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Persistent photoconductivity in ZnO nanostructures induced by surface oxygen vacancy

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ZnO nanowall networks grown on SiO_2/Si substrate were found to exhibit persistent photoconductivity (PPC). The relaxation rate of the persistent photocurrent is enhanced by a higher oxygen level in the ambient suggesting that PPC is closely related to the ZnO surface. Surface modification with hydrogen peroxide can significantly reduce the PPC relaxation time, implying that surface oxygen deficiency is responsible for the effect. The transition between the neutral and the metastable singly ionized states of the surface oxygen vacancy is suggested to account for the phenomenon and it is supported by the temperature and wavelength dependence of the PPC.

Owing to their low cost, fabrication ease, and unique properties, ZnO nanostructures are attractive in numerous fields and devices such as ultraviolet (UV) photodetectors. A high internal gain of 10^8 has been observed from ZnO nanowires [1]. In addition to the high sensitivity, the fast photoresponse bodes well for optoelectronic applications. Unfortunately, UV detectors based on ZnO nanostructures usually suffer from large persistent photoconductivity (PPC), a light-induced conductivity that persists for a long time after illumination has ceased. For instance, ZnO nanotubes [2], nanowires [3, 4], and nanoporous films [5] have been shown to exhibit PPC for several hours. A good understanding of the origin of PPC is thus crucial to the control and performance of ZnO UV detectors. Moreover, PPC itself has other interesting applications such as bistable optical switches and radiation detectors [6]. But unfortunately, there is still no consensus on the PPC origin. One school of thought is that it is closely related to oxygen photochemistry and associated with the spatial charge separation induced by surface oxygen adsorption [7]. However, there is no unequivocal proof that PPC lasting for hours or even days stems from oxygen adsorption/desorption. It has also been proposed that the large lattice relaxation between the ionized and neutral states of oxygen vacancy (V_O) creates an energy barrier for the decay of the metastable V_O and therefore leads to PPC [8, 9]. However, the main problem with this model is that the equilibrium concentration of V_O is too low (implying a large formation energy) to permit any observable PPC from ZnO [10].

In this Letter, by carefully examining the photoresponses in different ambients, we show that the PPC of ZnO nanowall-networks (NWNs) is related to the ZnO surface. More importantly, the surface oxygen vacancy is found to be the origin as revealed by surface modification experiments as well as the temperature and wavelength dependence.

ZnO NWNs were grown on SiO_2/Si substrates at 550 °C by thermal evaporation and the details of the synthesis process can be found in Ref. [11]. The surface morphology was examined by scanning electron microscopy (SEM). The effect of surface modification by hydrogen peroxide (H_2O_2) was evaluated by X-ray photoemission spectroscopy (XPS). Two Al contacts separated by 3 mm were deposited through a shadow mask by DC magnetron sputtering. An UV light-emitting diode (LED) with peak wavelength of $\lambda = 365$ nm, as well as the radiation from a

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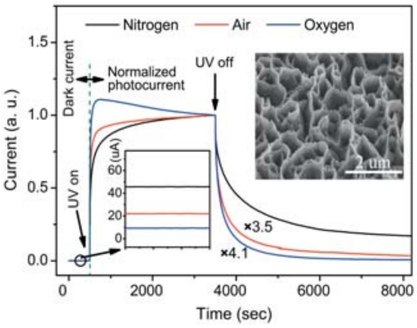

Figure 1 (online colour at: www.pss-rapid.com) Photoresponses observed from ZnO NWNs in different ambients excited by a 365 nm LED.

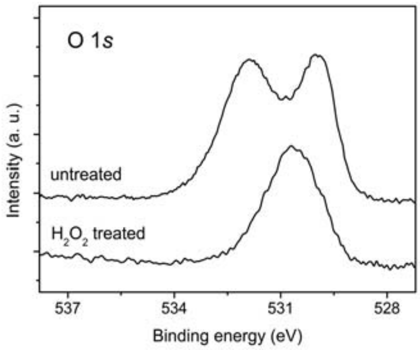

Figure 2 Comparison between the O 1s peaks obtained from the as-prepared and H_2O_2-treated ZnO NWNs.

halogen lamp dispersed by a grating monochromator, was utilized to produce the photocurrent. A bias voltage of 1 V was applied between the contacts during the measurements.

Figure 1 shows the photoresponses observed from the ZnO NWNs in different ambients. Both the dark current and photocurrent are largely enhanced in the nitrogen environment compared to oxygen-rich surroundings. This can be explained by the remarkable decrease in the conduction channel thickness caused by oxygen chemisorption [7], since the depletion width of ZnO is comparable to the nanowall thickness (as shown in the inset of Fig. 1). The most striking feature in Fig. 1 is that the PPC decay rate is retarded by reduced oxygen levels in the ambient. The PPC decay follows the stretched exponential function [6]

$$I_{\mathrm{PPC}}(t) = I_{\mathrm{PPC}}(0) \exp\left[-(t/\tau)^{\beta}\right] , \qquad 0 < \beta < 1 , \qquad (1)$$

where $I_{\mathrm{PPC}}(0)$ is the PPC buildup level at the moment when light excitation ceases, τ is the PPC decay time constant, and β is the decay exponent. The PPC time constant increases from 158 s in oxygen to 251 s in air to 1054 s in nitrogen.

The ambient dependent character found here is consistent with previous observations [12–14], implying that the observed PPC is a surface related effect and not a bulk one. A mechanism based on oxygen photochemistry suggests the important role played by the surface [7, 15]. According to this model, the chemisorption of oxygen leads to the formation of a surface barrier, which results in spatial separation between the electron–hole pairs and thereby the PPC. In such a scenario, the increase of oxygen level in the ambient would lead to a rise of the surface barrier height and thus a slower PPC decay. In nitrogen ambient, the oxygen adsorption-induced charge separation can be neglected [7], and the PPC decay should be faster than that in oxygen-rich surroundings. However, this expectation is contrary to our observations that the increase in oxygen level enhances the PPC decay rate. In order to fathom the microscopic origin and ambient dependence of PPC, the surface defects as well as their interactions with the ambient molecules should be taken into account.

Surface functionalization may provide clues to the microscopic origin of PPC. Our experiments disclose that the sample treated with H_2O_2 for 300 s exhibits a fast PPC decay with time constant of less than 3 s (not shown). XPS is employed to reveal the effects of H_2O_2 treatment on the ZnO surface, as shown in Fig. 2. Besides the O 1s signal at ~530 eV (lattice oxygen), another peak at ~531.9 eV corresponding to the adsorption of OH or oxygen [16, 17] can be observed from the untreated sample. These species are typically adsorbed on oxygen-deficient sites [18]. The adsorbed O 1s XPS signal is significantly reduced after the H_2O_2 treatment, indicating the number of surface oxygen-deficient sites is reduced [16]. This is further demonstrated by surface composition analysis, which reveals a sharp increase in the lattice [O]/[Zn] molar ratio from 0.44 to 1.13 after H_2O_2 treatment. These observations indicate that the H_2O_2 treatment alters the surface stoichiometry resulting in a conversion from a state of oxygen deficiency to that with excess oxygen. The results imply that PPC is closely related to the oxygen-deficient sites on the ZnO surface.

Surface V_O is a possible candidate responsible for the PPC observed in ZnO NWNs. According to first principles calculation, the large lattice relaxation between the singly ionized V_O (namely V_O^+) and neutral V_O creates an energy barrier, which impedes the decay of the metastable V_O^+ to V_O, leading to the PPC [8]. In fact, V_O was ascribed as the source of PPC in electron irradiated ZnO single crystals [19]. Unfortunately, the rather high formation energy results in a very low equilibrium concentration of V_O [10, 20] in the non-irradiated samples which cannot account for the PPC observed here. However, the vacancies on the surface have a lower formation energy than those in the bulk [18]. Thus one would expect considerable oxygen vacancies on or near the surface, especially on ZnO nanostructures due to their high surface-to-volume ratio. In fact, oxygen vacancies on ZnO surface act as active centers in the catalytic hydrogenation of CO to form methanol [21].

To obtain more proof, we measured the photocurrent decay at different temperature and the results are displayed in Fig. 3. The PPC decay rate is enhanced as the temperature increases, and the PPC time constants are determined by fitting the decay curves using Eq. (1). The inset of Fig. 3 shows the Arrhenius plot of the fitted time constants of the ZnO NWNs. In the measured temperature range,

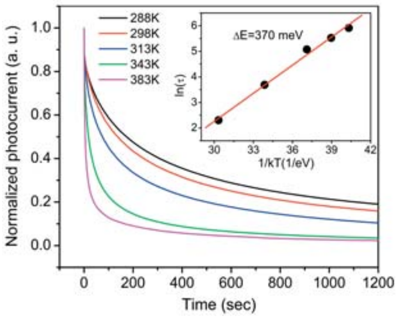

Figure 3 (online colour at: www.pss-rapid.com) Temperature dependence of the PPC decay of ZnO NWNs with the inset showing the Arrhenius plot of the PPC decay time constant τ, which yields an energy barrier of 0.37 eV.

τ exhibits a thermally activated behavior described by the following function:

$$\tau = \tau_0 \, e^{\Delta E/kT} \qquad (2)$$

where ΔE is the activation energy barrier determined to be 0.37 eV using a linear fit. This value is close to the calculated one of 0.3 eV for the $V_O^+ \to V_O^0$ transition [8] thereby supporting the postulate that surface V_O produces PPC.

The wavelength dependence of the PPC provides further confirmation. The photocurrent decays determined with different excitation photon energies are shown in Fig. 4. For photon energy $h\nu > 3.1$ eV, both the rise and fall of the photocurrent are rather slow, and the PPC decay can be well fitted by the stretched exponential function. When $h\nu < 3.1$ eV, both the photocurrent buildup and decay are governed by two competitive processes, namely fast and slow ones. The fast rise/decay part is more prominent for lower input photon energies, whereas the slow rise/decay part is still observable for excitation photon energy down to 2.1 eV. This value is identical to the threshold photon energy reported by Laiho et al. [22] in detecting V_O^+ by electron paramagnetic resonance, further corroborating that surface V_O is the source of the PPC observed here. It should also be noted that the fast rise/decay process which has a response time of less than 0.1 s (the resolution limit of our equipment) appears to be related to deep recombination centers. More work is being done in our laboratory concerning the detailed mechanism and the results will be reported in due course.

We now turn to the question why the PPC decay depends on the oxygen level in the ambient. The passivation of V_O by adsorbed oxygen molecules may be a possible answer. The adsorbed oxygen molecules deplete electrons from the ZnO NWNs forming $O_2^{\delta q-}$ [23]. For simplicity, here we do not consider the dissociation of oxygen molecules and suppose a charge transfer of δq. When $O_2^{\delta q-}$ adsorbs onto V_O, the site is passivated. Although some of the chemisorbed molecules are desorbed by light illumination, the $O_2^{\delta q-}$ ions are in equilibrium with the oxygen partial pressure. Passivation of V_O by $O_2^{\delta q-}$ hinders the $V_O^0 \to V_O^+$ transition under illumination leading to a fast photocurrent decay. On the other hand, the desorbed oxygen molecules immediately readsorb onto the ZnO surface when the illumination is turned off [1]. The readsorbed molecules capture the remaining electrons and thus facilitate the carrier relaxation process which may also contribute to the observed oxygen-accelerated PPC decay.

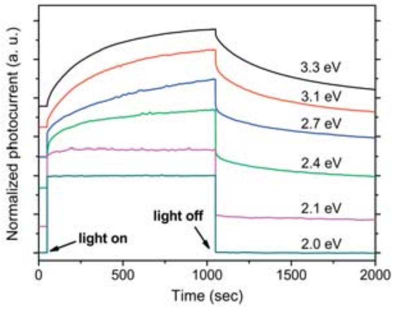

Figure 4 (online colour at: www.pss-rapid.com) Photoresponses of the ZnO NWNs obtained with different input photon energies. The PPC buildup level at the moment of light excitation being removed is normalized. The curves are shifted for clarity.

In summary, surface oxygen vacancy is recognized as the origin of PPC in ZnO NWNs following its temperature and wavelength dependence. This mechanism highlights the role of surface defects and their interactions with the surrounding molecules, and hence explains the ambient dependent behaviour of PPC. Our findings are helpful for gaining better insight into the PPC of oxide nanostructures.

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