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RESEARCH ARTICLE

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Synthesis of High Crystallinity ZnO Nanowire Array on Polymer Substrate and Flexible Fiber-Based Sensor

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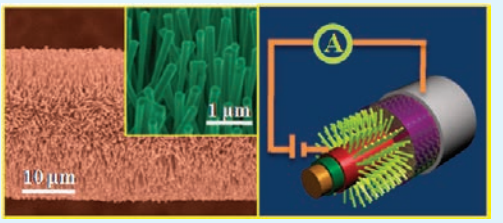
ABSTRACT: Well aligned ZnO nanowire (NW) arrays are grown on Kevlar fiber and Kapton film via the chemical vapor deposition (CVD) method. These NWs have better crystallinity than those synthesized through the low-temperature hydrothermal method. The average length and diameter of ZnO NWs grown on Kevlar fiber can be controlled from 0.5 to 2.76 μm and 30 to 300 nm, respectively. A flexible ultraviolet (UV) sensor based on Kevlar fiber/ZnO NWs hybrid structure is made to detect UV illumination quantificationally.



KEYWORDS: CVD method, ZnO nanowire array, flexible electronics, UV sensor

INTRODUCTION

One dimensional semiconductor nanomaterial is very important for future nanodevices.[1] Because of their semiconductor property, piezoelectric property, excellent mechanical property, and various morphologies, ZnO nanowires (NWs) have been widely studied to make ultraviolet (UV) laser,[2] solar cell,[3] nanogenerator,[4] piezotronic and piezophototronic nanodevices,[5] and every kind of sensor.[6−9] Generally, ZnO NWs can be synthesized via a low temperature hydrothermal method and high temperature physical vapor deposition (PVD) or chemical vapor deposition (CVD) method. A hydrothermal method has been used to grow ZnO NW arrays on polymer film and fiber.[10−12] However, the poor crystallinity and high defect concentration of NWs synthesized through this method weakened the device's performance,[13] which means that good crystallinity is necessary for the application of ZnO NW arrays. Compared with the hydrothermal method, a high growth temperature in CVD process can produce ZnO NW arrays with better crystallinity,[13] which is essential for the excellent performance of nanodevice. Applying this method, ZnO NW arrays has been perfectly grown on many different hard substrates,[14−16] but no attempt of the CVD method has been explored to grow ZnO NWs on flexible polymer substrate. Therefore, CVD synthesis of ZnO NW arrays on polymer substrate is valuable for high performance flexible nanodevices.

As a wide bandgap semiconductor, ZnO has wide application in solar blind UV sensors.[17,18] Although most of the studies about ZnO UV sensor are focused on how to increase the sensitivity, response velocity, and response current,[19−22] flexibility is a favorite character for nanodevices. Flexible fiber-based UV sensor will pave the way for wearable UV detection.

In this study, we successfully synthesized ZnO NW arrays with perfect crystallinity on Kevlar fiber and Kapton film by the CVD method. Furthermore, we use the microfiber/nanowire hybrid structure to fabricate a flexible fiber-based UV sensor, which can detect UV light quantificationally with high on/off current ratio.

EXPERIMENTAL DETAILS

ZnO NW array is synthesized on Kevlar fiber using pure Zn powder as source material, oxygen gas as reaction gas, and argon gas as carrier gas. The growth of ZnO NWs is determined by the mechanism of the CVD method.[23] Before experiment, the fiber is ultrasonically cleaned in acetone and ethanol for 20 min, respectively. Then, the well-cleaned fiber is put 10 cm away from the target at room temperature, and it is sputtered with 35 nm chromium (Cr) and 150 nm ZnO without annealing the fiber during the sputtering process. After that, fiber is placed at a position 0.5 to 8 cm away from the alumina boat in the furnace. At the beginning, the alundum tube is pumped to about 10 Torr, and then, 100 standard cubic centimeters per minute (SCCM) argon and 10 SCCM oxygen gas are introduced into the furnace in sequence. The furnace is heated to 560 °C with a heating rate of 10 °C per minute and then stays at this temperature. After being held at 560 °C for some time, the furnace is cooled down to room temperature. A similar procedure can be used to synthesize vertically aligned ZnO NW array on Kapton film.

Fiber-based flexible UV sensor is made from Kevlar fiber grown with ZnO NW array according to the following procedures. Most of the fiber is first immersed in P-type conductive polymer PEDOT/PSS to be covered by this polymer, and then, Ag is coated around the polymer at one end as one electrode of UV sensor. The other end of the fiber exposing ZnO NWs is another electrode of the sensor. Both electrodes are connected with the electrical measurement systems using copper wire and Ag paste. CHF-XM500 Xenon lamp (Beijing Trusttech Co. Ltd.) with a filter of 365 nm is used as the UV light source for UV detection.

RESULTS AND DISCUSSION

Typical scanning electron microscopy (SEM) images and transmission electron microscopy (TEM) images of the synthesized products are presented in Figure 1. As shown in Figure 1a,b, ZnO NW arrays grow radially on Kevlar fiber with very good uniformity. These ZnO NWs almost have the same diameter of

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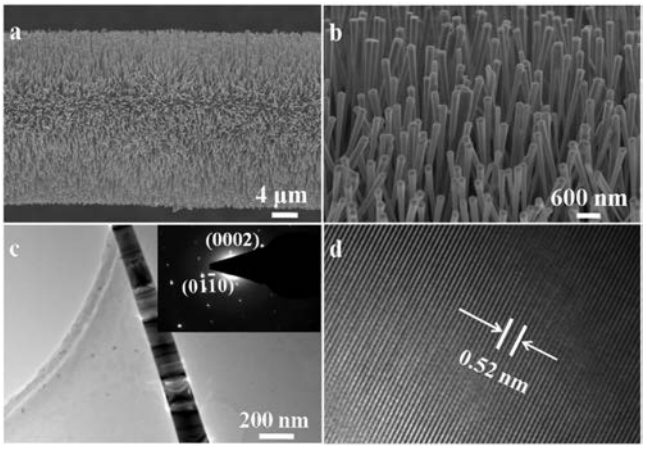

Figure 1. Morphology of ZnO NW arrays grown on Kevlar fiber via the CVD method. (a) and (b) are low magnification and high magnification SEM images. (c) TEM image of ZnO NW, its SAED pattern is shown in the inset. (d) HRTEM image of ZnO NW.

Table 1. Length and Diameter of ZnO NWs Grown at Different Temperature T^a

T (°C)	L (μm)	D (nm)
380	14.1 ± 1.5	350 ± 110
420	4.8 ± 1.3	125 ± 40
480	0.74 ± 0.21	325 ± 51
507	2.8 ± 0.71	300 ± 57
510	3.6 ± 1.1	740 ± 180

[a] The growth time of all samples is 90 min.

100 nm and same height of 1.5 μm. The distance between NWs is about several hundred nanometers. From SEM and TEM observation, the NWs' diameter gradually increases from 90 to 110 nm along the growth direction of ZnO NWs, which can be clearly seen from Figure 1c, too. Select-area electron diffraction (SAED) patterns (the inset of Figure 1c) shows the complete set of diffraction pattern, which implies that ZnO NW is of single crystalline wurtzite structure. Figure 1d displays high-resolution TEM (HRTEM) images, and the distance between the adjacent lattice planes is 0.257 nm, which represents the crystal face of (0002), consistent with the c-axis lattice constant of hexagonal ZnO (c = 0.521 nm) and implys that the growth direction of these ZnO NWs is [0001] direction.

Growth temperature of ZnO NWs is a very important factor for their nucleation and growth. The morphology evolution of ZnO NW arrays with growth temperature is shown in Table 1 and Figure 2. From Figure 2a−e, the growth temperature increases gradually from 380 to 510 °C. In Figure 2a, where the temperature was around 380 °C, ZnO NWs grow randomly on fiber. They are very long with a length of nearly 14 μm but very fine with small diameter about 350 nm and entangled with each other. Having a close-up view, nearly 70% NWs were perpendicular to the fiber' surface along their growth direction. When the deposition temperature was increased to 420 °C, as shown in Figure 2b, the synthesized NWs have a smaller diameter of about 125 nm and shorter length of about 4.8 μm, and the NWs' diameter gradually decreases along their growth direction, which results in a needle-like topography of NWs. At the

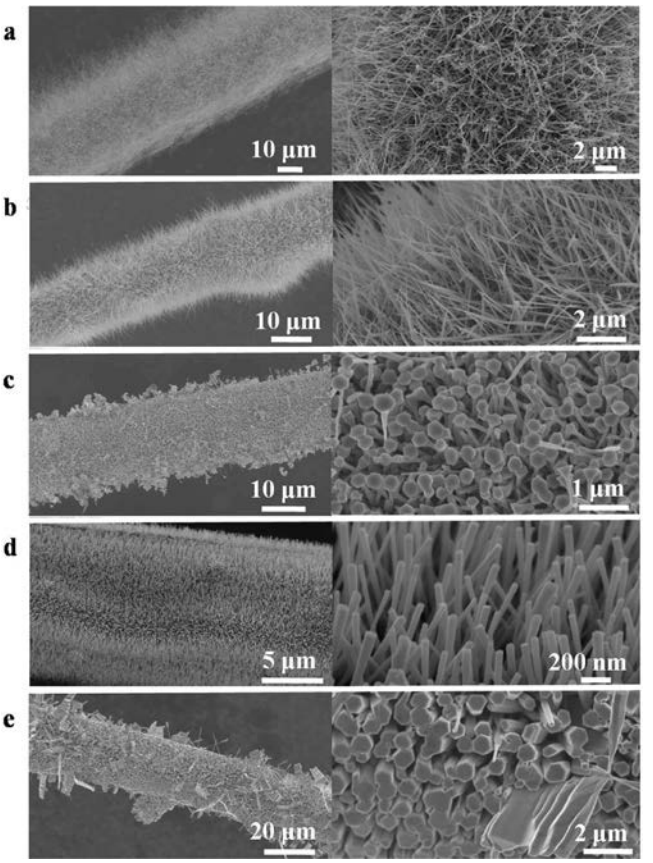

Figure 2. SEM images of ZnO NW arrays grown on Kevlar fiber at five different temperature zones. The left images are low magnification SEM images, and the right images are high magnification SEM images. From (a) to (e), the growth temperature of ZnO NW arrays is 380, 420, 480, 507, and 510 °C respectively.

same time, better radial orientation of NW arrays on fiber can be observed. This is probably due to larger Zn vapor concentration at 420 °C because it gradually reduces with the distance from the source position. At 480 °C, we can find an interesting nanostructure of a goblet, which is uniform thinner in the subjacent backbone with a diameter of 80 nm while much bulkier on the top with well-defined characteristic of hexagon on its head face with a diameter of 300 nm (Figure 2c). As the fiber is put at a 507 °C zone, it is covered by radial oriented NW arrays uniformly, which is shown in Figure 2d. The length of ZnO NWs is about 2.7 μm, and their diameter is about 300 nm. Nearly every ZnO NWs are uniform in diameter along the growth direction. It seems that this temperature is suitable for the growth of well-aligned ZnO NW arrays. When growth temperature is increased to 510 °C, ZnO NWs grow tightly with each other and their diameter and length are 740 nm and 3.6 μm, respectively (Figure 2e).

The influence of holding time on the growth of ZnO NWs was systematically studied by setting it to 15, 30, 60, and 90 min, respectively, keeping growth temperature at 507 °C. When keeping growth temperature at 507 °C for 15 minutes, synthesized ZnO NWs have rather small diameter of 30 nm and very short length of 0.5 μm (Figure 3a). Increasing holding time to 30 min, the diameter and length of NWs increase to 47 nm and 1.25 μm (Figure 3b). If the holding time is further increased, the

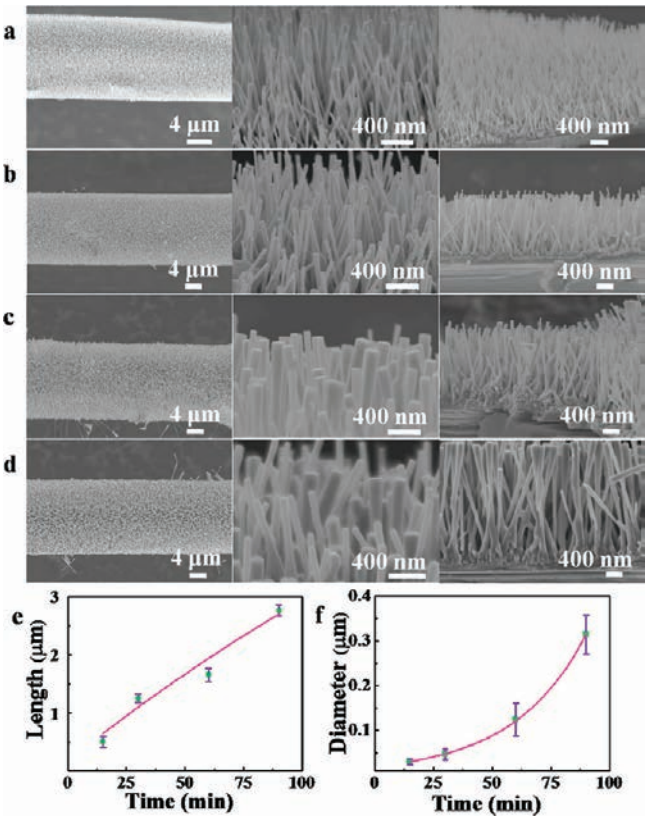

Figure 3. SEM images of ZnO NW arrays grown at 507 °C with different holding times of 15 min (a), 30 min (b), 60 min (c), and 90 min (d). The images from left to right are low magnification, high magnification, and cross-sectional SEM images. (e and f) The influence of holding time upon the length (e) and diameter (f) of ZnO NWs.

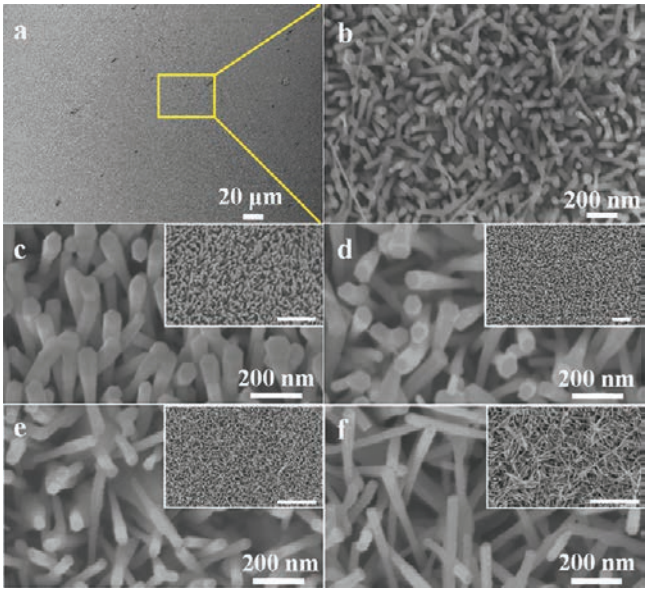

Figure 4. SEM images of ZnO NW arrays grown on Kapton film. (b) An enlarged image of the box area in (a). The growth temperatures for samples shown in panels (c), (d), (e), and (f) are 460, 450, 435, and 420 °C, respectively. The scale bar in (c)−(f) is 1, 1, 2, and 2 μm, respectively.

size of ZnO NWs will increase further too, which can be seen from Figure 3c,d. In general, the increase of holding time will

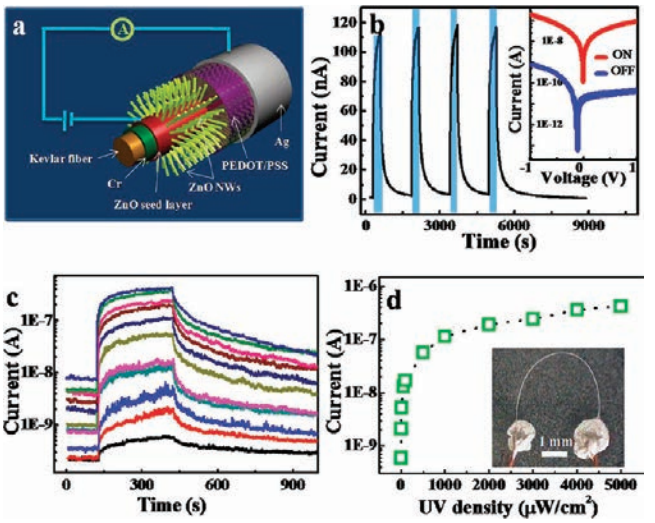

Figure 5. (a) Schematic diagram of UV sensor. (b) $I-t$ curves of UV response when UV light is on and off circularly. The inset shows $I-V$ curves under UV illumination (above) and $I-V$ curves without UV illumination (below). (c) $I-t$ curves under 11 kinds of different UV intensity. UV illumination from the top to bottom is 1, 5, 10, 50, 100, 500, 1000, 2000, 3000, 4000, and 5000 μw/cm^2. (d) The curve of response current with the increase of UV intensity. The inset is a bended fiber-based UV sensor like character "U".

make ZnO NWs grow more thicker and longer (Figure 3e,f) because ZnO molecules can continually deposit on them.

Figure 4 shows a 23 mm × 3 mm Kapton film grown with vertically aligned ZnO NWs. As shown in Figure 4a,b, NWs are uniformly and vertical to the film. The average diameter and length of NWs are 65 and 800 nm, respectively. Figure 4c−f shows ZnO NWs grown at temperature of 460, 450, 435, and 420 °C, respectively. Uniformity, vertical orientation, and diameter increase with the increase of temperature.

Kevlar fiber grown with ZnO NWs is very flexible, which makes it suitable for flexible devices. The uniform NW array shown in Figure 2d is used to fabricate a fiber-based UV sensor. Figure 5a is the schematic diagram of a fiber-based UV sensor. P-type conductive polymer PEDOT/PSS is used to form an internal electric field with ZnO NWs to speed up the UV response. The inset in Figure 5b shows $I-V$ curves of the UV sensor under UV light on and off. Schottky type IV curve under UV off depicts the formation of internal electric field between PEDOT/PSS and ZnO NWs. Time-dependent UV response is measured with 5 min UV illumination and 21 min without UV illumination. UV light intensity is 11mW/cm^2, and the applied voltage is 1 V. When UV light is turned on, the current increases from the dark current of 22 pA to 119 nA quickly, which displays a high on/off current ratio of 5400 (Figure 4b). Simultaneously, the flexible sensor shows good repeatability with UV light on and off. To study if the sensor can quantificationally detect the UV illumination, its response for different intensity UV illumination was measured (Figure 5c). When increasing UV light from 1 to 5000 μw/cm^2, the corresponding response current can be distinguished clearly, and from the response current, we can know the intensity of UV illumination (Figure 5d). To detect the flexibility of this fiber-based UV sensor, it was bent into the character like "U" as shown in the inset of Figure 5d. Even under bending status, it can detect

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UV light quantificationally. This means the fiber-based UV sensor has very good flexibility.

CONCLUSIONS

In summary, we have synthesized ZnO NW arrays on different polymer substrates via the CVD method. They have good crystallinity and flexibility, which makes them favorable for flexible and wearable electric devices. On the basis of these merits, the Kevlar fiber/ZnO NW array hybrid structure is used to fabricate a flexible UV sensor with high UV detection performance. The fiber-based sensor can precisely detect UV illumination with high on/off current ratio.

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