NANO LETTERS

2008
Vol. 8, No. 2
652−655

ZnO Tetrapods Designed as Multiterminal Sensors to Distinguish False Responses and Increase Sensitivity

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Received November 26, 2007; Revised Manuscript Received January 2, 2008

ABSTRACT

Individual zinc oxide tetrapods were designed as multiterminal sensors by the e-beam lithography method. Different from double-terminal sensors, these sensors can give multiple responses to a single signal at the same time. The designed tetrapod devices were employed to detect light with different wavelength. The results indicate that they are remarkable optoelectronic devices, sensitive to ultraviolet light, and have advantages on distinguishing noises and increasing sensitivity. This should be helpful for weak signal measurements of nanodevices.

In recent decades, sensors based on nanostructures have attracted great attention.[1−4] Compared to traditional sensors, these nanosensors exhibit obvious advantages. Generally, they are of comparable size to the detected biological or chemical targets. The detected targets can apply remarkable changes to the state of nanostructures,[5] and nanostructures are of high specific surface area. As we all know, the surface plays an important role in sensors. Therefore, the nanosensors often have excellent sensitivities. Moreover, they also show advantages on miniaturization, low cost, and low energy consumption. Especially, nanosensors based on electrical properties are direct and label-free and much more attractive.[5] Up to now, many groups have focused on these electrical nanosensors.[6−11] However, to some little targets, the response signals are often very weak. In this situation, unavoidable noises (false responses) become remarkable and cannot be distinguished from real responses easily. This hinders the development of highly sensitive and accurate nanosensors. In this letter, we report our recent work on designing individual nanostructured zinc oxide (ZnO) tetrapods as multiterminal sensors and employing them to detect light with different wavelength. The results exhibit these multiterminal sensors are beneficial for distinguishing false responses and increasing sensitivity.

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In our experiment, nanostructured ZnO tetrapods were synthesized without catalyst through thermal evaporation of zinc powder in a horizontal quartz tube with a simple chemical vapor deposition (CVD) method.[12] The four arms of a tetrapod are often joined through twin planes or a core in their geometrical center.[12−16] To fabricate individual multiterminal devices, ZnO tetrapods were ultrasonically dispersed into alcohol and then they were transferred onto a silicon wafer covered with a 500 nm thick thermal oxide film. ZnO tetrapods often stay on the wafer individually with three arms contacting with the oxide film and the fourth arm pointing upward. E-beam lithography (EBL, Raith-150) was used to pattern 200-nm-thick-Au/10-nm-thick Ni electrodes on the three arms contacting with the thermal oxide film. Figure 1a shows a typical field-emission scanning electron microscopy (FESEM) image of a fabricated device. Their electrical properties were measured with a Keithley-4200 at room temperature.

Figure 1b shows a schematic plan of the designed tetrapod devices. It can be seen that the tetrapod devices are obviously different from those devices based on a single nanowire/nanotube. They have three terminals connected to electrodes, respectively. The electrical properties between every two terminals (A−B, B−C, and C−A, as schematically shown in Figure 1b) were first characterized. The results demonstrate that the $I-V$ curves are similar and almost linear, indicating that there are good contacts between the electrodes and the arms of ZnO tetrapods (as shown in the inset in Figure 1a).

10.1021/nl073088o CCC: $40.75
Published on Web 01/25/2008

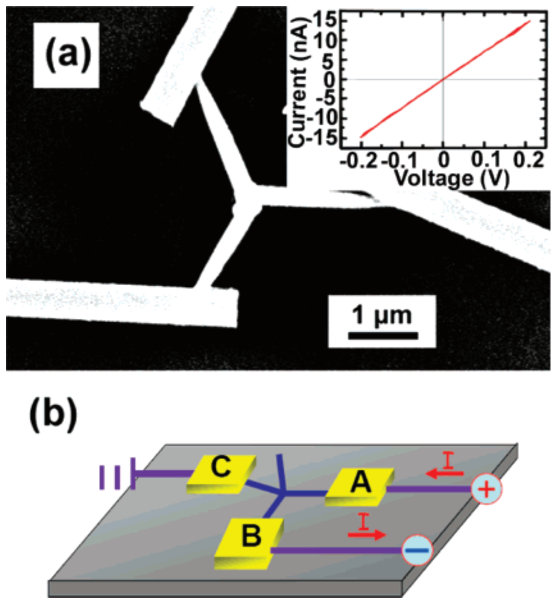

Figure 1. (a) FESEM image of a fabricated tetrapod device. The inset is a typical $I-V$ curve between two arms. (b) Schematic plan of the designed tetrapod devices.

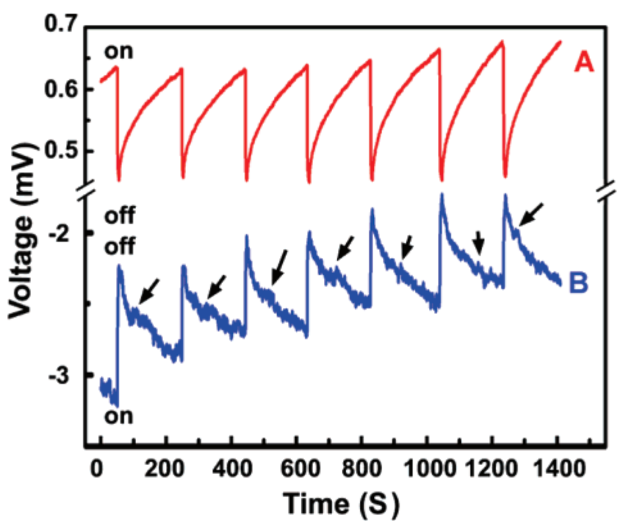

Figure 2. Typical time-dependent curves when the UV light (325 nm) is turned on or off. Applied current: ±10 nA. Curve A corresponds to the voltage between terminal A and C, and curve B to that between terminal B and C. While UV light is on or off, the two curves close rapidly or separate gradually. The arrowed intensities in curve B do not appear in curve A at the same time. They should be noises.

The tetrapod devices were further used to detect ultraviolet (UV) light with a wavelength of 325 nm. The light source is a He−Cd laser, and the light power is about 400 mW/cm^2. Before the UV light was turned on, the C electrode was grounded first and A and B electrodes were applied with two opposite constant currents of 10 nA, respectively (as schematically shown in Figure 1b). This means that the current between A and C is 10 nA, while the current between B and C is −10 nA. Figure 2 shows a typical result, exhibiting two accompanied time-dependent response curves to UV light corresponding to A and B terminals, respectively. The measurement was repeated for seven cycles. It can be seen from the image that the tetrapod device gives strong and rapid responses to the UV light and has a recovery time of about 200 s. The voltages decrease immediately while the UV light is turned on and increase gradually while the UV light is turned off. This repeats well. It is shown in the image that the two curves close while the UV light is on and separate from each other while the UV light is off. The phenomenon originates from the change of the charge carrier density and the design of the devices. When the UV light is turned on, the charge carrier density is enriched due to photogenerated electron−hole pairs. This results in the increasing of their conductivity. Thus, at the same current, the absolute value of the voltage will decrease. In the designed multiterminal tetrapod devices, two opposite currents are applied. That is to say, one is positive and the other is negative. Therefore, when the UV light is turned on, the positive voltage will decrease while the negative voltage will increase. When the UV light is turned off, the results are obviously reverse due to the recombination of electrons and holes.

The tetrapod devices were also employed to detect light with different wavelength generated by a 250 W Xe lamp source. As shown in Figure 3, the results show that the devices are sensitive to the light of 300 nm (power: ∼100 nW/cm^2) and 370 nm (power: ∼210 nW/cm^2) but not nearly to that of 410 nm (power: ∼280 nW/cm^2). As we all know, it is difficult to generate electron−hole pairs if the photon energy is smaller than the band gap energy. The band gap energy of the employed ZnO tetrapods is about 3.28 eV. (It corresponds to the light with a wavelength of 378 nm. See Supporting Information.) This energy is smaller than that of the light of 300 nm (∼4.14 eV) and 370 nm (∼3.36 eV) but bigger than that of 410 nm (∼3.03 eV). This results in the ZnO tetrapod devices being sensitive to the former two but not nearly to that of 410 nm.

Also, it can be seen from Figures 2 and 3 that the photoresponse times are quite different and the recovery times are very long (over 200 s). The photoresponse time to UV light from the He−Cd laser is much faster than that from the Xe lamp. Early studies[17−19] indicated that there are two processes in ZnO photoresponse: photogeneration−recombination of electron−hole pairs and adsorption−photodesorption of oxygen on the surface of materials. The absorbed oxygen will trap free electrons from ZnO and decrease its conductance,

$$O_2(g) + e^- \rightarrow O_2^-(ad)$$

While exposed to light, the absorbed oxygen will be photodesorbed by capturing photgenerated holes and increase its conductance,

$$h^+ + O_2^-(ad) \rightarrow O_2(g)$$

The former is quite fast, while the later is rather slow. Because of the high power of the light from the He−Cd laser (∼400 mW/cm^2), its photoresponse should be dominated by

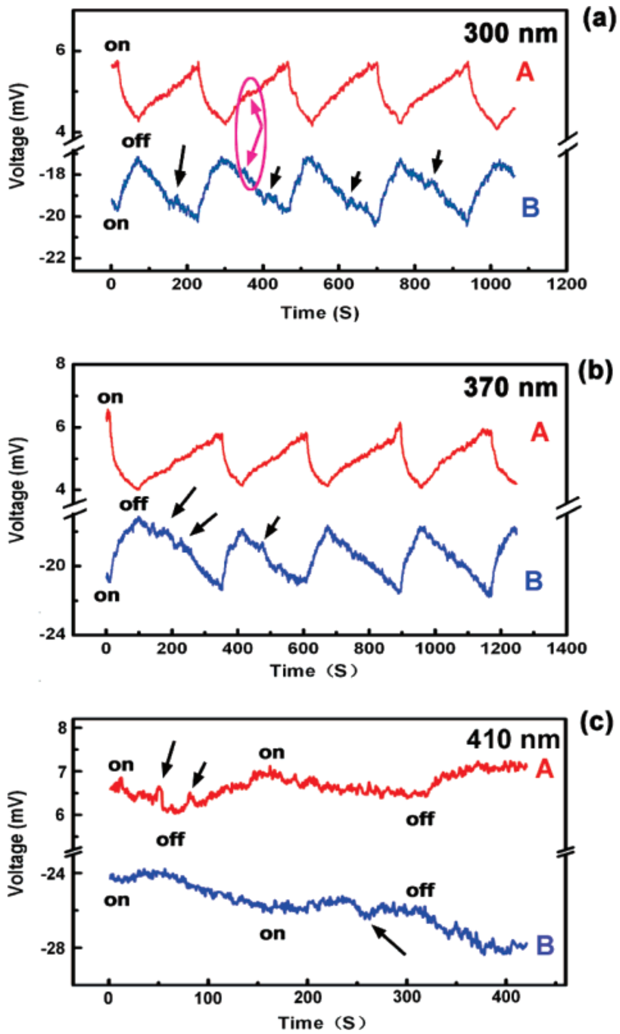

Figure 3. Typical time-dependent curves when the light is turned on or off. Applied current: ±10 nA. (a−c) correspond to 300, 370, and 410 nm respectively. Curve A corresponds to the voltage between terminal A and C, and curve B to that between terminal B and C. The arrowed intensities should be noises.

the former mechanism. Therefore, the process is rather rapid. Nanostructured materials often have a high specific surface area, and as seen in the Supporting Information, the employed ZnO tetrapods have a lot of oxygen defects. These will result in the enhancement of oxygen absorbed on the surface of the tetrapod devices. Because the power of the light from the Xe lamp is very low (only several hundred nW/cm^2), their photoresponse should be dominated by the oxygen absorption−photodesorption mechanism. This results in the process being very slow. The reabsorption of oxygen on the surface happens in all recovery processes. Thus, we can see that the recovery times are rather long.

The responsivities of the tetrapod devices were calculated in a similar way to that of Liu et al.[17]. For example, to the light of 300 nm, the change of the voltage of the "A" arm is about 1.5 mV at the applied current of 10 nA and its power is about 100 nW/cm^2. Then we can get the responsivity of the "A" arm to the light of 300 nm of about 15 kV·cm^2/W at 10 nA. We also calculated the responsivities of other results and list them in Table 1.

Table 1. Responsivities and Sensitivities of the Tetrapod Devices[a]

wavelength (nm)	325 (laser)	300 (Xe lamp)	370 (Xe lamp)	410 (Xe lamp)
responsivity of A arm (kV·cm^2/W)		~15	~8	~2
responsivity of B arm (kV·cm^2/W)		~31	~17	~4
whole responsivity (kV·cm^2/W)		~46	~25	~6
sensitivity of A arm (%)	>28	~27	~29	~10
sensitivity of B arm (%)	>22	~15	~17	~4
whole sensitivity (%)	>50	~42	~46	~14

[a] The responsivities are valued at 10 nA. For the light from laser, we did not give their responsivities due to fact that the photocurrents are far away from saturation.

Obviously, these kinds of multiterminal devices is different from traditional double-terminal devices based on a single nanowire/nanotube. They can simultaneously give two responses to a single outside signal at the same time. Compared to those double-terminal devices, they have obvious advantages.

This kind of multiterminal devices can distinguish noises. In electrical measurement process, especially to weak signals, noises are difficult to avoid. These noises may be from the measurement system or devices themselves. The characteristic of these noises is their randomicity. As mentioned above, the multiterminal devices can simultaneously give two responses at the same time. A real response must appear in both response curves at the same time. If some response appears in one response curve but not in another response curve at the same time (that is to say, the response does not appear in both response curves at the same time), this unexpected response can be decided as a false response. As shown in Figures 2 and 3, the arrowed intensities are found in curve B (or A) but not found in curve A (or B) at the same time. They should be judged as noises. Furthermore, even if the intensities appear in both curves at the same time, it is still difficult to decide that they are not false responses. For example, the two arrowed intensities circled in Figure 3a are present nearly at the same time in both response curves, but they are also false responses. In the designed tetrapod devices, real responses must respond to the out signals with opposite directions in two individual curves at the same time due to the opposite currents applied on, whereas, the two intensities circled are both "upward". Therefore, they are false responses too.

Perhaps most of these noises are easy to be ruled out due to the fact that they are weaker than real responses. But for some strong noises, these multiterminal devices will exhibit an obvious advantage. For example, the arrowed intensity in the "B" response curve in Figure 3c is so strong that it is difficult to be ruled out if there is no another reference response curve. The multiterminal devices give two simultaneous responses at the same time. These responses can be referred each other. Through this method, some noises can be ruled out.

The other advantage of this kind of multiterminal devices is that they could enhance sensitivity. The tetrapod devices can give two response curves simultaneously. These two curves respond to the out signals at the same time. Thus the tetrapod devices can be regarded as two individual similar sensors being assembled together. At this point, the sensitivity of the tetrapod devices should be the superposition of the two responses. The sensitivity can be defined as $S = (R_0 - R)/R_0$ (S is the sensitivity, R the response resistance, R_0 is the original resistance.). For the designed tetrapod devices, if the sensitivity of the "A" arm is S_A and that of the "B" arm is S_B, the sensitivity of the whole device should be $S = S_A + S_B$. The calculated sensitivities of the tetrapod devices to light are shown in Table 1. Here we note that it is not a general method to add the sensitivities of the two arms to get a higher sensitivity. If the two parts are extremely different on sensitivity, it is difficult for them to work well and cannot be used in practice. Indeed, for well-working multiterminal tetrapods devices, the different parts should be similar in sensitivity (Table 1).

The two simultaneous responses can be referred to each other. This can help to rule out not only whether the responses are noises or not (as mentioned above) but also whether they are real responses or not. This is especially helpful to weak responses. The responses to the light of 410 nm (see Figure 3c) are rather weak. If there is no another simultaneous reference curve, it is difficult to rule out that the devices are sensitive to the light, but in fact, the two simultaneous responses are changed correspondingly. They close or separate synchronally. Then we can decide that the devices have a weak response to the light. The reason should be due to the photogenerated electron−hole pairs resulting from multiple phonon absorption or that the used light is not single. At this point, it also can be said that the multiterminal devices can really enhance sensitivity.

In summary, individual ZnO tetrapods were used to design multiterminal sensors. Compared to double-terminal devices, these multiterminal devices can simultaneously give two responses at the same time. They were further employed to detect light with different wavelengths. The results show that they are sensitive to UV light and have advantages in distinguishing noises and enhancing sensitivity.

Acknowledgment. The work was supported by the National Science Foundation of China (no. 10334060) and the "973" National Key Basic Research Program of China (no. 2005CB623602). We acknowledge Prof. Gang Wang, Dr. Huajun Yuan, Dr. Yan Gao, Qiang Luo, Aizi Jin, and Dr. Haifang Yang for their discussions.

Supporting Information Available: Details of the photoluminescence spectrum of the employed ZnO tetrapods. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL073088O