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FIB fabrication of ZnO nanotetrapod and cross-sensor

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This article presents the fabrication of zinc oxide (ZnO) nanotetrapod and cross-nanorods-based sensors. This low-dimensional device is made in a focused ion beam set-up by using nanodeposition for metal electrodes. The gas response of the sensor based on an individual zinc oxide nanotetrapod and on crossed ZnO nanorod for detection of ultraviolet (UV) light and hydrogen at room temperature is presented. It is shown that ZnO tetrapod has potential application as UV and as chemical sensor with multi-terminal construction. The chemisorbed gas

molecules on the ZnO surface can extract or donate electrons to ZnO and this effect was used to monitor the electrical resistance values change of the tetrapod sensor. ZnO tetrapod sensor demonstrates sensitivity and selectivity in resistance upon exposure to UV light, H₂, O₂, NH₃, CO, CO₂, and LPG gas. The resistivity change is different for UV and for H₂ gas sensing. The presented ZnO sensor proves to be promising for application in various processes.

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Introduction Recently, wide-bandgap metal oxides architectures have attracted tremendous research interest due to their ultraviolet (UV) photoresponse and their optical transparency in the visible spectral range [1–6]. In particular, zinc oxide (ZnO) 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]. The low dimensions of such nanostructures promise increase in electronic device packing density, low power consumption, and also enhanced sensing properties. 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, 8], etc. ZnO nanostructures with multi-terminals came in the focus of researchers because it exhibits a large surface-to-volume ratio which makes them highly susceptible to altered electrical properties during gas and biologic molecules exposure too.

Thus, unique structure of ZnO branched rods [3] and ZnO tetrapods [6, 9] 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 multi-terminal 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 by Alivisatos and coworkers [10] in 2005. Newton et al. [9] has reported the ZnO tetrapod Schottky photodiodes [10] in 2006. Also, Zhang et al. [11] 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 cross-ZnO nanorod UV sensor. The main advantages of such nanostructures are: (a) multi-terminal nature and (b) the junctions between terminals, and (c) new functionality can be envisioned. As an example in a recent work, Huh et al. [12] suggests that the junction plays a decisive role in the electrical characteristics of the ZnO tetrapod devices.

Sensing with nanotetrapods and crosses is normally realized by monitoring the current–voltage (I – V) or the electrical conductance variation when exposed to UV, gas, or biologic molecules. It is expected to reach a higher sensitivity by using a single tetrapod as sensing element in devices.

The goal of this paper is to demonstrate that the *in situ* lift-out manipulation technique can be applied to the zinc oxide tetrapods prepared by hydrothermal technique and report the fabrication of a sensor device that uses characteristics of a single cross or tetrapod. We present investigations on synthesis, sensor fabrication, and on photo- and gas-response of ZnO tetrapod electronic device.

Experimental Current report was rendered possible based on recent success in synthesizing the ZnO nanoarchitectures by a simple aqueous solution method [8]. Transferable ZnO tetrapods and crosses were grown by an aqueous solution method as previously reported [5, 8]. This technique was found to have advantages of fast, efficient, easy scaling, and low cost.

Reagents used in the synthesis process were of analytical grade and used without further purification. The silicon substrates were cleaned according to procedure described in Refs. [8, 13]. Substrates were placed inside the reactor and filled with complex chemical solution [8]. Zinc sulfate and sodium hydroxide solution were added into 40 ml de-ionized water under stirring to obtain a transparent solution. Then, the substrates and complex solution were transferred inside an aqueous solution in a reactor of 50 ml capacity and sealed. The setup was mounted on a hot plate, and the temperature was increased to 95 °C and kept constant for 20–25 min and then cooled down naturally to room temperature. Afterwards, the samples were rinsed in de-ionized water and dried at 150 °C, 10 min. Variation of the synthesis conditions such as concentration of precursors and temperature allow control on the morphology of the obtained nanostructures.

The crystalline quality of ZnO nanowires were analyzed by X-ray diffraction (XRD). The structural characterization of a single nanowire was performed by high-resolution transmission electron microscopy (HRTEM) with a FEI Tecnai F-30 microscope operating at 300 kV. The morphology of the samples was studied by a scanning electron microscope (SEM, Hitachi, operating at 10 kV) equipped with an EDX spectroscope. The EDX spectroscope was used to explore the ZnO chemical composition (within a precision of 1 at.%).

The focused ion beam (FIB) was employed for the photodetector fabrication. I – V characteristics were measured using a semiconductor parameter analyzer with an input impedance of $2.00 \times 10^8 \Omega$. The UV and gas sensitivity was measured using a three-terminal ZnO tetrapod device and four terminal cross-nanorods. The UV source used in the photosensitivity responses and I – V characteristics measurements consists of an LED with a peak wavelength of 361 nm. Details on gas response characterizations can be found elsewhere [2–6].

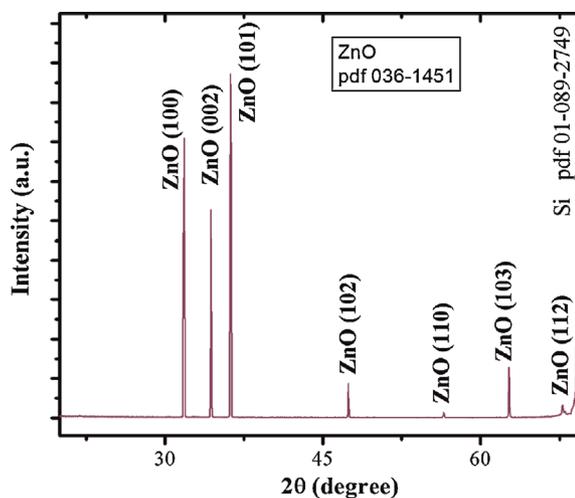


Figure 1 (online color at: www.pss-b.com) XRD spectrum for ZnO nanowires grown by aqueous solution method on a Si substrate.

3 Results and discussion

3.1 Structural characterization Figure 1 presents an indexed XRD scan in the range of 20–70° on the ZnO nanowires grown by our technique. One can see that all the diffraction peaks corresponds to crystalline ZnO with the hexagonal wurtzite structure [14, 15]. The calculated lattice constant $c = 0.521$ nm are consistent with the standard values. No characteristic peaks from other impurities are detected.

3.2 Morphologic characterization A typical SEM image taken from ZnO nanostructures grown by aqueous solution method is shown in Fig. 2. 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). Conversely, when experiments are conducted at the lower end of the temperature range, more tetrapods are observed. This suggests that while nanorods growth is kinetically driven, branching may encompass additional thermodynamic considerations. In Fig. 2 it is evident that the sample mainly consists of ZnO nanorods self-assembly into cross- and tetrapod-like morphologies. Closer observation (Fig. 2b) reveals that the products are actually composed of four legs perfectly grown/assembled. 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 3000 nm (Fig. 2b). An advantage of structure is that it has four legs. Any of the legs may be used latter for surface functionalization strategies, biofunctionalization, etc. A TEM studies (not shown) on an individual ZnO nanocross demonstrate that the lattice fringes in all examined regions reveal no dislocations or stacking faults.

According to our experimental results, the nanostructures obtained by aqueous solution process can be transferred

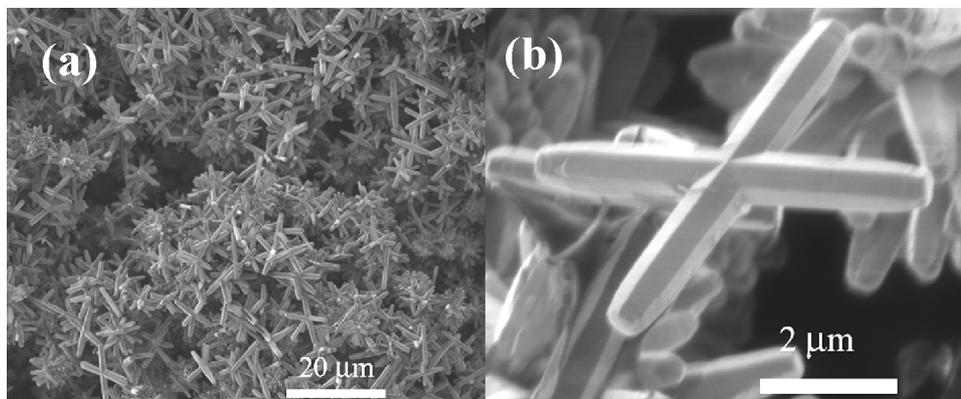


Figure 2 SEM images showing the as-grown zinc oxide nanostructures on silicon substrate (a) and zoom in cross (b).

to other substrates and can be handled by a FIB instrument in order to fabricate test devices.

For the nanosensor designing, the Si/SiO₂ substrates were used for tetrapods and crosses 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. Si/SiO₂ substrate was prepared using standard technique [8, 13]. After the transfer process we reduced the density of nanostructures on the surface of the substrate, which will facilitate the *in situ* FIB process of the crosses and tetrapods devices fabrication. 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 procedure. Details on *in situ* lift-out procedure are described in our previous works [2–6]. For the multi-terminal 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. Next, four metal

contacts were made (not shown) 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. 3). 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 3b shows the fabricated single crossed ZnO nanorods-based sensor.

By this technique, different shaped-nanosensors have been fabricated and investigated for their UV and gas sensitivity. In Fig. 3a 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 into account that nanorod synthesis was done in 15–20 min, we substantially improve the fabrication process of sensors. Our technique minimizes

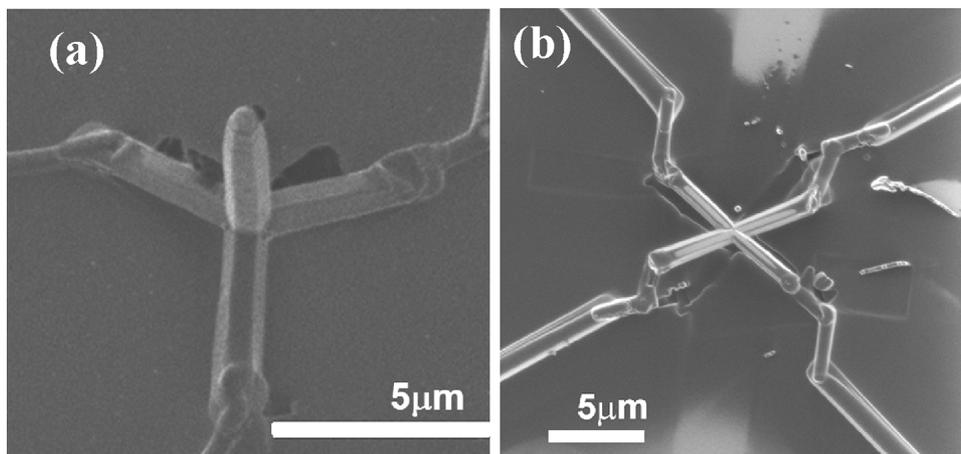


Figure 3 SEM images showing the steps of the *in situ* lift-out fabrication in the FIB/SEM system. (a) The ZnO tetrapod after welding its legs to the electrode/external connections as final sensor; (b) single crossed ZnO nanorod with uniform size after welding its legs to the electrode/external connections as final sensor.

the time to fabricate nanodevices using FIB and can be extended to other specific nanodevices.

Next, we measured the I - V curves (not shown) of the ZnO tetrapod with connections realized by *in situ* lift-out method. The I - V measurements were performed through all possible combinations by changing the bias voltages from +15 to -15 mV and *vice versa*. All the connections through legs pairs of the crossed ZnO nanorods or ZnO tetrapod displayed similar characteristics (not shown).

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 UV light. It was subjected to irradiation with an UV light with an incident peak wavelength of 361 nm with conductivity monitoring. The background atmosphere was air. It was found that conductivity increases linearly with intensity of UV irradiation. 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. When the UV light was turned off, the resistance increased within 10% of the initial value.

It is expected that a suspended nanorods-based tetrapod (Fig. 3) could have more surface area than a comparable nonsuspended structure such as cross-ZnO nanorod or individual nanorod [2–5], so the sensitivity can be further improved with suspended structure. 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.

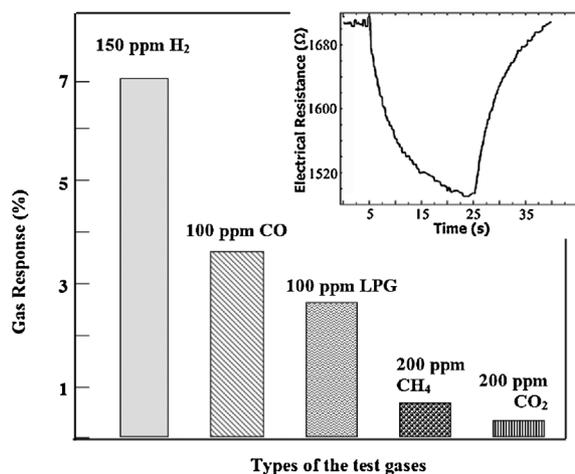


Figure 4 The gas response *versus* different types of test gases of the single ZnO nanotetrapod-based sensor fabricated by *in situ* lift-out technique in the FIB system. (Insert shows UV sensitivity.)

Several sensors on single tetrapod have been fabricated by *in situ* lift-out technique and investigated under identical conditions and similar UV response was observed. Spectral response (not shown) demonstrates that such device is indeed suitable for detecting UV in the range 300–400 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 [3–6]. The optical power on the detectors is 50 nW so the photoresponsivity at 361 nm is 40 A/W.

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. Also, in our experiments it was observed that a sensitivity of about 7% to 150 ppm H₂ gas. In Fig. 4 it is shown the gas response *versus* different types of test gases such as: 150 ppm H₂, 100 ppm CO, 100 ppm LPG, 200 ppm CH₄, and 200 ppm CO₂. It can be observed that developed sensor shows different sensitivity values to investigated gases. It can be concluded that device can be considered a selective one. Figure 4 (insert) illustrates the UV response of the single ZnO nanotetrapod-based UV sensor fabricated by *in situ* lift-out technique.

4 Conclusions In summary, fabrication of single ZnO-tetrapod UV and gas sensor by *in situ* lift-out technique in the FIB system is demonstrated. Our technique can fabricate sensors based on single nanowire/nanotetrapod or crossed ZnO nanorod.

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.

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