Profile-broaden ultraviolet lasing from whispering gallery mode cavity in crown-like zinc oxide*

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The crown-like zinc oxide (ZnO) samples, which are composed of a hexagonal cap and a tower-like shaft, are prepared by vapor transport method. The hexagonal cap, working as a whispering gallery mode (WGM) resonant cavity, demonstrates density-dependent ultraviolet (UV) lasing emission with a broadened and squared photoluminescence (PL) profile under UV excitation at 355 nm. Theoretical analyses based on Fermi golden rule show that the broadened spectrum profile results from the special optical mode density characteristics in a WGM micro-cavity, which is in agreement with the observed results.

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The small-scale dielectric resonators, applicable to photonic nano devices with low threshold is considered to be importance, because they can be used as low-power-consumption photonic and optoelectronic components in optical integrated circuits[1-3]. Among different kinds of resonators, the whispering gallery mode (WGM) has attracted much attention because of its efficient mechanism of luminescence enhancement in small-scale resonators. Due to its direct band gap, large exciton binding energy and lattice structure, zinc oxide (ZnO) has been thought of a promising candidate material for ultraviolet (UV) photonic devices, such as lasers, optical filters, optical limiting, all-optical switch and optical data storage based on WGM-enhanced emission performances[4-8].

In this paper, crown-like ZnO nanostructures composed of hexagonal caps and tower-like shafts are prepared by vapor transport method. After examining and characterizing their morphology and crystal structure by scanning electron microscopy (SEM), X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM), the crown-like ZnO samples are excited by nanosecond laser pulses. The low-threshold UV stimulated emission is observed from the sample, and the WGM-based photoluminescence (PL) characteristics are discussed.

The samples were grown on silicon substrate in a tube furnace by vapor phase transport method similar to our previous reports[1,6-8]. A small quartz boat filled with high purity Zn powders was placed in a slender quartz tube with both ends open. A strip of silicon wafer with (1000) plane was put into quartz tube downstream from the boat as a deposition substrate. The furnace was heated at a rate of 20 °C/min after the quartz tube being inserted in it, and the vapor pressure was maintained 50 kPa during the whole growing process. When the temperature in source region was raised to 750 °C, nitrogen was introduced into the furnace chamber with a flux rate of 200 cm^3/min. The growth process lasts 30 min. During the process, the temperature around the substrate was kept at about 500 °C. Fig.1 shows the SEM images of the crown-like ZnO samples.

The XRD pattern of the sample is illustrated in Fig.2. All diffraction peaks match the indexes of the wurtzite ZnO with lattice constants of a=0.325 nm and c=0.521 nm. The strongest (0002) peak of the sample shows a preferred growth orientation along the c-axis. It can be confirmed by the HRTEM images of a shaft and a cap shown in Fig.3(a) and (b), respectively. As shown in Fig.3(a), the 0.26 nm d-spacing matches (0001) interspacing of the wurtzite ZnO. This indicates that the shafts mainly grow along [0001] direction, which is consistent with the XRD pattern. It can be seen from Fig.3(b) that the HRTEM image of a disk-like cap is obtained by viewing from [0001] direction, and the atoms arrange regularly to form a sixfold symmetric projected structure. The 0.28 nm d-spacing between any two adjacent lattice fringes along six symmetric directions, corresponds to the interspacing of $\{10\bar{1}0\}$ in wurtzite ZnO, i.e., the cap is formed by (0001) plane closed by six symmetric $\{10\bar{1}0\}$, which is

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similar to the hexagonal ZnO nanorods and nanodisks as reported by J. Dai et al[4,5].

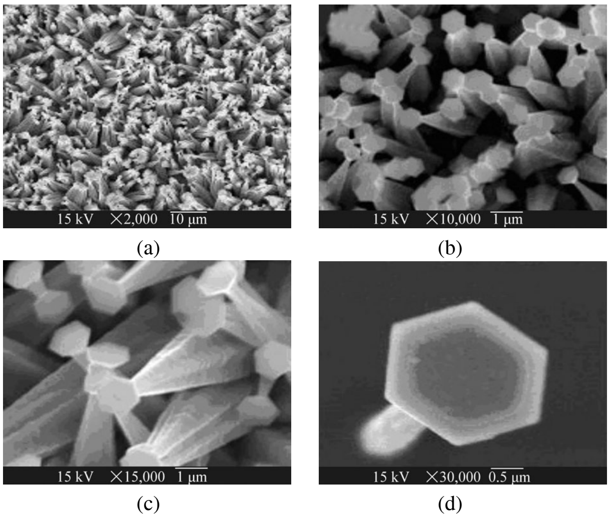


Fig.1 SEM images of the crown-like ZnO samples with (a) low, (b,c) medium and (d) high magnifications

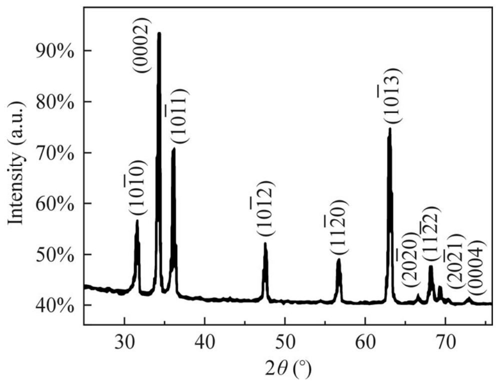


Fig.2 XRD pattern of the crown-like ZnO sample

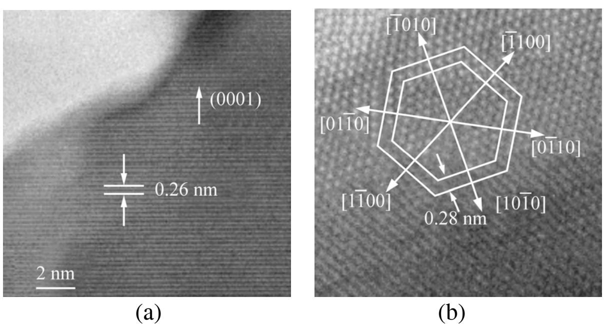


Fig.3 HRTEM images of (a) the shaft and (b) the disk-like cap

Fig.4 shows the lasing characteristics of the nanocap with diagonal of 8 μm under different excitation powers. At the low excitation power of 2.9 mW, the spectrum displays a weak spontaneous emission band centered at 394 nm. When the excitation power reaches 4.4 mW, some sharp peaks with the full width at half maximum (FWHM) of about 0.15 nm emerge out. As the excitation power increases to 10.4 mW, clear distinguished emission modes are observed in spectrum, while the mode spacing is abou 1.0 nm and the peak intensities of the discrete modes all increase dramatically.

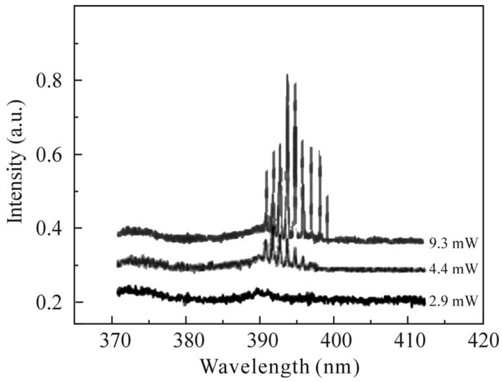


Fig.4 PL spectra from the cap with different excitation powers at 355 nm

This phenomenon may told us that there is a threshold of excitation power for the aforementioned PL performances. The threshold and the discrete modes reveal a transition from spontaneous emission to stimulated emission for the PL from the cap. Similar to the reports in Refs.[4–11], by estimating the $Q=\lambda/\Delta\lambda$ based on experimental data and comparing it with the calculation result of a hexagonal WGM cavity, according to the definition, Q is expressed as

$$Q=\frac{3\sqrt{3}\pi DnR^{3/2}}{2\lambda(1-R^{3})}, \qquad (1)$$

where D is the diagonal of the hexagon, R is the reflectivity of the side surface, λ is the wavelength of the emission mode, and n is the refractive index of ZnO. Good consistency between the two kinds of values means that the stimulated emission from the cap is WGM lasing. This reasonable ratiocination may be further confirmed by our measured result shown in Fig.5. Fig.5 shows the far-field lasing intensity distribution of the cap, and is measured around the axis of the shaft by rotating the optical multi-channel analyzer (OMA) around the cap. It can be seen from Fig.5 that there is a periodic distribution of the maximum and the minimum in the range of 360°. This experimental result is consistent with the numerical simulation result given by Wiersig[9] shown in the inset of Fig.5, in which the WGM lasing is predominantly emitted out at the corners of hexagon, and the intensity is periodically distributed around the cavity with a period angle of 60°. It directly proves the WGM resonant process in the hexagonal ZnO microcap.

Additionally, the profile of the lasing mode at high excitation power is more broaden than that under low excitation condition. In order to get more information on the resonant action in the hexagonal microcavities, the intensity-dependent lasing performance carries out in the same microcap as shown in Fig.6.

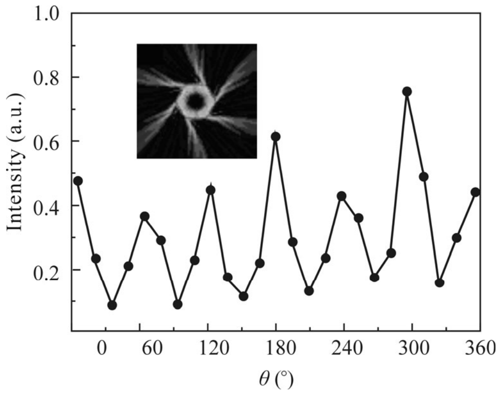
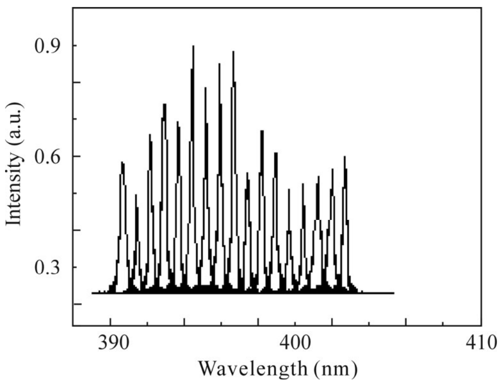
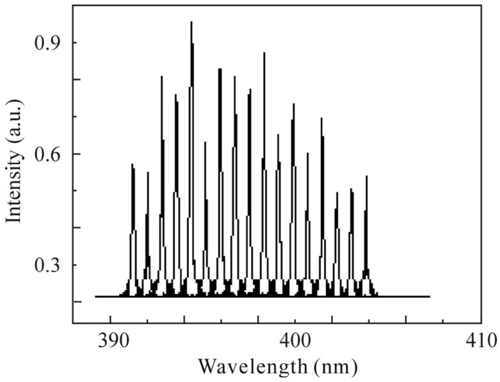


Fig.5 Far-field lasing intensity distribution around the cap (The inset is the numerical simulation result.)

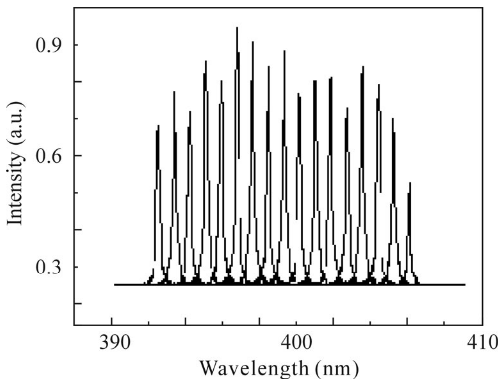
It is found from Fig.6 that more peaks emerge in a broadened and squared profile of all the lasing modes with the increase of excitation power, while the intensity of each lasing mode increases with different rates so that the profile tends to be more square, as well as with a totally red shift. This can be attributed to three reasons. The first is the behavior of band-gap shrinkage induced by intensive excitation condition according to the prediction of Varshni formula[3,5,6,9]. The second is the exciton-exciton inelastic collision. When the exciton concentration in the gain medium is raised as the excitation power, the main emission mechanism in ZnO becomes a change from exciton recombination to exciton-exciton inelastic collision. After this collision, the energy levels



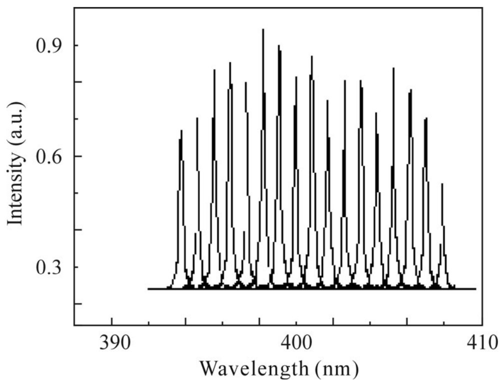
(a) 12.1 mW



(b) 15.2 mW



(c) 20.1 mW



(d) 24.3 mW

Fig.6 Broadened and squared profiles of PL from the cap at different excitation powers

of the exciton will follow the rule expressed as[6-8]

$$E_q = E_{\mathrm{ex}} - E_b^{\mathrm{ex}}(1-1/q^2) - 3kT/2\,, \tag{2}$$

where E_{ex} is energy of exciton in excited state, q is the charge of electron, T is the absolute temperature, and k is the state quantum number of the free exciton after collision. The shrinkage and collision make the electrons and holes with abundant occupied states. The last reason is determined by the quantized optical model density in WGM resonators. In free space, there is an optical mode density of a continuous function of the mode wavelength, but the modes with different wavelengths which can survive in a WGM resonator are quantized, and the each mode number can be deduced according to the resonant condition using plane wave method as[12,13]

$$l = \frac{3\sqrt{3}nD}{2\lambda} - \frac{6}{\pi}\tan^{-1}(n\sqrt{3n^2-4})\,. \tag{3}$$

In principle, the emission of photons due to electronic/hole transitions in condensed matter systems depends on the characteristics of initial and final states and the optical mode density. The radiative transition rate is given by[10,11]

$$R_{\mathrm{emission}} = \int_0^\infty R^{(l)}\rho(v_l)\mathrm{d}v_l\,, \tag{4}$$

where $R^{(l)}$ is the transition rate into an optical mode l, and $\rho(v_l)$ is the optical mode density.

Similar to the situation in Ref.[3-5], the fine-structured changes of the band-gap induced by increasing the excitation power combined the quantized optical mode density in WGM determines the broadened and squared profile of the lasing performance.

In conclusion, the UV WGM lasing with distinct mode structure is observed from the crown-like ZnO samples when its hexagonal cap works as a WGM cavity. Compared with the other hexagonal ZnO microstructures, such as nanorod and nanotube, it has a lower threshold for lasing emission. Meanwhile, a more and more broadened and squared profile of all the lasing modes is observed with the increase of excitation power. The theoretical and experimental investigations demonstrate that the broadened profile should be attributed to the influence of shrinkage of band-gap and the exciton-exciton inelastic collision on the electronic/hole initial and finial states, and the squared envelop is due to the quantized optical mode density in a WGM cavity. This is a good hint for the further investigation on WGM-based optical components.

References

[1] G. P. Zhu, C. X. Xu, J. Zhu and M. H. Wang, Journal of Materials Science **46**, 1877 (2011).

[2] Nitin R. Nand, Maxim Goryachev, Jean-Michel le Floch, Daniel L. Creedon and Michael E. Tobar, Journal of Applied Physics **116**, 134105 (2014).

[3] K. Saleh, G. Lin and Y. K. Chembo, IEEE Photonics Journal **7**, 5500111 (2015).

[4] J. Dai, C. X. Xu, K. Zheng, C. G. Lv and Y. P. Cui, Applied Physics Letter **95**, 241110 (2009).

[5] J. Dai, C. X. Xu, P. Wu, J. Y. Guo, Z. H. Li and Z. L. Shi, Applied Physics Letters **97**, 011101 (2010).

[6] Wang Mahua, Zhu Guangping, Zhu Hangqing and Zhao Zhengmin, Chinese Journal of Laser **39**, 154 (2012). (in Chinese)

[7] Wang Mahua, Zhu Guangping, Zhu Hanqing, Ju Yongfeng, Ji Rendong and Fu Lihui, Optoelectronics Letter **10**, 1 (2014).

[8] Wang Mahua, Zhu Guangping, Zhu Hanqing, Ju Yongfeng, Fu Lihui and Zhu Xia, Journal of Synthetic Crystal **42**, 1681 (2013). (in Chinese)

[9] J. Wiersig, Physics Review A **67**, 023807 (2003).

[10] CHEN Jin-zhong, CHEN Zhen-yu, SUN Jiang, LI Xu and GUO Shu-qing, Journal of Optoelectronics·Laser **24**, 1838 (2013). (in Chinese)

[11] WU Zhong-qing, CHENG Yin, ZHOU Wei-wei, WU Teng-yan and YANG Hai-jun, Journal of Optoelectronics·Laser **25**, 897 (2014). (in Chinese)

[12] E. F. Schubert, N. E. J. Hunt and A. M. Vredenbert, Applied Physics Letter **63**, 2603 (1993).

[13] Chinkyo Kim and Hyun Ha Kim, Applied Physics Letters **88**, 093104, (2006).