

Competitive surface effects of oxygen and water on UV photoresponse of ZnO nanowires

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UV photoresponse of ZnO nanowires is measured in air under different humidity conditions to study the competitive surface effects of oxygen and water vapor. During UV illumination, it was found that the current decreases gradually under high humidity, whereas the current increases under low humidity. In the recovery phase, a change of two to three orders of magnitude in the decay time is observed by varying the humidity. A model that takes into account the solid-state process of photocarrier generation/recombination and the competitive surface effects of oxygen/water is proposed to explain the observed variations in photoresponse under different humidity conditions. © 2009 American Institute of Physics. [DOI: 10.1063/1.3073042]

Conventional semiconductor photodetectors are expected to exhibit fast rises and decays in conductivity upon switching on/off light with photon energy above the semiconductor band gap. This is well explained in bulk by the fast creation of electron-hole pairs upon light illumination and their fast recombination after turning off light.¹ However, for ZnO nanowires, a slow decay of the photoresponse is observed and attributed to surface effects,² among which the surface adsorbed oxygen molecules have been reported to contribute greatly.¹⁻⁶ However, the effect of water vapor, another major adsorbed gas species, is still poorly understood in part due to the complex mechanism of water interaction with the surfaces of metal oxides such as ZnO, which is still a subject of intense research.⁷⁻¹² Some reports point to water adsorption as a cause for the shortening of the current decay process of ZnO photoresponses,¹⁻³ but still a conclusive data set and an up-to-date interpretation of the effects of oxygen and water on the ZnO photoresponse has not been presented.

In this letter, the surface effects of both oxygen and water on UV photoresponse of ZnO nanowires were studied by performing photoresponse measurements in air with different humidities. The obtained photoresponse curves showed drastic changes in dark, under illumination, and during recovery for different humidity conditions. A model taking the solid-state process of electron-hole generation/recombination and surface effects of oxygen and water into account was proposed to explain the drastic changes in the observed photoresponses. A better knowledge of these mechanisms would help in further understanding the chemistry and physics of ZnO surfaces and improving the performance of both ZnO UV detectors and gas sensors.

The ZnO nanowire UV detector was fabricated by chemical vapor deposition (CVD).¹³ In short, a Au catalyst was patterned on a quartz glass substrate using a comb-shaped mask and then ZnO was grown on the patterned substrate by CVD. The fabricated device is shown in Figs. 1(a) and 1(b). A thick ZnO layer was formed selectively on the Au-patterned areas and this layer served as native electrode. Ultralong (~100 μm) ZnO nanowires were grown across

the gap between the ZnO comb fingers and the nanowires served as the sensing elements of the detector. The experimental setup depicted in Fig. 1(c) was used to record the time-dependent photoresponse under different relative humidity (RH) conditions in air. The ZnO nanowire UV detector was placed inside a sealed glass chamber equipped with a gas inlet and outlet. A humidity recorder (T&D TR-72S) and a UV powermeter (Ushio UIT-150) were fixed near the sample. The glass chamber was placed on top of a UV transilluminator (3UV LMS-20E). Air with different RHs was generated by bubbling dry air from an air cylinder through pure water and adjusting the flow rates of dry air and wet air. The measured photoresponses shown in Fig. 1(d) reveal several interesting points. In the dark (0–30 s), the current level increases with RH. Under illumination (30–90 s), the current level is lower with high RH; besides, the current increases gradually under low RH, while it decreases gradually under high RH. In the recovery phase at 90–300 s, the current decays much faster under high RH. Table I lists the current decay times (decay to 10% and 1% of the value before switching off UV) estimated from the curves in Fig. 1(d). The decay times decrease drastically with high RH. These results are evidence for the effect of surface adsorbed water molecules on the carrier density and carrier lifetime in the nanowires. To explain these results, we propose a model that takes into account the surface effects of oxygen and water. The mechanisms of the photoresponse in dry air and wet air are summarized by the diagrams in Fig. 2.

In dry air, the photoresponse of ZnO is generally governed by adsorption and desorption of oxygen molecules on the surface. In the dark [Fig. 2(a)], oxygen molecules adsorbed on the surface of ZnO nanowires not only decrease the carrier density in the nanowires by trapping free electrons [$O_2(g) + e^- \rightarrow O_2^-(ad)$] of the *n*-type semiconductor but also decrease the mobility of the remaining carriers by creating depletion layers near the surface. This process also leads to upward band bending near the surface.² Due to their large surface-to-volume ratio, the adsorption of O_2 significantly decreases the conductivity of the nanowires. In Fig. 2(b), electron-hole pairs are generated [$h\nu \rightarrow e^- + h^+$] upon UV illumination. The photocarriers immediately affect the conduc-

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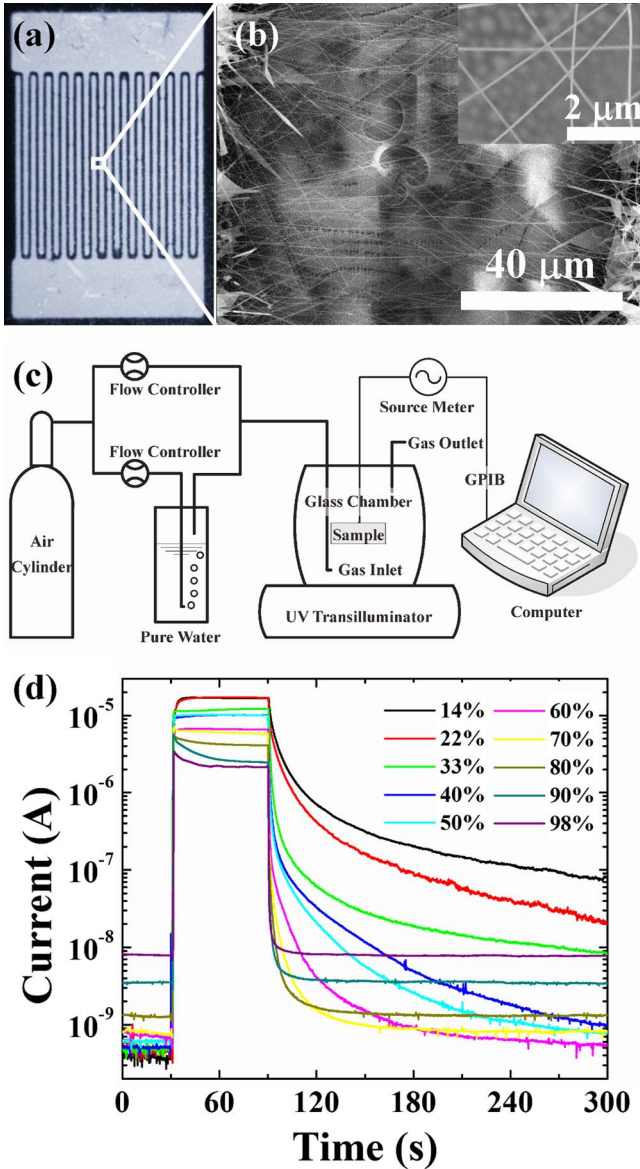


FIG. 1. (Color online) (a) Optical microscope and (b) scanning electron microscope images of the ZnO nanowire UV detector. The inset in (b) shows the nanowires across the gap. (c) Schematic of the experimental setup used to record photoresponses under different RHs. (d) Time-dependent photoresponses of the ZnO nanowire UV detector with an applied voltage of 5 V under different RHs. UV light ($\lambda=365$ nm) with an irradiance of 1.4 mW/cm² was switched on at 30 s and off at 90 s. The inset gives the RH values for the curves.

tivity due to the sudden increase in carrier density in the nanowires. Thereafter, holes migrate to the surface along the potential slope created by the band bending and recombine with the O₂-trapped electrons, thus releasing O₂⁻ from the surface [O₂(ad) + h⁺ → O₂(g)]. The remaining unpaired electrons become the major carriers that contribute to the current unless they are trapped again by readsorbed O₂ on the sur-

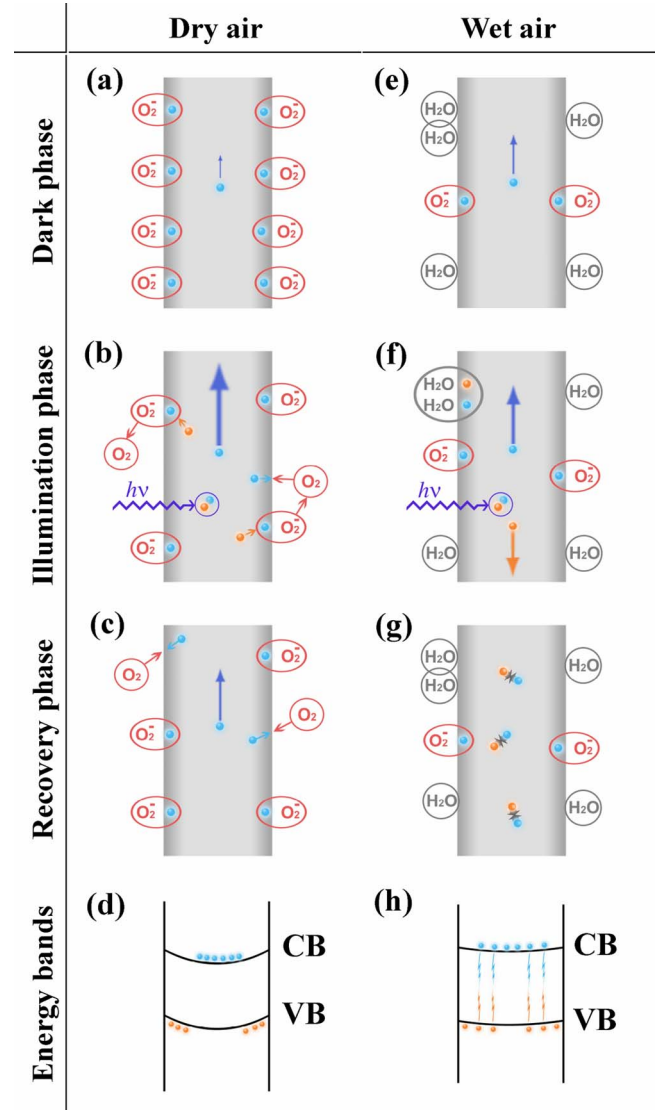


FIG. 2. (Color online) Schematic of the photoresponse process, the valence band and the conduction band of a ZnO nanowire in [(a)–(d)] dry air and [(e)–(h)] wet air. Blue and orange dots represent electrons and holes, respectively.

face. The unpaired electrons accumulate gradually with time until the desorption and readsorption of O₂ reach an equilibrium state, resulting in a gradual current rise until saturation during UV illumination. At the end of the illumination phase, the hole density is much lower than electron density in the nanowire. Although holes recombine quickly with electrons upon turning off UV light, there are still a lot of electrons left in the nanowires. O₂ molecules gradually readsorb on the surface and capture these electrons [Fig. 2(c)], which results in a slow current decay.

In wet air, the photoresponse is greatly affected by the presence of water molecules. In the dark [Fig. 2(e)], water

TABLE I. Decay times of the photocurrent under different humidity conditions.

	RH (%)										
	14	22	33	40	50	60	70	80	90	98	
Decay to 10% (s)	14	10	2.2	1.7	1.4	0.58	0.42	0.16	0.047	0.023	
Decay to 1% (s)	106	57	16	11	8.9	4.5	2.6	1.9	1.6	1.2	

molecules replace the previously adsorbed and ionized oxygen and hence release electrons from the ionized oxygen molecules, a process which partially annihilates the depletion layer,¹⁴ leading to a rise in conductivity. Upon UV illumination [Fig. 2(f)], the electron-hole pairs are generated and contribute to the current immediately. During UV illumination, the dissociated water molecules on the ZnO{10 $\bar{1}$ 0} crystallographic surfaces of the nanowires may take electrons and holes at the same time. Indeed, according to Meyer *et al.*⁸ and Dulub *et al.*,⁹ isolated water molecules are physisorbed on the ZnO{10 $\bar{1}$ 0} surfaces and remain undissociated. However, when a second water molecule adsorbs on a neighboring lattice site, it establishes a hydrogen bond that triggers the dissociation. The dissociated water molecules capture electrons and holes generated by UV light, decreasing the carrier density and creating a depletion layer, resulting in a gradual current decay during UV illumination. Since the water molecules either take both electrons and holes or do not interact with carriers, the number of unpaired electrons is decreased in this case. Thus, the number of holes is comparable to the number of electrons at the end of the illumination phase and, therefore, the electrons and holes recombine quickly upon switching off UV light [Fig. 2(g)], leading to a fast current decay.

The upward band bending near the surface created by the adsorption of O₂⁻ also affects the photoresponse of ZnO nanowires. As shown in Fig. 2(d), with more O₂⁻ adsorbed on the nanowire surface in dry air, the energy bands are more bended. The photogenerated electrons and holes are therefore segregated in different zones, so that the probability for them to recombine is lower. On the contrary, in wet air, the energy bands are less bended having less O₂⁻ adsorbed [Fig. 2(h)]. Electrons and holes recombine more easily with less bended bands, thus leading to a shorter carrier lifetime. The decrease in carrier lifetime with the increase in RH has two consequences on the photoresponse. First, the photocurrent level decreases with the increase in RH. Second, the current decay after switching off UV is faster with higher RH.

Based on the model given above, the observed photoresponse results can be explained. The increase in dark current level with increasing RH is attributed to the substitution of O₂⁻ by H₂O and the release of the electrons captured by O₂. The fast current rise process upon UV illumination originates in the electron-hole pairs generation upon UV exposure, which increases the carrier density in the nanowires. The lifetime of the photogenerated carriers shortens at high RHs because the energy bands are less bended. Thus, the photocurrent level decreases at high RHs. The slow current rise or decay process during illumination is due to the surface effects of both oxygen and water. On the one hand, desorption of O₂⁻ by the photogenerated holes increases the conductivity. On the other hand, the dissociated water molecules capturing the photogenerated electrons and holes decrease the conduc-

tivity. The result of the competition between these two processes determines the sign of the variation in the photocurrent. For low RH (<60%) cases, the effect of O₂⁻ desorption is more pronounced, so that the currents increase during UV illumination. For high RH (>60%) cases, the effect of the dissociated H₂O capturing electrons and holes becomes more significant, so that the currents decrease during UV illumination. The fast decay after turning off the UV light is due to the rapid recombination of holes with electrons. The slow decay is ascribed to the readsorption of O₂ on the surface, taking electrons from the nanowires and forming O₂⁻. The slow decay process dominates the current recovery under low RH, while the fast decay process dominates the current recovery under high RH. Thus, the current recovers faster under higher RH. The extremely fast current decay observed for RH > 70% is explained by a nearly equal number of holes and electrons and their quick recombination upon turning off the UV light. Previous works attribute the accelerated current decay in wet air to that water can effectively capture both electrons and holes while oxygen can only trap electrons.¹⁻³ However, we believe that this should not be the main reason for the accelerated current decay, because improving carrier-trapping efficiency by a factor of 2 could not lead to a decrease in the decay time by two to three orders as reported in Table I.

In conclusion, photoresponse measurements of ZnO nanowires under different RHs were conducted to study the surface effects of oxygen and water. In addition, we proposed a model that explained the observed results of the photoresponse experiments. The proposed model can help to better understand gas desorption and adsorption processes on the surface of metal oxide semiconductors, which play a central role in photodetection and gas sensing.

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