Aligned Ultralong ZnO Nanobelts and Their Enhanced Field Emission**

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One-dimensional (1D) semiconducting nanoscale materials have attracted considerable attention because of their importance in understanding the fundamental properties of low dimensionality in materials as well as in nanodevice applications. Many methods, including vapor–liquid–solid (VLS),[1] vapor–solid (VS),[2] and solution-based, have been developed to synthesize 1D semiconducting nanoscale materials such as nanoscale wires,[3–11] belts,[12–16] rods,[17,18] tubes,[19–22] and needles.[23,24] Usually, these methods require templates/catalysts and tedious operational procedures.

Here, we demonstrate a new strategy for the growth of aligned ultralong ZnO nanobelts, yielding an average length of 3.3 mm and widths up to 6 μm, on metal substrates in a one-step process via molten-salt-assisted template-free thermal evaporation. These ultralong nanobelts show enhanced field emission. The electric field for an emission current density of 1 mA cm–2 is 2.9 V μm–1, the lowest value ever reported for pure 1D ZnO nanostructures grown on flat surfaces, corresponding to a field-enhancement factor of about 1.4 × 10⁴. This approach is simple, efficient, and inexpensive, which significantly facilitates device fabrication.

By combining a general molten-salt process,[25] which is usually used to prepare micrometer-scale ceramic powders (although it was also used for the synthesis of ZnO nanorods[26] in a thermal evaporation process[16]), we have designed a new approach, molten-salt-assisted thermal evaporation, and we demonstrate that this approach can produce aligned ultralong ZnO nanobelts over a large area. The key point of this new approach is the evaporation of Zn metal powder in a liquid environment of molten sodium chloride (NaCl) salt.

A side-view camera photograph of the as-grown ZnO nanobelts on the Au substrate is shown in Figure 1a, indicating that the nanobelts can grow to several millimeters in length. Figure 1b shows a top-view optical microscopy photograph, demonstrating that the ZnO nanobelts are also transparent under an optical microscope. A higher-magnification optical microscopy image of the side-view is shown in Figure 1c, indicating nominal, though imperfect, alignment.

Figure 2 shows field-emission scanning electron microscopy (SEM) images of the as-grown ZnO nanobelts under different magnifications. The low-magnification image shown in Figure 2a indicates the alignment and length of 3.3 mm.
ure 2a indicates that the as-grown product exhibits a beltlike structure. High magnification, shown in Figure 2b, indicates that the width of the belts is up to 6 µm.

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were used to further characterize the microstructure of the as-grown ZnO nanobelts. Figure 3a shows a typical TEM image of a single belt. Although the width of the belt is about 5 µm, it is transparent to the electron beam, since the copper grid pattern below the belt can be clearly seen, meaning that the belt is very thin. The ripplelike contrast, resulting from strain and possibly small thickness variations, is clearly seen in Figure 3b. Figure 3c shows a TEM image of an individual belt used for selected area electron diffraction (SAED) and HRTEM. The rectangular SAED spot pattern (inset in Fig. 3c) can be indexed based on a hexagonal wurtzite cell with lattice parameters $a = 3.25$ Å and $c = 5.21$ Å (Joint Committee on Powder Diffraction Standards (JCPDS) No. 36-1451). Figure 3d shows a HRTEM image of the belt shown in Figure 3c. The clear lattice fringes demonstrate that the nanobelt is highly crystallized. The spacing of 0.52 nm corresponds to the (0001) planes of ZnO. Figure 3d shows that the (0001) planes are not perpendicular to the axis of the nanobelt, indicating that the growth direction of the nanobelt is not along [0001]. A detailed study of the SAED pattern indicates that the nanobelt grows along [01$\bar{1}$4], with its top/bottom surface $\pm$ (2$\bar{1}$10) and the side surfaces $\pm$(022$\bar{1}$).

The TEM observations reveal that there are no spherical droplets at the tips of the ZnO nanobelts, indicating that the nanobelts prepared via our current technique do not follow the VLS mechanism\textsuperscript{[1]} but the VS mechanism.\textsuperscript{[2]} Our experi-
ments indicate that a favorable molten-salt (NaCl) environment is essential for the formation of ZnO nanobelts. When the Zn metal powder is heated in the absence of molten NaCl, oxidation of Zn into ZnO happens very quickly so bulk ZnO forms instead of nanobelts. However, when the Zn metal powder is heated in the presence of molten NaCl, large quantities of ZnO nanobelts form because of the protection of NaCl on Zn, preventing Zn from oxidizing. The surfactant NP-9 (nonylphenol polyethylene glycol ether, chemical formula C₉H₁₉C₆H₄(OCH₂CH₂)₉OH) also plays an important role in the formation of the ZnO nanobelts, which we speculate to be as follows: First, by grinding Zn powder with NaCl in the presence of NP-9, the particle size of NaCl could be decreased, which may slightly lower the melting point of NaCl (below 800 °C). Second, burning NP-9 during heating increases the system temperature instantaneously to a value much higher than the melting point of NaCl, which liquifies in a very short time, completely dispersing all the Zn particles into the liquid. As soon as the liquid is formed, Zn starts to vaporize and deposits onto the Au sheet to nucleate ZnO with the help of oxygen in the air environment. Once the initial nucleation starts, epitaxial growth follows to form the nanobelts via a VS mechanism. Since the experiments were carried out in an open-atmosphere environment, Zn vaporizes continuously out of the molten NaCl to keep the growth going during the whole heating process, so that millimeter lengths can be achieved.

In principle, 1D ZnO nanostructures are very good field emitters because of their favorable aspect ratios. Field-emission properties of the ZnO nanobelts were measured using a simple planar diode configuration. The anode was a molybdenum disk with a diameter of 3 mm, and the gap between the tip of the nanobelts and the anode was 230 μm. The vacuum was kept at about 1 × 10⁻⁶ Torr (1 Torr = 1.333 × 10² Pa) during measurements. A typical field-emission current density–applied field (J–F) curve is shown in Figure 4a. For the as-grown ZnO nanobelts, the turn-on electric field, i.e., the field required to produce an emission current density of 10 μA cm⁻², is 1.3 V μm⁻¹. An emission current density of 1 mA cm⁻² (the minimum to produce the luminance of 300 cd m⁻² for a video graphics array field-emission display with a typical high-voltage phosphor screen efficacy of 9 lm W⁻¹) was achieved at 2.9 V μm⁻¹. Figure 4b shows the Fowler–Nordheim plot for the nanobelts, which fits well to the linear relationship given by

\[
\log(J/F^2) = \log(A \gamma^2/\phi) - B \phi^{3/2}/F \tag{1}
\]

where \( A = 1.54 \times 10^{-6} \) A eV V⁻², \( B = 6.83 \times 10^{3} \) eV⁻³/² μm⁻¹, \( \gamma \) is the field-enhancement factor, and \( \phi \) is the work function of the emitting materials.\[25\]

Our previous work has demonstrated that the field-emission performance of ZnO nanowires can be significantly enhanced by increasing the field-enhancement factor via either decreasing the area density of the nanowires, annealing with \( \text{H}_2 \)[27] or changing the geometry configuration (ZnO nanowires grown on carbon cloth).[26,29] It is generally accepted that the intrinsic field enhancement of an individual nanowire is approximately proportional to the aspect ratio \( l/r \), where \( l \) and \( r \) are the length and radius of the nanowire, respectively. In our present work, the average length of the ZnO nanobelts is 3.3 mm, and the thickness of the belts is in the scale of nanometers. Therefore, the as-grown ZnO nanobelts have a very high field-enhancement factor in the range of \( 10^4 \)–\( 10^5 \), which was confirmed by calculating the field-enhancement factor \( \gamma \) of \( 1.4 \times 10^4 \) from the slope of the straight line in Figure 4b, assuming \( \phi = 5.3 \) eV for ZnO. Thus, we believe that the enhanced field emission of the aligned ultralong ZnO nanobelts is the result of their high field-enhancement factor.

In summary, the lowest electric field (2.9 V μm⁻¹) for an emission current density of 1 mA cm⁻² due to the high field-enhancement factor (\( 1.4 \times 10^4 \)) indicates that field emission can be enhanced by increasing the length of 1D ZnO nanostructures. These long nanobelts may be very attractive for commercial applications as electron sources, and may also have impact in applications in electrical devices, microelectromechanical systems, and sensors.
Experimental

In a typical synthesis, 1 g of metal Zn powder was mixed with 8 g of NaCl and 4 mL of NP-9 (nonylphenol polyethylene glycol ether, chemical formula C_{9}H_{19}C_{6}H_{4}(OCH_{2}CH_{2})_{9}OH) in an agate mortar, then ground for 30 min by hand. The ground mixture was loaded into an alumina crucible covered with a gold (Au) sheet leaving an opening (about 10%) for vapor release. The whole assembly was placed in a box furnace and heated at 800 °C for 2 h, then cooled to room temperature in air. Transparent, aligned ultralong ZnO nanobelts were obtained on the Au cover facing the vapor.

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