

Selective Multiterminal Sensor on Individual ZnO Nanotetrapod

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ABSTRACT

This article presents a sensitive and selective sensor based on an individual zinc oxide nanotetrapod and on crossed ZnO nanorod for detection of UV light and hydrogen at low temperature. It is demonstrated that ZnO tetrapod has potential application as UV and as chemical sensor with multi-terminal construction. The chemisorbed gas molecules on a surface can extract or donate electrons to nano-material and this effect was used for monitoring the electrical resistance values change of the tetrapod sensor. We demonstrate that the ZnO tetrapod sensor demonstrate sensitivity and selectivity in resistance upon exposure to UV light, H₂, O₂, NH₃ and LPG gas. The resistivity change is different for UV and for H₂ gas sensing.

Keywords: ZnO nano-tetrapod, sensor, photosensor

1 INTRODUCTION

Recently, sensors based on semiconducting oxides nanostructures such as zinc oxide nanowires, nanotubes and nanorods have attracted vast and persistent attention for detecting ultraviolet (UV) radiation, gas and biological molecules [1-6]. Low-cost, nonpoisonous and highly sensitive and selective sensors are needed for detection of various gases in the environment. Among different materials, zinc oxide is in the focus of the practical applications as sensor material due to its sensitivity to different gases and ability to operate in harsh environments and in radiation facilities [7]. Its nanorods and nanowires exhibit many unique properties associated with their shape anisotropy. Several reports have demonstrated single ZnO nanorod/nanowire devices. Due to of the high aspect ratio of sensing material, the detection sensitivity may be increased to a single photon or a single-molecular detection level by monitoring changes of electrical characteristics [8]. Recently, it has been demonstrated that ZnO readily self-assembles into a diversity of nanocrystalline structures like nanorod-based spheres and radial spherical structures, branched nanorods, nanorod crosses, tetrapods [2-6,9] etc.

Thus, unique structure of ZnO branched rods [3] and ZnO tetrapods [10] with a natural junction attracted interest as possible building blocks of novel devices. At the same time, sensors based on ZnO crosses and tetrapods are multiterminal devices. In this way, ZnO tetrapod sensors can provide several different signals at the same time. The first report of electrical contacting of single tetrapod was fabricated by Alivasatos and coworkers in 2005 [11]. Newton et al. [10] has reported the first ZnO tetrapod Schottky photodiodes [10] in 2006. Also, Zhang et al. [12] showed individual ZnO tetrapod as a multi-terminal sensor which can yield simultaneous multiple responses to a single input signal. Chai et al. [5], on the other hand, fabricated first cross ZnO nanorod UV sensor in 2008. The main advantages of these types of nano-structures are: (a) their multi-terminal nature and (b) the junctions between different terminals, and (c) different from devices based on single nanowires, thus new functionality can be envisioned. For example in a recent report, Huh et al. strongly suggests that the junction plays a decisive role in the electrical characteristics of the ZnO tetrapods-devices [13].

So far, the ZnO tetrapods sensor reported were synthesized by chemical vapour transport technique. However it is well known that sensitivity of ZnO samples depends on its fabrication process. Here we applied the in-situ lift-out manipulation technique to the zinc oxide tetrapods prepared by hydrothermal technique and report the fabrication of a sensor structure that uses characteristics of a single cross or tetrapod. We present in details investigations on synthesis, sensor fabrication and on photo- and gas-response of ZnO tetrapod electronic device.

2 EXPERIMENTAL

2.1 Synthesis

This work was rendered possible by our recent success in synthesizing the ZnO nano-architectures by a simple aqueous solution method [9]. Transferable ZnO tetrapods were grown by an aqueous solution method as previously reported [9]. This technique was found to have advantages of fast, efficient, easy scaling and low cost.

All used reagents were of analytical grade and used without further purification. The glass substrates were cleaned according to procedure described in [9]. Substrates were placed inside of the reactor and filled with complex chemical solution [9]. ZnO nano-tetrapods with different architectures were also prepared with the same procedure. Zinc sulfate and sodium hydroxide solution were added into 75 ml DI-water under stirring to obtain a transparent solution. Then, the glass substrates and complex solution were transferred inside an aqueous solution in a reactor of 100 ml capacity and sealed. The setup was mounted on a hot plate, and the temperature was increased to 98 °C and kept constant for 20 min and then cooled down naturally to room temperature. Afterward, the samples were rinsed in deionized water and dried at 150 °C, 5 min. Variation of the synthesis conditions such as concentration of precursors and temperature allow certain degree of control on the morphology of the obtained nanorods.

2.2 Characterization

The phase composition and phase purity of ZnO tetrapods were identified by XRD analysis. Peak positions and relative intensities of synthesized architected material were compared to values from Joint Committee on Powder Diffraction Standards card for ZnO (JCPDS 036-1451).

The morphology of the products was obtained using a scanning electron microscope (SEM, JEOL) and high resolution transmission electron microscopy (TEM) (FEI Tecnai F30 TEM).

Current-voltage (*I-V*) characteristics were measured using a semiconductor parameter analyzer with an input impedance of $2.00 \times 10^8 \Omega$. The UV sensitivity was measured using a three-terminal ZnO tetrapod device and four terminal cross-nanorods. The UV source used in the photosensitivity responses and current-voltage (*I-V*) characteristics measurements consists of an LED with a peak wavelength of 361 nm. The peak power output of the LED is 0.7 mW at 20 mA. The readings were taken after a UV light was turned on.

3 RESULTS AND DISCUSSIONS.

Both straight and branched ZnO nanorods are grown at temperatures between 85 and 99 °C. Empirically, straight nanorods are grown at temperatures between 95 and 98 °C, while branched nanorods are grown at slightly lower temperatures (85-95 °C). When reaction is carried out at the high end of its temperature range, less tetrapod is observed. Conversely, when experiments are conducted at the lower end of the temperature range, more tetrapods are observed (Fig 1). This suggests that while nanorods growth is kinetically driven, branching may encompass additional thermodynamic considerations. In Figure 1 it is evident that the sample mainly consists of ZnO nanorods and most of them assembly into cross- and tetrapod-like morphologies.

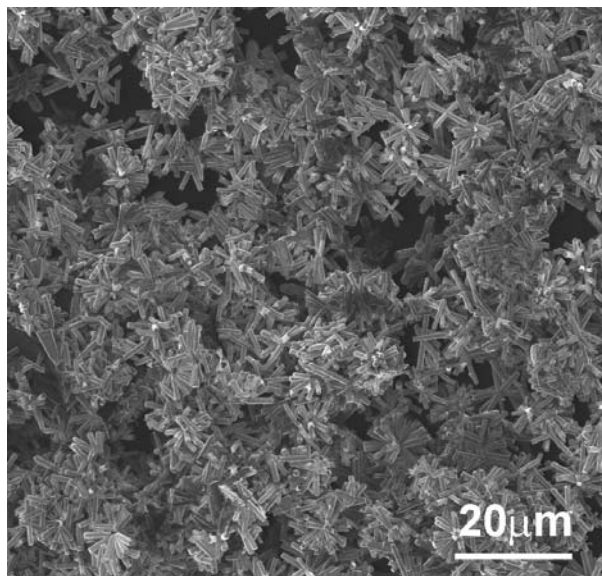


Figure 1: SEM images showing the as-grown zinc oxide nanostructures on glass substrate.

For the sensor fabrication, the Si/SiO₂ wafers were used as intermediate substrate for crosses and tetrapods transferring and individual distribution for further pick-up by in-situ lift-out technique. Crossed ZnO nanorods were transferred from the glass substrate to Si/SiO₂ substrate by direct contact of their faces (Figure 2a). SiO₂/Si substrate was prepared using standard technique [9]. We can see (Fig. 2a) that in the transfer process we reduced the density of nanostructures on the surface of the substrate by attaching of and the new substrate surface is relatively clean. This will facilitate the in-situ FIB/SEM process of the crosses and tetrapods devices fabrication. Closer observation (Fig. 3a) reveals that the products are actually composed of four legs touching the SiO₂/Si substrate. Furthermore, these nanorods have a uniform diameter along their length. The hexagonal cross-sectional radius was about 300 nm and the length of the nanorods was about 4 000 nm (Fig. 3a). An advantage of structure is that it has four legs. Any of the legs may be used latter for surface functionalization strategies, biofunctionalization, etc.

To separate an individual crossed ZnO nanorods or ZnO tetrapod for further processing an in-situ FIB micromanipulator needle is used for the in-situ lift-out technique. Details on in situ lift-out procedure are described in our previous works [2-4]. An in situ Keindiek Micromanipulator was mounted independent of the stage in the FIB/SEM permits navigation of a 1-2 nanometers along *z* direction and about 5-10 nm for the *x* and *y* directions. For the multiterminal device fabrication, the glass substrate was used and Cr/Au electrodes were deposited as template with external electrodes/connections. The needle used for the lift-out step was electro-polished tungsten wire. Figure 2b shows FIB needle with intermediate rod placed next to the crossed ZnO nanorods.

Next, four metal contacts were made to connect external Au electrodes with the four legs of an individual ZnO tetrapod on glass substrate. In the next step, the crossed ZnO nanorods or ZnO tetrapod was mounted and then fixed with one leg to the substrate by using FIB nanolithography with Pt deposition (Fig. 2c). The crossed ZnO nanorods or ZnO tetrapod is cut from an anchor point (end of intermediate point nanorod) and the needle rose away from the substrate. Then, the nanorod was fixed to the pre-deposited electrodes/external contacts. Figure 2c shows the fabricated single crossed ZnO nanorods -based sensor.

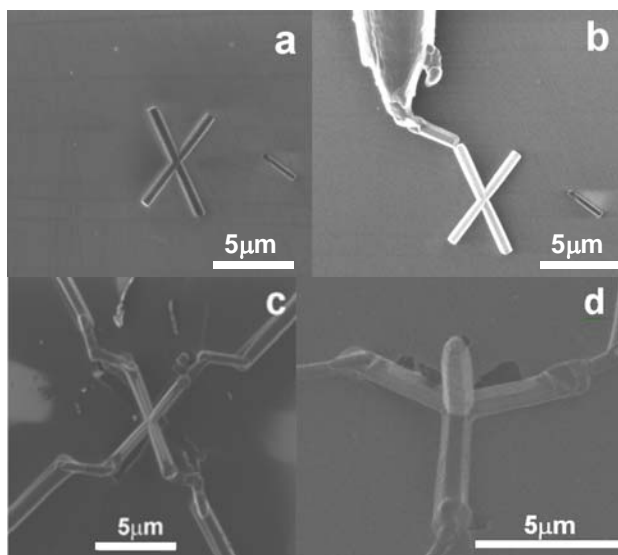


Figure 2: SEM images showing the steps of the in-situ lift-out fabrication in the FIB/SEM system. (a) single crossed ZnO nanorods with uniform size branched on Si/SiO₂ substrate; (b) the tungsten needle with an intermediate nanorod and is next to a single crossed ZnO nanorods selected for sensor fabrication; (c) the crossed ZnO nanorods after welding its four legs to the electrode/external connections as final sensor; (d) the ZnO tetrapod after welding its legs to the electrode/external connections as final sensor.

By this technique, different shaped-nanosensors have been fabricated and investigated for their UV and gas sensitivity. In Figure 4 (d) it is shown the ZnO tetrapod after welding its legs to the electrode/external connections as final sensor. The typical time taken to perform this in-situ lift-out FIB nanofabrication is about 20-25 min and our success rate is >95%. Also taken in the account that nanorod synthesis was done in 15 min, we substantially improve the fabrication process of sensors. Our technique minimizes the time to fabricate nanodevices using FIB and can be extended to other specific nanodevices.

Next, we measured the *I-V* curves of the ZnO tetrapod with connections realized by in-situ lift-out method. Figure 4 outlines the *I-V* characteristics of a four-terminal ZnO tetrapod based sensor in ambient air. The *I-V* measurements were performed through all possible combinations by

changing the bias voltages from +10 mV to -10 mV and vice versa. Since all the connections through legs pairs of the crossed ZnO nanorods or ZnO tetrapod displayed similar characteristics, only results from 1-2 will be presented here to avoid repetition (Fig. 3).

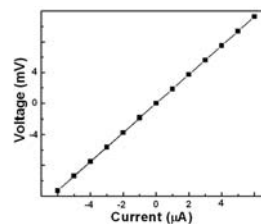


Figure 3: *I-V* characteristics of the zinc oxide – single tetrapod sensor.

It is known that electron-hole pairs will be generated in a semiconductor at a light wavelength of $\lambda=hc/E_g$, where h is Planck's constant, c is the velocity of light and E_g is the bandgap of the semiconductor (for ZnO E_g is ~ 3.37 eV). The UV sensitivity was measured using ZnO nanotetrapod device. The sensor was put in a test chamber to detect ultraviolet light. It was subjected to irradiation with an UV light using a lamp with an incident peak wavelength of 361 nm with conductivity monitoring. The background atmosphere was air. It was found that conductivity change increased linearly with ultraviolet intensity. Due to the fact that the photon energy is higher than the bandgap of ZnO, UV light was absorbed by the ZnO nanorod creating electron-hole pairs, which were further separated by the electric field inside ZnO nanorod contributing to the increase of the conductivity. When the ZnO nanorod photodetector was illuminated by 361 nm UV light, the resistance decreased with a time constant of a few minutes as shown in Fig. 4a. When the UV light was turned off, the resistance increased within 10% of the initial value (Fig. 4).

It is expected that a suspended nanorods-based tetrapod (Fig. 2d) could have more surface area than a comparable nonsuspended structure (cross ZnO nanorods or individual nanorod), so the sensitivity will be improved. Response time constants are on the order of few minutes and after the signal reach the equilibrium value after the UV light was applied. This suggests a reasonable recovery time.

Several sensors on single tetrapod have been fabricated by in-situ lift-out technique and investigated under identical conditions and was observed similar UV response. Spectral response demonstrates that such device is indeed suitable for detecting UV in the range 300 nm – 400 nm. The UV response is slow for ZnO sensor and can be explained by the adsorption and photodesorption of ambient gas molecules such as O₂ or H₂O [2-4]. The optical power on the detectors is 50 nW so the photoresponsivity at 361 nm is 40 A/W. In addition, ZnO has high crystal and optical quality [4], so μ_n will be high. Thus we can shorten the transit time by decreasing recombination of charge carriers.

Thus UV light will hit the nanorod surface and will be generated electron-hole pairs. Electrons must remain free

from holes long enough to zip along the nanorod and generate electric current under applied electric field and this will be the detection of light.

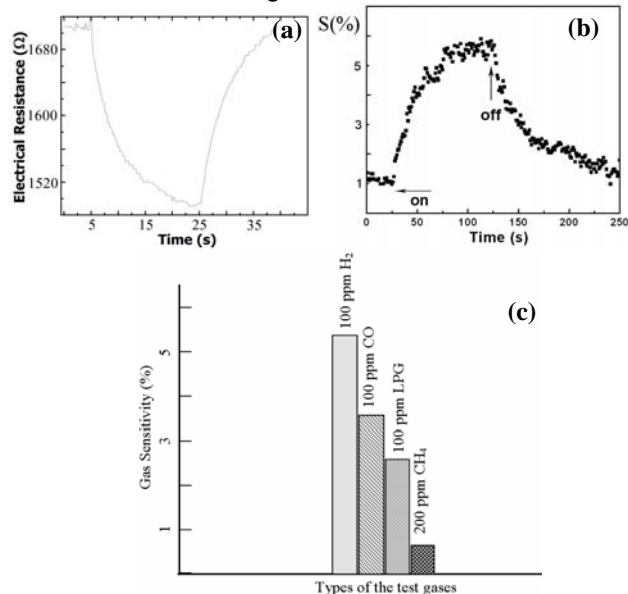


Figure 4: The response of the single ZnO nanotetrapod-based UV sensor fabricated by in-situ lift-out technique in the FIB system. (a) UV sensitivity; (b) H₂ sensitivity and (c) gas sensitivity versus different types of test gases.

Figure 4(b) illustrates the H₂ response of the single ZnO nanotetrapod-based UV sensor fabricated by in-situ lift-out technique in the FIB/SEM system. In our experiments was observed a sensitivity of about 5% to 100 ppm H₂ gas. In Figure 4(c) it is shown the gas sensitivity versus different types of test gases: 100 ppm H₂, 100 ppm CO, 100 ppm LPG and 200 ppm CH₄. It can be observed that developed sensor shows different sensitivity values to investigated gases. It can be concluded that our device can be considered a selective one.

4 CONCLUSIONS

In summary, fabrication of single ZnO –tetrapod UV and gas sensor by in-situ lift-out technique in the FIB/SEM system is demonstrated. Our technique can fabricate sensors on single nanowire/nano-tetrapod or crossed ZnO nanorod in order to study light detection with single photon sensitivity or single molecule detection.

Advantage of the proposed synthesis is its simplicity and fast growth method. An in-situ lift-out technique has been presented to fabricate single ZnO nanotetrapod –based sensor. The typical time taken to perform this in-situ lift-out FIB nanofabrication is 20-25 min. Also taken in the account that nanorod synthesis takes about 15 min, we contribute to overcome some obstacles for nanorods/nanowires sensor production.

Also, it is shown the gas sensitivity versus different types of test gases, like H₂, CO, LPG and CH₄. It was

observed that developed sensor shows different sensitivity values to investigated gases. Thus, can be concluded that fabricated device can be considered a selective one.

This technique has a great potential to be used to fabricate single ZnO tetrapod -based sensor which can help in understanding the uniqueness of branched nanorods for sensor and enable the design of novel devices.

In summary, the prototype device provides a simple method for nanotetrapod synthesis and demonstrated possibility of constructing nanoscale sensors for nano-applications.

Acknowledgments Drs. L.Chow and Lupan acknowledge financial support from US Department of Agriculture #58-3148-8-175, Apollo Technology, Inc and Florida High Tech Corridor Research Program. The research described here was made possible in part by an award 036/RF of ASM.

REFERENCES

- [1] Z. L. Wang, Oxide Nanobelts and Nanowires - Growth, Properties and Applications. *J.Nanosci.Nanotech.* 8, 27, 2008.
- [2] O. Lupan, G. Chai, L. Chow, *Microelectr.Eng.* 85, 2220, 2008.
- [3] O. Lupan, G. Chai, L. Chow, *Microelectronics Journal* 38, 1211, 2007.
- [4] O. Lupan, L. Chow, G. Chai, L. Chernyak, O. Lopatiuk, H. Heinrich, *Phys. Stat. Sol. A* 205, 2673, 2008.
- [5] G. Chai, O. Lupan, L. Chow, H. Heinrich, "Crossed zinc oxide nanorods for ultraviolet radiation detection." *Sensors & Actuators: A. Physical*, DOI information: 10.1016/j.sna.2008.12.020.
- [6] O. Lupan, G. Chai, L. Chow, *Technical Proceedings of the 2008 NSTI Nanotechnology Conference and Trade Show, NanoTech-2008.* 2008, v. 3, pp. 5-8.
- [7] F. D. Auret, S. A. Goodman, M. Hayes, M. J. Legodi, H. A. van Laarhoven, D. C. Look, *Appl. Phys. Lett.* 79, 3074, 2001.
- [8] J. S. Kim, *Journal of the Korean Physical Society*, 49, n4, 1635, 2006.
- [9] O. Lupan, L. Chow, G. Chai, B. Roldan, A. Naitabdi, A. Schulte, H. Heinrich, *Mater. Sci. Eng. B* 145, 57, 2007.
- [10] M. C. Newton, S. Firth, P. A. Warburton, *Appl. Phys. Lett.* 89, 072104, 2006.
- [11] D. J. Milliron, S. M. Hughes, Y. Cui, L. Manna, J. Li, L.-W. Wang, A. Paul Alivisatos, *Nature* 430, 190, 2004.
- [12] Z. Zhang, Li. Sun, Y. Zhao, Z. Liu, D. Liu, L. Cao, B. Zou, W. Zhou, C. Gu, S. Xie, *Nano Lett.* 8, 652, 2008.
- [13] J. Huh, G.-T. Kim, J.S. Lee, S. Kim, *Appl. Phys. Lett.* 93, 042111, 2008.
- [14] Z. Zhang, Li. Sun, Y. Zhao, Z. Liu, D. Liu, L. Cao, B. Zou, W. Zhou, C. Gu, S. Xie, *Nano Lett.* 8, 652, 2008.