ZnO nanowire Schottky barrier ultraviolet photodetector with high sensitivity and fast recovery speed

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ZnO nanowire (NW) ultraviolet (UV) photodetectors have high sensitivity, while the long recovery time is an important limitation for its applications. In this paper, we demonstrate the promising applications of ZnO NW Schottky barrier as high performance UV photodetector with high sensitivity and fast recovery speed. The on/off ratio, sensitivity, and photocurrent gain are 4×10^5, 2.6×10^3 A/W, and 8.5×10^3, respectively. The recovery time is 0.28 s when photocurrent decreases by 3 orders of magnitude, and the corresponding time constant is as short as 46 ms. The physical mechanisms of the fast recovery properties have also been discussed. © *2011 American Institute of Physics*. [doi:10.1063/1.3660580]

In recent years, one-dimensional (1D) semiconductor nanostructure materials have attracted much attention because of their potential applications in nanoscale electronic and optoelectronic devices, such as field effect transistors,[1,2] gas and chemical sensors,[3,4] and photodetectors.[5,6] Due to the wide bandgap (3.4 eV) and extraordinary optoelectronic properties, ZnO nanowires (NWs) have been widely investigated and exhibited potential applications in developing ultraviolet (UV) photodetectors.[7–12] In these 1D nanodevices, the 1D nanomaterials inevitably make two metal-semiconductor (MS) contacts with two electrodes. Recently, more and more researches begin to focus on the MS contacts of 1D nanomaterials, because the MS contacts have been found to have dominative influence on the transport behavior of 1D nanomaterials and promising applications in developing novel devices.[13–18] For example, the MS contact of carbon nanotube has been used to prepared Schottky rectifying diodes with high frequency up to 2.5 THz,[14] and the MS contact of ZnO NW has been used to prepare supersensitive gas and UV sensors.[15,16] In the previous studies in our group about the Schottky barrier (SB) contact between oxide NWs and metal, it is found that the surface states of NWs (Refs. 19 and 20) and the geometry structure of SBs (Ref. 21) have important influences on the transport properties of NW SBs, and light can effectively control the transport properties of NW SBs.[22] While, how to make use of SBs to improve the performance of NW-based optoelectronic devices is still a challenge.

In this paper, we demonstrate the photocurrent properties of a single ZnO NW SB with high sensitivity and fast recovery speed. The on/off ratio, sensitivity and photocurrent gain are 4×10^5, 2.6×10^3 A/W, and 8.5×10^3, respectively. Interestingly, the recovery time is 0.28 s when photocurrent decreases by 3 orders of magnitude, and the corresponding time constant τ_i (the recovery time when photocurrent decreases to its 1/e, i.e., 37%) is as short as 46 ms, which is much shorter than the previously reported τ_i values of ZnO NW UV photodetectors ranging from several seconds to several minutes.[7–12] In addition, the generation and recovery mechanisms of ZnO NW SB photocurrent have been discussed to explain the physical basis of the fast recovery properties.

The ZnO NWs were synthesized by thermal evaporating and assembled on Au electrodes by dielectrophoresis.[21] The I-V curves were measured at room temperature in ambient condition, and a 365 nm UV light with intensity 7.6 mW/cm^2 was used. Figure 1(a) shows the I-V curves of a single ZnO NW in dark and under UV light in log scale, Fig. 1(b) shows the I-V curve under UV light in linear scale, and the corresponding scanning electron microscopy (SEM) image of the NW is shown in the inset of Fig. 1(b). The nonlinear and cut-off properties of I_{dark} (current in dark) indicate that the ZnO NW makes two SB contacts with the two Au electrodes, and a back-to-back SBs structure is formed, in which the current is dominated by the reverse current of reverse biased SB.[13,20] As shown in Fig. 1, I_{light} (current under UV light) is nonlinear with voltage in low bias region ($-1.4\,\mathrm{V} < V < 1.6\,\mathrm{V}$), and $\ln(I_{light})$ is almost linear with voltage in this bias region. This curve properties have been discussed in detail in our previous report, which indicate that the current transport under UV light is still dominated by SB, and I_{light} is attributed to the tunneling current of SB.[22]

Under UV light, the current remarkably increases, and the ratio of I_{light} to I_{dark} at +5 V bias is up to 4×10^5. Photocurrent sensitivity (S) is the current value per unit optical power and is expressed as $S = I_{ph}/P_{opt}$, where $I_{ph} = I_{light} - I_{dark}$ and P_{opt} is the optical power absorbed in the interface of NW SB. Photocurrent gain (G) is the ratio of the number of electrons collected per unit time to the number of absorbed photon per unit time. If the absorption quantum efficiency of photon is assumed to be unit (all of the photons have been adsorbed), G can be expressed as[8,18]

$$G = \frac{I_{ph}/q}{P_{opt}/hv} = \frac{S}{q/hv}, \tag{1}$$

where q is elementary charge and v is the frequency of the adsorbed photon. For the photocurrent at +5 V bias, S and G are calculated as 2.6×10^3 A/W and 8.5×10^3, respectively.

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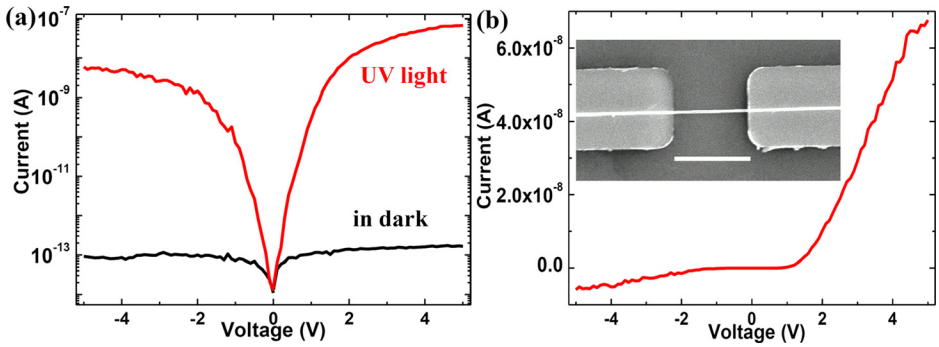

FIG. 1. (Color online) (a) The log-scale I-V curves of a single ZnO NW in dark and under UV light. (b) The linear-scale plot of the I-V curve under UV light; inset: the SEM image of the ZnO NW with scale bar of 5μm.

Figure 2(a) shows the time-resolved photocurrent at +5 V bias with multiple on/off cycles, in which the turn-on and turn-off time of UV light are both 10 s. It is clear that the recovery process of photocurrent contains a fast recovery process followed by a slow recovery process. The photocurrent recovery curves at various biases (+2, +3, +4, and +5 V) exhibit similar properties, all of them contains a fast and a slow recovery processes.[23] In the slow recovery process, the photocurrent completely recovery to the original current value in dark condition within about 70 s.[23] As shown in the magnification of a single on/off cycle at +5 V (Fig. 2(b)), the recovery time in the fast recovery process (t_{fp}) is only 0.28 s within which the photocurrent decreases by 3 orders by magnitude, and the current-time curve within t_{fp} can be well fitted by an exponential expression $I = I_{light}\exp(-t/\tau_i)$ by using $\tau_i = 46$ ms (the dash line), where τ_i is the corresponding recovery time constant. The statistical data of t_{fp} and τ_i from the multiple on/off cycles at +5 V have good stability and repeatability.[23] In the previously reported ZnO NW UV photodetectors, the typical values of τ_i range from several seconds to several minutes, and τ_i cannot remain constant in such a large photocurrent recovery range about 3 orders.[7–12] Compared to those ZnO NW photodetectors, the ZnO NW SB photodetector reported in this paper has excellent recovery performance.

The generation and recovery mechanisms of NW SB photodetector are different from that of NW photodetector, which forms the physical basis of the excellent photocurrent recovery behavior of ZnO NW SB. Figure 3(a) shows the barrier structure model of NW SB in dark condition, which is suitable for NWs with large diameter and has been discussed in our previous report.[21] In this model the surface depletion layer near the NW surface is formed by surface states, the NW SB is formed in the contacted region between surface depletion layer and electrode, and a nondepletion region exists inside NW. The barrier height of NW SB is determined by the surface states of NW but not by work function difference between NW and metal electrode, because of the Fermi level (E_F) pinning at surface states.[19,20] It has been widely accepted that oxygen molecule is an important type of surface states for ZnO NW, which is chemically adsorbed on NW surface by capturing free electrons $[O_2(g) + e^- \rightarrow O_2^-(ad)]$ and plays significant roles in forming depletion layer.[7,8] The barrier height of SB (φ) is expressed as

$$\varphi = \psi_{bi} + \xi = \frac{Q_S^2}{2qN_{SC}\varepsilon_s A^2} + \xi, \tag{2}$$

where ψ_{bi} is the build-in potential of SB depletion layer, ξ is the potential difference between the minimum of conduction band and E_F of NW, Q_S is the surface charges in SB interface, N_{SC} is concentration of space charges in depletion layer, ε_s is the dielectric constant, and A is the contact area of SB. The barrier structure model of NW SB under UV light is shown in Fig. 3(b). Under UV light, the photogenerated electron-hole pairs $[h\nu \rightarrow e^- + h^+]$ near SB are separated by build-in electric field in SB, and the holes migrate to SB interface. Some holes flow across the SB interface and enter metal electrode. Some holes are captured by O_2^- at SB interface, which discharge the negative charges of O_2^- and make O_2^- desorbed from SB interface $[h^+ + O_2^-(ad) \rightarrow O_2(g)]$.[7,8] Some holes stay at SB interface before they enter metal electrode, which generates holes in SB interface under dynamic equilibrium.[19] The desorption of O_2^- and the generation of holes in SB interface decrease the surface charges Q_S, as a result, the barrier height φ decreases according to Eq. (2). The decrease of φ will result in the exponential increase of tunneling current of NW SB,[13,22] which generates remarkable tunneling photocurrent of ZnO NW SB under UV light.

For ZnO NW SB photodetector, the photocurrent recovery is caused by the following two ways: one is the re-

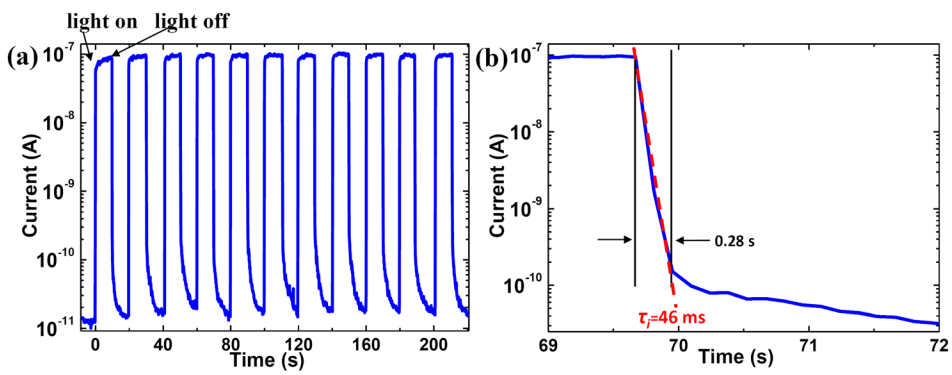

FIG. 2. (Color online) (a) The time-resolved photocurrent curve at +5 V with multiple on/off cycles. (b) The magnification of a single on/off cycle.

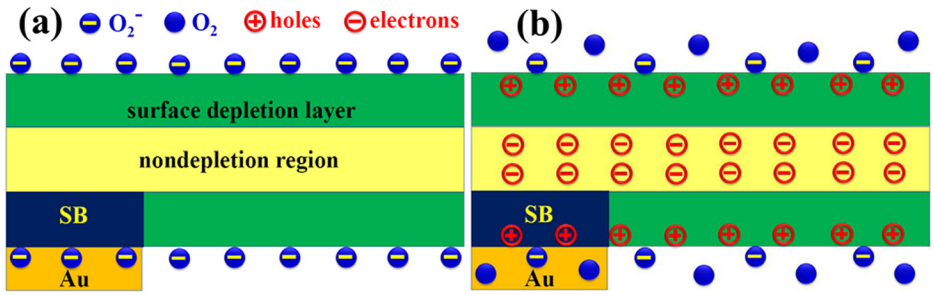

FIG. 3. (Color online) The barrier structure model of NW SB in dark (a) and under UV light (b), respectively.

adsorption of O_2^- in SB interface, the other one is the relaxation of the holes stayed in SB interface. Here, we define the total number of re-adsorbed O_2^- and relaxed holes in SB interface in the photocurrent recovery process of NW SB as $N_{SB-interf}$. According to Eq. (2) and the exponential dependence of tunneling current on φ discussed above, the photocurrent of NW SB has exponential-type dependence on $N_{SB-interf}$, and the photocurrent would reduce sharply with the increase of $N_{SB-interf}$. For ZnO NW photodetectors, the NW makes Ohmic contacts with the electrodes, and the photocurrent is linear with the number of photogenerated electrons in NW. Under UV light, the photogenerated electron-hole pairs are separated by the build-in electric field in surface depletion layer, the holes migrate to surface, and the unpaired electrons left in nondepletion region contribute to photocurrent. The photocurrent recovery of ZnO NW photodetector is caused by similar two ways: the re-adsorption of O_2^- in NW surface and the relaxation of the holes stayed in NW surface. Here, we define the total number of re-adsorbed O_2^- and relaxed holes in NW surface in the photocurrent recovery process of NW photodetector as $N_{NW-surf}$. The photogenerated electrons in NW linearly decrease with the increase of $N_{NW-surf}$, as a result, the photocurrent of NW photodetector has a linear dependence on $N_{NW-surf}$. According to above discussion, it is clear that the photocurrent of NW SB has more sensitive response to the number of re-adsorbed O_2^- and relaxed holes in SB interface, which is believed to be the major reason for the fast recovery speed of NW SB photodetector.

For NW photodetector, the holes stayed in NW surface are relaxed by recombining with the electrons in nondepletion region. However, the holes stayed in NW surface and the electrons left in nondepletion region are spacially separated, which decreases their recombination probability. For NW SB photodetector, besides the relaxation by recombining with electrons, the holes stayed in SB interface can directly flow across SB interface and enter metal electrode under the assistance of build-in electric field in SB. Therefore, the relaxation speed of holes stayed in SB interface is faster than that stayed in NW surface, which is considered to be another main reason for the fast recovery speed of ZnO NW SB photodetector.

In conclusion, the UV photodetector of ZnO NW SB with high sensitivity and fast recovery speed has been fabricated. The on/off ratio, sensitivity, and photocurrent gain are 4×10^5, 2.6×10^3 A/W, and 8.5×10^3, respectively. The recovery time is 0.28 s when photocurrent decreases by 3 orders of magnitude, and the corresponding recovery time constant τ_i is as short as 46 ms. The exponential-type dependence of photocurrent on $N_{SB-interf}$ and the faster relaxation speed of holes stayed in SB interface are the physical basis for the fast recovery speed of NW SB photocurrent. The high sensitivity and fast recovery properties of ZnO NW SB make it a promising candidate for high performance UV photodetectors and photoswitches.

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[23]See supplementary material at http://dx.doi.org/10.1063/1.3660580 for (1) the photocurrent recovery curves at various voltages, (2) the photocurrent recovery curve which contains whole recovery process, and (3) the statistical data of fast recovery process.