Journal of
Nanoscience and Nanotechnology
Vol. 11, 1–6, 2011

Growth of High-Aspect Ratio Horizontally-Aligned ZnO Nanowire Arrays

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A method of fabricating horizontally-aligned zinc-oxide (ZnO) nanowire (NW) arrays with full control over the width and length is demonstrated. SEM images reveal the hexagonal structure typical of zinc oxide NWs. Arrays of high-aspect ratio horizontal ZnO NWs are fabricated by making use of the lateral overgrowth from dot patterns created by electron beam lithography (EBL). An array of patterned wires are lifted off and transferred to a flexible PDMS substrate with possible applications in several key nanotechnology areas.

Keywords: Nanowire, Zinc Oxide, High-Aspect Ratio, PDMS, E-Beam Lithography, Horizontally-Aligned, Patterning.

RESEARCH ARTICLE

1. INTRODUCTION

ZnO, a direct wide-band-gap (3.37 eV) semiconductor and one of the most important functional materials, has attracted a wide range of interest in science and technology because of its exciting potential applications in optoelectronic devices,[1] sensors,[2] field emission devices,[3] solar cells,[4] and nanogenerators.[5] High quality, single crystalline ZnO nanowires are most commonly synthesized at elevated temperatures of 450–900 °C by metal-organic chemical vapor deposition (MOCVD),[6] chemical vapor transport,[7] and pulsed laser deposition.[8] These methods can produce NWs with lengths of several microns, however, these wires are in random alignment and therefore difficult to integrate into functional nanodevices. Patterned arrangement of aligned NWs has been obtained by a variety of techniques,[9] including photolithography,[10] nanosphere lithography,[11] and electron-beam lithography (EBL).[12]

The growth of vertically-aligned ZnO nanowire arrays has been extensively studied on a variety of important substrates such as GaN, SiC,[13] Si14 and Al_2O_3[15] substrates. Several techniques have been used in an effort to arrange the NWs into a controlled patterned alignment to make it amenable for device integration purposes. Standard photolithography in conjunction with an insulating template has been used to define growth of vertically aligned ZnO nanowire (NW) arrays.[16] Micromolding technique was used to fabricating micropatterned ZnO nanorods over a large area of the preconfined seed layer.[17] Xu et al. used a combination of EBL and wet chemical methods to successfully pattern and grow an array of horizontally aligned ZnO NWs.[18]

As compared to the vertically grown NWs, there are relatively fewer reports of horizontally grown NWs, even though these NWs may lead to many potential applications in nanotechnology. Qin et al. developed a general method for growing lateral NWs using combined effect from a side-wall patterned ZnO seed layer and catalytically inactive Cr (or Sn) by hydrothermal decomposition.[19] Although, this technique can be applied to a wide range of substrate materials, the alignment of the horizontal NW was poor and there was evidence of vertical NW growth too. Conley et al.[20] used physical vapor deposition to form an electrically accessible horizontal ZnO nanobridges devices on silicon-on-insulator substrates. This also resulted in sparsely oriented NWs. Recently, Xu et al. demonstrated the growth of patterned multisegmented ZnO NW superstructures using EBL.[21] Alignment of ZnO nanorods in solution phase using electric field also resulted in disordered alignment. The alignment can be controlled to an extent by controlling the concentration of the NW solution.[22] Others have used metal-organic chemical vapor deposition to grow horizontal ZnO NW on amorphous substrates,[23] however in this case too, the orientation of the wires was random.

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 1533-4880/2011/11/001/006 doi:10.1166/jnn.2011.4210

Although, catalyst assisted MOCVD method is fast and relatively low cost method to fabricate ZnO NWs of well-controlled properties, the high temperature required in such processes often a limiting factor in terms of the range of material which can be used as substrates. Elevated temperature synthesis processes can negatively impact material properties as well. In this work, EBL and a hydrothermal growth method were used to grow horizontally-aligned ZnO NW arrays on the {2110} surface of a single-crystalline ZnO substrate. Low temperature solution growth as described in this paper permits the integration of a wider range of materials and is compatible with organic and flexible substrates. Slit and dot patterns for growing horizontal ZnO NWs were produced by EBL. A hydrothermal method was used to grow high aspect ratio NWs by controlling the spacing of dot pattern and the dose value of the exposure during EBL writing process. In this paper, we have demonstrated full control over the length and width of horizontally grown ZnO nanowire arrays using a pattern created by EBL. The novel spacing of the dot pattern was used to create a very high aspect ratio NW array, with widths in sub-micron and nanometer range and length in millimeter range. Fabrication of a continuous high-aspect ratio NWs by EBL, without the use of an optimally spaced dot-pattern will utilize significant amount of expensive EBL time. The process described in this paper would save a lot of NW growth-time and can be scaled up easily by controlling the dot-spacing. We also showed that, these high-aspect ratio NWs can be lifted off and transferred to a flexible substrate such as PDMS, an insulating polymer. The ZnO substrate itself is brittle, not amenable to apply physical strains and is electrically conductive, which present a problem when it comes to device integration in applications such as flexible electronics, biological nano-generators. Transferring these arrays onto another insulating substrate is critical for fabricating NW integrated electronic devices. Extremely thin NWs (∼30 nm diameter)_aligned in a specific pattern were also grown.

2. EXPERIMENTAL DETAILS

The single crystal ZnO wafer {2110} or {0110} (MTI, California, US) was ultrasonicated consecutively in acetone, ethanol, IPA (isopropyl alcohol) and de-ionized water each for 10 minutes, then blew dry by nitrogen gas. The wafer was spun on a 100 nm thick layer of PMMA (polymethyl methacrylate, A2, Microchem, Molecular Weight −950,000) at a rotation speed of 6000 rotation per minute and baked on a hotplate at 180 C for 2 minutes. The pattern was defined by arrays of dots and slit pattern of different sizes with orientations along the {0001} direction of the wurtzite ZnO substrate. The area and dot dose used here was ranged from 260 μC/cm^2 to 360 μC/cm^2 and for dot dose ranged from 5 nAs-100 nAs with beam current −0.075 nA. Dosages and spacing between dots were optimized to get consistent results and these parameters were used for subsequent experiments. After electron beam exposure, the substrate was developed using a mixture of 1:1 (in volume) ratio of IPA and methyl isobutyl ketone (MIBK) for 30 sec. For the growth of NWs on the patterned substrate, 2.5 mmol/L aqueous solution of 1:1 ratio of zinc nitrate (Sigma–Aldrich) and water soluble HMTA (hexamethylenetetramine) (Sigma–Aldrich) were used as reagents. The substrates were floated on top of the growth solution such that the EBL patterned side faces the solution. The glass flask was kept at constant temperature of 90 °C for 5 hours and the process is carried out at atmospheric pressure. For the dot-pattern growth, PEI (branched, low molecular weight 4500, Aldrich) was added to the growth solution after 1 hour. The flask was cooled down to room temperature; the substrate was taken out of the growth solution and with IPA for 30 sec. The pH during all the experiments was maintained at 8. After the successful growth of NWs, E-beam resist was lifted-off and the as-grown horizontal ZnO nanowire arrays were characterized using LEO 1530 SEM.

3. RESULTS AND DISCUSSION

ZnO is a polar crystal, having positively charged Zn and negatively charged O surfaces resulting in a normal dipole moment and polarization along the *c*-axis. The basal O plane is negatively charged whereas the top Zn plane is positively charged, and the other planes are non-polar [{0100}, {0010} and {0110}—also known as {2110}]. The positive {0001} facet has the highest surface energy with fastest growth rate along the *c*-axis.[24, 25] Difference in growth velocities of various planes/facets gives rise to various crystal facets and will determine the final shape and aspect ratio of the ZnO crystal. The incoming molecules favorably adsorbed on the polar surfaces resulting in higher growth rate of the NW along {0001} and lower growth rates along low-energy, nonpolar surfaces. In hydrothermal solution growth, the NW size or width is controlled by the physical constraints (the dot or slit patterns created by EBL). If there is no physical pattern present, then the NW will grow in both vertical and horizontal directions. In presence of either dot or slit patterns, the NWs experience physical constraints of the patterns and grow accordingly. As the NWs grow out of the constraint slots, it can grow in any directions (both polar and nonpolar axis), however the growth is controlled by adsorption rates and the availability of precursors in the growth solution. ZnO NWs were grown using 0.4×2 μm^2 slits in PMMA, with the long axis parallel to the $\langle 0001 \rangle$ direction of the substrate. The growth kinetics favors NW growth parallel to the surface, along the *c*-axis ({0001} plane). With the slit approach, ZnO NWs were grown with a lateral expansion of the wires out of the photoresist slits.

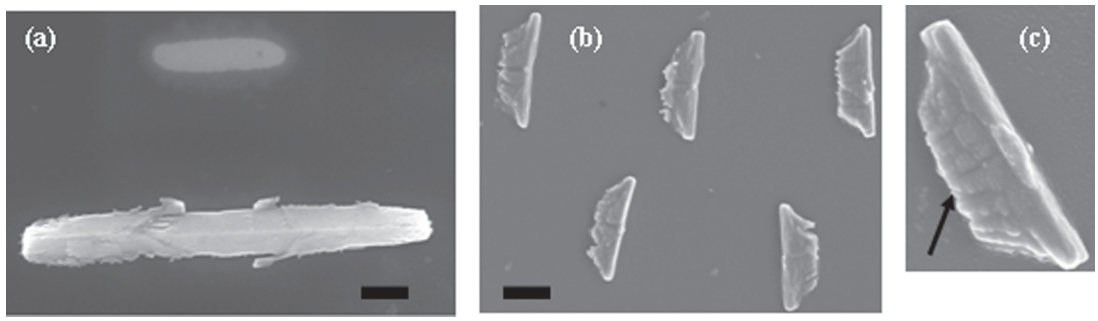

Fig. 1. Top view of zinc oxide NW grown horizontally on a substrate: (a) Top view of NW, also showing the slit defined by EBL (~400 nm × 2 μm), (b) Side view of an NW array (c) enlarged side view of a single NW grown from slit pattern. Black arrow shows the attachment area between the NW and the substrate. (Scale Bar: (a) 1 μm; (b) 4 μm).

The NWs are 8 μm long with width of 800 nm as shown in Figure 1(a), as determined by both physical confinement (slit) and growth rates and other variables such as temperature and growth time. ZnO {2110} wafers have high energy active sites along ⟨0001⟩ orientation. The slits parallel to {0001} orientation of the substrate resulted in fast growth of individual NWs.

For flexible electronics and hybrid nanodevice applications, it is important to lift-off horizontally grown NWs onto a flexible electrically insulating substrate. A PDMS casting method was used to detach arrays of ZnO NWs. Liquid PDMS was cured over a NW array and baked at 60 °C in an oven for 2 hours. After baking step, the PDMS polymer was detached from the substrate; however the lift-off process did not work. Use of shear force transferred few NWs onto the PDMS substrate as shown in Figure 1(b). Due to the shear force, the NWs were turned on their sides as illustrated in Figure 1(b). The increased surface area of contact between the substrate and the NW caused by the large slit written in the photoresist (black arrow in Fig. 1(c)) holds the NWs to the substrate. Therefore, the method of fabricating NWs using the slit approach will not be effective for applications which require transfer of large arrays of NWs onto various substrates. Instead of a slit pattern, a dot pattern was designed on the layout of the photoresist openings. After electron beam exposure, the substrate was developed and NWs were grown by a hydrothermal growth method using zinc nitrate and HMTA (hexamethylenetetramine).[26] ZnO NWs grow out of an array of dot patterns (~100 nm diameter) as illustrated in Figure 2(a).

PEI, a non-polar polymer and a cationic polyelectrolyte, which can be protonized over a range (pH 3–11) and positively charged, is often used to hinder radial or lateral growth of NWs in solution growth but allows axial growth of ZnO NWs. After the first hour of growth, low-molecular-weight poly(ethylenimine), PEI was added to the growth. The pH value of the growth solution in the present work is about 8, which allows protonization. When PEI is added to the solution, the positively charged PEI molecules adsorb on the non-polar lateral facets of the ZnO nanorods due to the electrostatic affinity, thus limiting lateral growth of NWs.[27] Although, addition of PEI increases the aspect ratio of the NWs, PEI also increases

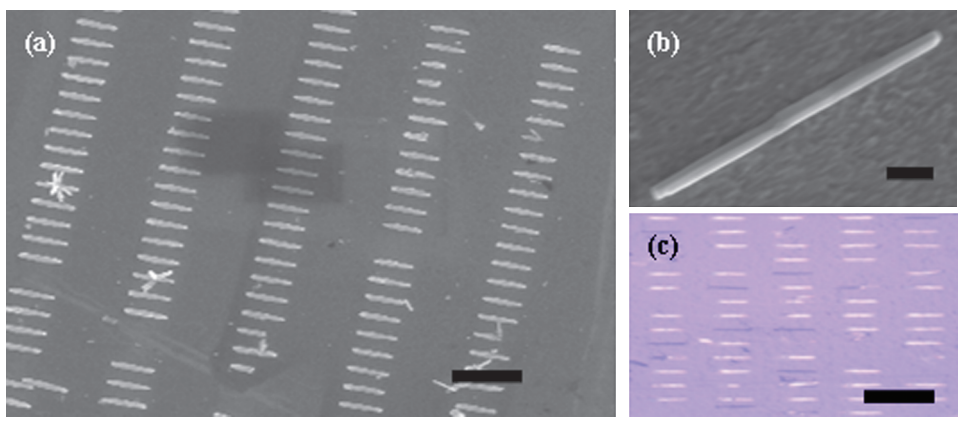

Fig. 2. (a) A dot pattern area (500 × 500 μm^2) was defined by arrays of dots (~100 nm diameter) made in the layout of the photoresist layer. The spacing between each dot row is 20 μm. SEM image shows an array of horizontally grown ZnO NWs on a {2 1 1 0} substrate (b) Uniform high aspect-ratio horizontally grown ZnO NWs. (c) Optical image shows an array of horizontally-grown NWs printed on a PDMS substrate. Most of the wires are able to detach from the ZnO substrate (white lines). (Scale Bar: (a) 10 μm; (b) 1 μm; (c) 10 μm).

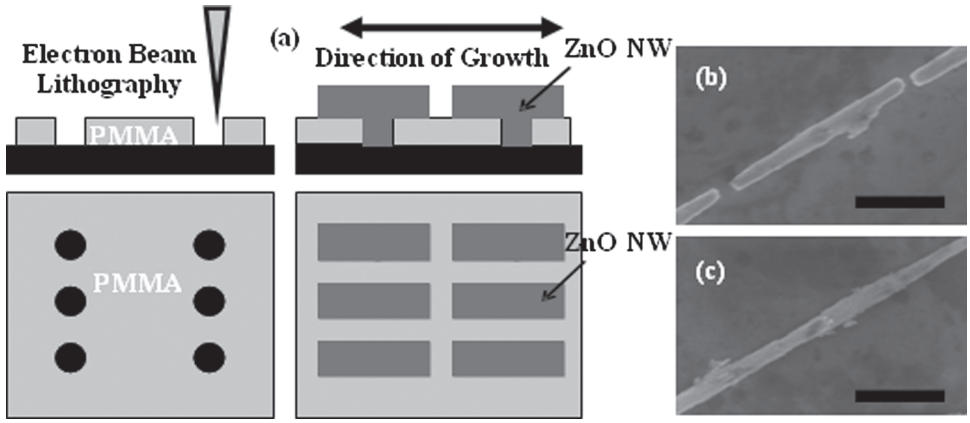

Fig. 3. (a) Schematic diagram of high-aspect ratio ZnO NW growth process (b) SEM image illustrating growth of ZnO NW from adjacent dot arrays exposed by EBL. (c) SEM image depicting the formation of a single high aspect ratio ZnO NW due to merging of adjacent NWs. The spacing between the exposed dots is optimized to 3 μm. (Scale Bar: (a) 2 μm; (b) 2 μm).

the growth time. In this paper, we have kept the PEI concentration low to achieve a balance between minimized lateral growth and optimal growth time.

The as-grown horizontal ZnO NW arrays were characterized by using a LEO 1550 scanning electron microscope at 5 kV. NWs grown using PEI via the dot pattern method (using ~100 nm dots) were well defined and uniform NWs (Fig. 2(b)) compared to the slit growth (Fig. 1(a)). The typical dimensions of these NWs are about 200–300 nm diameter and about 8–10 μm in length. With the dot pattern approach, the area of attachment for each NW to the substrate is only a small area (~100 nm diameter). A PDMS casting method was used to lift-off ZnO NWs arrays. Figure 2(c) shows optical image of printed NW from an array of ZnO NWs attached to a substrate grown using a dot-pattern. White lines are ZnO NWs (~10 μm long) while black, blank spaces on the sample represent some of the wires which did not detach. The ability to print large arrays of NWs onto flexible substrate is an important requirement for printable electronics and other applications. This method can be also scaled up for future practical applications.

Schematic diagram in Figure 3(a) illustrates the strategy of fabrication periodic high-aspect ratio NW arrays. Figure 3(b) shows a SEM image of growth of NWs out of adjacent dots spaced 3 μm apart. As the NW grows, the adjacent wires merge into one another and form a single NW (Fig. 3(c)). The wires are essentially non-tapered, showing that radial film deposition on the wire does not compete with axial nanowire growth. By optimizing the dot spacing, the NWs can be merged into one another, to form arrays of high aspect ratio NWs. A dose test was used to determine the exact dose required for continuous NW growth for high-aspect ratio NWs using dot-spacing of 3 μm. The dose increases in the direction of the white dashed arrow as shown in Figure 4. The NWs initially grow out of the dot pattern and subsequently start growing horizontally along the {0001} orientation of the wafer. At lower dosage (~5 nAs), the dimensions of the dot are small thereby impeding the crystal growth. Inset in Figure 4(c) shows an array of white dots suggesting some amount of ZnO crystal growth but not quite able to sustain the growth due to the smaller dimensions of the dot patterns. As the dose is increased, the dimensions of the dots defined by EBL are large enough for successful growth of NWs. At a dosage of 64 nAs and beam current of 0.075 nA, the NWs are ~100 μm long (Fig. 4(b)). As the dose in increased (100 nAs), the width of the NWs increases, until they are large enough to merge into adjacent aligned wires, forming a thick slab of ZnO (Fig. 4(a)). In this experiment, we have shown that careful placement of the dot patterns result in horizontal growth of NWs from adjacent sites resulting in formation of very high aspect ratio NWs. These experiments also give us information about the manipulation and control over orientation of the photoresist openings relative to the substrate.

A nanomanipulator tip was used to investigate the structural features of high-aspect-ratio horizontally-grown NWs. The ZnO substrates with arrays of NWs grown

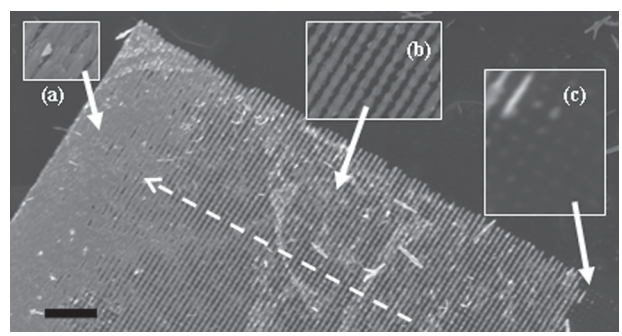

Fig. 4. Dose test to optimize the formation of high-aspect ratio NWs. Dose increases from 5 nAs to 100 nAs as shown by dashed white arrow. (a) Lower dose does not result in NW growth; (b) Intermediate dose result in formation of continuous ZnO NWs (~100 μm long); (c) Higher dose results in fusing of adjacent wires forming a ZnO slab. (Scale Bar: 10 μm).

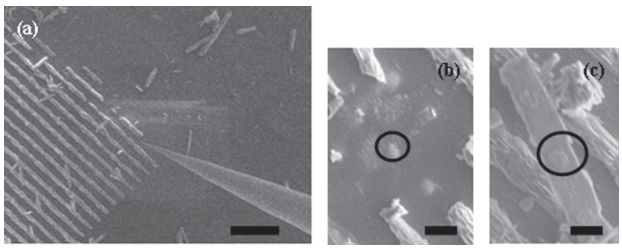

Fig. 5. (a) Tungsten tip of Zyvex nanomanipulator used for detaching high-aspect ratio NWs (b) White circular dots (∼100 nm) are attachment sites of individual NWs to the underlying substrate (schematically depicted by black circle) (c) Bottom side of a high-aspect ratio ZnO NW formed by fusing of 3 separate NWs. One of the circular stubs is represented by a black circle. Note: This pattern was grown without using low-molecular-weight poly(ethylenimine) PEI. (Scale Bar: (a) 10 μm; (b) 2 μm; (c) 2 μm).

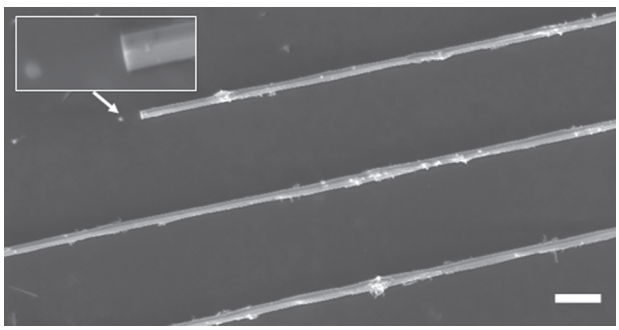

Fig. 6. Uniform arrays of ZnO NWs using hydrodermal growth having high-aspect ratio (Length > 50 μm) The c-axis is oriented parallel to the substrate, to foster horizontal growth of ZnO NWs. Inset: Careful control of the growth conditions resulted in ZnO nanowires with hexagonal cross section with a narrow diameter distribution. SEM image also shows a white circular dot (∼100 nm) which is the attachment site of a single NW. (Scale Bar: 5 μm).

in the absence of PEI, were mounted on an SEM stage and placed in an FEI Strata DB235 dual beam scanning electron microscope/focused ion beam (SEM/FIB) system equipped with a Zyvex S100 nanomanipulator. At the nanomanipultor's head, an electrochemically etched tungsten tip was mounted in order to probe the ZnO NW array. Each manipulator is designed to travel up to 50 mm with the accuracy of about 2 nm for three direction (x, y, z) movement. In the SEM mode, an array of ZnO NWs was identified (Fig. 5(a)). A tungsten probe in the manipulation system was driven to approach to a single NW. Using the fine movement mode of nanomanipulator, the tip apex was carefully brought to the end of a NW and pushed so as to dislodge the NW as shown in Figure 5(b). The SEM image shows circular white dots which are the attachments sites for the horizontally grown NWs. The underside of the same NW also shows 3 circular stubs which means that 3 adjacent NWs merged into one another during the crystal growth process to form a single NW (black circle shows one of the 3 attachment areas). NWs grown using a dot-pattern only have a small area attached to the underlying substrate thereby explaining the ease of detachment from the underlying substrate.

ZnO NWs growth using PEI and optimized dot patterns resulted in very well defined growth of high aspect ratio NWs as shown in Figure 6. The figure shows NWs more than 50 μm long with a hexagonal cross section, typically seen in ZnO NWs[28, 29] (Inset in Fig. 6). The diameter of these high aspect ratio NWs remain constant over the length of the >50 μm long NWs. Hexagonal cross section of the NWs implies that the c axis of ZnO NW is along its length direction.[29] SEM image also shows a white circular dot (∼100 nm) which is the attachment site of a single NW. In some of the growth studies involving spacing of 8–10 μm, we found growth of extremely thin NWs (diameter ∼30 nm) growing from the ends of the horizontally grown wires. Current efforts in our lab are towards investigating the growth mechanism and growth kinetics of these wires. Because of the anisotropic growth habits of the wurtzite ZnO NWs, these results should provide insight into the growth mechanics of these extremely thin NWs. To date, ZnO NWs of this dimension (∼20–30 nm diameters) have not been grown using low-temperature hydrothermal growth method. The well-placed array as shown in Figure 7 opens up possibilities to fabricate ZnO NW arrays for mechanical manipulation, nano-probes, force-sensing and nano-optical applications.

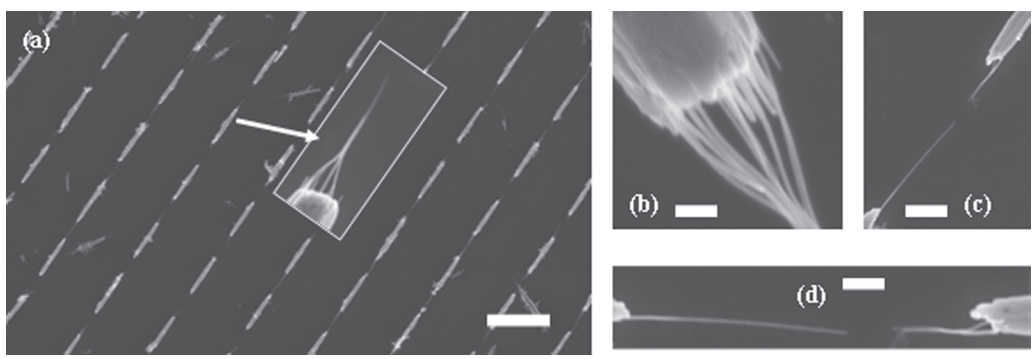

Fig. 7. Array of extremely thin ZnO NWs using hydrothermal growth technique. (Scale Bar: (a) 10 μm; (b) 0.3 μm; (c) 1 μm; (d) 1 μm).

4. CONCLUSION

We have demonstrated a simple and effective method for fabricating high-aspect ratio ZnO nanowire arrays using hydrothermal growth method and E-beam patterning. We were also able to transfer an array of NWs onto a PDMS flexible polymer substrate with applications in field of flexible electronics. Ordered array of extremely thin NWs ($\sim$20–40 μm) were also fabricated for potential applications in nanosensors.

Acknowledgment: The work is supported by grants to S. C. from the American Heart Association. We would also like to acknowledge the use of the core facilities in the Center for Nano- and Molecular Science and Technology at University of Texas at Austin.

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Received: 7 September 2010. Accepted: 17 December 2010.