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Citation: [Applied Physics Letters](#) **92**, 213116 (2008); doi: 10.1063/1.2938047

View online: <http://dx.doi.org/10.1063/1.2938047>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/apl/92/21?ver=pdfcov>

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Effectively enhanced oxygen sensitivity of individual ZnO tetrapod sensor by water preadsorption

K. H. Zheng,¹ Y. C. Zhao,¹ K. Deng,¹ Z. Liu,¹ L. F. Sun,^{1,a)} Z. X. Zhang,² L. Song,²
H. F. Yang,² C. Z. Gu,² and S. S. Xie²

¹National Center for Nanoscience and Technology, Beijing 100190, People's Republic of China and
Graduate School of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

²Beijing National Laboratory of Condensed Matter Physics, Institute of Physics, Chinese Academy of Science, Beijing 100190, People's Republic of China

(Received 30 March 2008; accepted 10 May 2008; published online 30 May 2008)

In this letter, individual ZnO tetrapod was designed as a multiterminal sensor. The gas-sensing properties of water and oxygen of the device have been investigated. We found that if water was preadsorbed on the device, the sensitivity of oxygen can be effectively enhanced; meanwhile, the response time can also be remarkably shortened. The mechanism of these phenomena, we propose, is the adsorption competition of the two kinds of molecules. Our results show that the preadsorption of appropriate gas can enhance the performance of the sensors, which is helpful for sensor designing. © 2008 American Institute of Physics. [DOI: 10.1063/1.2938047]

For the past several years, great interest has been paid to the development of gas sensor devices, which have a great impact in many areas, such as environmental monitoring, domestic safety, public security, etc.^{1,2} As the surface state and morphology of the material have great influence on their gas sensing properties, nanostructured materials present opportunities for enhancing the performance of gas sensors because of the much higher surface-to-volume ratio.³⁻⁵ ZnO is one of the most widely used gas-sensing materials owing to its high chemical stability, nontoxicity, and low cost.⁵⁻⁷ ZnO nanowires and nanorods have been investigated as sensors for various gases, such as C₂H₅OH, C₂H₂, CO, and other species.⁶⁻⁸ Compared to the sensors based on ZnO nanowires and nanorods, sensors with ZnO tetrapods will have the advantages of multiterminals, which can provide multisignals at the same time. As a typical nanostructure of ZnO,⁹ the physical properties of ZnO tetrapods, such as optical,¹⁰⁻¹² electrical,¹³ and gas-sensing properties,^{14,15} have already been investigated. However, due to the technological difficulties in making electrical contacts to the tetrapods, their gas-sensing properties were investigated based on a large amount of tetrapods.¹⁴⁻¹⁶ Very recently, we have synthesized ZnO tetrapods via vapor transportation deposition method,¹¹ and designed individual ZnO tetrapod as a multiterminal optoelectronic device, which has advantages of distinguishing false responses and increase sensitivity.¹⁷ In this letter, the fabricated tetrapod device has been investigated as oxygen and water gas sensor. We report that when the individual ZnO tetrapod was preadsorbed with water, the sensitivity of oxygen can be effectively enhanced, and the response time can also be shortened. We ascribe this phenomenon to the adsorption competition between water molecules and oxygen molecules. Our results provide a useful approach to design devices with higher performance.

In our experiment, the nanostructured ZnO tetrapods were synthesized via vapor transportation deposition process.¹¹ To fabricate the ZnO tetrapod devices, the as-prepared products were ultrasonically dispersed in ethanol

and transferred to the Si/SiO₂ substrate. ZnO tetrapods were spontaneously oriented with one arm directed upwards while other three arms contacting with the substrate. Three Ni/Au (10/120 nm) electrodes were made to contact each arm by electron beam lithography patterning, metal evaporating, and lift-off process. The device was loaded into a steel chamber (~0.8 L), which can be evacuated to 10⁻⁴ Pa. Moreover, the electrical response was measured with Keithley-4200 at room temperature. Voltage was swept across every two pairs of arms, respectively. The *I-V* characteristic shows a linear behavior [Fig. 1(a)], indicating the contact between the electrodes and ZnO tetrapod arms are Ohmic. A typical scanning electron microscopy (SEM) image of the fabricated device is shown in the inset of Fig. 1(a). Figure 1(b) shows a schematic structure of the tetrapod device. When measuring, electrode "C" is grounded while electrode "A" and "B" are

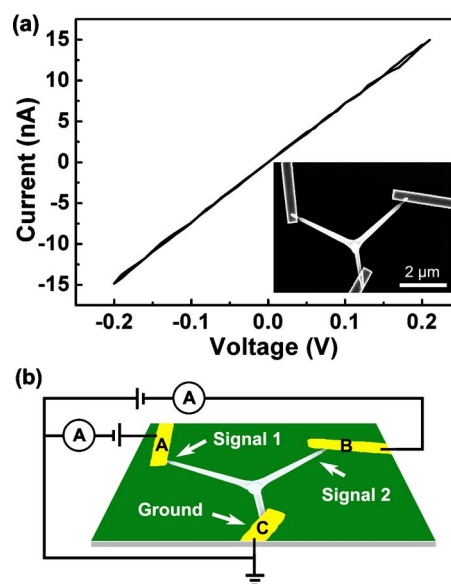


FIG. 1. (Color online) (a) Typical *I-V* characteristics between each two arms of ZnO tetrapod at room temperature. The inset shows the SEM image of an as-fabricated tetrapod device. (b) Schematic illustration of the experimental measurements.

^{a)} Author to whom correspondence should be addressed. Electronic mail: slf@nanocr.cn.

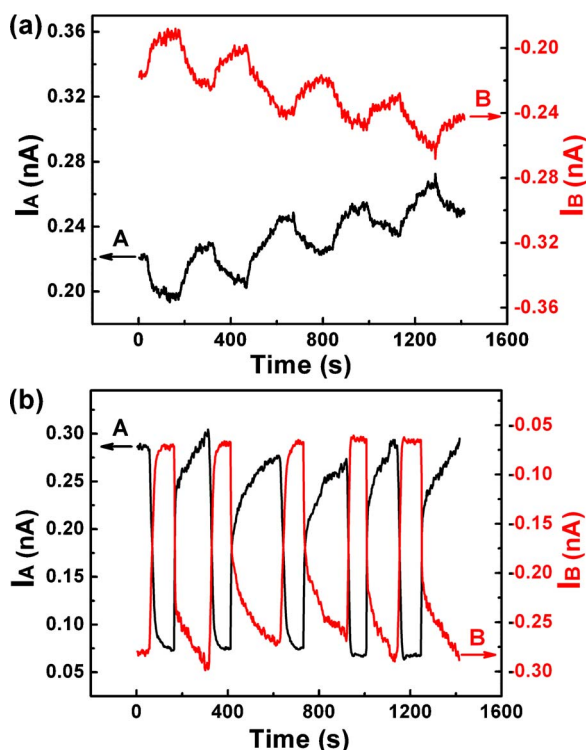


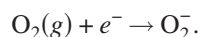
FIG. 2. (Color online) (a) Response and recovery characteristics of the ZnO tetrapod device exposed to oxygen (1 atm) and (b) water (10 μL) at room temperature. Curve A corresponds to the current between electrode A and C, and curve B to that between electrode B and C.

voltage biased, and the corresponding currents are recorded versus time.

Figure 2(a) shows the oxygen gas-sensing properties of the tetrapod device. The voltages of electrodes A and B are biased at 20 and -20 mV, respectively. Thus, two current signals can be measured at the same time: current A (positive) and current B (negative). When oxygen (1 atm, purity of 99.995%) was introduced into the chamber, the current A gradually decreased, while the current B increased correspondingly. After a period of 200 s, the chamber is evacuated and the current restored to its original value. As shown in Fig. 2(a), these processes can be well repeated. We can estimate the sensitivity of the device based on the formula,

$$S = \frac{G_V - G_{O_2}}{G_V} \times 100\%,$$

where S is the sensitivity, G_V is the conductance in vacuum (10^{-4} Pa), and G_{O_2} is the conductance in O_2 . The O_2 sensitivity of the device is about 10% and the response time is about 100 s. When the oxygen molecules are adsorbed on the oxygen vacancies of the zinc oxide surface, it captures the free electrons of the zinc oxide and the process can be described by



This creates a depletion layer near the surface and lowers the conductivity.^{18,19}

Figure 2(b) shows the water vapor sensing properties of the tetrapod device. Upon the chamber is evacuated to 10^{-4} Pa, 10 μL de-ionized water (Millipore, 18 $M\Omega\text{ cm}^{-1}$) is injected into the chamber and the currents are recorded versus time. In Fig. 2(b), we can find that the current decreases

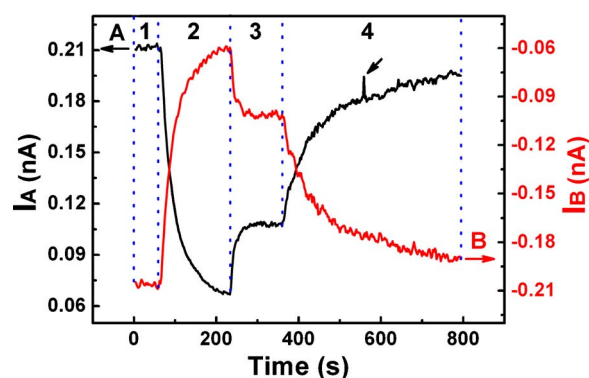


FIG. 3. (Color online) Typical response characteristics of the ZnO tetrapod sensor to oxygen (1 atm) with water (10 μL) preadsorption. Curve A corresponds to the current between electrode A and C, and curve B to that between electrode B and C. Region 1 corresponds to the current measured in high vacuum, region 2 the process of water preadsorption, region 3 exposed to oxygen, and region 4 the process of evacuation. The peak indicated by the arrow in curve A is judged to be a false signal.

(curve A) rapidly at first then slowly and reaches steady finally. At this moment, the chamber is evacuated again and the current rises quickly at first followed with a slower rising then becomes steady. The sensitivity of H_2O is about 73% which is much higher than that of O_2 . The different performance of the sensor toward water vapor or oxygen is due to the fact that water is a more effective oxidant than oxygen because the former molecule contains only single bonds while the latter contains double bonds.^{20,21}

Occasionally, we found that if water was preadsorbed on the device, unexpected result was found, as shown in Fig. 3. In this figure, region 1 corresponds to the current of the device in high vacuum and remains steady at 20 mV. In region 2, 10 μL water is added into the chamber and the current show similar behavior as reported above. At this point, high pure oxygen gas of 1 atm. is introduced into the chamber. Instead of decreasing, the current (curve A) increases rapidly at first and then becomes steady (region 3). In region 4, the chamber is pumped again to high vacuum and the current (curve A) restores to its original value. In this situation, the sensitivity of oxygen can be estimated based on a similar equation,

$$S = \frac{G_W - G_{O_2}}{G_W} \times 100\%,$$

where G_W is the conductance measured in water vapor. The calculated oxygen sensitivity is about 60% at room temperature (1 atm oxygen). The response time is about 30 s. Comparing with the oxygen sensing properties without water preadsorption, the oxygen sensitivity with water preadsorption has been remarkably enhanced, which is found to be six times higher (from 10% to 60%), while the response time has also been shortened from ~ 100 to ~ 30 s. Most importantly, the dynamic sensing characteristics of oxygen are quite different as displayed in region 3 of Fig. 3. When the oxygen was introduced in the chamber, the current increases rapidly and over half of the current change takes place in the first 2 s.

Furthermore, we have investigated the sensitivity at different oxygen concentration. Figure 4 shows a direct comparison of the sensitivity of the tetrapod device with and without water preadsorption. Therefore, we can conclude

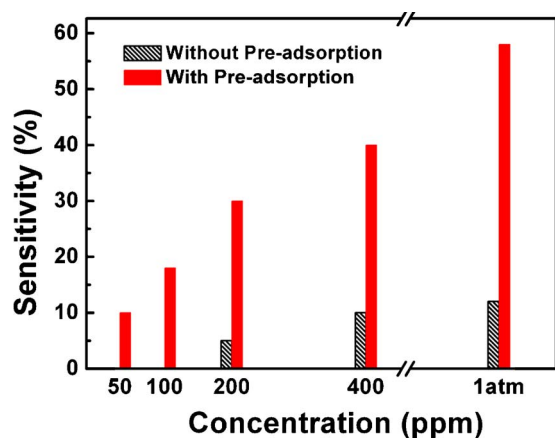


FIG. 4. (Color online) Comparison between the oxygen concentration and the sensitivity of the ZnO tetrapod sensor with and without water preadsorption. Oxygen gas of 50, 100, 200, and 400 ppm is added into the chamber with nitrogen as buffering gas.

that the corresponding sensitivity have been enhanced with the water preadsorption. It is notable that the device did not show detectable response when exposed to 100 ppm oxygen, while for the device with water preadsorption, even 50 ppm oxygen resulted in an obvious response with sensitivity of 10%.

As we have discussed above, the adsorption of both oxygen and water molecules captures the free electrons in zinc oxide, and thus the conductivity is decreased. However, if the device was preadsorbed with water, the addition of oxygen increased the conductivity, which was quite unexpected. When H₂O molecules are present, after certain duration, a dynamic equilibrium will be established, which means the adsorption rate equals to the desorption rate. And then oxygen gas is added into the chamber, the adsorption on the surface of zinc oxide tetrapod could involve in two different processes. First, the oxygen molecules can be adsorbed on the vacant sites in which process the conductivity will be decreased. Second, the oxygen molecules will compete for the adsorption sites with preadsorbed H₂O molecules. The physical mechanisms of the increased conductivity are attributed to the following: when the oxygen is induced into the system and adsorbed on the vacant sites, the total vacant sites for water molecules will be less, which results in less water molecules adsorbed comparing to that without introducing oxygen. Meanwhile, after oxygen has been adsorbed on the surface of ZnO tetrapod, the amount of oxygen vacancies is changed and affects adsorption behavior of water molecules.²² At the re-established equilibrium state, the quantity of absorbed water molecules will be less than that of without introduction of oxygen. The desorption of water molecules will increase the conductivity, while the adsorption of oxygen molecules will decrease it. As mentioned above, water molecules adsorption has a much larger effect on the conductivity of ZnO tetrapod than that of oxygen, and

thus the total conductivity is dominated by the desorption of water molecules. This results in the unexpected increase of current as shown in Fig. 3 (curve A).

An interesting feature can be found in Fig. 3. In curve A, there is an obvious peak as indicated by the arrow, while no corresponding one in curve B at the same time. For these multiterminal devices, the real signals should have responses in both curves at the same time. Therefore, this arrowed peak should be judged as “false response.” This is one advantage of this kind of multiterminal device.¹⁷

In summary, individual ZnO tetrapod was used to design multiterminal sensor. The gas-sensing property of water and oxygen on the multiterminal device has investigated. We show that the oxygen sensitivity can be effectively enhanced and the response time can be remarkably shortened by water preadsorption, which may be useful for designing other kinds of sensors.

This work is supported by the “100 Talents Program,” Knowledge Innovation Program of Chinese Academy of Sciences, “973” Program of Ministry of Science and Technology and National Science Foundation of China.

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