

Simple fabrication of a ZnO nanowire photodetector with a fast photoresponse time

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A zinc oxide (ZnO) nanowire photodetector was fabricated by a simple method of growing ZnO nanowires bridging the gap of two patterned zinc electrodes. The nanowire growth is self-catalytic, involving the direct heating of patterned Zn electrodes at 700 °C in an O₂/Ar gas flow of 20 SCCM (standard cubic centimeter per minute at STP)/80 SCCM, respectively, at atmospheric pressure for 3 h. The fabricated photodetector demonstrated fast response of shorter than 0.4 ms to UV illumination in air, which could be attributed to the adsorption, desorption, and diffusion of water molecules in the air onto the nanowire significantly influencing the photoresponse. © 2006 American Institute of Physics. [DOI: 10.1063/1.2190459]

Zinc oxide (ZnO) nanowires have attracted a considerable amount of research interest in recent years as potential candidates for short-wavelength optoelectronics applications such as nanoscale lasers,¹ light-emitting diodes,² and UV photodetectors.^{3–6} In applications as a photodetector, most of the devices reported have been fabricated by tedious and time consuming processing steps, often employing ZnO nanowires grown on a separate substrate, followed by sonification and dispersal of the isolated nanowires directly but randomly onto another substrate with prefabricated electrodes,^{3,5} or by electron-beam lithography to define the electrical contacts.³ Due to the random nature of the dispersal in such cases, the nanowire position could not be predetermined. Some degree of control over the alignment can be achieved by utilizing electric-field assisted assembly.⁶ Nonetheless, all these extra processing steps complicate the overall device fabrication. Although the methods described above enable us to study the characteristics of single-nanowire devices in order to demonstrate development potential, these fabrication techniques cannot be easily scaled up for mass fabrication of dense, low-cost nanowire-based photodetector device arrays.

In this letter, we demonstrate a simple method to fabricate a ZnO nanowire photodetector on a planar silicon nitride-coated Si substrate. The growth mechanism for forming our ZnO nanowires is discussed. The attractiveness of this work lies in the simplicity of the fabrication process, which could easily be scaled up, and paves the way for mass production of low-cost nanoscale UV photodetectors. In addition, the fabricated device demonstrated a fast response time to UV illumination in air at room temperature. Finally, the photoresponse mechanism is analyzed and discussed.

Two-level patterning was employed on a 150 nm thick silicon nitride (Si₃N₄) coated silicon (Si) substrate: the first level patterning was used to delineate a pair of gold (Au) electrodes leading to bond pads; the second level of patterning was used to pattern the two zinc (Zn) electrodes with a gap of 3 μm, connected to the Au electrodes. Next, thermal evaporation was carried out to deposit Zn onto the patterned electrode using 99.999% Zn wire as the source material, fol-

lowed by lift-off. An optical micrograph of the patterned Au/Zn electrode is shown in Fig. 1. The patterned sample was next placed in the middle of a quartz tube furnace. By directly heating the sample to 700 °C at atmospheric pressure with an O₂/Ar gas flow of 20 SCCM (standard cubic centimeter per minute at STP)/80 SCCM, respectively, for a duration of 3 h, ZnO nanowires were grown laterally bridging the gap between the patterned zinc electrodes. A Zn-coated Si₃N₄ membrane transmission electron microscopy (TEM) grid, with a few etched-through slots, was also processed together with the sample so as to characterize the as-grown ZnO nanowires using TEM.

The morphology of the interconnected ZnO nanowires grown was observed in a field-emission scanning electron microscopy (FE-SEM) (Phillips XL30 FEG) and shown in Fig. 2(a). The dimensions and the microstructure were analyzed by high-resolution transmission electron microscopy (HRTEM) (Phillips CM300). The diameters of the nanowires are typically around 20–40 nm. The nanowires are also single crystalline, as evidenced from the HRTEM micrograph shown in Fig. 2(b). The postulated growth mechanism for the lateral growth of our ZnO nanowires is as follows. The patterned zinc electrode consists of many randomly oriented hexagonal grains as seen in the SEM. When these zinc grains are heated above the melting point of Zn (approximately 419 °C), they start to melt to form liquid Zn droplets

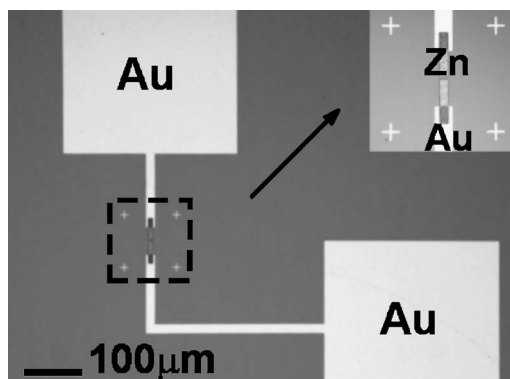


FIG. 1. Optical micrograph of the patterned sample. The inset is an enlarged view of the Au/Zn electrode.

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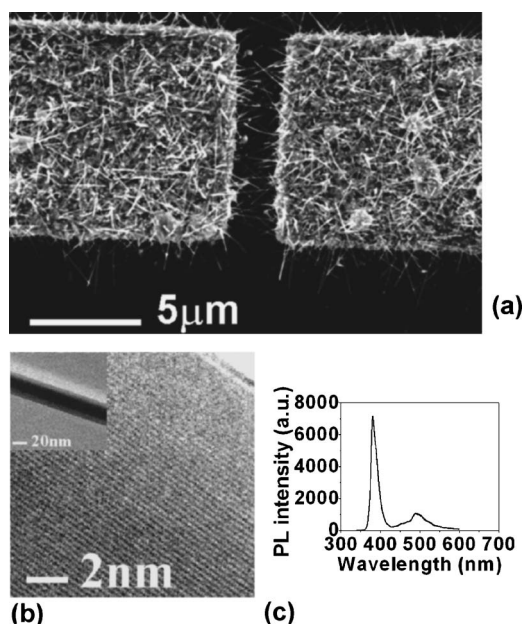


FIG. 2. (a) Plan view SEM image of the as-synthesized ZnO nanowires between the electrodes. (b) HRTEM micrograph of a ZnO nanowire indicating that it is a single crystal. The inset is a bright-field TEM micrograph of a typical ZnO nanowire. (c) Room temperature PL spectrum using an excited HeCd laser (325 nm).

which react with the low partial pressure of oxygen in the gas flow to generate ZnO nanoclusters.⁷ These ZnO nanoclusters at the apices of the Zn hexagonal grains act as nucleation sites for the preferential growth of the nanowires along the lateral direction at the apices of the hexagonal grains. Furthermore, due to poor wettability of the ZnO with Zn, these ZnO nanocluster nuclei would surface out rather than agglomerate, thereby promoting the one-dimensional growth of the nanowires.⁷ Our growth process does not make use of any transition-metal or noble metal catalyst particles; instead, only the predeposited Zn metal is used, which acts as both a reactant and a catalyst simultaneously. Therefore, the growth process could be considered as “self-catalytic.” Similar self-catalytic growth of ZnO nanowires by direct thermal oxidation of metal Zn powder above their melting points has been reported recently by Dang *et al.*⁸ and Fan *et al.*⁹ In addition, it is known that ZnO single crystals have three types of fast growth directions: $\langle 1120 \rangle$, $\langle 0110 \rangle$, and $[0001]$.⁹ In our case, TEM selected area electron diffraction (SAED) results (not shown) reveal that the growth direction of our ZnO nanowires is along the $\langle 1120 \rangle$ (a axis) direction. The preferential lateral growth of our ZnO nanowires at the apices of the hexagonal Zn grains was confirmed in a separate experiment using a sparse distribution of hexagonal Zn grains deposited on a similar substrate, and oxidized under identical conditions. Recently, similar lateral growth of the ZnO nanowires along the a -axis growth direction at the apex of hexagonal Zn nanograins has been reported by Kim *et al.*¹⁰ and Fan *et al.*,⁵ under different thermal oxidation conditions.

Room temperature photoluminescence (PL) measurement of the as-grown ZnO nanowires was carried out using a HeCd laser (325 nm wavelength line) as the source of excitation. Figure 2(c) shows the PL spectrum with a strong luminescence peak centered around 390 nm, indicating the near-band-edge (3.37 eV) emission and the free-exciton

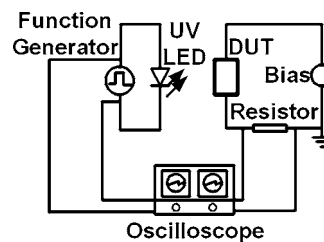


FIG. 3. Schematic diagram of the photoresponse measurement setup.

peak, and a weak broad band, centered around 500 nm, which could be attributed to deep-level defects in the ZnO crystals.^{11–13}

The time-dependent photoresponse of the ZnO nanowire-based photodetector to UV illumination at room temperature was investigated. Figure 3 shows a schematic diagram of the measurement setup. The UV illumination was provided by a UV light-emitting diode (LED) with a peak wavelength of 370 nm, which was driven by a 600 Hz square wave from a function generator to provide pulsed illumination. The photodetector [device under test (DUT)] was biased at 5 V. A small resistor in series with the circuit was used to monitor the current with a digital oscilloscope (sampling interval of 0.4 μ s).

The photoresponse of the photodetector in air is shown in Fig. 4(a). It was observed that the photoresponse to UV illumination in air follows an exponential growth and decay trend. Upon illumination, the photoresponse follows a first-order exponential growth function with an estimated time constant of $\tau_g = 0.1$ ms. When the UV light is turned off, the photoresponse follows a second-order exponential decay function, with estimated time constants of $\tau_{d1} = 0.09$ ms and $\tau_{d2} = 0.36$ ms, and relative weight ages of 0.47 and 0.53, respectively. The inset of Fig. 4(a) shows a corresponding measurement of the photoresponse in 10^{-5} mbar vacuum ambience. The I - V characteristics of the photodetector in air with and without UV (370 nm) illumination were also measured separately as shown in Fig. 4(b).

The observed fast photoresponse of shorter than 0.4 ms of our device to UV illumination in air could be attributed to the water vapor from the air having a significant influence on the photoresponse of the ZnO as discussed in Refs. 5, 14, and 15. Water vapor in the air is known to play a more effective role in influencing the photoresponse characteristics of ZnO thin films or nanowires than oxygen (O_2) molecules due to two mechanisms. The first mechanism is that the water vapor can capture both electrons as well as holes in ZnO, unlike O_2 molecules which only capture electrons, and thus more effectively shortens the photoresponse. The second mechanism is that water is more effective in taking up O_2 vacancies in ZnO than O_2 molecules due to its single bonding unlike the double-bonded O_2 molecules. In our case, when UV illumination is turned off, the second-order exponential decay function could be explained as follows. The fast decay response ($\tau_{d1} = 0.09$ ms) could be attributed to the water molecules oxidizing the oxygen vacancies and capturing both electrons and holes on the ZnO surface upon adsorption,¹⁵ while the slower decay response ($\tau_{d2} = 0.36$ ms) could be attributed to the relatively slow diffusion of the water molecules into the ZnO to bind to the oxygen vacancies.¹⁴ Upon UV illumination, the growth response follows only a single-order exponential function due

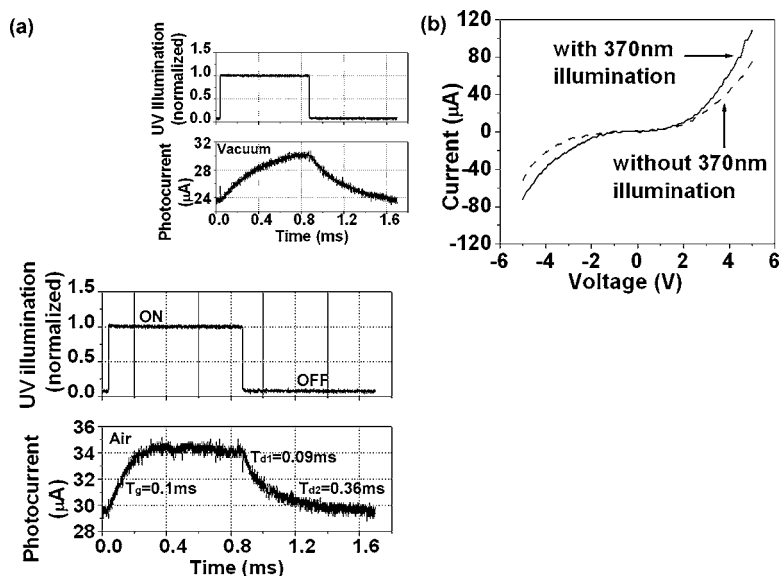


FIG. 4. (a) Time dependent photocurrent response to input UV illumination (normalized) in air changing with a period of 1.7 ms. The inset shows the corresponding time dependent photocurrent response in vacuum. (b) I - V characteristics of the photodetector with and without UV (370 nm) illumination.

to the external light providing dominant and sufficient energy source for both desorption and diffusion processes.^{14,15} The effect of water vapor in the air influencing the photoresponse of our device is evident from the measured response in vacuum [Fig. 4(a), inset] which shows slower growth and decay responses; similar observations of a slower photocurrent response in vacuum than air for ZnO-based nanowire photodetectors have been reported in Refs. 4 and 5.

Photoresponse times of the various ZnO nanowire-based photodetectors to UV illumination in air reported to date have shown a large variation (reported rise times range from 1 to 3750 s; reported fall times range from 1 to 11250 s).^{3-5,14,16} Kind *et al.*³ reported a rise and fall times of less than 1 s, but were not able to measure below 1 s, due to equipment limitation. Our measured results provide further information on how the photoresponse characteristics evolve below the 1 s limit and the mechanisms involved as explained above. In addition, it is known that the photoresponse characteristics of ZnO are significantly influenced by a number of factors such as the presence of different amounts of defect concentration in the ZnO grown, crystallographic orientation, grain size, and processing condition (such as annealing treatment in H_2/O_2).¹⁷ These factors could be at interplay to influence the photoresponse characteristics. This could explain the large variation in photoresponse times previously reported by various groups.

In summary, a simple and controlled method for fabricating a ZnO nanowire photodetector on a planar substrate has been described. The fabricated nanowire photodetector demonstrated fast response to UV illumination in air. Our results open up the possibility of mass production of simple, low-cost ZnO nanowire-based UV photodetectors.

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