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Synthesis of Various Sized ZnO Microspheres by Laser Ablation and Their Lasing Characteristics

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We have succeeded in synthesizing ZnO nano/microspheres by a simple laser ablation method in the air and demonstrated whispering-gallery-mode (WGM) lasing from the ZnO sphere excited by a pulsed-ultraviolet laser beam. The spheres with diameters of up to 10μm were simply prepared by laser ablation of a ZnO sintered target by a Q-switched Nd:YAG laser in the air. In this study, we succeeded synthesizing large microspheres with diameters of larger than 20μm by the Nd:YAG laser without Q-switching. The mode spacing of the large sphere was in good agreement with the WGM theory.

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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 that of gallium nitride (28 meV) and the thermal energy at room temperature (26 meV). Therefore, ZnO is an excellent candidate material for ultraviolet (UV) emitting devices, such as UV light emitting diodes and UV lasers. In addition, ZnO nano/microstructures have attracted considerable attention because of their high crystalline quality and unique structures. Those ZnO nano/microstructures typically consist of single crystalline and can serve as good resonance cavities without additional mirrors due to the high refractive index of ZnO. UV light is confined in a single nano/microcrystal, and the oscillation route is formed within it. Lasing from several ZnO micro/nanocrystals, for example, nanowire [1], nanosheet[2], microdisk[3], have been demonstrated. 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[4]. The spheres with diameters of up to 10 μm were simply prepared by laser ablation of a ZnO sintered target by a Q-switched Nd:YAG laser in the air. Recently, we succeeded synthesizing large microspheres with diameters of lager than 20 μm by the Nd:YAG laser without Q-switching. In this study, we report the morphological and lasing characteristic of the large microspheres.

2. Experiment

Our synthesizing method is a quite simple process, which is laser ablation of a ZnO bulk target in the air. The ZnO microspheres were 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 crystals were obtained. The pulse width of the Nd:YAG laser was typically 10 ns under Q-switch operation. On the other hand, when the laser was operated without Q-switching, several pulses were output at each shot, as shown in Fig.1. Output duration of the pulse group was about 45μs due to no Q-switching. Though the flash lamp of the Nd:YAG laser pump at 10 Hz, the repetition rate of the pulses was approximately estimated to be 200 kHz (= 1 sec/(45 μs/9 pulses)), that is, these high-repetition rate pulse group (about 9 shots) was output at 10 Hz.

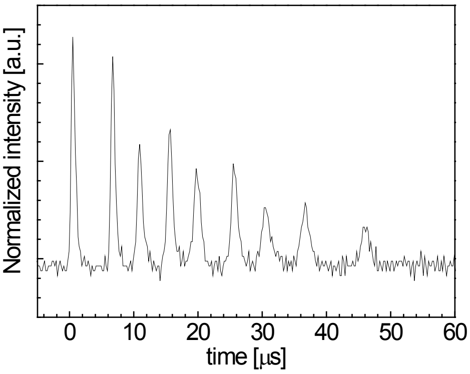

Fig. 1 Pulse shape of the Nd:YAG laser beam without Q-switching.

3. Results and discussions

3.1 Synthesis of ZnO microspheres

ZnO spheres collected on indium tin oxide (ITO) thin film were observed by a scanning electron microscope

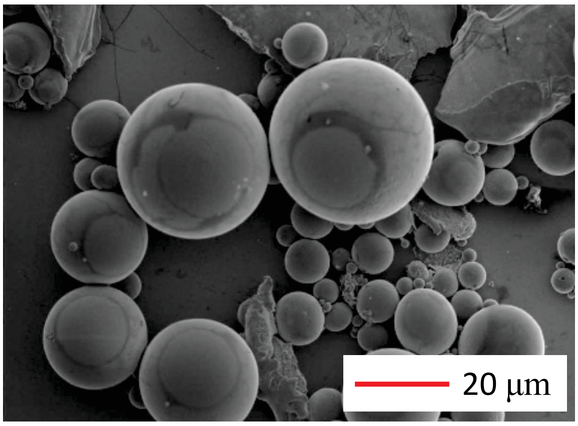

Fig. 2 SEM image of the various sized ZnO microspheres synthesized by laser ablation.

(SEM), as shown in Fig. 2. Several sized ZnO microsphere were synthesized. Most of the spheres have completely spherical in shape, and the diameters were from 500 nm to 35 µm. A small amount of non-spherical flakes were also produced. It was confirmed that the synthesized ZnO spheres have wurtzite-structured ZnO crystal from the X-ray diffraction and micro-Raman measurement[4].

The synthesis method of ZnO spheres, which is laser ablation in the air, was very simple and productive without any time-consuming crystal-growth process. However, the diameters of the ZnO spheres have been limited to up to 10 µm by this method using a Q-switch Nd:YAG laser. In this study, large ZnO spheres with diameters of over 30µm were obtained by no Q-switching laser pulses. This result can be explained by heat accumulation by long pulse duration and high repetition rate pulses[5]. In the experiment, the average power of the laser pulses was the same in both of the Q-switching and non-Q-switching mode. For instance, the peak power in the Q-switch mode can be simply estimated to be 1 MW from a 10 mJ/pulse and a pulse duration of 10 ns. In contrast, the peak power in the non-Q-switching mode was 0.6 to 3.5 kW, which is much less than that of in the Q-switching mode, because of the pulse durations of 300 ns to 1.5 µs. Though the peak power decreased in the non-Q-switching mode, target heating was enhanced by a much longer duration pulse. In addition, thermal conductivity of ZnO single crystals decreases along with increasing of its temperature[6,7]. When the interval of laser pulse is shorten, which means shortage of cooling time, the temperature of laser-irradiated ZnO surface will increase due to heat accumulation by multi-pulses. For this reason, the interior of the ZnO target is not cooled to room temperature until the next pulse comes when the repetition rate is higher than a threshold value[8,9]. In the case of ZnO, the effect gradually appears at larger than 100 Hz[5]. Therefore, melted volume provably increased, and then the large sized droplets generate by high repetition rate pulses.

3.2 Lasing characteristic of ZnO microsphere

Figure 3(a),(b) show the images of single ZnO microsphere captured by a color CCD camera and SEM, respectively. The diameter of the sphere was 23.8µm. The sphere on the transparent substrate was excited by the third harmonics of a Q-switched Nd:YAG laser (355 nm, 5 ns), and

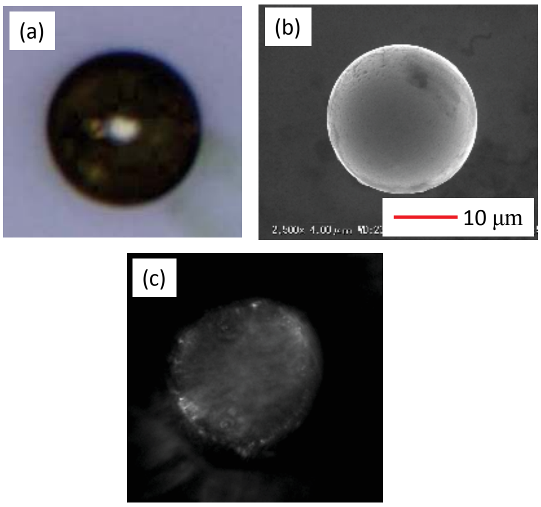

Fig. 3 Images of the ZnO microsphere captured by (a) color CCD camera, (b) SEM, and (c) monochrome CCD under optical excitation.

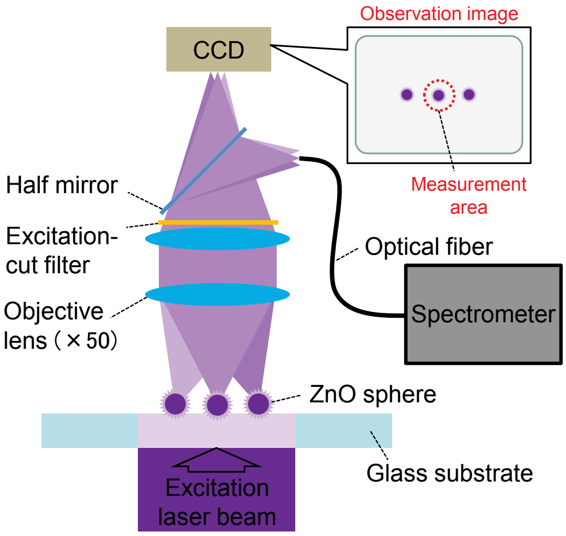

Fig. 4 Schematic of the microscopy system for measuring emission spectrum from a single ZnO microsphere.

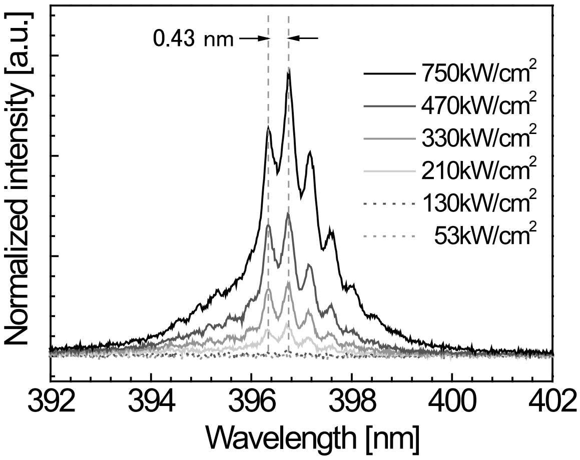

Fig. 5 Lasing spectra from the ZnO microsphere excited by the pulsed UV laser beam with different power

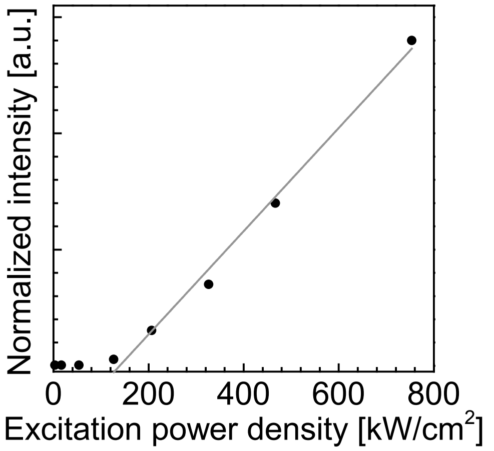

Fig. 6 Normalized peak intensities plotted as a function of the excitation power densities at 396.7nm in Fig. 5.

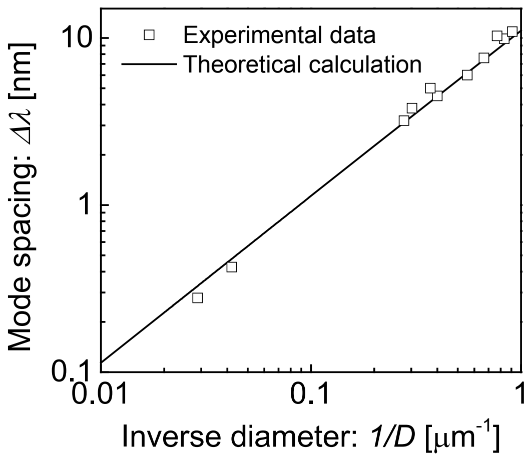

Fig. 7 Experimental results of mode spacing and inverse diameter of ZnO microspheres were plotted, and WGM-theoretical relationship was also shown.

the emission was measured by the microscopic-spectroscopy system, as shown in Fig. 4. In this system, many spheres dispersed on the substrate are excited at once. But, we can measure the emission from single ZnO microsphere using an x-y micro stage and a small observation area. Figure 3(c) shows the monochrome CCD image of the ZnO sphere under excitation by the Nd:YAG laser beam. Figure 5 shows the emission spectra from the microsphere observed by the spectrometer. Lasing spectra with modal structure from the ZnO microsphere were observed in UV region, which corresponds to the near band edge emission in ZnO. Figure 6 show the plotted peak intensities at 396.7 nm as a function of excitation power density. A clear threshold behavior of the peak intensity was observed, indicating that lasing took place within the microsphere. In addition, the ZnO microsphere prepared by this method has considerably lower threshold compared to random lasing, resulting from WGM-cavity lasing. The mode spacing of the lasing spectra from the microspheres with diameters of 23.8 μm was 0.43 nm. The WGM-theoretical mode spacing $\Delta\lambda$ is expressed as the following equation[4]:

$$\Delta\lambda = \frac{\lambda_m^{\,2}}{Da\sin(\pi/a)}\left(n_m - \lambda_m\frac{dn}{d\lambda} + \frac{\lambda_m}{Da\sin(\pi/a)}\right)^{-1}$$

where D is the diameter of the microsphere, and m is a modal number with an integer, $dn/d\lambda$ is the wavelength dispersion, and n_m and a are the refractive index of the microsphere and the reflection time of the confine light within a microsphere, respectively. The mode spacing was estimated around λ_m =400 nm, and the values of the refractive index and wavelength dispersion were n_m =2.3 and $dn/d\lambda$ =0.0054 nm^{-1}, respectively[10]. Those values were assigned to the equation, and the relationship between $\Delta\lambda$ and 1/D was shown in Fig. 7, where the reflection times a was assumed to be 15. The experimental results were also accompanied in Fig. 7. The experimentally observed results from not only several micrometer spheres but also large sized spheres of 23.8 μm and 34.6 μm were in good agreement with the theoretical prediction.

The experimental Q factor of the lasing spectra in Fig. 4 was calculated. The full-width half-maximum (FWHM) of the one peak was estimated to be 0.4 nm by Gaussian fitting though the lasing peaks were overlapped due to the small mode spacing. Thus, the Q factor was calculated to be about 10^3. This result confirmed that the WGM-cavity lasing took place within the ZnO sphere because of high light-confinement.

4. Conclusions

We synthesized ZnO microspheres by a simple atmospheric ablation method of ZnO sintered target. Large size ZnO microspheres of over 30μm were synthesized by laser ablation using a Nd:YAG laser without Q-switching. The synthesized ZnO microspheres had wurtzite structure and completely spherical in shape. Lasing characteristics of ZnO microspheres were investigated using an optical pumping, and WGM-mode lasing in UV region could be observed from the ZnO microsphere because of high light-confinement property resulted from the spherical micro-cavity effect. Experimental results were in good agreement with WGM theories in terms of mode spacing, and the high Q factor of about 10^3 was obtained from the 23.8 μm microsphere.

Acknowledgments

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