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A General Approach for Fabricating Arc-Shaped Composite Nanowire Arrays by Pulsed Laser Deposition

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Here, a new method is demonstrated that uses sideways pulsed laser deposition to deliberately bend nanowires into a desired shape after growth and fabricate arc-shaped composite nanowire arrays of a wide range of nanomaterials. The starting nanowires can be ZnO, but the materials to be deposited can be metallic, semiconductor, or ceramic depending on the application. This method provides a general approach for rational fabrication of a wide range of side-by-side or "core–shell" nanowire arrays with controllable degree of bending and internal strain. Considering the ZnO is a piezoelectric and semiconductive material, its electrical properties change when deformed. This technique has potential applications in tunable electronics, optoelectronics, and piezotronics.

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1. Introduction

Controlling the shape of nanostructures is very useful for building nanometer-scale devices[1–4] and realizing special nanostructure-induced surface properties.[5–7] There are generally two approaches to create nanostructures with desired shapes. One is 'top down', which is the fabrication of nanostructures by cutting, etching, and milling bulk pieces of materials.[8] The other is 'bottom up', which is to grow nanostructures by using catalysis and/or templates. A lot of work has been done to grow useful nanomaterials with various morphologies such as nanowires,[9,10] nanotubes,[11] nanobelts,[12] nanohelices,[13] nanorings,[14] nano-tetrapods,[15] etc. However, further modification of the shapes of these nanomaterials post growth[7] is still a big challenge. In this paper, we demonstrate a new method that uses sideways pulsed laser deposition (PLD) to deliberately bend nanowires into a desired shape after growth and fabricate arc-shaped composite

2. Results and Discussion

To demonstrate the method of sideways PLD to deliberately bend nanowires, a starting nanostructure/template of patterned vertically aligned ZnO nanowires (Fig. 1B) was synthesized by e-beam lithography assisted wet chemical growth.[19] These nanowire arrays and target materials were mounted in a vacuum
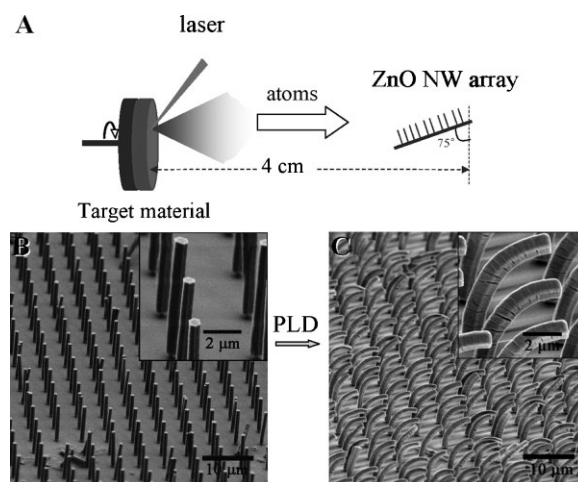
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Figure 1. A) Schematic of the experimental set up to fabricate the bent ZnO nanowires using PLD. B,C) Patterned ZnO nanowires before and after PLD deposition, respectively.
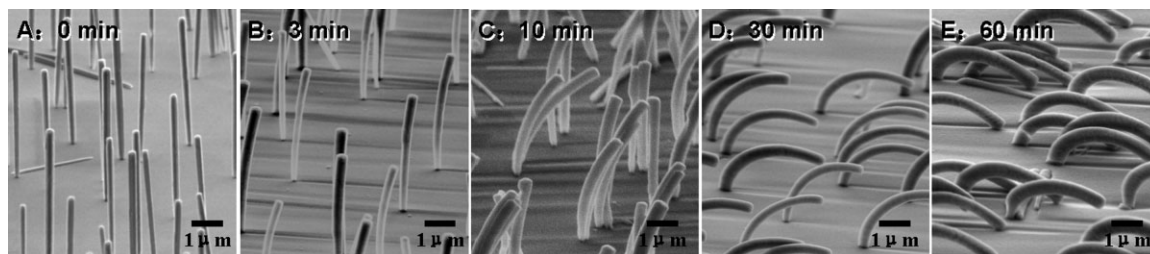
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Figure 2. ZnO nanowires after PLD deposition of a thin ZnO layer for different times, showing the induced bending shape of the nanowires.

chamber (pressure $< 1 \times 10^{-6}$ torr) as shown in Figure 1A. In this case, we used ZnO as the target material, which was ablated by a focused KrF excimer laser (wavelength $=248$ nm, energy per pulse $=100$ mJ, energy density $=10$ J cm^{-2}, repetition rate $=5$ Hz). After 1 h deposition, the nanowires were bent and became arc-shaped nanostructures as shown in Figure 1C. All of the nanowires are bent uniformly in the direction along which the deposition was made. The thick ZnO deposition resulted in the formation of cracks perpendicular to the nanowires, but the nanowires hold their shape without fracture.

The degree of bending can be controlled by adjusting the deposition time. Here, we used vertical ZnO nanowires as the starting nanostructure.[20] As shown in Figure 2, the degree of bending increased when the deposition time was extended. Eventually, the nanowires were so bent that the upper ends even touched the substrate.

The bent nanowires were observed by high-resolution transmission electron microscopy (TEM). The cracks that developed in the nanowire after depositing a thick layer of ZnO are visible (Fig. 3A). Bright-field and dark-field images reveal the build up of strains in the bent nanowires (Figs 3B and C).

The target materials can be any material that can be ablated by the laser, such as ZnS, GaN, Al$_2$O$_3$, Zn$_3$P$_2$, BaTiO$_3$, indium tin oxide (ITO), and Au (Fig. 5). All of them were found to be able to bend the ZnO nanowires. Under the same experimental conditions, the degree of bending introduced to the nanowires varies for different target materials (Fig. 5) because of the different nature of these materials. Among the targeted materials we have examined, ZnO, GaN, and ZnS appear to introduce the maximum degree of bending, which may be related to the similar wurtzite structure of the target material in reference to the template ZnO.
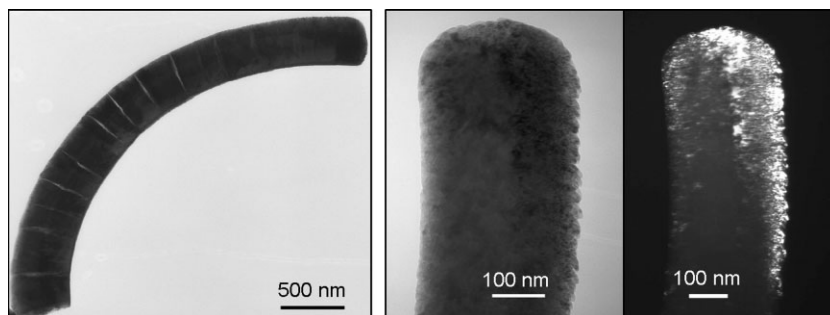
X-ray diffraction (XRD) was applied to examine the microstructural properties in the bent ZnO. A traditional θ–2θ scan of ZnO (0002) peak was processed at different sample tilt angles (Ω). For each Ω, the intensity, the position, and the width of the ZnO (0002) peak were recorded. Considering that the nanowires were bent (as observed in the scanning electron microscopy (SEM) images), different parts of the nanowires and the corresponding atomic planes along their length had different tilt angles with respect to the substrate surface. Signals can only come from the part in which the (0002) plane satisfies Bragg's law. When the ZnO (0002) peak was scanned at different Ω we were acquiring the diffraction from different parts of the bent nanowires. To make sure that we were studying signals from the original ZnO nanowires instead of signals from the polycrystalline deposited layer, we used ZnO nanowire arrays bent by GaN deposition as the test sample. The GaN deposition time was changed from 0 to 60 min, and the results are plotted in Figure 4.

With the increase of the deposition layer, the intensity of the ZnO (0002) peak shifts towards a negative tilt angle. This is statistical proof that the nanowires are bent in only one direction. The peak position shifted to lower angle, which means there was an average tensile strain in the original nanowires. The maximum of the strain was 0.167%. The width of the ZnO (0002) peak becomes larger after bending, which indicates the buildup of strain in the nanowires. The integral breadth of the diffraction peaks increase with Ω, which indicates the presence of a strain gradient along the bent wire.

Crack-free bent nanowires have also been achieved by simply using thinner nanowires, which tolerate a large degree of bending (Fig. 6).[21] Vertically aligned ZnO nanowires with a diameter of around 20 nm were made by topside PLD at relatively higher temperature and higher pressure.[22] These nanowires were then bent by sideway PLD deposition of ZnO and Al$_2$O$_3$, respectively. No cracks were observed using TEM (Fig. 6). By high resolution TEM, we can see that the original ZnO core remained single crystalline. Energy dispersive X-ray spectroscopy analysis showed that the chemical composition of the coated layer was the same as the target materials.

There are possibly two effects that contribute to the bending of the nanowires after PLD deposition. During the PLD process, target materials are ablated by focused high energy laser pulses and high energy atoms are released.[23] Perriere and Millon studied the velocity of zinc and oxygen ions in a
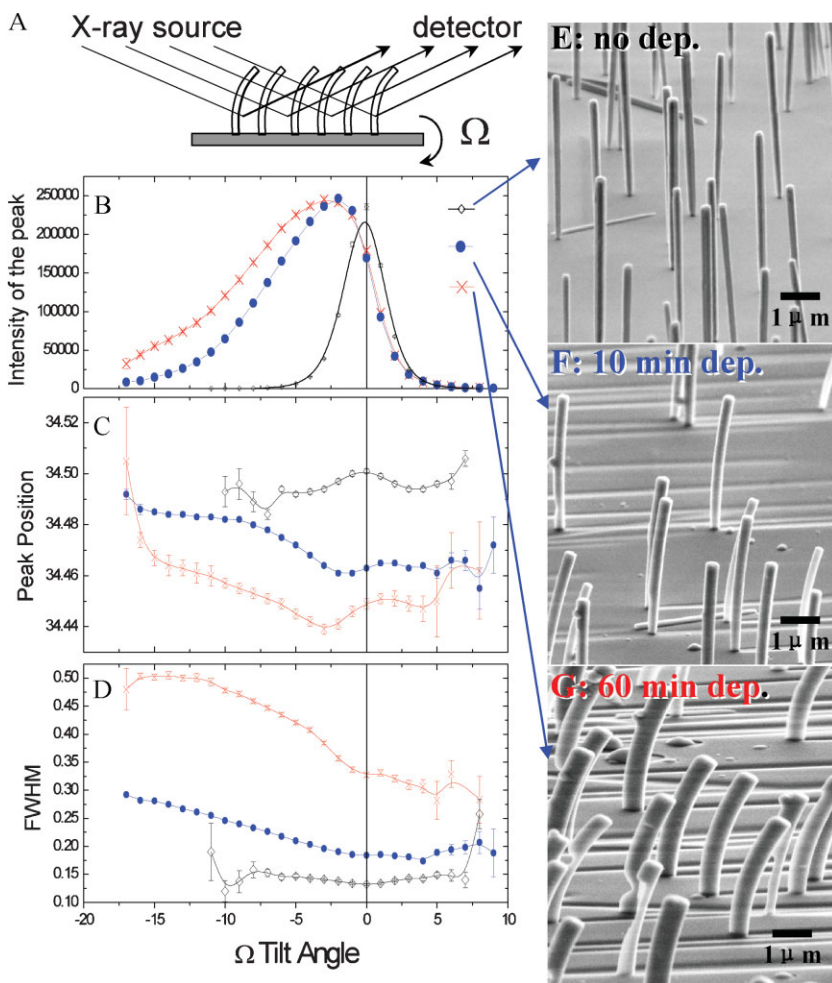

Figure 3. TEM images of a bent ZnO nanowire after deposition with ZnO showing the polycrystalline nature of the deposited material.

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Figure 4. X-ray diffraction analysis of the strain distribution along the length of the bent ZnO nanowires.

nanosecond laser ablation process under similar experimental conditions as used by us.[24] They concluded that the average velocity of the released atoms was around 5×10^3 m s^{-1}. However, the velocity of the leading 1% atoms was around 4×10^4 m s^{-1}. When these atoms hit on one side of the nanowires, their lateral impact creates a horizontal force on the nanowires, causing them to bend. As more material is deposited on one side, a hit-stick-hold process of the deposited atoms may create and hold the shape of the nanowires. Alternatively, the fastest atoms may penetrate into the nanowire and thus implant into the surface, which may induce strain on the stretched side of the nanowire.[25]

We can also see from Figure 5 that the degree of bending may also be influenced by the coherence of the material between the deposited layer and the original nanowire. This may be because similar materials have a stronger adhesive force between each other. Figure 7 helps to clarify this effect. For he two samples in Figure 7, one was with and one without the poly(methyl methacrylate) (PMMA) photoresist at the root during PLD. When PMMA was not removed, incoming atoms bombarded the organic molecules knocking them out of the surface, and some organic contaminants may adhere on the sidewalls of the nanowires. The adhesion between the newly deposited material and the original ZnO nanowire was strongly affected. Therefore, some parts of the deposited layer broke away from the original nanowires, and as a result the nanowires did not bend as much. For the sample without the PMMA layer, there was no organic contamination at the
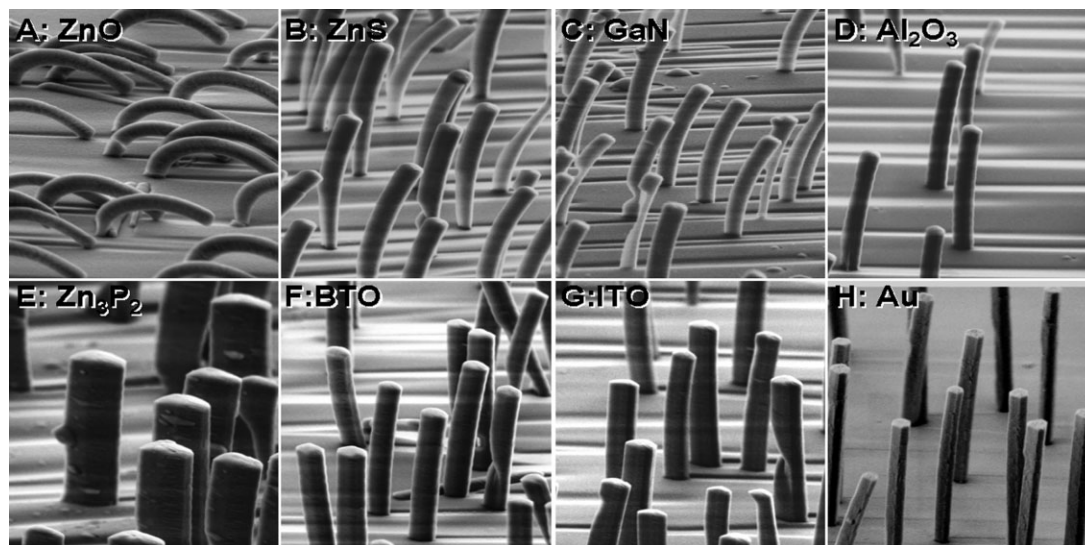

Figure 5. ZnO nanowires bent by various target materials as indicated, showing the universal application of the PLD method.

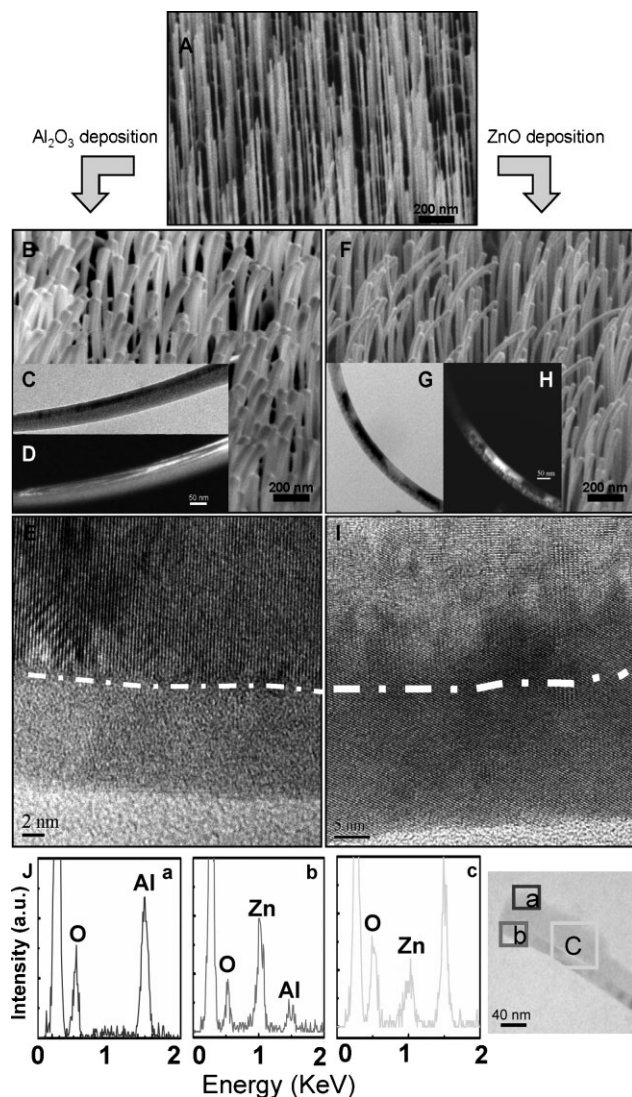**Final page numbers not assigned**

Figure 6. Crack-free PLD bent ZnO nanowires with small diameters. A) Original thin ZnO nanowires with high aspect ratio. B–E) SEM, bright field TEM, dark field TEM, and HRTEM images of Al_2O_3-coated thin ZnO nanowires, respectively. F–I) SEM, bright field TEM, dark field TEM, and HRTEM images of ZnO-coated thin ZnO nanowires, respectively. The dash-dot lines indicate the separation between the nanowires (upper part) and the PLD deposited material (lower part). J) EDS analysis of different parts of an Al_2O_3-coated ZnO nanowire, showing the local chemical compositions from the areas as marked in the inset TEM image.

nanowire surface during the PLD process; a strong adhesion and bonding of the newly deposited materials and the nanowires resulted in their bending.

3. Conclusions

In summary, we have developed a new method to fabricate arc-shape side-by-side composite nanowire arrays using pulsed laser deposition. The materials to be deposited on can be of any kind, but the degree of arc bending depends on the nature of the materials. The direction and degree of bending can be controlled by the
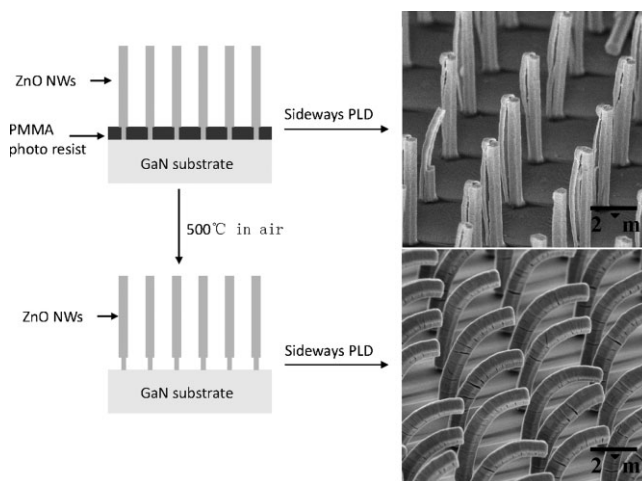

Figure 7. The influence of the presence of the PMMA layer at the root of the ZnO nanowires on the PLD deposition.

deposition time. Although the mechanism related to the shape deformation is not completely understood, the method demonstrated provides a general approach for nanomaterial manipulation and fabrication post growth. The technique can be generally utilized to control the shape and internal strain of nanowires, with potential applications for fabricating desired nanodevices.

4. Experimental

Chemical Synthesis of Patterned Vertical ZnO Nanowires: Patterned ZnO nanowires were synthesized by e-beam lithography (EBL)-assisted wet chemical growth. A PMMA photoresist was spin-coated on a GaN substrate and annealed at 180 °C for 1 min. EBL was used to make a 100 nm dot square array on the PMMA film. The substrate was then placed face down on a 2×10^{-3} M zinc nitrite and hexamethylenetetramine (HMTA) 1: 1 solution. Because of the surface tension, the substrate floats on the solution. The solution was then heated to 85 °C in a mechanical convection oven (model Yamato DKN400, Santa Clara, CA) and maintained at this temperature for 8 h. With the decomposition of HMTA and hydrolysis of zinc nitrate, ZnO nanowires were grown vertically from the dots made by EBL. After the growth of the nanowires, these arrays were annealed in air at 500 °C for 5 h to remove the organic PMMA mask.

Chemical Synthesis of Randomly Aligned Vertical ZnO Nanowire Arrays: Ti (10 nm) and Au (50 nm) were sputtered on a cleaned Si (100) wafer consecutively to obtain a flat Au (111) textured surface as the substrate. The substrate was placed face down to float on a zinc nitrate and HMTA (1×10^{-3} M) 1: 1 aqueous solution at 70 °C for 24 h.

PLD Synthesis of Vertical Thin ZnO Nanowire Arrays: The nanowires with diameters of around 20 nm were prepared on a silicon substrate by a pulsed laser deposition (PLD) technique. The Si substrate was mounted vertically to the direction of the plume so that the deposition was from the topside. The growth temperature and pressure were 800 °C and 4.4 torr under an Ar atmosphere, respectively.

Sideway PLD Bending of Thin ZnO Nanowires: The thin nanowires were bent by Al_2O_3 and ZnO sideway PLD. The laser energy per pulse was 150 mJ. The frequency was 5 Hz. The deposition time was 1 min for Al_2O_3 and 5 min for ZnO.

Instruments and Measurements: A pulsed UV laser was emitted from a Coherent Complex 205 KrF excimer laser source. SEM was performed using a Leo 1550 scanning electron microscope at 5 kV. TEM and EDS results were obtained from a JEOL 4000EX and a Hitachi HF-2000. XRD

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results were obtained using a PAnalytical X'pert Pro MRD X-ray diffraction system.

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