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COMMUNICATIONS

Published on Web 03/29/2003

Dendritic Nanowire Ultraviolet Laser Array

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Hierarchical assembly of nanoscale building blocks (nanocrystals, nanowires, and nanotubes) is a crucial step toward realization of functional nanosystems and represents a significant challenge in the field of nanoscale science.[1] In this regard, one can learn from nature where exquisite structures of highly organized matter[2,3] such as diatoms, sea urchins, dendrite spines, and ferns are routinely self-organized. Here we exploit the self-organized dendritic crystal growth[4] to assemble uniform semiconductor nanowires into highly ordered one-dimensional (1D) microscale arrays that resemble comb structures. The individual ZnO nanowires have uniform diameters ranging from 10 to 300 nm. They are evenly spaced on a stem with a regular periodicity of 0.1−2 μm. Under optical excitation, each individual ZnO nanowire serves as a Fabry−Perot optical cavity, and together they act as a highly ordered nanowire ultraviolet laser array.

By precisely controlling the oxide nanowire growth process developed in the Yang lab,[5,6] we were able to synthesize a high yield of microscale comblike structures made of periodic arrays of single-crystalline ZnO nanowires. The samples were synthesized within a chemical vapor transport and condensation system.[6] Zn powder was placed in an alumina boat as the Zn source. The boat was centered inside a quartz tube in the tube furnace. A clean Si (100) substrate was put on top of the alumina boat to collect the products. A 5−10% oxygen/argon mixture was used as the carrier gas. The flow rate was about 8−10 sccm. The reaction was kept at 800−900 °C for 10 min. After the reaction, the substrate was coated with a thin layer of white powder, consisting of over 90% comblike structures.

Figure 1A,B shows typical scanning electron microscopy (SEM) images of beautiful ZnO nanowire comb structures. Morphologically, they resemble *Todea barbara*, a unique type of King Ferns existing in the Canberra region. These nanowire branches have uniform diameters and are evenly distributed at one or both sides of the stem with a periodicity of 0.1−2 μm. The diameters of the nanowires range from 10 to 300 nm, and their lengths are 0.5−10 μm. X-ray diffraction (XRD) confirms the wurtzite structure of the entire comb structure. Additional structural characterization was carried out using transmission electron microscopy (TEM). Figure 1C shows a TEM image of such a 1D nanowire array. These hierarchically ordered nanowire arrays are monolithically single crystalline as evidenced by the selected electron diffraction pattern (Figure 1D) obtained on the comb structure. Figure 1E−H shows high-resolution TEM images taken in different areas (see Figure 1C) on this array. The lattice spacing of 2.56 ± 0.05 Å between adjacent lattice planes in each of these images corresponds to the distance between two (0002) crystal planes, confirming [0001] as the preferred growth direction for all ZnO nanowires and the monolithically single-crystalline nature of the entire comb structure. We note that the tips of each nanowire branch are atomically sharp (Figure 1E), raising the possibility of their use as scanning probe or sensor arrays. For relatively thick nanowire branches (diameter > 100 nm), each nanowire exhibits atomically flat end surfaces.

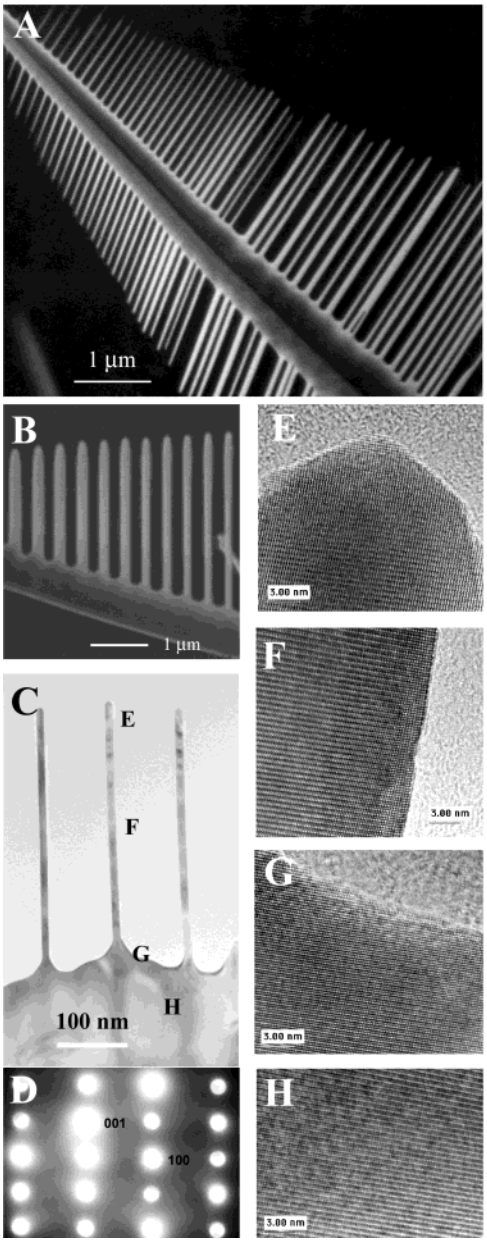

Figure 1. (A,B) Scanning electron microscope images of comb structures made of ZnO nanowires. (C) Transmission electron microscope image of an electron-transparent comb structure. (D) Electron diffraction pattern recorded on the entire comb structure in (C). (E−H) High-resolution TEM images recorded in different regions of the comb structure in (C).

Previously, there have been several reports on the generation of various morphologies within this interesting ZnO system, including,

10.1021/ja034327m CCC: $25.00

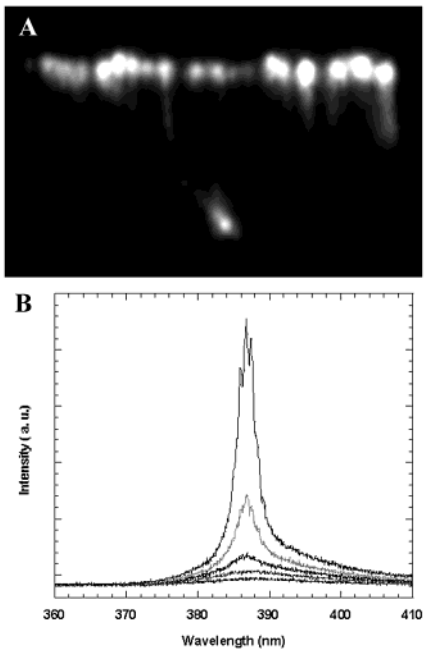

Figure 2. (A) Far-field optical image of spatially resolved light emission from individual nanowires of the comb structures. The spacing between the wires is ca. 1 μm. (B) Power-dependent emission spectra recorded on the comb structure. From bottom up, the excitation energy densities are 252, 505, 580, 707, 883 nJ/cm^2, respectively. Lasing behavior is evidenced by the appearance of sharp cavity modes in the top two traces.

for example, nanobridges, nanonails, tetrapods, ribbons, and webs.[7−11] The dendritic growth of nanowire arrays into microscale comb structures represents another important example of spontaneous organization of vapor molecular species into nanoscale wires and their microscale assemblies in one step. The appearance of dendritic crystals is fairly common in bulk crystal growth and usually results from rapid crystallization at large supersaturation.[4] It is, therefore, consistent with our current experimental process where the evaporation of zinc metal induces large supersaturation and fast condensation in an oxygen environment.

Despite the observation of these interesting hierarchically ordered structures, their optical properties have not been explored so far. Recently, UV lasing has been demonstrated by our groups for the ZnO and GaN nanowire systems.[5,7,12,13] In these earlier studies, the entire facetted nanowire (generally with diameter > 100 nm) serves both as gain medium and as the Fabry−Perot optical cavity. We took a similar strategy to examine the light emission from these ordered arrays.[14] The present nanowire array offers an excellent model system to study possible nanolaser interference, coupling, and other nonlinear collective effects.[15] Because of the spatial resolution of our current far-field optical imaging system (0.5−1 μm), we were not able to resolve the light emission from individual nanowire arrays with submicrometer spacing. We, therefore, examine the array with large nanowire spacing (1−2 μm) and large diameter (200−300 nm). In these cases, we successfully resolved the emission from individual nanowires (Figure 2). Each bright emission spot in Figure 2A corresponds to a single tip of the nanowire array. Figure 2B shows power-dependent photoluminescence spectra recorded on the comb structure. Clearly, at low excitation power, the structure displays broad emission near 385 nm, and these emissions are waveguided to the tips of each nanowire. Above an excitation threshold, amplified spontaneous emission was observed from these nanowire arrays. Sharp features centered at ~387 nm appear above the threshold (in this case, ~707 nJ/cm^2), indicating the onset of lasing emission. The integrated emission intensity also exhibits a superlinear increase above the threshold. It is noted that the lasing threshold for these comb structures is about 2−5 times higher than those obtained for individual nanowires and two-dimensional arrays.[5,13] The exact reason is not clear at this stage, but it might be related to the cavity length fluctuation between neighboring nanowires, the lack of second reflecting mirror surfaces, and other yet-to-be-explored nanolaser near-field coupling mechanisms.

In summary, we report here the self-organization of comb structures made of ordered arrays of ZnO nanowires that are monolithically single crystalline. Under optical excitation, an ultraviolet laser array was demonstrated for these comb structures. In addition, these nanowire arrays might have implications in other applications such as one-dimensional photonic crystals,[16] laser interference/coupling, nonlinear collective effects, and the nanometer electromechanical system (NEMS). The microscopic nature of these nanowire ensembles would also enable their facile manipulation into desired system architectures such as crossbar junction arrays.

Acknowledgment. This work was supported by the Camille and Henry Dreyfus Foundation, Beckman Foundation, and National Science Foundation (J.J., R.J.S., H.Y., P.Y.). P.Y. is an Alfred P. Sloan Research Fellow. Work at the Lawrence Berkeley National Laboratory was supported by the Office of Science, Basic Energy Sciences, Division of Materials Science of the U.S. Department of Energy. We thank the National Center of Electron Microscopy for the use of their facilities.

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(14) The optical studies were carried out on isolated comb structures.[12,13] The pulsed UV radiation is derived from the frequency-quadrupled output of an optical parametric amplifier (OPA). The OPA is seeded with regeneratively amplified light at 800 nm, from a home-built Ti:sapphire oscillator (88 MHz) and commercial regen/bowtie amplifier (1 kHz, 2.5 mJ). The UV pulses are approximately 100−200 fs in duration, with pulse energies of 2−3 μJ (photon density: $(1.3 \times 10^{17})-10^{18}$ cm^{-3}). The pulses are attenuated with a variable neutral density filter, and the UV is spectrally isolated using a black glass band-pass filter (Edmund, UG11). The samples have also been excited by the 266 nm laser (the fourth harmonic of Nd:YAG laser, Spectra Physics). The laser pulse is about 8 ns in duration, with a pulse energy of 2−4 mJ. The spatial resolution of the microscope is about 0.5−1 μm. A removable mirror redirects the emission to an optical fiber, which is routed to a spectrograph and CCD (Roper Scientific) used for spectra collection.
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JA034327M