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Nanowire Array Based UV Detectors

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Abstract: ***Low temperature hydrothermal fabrication of high performance nanostructured detectors possesses a great potential for the next generation of smart low cost electronic devices. In this work, the fabrication of a low-cost metal–semiconductor–metal photodetectors based on ZnO nanowire array as the active layer is presented. The nanowire array UV detector 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 detectors at large scale and low cost.***

Keywords: Nanowires, ZnO, sensors, photodetector, array

1. Introduction

Hydrothermal preparation of metal oxide nanostructures has evolved impressively lately due to its importance in the fabrication and development of many devices [1-5]. Zinc oxide (ZnO) is an important material in technology and is used for a variety of devices such as laser diodes, light-emitting diodes, piezoelectric transducers, and ultraviolet (UV) detectors [6-9]. UV photodetectors in particular have been used in different key applications including pollution monitoring, secure space communications, water purification, flame and missile plume detection, etc. In these entire applications high sensor performance (i.e. high sensitivity and short response time) is essential.

In the literature there are many reports on the growth of ZnO nanostructures using different techniques and their use in UV detection [6-9]. Among these different synthesis techniques, hydrothermal methods are attractive for many reasons including: simplicity, cost effectiveness, suitability to large area scalability [1-4], low processing temperature, non-hazardous nature, reproducibility, and compatibility with flexible organic substrates.

Benefiting from large surface-to-volume ratio and high crystal structure, nanostructures are considered a great choice to fabricate UV detectors with superior sensitivity, responsivity, and speed of response. Until now, most of the reports on nanostructured UV detectors are based on single one dimensional (1D) nanostructures. The working principles and mechanism of photosensitivity are explained by oxygen mediation on the surface of ZnO. However, for the 1D nanostructure configuration, only a small fraction of light interacts with the active area of the nanowires which is not practical for UV detection. Furthermore, the fabrication process of single nanowire devices is expensive, challenging, and time consuming. On the other hand, nanowire arrays are very attractive as active materials for photodetectors because they are easy to fabricate and can achieve high photosensitivity due to their capability to trap more light than single nanowires.

In this work, the hydrothermal synthesis of ZnO nanowire array and analysis of UV detectors based on the grown arrays are reported. First, the morphological and structural characterizations of the grown nanowire arrays are presented together with a growth mechanism. Next, UV detectors based on ZnO thin film and nanowire array are fabricated and their performance as fully solution processable large area UV detectors in terms of photosensitivity, photoresponsivity, external quantum efficiency, and response and recovery times is presented. The detection mechanism is finally discussed in terms of the role of adsorbed oxygen on the surface of ZnO nanowires.

2. Experimental details

All reagents in this work were analytical grade. The growth of ZnO nanowire array starts by preparing a seeded substrate. Pre-patterned Si/SiO2 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)2.2H2O 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 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

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rinsed with DI water and dried in air at 150 °C for 30 min.

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.

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.

3. Results and discussion

3.1 Morphology and structure of ZnO nanowires

Figures 1(a)-1(c) show side and top view SEM images of the grown ZnO nanowire array. From these images one can see the high uniformity and density of the nanowires. Figure 1(d) depicts the XRD pattern of the grown nanowires showing high crystallinity of a hexagonal wurtzite-type ZnO (JCPDS No.36-1451). Signals of impurities were not identified suggesting that the only crystalline material to which the precursor was converted to during the 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 NWs are single crystal structures growing along the [0001] direction stretching their nonpolar side facets and minimizing their polar facets.

3.2 UV detection properties

Initially, the UV detection properties of a ZnO thin film, which was fabricated originally to serve as a seed layer to fabricate the ZnO nanowire array detector, has been tested as a reference. Figure 2 shows the photoresponse

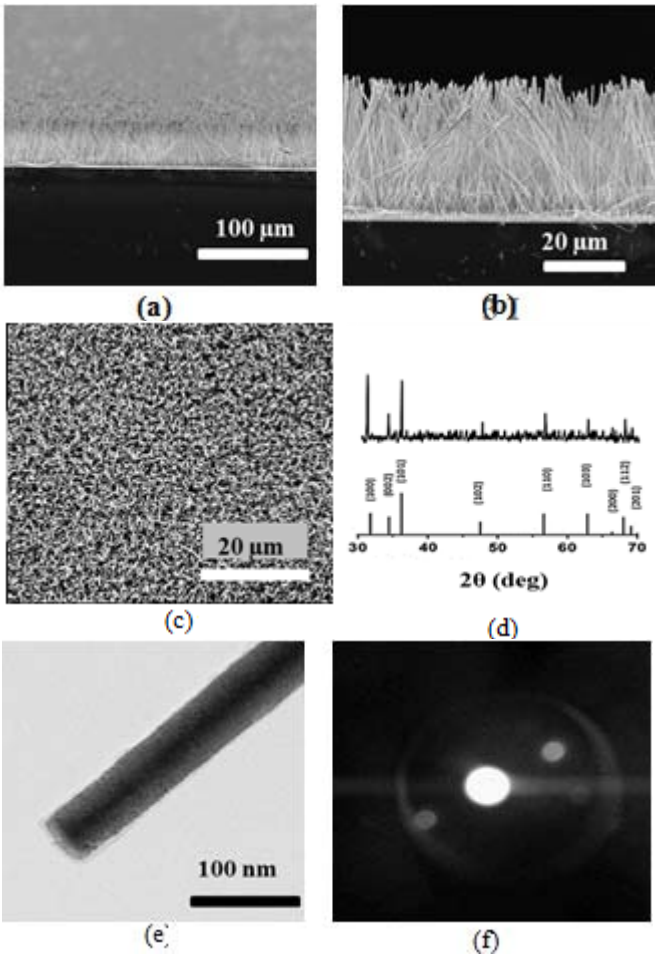


Figure 1 (a) Low magnification side view, (b) high magnification side view, and (c) top view SEM image of a ZnO nanowire array. (d) XRD pattern, (e) STEM image, and (f) the corresponding SAED pattern of a single ZnO nanowire.

Characteristics of ZnO thin film UV detector. The photosensitivity of the device is calculated to be 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].

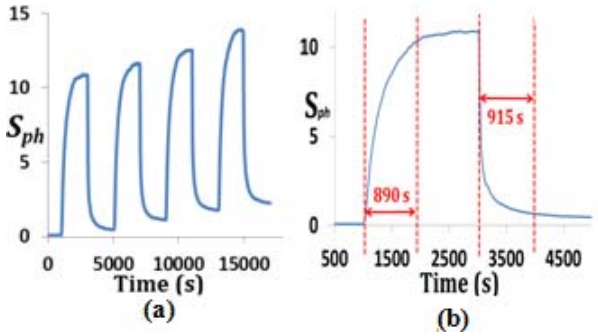


Figure 2: (a) and (b) the photoresponse characteristics of the ZnO thin film detector.

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Figure 3 shows the schematic and photoresponse characteristics of the ZnO nanowire array photodetector. The photosensitivityof this device is around 30, which is three times that of the thin film detector. The photocurrent of this detector was measured around ~7.5 μA, while the dark current was ~0.25 μA. From figure 5.3(b) the response-time and the recovery-time are 42 and 55 s (20 times faster than the thin film detector), respectively.

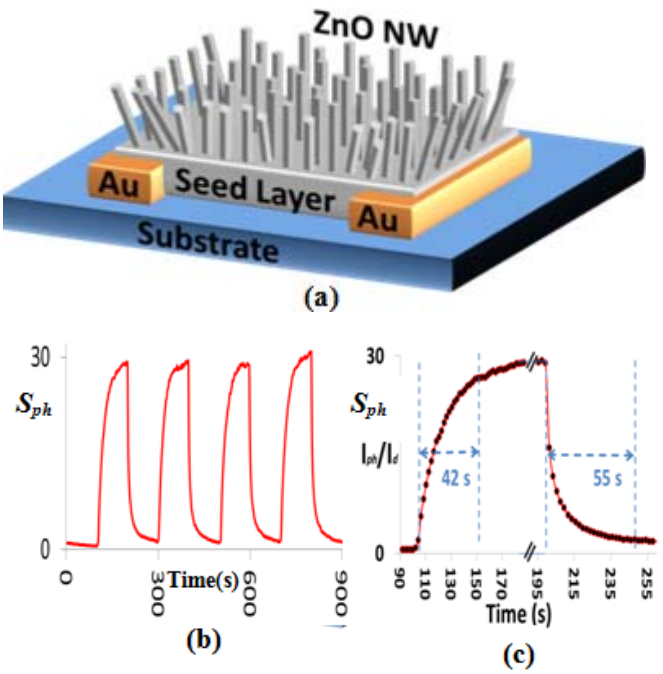


Figure 3: (a) Schematic, (b), and (c) photoresponse characteristics of the ZnO NWA detector

Figure 4 illustrates a charge transport model in the nanowire array detectors. Initially oxygen molecules (O2) are adsorbed on the surface of the ZnO nanowires and become negatively charged ions (O2−) by catching electrons from ZnO [12-15]. This in turn causes the formation of a depletion layer between the negatively charged surface and the NW axis (figure 4(a)). UV illumination on the ZnO creates electron–hole pairs. After that, the holes move to the surface of ZnO motivated by the depletion field and free the trapped electrons (figure 4(b)). The improved photosensitivity in the nanowire array detector can be understood from the following aspects. First, the nanowire array structure improves the absorption of light [12]. Second, reduced dimensionality and confinement of the nanowire building blocks of the detector improve the photogeneration of electron–hole pairs and lowers the time needed for electrons to reach electrodes [13]. Finally, the increased surface-to-volume ratio enhances surface-state trapping allowing longer life time for carriers in the nanowires. The combination of these aspects increased the photosensitivity and speed of response and recovery in comparison with the thin film device.

4. Conclusion

In conclusion, we present a one-pot, low temperature, hydrothermal synthesis method to grow single crystal ZnO nanowires. We demonstrate a MSM ZnO UV detector based on nanowire array and show the effects of charge confinement in the low dimensional structure. The nanowire array detector showed an enhanced photoresponsivity and speed of 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 detectors.

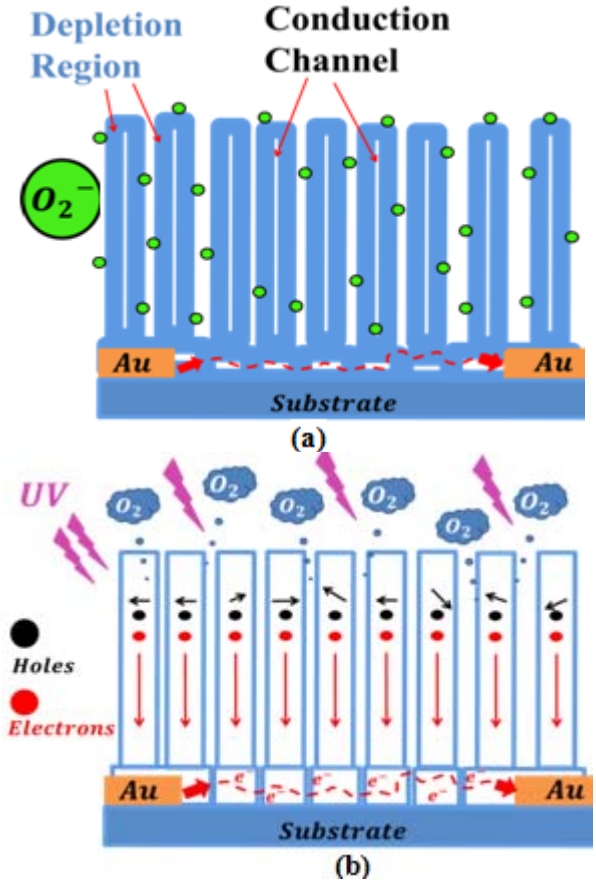


Figure 4: A schematic illustration of the ZnO NWA (a) under dark condition and (b) under UV illumination.

5. Acknowledgment

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