Room-Temperature Ultraviolet Nanowire Nanolasers

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Room-temperature ultraviolet lasing in semiconductor nanowire arrays has been demonstrated. The self-organized, <0001> oriented zinc oxide nanowires grown on sapphire substrates were synthesized with a simple vapor transport and condensation process. These wide band-gap semiconductor nanowires form natural laser cavities with diameters varying from 20 to 150 nanometers and lengths up to 10 micrometers. Under optical excitation, surface-emitting lasing action was observed at 385 nanometers, with an emission linewidth less than 0.3 nanometer. The chemical flexibility and the one-dimensionality of the nanowires make them ideal miniaturized laser light sources. These short-wavelength nanolasers could have myriad applications, including optical computing, information storage, and microanalysis.

The interest in developing short-wavelength semiconductor lasers has culminated in the realization of room-temperature green-blue diode laser structures with ZnSe and $In_xGa_{1-x}N$ as the active layers (*1–3*). ZnO is a wide band-gap (3.37 eV) compound semiconductor that is suitable for blue optoelectronic applications, with ultraviolet lasing action being reported (*4–6*) in disordered particles and thin films. For wide band-gap semiconductor materials, a high carrier concentration is usually required in order to reach an optical gain that is high enough for lasing action in an electron-hole plasma (EHP) process (*7*). Such an EHP mechanism, which is common for conventional laser diode operation, typically requires high lasing thresholds. As an alternative to an EHP process, excitonic recombination in semiconductors is a more efficient radiative process and can facilitate low-threshold stimulated emission (*8, 9*). To achieve efficient excitonic laser action at room temperature, the binding energy of the exciton must be much greater than the thermal energy at room temperature (26 meV). In this regard, ZnO is a good candidate because its exciton binding energy is ~60 meV, substantially larger than that of ZnSe (22 meV) and GaN (25 meV).

To further lower the threshold, low-dimensional compound semiconductor nanostructures have been fabricated, in which quantum size effects yield a substantial density of states at the band edges and enhance radiative recombination due to carrier confinement. The use of semiconductor quantum well structures as low-threshold optical gain media represents a sizable advancement in semiconductor laser technology (*10*). Light emission from semiconductor nanowhiskers has been previously reported in GaAs and GaP systems (*11, 12*). Stimulated emission and optical gain have also been demonstrated recently in Si and CdSe nanoclusters and their ensembles (*13, 14*). Here, we demon-

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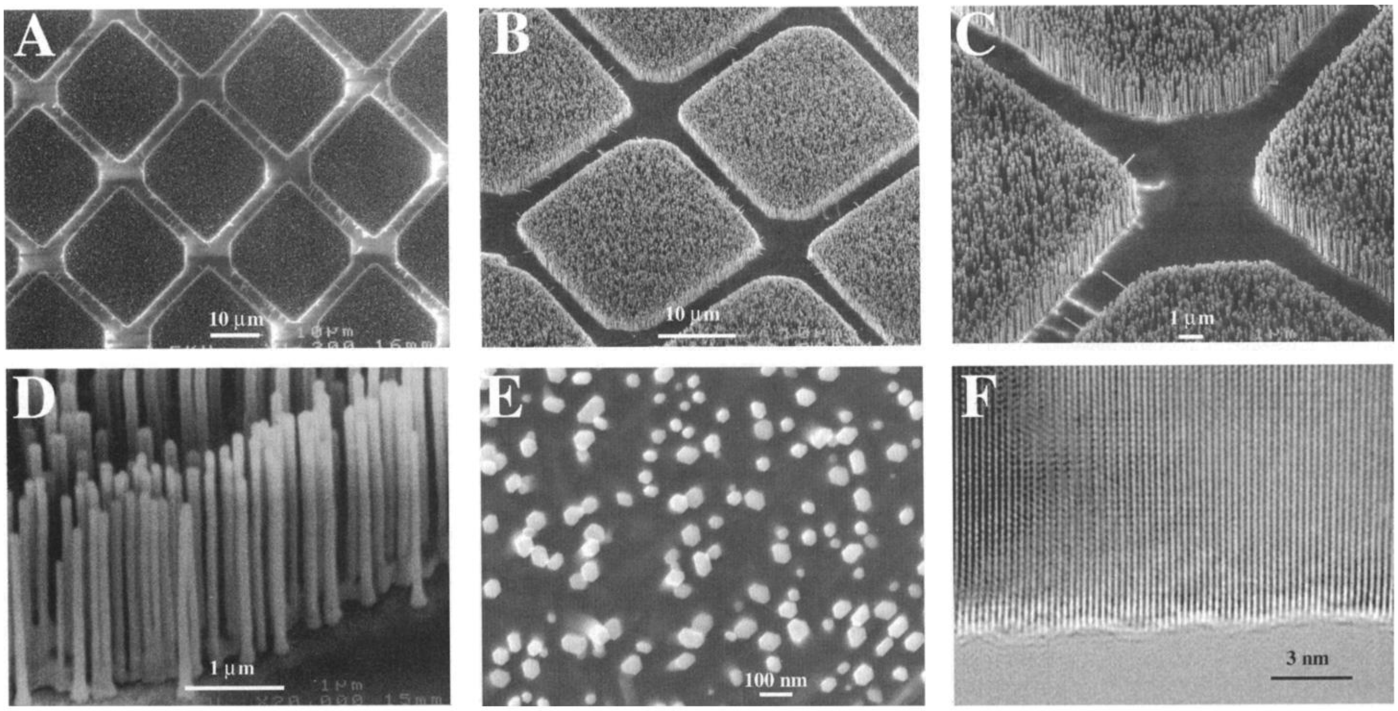

Fig. 1. (**A** through **E**) SEM images of ZnO nanowire arrays grown on sapphire substrates. A top view of the well-faceted hexagonal nanowire tips is shown in (E). (**F**) High-resolution TEM image of an individual ZnO nanowire showing its <0001> growth direction. For the nanowire growth, clean (110) sapphire substrates were coated with a 10 to 35 Å thick layer of Au, with or without using TEM grids as shadow masks (micro contact printing of thiols on Au followed by selective etching has also been used to create the Au pattern). An equal amount of ZnO powder and graphite powder were ground and transferred to an alumina boat. The Au-coated sapphire substrates were typically placed 0.5 to 2.5 cm from the center of the boat. The starting materials and the substrates were then heated up to 880° to 905°C in an Ar flow. Zn vapor is generated by carbothermal reduction of ZnO and transported to the substrates where ZnO nanowires grow. The growth generally took place within 2 to 10 min (*15*).

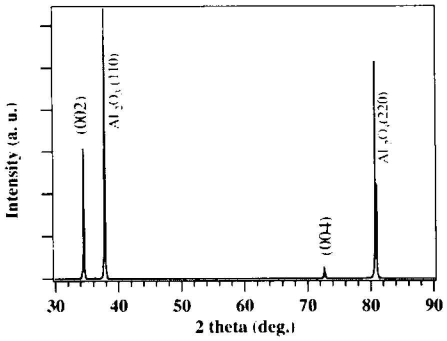

Fig. 2. X-ray diffraction pattern of ZnO nanowires on a sapphire substrate. Only (000*l*) peaks are observed, owing to their well-oriented growth configuration. The diffraction pattern is taken on a Siemens Z5000 x-ray diffractometer. a.u., arbitrary units.

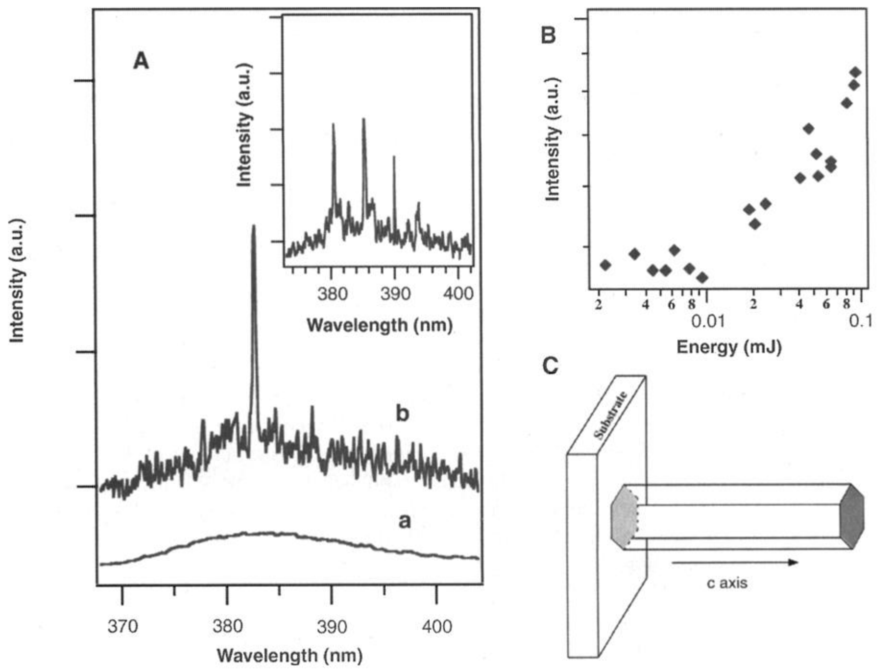

Fig. 3. (**A**) Emission spectra from nanowire arrays below (line a) and above (line b and inset) the lasing threshold. The pump power for these spectra are 20, 100, and 150 kW/cm^2, respectively. The spectra are offset for easy comparison. (**B**) Integrated emission intensity from nanowires as a function of optical pumping energy intensity. (**C**) Schematic illustration of a nanowire as a resonance cavity with two naturally faceted hexagonal end faces acting as reflecting mirrors. Stimulated emission from the nanowires was collected in the direction along the nanowire's end-plane normal (the symmetric axis) with a monochromator (ISA, Edison, New Jersey) combined with a Peltier-cooled charge-coupled device (EG&G, Gaithersburg, Maryland). The 266-nm pump beam was focused to the nanowire array at an angle 10° to the end-plane normal. All experiments were carried out at room temperature.

strate excitonic lasing action in ZnO nanowires with a threshold of 40 kW/cm^2 under optical excitation.

ZnO nanowires were synthesized with a vapor phase transport process via catalyzed epitaxial crystal growth (*15*). Using Au thin film as the catalysts for nanowire growth, we epitaxially grew the nanowires, which are highly oriented, on the substrate. Selective nanowire growth can be readily achieved by patterning the Au thin film before growth. Typical scanning electron microscopy (SEM) images of nanowire arrays grown on sapphire (110) substrates with patterned Au thin film (Fig. 1) confirm that the ZnO nanowires grow only in the Au-coated areas. The diameters of these wires range from 20 to 150 nm, whereas more than 95% of them have diameters of 70 to 100 nm. The diameter dispersity is due to the inhomogeneous sizes of the Au nanocluster catalysts when the substrate is annealed during the growth process. The lengths of these nanowires can be varied between 2 and 10 μm by adjusting the growth time. The capability of patterned nanowire growth allows us to fabricate nanoscale light emitters on the substrate in a controllable fashion.

Because of the good epitaxial interface between the (0001) plane of the ZnO nanowire and the (110) plane of the substrate (*16*), nearly all of the nanowires grow vertically from the substrates (Fig. 1, A through D). The *a* plane (110) of sapphire is twofold symmetric, whereas the ZnO *c* plane is sixfold symmetric. They are essentially incommensurate, with the exception that the *a* axis of ZnO and the *c* axis of sapphire are related almost exactly by a factor of 4, with a mismatch of less than 0.08% at room temperature. Such a coincidental matchup along the sapphire [0001] direction, along with a strong tendency of ZnO to grow in the *c* orientation and the incoherence of interfaces in directions other than sapphire [0001], leads to the unique vertical epitaxial growth configuration. The anisotropy of the sapphire's *a* plane is critical for growing high-quality *c*-oriented ZnO nanowire arrays.

Hexagon end planes of the nanowires can be clearly identified in the SEM image of the nanowire array (Fig. 1E), providing strong evidence that these nanowires grow along the <0001> direction and are indeed well-faceted at both the end and side surfaces. The well-faceted nature of these nanowires will have important implications when they are used as effective laser media. Additional structural characterization of the ZnO nanowires was carried out with transmission electron microscopy (TEM). The high-resolution TEM image of a single-crystalline ZnO nanowire (Fig. 1F) shows that spacing of 2.56 ± 0.05 Å between adjacent lattice planes corresponds to the distance between two (0002) crystal planes, further proving <0001> to be the preferred growth direction for the ZnO nanowires. This <0001> preferential nanowire growth on the sapphire substrate is also reflected in the x-ray diffraction pattern (Fig. 2). Only (000*l*) peaks are observed, indicating excellent overall *c*-axis alignment of these nanowire arrays over a large substrate area.

Photoluminescence spectra of nanowires were measured with a He-Cd laser (325 nm) as an excitation source. Strong near–band-gap edge emission at ~377 nm has been observed (*15*). In order to explore the possible stimulated emission from these oriented nanowires, the power-dependent emission has been examined. The samples were optically pumped by the fourth harmonic of Nd: yttrium-aluminum-garnet laser (266 nm, 3-ns pulse width) at room temperature. The pump beam was focused on nanowires at an incidence angle 10° to the symmetric axis of the nanowire. Light emission was collected in the direction normal to the end surface plane (along the symmetric axis) of the nanowires. In the absence of any fabricated mirrors, we observed lasing action in these ZnO nanowires during the evolution of the emission spectra with increasing pump power (Fig. 3, A and B). At low excitation intensity, the spectrum consists of a single broad spontaneous emission peak (Fig. 3A) with a full width at half maximum of ~17 nm. This spontaneous emission is 140 meV below the band gap (3.37 eV) and is generally ascribed to the recombination of excitons through an exciton-exciton collision process, where one of the excitons radiatively recombines to generate a photon (*4*–*6*). As the pump power increases, the emission peak narrows because of the preferential amplification of frequencies close to the maximum of the gain spectrum.

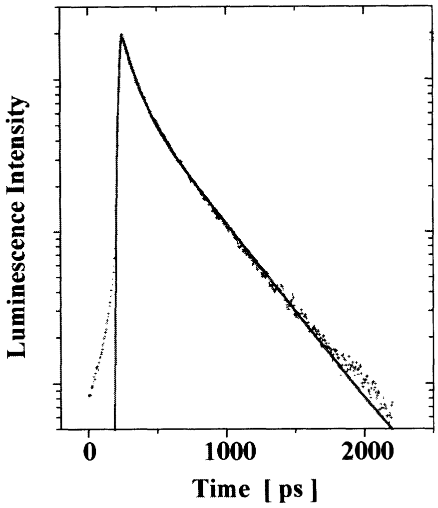

Fig. 4. The decay of the luminescence from the ZnO nanowires was studied with a frequency-tripled mode-locked Ti:sapphire laser for pulsed excitation (200-fs pulse length) and a streak camera with picosecond resolution for detection. A good fit (solid line) to the experimental data (dotted line) recorded at room temperature is obtained with a biexponential decay model assuming a fast and a slow process with time constants of ~70 and 350 ps, respectively. The time-resolved spectrum was recorded at an excitation power of 6.39 mW.

When the excitation intensity exceeds a threshold (~40 kW/cm^2), sharp peaks emerge in the emission spectra. The linewidths of these peaks are <0.3 nm, which are >50 times smaller than the linewidth of the spontaneous emission peak below the threshold. Above the threshold, the integrated emission intensity increases rapidly with the pump power (Fig. 3B). The narrow linewidth and the rapid increase of emission intensity indicate that stimulated emission takes place in these nanowires. The observed single or multiple sharp peaks represent different lasing modes at wavelengths between 370 and 400 nm. The lasing threshold is quite low in comparison with previously reported values for random lasing (~300 kW/cm^2) in disordered particles or thin films (*4*). These short-wavelength nanowire nanolasers operate at room temperature, and the areal density of these nanolasers readily reaches 1.1 × 10^{10} cm^{-2}.

The observation of lasing action in these nanowire arrays without any fabricated mirror prompts us to consider these single-crystalline, well-faceted nanowires as natural resonance cavities (Fig. 3C). It is possible that the giant oscillator strength effect (*8*), which can occur in high-quality nanowire crystals with dimensions larger than the exciton Bohr radius but smaller than the optical wavelength, enables the excitonic stimulated emission in these nanowire arrays. For II-VI semiconductors, the cleaved edge of the specimen is usually used as a mirror (*1–3, 17*). For our nanowires, one end is the epitaxial interface between the sapphire and ZnO, whereas the other end is the sharp (0001) plane of the ZnO nanocrystals. Both can serve as good laser cavity mirrors, considering that the refractive indexes for sapphire, ZnO, and air are 1.8, 2.45, and 1, respectively (*18*). This natural cavity or waveguide formation in nanowires suggests a simple chemical approach to forming a nanowire laser cavity without cleavage and etching. In fact, when multiple lasing modes were observed for these nanowires (Fig. 3A, inset), the observed mode spacing is ~5 nm for ~5-μm-long wires, which agrees quantitatively well with the calculated spacing between adjacent resonance frequencies $v_F = c/2nl$ (*17*), where v_F is emission mode spacing, c is the speed of light, n is the refractive index, and l is the resonance cavity length.

Furthermore, lifetime measurements (Fig. 4) show that the radiative recombination of the excitons is a superposition of a fast and a slow process with time constants of ~70 and 350 ps, respectively. The luminescence lifetime is mainly determined by the concentration of defects, which trap the electrons and/or holes and eventually cause their nonradiative recombination. Although the exact origin of the luminescence decay remains unclear at this stage, the long lifetime measured for these wires [350 ps, as compared with 200 ps for ZnO thin films (*4*)] demonstrates the high crystal quality achieved with the nanowire growth process.

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18. A simple estimation of the possible number of transversal modes that a waveguide can support indicates that our nanowires with diameters between 80 and 120 nm are actually single-mode waveguides for ultraviolet light.
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Ultraviolet Emission from a Diamond pn Junction

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We report the realization of an ultraviolet light–emitting diode with the use of a diamond pn junction. The pn junction was formed from a boron-doped p-type diamond layer and phosphorus-doped n-type diamond layer grown epitaxially on the {111} surface of single crystalline diamond. The pn junction exhibited good diode characteristics, and at forward bias of about 20 volts strong ultraviolet light emission at 235 nanometers was observed and was attributed to free exciton recombination.

The wide energy band gap of diamond (5.47 eV) is attractive for the opto-electronic applications because it allows the possibility of ultraviolet (UV) light–emitting devices. Although diamond has an indirect band gap, cathodoluminescence (CL) and photoluminescence (PL) studies have revealed UV luminescence. The UV luminescence is related to exciton recombination from diamond crystals, which have high crystalline perfection. The main luminescence peaks appear at 5.27 eV (235 nm) for free exciton recombination with the assistance of transverse-optical (TO) phonon transition for intrinsic diamond (*1, 2*), and 5.21 eV (238 nm) (*1, 3*) and 5.18 eV (239 nm) (*4*) for bound exciton recombination for doped diamond. The energies of these luminescence peaks are considerably higher than those observed from gallium nitride (GaN) at 3.47 eV (357 nm). Recent studies provided

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