

Effect of hydrogen plasma treatment on the luminescence and photoconductive properties of ZnO nanowires

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ABSTRACT

ZnO nanowires with strong green emission synthesized by chemical vapor deposition were treated using hydrogen plasma. The effect of hydrogen plasma treatment was studied by means of photoluminescence and photoconductivity. A strong passivation of the green emission and a significant enhancement of the near band edge emission were found after the hydrogen plasma treatment. The conductivity of the nanowires in dark was increased by more than 3 orders of magnitude. The photoconductivity also increased after the hydrogen plasma treatment. The observed changes in the luminescence and photoconductive properties of the ZnO nanowires were likely caused by hydrogen atoms occupying both oxygen vacancies and interstitial sites.

INTRODUCTION

Zinc oxide (ZnO) is a wide-band-gap semiconductor with unique piezoelectric, optical, and electrical properties which has many technological applications [1, 2]. ZnO almost always shows strong n-type conduction due to unintentional doping. The origin of the n-type conductivity has been widely debated. It was traditionally thought that the native defects, including zinc interstitials and oxygen vacancies, should be responsible for the n-type conductivity [3, 4]. However, Vanheusden *et al.* [5, 6] proved through their experiments that the oxygen vacancies should not be the source of donor since the free carrier concentration was much larger than the concentration of oxygen vacancies. A first-principles study showed that the energy levels of oxygen vacancies and zinc interstitials were too deep in the band gap to contribute to the conductivity [7]. Therefore, the n-type conduction of ZnO must be attributed to impurities that are unintentionally incorporated. Hydrogen was then proposed as a cause of doping in ZnO [8]. The influence of hydrogen on defects in ZnO bulk crystals or powders were studied using cathodoluminescence (CL) [9], photoluminescence (PL) [10], and Raman [11]. ZnO nanowire (NW) is a good starting material for study the effect of hydrogen. Because of their small size and large surface-to-volume ratios, hydrogen can be easily incorporated into ZnO NWs. Besides, ZnO NWs can be synthesized with controllable properties using simple methods. The understanding of the effect of hydrogen in ZnO NWs is also very important for their future device applications.

In this report, the effect of H₂-plasma treatment on the luminescence and photoconductive properties of ZnO nanowires was studied. ZnO NWs with strong green

emission were first grown by chemical vapor deposition (CVD). The fabricated sample consisted of ZnO NWs bridged between thick ZnO electrodes, which are used to record the electrical properties of the bridged NWs [12-14]. H₂-plasma treatment was carried out on the ZnO NWs to incorporate H into the NWs. The PL and photoconductive (PC) properties of the ZnO NWs were measured before and after the H₂-plasma treatment.

EXPERIMENT

ZnO bridging NWs were fabricated by a CVD process in a horizontal vacuum tube furnace. A thin (~2 nm) gold discontinuous layer was sputtered on a quartz silica substrate through a shadow metal mask. A gap with a length of ~ 0.5 mm and a width of ~ 0.1 mm was created between two Au patterns. A powder mixture of 0.24 g ZnO (Koch Chemicals, 99.999 % purity) and 0.12 g graphite (NewMet Koch, 99.999 % purity) was charged in an alumina boat located at the center of the furnace. The substrate was placed 5 cm away from the source and downstream of the carrier gases. Argon and oxygen with a ratio of 3:2 were used as the carrier gases at a working pressure of 50 mbar. The temperature of the furnace was kept at 1000 °C for 30 min and then cooled down naturally to room temperature.

H₂-plasma treatment was performed at room temperature for 1 min in a reactive ion etching (RIE) system (SAMCO, RIE-10NRU). The RIE system had a parallel-plate type plasma reactor and was operated at an RF frequency of 13.56 MHz. The H₂ plasma was generated under an applied RF power of 100 W, a gas flow of 100 sccm, and a pressure of 100 Pa.

Scanning electron microscopy (SEM) images of the sample were taken with a Hitachi S3000N. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2010F under an acceleration voltage of 200 kV. The PL spectra were measured with a fiber optic spectrometer (Ocean Optics, USB4000) using a 325 nm He-Cd laser as the excitation source. For the PC measurements, the sample was installed into a tailor-made chamber and the ZnO NW layers were contacted using Al probes. The chamber was sealed and filled with dry air before the measurements. The current was measured using a source meter (Keithley, 2400) connected with a GPIB controller to a computer. A mercury arc lamp was used as the UV light source, and an excitation filter centered at 350 nm (± 30 nm) was inserted in the beam. The UV irradiance was measured with an optical power meter (Ophir, PD300-UV). The UV illumination was switched on and off using a mechanical shutter.

DISCUSSION

After the CVD process, ZnO NW layers were found to grow selectively on the Au-patterned areas, as shown in Figure 1a. These thick ZnO NW layers having high conductivity can be directly used as electrodes for electrical property measurements. The gap between the ZnO NW layers was bridged by many NWs with lengths of ~100 μ m and diameters in the range of 80-150 nm, as shown in Figure 1b. The bridging NW structure is very convenient for studying the PC properties of the ZnO NWs. No change in the morphology of the NWs upon plasma treatment was observed by SEM. The TEM images of the ZnO NWs before (Figure 2a) and after (Figure 2b) the H₂-plasma treatment also show similar structure and surface roughness, which suggests that the H₂-plasma treatment did not cause structural damage to the NWs.

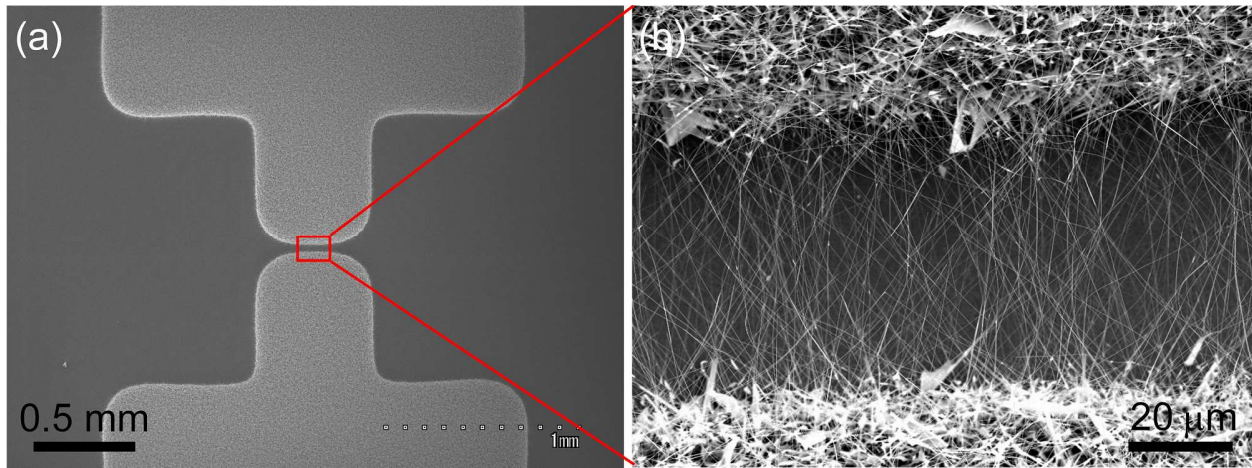


Figure 1. (a) SEM image of the ZnO bridging NW structure, ZnO NW layers were formed selectively on the Au-patterned areas. (b) SEM images of the ZnO bridging NWs in the gap between ZnO NW layers.

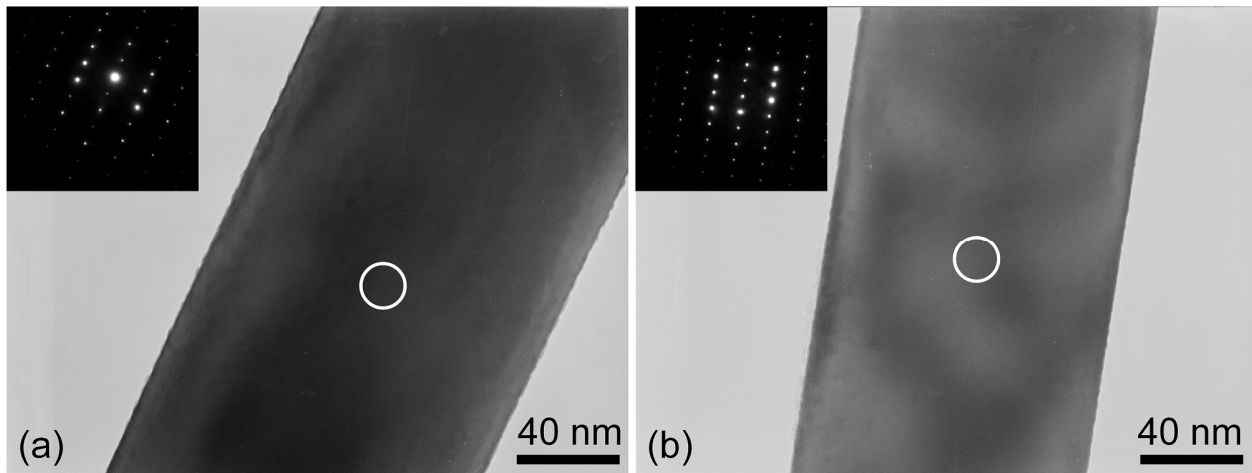


Figure 2. TEM images of (a) as-grown ZnO NW and (b) ZnO NW after H₂-plasma treatment. The corresponding selected area (indicated by the white circles) electron diffraction patterns are given in the insets.

Figure 3 shows the PL spectra of the ZnO NWs before and after H₂-plasma treatment. The as-grown ZnO NWs had a strong peak in the visible range centered at ~520 nm. The near band edge UV emission at ~380 nm, which is associated with free-exciton recombination, was almost invisible in the PL spectrum. After H₂-plasma treatment, the visible peak almost disappeared in the PL spectrum. In sharp contrast with the PL spectrum before plasma treatment, the PL spectrum after plasma treatment showed an intensive peak at ~380 nm. This sharp peak corresponded to the near band edge emission of ZnO. The green luminescence of ZnO is thought to be due to oxygen vacancies in ZnO [15-16]. Therefore, the as-grown ZnO NWs had high density of oxygen vacancies. After H₂-plasma treatment, the oxygen vacancies were occupied by H atoms which resulted in the drastic decrease of green emission and the enhancement of UV emission. This is consistent with the result of Windisch *et al.* [11], where the intensity of Raman bands associated with the oxygen vacancies was reduced after hydrogenation. The long term stability of the effect of the H₂-plasma treatment was also examined. As shown by the green line

in Figure 3, almost no change in the PL spectrum was observed 42 days after the H₂-plasma treatment. This result is evidence for the stability over time of H atoms in the oxygen vacancies. The great enhancement of the UV emission of ZnO NWs can be used to improve the performance of UV light emitting devices such as ZnO NW light-emitting diodes [17] and nanolasers [18].

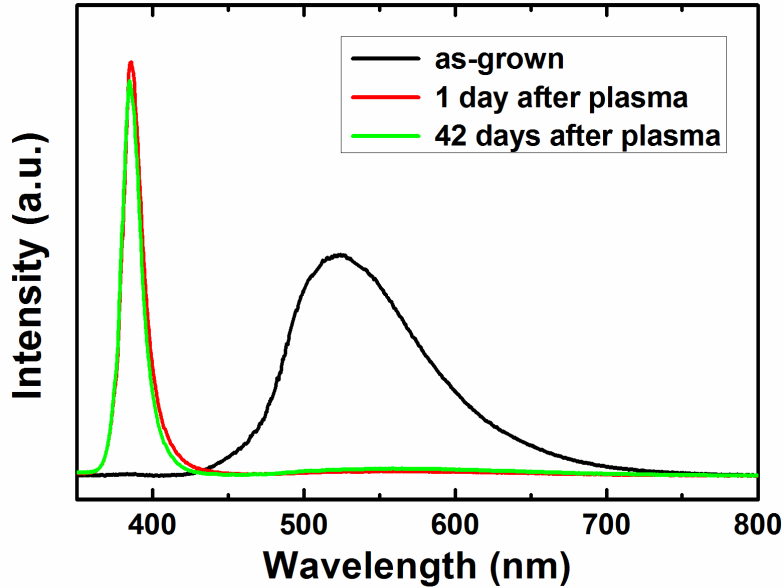


Figure 3. PL spectra of the ZnO NWs before (black line) and after (red and green lines) H₂-plasma treatment.

The PC properties of the ZnO bridging NWs before and after H₂-plasma treatment are presented in Figure 4. Before H₂-plasma treatment, the dark current (under 1 V bias) were only ~1.5 nA. The current increased drastically by more than 3 orders of magnitude upon UV illumination. The photocurrent (defined as $I_{UV} - I_{dark}$) was ~3 μ A. After switching off the UV light, the current decreased rapidly to the dark level. After the H₂-plasma treatment, the dark current increased by $\sim 4 \times 10^3$ times to ~7 μ A, the photocurrent was ~7 μ A, and I_{UV}/I_{dark} was only ~2. The current decay after switching off the UV light was slower than before H₂-plasma treatment. The increase in the dark current level indicates that the H atoms occupied interstitial sites in addition to the oxygen vacancies [11]. The increase in the photocurrent may be due to the reduction of defect density by H₂-plasma treatment which results in an increase of the photogenerated carrier life time. This could also explain the slower current decay after switching off the UV light. The PC properties of the ZnO bridging NWs after H₂-plasma treatment were also very stable over a long period of time.

The *I-V* characteristics of the ZnO bridging NWs before and after H₂-plasma treatment were also measured in dark and under UV. As shown in Figure 5a, the *I-V* curve of the as-grown ZnO bridging NWs in dark is nonlinear, which suggests that there are potential barriers in the device. After H₂-plasma treatment, the dark *I-V* curve became linear as shown in Figure 5c. This means that the potential barriers in the ZnO bridging NW structure were eliminated by the H₂-plasma treatment. Under UV illumination, the linear *I-V* curves were always linear, as shown in Figure 5b and 5d. The barriers in the as-grown ZnO bridging NWs were eliminated by the UV illumination.

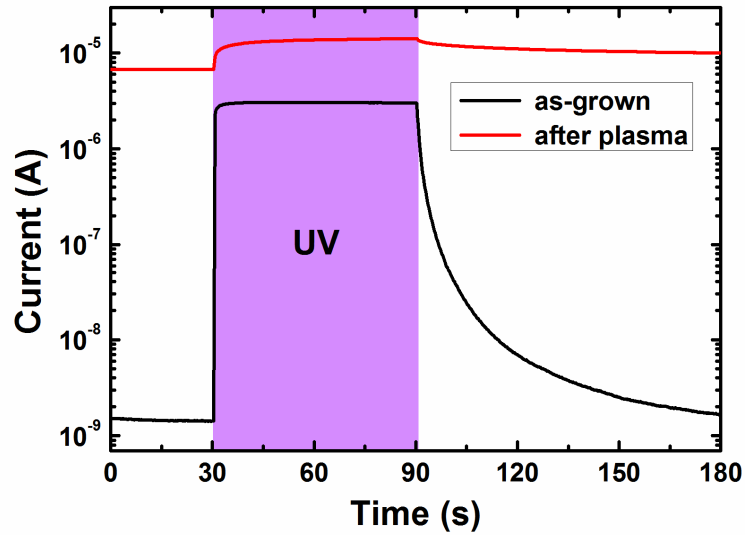


Figure 4. PC properties of the as-grown ZnO bridging NWs (black line) and the H₂-plasma treated ZnO bridging NWs (red line). The bias voltage was 1 V and the UV irradiance was ~48 mW/cm².

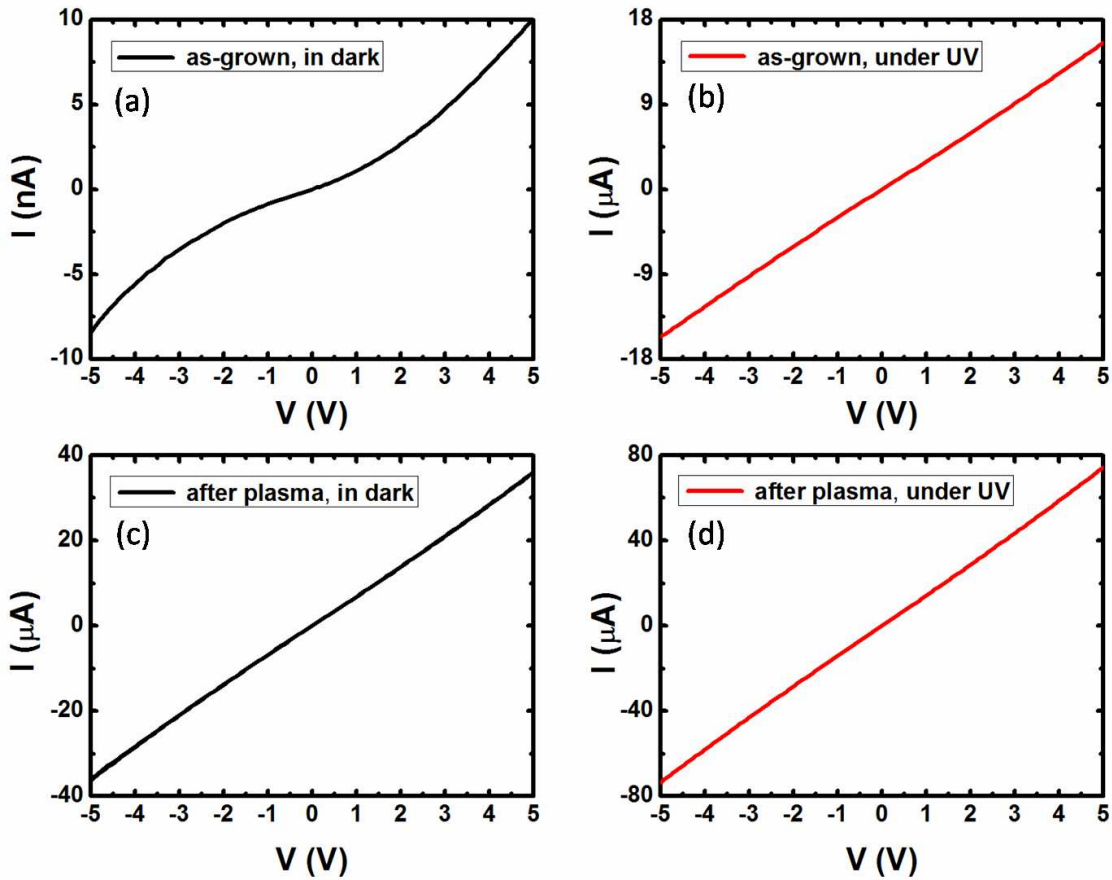


Figure 5. *I-V* characteristics of the as-grown ZnO bridging NWs (a) in dark and (b) under UV. *I-V* characteristics of the ZnO bridging NWs after H₂-plasma treatment (c) in dark and (d) under UV.

CONCLUSIONS

In conclusion, the effect of H₂-plasma treatment on the PL and PC properties of ZnO NWs was studied. Hydrogen was found to be effectively incorporated into ZnO NWs. The H atoms occupied both the oxygen vacancies and the interstitial sites in the ZnO NWs, which result in the passivation of the green emission, the enhancement of the near band edge UV emission, and the drastic increase in the conductivity of the ZnO NWs. The results demonstrate that H doping could be used to improve the UV emission efficiency in ZnO NW light emitting devices.

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