

Ultraviolet amplified spontaneous emission from self-organized network of zinc oxide nanofibers

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Self-organized zinc oxide (ZnO) nanofiber network with six-fold symmetry was fabricated on ZnO-buffered (0001) sapphire substrate with patterned gold catalyst by vapor-phase transport method. From the ZnO buffer layer, hexagonal ZnO nanorods with identical in-plane structure grew epitaxially along [0001] orientation to form vertical stems. The nanofiber branches grew horizontally from six side-surfaces of the vertical stem along [0110] and other equivalent directions. The aligned network structure constructed a waveguide array with optical gain. Ultraviolet amplified spontaneous emission was observed along the side-branching nanofibers when the aligned ZnO network was excited by a frequency-tripled Nd:YAG laser. © 2005 American Institute of Physics. [DOI: 10.1063/1.1847716]

One-dimensional nanostructural materials have attracted great interest because of their unique properties and promising applications in electronics, photonics, and biochemistry. How to organize the nanostructural materials into functional nanodevices is the most critical issue faced by researchers. Lieber's group¹ has developed a fluidic alignment technology to assemble one-dimensional nanostructures. Electron beam lithography² and scanning probe microscopy³ have also been utilized to prepare the nanowires through the so-called top-down approach. Though various desired structures could be fabricated in principle through these advanced tools, the fabrication process is relatively slow and inconvenient. Self-assembly is an economic and convenient approach to fabricate nanostructural networks. So far, the alternative self-assembling approaches include diffusion-controlled aggregation,⁴ nanocluster⁵ and template-assisted growth,⁶ atomic adsorption along stress lines on flat surface,⁷ dealloying a chemical etched Al-Si thin film,⁸ surfactant-induced mesoscopic organization,⁹ and hydrogen/oxygen plasma exposure.¹⁰ Although various nanomaterials have been employed in the above-mentioned reports, all reported nanostructural networks were random.

In recent years, various nanostructural ZnO such as nanowires,¹¹ nanotubes,¹² nanoribbons,¹³ nanopins,¹⁴ and hierarchical nanorods^{15,16} have been fabricated. The aesthetic morphologies and its wide band gap and strong excitonic binding energy have triggered great interest in the nanoscience and nanotechnology based on ZnO. In this letter, we report a six-fold symmetric self-organized network of ZnO nanofiber fabricated on sapphire substrate through vapor-phase transport assisted by [0001]-oriented ZnO buffer layer and Au-patterned catalyst.

One promising application of ZnO is to be used as ultraviolet light source, such as UV light emitting diodes and laser diodes. In recent years, the UV laser of ZnO has been observed in powder, thin film and nanowire samples based on the positive feedback in random and Fabry-Perot cavities.¹⁷⁻¹⁹ The amplified spontaneous emission (ASE) has also been investigated in ZnO powders and patterned films with incoherent and coherent feedback in the gain media.^{20,21} In this letter, we shall also report observation of ASE from the aligned ZnO network.

Before preparation of ZnO network, a ZnO buffer layer was fabricated on (0001) sapphire by filtered cathodic vacuum arc technology.^{22,23} Using a copper grid with 400 mesh as the mask, a patterned array of thin gold film was prepared on the ZnO buffer layer by thermal evaporation. ZnO nanofiber network was fabricated on the patterned substrate by vapor-phase transport method.^{11,14} The growth was carried out in a quartz tube using a mixture of ZnO and graphite powders as source materials. The source temperature was 1100 °C and the growth temperature was about 700 °C. A white layer of product was observed on the collector after sintering for 30 mins.

Figure 1 shows the XRD patterns of the ZnO buffer layer and the nanofiber network. Only (0002) peak was observed from the ZnO thin film, which demonstrates that the ZnO buffer layer grows along [0001] direction with good crystal quality. The XRD spectrum illustrates multipeaks after the ZnO nanostructure was fabricated on the buffer layer. As indexed in Fig. 1, all diffraction peaks match the wurtzite ZnO structure with the lattice constants of $a=3.250$ Å and $c=5.207$ Å.

Figure 2(a) shows the scanning electron microscopy (SEM) image of the product. Due to the catalyst dominated position-selected growth, the surface was covered with patterned arrays of ZnO nanostructures corresponding to the inserted gold pattern [insert of Fig. 2(a)]. It is clearly seen that the nanofibers grow along six specific directions parallel to the substrate surface. The size of the nanofibers is about

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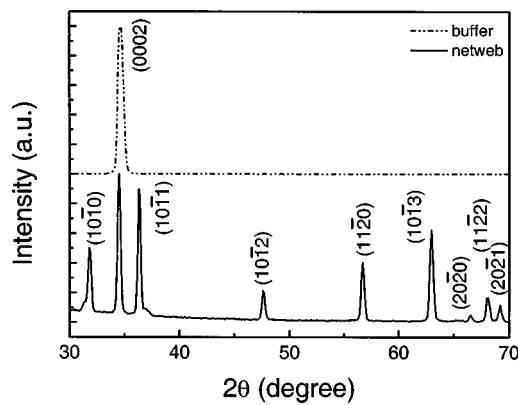


FIG. 1. XRD patterns of ZnO buffer layer and as-grown ZnO nanofiber network.

500–800 nm in diameter and several tens of microns in length. Each cell is composed of six-fold symmetric branches that interconnect adjacent cells to form a network with regular structure. Figure 2(b) shows the enlarged SEM image of the nanowhisker morphology corresponding to the center of a cell as circled in Fig. 2(a). Each whisker is composed of a stem with hexagonal cross section and several branches grown radially around the sides of the stem. It is noted that the stems are perpendicular to the substrate, and the branches from either the same or different stems are parallel to the substrate along the pre-defined six-fold symmetric directions as indicated by the arrows in Fig. 2(b).

Figures 2(c) and 2(d) show the high resolution transmission electron microscopy (HRTEM) images taken from different parts of a nanowhisker as inserted between Figs. 2(c) and 2(d). The lattice fringes of the stem with the d spacing of 0.26 nm match the interspacing of (0002) planes of the wurtzite ZnO, while the lattice fringes of the branch nanofiber with the d spacing of 0.28 nm coincide with the spacing of (0110) planes. These results demonstrate that the hexagonal nanorods grew epitaxially along [0001] direction from the ZnO buffer layer to form vertically aligned stems with hexagonal structure, and the branch nanofibers grew around the side surfaces along $\langle 01\bar{1}0 \rangle$ orientations to form a six-fold

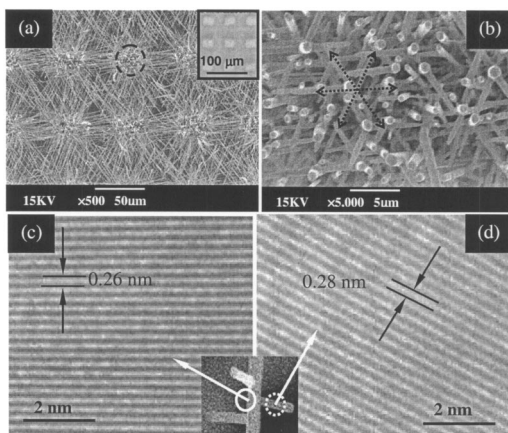


FIG. 2. SEM and HRTEM images of the ZnO network. (a) Six-fold symmetrically aligned ZnO array corresponding to the inserted gold pattern on ZnO buffer layer. (b) The enlarged SEM image of the center area of a cell circled in (a). The arrows drawn in (b) indicate the growth directions of the branches parallel to the substrate. (c) and (d) The HRTEM images taken from the inserted stem (left) and the branch (right), respectively.

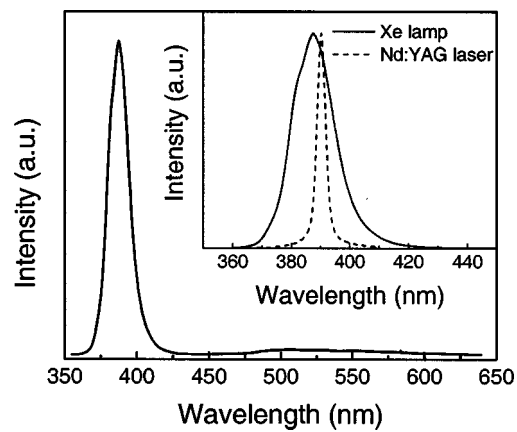


FIG. 3. PL spectra of the ZnO nanofiber network excited by 355 nm light from Xe lamp inserted with the normalized UV emission bands excited by 355 nm light from Xe lamp and 312 kW/cm² frequency-tripled Nd:YAG laser as light sources, respectively.

symmetric structure. The growth mechanism will be analyzed separately in another paper.

Figure 3 shows the PL spectrum of the ZnO network excited by 355 nm UV light selected from a Xe lamp. The PL spectrum contains a strong narrow UV band peaking at 386 nm and a very weak broad green band centered at about 520 nm. The UV emission is originated from excitonic recombination corresponding to the band-edge emission of ZnO and the green one is related to the defects in ZnO such as oxygen vacancies. Consistent with the results of XRD and HRTEM, the strong UV and weak green bands imply good crystal quality and low concentration of defects in the ZnO network. It is noted that the width of the UV emission band is narrowed dramatically when the sample was excited by a strong pulsed Nd:YAG laser (355 nm, 6 ns, and 10 Hz), as shown in the insert in Fig. 3, which was obtained in a configuration that the direction of the incident laser was along the stem fibers of the hierarchical structures (perpendicular to the substrate surface) and the PL signal was measured in the perpendicular directions around the stems (parallel to the side branches and substrate). It can be seen from Fig. 3 that the full width at the half maximum (FWHM) of the spontaneous UV emission band excited by the Xe lamp was about 17 nm. However, excited by a frequency-tripled Nd:YAG laser with a power of 312 kW/cm², an ASE process was obviously observed, which showed a narrowed UV spectrum with the FWHM of 3 nm.

In order to understand the ASE process in the network structures, we explored the relationship of the output intensity and the spectral FWHM on the excitation intensity (Fig. 4). It can be seen that the output intensity is low and increases slowly with the increase of the pumping power under 300 kW/cm². In this region of pumping power, the UV emission shows a broad band, for example, the FWHM is about 11 nm at 35 kW/cm². When the excitation intensity was above 300 kW/cm², the FWHM of the UV spectra quickly narrowed to 3 nm (insert of Fig. 4) and the output intensity increases rapidly with the increase of the pumping power. It is estimated that the threshold of the ASE is about 300 kW/cm². It is worth mentioning that the ASE signal could hardly be detected if the detector is positioned at an oblique angle to the substrate, which indicates that the aligned nanofibers act as waveguides and the positive feedback happened in the branching fibers of the ZnO network.

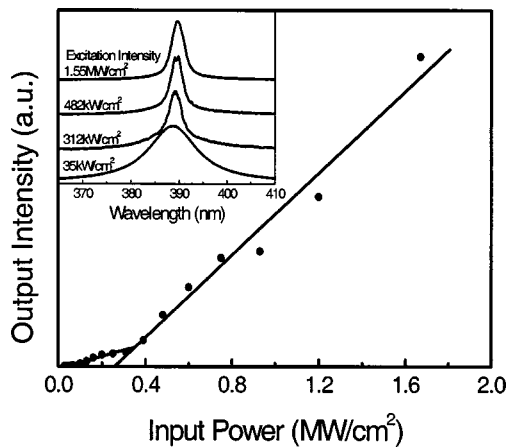


FIG. 4. Dependence of the PL intensity and the narrowing spectra (insert) on the excitation power of the pumping laser (355 nm frequency-tripled Nd:YAG).

ASE is a light emission process in which spontaneously emitted photons are amplified by stimulated emission as they travel through a gain medium.²⁴ A typical method to obtain ASE is by fabricating a waveguide array of the gain medium. For example, Yang *et al.*²⁴ fabricated a mesostructural silica stripe array doped with rhodamine 6G by soft lithography and obtained ASE with FWHM of 7 nm. Recently, Yu *et al.*²¹ observed ASE with FWHM of 9 nm and threshold of 1.9 MW/cm² from ZnO ridge waveguide. In those reports, an etching process has to be employed to pattern the waveguide structure and the width and height of each ridge are usually about several microns. In the present case, the aligned array of ZnO is self-organized in six symmetrical directions and the diameter of the fibers is about several hundreds of nanometers, and the ASE present a FWHM of 3 nm with a threshold of about 300 kW/cm². The regular structural ZnO network constructs the aligned waveguide arrays along the six symmetrical directions (ZnO side branches) because the refractive index of ZnO (2.1–2.45)^{21,25} is higher than that of air and even sapphire substrate (1.76), therefore, it is reasonable that the ASE is confined in the branch nanofibers and emits from the ends of them. When the excitation power exceeds the threshold, every photon generated a second photon by stimulated emission before leaving the gain medium. Further increasing the pumping power will trigger a “chain reaction,” i.e., one photon generates two photons, and two photons generate four photons, etc.²⁰ The drastic increase of photon density at the frequency of gain maximum results in PL intensity enhanced superlinearly and spectral width narrowed dramatically.

In summary, employing an epitaxial ZnO buffer layer on sapphire, a regular network of ZnO nanofibers was fabricated by vapor-phase transport method using the mixture of ZnO and graphite powders as source materials and patterned-Au as catalyst. From the buffer layer, the ZnO nanorod grew epitaxially along [0001] orientation to form a stem with hexagonal cross section, while the branch nanofibers grew around the stem from its six side surfaces to form a hierar-

chical structure with six-fold symmetry. Due to the good crystal quality, the nanostructural network presented strong excitonic recombination and weak defect-related recombination when it was excited by the Xe lamp. The ASE was observed in the self-organized waveguide array formed by the aligned branching nanofibers when intense laser light was vertically pumped into the nanowork. The self-organized ZnO network with regular structure may be used for electronic or photonic interconnect and other advanced applications.

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