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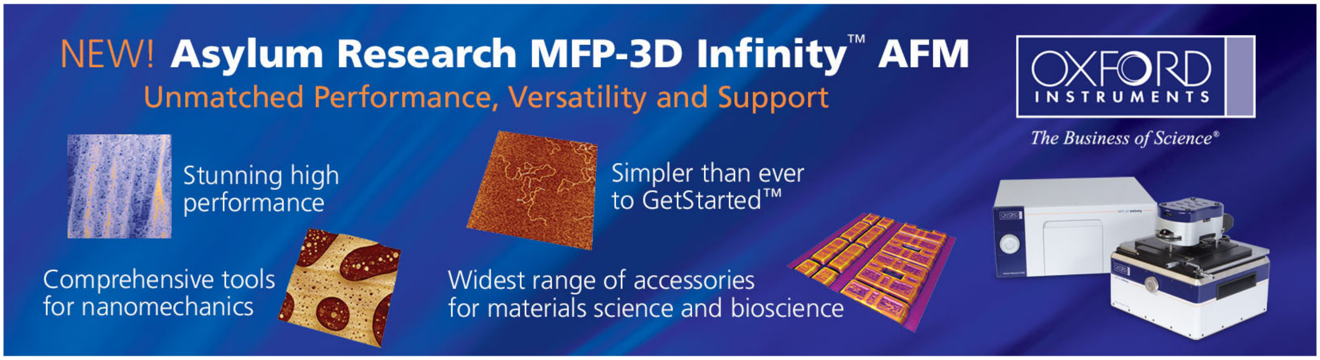

APPLIED PHYSICS LETTERS **89**, 013101 (2006)

# Band gap engineering and stimulated emission of ZnMgO nanowires

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We report a simple method for fabricating heterostructured ZnMgO nanowires by annealing the preformed ZnO/MgO core-shell structure. Photoluminescence from the alloy nanowires shows strong near-band-edge (NBE) emission, reflecting good material quality. A blueshift of the NBE emission at room temperature after the annealing treatment is attributed to the diffusion of Mg from the shell into the core ZnO of the nanowires to form a ternary ZnMgO alloy. Band gap engineering and stimulated emissions of ZnMgO nanowires with different Mg doping concentrations are also demonstrated. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2218813]

One-dimensional nanostructures have attracted a great deal of attention for their special properties and applications in microsensing for chemical-biological agent detection, solar energy conversion, solid-state lighting, and the like.[1–5] ZnO, with a wide gap of 3.37 eV and a large exciton binding energy of 60 meV, has been recognized as a key photonic material in the blue-UV region.[6,7] The greatest challenges in realizing photonic devices based on ZnO nanowires are heterostructure, *p*-type doping, and band gap engineering. In practical applications, the ability to fabricate a laser of a predetermined wavelength is critical.

Alloying the ZnO phase with MgO and ZnS has been investigated for widening the band gap of ZnO-based nanowires.[8–14] A blueshift of the UV emission with respect to that of the pure ZnO nanowires has been observed while the ZnO nanowires were doped with sulfur.[10,11] The room-temperature photoluminescence[12] and absorption spectra[13] of the ZnMgO nanowires were tuned by adjusting the Mg concentration. However, there are no reported studies on stimulated emissions (SEs) from ZnMgO alloy nanowires at room temperature. In this letter, we demonstrate a simple method to achieve the band gap engineering in ZnO/MgO core-shell nanowires by using Mg diffusion. While the annealing temperature increases, the diffused concentration of Mg increases, which results in a blueshift of PL UV-emission spectra at room temperature. Furthermore, we report the observation of optically pumped stimulated emissions from the ZnMgO nanowires.

Synthesis of ZnMgO nanostructures was carried out in a simple vapor transport process. A mixture of zinc powder (99.9999%) and magnesium powder (99.6%) with Mg:Zn weight ratios of 1:19 was placed in a ceramic boat as the starting materials and an *a*-plane sapphire wafer was used as a substrate. The boat was positioned in the center of the quartz furnace tube and the substrate was placed 10 mm downstream from the mixed powders. Before heating the furnace, the quartz tube was purged twice with high-purity argon gas for 3 min periods. The system was then heated to 570 °C (at a heating rate of 50 °C/min) with an Ar flow rate of 500 SCCM (SCCM denotes cubic centimeter per minute at STP) and was kept at this temperature for 60 min. At the end of the process the products were treated under ambient atmospheric pressure for 120 min at temperatures ranging from 800 to 1000 °C.

The morphology, composition, and crystallinity of the products were characterized through the use of scanning electron microscopy (SEM), energy dispersive x-ray (EDX), x-ray diffraction (XRD), and transmission electron microscopy (TEM). For the continuous-wave (cw) PL measurement, we used a He–Cd laser (3.81 eV) as the excitation source, while for the stimulated emission measurement, we used the third harmonic of a pulsed-pumped Nd:$YVO_4$ (yttrium vanadate) laser (3.51 eV) with a pulse width of ~500 ps and a repetition rate of 1 kHz.[15] The emission light was dispersed in a 32 cm monochromator and detected by an UV-sensitive photomultiplier tube.

Figure 1(a) shows the SEM images of the as-grown products. All the products are nanowires with a diameter of 200–500 nm and a length of over 5 $\mu$m. Figure 1(b) shows the EDX pattern of the as-grown nanowires, which are composed mainly of Mg and O with a small amount of Zn. The typical XRD pattern of the nanowires is shown in Fig. 1(c). All sharp diffraction peaks can be perfectly indexed to a high crystallinity in the hexagonal structure of ZnO and the face-centered-cubic structure of MgO. The TEM image of the as-grown nanowires in Fig. 2(a) shows that an individual nanowire displays good contrast, distinguishing the core and sheath regions. The core has a diameter of about 90 nm and is capped with a sheath about 200 nm thick. The EDX pattern in Fig. 2(b) indicates that the nanowire is composed of Mg and O with a small amount of Zn. The high resolution TEM (HRTEM) image in Fig. 2(c), which is taken from the edge (sheath region) of the nanowire, shows a perfect lattice plane with an interplanar spacing of 2.1 nm, which is in good agreement with the (002) spacing of MgO. The selection-area electron diffraction (SAED) pattern of this region [see Fig. 2(d)] shows that the outer layer of the nanowires is single-crystalline MgO with a cubic rocksalt structure. Based on these observations, we proposed that the nanowires should be formed of a ZnO/MgO core-shell heterostructure as illustrated in Fig. 2(e).

The growth of the ZnO/MgO core-shell nanowires discussed above was accomplished by simple thermal evaporation of Zn and Mg powders. The proposed growth process follows: Because the melting point of Zn (~419 °C) is

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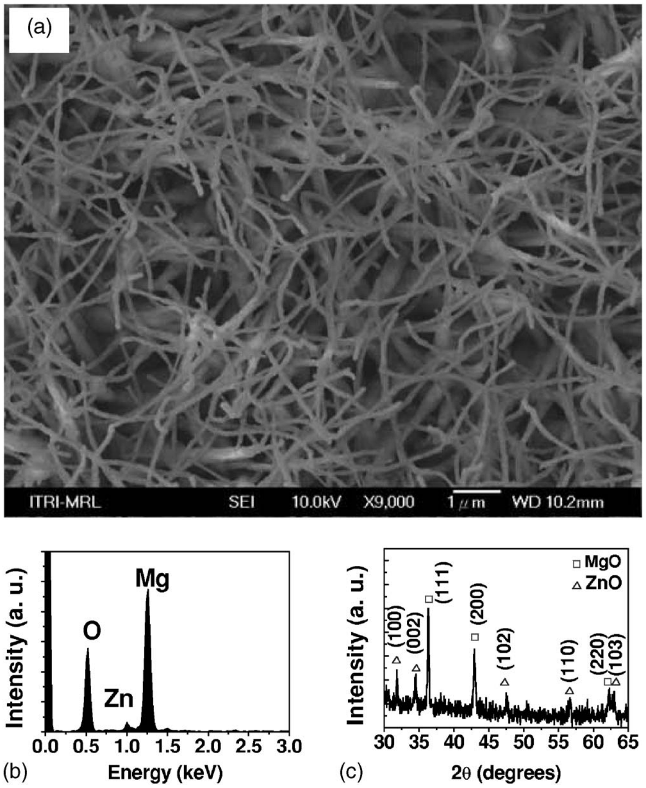

FIG. 1. (a) Typical SEM image (b) EDX pattern, and (c) XRD of the as-grown nanowires.

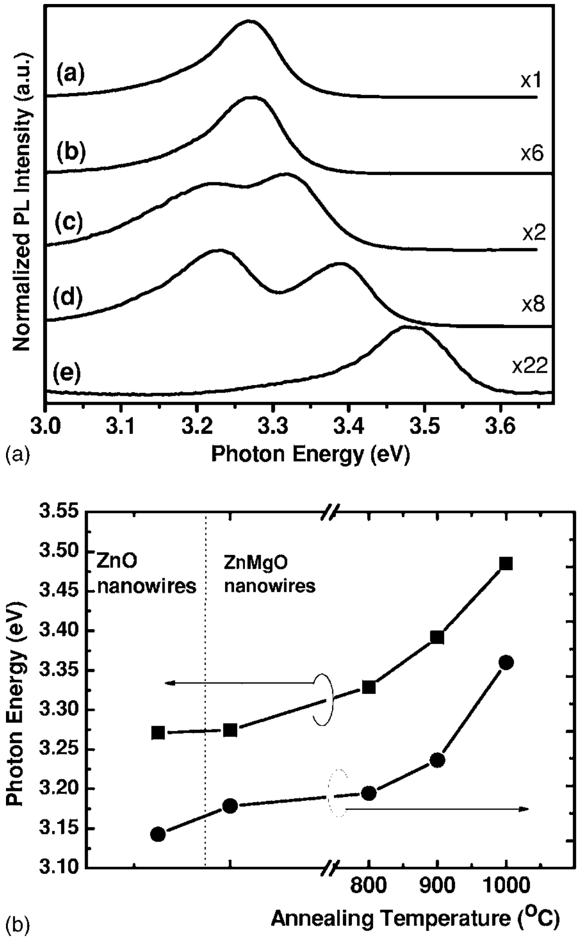

FIG. 3. (a) Room-temperature PL spectra of (a) pure ZnO nanowires and (b) the as-grown ZnO/MgO core-shell nanowires annealed at different temperatures ranging from (c) 800, (d) 900, and (e) 1000 °C. (b) shows the peak energy of excitonic emission of ZnO/MgO core-shell nanowires and the corresponding FWHM as a function of annealing temperature.

lower than that of Mg (650 °C), the Zn powder would evaporate before the Mg powder does as the processing temperature increases. In the present case, because no evidence for catalyst particles can be observed on any tip of the synthesized nanowires, the vapor-solid (VS) mechanism would be a reasonable explanation for the growth of the core ZnO nanowires. The follow-up vaporization of Mg would condense on the ZnO nanowires and be oxidized rapidly to form the MgO sheath structure and to lead to the formation of the ZnO/MgO core-shell nanowires.

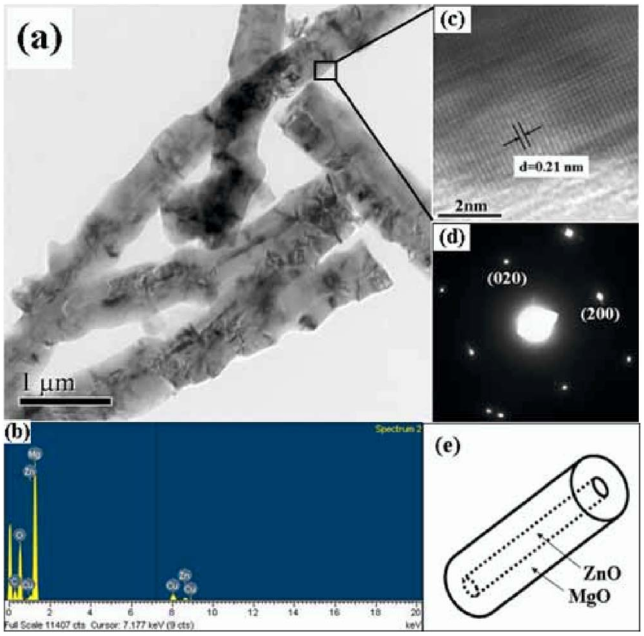

FIG. 2. (Color online) (a) TEM image of the as-grown nanowires; (b) EDX analysis showing the nanowire is composed of Zn, Mg, and O; (c) HRTEM image showing the edge of the nanowire; (d) SAED at the edge of the nanowire showing single-crystalline cubic rocksalt structure; (e) schematic model of the core-shell nanowire.

Figure 3(a) shows the room-temperature PL spectra of the ZnO/MgO core-shell nanowires annealed at temperatures ranging from 800 to 1000 °C. The PL of the pure ZnO is also shown in Fig. 3(a) as a reference. For the undoped ZnO nanowires and the as-grown ZnO/MgO core-shell nanowires, a near-band-edge (NBE) emission peak of 3.27 eV with the full width at half maximum (FWHM) of ~85 meV is the result of the free exciton emission.[16–18] As shown in Fig. 3(b), the excitonic transition energy and linewidth increase as a function of the annealing temperature. Meanwhile, another peak appears at 3.23 eV on the low-energy side of the excitonic band. The origin of the emission peak should be attributed to the free exciton emission of the residual inner core of the nondiffused ZnO nanowires. When the thermal treatment temperature reaches 1100 °C, the peak at 3.23 eV vanishes, indicating that the interdiffusion process is completely finished. The dramatically blueshifted emission can be attributed to the increase in Mg composition in the ternary ZnMgO through interdiffusion. The broadening of the main peak reflects the increase in fluctuation of the composition and lattice disorder in the alloy. A decrease of the PL intensity with increasing Mg concentration results from the

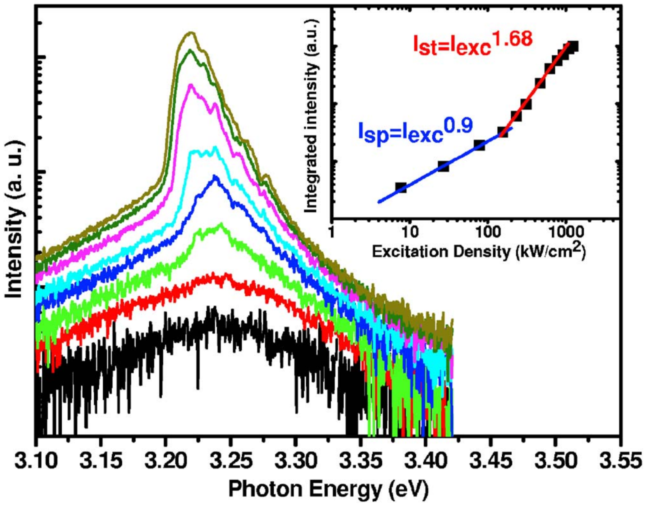

FIG. 4. (Color online) The RT emission spectra as a function of excitation intensity for 800 °C-annealed ZnO/MgO core-shell nanowires. The inset shows its log-log plots of integrated emission intensity vs the excitation intensity.

increase in nonradiative recombination processes.

Figure 4 shows a semilog plot of the typical NBE spectrum and the corresponding peak intensity as a function of excitation density ($I_{\mathrm{exc}}$) under pulsed pumping for the sample annealed at 800 °C. At low excitation densities, only a broad spontaneous emission peak can be observed at 3.25 eV with the FWHM of ~0.1 eV. As shown in the inset in Fig. 4, the emission intensity was found to be approximately linearly proportional to the excitation power density, indicating that the broad emission is typical spontaneous emission. As the excitation pump density increases to a value exceeding a threshold of about 200 kW/cm$^2$, a spectrally narrower peak with the FWHM of 24 meV appears at the top of the low-energy shoulder of the spontaneous emission. The emission intensity of this narrower feature becomes dominant as the pumping power density is increased to above the threshold. The strong, narrow emission exhibits a superlinear increase, indicating the appearance of SE. The SE is attributed to the stimulated recombination of exciton-exciton scattering,[19,20] which is a two-particle process; therefore, a dependence of $I_{\mathrm{exc}}$ as $I_{\mathrm{SE}} \propto I_{\mathrm{exc}}^{\alpha}$, with $\alpha \sim 2$, can be expected. Our analysis shows a value of $\alpha=2.08$ for the as-grown sample and $\alpha=1.68$ and $\alpha=1.45$ for the samples with annealed temperatures of 800 and 900 °C, respectively. As expected, the exponent $\alpha$ is 2.08 for the as-grown samples; however, it decreases to 1.45 for the 900 °C-annealed sample. This result indicates that the material quality degrades after the Mg diffusion process, owing to the additional scattering centers introduced by impurities and defects. Many nonradiative centers or other loss mechanisms formed after more diffusion of the Mg and caused a reduction in the cross section (or probability) of exciton-exciton scattering. Thus, the efficiency of the stimulated emission decreased.

In conclusion, we have synthesized heterostructured Zn-MgO alloy nanowires by a simple evaporation route. The formation of the ZnO/MgO core-shell structure is based on the melting point of Zn being lower than that of Mg. After the annealing treatment, a blueshift in the near-band-edge emission at room temperature is attributed to Mg diffusion into the core ZnO nanowires to form a ternary ZnMgO alloy. Band gap engineering and stimulated emission of ZnMgO nanowires with different Mg doping concentrations are also achieved. This demonstration of the stimulated emission at room temperature from MgZnO nanowires could be used for light-emitting device applications.

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