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Ultraviolet lasing and field emission characteristics of ZnO nano-rods synthesized by nano-particle-assisted pulsed-laser ablation deposition

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ABSTRACT We describe the lasing and the field emission characteristics of ZnO nano-rod crystals synthesized by nano-particle-assisted pulsed-laser ablation deposition, where nano-particles formed in the gas phase by the condensation of the laser-ablated species are transported on to the substrate to form nanorods. The nano-rod crystals having a hexagonal shape with a pyramidal top were synthesized on a sapphire substrate by a single-step process. The nano-rod crystals act as an efficient ultraviolet emitter showing the stimulated emission under an optical excitation and also act as field emitters with a current density of 1 mA/cm^2 at an electric field strength of 16 V/μm.

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1 Introduction

Zinc oxide (ZnO) is a wide-gap compound II-VI semiconductor and has the direct band gap of about 3.37 eV at room temperature. Furthermore, its large exciton binding energy of about 60 meV, that is significantly larger than the thermal energy at room temperature (26 meV), can ensure an efficient exciton emission at room temperature under low excitation energy [1]. Thus, ZnO is one of the most promising materials suitable for generating ultraviolet (UV) light. UV stimulated emission, so-called random laser, at room temperature from an optically-pumped nano-wire-array has also been reported [2, 3]. ZnO has another function other than UV emission that is useful for the device application. Recently it has been reported that nano-structured ZnO crystals also show the good field emission characteristics [4–6].

Various methods have been applied to grow ZnO crystals, including nano-structured ZnO crystals. The crystals made by the chemical liquefied methods often show the green emission originated oxygen-deficient defect. Better ZnO crystals have been obtained by the gas-phase synthesis, such as chemical vapor deposition [7], physical vapor deposition [8], molecular beam epitaxy [9], and so on. ZnO nano-wires have been synthesized simply by heating Zn powders containing catalyst nano-particles [10], where the vapor–liquid–solid (VLS) mechanism is responsible for the nano-wire growth, in which a metal or an oxide catalyst is necessary to dissolve feeding source atoms in a molten state initiating the growth of nano-materials.

Pulsed-laser ablation deposition (PLD), on the other hand, is a powerful method for the synthesis of functional materials and already has been used for the synthesis of ZnO thin films. In the case of the conventional PLD, however, ZnO thin films have been deposited in an oxygen background gas at a relatively low pressure of around 10 Pa or less [11–15]. In the previous reports, we have succeeded in growing large quantities of ZnO nanorods by a newly developed nano-particle-assisted PLD (NAPLD) without using any catalyst [16–18]. By using NAPLD, we obtained hexagonal ZnO nano-rods having a sharp pyramidal surface at an end-surface of the nano-rods by a single-step process. In this paper, the ultraviolet lasing and the field emission characteristics of the ZnO hexagonal nano-rods synthesized by NAPLD are reported. The ZnO hexagonal nano-rods with the sharp pyramidal surface may be very useful for building a large area directional UV emitter using the stimulated emission.

2 Preparation of samples

The ZnO nanorods crystals were synthesized as follows. A sintered ZnO target (purity 99.99%) was ablated by a KrF excimer laser with a fluence of about 3 J/cm^2 at a repetition rate of 20 Hz. The ZnO crystals were grown on a sapphire(0001) substrate placed at a substrate–target distance in the range from 20 mm to 70 mm. The substrate was heated in the range from 500 °C to 800 °C. In NAPLD, ZnO crystals are synthesized at a higher background gas in the range from 133 Pa to 1.3 kPa [16–18]. At such a high pressure, nano-particles are generated in the gas phase by the condensation of the ablated species [19] and they are the major species transported on to the substrate [16]. This enables the low-temperature growth of the crystals with the help of a low melting temperature of nanoparticles [17]. The samples of the crystalinity and morphology were characterized by an X-ray diffract meter

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(XRD) and a scanning electron microscope (SEM).

3 Results and discussion

3.1 *Optical property*

Figure 1a, b and c show the photoluminescence spectra from ZnO films deposited on sapphire substrate heated at 700 °C by NAPLD at different O_2 pressures of 13.3 Pa, 133 Pa and 2.7 kPa, respectively. The films were excited by a XeCl excimer laser at 308 nm. In Fig. 1, the SEM images of each ZnO film are also shown on the right-hand side of corresponding photoluminescence spectra. At a low O_2 pressure of 13.3 Pa, micro-crystals were observed on a smooth film, as shown in the SEM images of Fig. 1a. The size of the crystals ranged from 1 to 2 μm and have a hexagonal-pyramidal top-surface. When the film was excited by the XeCl excimer laser, a broad fluorescence spectrum peaked at 385 nm was observed. When the excitation power was increased, sharp fluorescence spectra peaked at 395 nm became observable as marked by the thick arrows in the spectra of Fig. 1a, indicating the on-set of the stimulated emission.

When the background gas pressure increased from 133 Pa to 665 Pa hexagonal ZnO nano-rods with pyramidal top-surfaces grew. The size of nano-rods was in the range from 300 to 500 nm at 133 Pa, as shown in the SEM image in Fig. 1b. It became larger in the range from 500 to 1000 nm at 665 Pa. It was confirmed that these nanorods were separated from each other and grew directly from the substrate [16]. The size can be controlled by varying the deposition conditions such as the distance between the target and the substrate and/or the background gas pressure [18]. The detailed dependence of the crystal morphology on the deposition conditions such as a kind of gas, a kind of substrate, background gas pressure and son has been reported in [20]. The fluorescence spectra from nano-rod crystals also showed the sign of the on-set of the stimulated emission near 390 nm as marked by the thick arrows in Fig. 1b. However, the spectra due to the stimulated emission were broader than those observed from the film of Fig. 1a. When the pressure was further increased to more than 1.3 kPa, all the nanorods fused together and the surface became flattened, as shown in Fig. 1c. In this case, the spectra due to the stimulated emission were observed near 390 nm with a smaller excitation power than in Fig. 1a and b. No blue fluorescence, which is attributed to the defect due to oxygen deficiency, was observed for all films, indicating the high quality of the crystals.

Figure 2a shows the SEM image of ZnO crystals deposited on a sapphire substrate at 700 °C in a 400 Pa He background gas, and Fig. 2b is the fluorescence spectra under the excitation by the XeCl laser. In this case, hexagonal micro-crystals were obtained as in a low O_2 background gas at 13.3 Pa Torr. The stimulated emission spectra similar to those from the films in Fig. 1a were observed, but at much lower excitation intensity. This may be due to more perfect crystal shape in Fig. 2 than in Fig. 1a.

The optical cavity that is responsible for the onset of the stimulated emission is not clear at present. In the previous report [17], we observed the stimulated emission even from isolated ZnO nano-rods which were taken out of the ZnO nano-rods films similar to that shown in the SEM image of Fig. 1b. At least regarding the film in Fig. 1b, this indicated that each ZnO nano-rods are capable of lasing and so-called random lasing mechanism [21] due to multiple scattering among many ZnO nano-rods crystals is not always necessary for the stimulated emission. In this case, one possible optical cavity is formed between the pyramidal roof top and the other flat end surfaces, as depicted in Fig. 3. According to the cross sectional SEM observation of the ZnO nano-rods, the angle of the pyramidal roof is about 90 degrees. The pyramidal roof can act as a total reflector such as corner cube mirror and the rods act as a waveguide, in

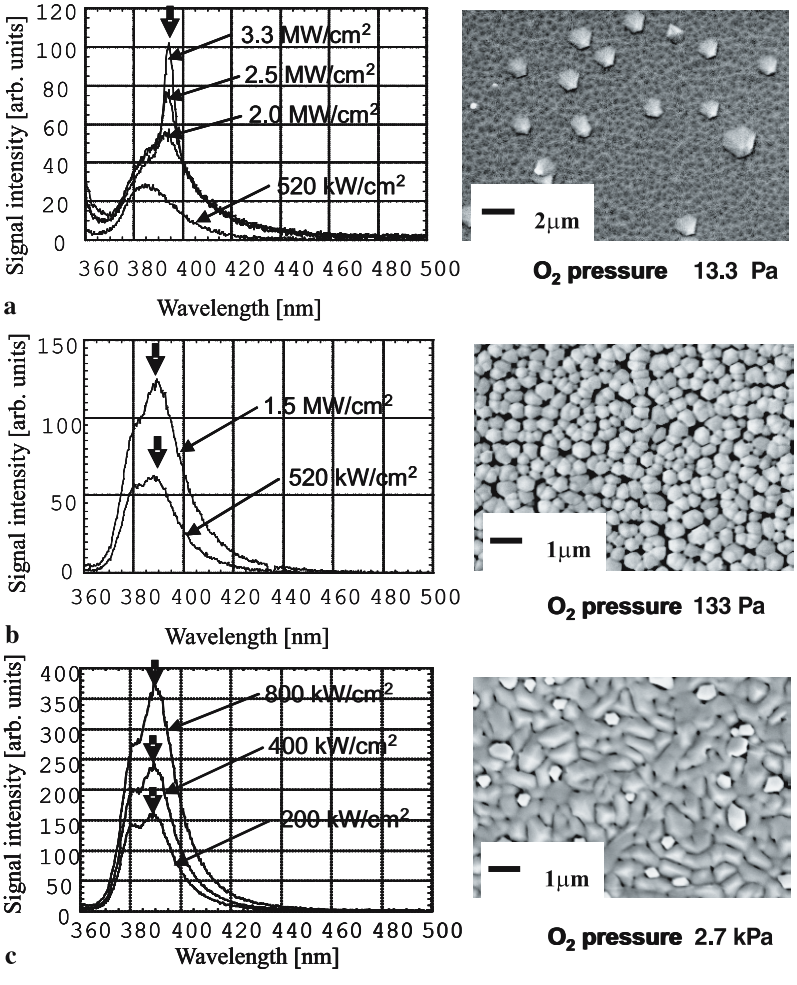

FIGURE 1 Photoluminescence spectra from ZnO films deposited at different O_2 pressure of (**a**) 13.3 Pa, (**b**) 133 Pa and (**c**) 2.7 kPa. SEM images of the ZnO films are shown in *right-hand side* of the spectra

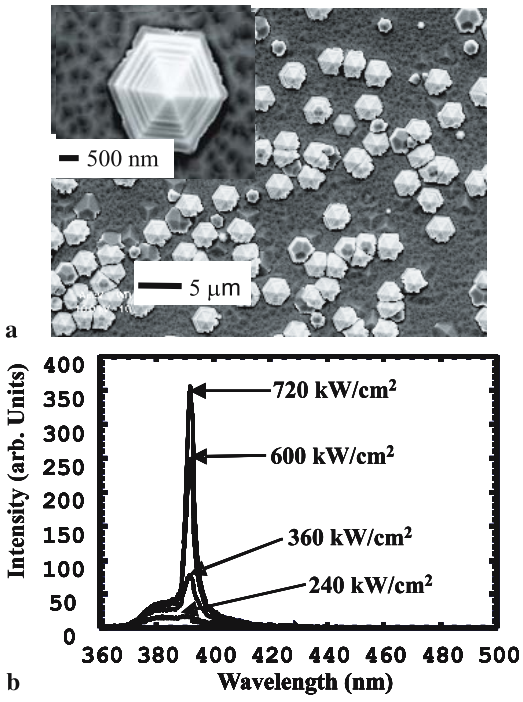

FIGURE 2 Photoluminescence spectra from ZnO films deposited at 400 Pa He background gas. SEM image of the ZnO film is shown in the *right-hand side*. The *inset* is the magnified SEM image

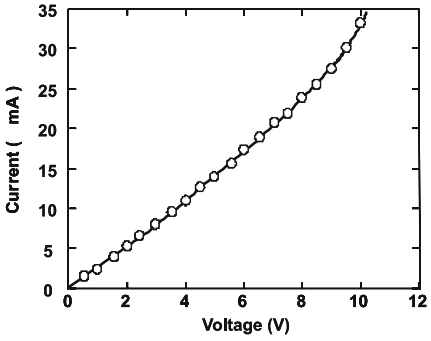

FIGURE 4 Typical I–V characteristics of ZnO film

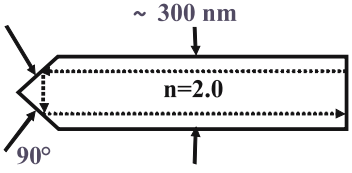

FIGURE 3 Schematics of possible optical cavity in ZnO nano-rods

taking into account the refractive index of the ZnO crystal that is 2.0.

3.2 *Field emission property*

It is expected that the pyramidal top-surface of the crystals is suitable for the field emission due to the field enhancement at the tip of the pyramidal surface. The field emission property was measured using a plane parallel electrode arrangement. The anode electrode is made by stainless steel with a diameter of 2 mm and the cathode is the ZnO film itself. Before measuring the field emission, we measured the electrical property of the films by contacting the anode electrode on the films. An example of the measured I–V characteristics is shown in Fig. 4. The film was conductive with slightly semiconductive nature.

Next, the field emission property was measured in keeping the anode–cathode distance at 50 μm. The field emission property is shown in Fig. 5a, where the emitted current is plotted as a function of the applied electric field strength. The SEM images of the sample is also shown in the inset. The threshold of the field emission was about 10 V/μm and an emission current of 1 mA/cm^2 was obtained at an electric field strength of about 16 V/μm. The field emission property was analyzed by the Fowler–Nordheim (F–N) plot, that is given as follows.

$$J = \frac{A\beta^2 E^2}{\phi} \exp\left(-\frac{B\phi^{3/2}}{\beta E}\right) \tag{1}$$

where J is the current density, ϕ is the potential barrier for electron emission of ZnO that is 5.3 eV, E is the field strength, A is 1.56×10^{-10} A/V^{2}eV and B is 6.83×10^3 VeV$^{-3/2}$ μm^{-1}. β is the field enhancement factor. The F–N plot

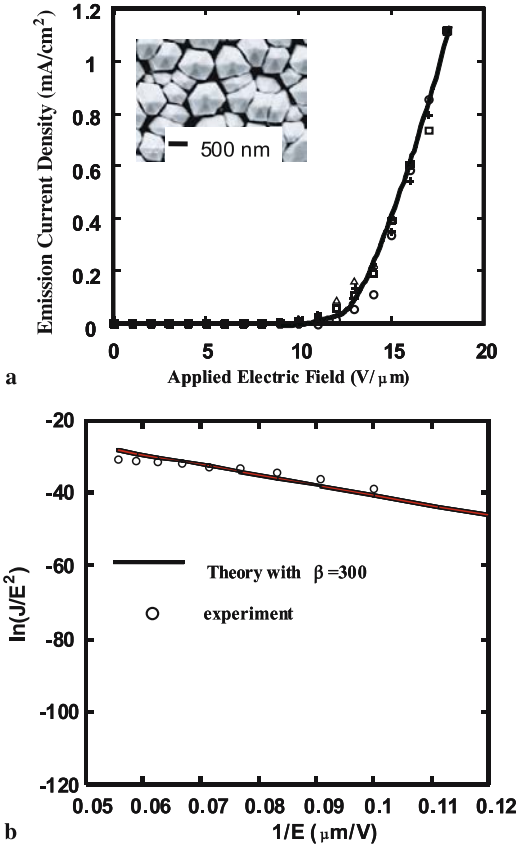

FIGURE 5 Field emission characteristics of ZnO rod-crystal. (**a**) field emission current as a function of field strength and (**b**) F–N plot. SEM image of the ZnO rod-crystals is shown in the *inset* of (**a**)

with $\beta = 300$ is shown in Fig. 5b by the solid line along with the experimental data given by open circles. We can expect further improvement of the field enhancement factor by optimizing the surface density of the pyramidal rods, although the value of $\beta = 600$ is roughly a half of that of a ZnO nano-pin [4] and much smaller than that of ZnO nanowires [5].

4 Conclusion

In conclusion, we have investigated the ultraviolet emission and the field emission characteristics of ZnO nano-rod crystals that were synthesized by the nanoparticles assisted pulsed-laser deposition (NAPLD) technique. The hexagonal ZnO nanorods with a pyramidal top-surface were obtained under limited growth conditions. It was demonstrated that the nano-rod crystals simultaneously act as an efficient ultraviolet emitter showing the stimulated emission under an optical excitation at 308 nm and also as a field emitter with a current density of 1 mA/cm^2 at an electric field strength of 15 V/μm. Using the hexagonal nano-rods with the pyramidal roof end, we constructed an efficient ultraviolet emitter excited by the field-emitted electrons only with ZnO nano-rod crystals synthesized by NAPLD with a single-step process, as schematically shown in Fig. 6 where the large area ZnO micro-nano-crystal arrays excited by electrons from a field emitter is proposed as a stimulated emission UV emitter.

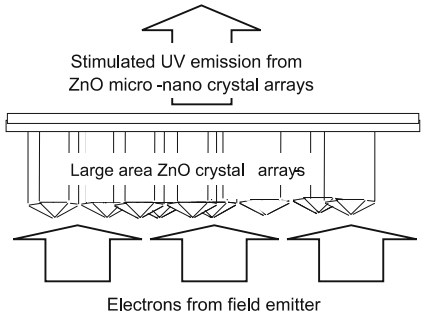

FIGURE 6 Schematics of efficient ultraviolet emitter using ZnO crystal arrays synthesized by NAPLD

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