Optical Characterization of ZnO Microsphere Produced by Laser Ablation in Air

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We have succeeded in growing the ZnO microspheres by a simple laser ablation in the air, and we have obtained UV whispering-gallery-mode (WGM) lasing from the sphere under pulsed laser excitation. In this study, we observed resonances of WGM in visible region under cw laser pumping. In addition, possible refractive index of the ZnO microsphere was estimated from the WGM peaks. Furthermore, we obtained room-temperature electroluminescence from the ZnO microsphere/p-GaN heterojunction under forward bias.
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1. Introduction

Zinc oxide (ZnO) has a direct wide band-gap of 3.37 eV and a large exciton binding energy of 60 meV, which is much larger than the thermal energy at room temperature (26 meV). Therefore, ZnO is one of the excellent candidate materials for ultraviolet (UV) emitting devices, such as UV light emitting diodes and UV lasers. In addition, ZnO nano/microstructures have attracted a great deal of attention as building blocks because of their high crystalline quality and unique structures. Those ZnO nano/microcrystals can be synthesized by several methods such as carbothermal CVD [1,2], hydrothermal method [3,4], nanoparticles assisted pulsed laser deposition (NAPLD) [5-7], and so on. Interestingly, the ZnO nano/microcrystals can serve as good resonance cavities without additional mirrors due to the high refractive index of ZnO. Light is confined in a single nano/microcrystal, and the oscillation route is formed within it. Lasing from ZnO nanowire [7-9], ZnO nanosheet [2], ZnO microdisk [10], ZnO ring [11], and ZnO nanonail [12] have been demonstrated under pulsed laser excitation. In our study, we have succeeded in synthesizing ZnO nano/microspheres by simple atmospheric laser ablation method, and demonstrated whispering-gallery-mode (WGM) lasing from the spheres [13,14]. In order to investigate the lasing properties of these nano/microcrystals, pulsed laser excitation is generally used because it induces population inversion due to the high peak power. Recently, we observed resonances of WGM in visible region from the ZnO microsphere under cw laser excitation, which is used for investigating the luminescence properties. In addition, room-temperature electroluminescence (EL) from the ZnO microsphere/p-GaN heterojunction under forward bias [15]. In this paper, we report the optical characteristics of optically- and electrically-pumped single ZnO microsphere. Furthermore, possible refractive index of the ZnO microsphere estimated from the WGM peaks are discussed.

2. Experimental details

2.1 Synthesis of ZnO microsphere

A ZnO microsphere synthesis method is laser ablation of a ZnO bulk target in the air, which is a quite simple laser process. The ZnO microspheres are synthesized by ablating the ZnO sintered target on which Nd:YAG laser beam (λ = 1064 nm, 10 Hz) was focused at a fluence of 5-40 J/cm^2. The atmospherically ablated ZnO droplets were collected on a proper substrate which was located at approximately 5 mm away from the focal point on the target, and then the spherical ZnO microcrystals were obtained. For a more detailed description of the ZnO microsphere synthesis, please refer to Refs. 13 and 14. The morphology of the microspheres were observed by scanning electron microscopy (SEM) and an optical microscope.
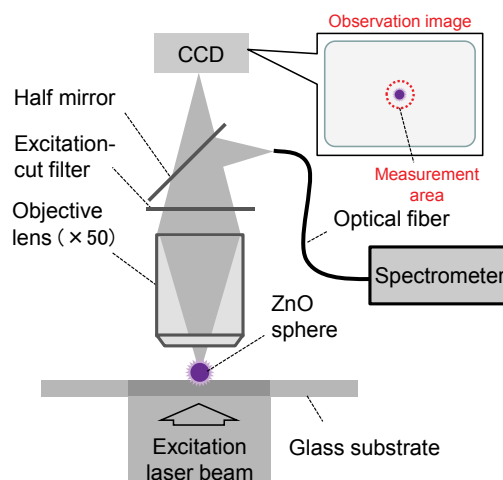

Fig. 1 Schematic of the microscopy system for measuring emission spectrum from a single ZnO microsphere.

2.2 Optical characterization of ZnO microsphere

The emission from the ZnO microsphere was measured by a microscopic-spectroscopy system, as shown in Figure 1. The microspheres were excited by the third harmonics of a Q-switched Nd:YAG laser (355 nm, 5 ns) or cw He-Cd laser. In this system, many microspheres dispersed on the substrate are excited at once. But, we can measure the emission from a single ZnO microsphere using an x-y micro stage and a small observation area captured by an optical fiber.

3. Results and discussion

3.1 Lasing characteristic of ZnO microsphere under pulsed laser excitation

Fig. 2 shows the emission spectra from the ZnO microsphere excited by the Nd:YAG laser. Inset is the SEM image of the microsphere, which has a radius, a, of 1.6 μm. We have confirmed that the synthesized ZnO microspheres have wurtzite-structured ZnO crystal from the X-ray diffraction and micro-Raman measurement [13] Lasing spectra with modal structure from the ZnO microsphere were observed in UV region, which corresponds to the near band edge emission in ZnO. These sharp peaks show a clear threshold behavior with the threshold power density of around 100 kW/cm^2, indicating that lasing took place within the microsphere. The mode spacing of the lasing spectra from the microspheres was 3.6 nm, which corresponds to the WGM-theoretical mode spacing $\Delta\lambda$ expressed as the following equation [13]:

$$\Delta\lambda = \frac{\lambda_i^2}{L}\left(n_i - \lambda_i \frac{dn_i}{d\lambda} + \frac{\lambda_i}{L}\right)^{-1} \qquad (1)$$

where L is the cavity length, and i is a modal number with an integer, $dn/d\lambda$ is the wavelength dispersion, and n_i is the refractive index of the microsphere. The cavity length L approaches to the circumference of the sphere if the modal number is large, resulting in $L \approx 2\pi a$. The theoretical mode spacing of 3.64 nm was estimated around λ_m =395 nm, and the values of the refractive index and wavelength dispersion were n_i =2.29 and $dn_i/d\lambda$ = -0.0049 nm^{-1},
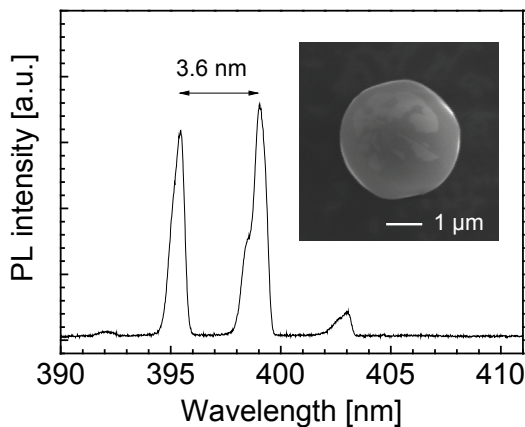

Fig. 2 Lasing spectra from the ZnO microsphere excited by the pulsed UV laser beam. Inset is the SEM image of the ZnO microsphere.
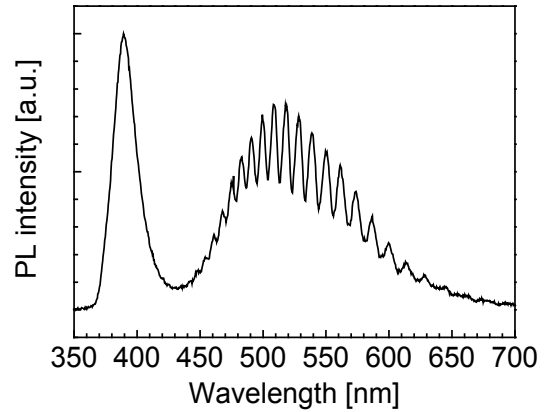

Fig. 3 PL from the ZnO microsphere excited by cw He-Cd laser beam.

respectively [15], and it showed good agreement with the experimental result.

3.2 Photoluminescence of ZnO microsphere under cw laser excitation

Fig. 3 shows the photoluminescence (PL) from the ZnO microsphere with a diameter of 3.6μm under cw He-Cd laser (325 nm) excitation. A strong UV emission, which corresponds to the near-band-edge emission of ZnO, and a broad visible emission with a modal peaks were observed. The visible emission was usually observed from ZnO under cw He-Cd laser excitation [2,16], and it is defect-related emission which is attributed to the deep-level oxygen vacancy [17,18]. It was confirmed that the modal peaks in visible region also correspond to WGMs from Eq. (1).

The WGMs in a spherical microcavity are characterized by a set of quantum numbers that describe the angular momentum mode number i and radial mode number l. Assuming a is much larger than λ, the relation between size parameter $x_i^{(l)} = 2\pi a/\lambda$ and i, l can be expressed in powers of $\nu^{-1/3}$ [19,20]:

$$n_s x_i^{(l)} = \nu - \zeta_l\left(\frac{\nu}{2}\right)^{\frac{1}{3}} + \sum_{k=0}^{k_{max}} \frac{d_k(m,\zeta_l)m}{\nu^{1/3}(m^2-1)^{(k+1)/2}} \qquad (2)$$

where $\nu = i+1/2$ and $m = n_s/n_e$ is the relative refractive index between the sphere and the surrounding medium. The coefficients d_k depend on the polarization (TM or TE) of the mode [20]. The lth zero of the Airy function is denoted as ζ_l.

Using Eq. (2), the refractive index of the ZnO microsphere was estimated because some papers reported that the dispersion of ZnO micro/nanocrystals was different from that of ZnO bulk or film [10,12]. In order to apply the ZnO microsphere to sensing devices [21], the absolute value of n_s is very important for its sensitivity and reliability. Fig. 4 shows the refractive indexes calculated using the experimental WGM peak wavelengths, where the first radial order (l=0) and TE mode were estimated since they are more likely to be longer-lived than other WGMs [22]. In Fig. 4, different angular momentum mode number series were assigned, that is, i= 41-45 at λ=482.8 nm. The dispersion curve with i=43 (@λ=482.8 nm) series is very close to that
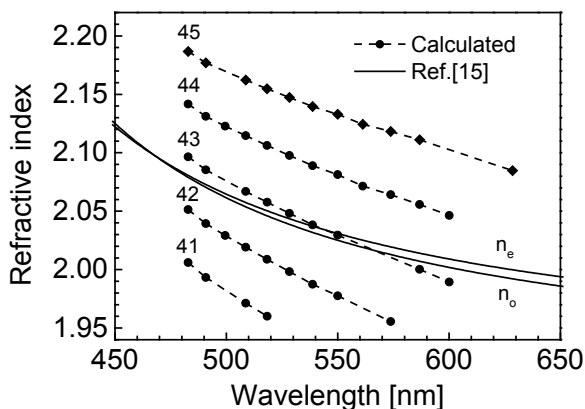
Fig. 4 Estimated refractive index of the ZnO microsphere.

of bulk ZnO [15], which probably shows the possible refractive index of the ZnO microsphere, because the dispersion of ZnO in visible region is small compared with that in UV region. The difference in the refractive index between the ZnO microcrystal and bulk ZnO was also reported [12,22], though the reason remains unclear. The difference may be induced by the size of the ZnO crystal. Although a much more detail investigation is required, possible refractive index of the ZnO microsphere could be estimated from the WGM peaks.
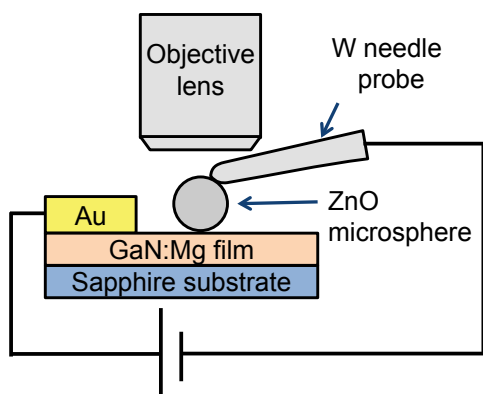

Fig. 5 Schematic of the ZnO microsphere/p-GaNfilm heterostructure for electrical excitation of the microsphere.

3.3 Emission characteristic of ZnO microsphere under electrical excitation

It is desirable to fabricate light emitting diodes and laser diodes based on ZnO microspheres to realize electrically pumped WGM emitter and lasing. Here, an optical property of the ZnO microsphere under electrical excitation was investigated. We fabricated the ZnO microsphere/p-GaN heterostructure, as shown in Fig. 5. In the experiment, the microsphere with a radius of 5 μm was used. The ZnO microsphere and the p-GaN film grown on the sapphire substrate formed a microsized junction on the interface. It was confirmed that Ohmic contacts were formed on the top ZnO buffer layer in contact with a W needle probe and the p-GaN film by depositing Au. EL emission of the ZnO microsphere/p-GaN heterostructure was observed under various forward biases, as shown in Fig. 6. Inset is the peak intensity at 400 nm as a function of the forward bias. The

near-UV emission peak at 400 nm was intensified with increasing the applied voltage up to 20 V. The *I–V* curves of the heterojunction clearly show the nonlinear increase of the current under forward bias. Rectifying characteristics with a threshold voltage of about 5 V was obtained, which is larger than that of nanowire-based heterojunction [23]. The heterojunction interface of the ZnO microsphere/p-GaN film probably decreased the electron injection from the ZnO microsphere to the p-GaN films due to poor contact, and reduced the electron–hole recombination when the forward bias is applied. Unfortunately, no WGM lasing from the ZnO microsphere was obtained though the EL emission was observed from the heterostructure. In this case, light generated at the heterojunction leaked to GaN film because the refractive index of GaN is larger than that of ZnO at 400 nm. Other p-type material having a low refractive index will serve a high light confinement and lasing from the ZnO microsphere under electrical excitation.
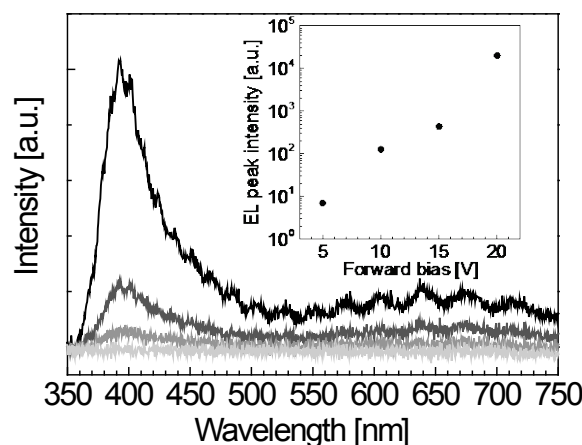

Fig. 6 EL spectra of the ZnO microsphere/p-GaNfilm heterostructure under forward bias. Inset is the peak intensities as a function of the forward bias.

4. Conclusion

We have achieved the ZnO microspheres by a simple atmospheric ablation method. The synthesized ZnO microspheres had wurtzite structure and completely spherical in shape. The UV WGM lasing of ZnO microspheres under pulsed laser excitation was obtained because of high light-confinement property resulted from the spherical microcavity effect. In addition, WGM resonances in visible region was also observed from the ZnO microsphere pumped by a cw He-Cd laser. Experimental results were in good agreement with WGM theory. Using the WGM theory, possible refractive index of the ZnO microsphere was estimated from the experimental WGM peaks. Furthermore, room-temperature electroluminescence with peak wavelengths of 400 nm was observed from ZnO microspere/p-GaN heterojunction under forward bias.

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