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# Enhanced UV photoresponse in nitrogen plasma ZnO nanotubes

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## Abstract

The photoresponse behavior of one-dimensional ZnO nanowires (NWs) and nanotubes (NTs) grown on ITO-coated glass substrates via a wet-chemical route was investigated. The photoluminescence spectra exhibited a decrease in the deep-level intensity, indicating that the oxygen defects and impurities are occupied by the presence of N ions in the ZnO NT matrix after a nitrogen plasma treatment.  $I$ - $V$  tests demonstrate an enhanced dark current ( $4.83 \times 10^{-7}$  A) after an extended plasma treatment of up to 900 s for ZnO NTs compared to that ( $0.571 \times 10^{-7}$  A) of NWs. Furthermore, the ZnO NTs show the highest reliable photoresponse, 20 times that of NWs under UV irradiation (325 nm) in air at room temperature. It is believed that nitrogen plasma ZnO nanotubes can potentially be useful in the designs of 1D ZnO-based solar cells and optoelectronic devices.

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

## 1. Introduction

One-dimensional (1D) zinc oxide (ZnO) is a promising semiconductor material in nanoscale electronics, optoelectronics and light-emitting device applications [1–13, 19, 20] because of its wide band gap ( $E_g = 3.34$  eV), high electron–hole binding energy (60 meV) and the ease of cheap wet-chemical synthesis. The diversity of novel ZnO nanostructures, such as nanobelts (NBs) [1], nanowires (NWs) [2–11] and nanotubes (NTs) [14–16], has attracted attention due to the ways that its dimensionality corresponds to physical and chemical properties.

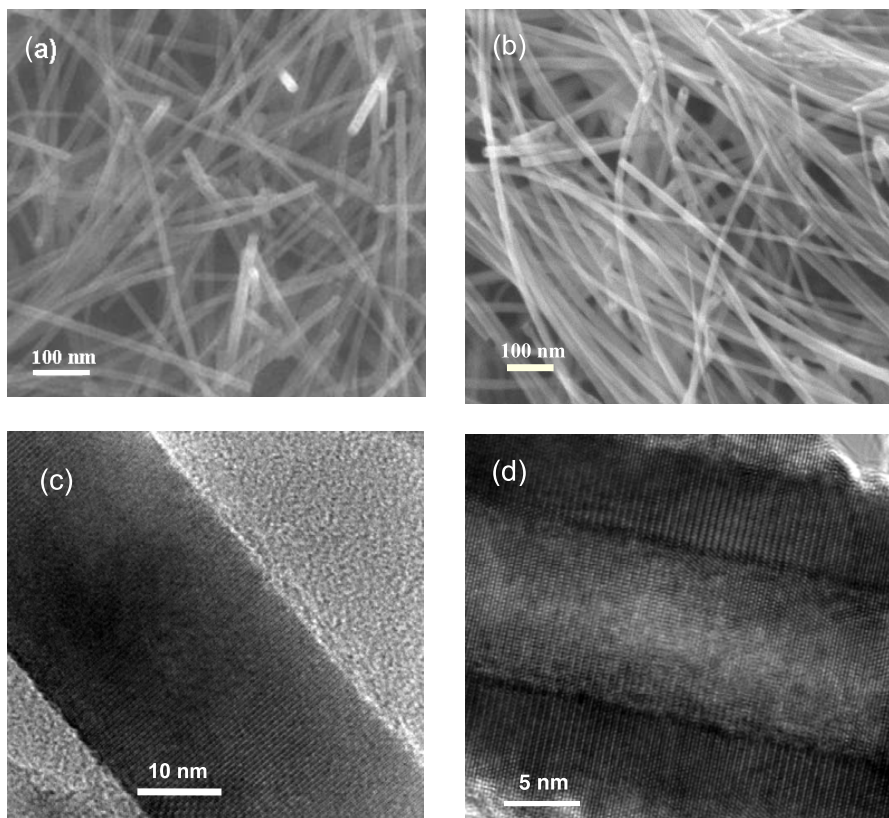
Up to now, wet-chemical approaches have been widely used to synthesize ZnO nanostructures. However, several defects may be generated on the surface of ZnO nanorods grown with an aqueous solution process. Recently, Sun *et al* reported that the existence of hydroxyl groups (OH) and physisorbed water molecules on the surface of ZnO nanorods that can generate oxygen vacancies and defects, which affect the PL characterization and apparent photocurrent. Yuan

*et al* proposed that the gaseous dopant N<sub>2</sub>O on ZnO NWs could compensate the intrinsic donor defects and achieve controlled electron-transport properties. A recent study by Le *et al* demonstrated that nitrogen (N) incorporation into ZnO nanorods (NRs) under plasma exposure can efficiently induce the relative chemical bonding (increased O–Zn), but that it may result in the occurrence of lattice disorder.

Recently, ZnO nanotubes have been fabricated by many methods, such as a hydrothermal process, a template-assisted method and a thermal oxidation process [14–16]. Based on the high surface-to-volume ratio of ZnO NTs, it was believed that ZnO NTs have the possibility of improving charge collection and charge carrier transportation, thus enhancing performance and activity. Furthermore, the direct flow of electrons along a large interfacial surface area may contribute to a higher photocurrent generation.

Therefore, in this investigation, ZnO nanotubes (NTs) were produced by a low-cost chemical method, followed by the application of a nitrogen plasma. In order to better understand the photoresponse of NTs, ZnO nanowires (NWs) were also prepared for comparison. This letter discusses, for the first time, the photoresponse and photoluminescence behavior of

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**Figure 1.** FESEM images: of (a) ZnO NWs and (b) NTs; HRTEM images (c) NWs and (d) NTs on ITO-coated glass substrates subjected to postannealing at 300 °C and nitrogen plasma treatment.

nitrogen plasma-treated, chemically grown ZnO NTs. The nitrogen-treated ZnO NTs show a very good photoconductivity under long wavelength UV irradiation, as well as durability with extended exposure time, which can benefit ZnO-based solar cell devices.

## 2. Experimental details

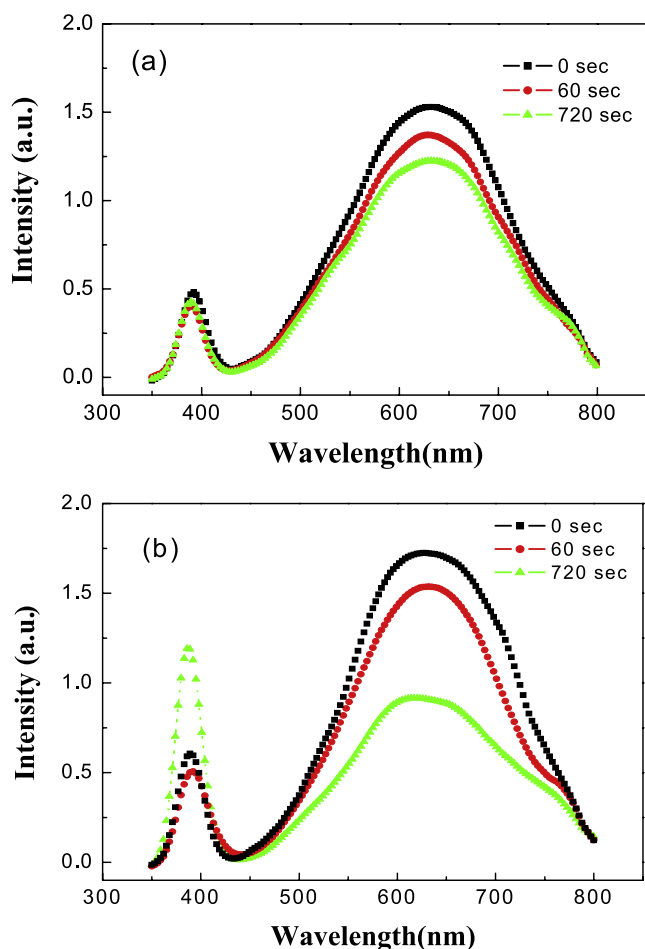
For the wet-chemical reaction, we prepared an equimolar (5 mM) mixture of zinc nitrate hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and hexamethylenetetramine (HMT) in DI water with ratios of 2:1 and 1:1 for the ZnO NWs and NTs, respectively. Subsequently, an ITO-coated glass substrate was immersed in the aqueous solution at 95 °C for 24 h to obtain pure NWs or NTs on the substrate. After removal from the aqueous solution, the sample was rinsed in DI water several times and dried in air. Following a thermal annealing at 300 °C, both ZnO samples were exposed to nitrogen plasma for 60, 180, 300, 480, 600, 720 and 900 s at 100 mTorr in an inductively coupled plasma (ICP) with the ICP power fixed at 100 W. A transmission electron microscope (TEM, JEOL 2100), operated at 200 keV, and a field emission scanning electron microscope (SEM, JEOL JSM-6700F) were used to examine surface morphology of the 1D ZnO. Room-temperature PL measurements were performed at 325 nm using a He–Cd laser (325 nm) and taken over a wavelength range of 350–800 nm. Both the  $I$ – $V$  characteristics and  $I$ – $t$  photoresponse were measured at room temperature in air and under additional UV illumination

( $\lambda = 325$  nm), which was vertically positioned at 15 cm from the samples.

## 3. Results and discussion

Figures 1(a) and (b) show scanning electron microscopy (SEM) images of ZnO NWs and NTs subjected to the nitrogen plasma treatment. Each NW, or NT, is 2–5  $\mu\text{m}$  in length and has a uniform width over its entire length. After thermal annealing at 300 °C and longer plasma treatments, both ZnO nanostructures still show a uniform surface morphology. The high-resolution TEM image of the ZnO NWs in figure 1(c) shows that the synthesized ZnO nanowires grow along the preferential [0002]  $c$ -axis direction with a diameter of around 25 nm. For the ZnO NTs, figure 1(d) displays tubular structures with wall thicknesses of about 5–10 nm and inner diameters of about 10–15 nm. Furthermore, it was found that the diameters of both the ZnO NTs and NWs are very close in size, which can be attributed to the disappearance of the  $c$ -axis plane of the ZnO nanowires to form nanotubes [4, 7].

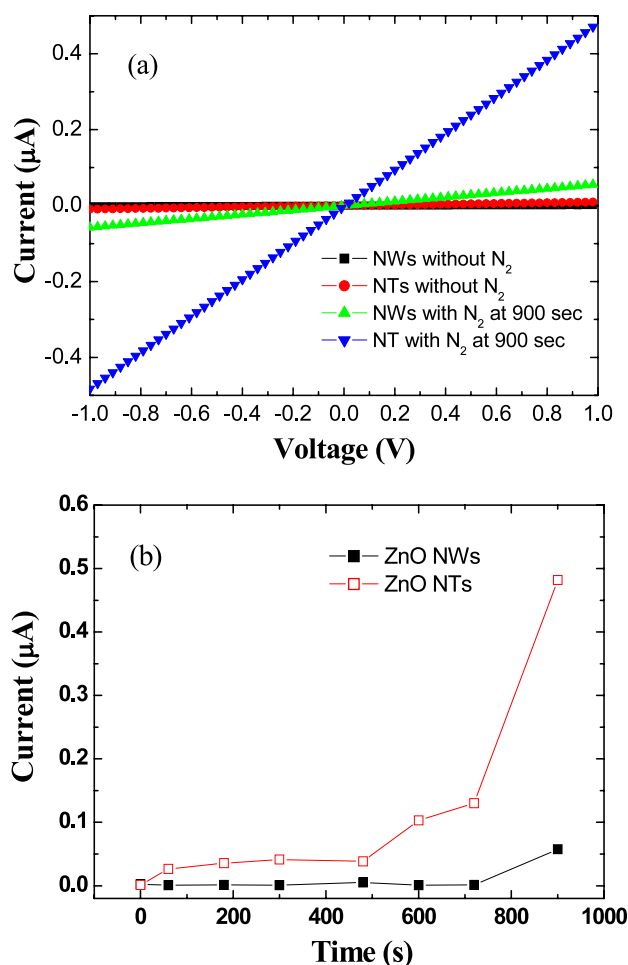
Figure 2 shows the room-temperature photoluminescence (PL) spectra of both ZnO NWs and NTs treated with different exposure times (0, 60 and 720 s) in a nitrogen plasma. Two distinct emission bands were observed: UV emission related to free exciton recombination at around 384 nm, and broadband deep-level emission related to native defects, such as oxygen vacancies and zinc interstitials. After nitrogen plasma treatment, no damage was observed for both the NWs



**Figure 2.** Photoluminescence spectra measured at room temperature for a nitrogen plasma treatment of 0, 60 and 720 s for (a) ZnO NWs and (b) NTs.

and NTs, and the emission intensity of the deep-level band was reduced, which is consistent with the report of Le *et al*, who found that a  $N_2$  plasma treatment can passivate the surface defects of ZnO nanorods. However, it was observed that the effect on the ZnO NWs was not as remarkable as the effect on the ZnO NTs, indicating the ZnO NTs show a greater relative reduction in surface defects than the NWs after the  $N_2$  plasma treatment. Furthermore, it was noted that a long plasma treatment at 720 s caused enhanced UV and decreased deep-level bands in terms of peak intensity, indicating that a surface reaction between the N ion and  $V_o^+$  occurs on the ZnO. It is assumed that with a long plasma treatment, the  $N_i$  ions diffuse further into the core layer of the NTs and induce more nitrogen interstitials ( $N_i$ ) to fill the  $V_o^+$  defects of the NTs. Therefore, enhanced UV can be obtained.

Figure 3(a) shows the current as a function of applied voltage with and without  $N_2$  treatment for 900 s. The dark currents of untreated and  $N_2$  plasma-treated NWs and NTs show linear  $I$ - $V$  characteristics, which indicate an ohmic nature in both cases. It was found that without  $N_2$  treatment, both ZnO NWs and NTs generate a slight current ( $1.81 \times 10^{-9}$  and  $9.53 \times 10^{-9}$  A, respectively). In contrast, a rapid rise in the dark current was observed for the ZnO NTs treated with



**Figure 3.** (a) Current as a function of applied voltage for both ZnO NWs and NTs, with and without a 900 s nitrogen treatment. (b) Dark current dependence versus  $N_2$ -exposure time.

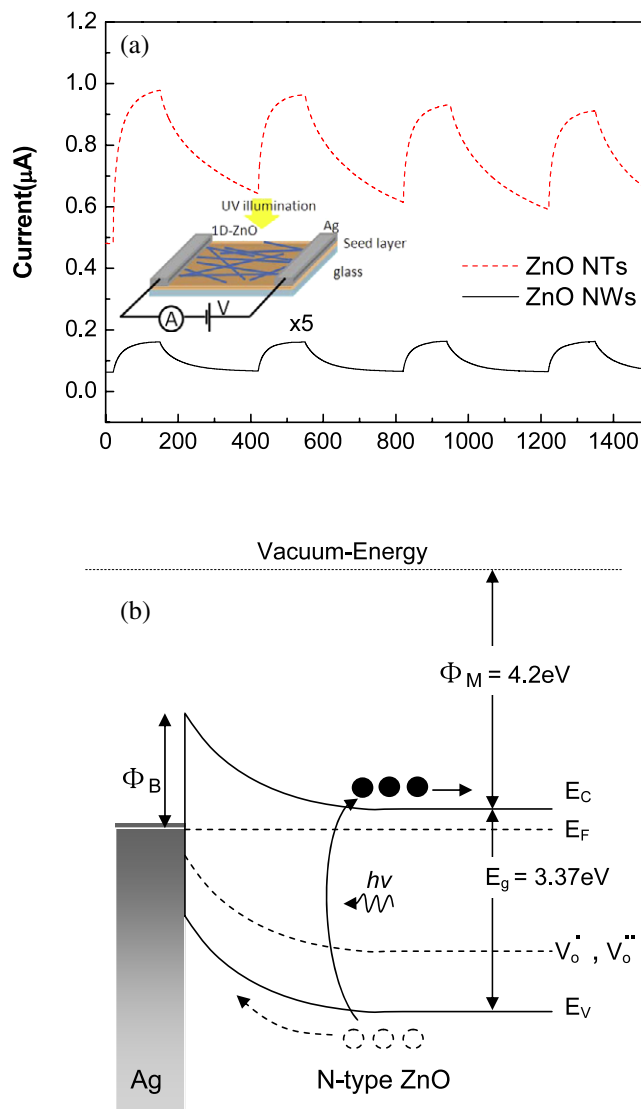
$N_2$  plasma compared to those without treatment and to  $N_2$ -treated ZnO NWs. The current in the NTs is increased by a factor of 20 over that in the NWs after  $N_2$  plasma treatment, which might be correlated with the larger surface area and thinner walls ( $\sim 10$  nm) in ZnO NTs. Normally, ZnO can be doped to be an n-type material due to the existence of oxygen defects, which contribute to the apparent photocurrent via filling or removal of the oxygen defect sites in the ZnO nanowires. Ahn *et al* studied the photocurrent of a single ZnO nanowire synthesized by the sol-gel route and found that, in vacuum, the dark current was larger than in air; this can be attributed to the release of the available charge carriers by the desorption of physisorbed water molecules [11]; this might also be applicable to this work. The dark current of the ZnO NTs can be further enhanced after  $N_2$  plasma treatment compared to ZnO NWs, because NTs have a relatively high surface to volume ratio and more electrons captured on the surface can be released. Figure 3(b) illustrates the dark current of both ZnO NWs and NTs with different  $N_2$  plasma exposure times. It was found that the dark current of the NTs shows a slight change after implant durations of 30–480 s. Beyond that, the enhancement in dark current is more remarkable for NTs after a long duration  $N_2$  plasma treatment. The current

can be increased up to  $4.82 \times 10^{-7}$  A at 900 s, which is much larger than that in ZnO NWs. It is believed that the surface defects in the solution-synthesized ZnO nanostructures normally have positively charged sites on their surfaces; these capture the electrons of ZnO electrostatically, reducing the available carriers in the air. According to our experiment, the N<sub>2</sub> plasma treatment can detach the surface defects, releasing the captured electrons and resulting in an increase of the conductance, especially under ion bombardment for a longer duration (>600 s) at an ICP power of 100 W, where there is the possibility of accumulating more energy to release further charge carriers by the detachment of physisorbed defects, such as water molecules inside the ZnO nanotubes. Therefore, an enhanced dark current can be obtained for the NTs after a long duration N<sub>2</sub> plasma treatment.

Figure 4(a) shows the  $I-t$  plots and the photocurrent onsets generated by the excitation of UV irradiation in air at room temperature with a bias voltage of 1 V. After a longer N<sub>2</sub> treatment (900 s) for ZnO NWs and NTs, the ON-OFF cycles were exponential in generating a photocurrent with a reproducible response. It was noted that the N<sub>2</sub> plasma treatment for the NTs not only induced an increase in the dark current, but also enhanced the absolute magnitude of the photocurrent. The photoresponse enhancement for the NTs shows a remarkable increase by one order of magnitude over that of the NWs. It was assumed that the generation of an oxygen defect normally releases two electrons according to  $O_o^x \rightarrow 1/2O_2 + V_o^{2+} + 2e^-$ , which contributes to the intrinsic n-type nature of the ZnO nanostructure. This implies that oxygen defect vacancy ( $V_o^+$ ) sites in the depletion layer are produced and become so unstable that they tend to be stabilized by combining with ambient negative charges, such as OH<sup>-</sup> from physisorbed water molecules in the surrounding atmosphere (air), to form  $V_o^+-OH$  bonds, which result in a decrease in free electrons. Therefore, under UV excitation,  $V_o^+-OH^-$  pairs are broken, and electrons can be released from the detached hydroxyl OH<sup>-</sup> groups on the surface of the ZnO nanostructures; this results in an apparent enhancement in photoresponse due to the larger surface/volume ratio of ZnO nanotubes without position dependent measurements of the UV illuminated lamp.

On the contrary, the slow decay in the NTs at light-off suggests a better stability and a more gradual electron-hole recombination than that found in NWs, which might be related to the defect sites, which capture or release the bypassing electrons and slow the reduction of the mobility of the photoexcited carriers in the ZnO NTs.

Figure 4(b) shows a schematic diagram to illustrate the electronic band behavior for ZnO NTs. A sufficient photon energy can generate electron-hole pairs, then excited electrons in the conduction band and unpaired holes neutralize oxygen ions at the surface [11, 12, 17, 18]. Due to the higher surface-to-volume ratio of the lower-dimensional NTs, the abundance of incident photons at the N<sub>2</sub>-treated surface can readily break down the  $V_o^+-OH$  bonds, and the electrons transferred can subsequently overcome the large band gap. Evidently, the conductivity is governed by the carrier concentration, which is associated with the surface morphology of the ZnO NTs. The



**Figure 4.** (a) Time traces of the current with the chopped light for samples measured after a 900 s N<sub>2</sub> plasma exposure under an applied voltage of +1 eV (electron conduction). The inset shows the schematic diagram of the corresponding measurement method. (b) Energy-band diagram for 300 °C annealed and N<sub>2</sub> plasma-treated ZnO under UV illumination.

large direct band gap of the NTs (3.208 eV) demonstrates the enhanced carrier concentration, which leads to a decrease in the band gap and the Schottky barrier ( $\Phi_B$ ) at the grain boundaries.

#### 4. Conclusion

In summary, a chemically based approach was used to develop ZnO nanotube (NT) and nanowire (NW) structures. The PL results show that a longer nitrogen plasma exposure can significantly improve the UV emission of ZnO nanotubes. Furthermore, the current-voltage characteristics show that the photocurrent ( $4.82 \times 10^{-7}$  A) of NTs can be remarkably enhanced compared to that ( $0.571 \times 10^{-7}$  A) of ZnO NWs after exposure to N<sub>2</sub> plasma for 900 s. This treatment also enhances the photoresponse behavior of the plasma-treated

NTs (by a factor of 20 over that of NWs). Such a promising NT structure using a nitrogen plasma treatment may offer a method of producing high optical quality ZnO nanostructures and could potentially be useful in the designs of 1D ZnO-based solar cells and optoelectronic devices.

### Acknowledgment

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