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# Laser Processing for Growth Control of ZnO Nanocrystals by Nanoparticle – Assisted Pulsed Laser Deposition

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## Abstract

ZnO nano/micro crystals exhibit unique optical and electrical properties, and have gained considerable attention as building blocks of optoelectronic devices. We have succeeded in synthesizing ZnO nanocrystals by nanoparticle-assisted pulsed laser deposition (NAPLD), which is catalyst-free method. For development of ZnO nanocrystal-based devices, control of shape, density and position of ZnO nanocrystals is essentially required. In our study, we proposed combining NAPLD and laser interference patterning for position control of ZnO nanocrystal. Periodic ZnO cylinder-shaped crystals were obtained on pre-deposited ZnO buffer layer patterned by four-beam interference laser. Each cylindrical wall was formed by connecting the high-density ZnO nanowires grown on patterned edge. In addition, shape of ZnO nanocrystal tip was modified by laser irradiation. Photoluminescence emission from the patterned ZnO crystals under 355 nm laser excitation showed strong emission peaked at 390 nm due to a near band edge recombination of ZnO, and defect-related emission was reduced after laser irradiation. This technique can be useful for control not only position but also shape and density of the ZnO nanocrystals.

Keywords: ZnO, PLD, interference patterning, laser annealing

## 1. INTRODUCTION

Currently, gallium nitride (GaN) based semiconductors are used for near ultraviolet light emitting devices such as blue diodes. However, since gallium is a rare metal, the light emitting element has been moving at a high price. So we focused on zinc oxide (ZnO) which has a potential to emit light with high efficiency in the same wavelength region as an alternative material for gallium nitride. ZnO has potential in many applications area, including short-wavelength ultraviolet lasers [1,2] and blue–green optoelectronic devices [3] due to the wide direct band-gap (3.37 eV) and large exciton binding energy (60 meV) at room temperature. ZnO is also resource-rich, inexpensive and it is easy to fabricate nanostructures by self-organization. In addition, ZnO nano/micro crystals exhibit optical and electrical properties that cannot be obtained with bulk or thin film, and have received great attention as building blocks for optoelectronic devices. Control of crystal shape, density and position is important for development of ZnO nanocrystal-based devices.

A large number of methods have been developed to fabricate ZnO nano/micro crystals, including chemical vapor deposition (CVD) method [4], metal-organic CVD (MOCVD) [5] and hydrothermal synthesis [6]. Basically, MOCVD method requires liquid phase medium and vaporizer, so that the equipment becomes large. On the other hand, we have developed nanoparticle-assisted pulsed laser deposition (NAPLD) in which a typical PLD chamber can be used. This method can produce nano/micro crystals without any catalyst. We have succeeded in synthesizing various ZnO crystals such as nanoparticles [7], nanowalls [8] and nanorods [9] by using NAPLD method. Furthermore, we have succeeded in growing periodic ZnO crystals by combining the NAPLD method and laser interference patterning [10]. Each ZnO crystals of the periodic structure has unique shape such as cylinder [11] and sub-micron rod [12] so that they may be applicable to micro-cavity array. However, in order to realize the micro-cavity lasing, light confinement structure is inevitably required. In this study, we fabricated ZnO nanocrystals by NAPLD with interference patterning, and performed laser irradiation to the nanocrystals to modify the shape and to improve the photoluminescence (PL) property.

## 2. EXPERIMENT

### 2.1 Preparation of ZnO film as buffer layer using pulsed laser deposition

In order to fabricate periodic ZnO nanocrystals, a ZnO thin film was firstly prepared on a substrate as a buffer layer. An experimental schematic is shown in fig.1.

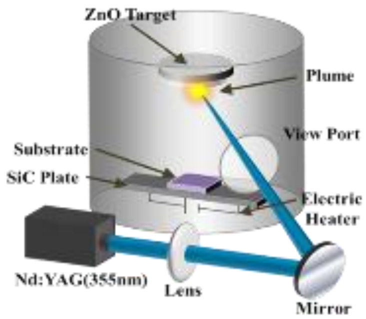


**Fig.1 Schematic of PLD and NAPLD**

A ZnO sintered target was set in a vacuum chamber, and irradiated by Nd:YAG laser (355 nm, 10 ns, 10 Hz). ZnO thin film was grown on a-cut sapphire substrate at substrate temperature of 500 oC with an ambient oxygen gas pressure of 3 Pa for the deposition time of 10 min. The thickness of the

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buffer layer was about 80 nm.

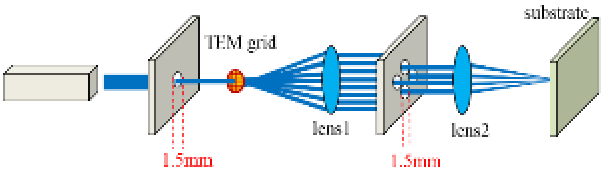


**Fig. 2 Schematic of four-beam interference laser patterning**

### 2.2 Four-beam interference laser patterning

Subsequently, we patterned on ZnO buffer layer with four-beam interference laser. An experimental schematic is shown in fig. 2. A TEM grid (400 mesh, 63.5 μm pitch) was used as a transmission beam splitter. Nd:YAG laser beam (355 nm, 10 ns) was diffracted and converted to parallel light by first lens. Four beams were extracted by a special filter, and focused on the ZnO buffer layer though the second lens. The irradiation fluence was 0.7~1.6 J/cm$^2$.

### 2.3 ZnO nanocrystal fabrication by NAPLD

The patterned ZnO film was again placed in the vacuum chamber, and ZnO nanocrystals were grown on the film by NAPLD method at substrate temperature of 750 °C. An ambient argon gas pressure was 1.3 × 10$^4$ Pa. In the relative high gas pressure, the nanoparticles are formed by the aggregation of the ablated species, and the nanoparticles play an important role in the formation of nanocrystals without catalyst. In the experiment, the deposition time was 20 min for the growth of ZnO nanocrystals.

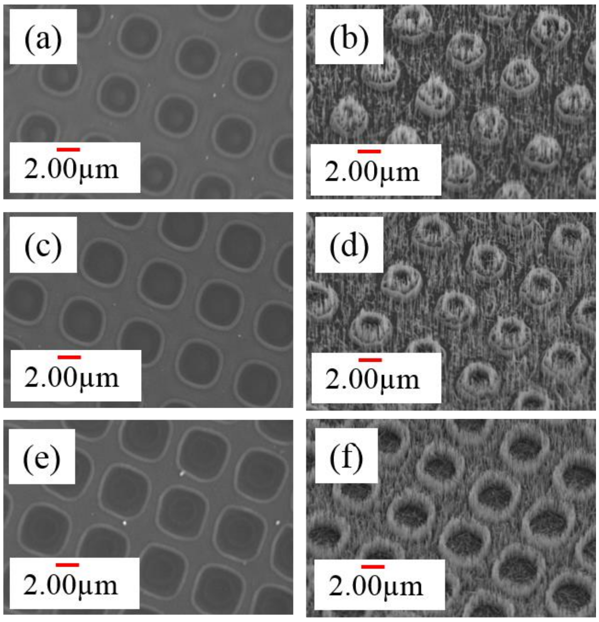


**Fig. 3 SEM images of patterned ZnO buffer layer and nanocrystals with different patterning fluences of (a, b) 0.8 J/cm$^2$, (c, d) 1.1 J/cm$^2$ and (e, f) 1.6 J/cm$^2$**

### 2.4 Laser irradiation to ZnO nanocrystals

After growth of the ZnO nanocrystals, laser irradiation was performed in atmosphere using KrF excimer laser (248 nm, 60 mJ/cm$^2$) in order to anneal the nanocrystals and modify the shape.

## 3. RESULTS AND DISCUSSIONS

Scanning electron microscope (SEM) images of the patterned buffer layer and fabricated ZnO nanocrystals after NAPLD are shown in fig. 3. From fig. 3(a, c, e), we confirmed dot pattern formation on the buffer layer, which corresponds to the four-beam interference pattern. Vertical ZnO cylinder like crystals were grown on ZnO buffer layer as shown in fig. 3(b, d, f). It is because edge of the laser-irradiated dot promoted nucleation of ZnO nanowire, and dense nanowires connected each other. On the other hand, vertical ZnO nanowires with a diameter of 50 nm to 100 nm were grown on the non-irradiated area.

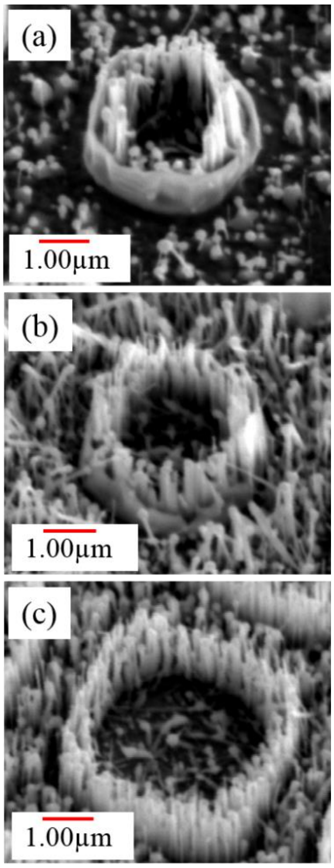


**Fig. 4 High magnification SEM images of laser-irradiated ZnO nanocrystals with patterning fluence of (a) 0.8 J/cm$^2$, (b) 1.1 J/cm$^2$ and (c) 1.6 J/cm$^2$**

Figure 4 shows high magnification SEM images of the ZnO nanocrystals irradiated by KrF excimer laser with 60 mJ/cm$^2$. It was confirmed that the tip of the nanowire was changed to a spherical shape. It is considered that the tip of the nanowire was melted by laser irradiation and changed to a spherical shape due to surface tension, and then recrystallized immediately with keeping the shape. The diameter of the produced tip sphere was about 100 to 200 nm. Figure 5 shows PL spectra of the ZnO nanocrystals before/after laser irradiation. Reduction of visible light emission, which was defect-related emission, was confirmed after laser irradiation (red-line) compared with before laser irradiation (blue-line). In fig. 5(a), an increase in ultraviolet emission was observed, and a change in visible emission peak was observed. However, lasing behavior was not observed. We have observed whispering gallery mode (WGM) lasing from ZnO microsphere under optical excitation [13]. In order to obtain laser oscillation from the spherical ZnO cavity more than 500 nm diameter may be required, otherwise light confinement inside sphere cannot be achieved.

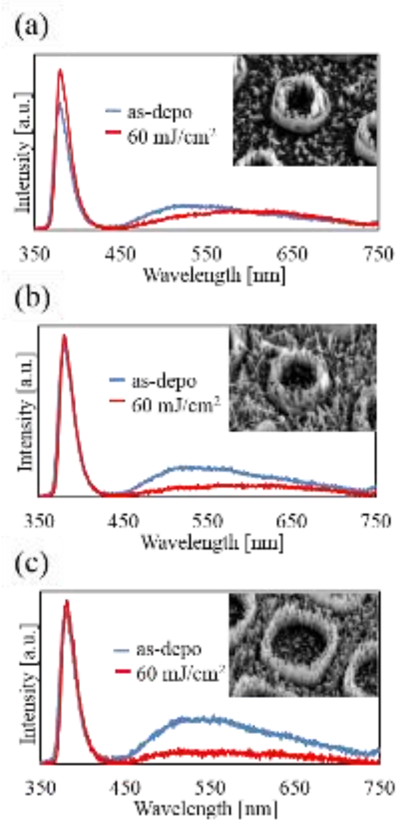


**Fig. 5 PL spectra of ZnO nanocrystals before/after laser irradiation with patterning fluence of (a) 0.8 J/cm$^2$, (b) 1.1 J/cm$^2$ and (c) 1.6 J/cm$^2$**

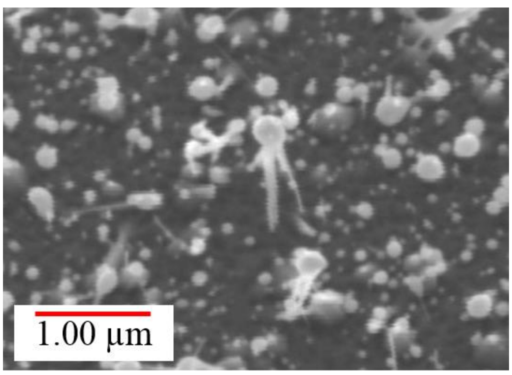


**Fig. 6 SEM image of ZnO tip sphere with a fluence of 100 mJ/cm$^2$.**

So laser irradiation conditions such as fluence and shot number were changed to increase the diameter of the tip spheres. When the laser fluence was increased to be 100 mJ/cm$^2$, the diameter of the tip sphere was increased to about 400 nm as shown in fig. 6. It is due to an increase in the amount of molten nanowires. However, the produced spheres and nanowires were blown off by laser ablation. Next, the number of laser shots was increased with a fluence of 50 mJ/cm$^2$. No change in the diameter of the tip sphere was observed. This is because the tip sphere produced by former laser irradiation was blown off and other tip spheres were newly produced from remained nanowires by further laser irradiation.

A diameter of more than 500 nm is necessary to realize WGM lasing from ZnO sphere. However, it is difficult to produce such large tip sphere from the ZnO nanowire with a diameter of 50 nm to 100 nm by laser irradiation, because thin nanowire is fragile and molten volume is limited. Although we have expected a few tip spheres aggregate each other, each nanowire independently formed a tip sphere as shown in fig. 4. On the other hand, a tip sphere of about 400 nm could also be obtained at high fluence of 100 mJ/cm$^2$, though the many nanowires were blown off by the impact of the laser irradiation. Therefore, in order to fabricate a sphere of more than 500 nm at the wire tip, preparation of thick ZnO nanowires with a diameter of about 300 nm will be effective. We can increase diameter of ZnO nanowire by NAPLD with optimization of growth condition, and it will be revealed by future research.

## 4. CONCLUSION

We succeeded in fabricating periodic ZnO nanocrystals by NAPLD and laser interference patterning. In addition, tip of the nanocrystals was changed to a spherical shape by laser irradiation. PL characteristics of the laser-irradiated ZnO nanocrystals showed increase of ultraviolet emission and the reduction of defect-related visible emission. However, WGM lasing at the tip sphere could not be observed because the diameter of the sphere was too small for light confinement. In order to increase diameter of the tip sphere different laser irradiation conditions of fluence and shot number were investigated, and the diameter of the tip sphere was increased to be 400 nm. However, it is difficult to increase the diameter of the tip sphere more than 500 nm to achieve WGM lasing. One approach will be to prepare large diameter nanowires by the NAPLD and laser interference patterning.

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