Photolithographically Constructed Single ZnO Nanowire Device and Its Ultraviolet Photoresponse

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Abstract

Sparse ZnO nanowire array with aspect ratio of ca. 120 and growth rate of 1 µm/h was synthesized by controlling density of seeds at initial stage of nanowire growth. The spatially-separated nanowires were cut off from growth substrate unbrokenly, and thus facilitate to construct a single-nanowire device by photolithography. The device exhibited a linear current-voltage characteristic associated with ohmic contact between ZnO nanowire and electrodes. The device further demonstrated reliable photoresponse with an $I_{UV}/I_{dark}$ of ~100 to ultraviolet light irradiation.

Keywords: ZnO nanowire, single nanowire device, photolithography, ultraviolet photodetector
Introduction

Single zinc oxide (ZnO) nanowire devices have been widely produced not only for research about intrinsic properties of ZnO at confined nanospaces but also for application in light-emitting diodes, photodetectors, bio- and gas-sensors. In general, the devices require high aspect ratio nanowires and use of costly electron beam (EB) lithography apparatuses which present challenges to some researchers fabricating single nanowire devices. For the first challenge, although metal–organic chemical vapor deposition (MOCVD) can yield high aspect ratio ZnO nanowires, the severe experimental conditions, and high apparatus cost prevent it from being widely adopted. For less hazardous synthesis, flexible control by nutrient solution composition and low cost, researchers generally select hydrothermal synthesis to produce ZnO nanowires. In the hydrothermal synthesis, typical approaches to increase aspect ratio of ZnO nanowires are, 1) adding polyethylenimine (PEI) in growth solution to inhibit nanowire radial extension and prolonging growth time, 2) adding NH$_3$·H$_2$O to promote nanowire axial growth and a PEI to inhibit radial extension. For these two approaches, the former suffers from serious fusion at the bottom part of nanowires, and the latter is bound by its slow growth rate. For the second challenge of single nanowire device fabrication with transferring single nanowire to a predefined location, single nanowire devices are able to be practically fabricated by photolithography, but complicated operation of picking up and transferring of single nanowire has to be implemented.

In the current work, we demonstrate a facile technique to hydrothermally synthesize sparse ZnO nanowire array with high aspect ratio by suppressing the fusion at the bottom of nanowires.
The fabricated nanowires were unbrokenly cut off from growth substrate. Single-nanowire device was constructed via photolithography technique equipped with a micrometer control stage, instead of conventional EB lithography. Using the single-nanowire devices, we characterized the electrical conduction properties of ZnO nanowires as well as their photoresponse to ultraviolet (UV) light irradiation.

**Experimental**

*Growth and characterization of nanowires*

Silicon substrates (N type) with a size of $20 \text{ mm} \times 10 \text{ mm} \times 0.625 \text{ mm}$ were cleaned by heating them in a mixture of 98 % concentrated sulfuric acid and 35 % hydrogen peroxide (3 : 1 by volume) at $180 \text{ °C}$ for 2 h, and then washing them with ultrapure water and blowing them dry with a nitrogen gas flow. Radio frequency sputtering was used to prepare a 50 nm thick ZnO seed layer on the clean substrates. Next, the substrates were immersed into 50 mL nutrient solution in individual Teflon cups containing 50 mM equimolar of zinc nitrate hexahydrate and hexamethylenetetramine. Ammonia concentration was adjusted to 800 mM by adding commercial 25 % ammonia solution. 2 mM PEI (branched, low molecular weight, Aldrich) was added to the nutrient solution as a nanowire radial growth inhibitor, to result in a decreased nanowire areal density. The Teflon cups were covered with glass dishes and they were put into an oven, preheated to $95 \text{ °C}$, for 3 h. After 3 h, the substrates were immersed into fresh solution in order to obtain long wire arrays; this was repeated 10 times (total immersion time of 30 h). In this way we were able to synthesize a 30 µm length nanowire array on each substrate in 30 h. Finally, the samples were washed with ultrapure water and acetone, before
being dried on an 80 °C hot plate for 10 min. We imaged the fabricated nanowires using a scanning electron microscope (SEM; Zeiss Supra 40 VP).

Device fabrication

The nanowires were cut from the substrates by a scalpel and suspended in isopropanol. The suspension was dropped onto a 20 mm × 20 mm SiO2/Si substrate using a micropipette and dried in air. A layer of hexamethyldisilazane as tackifier was spin coated on the dried substrate with the nanowires at 3000 rpm for 8 s, and then this was covered with photoresist AZ 5200-E (purchased from Tokyo Ohka Kogyo) by spin coating at 1000 rpm for 120 s. Suitable nanowires were selected and they were exposed for the electrode pattern using a photolithography equipment (Model DDB-700, Neoark Corporation). After pattern development, sputter-deposited electrodes were obtained that consisted of layers of Ti (10 nm), Pt (50 nm) and Au (100 nm).

Measurement of electrical resistivity

We measured resistance of the ZnO nanowires by the 4 probes measurement. A source meter (Model 2401, Keithly) was connected to two outer electrodes to provide the voltage and measure the current in circuit. A digital multimeter (34461A, Keysight) was connected to two inner electrodes and used for component voltage measurement. In photoresponse detection, the source meter was connected to two inner electrodes to provide a voltage and measure current. A hand hold UV lamp with wavelength of 365 nm (0.29 mW/cm²) was used to illuminate the devices. The measurement was carried out in the dark in air.

Results and Discussion
Research studies have shown that a certain amount of PEI hinders lateral growth of ZnO nanowires in solution\textsuperscript{13-16}. In the current work, we carry out ammonia-assisted seed engineering and PEI as cation surfactant to control density of the seeds, realizing synthesize sparse nanowire arrays with ~120 aspect ratio at a 1 \( \mu \text{m/h} \) growth rate. According to the SEM images in Fig. 1 A, it is clear that the areal density of the nanowires gradually decreases with the increased amount of added PEI. The statistical analysis in Fig. 1 B confirms the inverse trend between nanowire areal density and the added PEI weight. PEI plays a significant role to control the amount of rebuilt seed templates. The statistical results in Fig. 1 C demonstrate a small quantity of PEI have almost no effect on nanowire diameter and growth rate. We are able to boost the nanowire growth rate from 0.3 to 0.5 \( \mu \text{m/h} \) in typical experiments\textsuperscript{15, 16}, to 1 \( \mu \text{m/h} \) and produce an ultralong sparse ZnO nanowire array with ~120 aspect ratio. What is more, because of the low areal density, the serious fusion phenomenon of nanowires in the bottom part of the array is almost completely avoided (shades of light red in Fig. 1 A). As show in Fig.1 D, the fusion length proportion of total length gradually decreases with the increase of added PEI amount. The decrease of this proportion means that nanowires keep enough length for device fabrication after they are cut from the substrate.

According to XRD spectra of ZnO (JCPDS Card No. 36-1451), typical crystallographic peaks of ZnO nanowires (2 mM PEI, 27 h growth, ~ 30 \( \mu \text{m} \) length) are clearly seen in the XRD patterns (Fig. 2 A). A significant raise of (002) peak intensity is measured after annealing nanowires at 600 °C in vacuum for 2 h. The preferential nanowires growth orientation of (0001) plane and improvement of crystallinity after annealing explain the prominent raise of (002) peak. The room temperature photoluminescence (PL) spectra and multiple Gaussian
peak fitting (inset is fitting result of annealed ZnO nanowires) of green-yellow (~565 nm) and yellow-orange (~620 nm) defect emission in as-grown and annealed ZnO nanowires are shown in Fig. 2B. The dominant defect emission changes from green-yellow to yellow-orange after annealing indicating reduction and restoration of crystal structure in nanowires. We consider the redshift of defect emission is caused by the decomposition of the residual Zn(OH)$_2$ on nanowire surface$^{18}$, and the involvement of interstitial oxygen$^{19}$. The possible bond breaking of the interstitial oxygen is supposed to be significant weakening of defect emission$^{20}$. After a heat treatment at 600 °C in vacuum, an intensity reduction and a redshift of the broad defect peak indicates a decrease in the point defect concentration and enhancement of crystallinity.

After obtaining ultralong nanowires, we employed a photolithography method to obtain single nanowire devices. The fabrication procedure is described in experimental section as show in Fig. 3 A. Fig. 3 B intuitively presents nanowires cut from the substrate and scattered around a SiO$_2$/Si substrate using a micropipette and allowed to dry naturally. From the SEM image of the fabricated device shown in Fig. 3 C, we can see that a four-terminal single nanowire device was neatly fabricated with a 5 µm gap between two electrodes. Here, we carry out photolithography instead of electron beam irradiation to realize the structure of our single nanowire devices. The simpler procedures and less costly equipment will encourage more researchers to examine the electrical and optical properties of nanowires.

For a characterization of the nanowire electrical property, we measured electrical resistivity of nanowire the nanowire electrical resistivity by the 4-T sensing method (Fig. 4 A). Fig. 4 B presents the I-V characteristics of the nanowires; we see that linear behaviors were
achieved between [-0.25 V, +0.25 V]. The result demonstrates that good ohmic contacts between nanowires and metal electrodes have been realized. We estimated nanowire resistivities by Ohm’s law based on the measurement of nanowire diameters and channel lengths between inner two electrodes. Existence of the shallow energy level defects, possibly the oxygen vacancy or the Zn interstitial defects result in an effective enhancement of electrical conductivity. The calculated resistivities vary in a range from 2.8 to 26.9 Ω·cm, which are comparable with previous studies. To characterize the nanowire photoconductive properties, electrical measurements were performed in the states of UV light on and UV light off. Fig. 4C compares the current-voltage (I-V) curves measured on a device with 5 µm length nanowire channel. Results show that, without UV illumination, the detected average resistance is above 15.1 MΩ and that indicates the nanowire is highly insulated in the dark; while when the device is exposed to UV light, the nanowire resistance is 1.9 MΩ, and that is a decrease by almost 1 order of magnitude. What is more, no matter with or without UV light irradiation, the current-voltage curves exhibit quite good linear behavior. On the one hand, this linear behavior can be attributed to a reduction of contact energy barrier by the sputtered layer of Ti which possesses a work function of ~4.33 eV, is close to the ZnO electron affinity of ~4.35 eV; and on the other hand, this is good evidence that our photolithography method offers flexibility for single nanowire device fabrication. The characteristics of the photoconductive ZnO nanowire suggest that it is a good candidate for a UV photodetector. Fig. 4D shows the photo response to UV light being turned on and off as a function of time. Significant differences of the detected current clearly indicate that the fabricated UV detector can be reversibly switched between the low (dark) and the high (UV) conductivity states. With 1 V bias, our UV detector
exhibits a $\sim 100 \ (I_{UV} / I_{dark})$ sensitivity, 23 s response time and 70 s recovery time. The photoconductive nanowire seems to be a good candidate for highly sensitive UV light detectors, and chemical or biological sensors when combined with suitable surface modification.

**Conclusions**

In summary, we successfully suppressed the fusion of nanowires at their bottom part and promoted nanowire growth rate to 1 $\mu$m/h by ammonia-assisted seed engineering and PEI as cation surfactant to control areal density of the seeds. With $\sim 120$ aspect ratio, nanowires were used to fabricate single nanowire device by a manageable photolithography apparatus. We estimated nanowire resistivities to be in the range of 2.8 to 26.9 $\Omega \cdot$ cm due to ohmic contacts between single nanowire and metal electrodes. Device exhibited a $\sim 100 \ (I_{UV} / I_{dark})$ sensitivity on exposure to UV irradiation, which enabled it to serve as UV light detector or switching device.

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Figure Captions

**Fig. 1** Morphology analysis of ZnO nanowires.  
A. SEM images of ZnO nanowires grown in nutrient solutions containing 800 mM ammonia and various weights of added PEI.  
B. Numbers of nanowires in a unit area.  
C. Nanowire diameter vs. its length for different weights of added PEI. The red line is a linear fit to the statistical data, and the error bars represent the standard deviation.  
D. The proportion of bottom fusion length in the total length of the nanowires for different weights of added PEI.

**Fig. 2** Characterization of ZnO nanowires.  
A. XRD patterns of ZnO nanowires and Si substrate with sputtered ZnO seed layer. Peaks with numbers on them indicate typical peaks for wurtzite characteristics.  
B. Room temperature photoluminescence spectra of ZnO nanowires.

**Fig. 3** Schematic drawings of the fabrication of the single nanowire device and SEM images of the device.  
A. Schematic drawings of the fabrication. (a). Applying a suspension containing nanowires to a substrate followed by drying. (b). Covering with photoresist. (c). Selecting the suitable nanowires, and exposing the pattern. (d). Developing the pattern. (e). Sputter-depositing the metal electrodes. (f). Lifting-off excess photoresist and metal layer.  
B. SEM image of ZnO nanowires cut from the substrate before (inset) and after 2 s ultrasonic dispersion.  
C. SEM image of the single nanowire device. Distance between two adjacent electrodes was 5 µm.
Fig. 4 Schematic of the 4-T sensing method and device photoelectric properties.  
A. Schematic of the 4-T sensing method. Partial voltage between the two inner electrodes was measured by a digital multimeter. A source meter was used to apply the voltage and measure current.  
B. Current-voltage (I-V) curves of several devices.  
C. I-V curves of dark current (blue) and photocurrent (red) of a single ZnO nanowire device under UV illumination.  
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