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Aligned growth of ZnO nanowires and lasing in single ZnO nanowire optical cavities

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ABSTRACT Ordered ZnO nanowire arrays have been fabricated in N_2 background gas by catalyst-free nanoparticle-assisted pulsed-laser deposition. A single ZnO nanowire was collected in an electrode gap by dielectrophoresis. Under the optical pumping above an exciting laser ($\lambda = 355$ nm) threshold of $\sim 334\ \mathrm{kW/cm^2}$, ultraviolet lasing action in a single ZnO nanowire was observed at room temperature, indicating that the as-synthesized nanowires in pure N_2 background gas are of high quality. The crystalline facets of both ends of the nanowire acted to form an optical cavity. Therefore, the mode spacings corresponding to cavity lengths of the respective nanowires were observed in photoluminescence spectra.

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1 Introduction

Recently, semiconductor nanostructures are attracting tremendous attention as building blocks for next-generation nanodevices [1]: nanolasers [2], waveguides [3], frequency converters [4], optical switches [5], and sensors [6]. In particular, the transverse nanoscale and longitudinal microscale dimensions as well as the well-defined faceting nature of such nanostructures enable the observation of unique optical confinement and microcavity effects [7]. The direct wide band gap of 3.37 eV at room temperature and the high exciton binding energy of 60 meV make ZnO one of the most promising candidates to realize ultraviolet lasing action at room temperature. ZnO has also displayed an astonishing series of nanostructures with different morphologies [8]. Among many others, the nanowires and nanoribbons are highly interesting for their fundamental significance in revealing microcavity effects as well as near-field optical coupling phenomena [9]. They are expected to have a lower threshold power density for lasing, because quantum effects result in substantial density of states near the band-gap edges and enhance radiative recombination due to carrier confinement.

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In this work, vertically aligned growth of ZnO nanowires has been successfully realized in pure N_2 background gas by catalyst-free nanoparticle-assisted pulsed-laser deposition (NAPLD). Furthermore, we successfully observed excitonic lasing from ZnO single nanowires with different dimensions synthesized by NAPLD. It is noteworthy that excitonic lasing from ZnO nanowires occurs without an external cavity, because crystalline facets of both ends of the nanowire act to form a cavity. In addition, we report on the lasing-cavity mode formed and the lasing properties.

2 Synthesis and characterization of vertically aligned ZnO nanowires

2.1 *Synthesis of* ZnO *nanowires*

A sintered ZnO target with 99.99% purity was used as source material in synthesizing ZnO nanowires. This material was ablated with a KrF excimer laser with a fluence of $4\ \mathrm{J/cm^2}$ in a chamber filled with nitrogen background gas for 20 min, which operated at a repetition rate of 20 Hz and an energy of 240 mJ. The substrate–target distance was fixed to 15 mm and the typical values of chamber pressure and temperature in a horizontal electrical tube furnace were 260 Torr and 1000 °C, respectively. Ablated species were then deposited on a (0001) sapphire substrate (1 cm × 1 cm), which had been annealed at 1000 °C for 1 h in a programmable box-type electric-resistance furnace in order to improve the surface morphology and favor the vertical growth of ZnO. In our experiment, ZnO nanowires were synthesized at a higher background gas pressure. When the deposition is carried out at a lower pressure, there are virtually no collisions between ejected species and nitrogen gas before they reach the substrate. Therefore, our experimental pressure would be critical, as the cooling of the energetic ablated species by collision with the nitrogen gas could reduce the deposited atom mobility on the surface and result in columnar growth forming 3D islands.

The morphology and the crystallinity of the as-deposited products were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis. The optical properties of ZnO nanowires were investigated by observing the photoluminescence (PL).

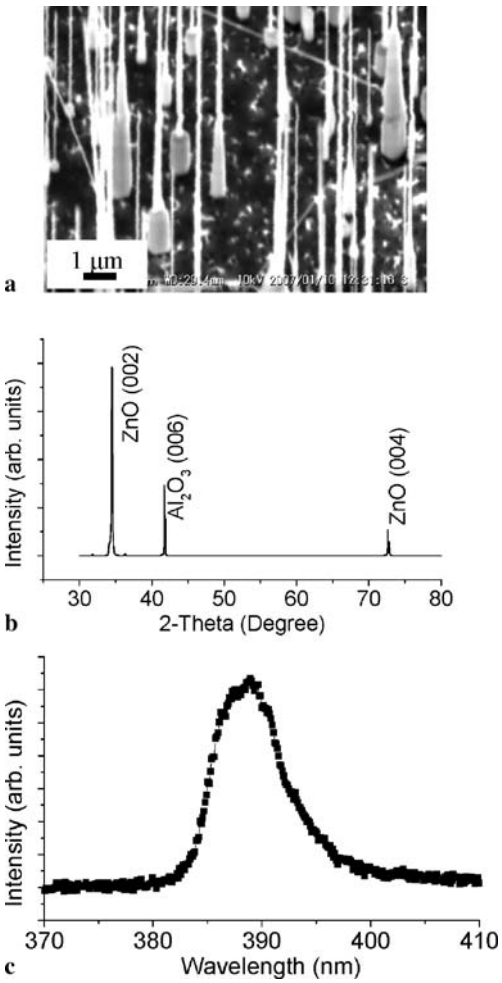

FIGURE 1 (**a**) SEM image, (**b**) XRD pattern, and (**c**) PL spectrum of ZnO nanowires grown in N_2 background gas by NAPLD

2.2 *Morphology, crystallinity, and PL of* ZnO *nanowires*

As shown in Fig. 1, this synthesis method could produce vertically aligned ZnO nanowires, which had an average diameter of less than 200 nm and a length in the micrometer range. And, only the diffraction peaks of ZnO(002) and (004) appear in the XRD pattern, indicating that the ZnO nanowires grown on substrates were preferentially oriented in the *c*-axis direction. The room-temperature PL spectrum shows a broader UV peak at around 390 nm, which is the contribution of the near band edge emission of the wide band gap ZnO. Further study of electrical properties of ZnO nanowires grown in nitrogen gas is proceeding.

3 Lasing characteristics of single ZnO nanowire

3.1 *Preparation of single* ZnO *nanowire*

To observe the photoluminescence from a single ZnO nanowire, the nanowires were removed from the growth substrate by ultrasonication in ethanol and dispersed onto a glass substrate on which an interdigitated chrome microelectrode was patterned. Figure 2 shows the image of the microelectrode pattern and the schematic of the dielectrophoresis (DEP) experiment. It can be seen from Fig. 2 a that the electrode had a sawtooth pattern in order to form high and low electric field regions periodically. Each electrode finger, which was respectively marked with characters A, B, C, ..., T, had 5-mm length and 5-μm minimum gap. Each tooth-like part was a triangle with sides of 50 μm and every ten teeth was marked with numbers 1, 2, 3, ..., 10. With the help of these characters and numbers, we can locate the trapped single nanowire by an optical microscope with ease. In addition, SEM observation is required to measure the size of the nanowire whose PL spectra were measured. Therefore, according to the location of the nanowire, it is very convenient to obtain further necessary information about the size and the morphology of a single nanowire under PL measurement by SEM, which cannot be obtained by a low-resolution optical microscope due to the small size of the nanowire. In a word, the DEP technique was used in this work to collect the single nanowire in order to offer the information about the location of the nanowire which is useful for SEM observation. The DEP was performed with an ac voltage of 100-kHz frequency and 20-V amplitude (peak to peak value) [10].

The size and morphology of a single nanowire collected in the electrode gap were observed by scanning electron microscopy (SEM). The photoluminescence of a single nanowire was observed under excitation at 355 nm using a frequency-tripled Q-switched Nd:YAG laser. PL images of the single nanowire were enlarged by using a long-distance microscope to detect PL from only a single nanowire from those dispersed on the glass substrate with patterned microelectrode. In order to measure the PL spectra, single nanowires whose crystalline facets were of good quality were selected, because it was expected that the nanowires with good crystalline facets could act as self-formed cavities and result in successful lasing.

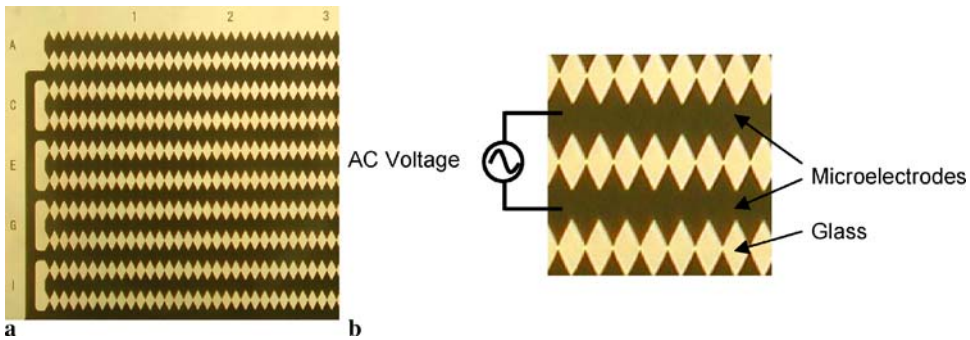

FIGURE 2 (**a**) Image of microelectrode pattern, (**b**) schematic of DEP experiment

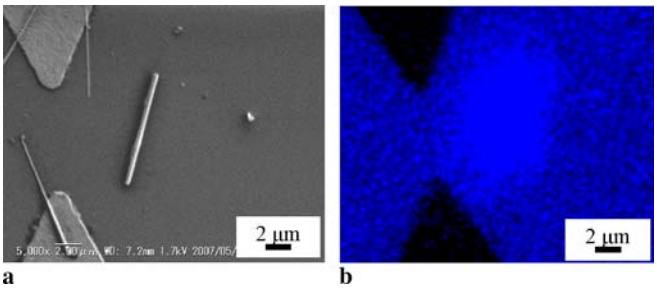

FIGURE 3 (**a**) SEM image of a single nanowire in the electrode gap, (**b**) PL image of the nanowire under optical excitation

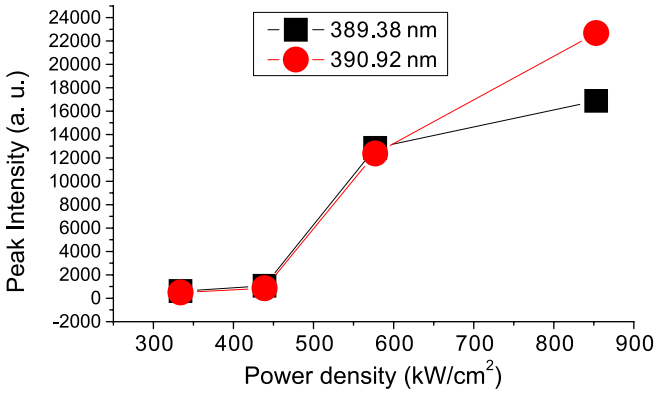

FIGURE 5 Excitation power dependence on the dominant peak intensity

3.2 *Lasing in single* ZnO *nanowire optical cavities*

Figure 3 shows the SEM image of the single nanowire whose PL spectra were measured and its typical photoluminescence (PL) image. It can be seen that the single nanowire was collected in the electrode gap where the electric field became higher and aligned along the electric field line. The dimensions of the selected nanowire are about 18.5 μm in length and ∼ 600 nm in diameter. As shown in the PL image, strong emission was observed from the body of the nanowire cavity and also some signal can be detected from the ends of the nanowire. Figure 4a shows the excitation-intensity dependence of PL spectra of a ZnO single nanowire at room temperature. In Fig. 4b, the lowest PL spectrum was obtained under a weak excitation density of 286 kW/cm^2 and exhibits a very weak broad PL band which consists of PL bands due to free excitons and their phonon replicas [11]. With increasing excitation intensity, two sharp peaks abruptly appear at 387.97 nm and 389.62 nm above an excitation threshold of about 334 kW/cm^2. Considering that the PL peaks appear above a certain threshold power, it is concluded that stimulated emission occurs.

Upon increasing the excitation level further, the intensity of the sharp peaks at the same positions increases and the number of peaks increases on the longer-wavelength side. As shown in Fig. 4a, the single ZnO nanowire exhibited UV emission at around 390 nm with several sharp peaks whose energy spacings are almost constant, which greatly differs from the broad UV emission of the film with many nanowires shown in Fig. 1c, indicating that lasing occurs in the nanowire. It is considered that the self-formed cavity of the nanocrystal brings about lasing in the cavity modes formed in the nanowire. The cavity modes appear as the several peaks with almost constant energy spacing in the PL spectra [11]. An important aspect is that this lasing action occurs without external mirrors and the nanolaser cavity is formed by the crystalline facets alone. This PL from the nanowire was detected in the vertical direction of the electrode chip. In fact, the lasing was also observed along the length of the nanowire.

Figure 5 shows the incident laser power dependence on the dominant peak intensity at 389.38 nm (black squares) and at 390.92 nm (red circles). Excitation power dependent measurements indicate that the peak intensity at 390.92 nm increases rapidly and becomes dominant at higher excitation powers, while at lower excitation intensities the peak intensity at 389.38 nm presents the highest feature in the PL spectra.

In order to examine the relation between the cavity and its lasing action further, series of lasing spectra from a single nanowire were collected at several wire lengths. As shown in Fig. 6a, one clear trend is that the mode spacing increases with decreasing nanowire length. If we assume that these nanowires serve as Fabry–Pérot optical cavities, the longitudinal mode spacing is expected to be determined by the equation $\Delta\lambda = \lambda^2/2nL$, where n is the group refractive index and L is the effective cavity length [9]. Figure 6b shows the relationship calculated by this equation.

As shown in Fig. 6, not all modes agree well with the pure axial Fabry–Pérot type. Some of the peak spacings observed in the PL spectra of the respective nanowires were less than the mode spacings estimated from the equation. The hexagonal (or near-circular) cross-section nanowire geometry resembles many microfabricated laser structures based

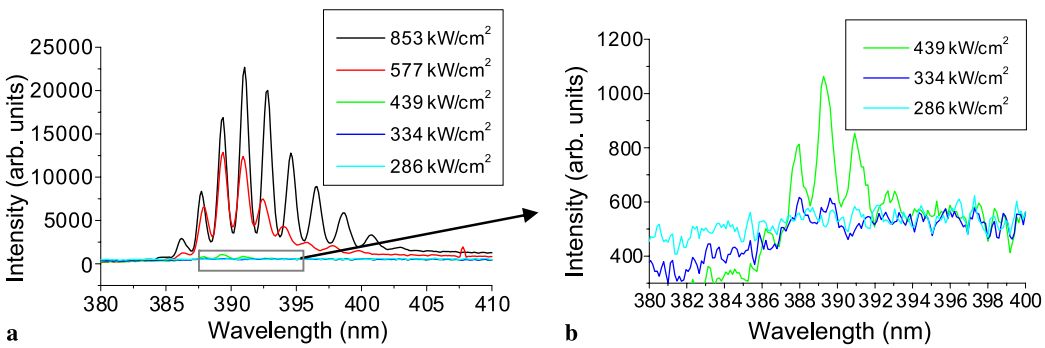

FIGURE 4 PL of a single ZnO nanowire collected at different power densities

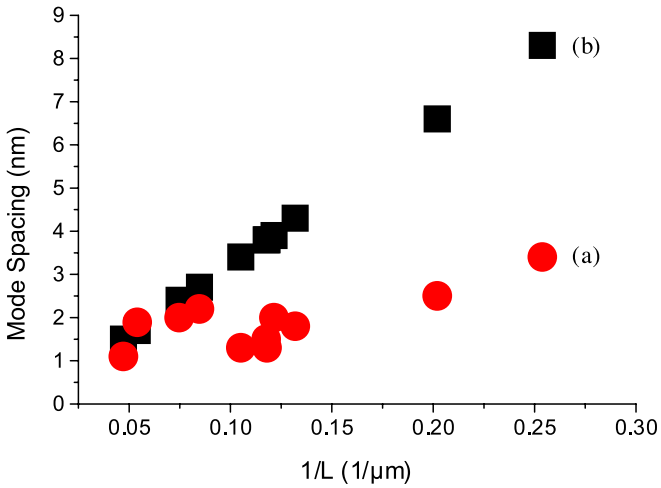

FIGURE 6 The relation between the mode spacing and the reciprocal nanowire length $1/L$: (**a**) given by experimental data, (**b**) given by the equation $\Delta\lambda = \lambda^2/2nL$

on strip waveguide geometry. Either single-transverse mode or multiple modes can be sustained within such microcavities depending on the dimensions of the structures [9]. Based upon classical waveguide theory [12], single-mode operation occurs for an infinite symmetric wire waveguide with the radius being the critical dimension. Thus, one would expect a complicated set of transverse modes as the radius of the wire waveguide increases. However, the axial symmetry of wires is not perfectly present in the above-selected samples, which also have larger radii with decreasing lengths. The exact transverse mode structures will be more complicated and also depend on the wire radius.

The spacing of the longitudinal modes that accompany each transverse mode depends critically on the effective path length of the mode, which for Fabry–Pérot resonators would simply be the wire length. However, when primarily axial modes may not experience sufficient gain to sustain lasing, it would not be expected that all modes would be of the pure axial Fabry–Pérot type, but instead some of them might contain significant non-axial wave vectors such as 'bow-tie' modes with large transverse wave vectors and larger effective cavity lengths, which is expected to narrow the effective mode spacing and modify the directional emission properties [9]. Therefore, this effect could be observed in the lasing spectra, as the mode spacing for $L < 10$ μm does not follow the typical $1/L$ dependence (Fig. 6).

4 Conclusions

In summary, we have succeeded in synthesizing vertically aligned ZnO nanowires in pure N_2 background gas without any catalyst using NAPLD. The room-temperature lasing phenomenon was observed in single ZnO nanowire microcavities, indicating that the as-synthesized nanowires in pure N_2 background gas are of high quality. With increase in excitation power, more cavity modes and higher peak intensities would emerge. The highly nonlinear gain combined with distinct cavity modes is a clear indication of the lasing process. The crystalline facets of the nanowires acted as laser-cavity mirrors. Therefore, mode spacings corresponding to cavity lengths of the respective nanowires were observed in photoluminescence spectra. In other words, lasing occurred within the self-formed cavity of the nanowire.

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REFERENCES

1 D. Appeli, Nature (London) **419**, 553 (2002)
2 J.A. Zapien, Y. Jiang, X.M. Meng, W. Chen, F.C.K. Au, Y. Lifshitz, S.T. Lee, Appl. Phys. Lett. **84**, 1189 (2004)
3 X. Duan, Y. Huang, R. Agarwal, C.M. Lieber, Nature **421**, 24 (2003)
4 J.C. Johnson, H. Yan, R.D. Schaller, P.B. Petersen, P. Yang, R.J. Saykally, Nano Lett. **2**, 279 (2002)
5 H. Kind, H. Yan, B. Messer, M. Law, P.D. Yang, Adv. Mater. **14**, 158 (2002)
6 Z.L. Wang, Adv. Mater. **15**, 432 (2003)
7 M. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, P. Yang, Science **292**, 1897 (2001)
8 H. Yan, R. He, J. Pham, P. Yang, Adv. Mater. **15**, 402 (2003)
9 H. Yan, J. Johnson, M. Law, R. He, K. Knutsen, J.R. McKinney, J. Pham, R. Saykally, P. Yang, Adv. Mater. **15**, 1907 (2003)
10 J. Suehiro, N. Nakagawa, S. Hidaka, M. Ueda, K. Imasaka, M. Higashihata, T. Okada, M. Hara, Nanotechnology **17**, 2567 (2006)
11 K. Bando, T. Sawabe, K. Asaka, Y. Masumoto, J. Luminesc. **108**, 385 (2004)
12 A.W. Snyder, J.D. Love, *Optical Waveguide Theory* (Kluwer, London, 1983)