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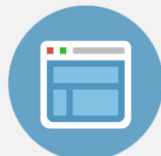
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Ultralow-frequency photocurrent oscillation in ZnO nanowires

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We report experimental results of ultralow frequency photocurrent oscillation in individual ZnO nanowires. Consecutive photocurrent and photoluminescence measurements corroborate the process of capture and release of photogenerated holes by surface trap states. The dynamic process results in the oscillation of the thickness of surface depletion region, which is believed to be responsible for the observed photocurrent oscillation. © 2010 American Institute of Physics.

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ZnO nanostructures exhibit many interesting properties including piezoelectric effect,¹ high photoconductive gain,² optical pumped lasing,³ and chemical⁴ and gas sensing.⁵ ZnO nanowires have been used to construct all kinds of nanodevices, such as p-n junctions,⁶ nanogenerators,⁷ photovoltaic cells,^{8,9} field effect transistors,¹⁰ and light emitting diodes.¹¹ Due to the large surface-to-volume ratio surface effect will strongly influence the physical properties of ZnO nanowires.^{12,13} Especially, for the photoelectric response of ZnO nanowires the surface trap states significantly affect the processes of carrier generation, recombination, and diffusion.^{14,15} In this work, we reported the ultralow frequency photocurrent oscillation induced by the dynamic variations in the surface depletion region in single ZnO nanowires.

ZnO nanowires were fabricated via a simple chemical vapor deposition method as previously described.¹⁶ The as-grown nanowires were mechanically transferred onto a Si substrate with a 500-nm-thick SiO₂ layer. Ti/Au electrodes were fabricated contacting with one nanowire using electron beam lithography and magnetron sputtering metal deposition. The device configuration is shown in the inset in Fig. 1 by the scanning electron microscope (SEM) image. The nanowire diameter is about 60 nm and the length spanning the two electrodes is $\sim 1.8 \mu\text{m}$. The sample was placed in a vacuum chamber ($\sim 10^{-6}$ Torr) of a Janis microcryostat. The photoelectrical properties were measured by a Keithley 6430 Source-Measure Unit with the excitation of a 325 nm He-Cd laser guided by a Renishaw Raman microscope.

Figure 1 shows the dark and photoexcited current-voltage (I-V) curves of the ZnO nanowire measured at 300 K. The high dark-resistance $\sim 10 \text{ G}\Omega$ is due to the oxygen molecules adsorbed on the nanowire surface which can however capture free electrons and deplete the thin nanowires.¹⁷ The photoexcited I-V curves correspond to three consecutive measurements with the same condition. It is evident that the conductance increases with the UV irradiation duration, for example, the conductance of the third measurement (the blue line) is larger than that of the second measurement (the green line). It takes about several seconds

to collect an I-V curve. Therefore, it is interested to know how the photoconductivity depends with time.

The photocurrent of the nanowires as a function of time is shown in Fig. 2. As the laser illumination was turned on, the current quickly increased and then showed an oscillating characteristic. At temperature of 10 K, the frequency of this oscillation is about 0.0016 Hz, and the rise time and fall time are about 380 s and 250 s, respectively. At 100 K, the frequency of the oscillation is about 0.0011 Hz, and the rise time and fall time are about 300 s and 600 s, respectively. As illustrated in Fig. 3, the oscillation can be explained by considering the variation in the surface depletion region caused by the surface adsorbed oxygen molecules which can capture free electrons.¹² Under illumination, photogenerated electron-hole pairs are separated by the built-in electrical field of the surface space charge region. The holes move toward the nanowire surface and trapped by the surface adsorbed oxygen anions [see Fig. 3(b)]. Due to the effective separation of the electron-hole pair, the lifetime of the photogenerated electrons will gradually increase, which corresponds to the slow increase in the photocurrent in Fig. 2. As the surface negatively-charged oxygen molecules were neutralized by the holes as well as the electron concentration inside the nanowire was increased, the thickness and magni-

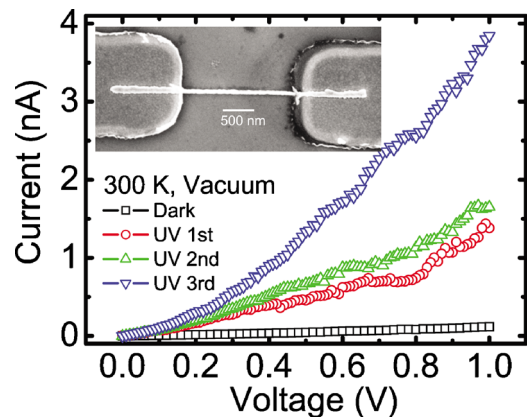


FIG. 1. (Color online) The dark and photocurrent I-V curves of single ZnO nanowire measured at 300 K and vacuum conditions. The photocurrent I-V curves correspond to three consecutive measurements with the same condition. Inset: the SEM image of single ZnO nanowire device.

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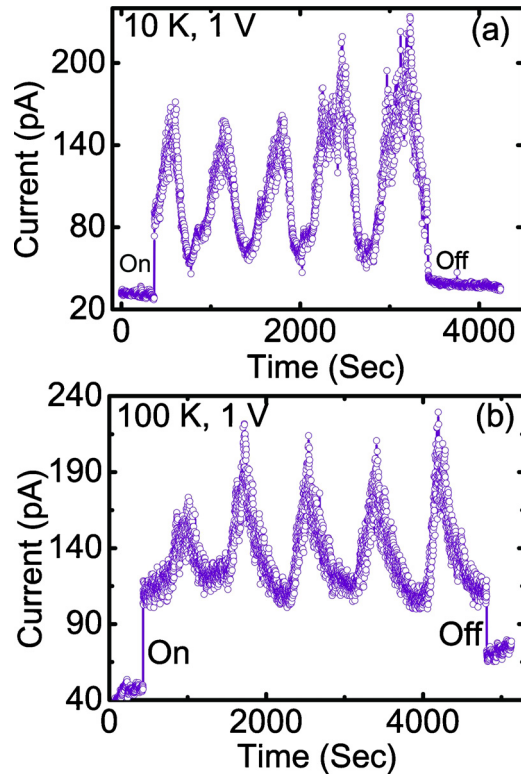


FIG. 2. (Color online) Applying 1 V bias voltage, under illumination with a 325 nm laser, the photocurrent oscillations measured at temperature of (a) 10 K, and (b) 100 K.

tude of the barrier potential of the surface depletion layer will be gradually reduced.

The decreasing depletion region described in Fig. 3 was verified by the photoluminescence (PL) spectrums measured with consecutive cycles (seen in Fig. 4). First, it shows that for the first measurement the excitonic emission intensity is much larger than that for the second measurement. Because the photogenerated holes were continuously captured by the surface trap states, the amount of irradiative recombination was reduced and thus lowered the excitonic emission intensity. Second, it is also found that the peak position of the excitonic emission for the second measurement has a redshift comparing with that for the first measurement, which is attributed to the band filling effect (Burstein–Moss effect).¹⁸ As described above, the number of holes in the valance band decreased and raised the filling energy level of the valance

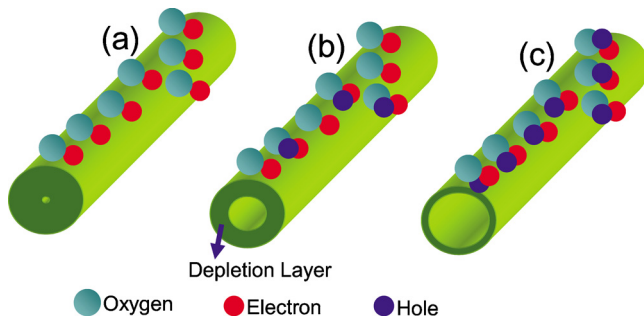


FIG. 3. (Color online) Sketches of the surface depleted status of single ZnO nanowire, (a) almost totally depleted by surface absorbed oxygen, (b) the surface depletion region is reduced through capturing photogenerated holes, and (c) the depletion region is further reduced and the holes can tunnel back through the thin surface depletion layer.

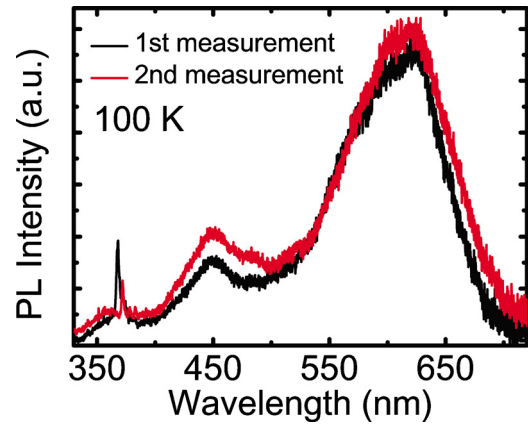


FIG. 4. (Color online) The PL spectrums of a single ZnO nanowire measured at temperature of 100 K with two consecutive measurement cycles.

band. Consequently, the photon energy coming from the radiative recombination between states in the conduction and valence bands also decreased. Therefore, the PL measurements gave an evidence of the photogenerated holes can be trapped by the surface trap states and thus reducing the surface depletion region.

As further decreasing the surface depletion layer, the surface trapped holes can tunnel through the thin depletion layer and back to the inside of the nanowire, as seen in Fig. 3(c). Since the holes have a certain probability to recombine with the free electrons, the lifetime of the photogenerated electrons will decrease. Therefore, the number of carriers that can transit through the nanowire within the lifetime will decrease, which results in the decrease in photocurrent in Fig. 2.

The photocurrent oscillation can be further analyzed by considering the thickness variation in the surface depletion region. The thickness of the depletion region $\zeta(t)$ is proportional to the number of surface charged oxygen molecules $Q(t)$, that is, $\zeta(t) = CQ(t)$, where C is related to the electron concentration and the cross section area of the nanowire and here simply as a constant. As the holes move toward the surface and are trapped by the charged oxygen, the charged oxygen becomes neutral oxygen reducing the number of Q . Thus, the variation in the Q can be written as

$$dQ(t) = -p_{e-h}\zeta(t)dt, \quad (1)$$

where p_{e-h} is the number of the electron-hole pair generated within unit time and unit thickness in the depletion region. Thus, $dQ(t) = -p_{e-h}CQ(t)dt$, and

$$Q(t) = \exp(-p_{e-h}Ct). \quad (2)$$

Here, the exponential decrease in surface charged oxygen is well consistent with the exponential increase in the photocurrent in Fig. 2. As temperature increasing, the p_{e-h} will increase due to the contribution from thermal energy. Therefore, the growth time of the photocurrent decrease with increasing temperature, which is consistent with experimental observation in Fig. 2.

For the decrease process of the photocurrent, the holes tunnel back into the inside of the nanowire. The increase in the Q is related to the value of Q and the tunneling rate of the hole through the depletion layer. Thus,

$$dQ(t) = Q(t)B e^{-\sqrt{2m^*(U-E)\zeta(t)/h} dt}, \quad (3)$$

where B is the tunneling coefficient, m^* is the effective mass of hole, U is the potential of the surface depletion region, h is the Planck's constant and E is the energy of the trapped hole. To catch the main physical picture, we simplify the equation as

$$Q(t) = \exp(Bte^{-\sqrt{2m^*(U-E)\zeta(t)/h}}), \quad (4)$$

which can well explain the exponential decay of photocurrent in Fig. 2. The energy E of the hole may mainly come from the excitation photon and is not sensitive to temperature, because the photon energy is much larger than the thermal energy. Thus, E can be considered as a constant. As increasing temperature to above the oxygen condensed point of 90.2 K, the total oxygen gas molecules in the vacuum chamber will increase. Therefore, the surface adsorbed oxygen and thus the depletion ζ will increase as the temperature is increased from 10 to 100 K. According to Eq. (4), the decay time of photocurrent increasing with increasing ζ . Thus, it can be inferred that the photocurrent decay time at temperature of 100 K is larger than that at 10 K, which is consistent with the observation in Fig. 2.

The deep defect energy centers also influence the photoconductivity of the nanowire. The PL peaks centered at 449 and 624 nm (seen in Fig. 4) indicate the existence of deep defect energy levels in the ZnO nanowire. At low temperature of 10 K, the carriers generated from the deep trap centers under laser illumination also contribute to the photoconductivity. After the laser illumination was switched off, at 10 K the carriers will be recaptured by the deep trap states, which results in the slow decay of the dark current in Fig. 2(a). However, at medium temperature of 100 K, the defect trap states may mostly be thermally activated. Under laser illumination, large numbers of photogenerated carriers upset the original dynamic balance between the number of activated trap state and the number of free carrier, and the photogenerated carriers will fill in the trap states to reach a new balance. After turning off the laser illumination, the carriers are slowly returned from the trap states due to thermal activation, which results in the slow increase in the dark current in Fig. 2(b).

In conclusion, ultralow frequency photocurrent oscillation from a single ZnO nanowire has been observed. Under illumination, the variation in the surface depletion region was responsible for the oscillating photocurrent. The influence of the deep traps on the photoconductivity was also discussed.

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