Stimulated Emission and Field Emission Characteristics of ZnO Nano-Rods Synthesized by Laser Ablation

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Stimulated Emission and Field Emission Characteristics of ZnO Nano-Rods Synthesized by Laser Ablation

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Abstract. We describe the stimulated emission and the field emission characteristics of ZnO nano-rod crystals synthesized by laser ablation in a background gas. A various type of nano-structured ZnO crystals were successfully synthesized on sapphire substrates, and ZnO crystals were taken out of the substrate by a laser brow-off technique and sonification. ZnO crystals taken out of the substrate showed a lower stimulated emission threshold than those as grown on the substrate under optical excitation, indicating a high quality of the crystalinity.

1. Introduction

Zinc oxide (ZnO) is a wide-band-gap II-VI semiconductor that has the direct band gap of about 3.37 eV at room temperature, and is a well-recognized as the functional material suitable for opto-electronic applications. In the past few years, nano-structured ZnO crystals, such as nano-rods, nano-wires and nano-balls have been of growing interest due to their importance both in scientific and technological researches. Considerable efforts have been paid on the synthesis and on the study of nano-structured ZnO crystals. Nano-structured ZnO crystals have been synthesized by various methods, such as chemical vapour deposition [1], physical vapour deposition [2], molecular beam epitaxy [3] or a simple method just by heating Zn powders containing catalyst nanoparticles [4]. Ultraviolet stimulated emission from optically-pumped nano-wires [5,6] and the field emission have been reported [7-9].

Laser ablation in a background gas is also powerful technique for the synthesis of nano-structured ZnO crystals. In the previous reports, we have succeeded in the growth of large quantities of ZnO nano-rods by pulsed-laser deposition in a relatively high O_2 background gas around 10 Torr, where nano-particles formed by condensation of ablated species in high pressure gas phase play an important role in the ZnO nano-rod growth [10-14]. In this paper, we describe the stimulated emission under an optical excitation at 355 nm and the field emission characteristics of nano-structured ZnO crystals synthesized by laser ablation in a higher background gas.

2. Preparation of nano-structured ZnO crystals

A various kind of nano-structured ZnO crystals was synthesized on *c*-cut sapphire substrates by laser-ablating a sintered ZnO ceramics target in a background gas. Typical SEM images of ZnO crystals are shown in Figs. 1 (a), (b) and (c). The crystals in Figs. 1 (a) and (b) were synthesized on sapphire substrates heated at 700 ^{o}C in a O_2 gas pressure of 3 Torr at room temperature for 10 minutes and 30 minutes., respectively. On the other hand, the crystals in Fig. 1 (c) were synthesized on a sapphire

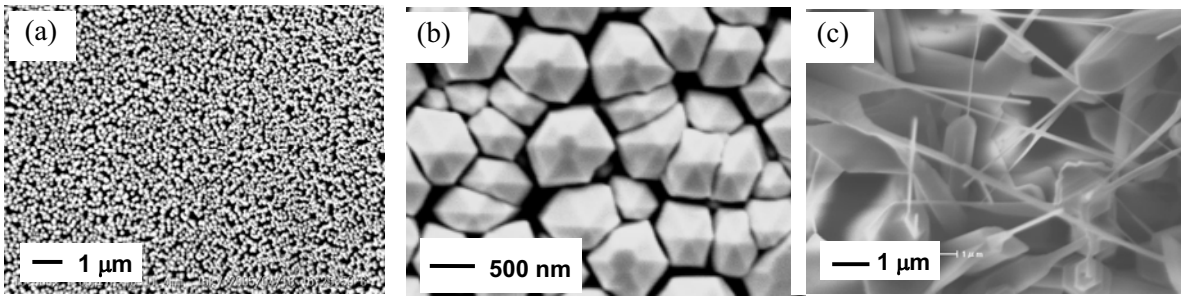

Fig. 1 SEM images of nano-structured ZnO crystals. (a) and (b) nano-rods crystals and (c) nano-wire pig-tailed micro crystals.

substrate in a Ar gas pressure of 260 Torr at 900 ^{o}C for 90 min.. In the case of Fig. 1(a), ZnO nano-rods with a diameter of about 100 nm were grown uniformly on the sapphire substrate and much larger crystals with a pyramidal top were obtained for a longer deposition time. It was found that Both crystals were c-axis oriented. The lengths of the rods were about 900 nm in Fig. 1 (a) and 6 μm in Fig.1 (b).

In Fig. 1 (c), on the other hand, ZnO nano-wires with a diameter of about 100 nm and 5 to 10 μm in length were grown on micrometer-size ZnO crystals. Although the crystals were grown on a *c*-cut sapphire substrate in Fig. 1 (c), the orientation of the crystal axis was random. The mechanism that produced such a unique structure was not known at present.

In order to take individual nano-crystals out of the substrate, two methods were examined. One is a laser brow-off technique in which nano-crystals were brown off by irradiating the 3rd harmonics of a Q-switched Nd:YAG laser beam through a sapphire substrate and crystals brown-off were collected on an another substrate. A typical SEM image of crystals, which were brown-off from the substrate shown in Fig. 1 (c), is shown in Fig. 2 (a). In this case, only ZnO crystals which still contained many rod and wire crystals were obtained. A similar result was obtained for the crystals shown in Fig. 1 (a). Another method is sonication. In sonication, an original substrate in a solvent of ethanol was sonicated for 5 to 10 minutes, and then individual crystals were scattered on a proper substrate by putting a drop of ethanol solution and drying it. A typical image of nano-wire crystals is shown in Fig. 2 (b), where only nano-wire crystals were obtained without micrometer-size crystals on which the nano-wires were grown. In the case of crystals shown in Figs. 1(a) and (b), sonification was not successful in taking the crystals out of the substrate. So, further development is required for taking off single and isolated ZnO rod-crystal from the substrate.

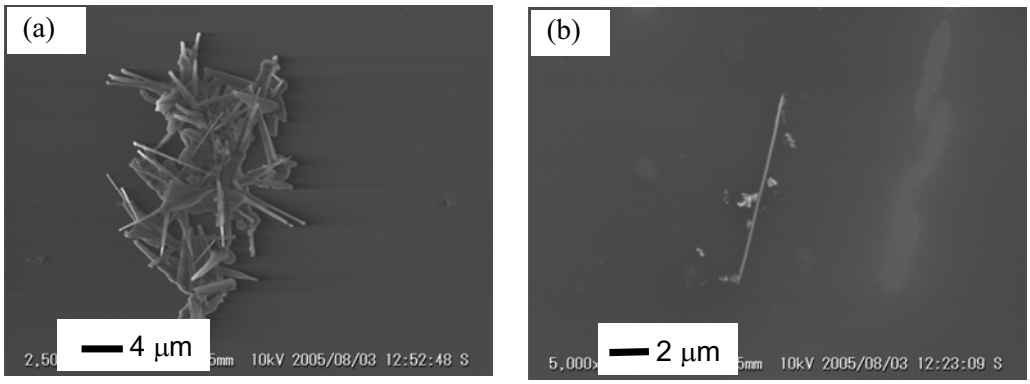

Fig. 2 ZnO nano-crystals taken out of the substrate shown in Fig. 1(c), by laser brow-off (a) and sonification (b).

3. Photoluminescence property

Photoluminescence spectra were observed with a multi-channel spectrometer by exciting the ZnO crystals with the third harmonics of a Q-switched Nd:YAG laser. First the ZnO crystals as gown on the substrate in Fig. 1 were examined by exciting an unfocused laser beam. In this case, many crystals were excited simultaneously and the sum of the photoluminescence light from many crystals was observed. Figure 3 shows the photoluminescence spectra from the crystals shown in Fig. 1 (a) as a function of excitation fluence. When the pump fluence increased, the peak wavelength shifted to the longer wavelength and a narrow peak became observable around 390 nm at a fluence of 5.3 mJ/cm^2, indicating the onset of the stimulated emission.

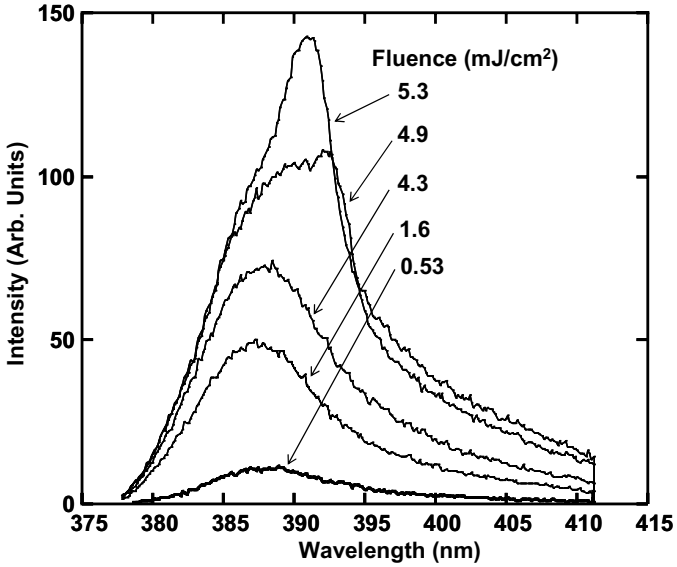

Fig. 3 Photoluminescence spectra as a function of pump fluence for nano-rods shown in Fig. 1 (a).

It was observed that the threshold fluence for the stimulated emission was lowered when the individual crystals taken out of the substrate were excited. Figure 4 (a) and (b) shows the photoluminescence spectra at a fluence of 0.6 mJ/cm^2 for the ZnO crystals shown in Fig. 1 (c) and for the crystals shown in Fig. 2 (a) that were taken out of the substrate shown in Fig. 1 (c), respectively. In the case of Fig. 4 (b), the photoluminescence signal only from the lump of the crystals shown in Fig.

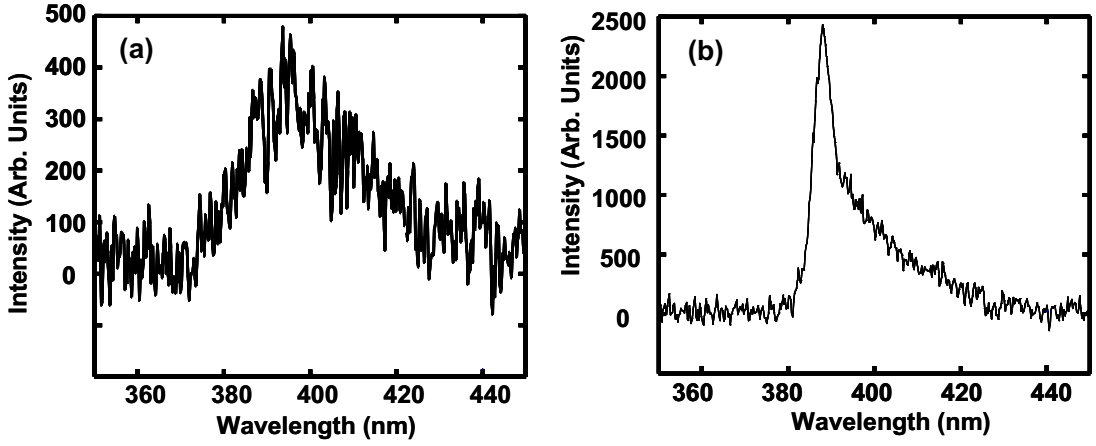

Fig. 4 Photoluminescence spectra. (a) for crystals shown in Fig. 1 (c), and (b) for lump crystals shown in Fig. 2 (a) that was taken from crystals in Fig. 1 (b) by laser brow-off.

2(a) was observed by an optical microscope. In the case of ZnO crystal as grown on the substrate in Fig. 1 (c), just broad spectrum was observed near the band gap of ZnO and no stimulated emission was observed at a fluence of 0.6 mJ/cm^2. In the case of the lump crystals shown in Fig. 2 (a), on the other hand, a narrow spectral peak was observed on a broad fluorescence spectrum even at a fluence of 0.6 mJ/cm^2. At present, it was not identified which crystals in the lump crystals shown in Fig. 2 (a) are lasing. It is also very interesting to examine the lasing characteristics of the ZnO nano-wire, and it is now in progress.

4. Field emission property

It is expected that the pyramidal top-surface of the crystals in Fig. 1 (b) 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 pair of plane-parallel electrodes. The field emission property was measured in keeping the anode-cathode distance at 50 μm. It was observed that the threshold of the field emission was about 10 V/μm and an emission current of 1 mA/cm^2 was obtained at an electrical field strength of about 16 V/μm. It is also expected that nanowire pig-tailed ZnO crystals shows a good field emission characteristics due to the field enhancement at the tip of the nanowire. For the purpose, however, we have to control the growth direction so that the nanowires were directed along substrate normal.

Conclusion

We have successfully synthesized a various kinds of nano-structured ZnO crystals by laser ablation in a background gas. Synthesized ZnO crystal showed the stimulated emission under an optical pumping at 355 nm, indicating that the high quality of the crystalinity. Some of the ZnO crystals also showed a field emission characteristics.

Acknowledgments

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