

# Splendid One-Dimensional Nanostructures of Zinc Oxide: A New Nanomaterial Family for Nanotechnology

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Zinc oxide (ZnO) is a wide band gap (3.37 eV) semiconductor having a high electron–hole binding energy (60 meV) and important applications in electronics, optics, optoelectronics, lasers, and light-emitting diodes.<sup>1,2</sup> The piezoelectric and pyroelectric properties of ZnO make it a great candidate for sensors, transducers, energy generators, and photocatalysts for hydrogen production. ZnO is also a “green” material that is biocompatible, biodegradable, and nontoxic for medical applications and environmental science.<sup>3</sup>

Research in ZnO nanostructures was first inspired by the discovery of oxide nanobelts in 2001.<sup>4</sup> As for one-dimensional (1-D) nanostructures, ZnO has equal importance to silicon-based 1-D nanostructures, according to published articles in the literature (Figure 1), and it is playing an increasingly key role in developing nanoscience and nanotechnology. It is fair to state that carbon nanotubes, silicon nanowires, and ZnO nanowires/nanobelts are probably the most important 1-D nanomaterials in today’s research. One-dimensional nanostructures of ZnO can be synthesized by either physical vapor deposition methods at high temperature (500–600 °C) or chemical approaches at low temperature (~70 °C) on a wide range of substrates without using sophisticated or expensive equipment. Its diverse and versatile morphologies are probably greater than any material known today.

**Vapor–Solid Growth of Nanobelts and Polar Surface-Dominated Nanostructures.** Nanostructures of ZnO are one of the most splendid families of nanomaterials.<sup>5,6</sup> The wurtzite structure of ZnO is unique for its noncentral symmetry and the polar surfaces. The structure of ZnO can be described as a num-

ber of alternating planes composed of tetrahedrally coordinated O<sup>2-</sup> and Zn<sup>2+</sup> ions, stacked alternatively along the *c*-axis. The oppositely charged ions produce positively charged (0001)-Zn and negatively charged (000 $\bar{1}$ )-O polar surfaces, resulting in a normal dipole moment and spontaneous polarization along the *c*-axis as well as a divergence in surface energy. The electrostatic interaction energy and distinct chemical activities of the polar surfaces result in the formation of a wide range of nanostructures, such as nanosprings,<sup>7</sup> nanorings,<sup>8</sup> nanobows,<sup>9</sup> and nanohelices<sup>10</sup> (Figure 2).

Nanobelts and the unique nanostructures shown in Figure 2 for ZnO were grown using a vapor–solid process without introducing a metal catalyst.<sup>4</sup> Using a tube furnace and ZnO powder as a source material, heating the furnace to a peak temperature of 900–1300 °C results in the growth of nanobelts on a substrate placed in a temperature zone of 500–600 °C. For a nanobelt that is dominated by the polarized  $\pm(0001)$  facets, owing to the positive and negative ionic charges on the zinc- and oxygen-terminated  $\pm(0001)$  surfaces, respectively, spontaneous polarization is induced across the nanobelt thickness. As a result, a nanospring is formed by rolling up a single-crystal nanobelt (Figure 2a);<sup>7</sup> this phenomenon is attributed to being a consequence of minimizing the total energy contributed by spontaneous polarization and elasticity. Alternatively, a nanoring can be initiated by circular folding of a nanobelt so that the polar surfaces of opposite charges on the side surfaces can meet face-to-face (Figure 2b).<sup>8</sup> Coaxial and uniaxial loop-by-loop winding of the nanobelt forms a complete ring. Short-range chemical bonding

**ABSTRACT** Zinc oxide is a unique material that exhibits exceptional semiconducting, piezoelectric, and pyroelectric properties. Nanostructures of ZnO are equally as important as carbon nanotubes and silicon nanowires for nanotechnology and have great potential applications in nanoelectronics, optoelectronics, sensors, field emission, light-emitting diodes, photocatalysis, nanogenerators, and nanopiezotronics. Fundamental understanding about the growth of ZnO nanowires is of critical importance for controlling their size, composition, structure, and corresponding physical and chemical properties. The papers by She *et al.* and Ito *et al.* in this issue describe the controlled growth and field-emission properties of individual nanostructures, respectively. These studies provide new approaches and insight into the controlled growth and electrical properties of ZnO nanostructures.

See the accompanying Article by She *et al.* on p 2015, and by Ito *et al.* on p 2001.

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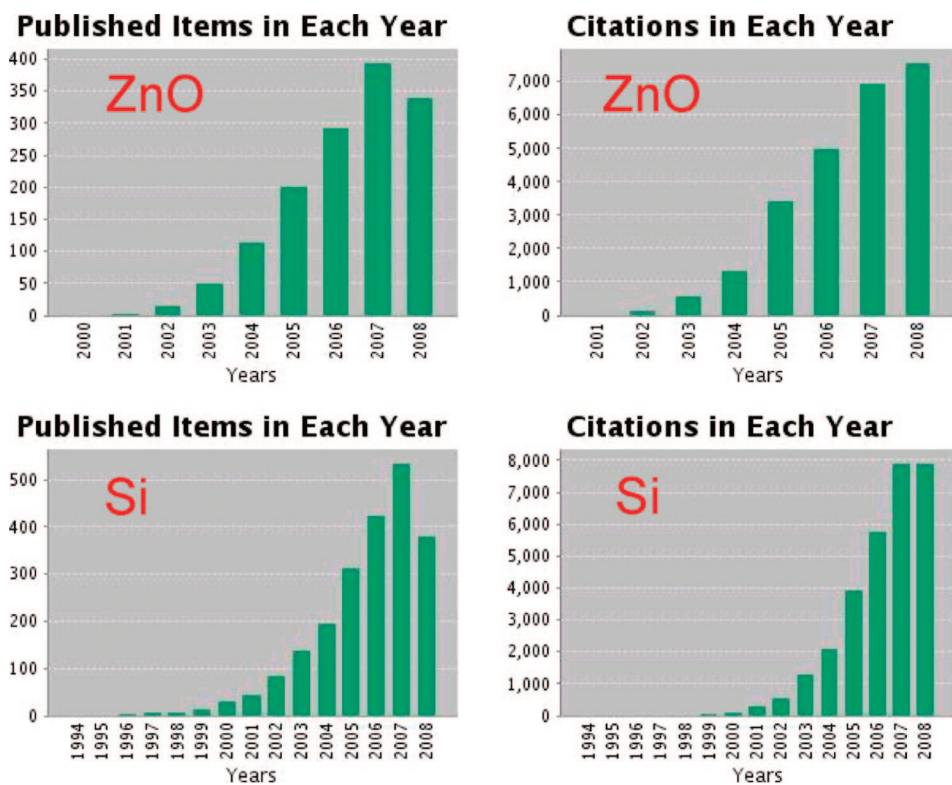


Figure 1. Publication statistics on one-dimensional nanostructures for (a) ZnO and (b) Si and their corresponding citation report. The data were compiled on September 20, 2008 through the database from Institute of Scientific Information using the following keywords that appear in the title, abstracts, and keywords: ZnO (or zinc oxide) vs Si (or silicon) together with nanowire, nanobelt, nanoribbon, nanorod, nanotip, nanoring, nanofiber, nanospring, nanohelix, nanoflower, or nanobrush.

among the loops results in a single-crystal structure. The self-coiling is likely to be driven by minimizing the energy contributed by polar charges, surface area, and elastic deformation.

A rigid helical structure of ZnO consisting of a superlattice-structured nanobelt has been formed spontaneously in a vapor–solid growth process for ZnO (Figure 2c).<sup>10</sup> The nanohelix

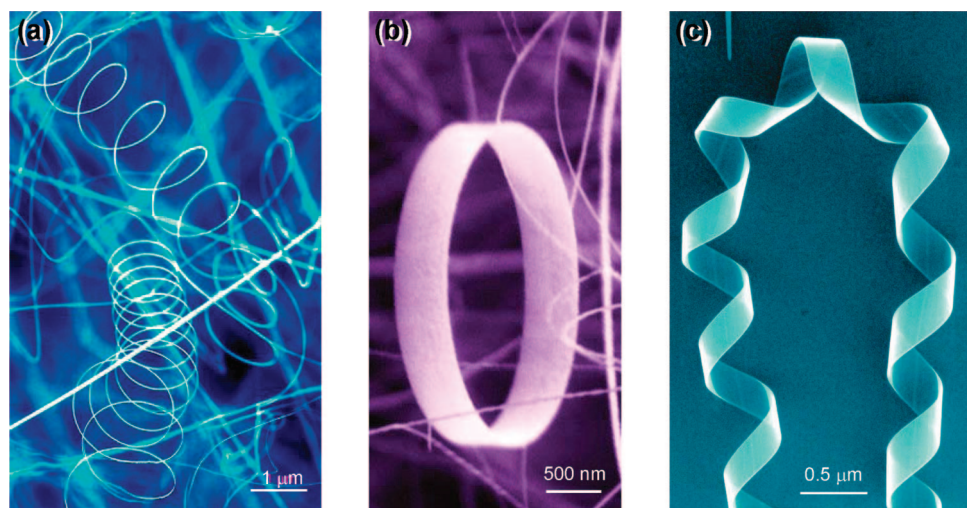


Figure 2. Polar-surface-induced formation of (a) nanospring, reprinted with permission from ref 5, copyright 2004 by Elsevier Ltd. ([www.materialstoday.com](http://www.materialstoday.com)), (b) nanoring, reprinted with permission from ref 8, copyright 2004 by AAAS ([www.sciencemag.org](http://www.sciencemag.org)), (c) nanohelix formed by a single-crystal ZnO nanobelt that is dominated by {0001} polar surfaces. Reprinted with permission from ref 28, copyright 2007 by MRS Bulletin ([www.mrs.org/bulletin](http://www.mrs.org/bulletin)).

was made of two types of alternating and periodically distributed long crystal stripes, which were oriented with their *c*-axes perpendicular to each other. Lattice strain between the crystal stripes may twist the nanobelt to coil along its growth direction, resulting in the formation of a nanohelix.

**Catalyst- or Seed-Assisted Growth of Patterned Nanowire Arrays.** Vertically aligned ZnO nanowires have a variety of astonishing applications in electronics, optoelectronic, and electromechanical nanodevices, such as solar cells,<sup>11</sup> field-emission devices,<sup>12</sup> UV lasers,<sup>13</sup> light-emitting diodes,<sup>14</sup> and piezo-nanogenerators.<sup>15–17</sup> Aligned growth of ZnO nanorods has been successfully achieved on solid substrates using vapor–liquid–solid (VLS) or vapor–solid–solid (VSS) processes with the use of Au nanoparticles as

catalysts,<sup>13,18</sup> in which the catalyst initiates and guides growth, and the epitaxial orientation relationship between the nanorods and the substrate leads to aligned growth.<sup>19</sup> The spatial distribution of the catalyst

particles determines the pattern of the nanowires grown. By choosing an optimum match between the substrate lattice and the nanowires to be grown, the epitaxial orientation relationship between the nanowire and the substrate results in the aligned growth of nanowires normal to the substrate. The distribution of the catalyst particles defines the locations of the nanowires, and the epitaxial growth on the substrate results in the vertical alignment.

The paper by Ito *et al.* reports a novel method for selective growth of vertical



Vertically aligned ZnO nanowires have a variety of astonishing applications in electronics, optoelectronic, and electromechanical nanodevices.

ZnO nanowire arrays using patterned Au nanoparticles *via* self-assembly.<sup>20</sup> First, a patterned ZnO seed layer was fabricated using lithography. Gold nanoparticles functionalized with a layer of phosphonic acid were synthesized with uniform size. Then, using the charge interactions on surfaces of the ZnO seed layer and the Au nanoparticles, a monolayer of self-assembled Au nanoparticles was selectively deposited on the areas covered by ZnO seeds. Growth using a VLS process at 900 °C peak temperature resulted in aligned nanowire arrays on the patterned areas. This growth technique is likely to produce nicely patterned structures on any inorganic substrate—regardless of whether it is crystalline or amorphous—for a wide range of applications such as sensors, field-emitting devices, and light-emitting devices.

The uniqueness of the work by Ito *et al.* is that it introduces an effective method for utilizing a self-assembled system that has the great potential of incorporating many different selective ligand–substrate interactions based on well-known surface chemistries. The methodology illustrated could be used to synthesize nanowire arrays of other materials *via* VLS processes.

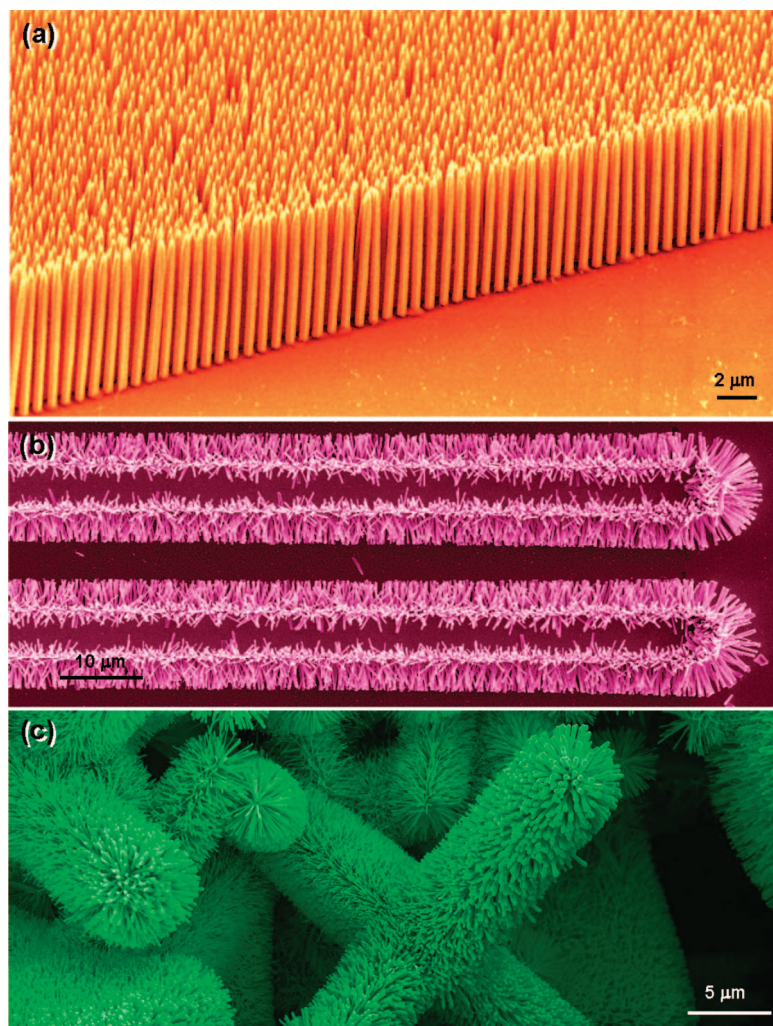


Figure 3. (a) Vertically aligned ZnO nanowire array grown on a GaN substrate *via* a chemical approach. Previously unpublished data. (b) Laterally aligned ZnO nanowire array grown *via* chemical approach on a general substrate as long as it is flat. Previously unpublished data. (c) Radially grown ZnO nanowires around fine wires using vapor–liquid–solid growth. Reprinted with permission from ref 22, copyright 2007 by Taylor & Francis Ltd. ([www.tandf.co.uk/journals](http://www.tandf.co.uk/journals)).

**Chemical Growth of Aligned Nanowire Arrays at Low Temperature.** To grow high-quality ZnO nanowire arrays, an approach that can meet the following three requirements is needed. First, the growth has to be at low temperature so that the nanowires can be integrated with general substrates. Second, the nanowires have to be grown following a designed pattern, with a high degree of control in size, orientation, dimensionality, uniformity, and possibly shape. Finally, the catalyst may need to be eliminated for integration with silicon-based technology. The nonepitaxial growth of ZnO nanowire arrays on Si wafers, for example, was assisted by a thin

film of polycrystalline ZnO seeds evaporated on the wafer followed by annealing. Electron-beam lithography was employed to generate a patterned mask, which was made of poly(methyl methacrylate) (PMMA), over the ZnO seed film. Hydrothermal growth was conducted in a solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and hexamethylenetetramine (HMTA) to grow ZnO nanowires (Figure 3a). This growth technique can be expanded to a general inorganic substrate that may or may not have an epitaxial orientation relationship with ZnO.

Laterally aligned ZnO nanowire arrays parallel to a substrate offer a potential benefit for fabricating in-

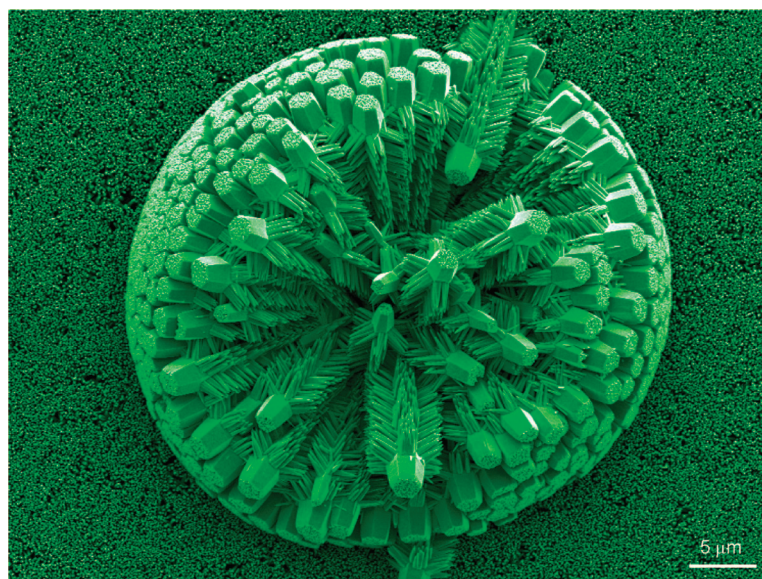


Figure 4. Hierarchical nanostructure of ZnO formed during the growth of nanowire arrays. Image courtesy of Dr. Jun Liu, Pacific Northwest National Laboratory).

tegrated nanodevice arrays. Taking advantage of the lattice match between ZnO and sapphire, Nikoobakhht *et al.* received ZnO nanowires grown from two sides of gold pads deposited on a sapphire substrate.<sup>21</sup> However, the growth temperature ( $\sim 900$  °C) and the choice of substrate are rather limited, which greatly restricts the integration of nanowires with silicon- or polymer-based devices. A general method has been developed to grow laterally aligned and patterned ZnO nanowire arrays on a general substrate as long as it is flat (Figure 3b). Orientation control is achieved using the combined effect from a ZnO seed layer and the catalytically inactive Cr layer for nanowire growth. The growth temperature ( $< 100$  °C) is so low that the method can be applied to a wide range of substrate materials that can be inorganic, organic, single crystal, polycrystalline, or amorphous. Finally, ZnO nanowires can be grown on any substrate of any shape. Figure 3c shows aligned nanowires grown radially around fine wires.<sup>22</sup> In some cases, spectacular hierarchical nanostructures can be formed (Figure 4).<sup>23</sup> ZnO has three fastest growth directions:  $\{0001\}$ ,  $\langle 1_{\bar{1}}00 \rangle$ , and  $\langle 2_{\bar{1}}\bar{1}0 \rangle$  and the corresponding facets. The struc-

ture shown in Figure 4 is a combination of these fastest growth directions following the six-fold symmetry around the *c*-axis and the formation of the following facets:  $\{0001\}$  at the top,  $\{1\bar{1}00\}$  and  $\{2\bar{1}\bar{1}0\}$  facets at the sides.

Fundamental understanding of the physical properties of 1-D nanostructures is important for technological advances. Due to the diversity in morphologies and structures, the properties of individual nanostructures can have large variations. In order to correlate the structure with performance directly, *in situ* measurements of the properties of a single nanostructure are essential. Techniques have been demonstrated for characterizing the mechanical,<sup>24</sup> electrical,<sup>25</sup> and field-emission<sup>26</sup> properties of 1-D nanostructures. In the paper by She *et al.*,<sup>27</sup> electrical conduction and field-emission measurements were performed on individual ZnO 1-D nanostructures of three shapes: an agave-like structure with a tip shape, a hierarchical structure consisting of a nanowire on the top and a microcolumn at the bottom, and a pencil-like structure with a sharp tip on a thick trunk. They used a metal ball to contact a single nanostructure to first characterize the total resistance of the system. By ig-

oring the contact resistance between the metal ball and the tip and with considering the observed dimensionality and geometrical shape, they calculated the conductivity of the ZnO nanostructure based on the measured resistance. This type of calculation assumes the transport was quasi-ohmic.

Then, She *et al.* separated the ball from the nanostructure and kept both at a specific distance and measured the corresponding field-emission properties of the nanostructure. The conductivity, field-emission properties, and vacuum breakdown behavior for each type of nanostructure was specifically investigated *in situ*. They found that, in the same type of 1-D ZnO nanostructure, emitters with lower resistance exhibited better field-emission performance. The vacuum breakdown event might be initiated at a local position where local resistance was highest. They concluded that the conductivity is a very important factor affecting the field-emission properties. Such a study provides a direct correlation between the field-emission performance and the electrical conductance of the nanostructures. A key conclusion is that, in addition to the uniformity and shapes of the nanostructures that affect the field-emission properties, a local fluctuation in conductance is also important. Such a conclusion can greatly impact the applications of carbon nanotubes for field-emission because some graphitic shells are metallic and some are semiconducting, depending on their chiralities.

**Outlook.** ZnO nanostructures have equal importance to carbon nanotubes and silicon nanowires for nanotechnology. Growth of high-quality ZnO nanowire arrays and knowledge of their physical properties are fundamental for their applications as sensors, field emitters, light-emitting diodes, photocatalysts, nanogenerators, and nanopiezotronics. Near-term research in ZnO nanostructures is likely to address the following:



Future applications and nanomanufacturing will strongly rely on designed growth with control of the location, orientation, distribution, and uniformity of nanowires.

1. *Fundamental understanding of growth kinetics.* Growth of 1-D nanostructures is a thermodynamically nonequilibrium process, and it is controlled by kinetics, but growth kinetics are rather complex. A solid understanding on growth kinetics is essential for controlling the growth process.
2. *Structurally, morphologically, and dimensionally controlled synthesis.* For large-scale integration, we need nanostructures that have uniform dimensionality and well-defined morphology. Property control is possible only if structural control is achieved. Techniques are required to grow the designed structure with superior controllability in size, size distribution, shape, crystal structure, defect distribution, and even surface structure.
3. *Large-scale, low-cost, patterned, and designed growth as well as self-organization.* Future applications and nanomanufacturing will strongly rely on designed growth with control of the location, orientation, distribution, and uniformity of nanowires.
4. *Fundamental study of the properties of individual nanostructures in correlation with their corresponding crystal, chemical, and surface structures.* Studies of nanowires have been focused

mainly on the sizes of the nanowires, but with little attention to the surface structures of the nanowires, such as crystallographic planes, sizes of facets, and surface reconstructions. The surface science in nanowire/nanostructure studies is likely to be important for understanding their physical and chemical performance.

5. *Fabrication, characterization, and integration of arrays of devices made using aligned nanowire arrays.* Numerous studies have demonstrated using individual nanowires as nanodevices. The future will employ arrays of devices with distinct properties and performances.

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