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UV Sensor Based on Single Metal Oxide Nanowire

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Abstract

Nanostructures with high surface-to-volume ratios are great candidates for the next generation of high performance electronic devices. Low temperature hydrothermal synthesis techniques to produce such nanostructures at low cost and large scale are very desirable. In this work, the fabrication of a low-cost metal–semiconductor–metal UV sensor based on single ZnO nanowire as the active material is presented. The single nanowire UV sensor demonstrates a 272% enhancement in sensitivity and 21 times faster in response compared with a thin film detector. The improvement in the device performance is attributed to the high quality of the grown nanowires as well as their high aspect ratio and reduced dimensionality. This work represents a low cost method to produce efficient ZnO UV sensors at large scale and low cost.

Keywords: Nanowire, nanostructure, ZnO, hydrothermal, UV, sensor

Introduction

Low temperature growth methods of nanostructured metal oxide materials have progressed remarkably in recent years. This is mainly due to the need for such growth methods in the production and improvement of many devices [1-5]. Zinc oxide (ZnO) is a key material in industry and technology and is used in many devices including laser diodes, light-emitting diodes, piezoelectric transducers, and ultraviolet (UV) detectors [6-9]. UV sensors have been used in a numerous applications ranging from pollution monitoring, secure space communications, and water purification to flame and missile plume detection.

One can find numerous reports and studies on the synthesis and fabrication of nanostructured ZnO UV sensors [6-9]. One attractive synthesis technique among them is the hydrothermal synthesis because of its simplicity, cost effectiveness, suitability to large area scalability [1-4], low processing temperature, non-hazardous nature, reproducibility, and compatibility with flexible organic substrates.

Nanostructures are great candidates and hold high expectations as high performance UV sensors due to their large surface-to-volume ratio and high crystal structure. However, the cost of fabrication of nanostructured UV sensors is still very high and the process is time consuming.

In this work, the hydrothermal synthesis of ZnO nanowires and analysis of UV sensors based on single nanowire are reported. First, the morphological and structural characterizations of the grown nanowires are presented together with a growth mechanism. Next, the fabrication of UV sensors based on ZnO thin film and single nanowire as well as their performance in terms of photosensitivity and response and recovery times are presented. We finally discuss the sensing mechanism is in terms of the role of adsorbed oxygen on the surface of ZnO nanowire.

Materials and methods

Synthesis

All reagents in this work were analytical grade. First a ZnO seed layer was prepared on a substrate as follow. Si/SiO_2 substrates were cleaned by sonication in acetone, isopropyl alcohol (IPA), ethanol, and deionized water for 10 min each, consecutively. Further, it was dried with nitrogen gas and baked on a hotplate at 150˚C for 5 min. The substrate was then spin coated with 5 mM zinc acetate dehydrate $Zn(CH3COO)_2.2H_2O$ solution in ethanol at 1000 rpm for 30 s. The spin-cast layer on the silicon substrate was cured on a hot plate 150˚C for 5 min to stabilize the film structure. The spin coating and curing processes were repeated five times in order to obtain a uniform film, which served as the seeding layer. Afterwards, the film was thermally annealed at 350˚C for 30 min, and then allowed to cool down. The thermal decomposition (of the zinc

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acetate) created ZnO nanocrystals on the substrate that act as a seed layer for subsequent ZnO array growth. The precursor solution for the hydrothermal reaction consists of (25-50 mmol) zinc nitrate, (12.5-25 mmol) HMTA, and (0.35-0.45 mol) ammonium hydroxide. The seeded substrate was then placed in a vial that contains (15 mL) of the growth solution. (5 mmol) polyethylenimine (PEI) (end-capped, molecular weight 800 g/mol LS, Aldrich) were also added to the growth solution as a capping agent to control the diameter of the nanowires. The vial was covered and then placed in an oven which had been preheated to 90˚C to start the growth of ZnO arrays. It takes several minutes for the growth solution to reach 90˚C. The vial was taken out of the oven after 24 h, and the silicon substrate was transferred to a new vial containing only warm DI water for another 24 hours to dissolve PEI residuals. The substrate was then rinsed with DI water and dried in air at 150 °C for 30 min.

Morphology and structure

The morphology and crystal structure of the grown structures were observed using Philips XL-20 scanning electron microscope (SEM) at 10 kV. The grown structures were also through powder X-ray diffraction (XRD) using a Panalytical X-pert diffractometer with Cu Kα radiation. Scanning transmission electron microscopy (STEM) and electron diffraction characterizations were applied using a Hitachi HD2300A microscope operating at 200 kV. STEM samples were prepared by depositing a drop of diluted suspension of the nanostructure in ethanol on a carbon film coated copper grid.

UV sensing

The electrical characteristics of the fabricated devices were recorded using a probe station attached to Keithley 4200 semiconductor analyzer. The excitation source for the UV detection properties was a monochromatic UV lamp (UVGL-55 Hand Lamp from UVP LLC) with 50 µW/cm2 intensity at a wavelength of 365 nm.

Results and discussion

Morphology and structure

Side and top view SEM images of the grown ZnO nanowire arrayare shown in figures 1(a)-1(c). these SEM images clearly present the great uniformity and high density of the hydrothermally grown nanowires. Figure 1(d) represents the XRD pattern of the grown nanowires showing high crystallinity of a hexagonal wurtzite-type ZnO (JCPDS No.36-1451) with no identified impurity signals. This is an indication that the only crystalline material to which the precursor was transformed to in this reaction is ZnO. However, the diffraction intensity of (002) is low relative to (101), which is unlike the usual observation in the literature of high intensity (002) peak in XRD analysis of ZnO NW array [1,2]. The high intensity ZnO (002) peak represents the good alignment of the NWs growing in the c-axis direction normal to the substrate. The low intensity (002) peak for the NWs is due to the poor alignment of the NWs in the sample during characterization. Figures 1(e) and 1(f) show a TEM image of single ZnO NW along with the corresponding SAED pattern, respectively. These images show that these nanowires are single crystal structures growing along the [0001] direction stretching their nonpolar side facets and minimizing their polar facets.

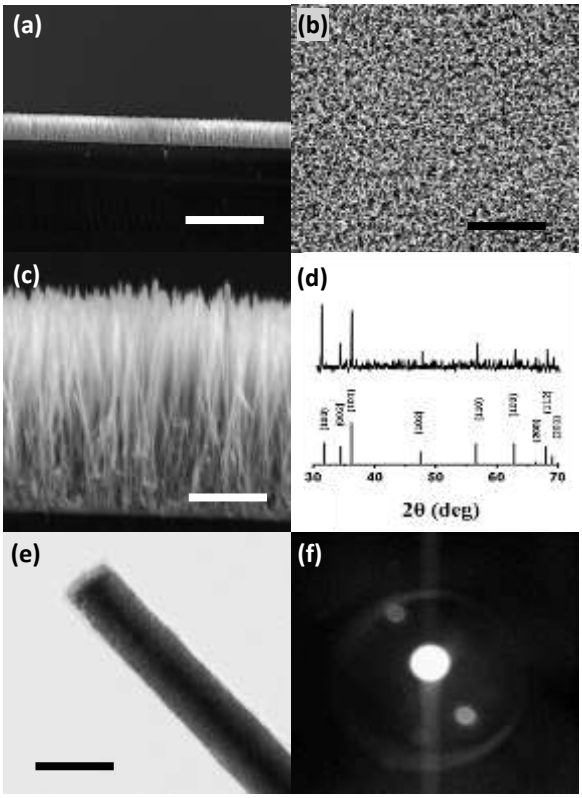

Figure 1 (a) Low magnification side view, (b) top view, and (c) high magnification side view SEM image of a ZnO nanowire array. (d) XRD pattern, (e) STEM image, and (f) the corresponding SAED pattern of a single ZnO nanowire.

UV sensing

First, a ZnO thin film UV sensor was fabricated and tested under ambient conditions to be used as reference. Figure 2 shows the ZnO thin film UV sensor response characteristics. The photosensitivity of the device is calculated to be

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about 11, while the response time and recovery time are 890 s and 915 s, respectively. The photocurrent of this device was measured around ~5 µA, while the dark current was ~0.45 µA. This photosensitivity value is comparable to previously reported values for thin film detectors. For example, Xu et al. reported a UV detector fabricated based on RF sputtered ZnO thin film on quartz substrates with a photosensitivity value of 20 [10]. In a similar report, a sol–gel synthesized ZnO thin film UV detector showed a photosensitivity of 6 [11].

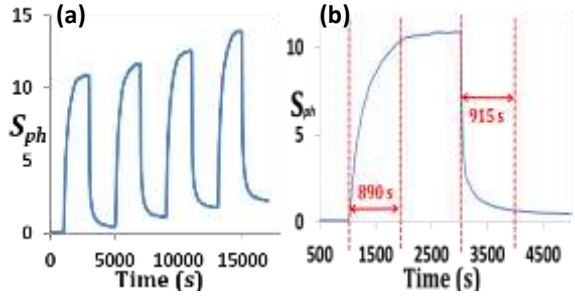

Figure 2 The photoresponse characteristics of the ZnO thin film detector.

Figure 3 shows SEM image and photoresponse characteristics of the ZnO nanowire UV sensor. The photosensitivity of this device is around 1200, which is 100 times that of the thin film sensor. The photocurrent of this detector was measured around ~3.6 µA, while the dark current was ~3 nA. The response-time and the recovery-time are 11 and 15 s, respectively indicating that this sensor is 80 times faster than the thin film sensor.

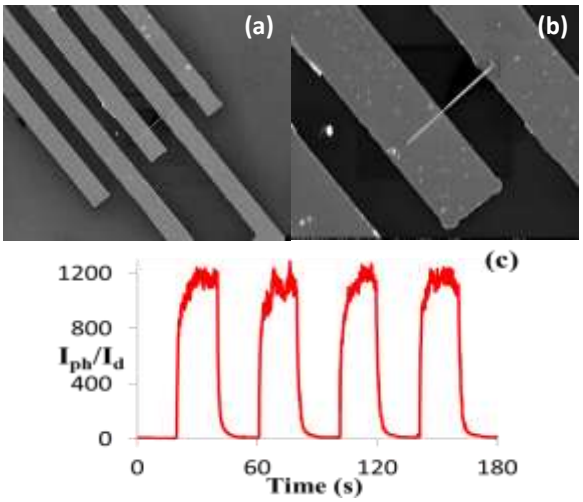

Figure 3 (a), (b) SEM images, and (c) photoresponse characteristics of the single nanowire UV sensor.

The improvement in the sensor performance is attributed to the reduction in the dimensionality of the nanowires compared with thin film sensor. The higher surface-to-volume ratio should extend the carrier life time by creating more surface state traps. Additionally, the reduction in dimensions presents confined active area deceasing the time needed for transient. [12-15] The combination of these two aspects clearly presents a significant enhancement in the overall detector performance.

The photodetection mechanism is illustrated in the schematic in figure 4. When the ZnO nanowire is in dark and room temperature conditions, oxygen molecules (O_2) are adsorbed on its surface and become negative ions (O^{2-}) seizing electrons from the conduction band of ZnO. [12-15] Subsequently, this builds a depletion layer close to the surface (figure 4(a)). Upon UV illumination, electron–hole pairs are photogenerated lowering the thickness of the depletion layer and increasing the number of free electrons in the ZnO nanowire as shown in figure 4(b). After turning the UV light off, oxygen molecules are readsorbed again on the surface of the ZnO nanowire decreasing its conductivity. [12-15] Therefore, the charge transport in the nanowire UV sensor is controlled by the surface oxygen exchange process.

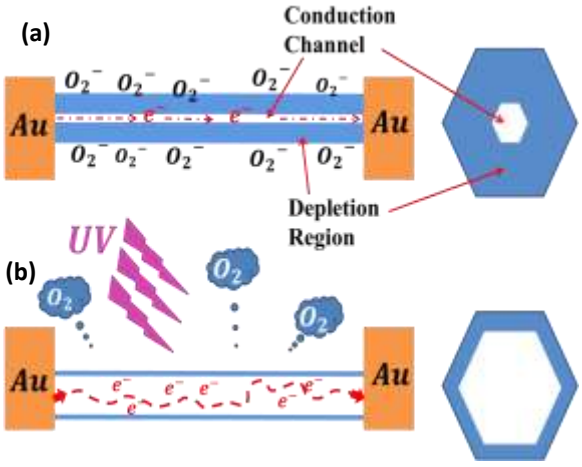

Figure 4 A schematic illustration of the ZnO SNW (a) under dark condition and (b) under UV illumination.

Conclusion

In conclusion, we presented a simple low temperature hydrothermal synthesis method to grow single crystal ZnO nanowires at low cost and large scale. We fabricated a MSM ZnO UV sensor based on a single nanowire and showed the effects of charge confinement in the low dimensional structure. The single nanowire UV sensor demonstrated an improvement in photoresponsivity and speed of

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response in comparison with the thin film structure. The enhancement is attributed to the high quality of the grown nanowires as well as high aspect ratio and reduced dimensionality. This work represents a low cost method of producing efficient ZnO UV sensors.

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