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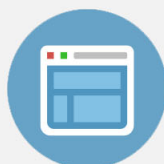
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Stimulated emission and lasing of random-growth oriented ZnO nanowires

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We report room-temperature ultraviolet stimulated emission and lasing from optically pumped high-quality ZnO nanowires. Emission due to the exciton-exciton scattering process shows apparent stimulated-emission behavior. Several sharp peaks associated with random laser action are seen under high pumping intensity. The mechanism of laser emission is attributed to coherent multiple scattering among the random-growth oriented nanowires. The characteristic cavity length is determined by the Fourier transform of the lasing spectrum. © 2005 American Institute of Physics. [DOI: 10.1063/1.1862312]

I. INTRODUCTION

One-dimensional semiconductors have become the important fundamental building blocks because of their fundamental physical properties and their potential applications for nanoelectronic and nanophotonic devices.^{1–3} ZnO nanowires are especially interesting because they exhibit large exciton binding energy (60 meV), wide band gap (3.37 eV), and low threshold ultraviolet lasing.⁴ Recent progress in lasing or stimulated emission has been achieved from a variety of low-dimensional ZnO structures such as microcavity,⁵ nanowires,^{4,6–9} nanorods,^{10–12} and nanoribbons.¹³ For a large diameter such as ZnO microcavity,⁵ the lasing mechanism results from whispering gallery modes (WGMs). The light is trapped proximity to the perimeter of the nanowire by the total internal reflections (TIR). When the diameter of the ZnO nanowire is smaller than the optical wavelength, the WGMs will experience high scattering loss as a result of diffraction. Fabry–Perot resonator has been used to explain the lasing mode in the individual single nanostructure^{4,13–15} and long whiskers^{16,17} in which two well-aligned end facets of the nanowire serve as the Fabry–Perot cavity.

However, in a disorder system of randomly oriented nanowires, coherent photon may exist during multiple scattering among these disordered nanowires. Unlike the conventional laser, the random laser emission in disorder media of polycrystalline ZnO films and powders is a result of the coherent photon scattering that did not contain any conventional Fabry–Perot cavities.^{18–20} The key factor to random lasing is the existence of a high-gain medium and efficient light scattering in the samples to provide the necessary coherent feedback. Due to the high-gain characteristic of the ZnO nanowires,⁴ random lasing also acts in high-density vertically aligned ZnO nanorod arrays.²¹ The different resonant cavities formed by multiple scattering could have different lasing directions. In this article, we demonstrate the stimulated emission and lasing of randomly oriented disordered ZnO nanowires and discuss their relevant mechanisms. By

Fourier transforming the lasing spectrum, we obtained a characteristic loop length of random lasing cavity.

II. EXPERIMENTAL PROCEDURES

ZnO nanowires were synthesized in a simple vapor transport method mediated by vapor-liquid-solid (VLS) growth. More detail of this growth process has been published elsewhere.²² For continuous-wave (cw) photoluminescence (PL) measurement, we used a He–Cd laser (325 nm) as the excitation source; for pulsed pumping, we used the third harmonic of Nd:YVO₄ (yttrium orthovanadate) laser (3.51-eV photon energy) with a pulse width of ~500 ps and repetition rate of 1 kHz. The excitation laser beam was directed normally and focused onto the sample surface with power being varied with an optical attenuator. The spot size on the sample is about 100 μm . Spontaneous and stimulated emissions were collected by a fiber bundle and coupled into a 0.32-cm focal-length monochromator with a 1200 lines/mm grating, then detected by either an electrically cooled charge-coupled device (CCD) or a photomultiplier tube (PMT) detector. All of the experiments were performed at room temperature.

III. RESULTS AND DISCUSSION

The electron microscopy image provides the general morphology of the as-grown products. As shown in Fig. 1(a), the typical scanning electron microscopy (SEM) micrograph clearly reveals that there are random-growth oriented ZnO nanowires on the substrate with their lengths normally exceeding 3 μm and diameters ranging between 60 and 200 nm. Figure 1(b) shows the transmission electron microscopy (TEM) image of a single nanowire of 120 nm in diameter. The selected-area electron diffraction (SAED) pattern of an individual nanowire shown in Fig. 1(c) reveals a complete diffraction pattern. It indicates that the ZnO nanowire is single crystalline and can be indexed to the hexagonal ZnO (110) diffraction with growth direction of [002].

Figure 2(a) shows the typical emission spectra of the ZnO nanowires measured at various pumping intensities. As a reference, the cw-PL is also shown at the bottom of Fig. 2(a). At low pumping intensity, only a spontaneous emission

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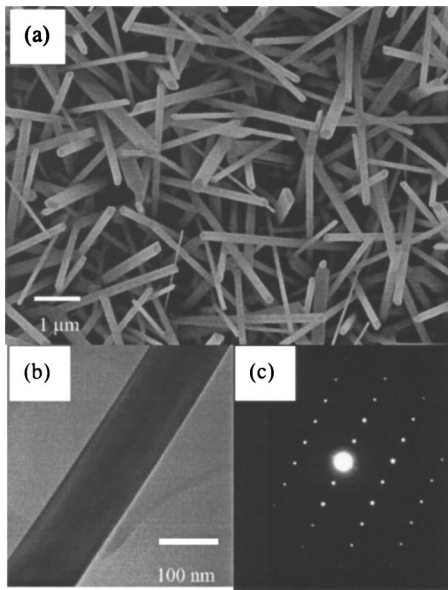


FIG. 1. (a) SEM micrograph of the ZnO nanowires. (b) TEM image of an individual nanowire. (c) SAED pattern showing a single crystalline structure.

peak at 3.26 eV with a full width at half maximum (FWHM) of 110 meV is attributed to the exciton emission. With increasing the pumping intensity, a narrow emission appears on the low-energy shoulder of the exciton band. By decomposing the emission spectrum into a broad spontaneous emission and a sharper peak, we observed that the integrated intensity of the broad spontaneous emission increases almost linearly with pumping intensity ($I_{sp} = I_p^{0.95}$), illustrated as close circles in Fig. 2(b); however, the integrated intensity of the narrower peak at 3.22 eV experiences a strong superlinear dependence ($I_{st} = I_p^{2.95}$) of the excitation intensity (open circles). As shown in Fig. 2(c), the FWHM of the sharper peak is only 20 meV. These results indicate a clear evidence of stimulated emission. The stimulated emission process was interpreted in terms of inelastic exciton-exciton scattering in which one exciton is scattered into a photonlike polariton state giving rise to luminescence, while the other exciton is scattered into an excited state with a larger quantum number or a totally dissociated state.²³

When the pumping intensity exceeds a certain threshold at a specific position of the sample, shown in Fig. 3(a), we found that several sharp peaks emerge from 3.20 to 3.25 eV with FWHM ~ 2 meV. Note that the redshift of the PL peak with increasing excitation intensity is caused by the band-gap renormalization.

There are two possible optical resonance modes in ZnO nanowires for laserlike action. The first resonance mode is the Fabry–Perot mode of the natural optical cavity formed by the two-end facets of the well-organized nanowires which is a well-accepted reason for explaining the lasing behavior in a single ZnO nanowire⁴ and GaN nanowire.¹⁵ Another possible lasing mechanism results from light amplification due to photon coherent scattering in the random media.^{18–20} Compared with the previous reports of lasing from ZnO nanowires,⁴ our samples show an unobvious feature of Fabry–Perot modes. The longitudinal modes spacing can be determined by the equation,

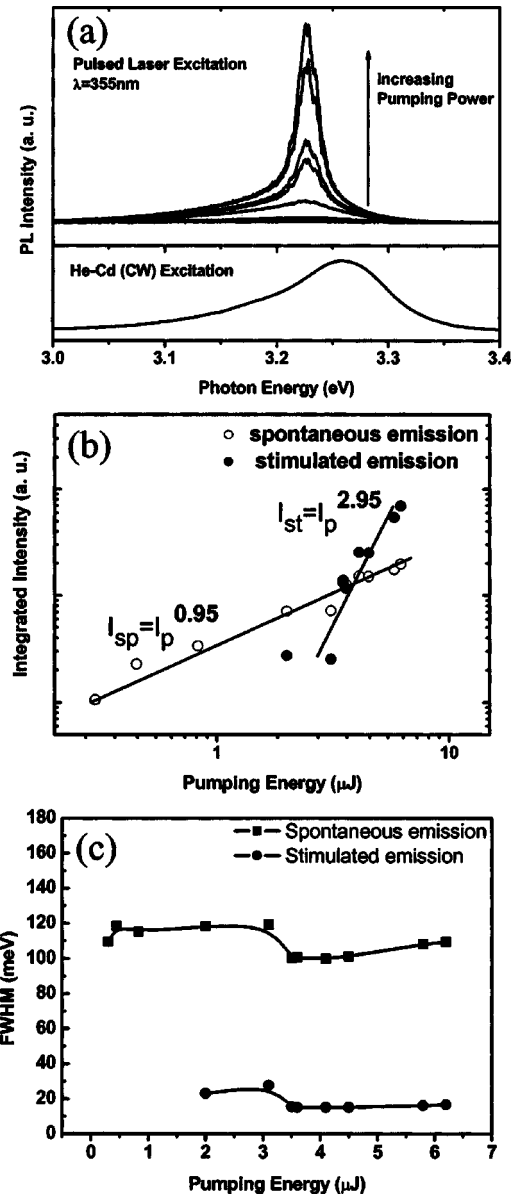


FIG. 2. (a) Excitation power dependence of the emission spectra of ZnO nanowires. (b) Plot of integrated intensity of the stimulated emission of ZnO nanowires vs the pumping intensity. (c) The FWHM of the emission peaks vs pumping intensity.

$$\Delta\lambda = \lambda^2/(2nL). \quad (1)$$

Here L is the laser cavity length, n is the refractive index (2.45), and is the resonant wavelength (~ 390 nm). For a ZnO nanowire with length of about $3 \mu\text{m}$, the mode spacing between the closest longitudinal modes is expected to be 10 nm. It should exist only a single Fabry–Perot mode in the whole measured PL range (3.0–3.4 eV) and may become a broad lasing spectrum due to averaging out the emission spectra of the single Fabry–Perot modes having different lengths. However, we did observe several sharp lasing modes under high pumping intensity. Therefore, we further considered the other possible lasing action from coherent photon scattering in the random medium.

To confirm the origin of the laserlike emission peaks, we studied the influence of the excitation area on the number of modes in the random lasing. Figure 4 plots the emission

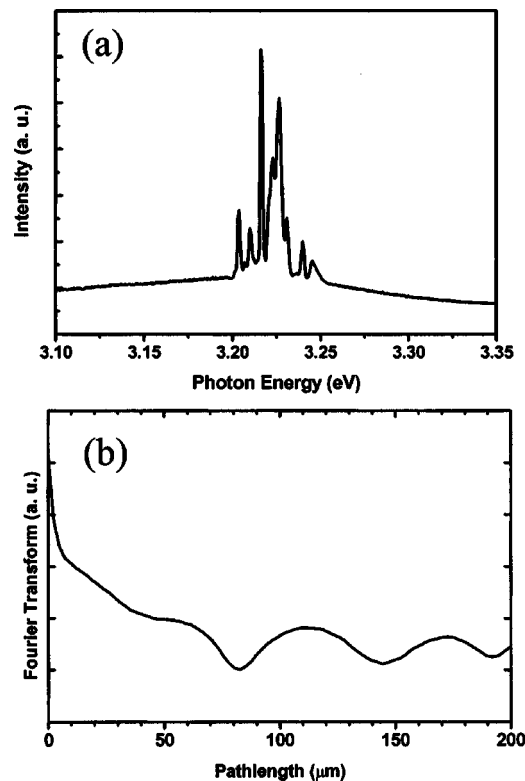


FIG. 3. (a) Typical lasing spectra of the ZnO nanowire. The excitation intensity is about 2 MW/cm²; (b) Fourier transform of the lasing spectrum shown in Fig. 3(a).

spectra measured at different s slightly above the lasing threshold. Under the smallest excitation area, 7.9×10^{-5} cm² no narrow emission peak was observed. With increasing the excitation area, several sharp laserlike emission peaks appear. In addition, the number of sharp laserlike peaks tends to increase with an increase of the excitation area. According to the previous report on random lasing,¹⁸ the laser oscillation would not have occurred if the closed-loop paths were too short to provide enough amplification. This result clearly indicates that the sharp emissions result from the random lasing action. The scattering probability of coherent photon in random-oriented ZnO nanowires is higher than that in well-aligned ZnO nanowires. We found no distinct sharp peaks from the well-aligned ZnO nanowires grown on a quartz glass²⁴ with optical pumping. Hence, ran-

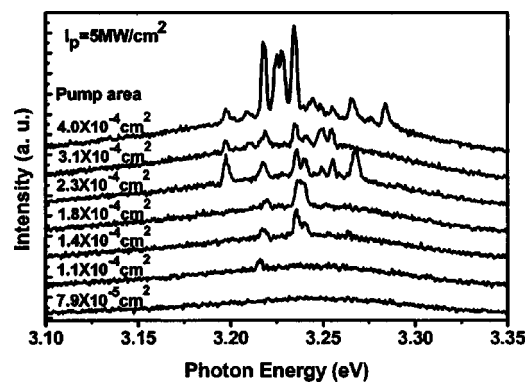


FIG. 4. Lasing spectra of the sample of different excitation areas (from top to bottom for decreasing area).

dom laser only acted in high-density vertically aligned ZnO nanowires²¹ or disorder-oriented ZnO nanowires.

To further determine the cavity length of the closed-loop random lasing, a simple and powerful technique which is Fourier transform (FT) of the lasing spectrum is used.^{25,26} The unit of the FT result is in length provided that the unit of the lasing spectrum is in wave number (1/length). For a traditional Fabry–Perot laser cavity, the separation of harmonics in FT of the lasing emission is nL/π . We assume that the closed-loop paths of the coherent photon are approximately circles, then the optical path $2L$ is replaced by the circumference of the loop, and the resultant FT harmonics appear at the multiples of $nD/2$, where D is the loop diameter.

Figure 3(b) is the FT of the laser emission spectrum of Fig. 3(a). We found a broad peak at 20 μ m and a series of peaks of the harmonics that appear at 56, 112, and 168 μ m, respectively. In fact, the broad peak contains many individual peaks that are belonging to several short laser cavities within the illuminated area. The fundamental resonator of random lasing has a diameter of 46 μ m and the second-harmonic peak is due to the light passing through twice trips of the resonant loop, and so on. The calculated loop diameter of the random laser is smaller than the spot size of the pumping laser beam on the sample.

IV. CONCLUSIONS

In summary, we have shown stimulated emission of randomly grown oriented ZnO nanowires under optical pumping. Below the lasing threshold, the stimulated emission shows the superlinear dependence of the pump intensity. Above the lasing threshold, several sharp peaks with FWHM ~ 2 meV were observed. The random laser action requires a long enough path length of closed loop to generate photon amplification via coherent feedback scattering. If the path length of the closed loop was reduced to below a critical length, the laser action stopped. Random lasing is more easily realized in disorder-grown oriented ZnO nanowires than well-aligned ZnO nanowires because of the short mean free path of coherent light scattering in the former case. Finally, the typical cavity length of the random laser can be roughly determined by Fourier transforming the lasing spectrum.

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¹X. F. Duan, Y. Huang, R. Agarwal, and C. M. Lieber, *Nature (London)* **421**, 241 (2003).

²S. S. Wong, E. Joselevich, A. T. Woolley, C. L. Cheung, and C. M. Lieber, *Nature (London)* **394**, 52 (1998).

³X. F. Duan, Y. Huang, Y. Cui, J. F. Wang, and C. M. Lieber, *Nature (London)* **409**, 66 (2001).

⁴M. H. Huang, S. Mao, H. Feick, H. Q. Yan, Y. Y. Wu, H. Kind, E. Weber, R. Russo, and P. D. Yang, *Science* **292**, 1897 (2001).

⁵X. Liu, W. Fang, Y. Huang, X. H. Wu, S. T. Ho, H. Cao, and R. P. H. Chang, *Appl. Phys. Lett.* **84**, 2488 (2004).

⁶C. H. Liu, J. A. Zapfen, Y. Yao, X. M. Meng, C. S. Lee, S. S. Fan, Y. Lifshitz, and S. T. Lee, *Adv. Mater. (Weinheim, Ger.)* **15**, 838 (2003).

⁷J. H. Choy, E. S. Jang, J. H. Won, J. H. Chung, D. J. Jang, and Y. W. Kim,

- Appl. Phys. Lett. **84**, 287 (2004).
- ⁸J. C. Johnson, H. Q. Yan, P. D. Yang, and R. J. Saykally, J. Phys. Chem. B **107**, 8816 (2003).
- ⁹Z. R. Qiu, K. S. Wong, M. M. Wu, W. J. Lin, and H. F. Xu, Appl. Phys. Lett. **84**, 2739 (2004).
- ¹⁰J. H. Choy, E. S. Jang, J. H. Won, J. H. Chung, D. J. Jang, and Y. W. Kim, Adv. Mater. (Weinheim, Ger.) **15**, 1911 (2003).
- ¹¹Y. K. Tseng, H. C. Hsu, W. F. Hsieh, K. S. Liu, and I. C. Chen, J. Mater. Res. **18**, 2837 (2003).
- ¹²A. B. Hartanto, X. Ning, Y. Nakata, and T. Okada, Appl. Phys. A: Mater. Sci. Process. **78**, 299 (2004).
- ¹³H. Q. Yan, J. Johnson, M. Law, R. R. He, K. Knutsen, J. R. McKinney, J. Pham, R. Saykally, and P. D. Yang, Adv. Mater. (Weinheim, Ger.) **15**, 1907 (2003).
- ¹⁴J. A. Zapien, Y. Jiang, X. M. Meng, W. Chen, F. C. K. Au, Y. Lifshitz, and S. T. Lee, Appl. Phys. Lett. **84**, 1189 (2004).
- ¹⁵J. C. Johnson, H. J. Choi, K. P. Knutsen, R. D. Schaller, P. D. Yang, and R. J. Saykally, Nat. Mater. **1**, 106 (2002).
- ¹⁶D. X. Zhao, Y. C. Liu, D. Z. Shen, Y. M. Lu, L. G. Zhang, and X. W. Fan, J. Appl. Phys. **94**, 5605 (2003).
- ¹⁷Y. G. Wang, C. Yuen, S. P. Lau, S. F. Yu, and B. K. Tay, Chem. Phys. Lett. **77**, 329 (2003).
- ¹⁸H. Cao, Y. G. Zhao, S. T. Ho, E. W. Seelig, Q. H. Wang, and R. P. H. Chang, Phys. Rev. Lett. **82**, 2278 (1999).
- ¹⁹R. K. Thareja and A. Mitra, Appl. Phys. A: Mater. Sci. Process. **71**, 181 (2000).
- ²⁰X. H. H. Wu, A. Yamilov, H. Noh, H. Cao, E. W. Seelig, and R. P. H. Chang, J. Opt. Soc. Am. B **21**, 159 (2004).
- ²¹S. F. Yu, C. Yuen, S. P. Lau, W. I. Park, and G.-C. Yi, Appl. Phys. Lett. **84**, 3241 (2004).
- ²²H. C. Hsu and W. F. Hsieh, Solid State Commun. **131**, 371 (2004).
- ²³C. F. Klingshirn, *Semiconductor Optics* (Springer, Berlin, 1995).
- ²⁴S. Yang, H. C. Hsu, W. R. Liu, and W. F. Hsieh, Nanotechnology(submitted).
- ²⁵R. C. Polson, A. Chipouline, and Z. V. Vardeny, Adv. Mater. (Weinheim, Ger.) **13**, 760 (2001).
- ²⁶R. C. Polson, G. Levina, and Z. V. Vardeny, Appl. Phys. Lett. **76**, 3858 (2000).