Fabrication of ZnO bridging nanowire device by a single-step chemical vapor deposition method

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ABSTRACT

ZnO nanowires are directly integrated into a working device by a single-step chemical vapor deposition (CVD) method. Gold catalyst is patterned on a quartz glass substrate using a comb-shaped shadow mask and then ZnO is grown on the patterned substrate by CVD. Thick ZnO layers formed on the gold-patterned areas serve as native electrodes. Ultra-long (~100 µm) ZnO nanowires grown across the gap between the ZnO electrodes and the nanowires serve as the sensing elements of the device. The device exhibits high sensitivity and fast response to UV illumination in air. Our method can be used to fabricate other metal oxide semiconductor bridging nanowire devices, which have promising applications in photodetection and gas sensing.

INTRODUCTION

Zinc oxide is a direct, wide bandgap ($E_g \approx 3.4$ eV) semiconductor material with a wide range of properties from UV detection to gas sensing [1-5]. The sensing properties of ZnO and other metal oxides are governed by the charge-exchange reactions with adsorbants on the surface [6]. Due to their inherently high surface-to-volume ratio, ZnO nanowires offer the promise of high sensitivity. Although the nanowires can be grown by simple thermal evaporation or chemical vapor deposition (CVD) methods with relatively low cost [7-9], the integration of the nanowires into working devices still remains a challenge. The integration of nanowires is usually done by “bottom-up” and then “top-down” processes. The nanowires are grown by “bottom-up” processes such as thermal evaporation or CVD. Then, they are collected from substrates and dispersed in a solution. After that, the nanowires are randomly deposited on an insulating substrate. The positions of the nanowires are noted under scanning electron microscope (SEM) observation with the assistance of pre-patterned markers on the substrates. Thereafter, metallic contacts to the nanowires are fabricated by “top-down” techniques such as photolithography [10], electron beam lithography [11], or focused ion beam lithography [12]. Because of its complexity, low efficiency and high cost, this method is limited to fundamental studies of properties of nanowires. In recent years, a new process has been developed to integrate nanowires into working devices. It is based on the concept of bridging nanowires between electrodes by self-organized growth of nanowires [13-19]. On contrary to the first method, the bridging method employs a “top-down” process to make the electrodes, and then uses a “bottom-up” process to grow the nanowires. A single crystal substrate is usually used to make a trench and form
electrodes on both sides of the trench by a “top-down” process. Then, nanowires are grown across the trench from one electrode to the other, forming bridges directly in the “bottom-up” growth process. The integration process is more efficient in comparison to the first method. However, expensive single crystal substrates are used to make the trench so as to achieve epitaxial nanowire growth and thus form ohmic contacts between the trench walls and the nanowires. Besides, “top-down” techniques such as photolithography, lift-off, and reactive-ion-etching are still needed to fabricate the trenches. Here, we report the fabrication of a ZnO bridging nanowire device by a single-step CVD method without resorting to any “top-down” process. In our method, the electrodes and the sensing elements are formed simultaneously during the CVD process. Despite of the simplicity of the fabrication process, our device is extremely sensitive to UV illumination.

EXPERIMENT

The schematic illustration of the experimental setup for growing ZnO bridging nanowires is shown in Figure 1. The device was fabricated by a CVD process in a horizontal vacuum tube furnace. A thin (~2 nm) gold discontinuous layer was sputtered on a quartz glass substrate through a comb-shaped shadow mask. The number of comb fingers was 25, their length was 5 mm, and the width of the fingers and the gap between them were both 100 µm. A powder mixture of 0.6 g ZnO (Koch Chemicals, 99.999 % purity) and 0.3 g graphite (NewMet Koch, 99.999 % purity) was charged in an alumina boat located at the center of the furnace. The substrate was placed 4-6 cm away from the source and downstream of the carrier gases. Argon and oxygen with a ratio of 10:1 were used as the carrier gases at a working pressure of ~70 mbar. The temperature of the source was kept at 1050 °C for 30 min, while the temperature of the substrate was around 1000 °C. Then, the furnace was cooled down at a rate of 10 °C min⁻¹ to room temperature. SEM images of the sample were taken with a Hitachi S3000N. For electrical measurements, copper wires were fixed by indium granules on both pads of the ZnO combs. The time-dependent photoresponse was measured using a source meter (Keithley, 2400) connected with a GPIB controller to a computer. A mercury arc lamp was used as the UV light source, and an excitation filter centered at 350 nm (±30 nm) was inserted in the beam. The UV irradiance was varied using neutral density filters and measured by an optical power meter (Ophir PD300-UV). A mechanical shutter was used to turn on and off the UV illumination on the sample.

Figure 1. Schematic illustration of the experimental setup (top view) for the growth of ZnO bridging nanowires.
DISCUSSION

The idea of fabricating ZnO bridging nanowire devices was inspired by the observation of different morphologies of ZnO products on different areas of the substrate. In our preliminary experiments, it was found that under the CVD conditions described in the experiment section, a thick ZnO layer was formed on top of a quartz glass substrate sputtered with a layer of gold (2 nm in thickness). Under SEM observation, it was found that this thick layer consisted of tangling ZnO nanowires and nanosheets, as shown in Figure 2a. The thickness of the layer is of the order of tens of microns and the resistance of the layer is very low according to our measurements. At the edges of the substrate, ZnO nanowires grow very long and are quite uniform because there is enough space for the nanowires to grow laterally, as exhibited in Figure 2b. The diameter of the nanowires is about 100 nm and their length around 50-100 µm. These results are very interesting because if two thick ZnO layers are close enough to each other, the long and oriented nanowires at their edges can bridge between them. Thus direct integration of nanowires into a working device is made possible, because the thick layers may serve as electrodes and the bridging nanowires can work as sensing elements.

Based on this idea, we have successfully fabricated ZnO bridging nanowire device by a single-step CVD process using quartz glass substrate sputtered with Au discontinuous thin film with defined shape. As shown in Figure 3a, ZnO thick layer was formed selectively on the gold sputtered areas, that is, the pads and the fingers of the comb-shaped structures. The morphology of the layer is the same as that shown in Figure 2a. Figure 3b and 3c show the details of the gap

Figure 2. SEM images of ZnO nanostructures grown (a) on top of the quartz glass substrate and (b) at the edge of the substrate. The scale bars are both 20 µm.

Figure 3. SEM images of the fabricated ZnO bridging nanowire device. The positions of images (b) and (c) are outlined in black in (a). The scale bars are (a) 500 µm, (b) 30 µm, and (c) 30 µm.
between the comb fingers. It can be seen that the gap between the fingers are bridged by some long nanowires. Because the resistance of the bridging nanowires is much larger than that of the thick layers on the pads and fingers, the sensing performance should mainly depend on the bridging nanowires. Due to the large surface-to-volume ratio of the bridging nanowires, the device is promising for high sensitivity gas detection and photon detection. The two interlacing combs made of thick ZnO layers serve as electrodes to collect electrical signals. The electrodes and the sensing elements are made simultaneously in the CVD process using our method, which makes the fabrication process very simple and highly efficient. Besides, the contamination to the nanowire surface is also minimized because no post treatment is needed to fabricate electrodes.

Selective growth of ZnO thick layer on the substrate is the key factor for achieving this bridging nanowire device. Thus, the selection of catalyst and substrate is very important for our method. Au atoms have a strong binding affinity to ZnO [20], so that ZnO particles in the gas flow can be caught easily by Au catalysts on the substrate. Moreover, the quartz glass has a very low surface energy of ~1.8 J m\(^{-2}\) [21], so that ZnO nucleation events do not take place without the presence of Au on the quartz glass substrate. Although the exact role of Au in the growth of the bridging nanowires is still unclear, three possible growth modes have been reported that may take place at the same time. First, the nanowire growth follows a vapor-liquid-solid (VLS) growth, where the Au nanoparticles act as nuclei for the nanowire and subsequently as growth sites. This is evidenced by the observation of an Au droplet at the tip of some of the ZnO nanowires. Second, the nanowires grow from the ZnO nuclei formed on the Au nanoparticles [22]. In this case, the Au nanoparticles are at the root of the nanowires. Third, the nanowires grow from the ZnO layers formed on top of Au layer. This type of nanowire growth follows a catalyst free process. Catalyst free growths of ZnO nanostructures usually involved ZnO seeds [23], so this type of growth is also possible for our sample.

The performance of the ZnO bridging nanowire device was tested by time-dependent photoresponse measurements. Figure 4 shows the photoresponse measured by switching on and off the UV illumination repeatedly over six cycles. Under a bias voltage of 5 V, the dark current level is below 10\(^{-9}\) A. Upon UV illumination, the current rises immediately to \(\sim 2 \times 10^{-5}\) A. The

![Figure 4. Photoresponse of the ZnO bridging nanowire device upon UV illumination switching on (for 60 s) and off (for 60 s) over six cycles. The bias voltage was 5 V and the irradiance was 0.8 mW cm\(^{-2}\).](image-url)
current increases by more than four orders of magnitude under an irradiance of 0.8 mW cm⁻². After switching off the UV illumination, the current decreases quickly to the dark level. As can be seen from the curve, the current fully recovers within 60 s, which is much faster than most reported results. By fitting the current decay data with an exponential decay formula \( y = y_0 + Ae^{-xt} \), decay time for the six decays was obtained, giving an average decay time of only 0.3 s. The photoresponse also shows high reproducibility as evidenced by the nearly identical rises and decays over the six cycles. The above results demonstrate that the ZnO bridging nanowire device is highly sensitive to UV illumination. Our fabrication method provides a simple and cost-effective way to make high-performance UV detectors. The detailed UV sensing properties of the ZnO bridging nanowires have been reported elsewhere [24, 25].

In order to prove that the high sensitivity of the device is truly attributed to the bridging nanowires, we have measured the photoresponse of the thick ZnO layers made of tangling ZnO nanowires and nanosheets. As shown in Figure 5, the current increases by four orders of magnitude upon UV illumination for photoresponse measured between the two interlaced combs. However, the current increases by only four times upon UV illumination when the photoresponse is measured between the points B and C of the same comb pad (see Figure 5). Furthermore, the current recovery of the bridging nanowires (points A and B) is faster than that of the thick layer (points B and C). Therefore, the high sensitivity and fast response of the device is ascribed to the nanowires bridging the fingers of the interlaced combs.

![Figure 5](image-url)

**Figure 5.** Photoresponse measured under the same UV illumination (0.77 mW cm⁻²) and bias voltage (5 V) in air between the points A and B (solid line), and between the points B and C (dotted line). The location of the points A, B, and C is indicated in the inset showing an optical microscope image of the fabricated device.

**CONCLUSIONS**

In conclusion, we have fabricated a ZnO bridging nanowire device by a single-step CVD method. The electrodes and the sensing elements were fabricated simultaneously in the CVD process, which is due to selective growth of thick ZnO layers on Au catalyst covered areas and lateral growth of ultra-long ZnO nanowires at the edges of the thick layers. The device exhibited
high sensitivity, fast response, as well as high reproducibility to UV illumination. The high performance of the device was proved to be attributed to the bridging nanowires. The device is also expected to have high sensitivity to gas sensing. Our one-step growth method provides a simple, efficient, and cost-effective way to fabricate UV or gas sensors for practical applications.

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REFERENCES