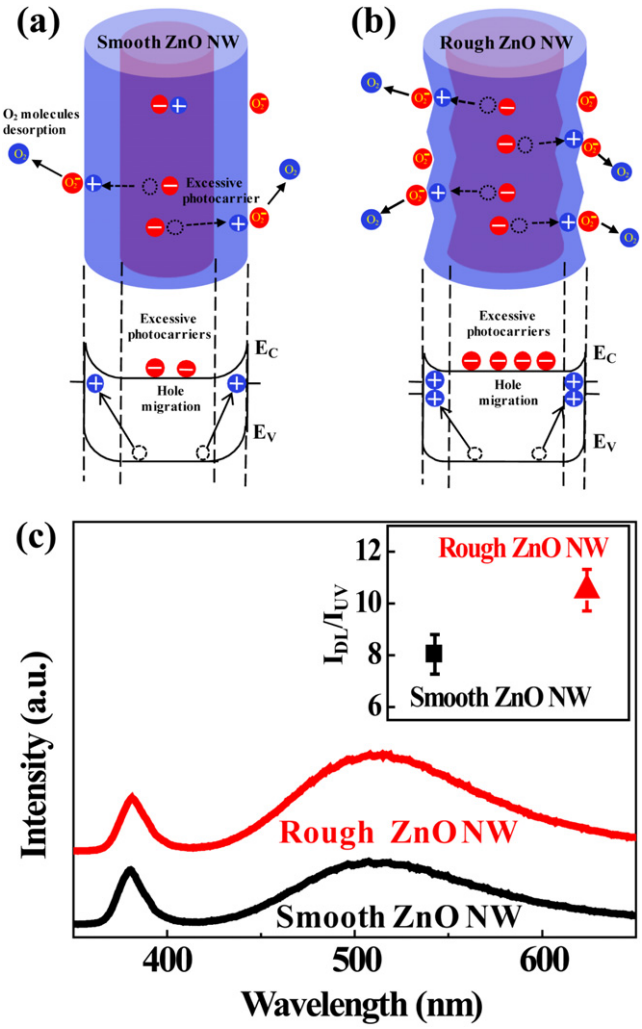


**Figure 5.** (Top) Schematic illustration of the mechanism of photocarrier generation and (bottom) the corresponding energy band diagrams of (a) smooth and (b) rough ZnO NWs under UV illumination. $E_C$ is the conduction band and $E_V$ is the valence band of ZnO NWs. (c) PL spectra of smooth (black line) and rough ZnO NWs (red line). To allow for clear comparison, the red line was shifted vertically. The inset displays the PL intensity ratios ($I_{DL}/I_{UV}$) for two cases.

the data shows in figures 2, 3 and 4(a). The results indicated that roughening NW surfaces is an effective method for enhancing the photoresponsivity of ZnO NW photodetectors.

Figure 5(c) shows the PL data of smooth (black line) and rough (red line) ZnO NWs. The PL spectrum of ZnO consists of an ultraviolet (UV) emission band (375–380 nm) and a defect-level (DL) emission band [7]. The energy bandgap of the material can be estimated from the UV emission band, while the deep-level surface defects can be estimated from the DL emission band. In smooth ZnO NWs, the DL emission peak was weak compared to the UV emission peak; however, in rough ZnO NWs, the DL emission peak was considerably larger than the UV emission peak. This result indicates that the density of the deep-level surface traps was increased significantly in ZnO NWs treated with IPA. The inset of figure 5(c) shows the DL-to-UV emission intensity ratios ($I_{DL}/I_{UV}$) of both types of ZnO NWs. The error bars were determined by evaluating several NWs and performing statistical analyses. As shown in the inset, the intensity ratio increased significantly, after the ZnO NWs were submerged in IPA for 30 days, due to the introduction of surface trap sites induced by surface roughness [7, 18]. These results support our proposed surface absorption model in figures 5(a) and (b) and explain the enhanced photoresponse from the roughened ZnO NWs FET in figure 2.

## 4. Conclusions

In summary, we demonstrated that a simple solvent-based process improved the photoresponsivity of ZnO NW devices. By immersing ZnO NWs in isopropyl alcohol, the NW surfaces were significantly roughened. As a result, roughness-induced surface traps were generated and the photoresponsivity of ZnO NW devices were improved. Specifically, higher photocurrent to dark current ratio and faster photoswitching speed were observed in devices using roughened ZnO NWs. This study indicates that the performance of ZnO NW photodetectors can be improved by employing a solvent-induced NW surface-roughening technique.

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