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ZnO nano-rods synthesized by nano-particle-assisted pulsed-laser deposition

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ABSTRACT We succeeded in synthesizing ZnO nanorods by nanoparticle assisted pulsed-laser deposition (PLD) without using any catalyst where nanoparticles formed by condensation of ablated particles play an important role. The nanorods have an average size of about 120 nm. Stimulated emission was observed from ZnO nanorods at 388 nm by optical pumping. The size-controlling of nanorods can be achieved by controlling the size and the density of these nanoparticles.

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1 Introduction

In the past few years, nano-sized wide-gap semiconductor materials, such as nanorods, nanowires and nanobelts, have been of growing interest due to their importance both in scientific research and potential technological applications, including nano-optical devices. Zinc oxide (ZnO), a wide-gap compound II–VI semiconductor that has the direct band gap of about 3.37 eV at room temperature, is a well-known material suitable for generating ultraviolet (UV) light. Furthermore, a large exciton binding energy of about 60 meV in ZnO, which 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, considerable efforts have been made on the synthesis and study of nano-scale ZnO materials. For example, ZnO nano-materials have been synthesized by various approaches, such as chemical vapor deposition [2], physical vapor deposition [3], molecular beam epitaxy [4] or a simple method just by heating Zn powders containing catalyst nanoparticles [5]. All these approaches apply the vapor-liquid-solid (VLS) mechanism for nanowire growth, in which a metal or oxide catalyst is necessary to dissolve feeding source atoms in a molten state initiating the growth of nano-materials. UV stimulated emission at room temperature from optically-pumped nanowires has also been reported [6]. ZnO nanobelts have been successfully synthesized by simply evaporating ZnO powders without the presence of catalyst [7]. But, a very high temperature, as high as the melting point of bulk ZnO, will be needed in such a method.

Pulsed-laser deposition, on the other hand, is also a very simple method and widely used for the synthesis of various thin films. But there are only a few efforts to employ this method in the synthesis of nano-scale ZnO materials, such as nanowires or nanorods. In the previous letter, we have reported the growth of large quantities of ZnO nanorods by pulsed-laser deposition without using any catalyst [8]. We have also demonstrated that nanoparticles formed by condensation of ablated species in high pressure gas phase play an important role in the ZnO nanorods growth [9]. In this letter, we report on the size-controlling of the nanorods synthesized by pulsed-laser deposition. We found that by controlling the size and the density of the nanoparticles in the gas phase, it is possible to control the size of the nanorods.

2 Experiment, result and discussion

In our experiment, a sintered ZnO target with 99.99% in purity was used as source material in synthesizing nanorods. This material was ablated with a KrF eximer laser, which operates at a repetition rate of 20 Hz and a fluence of about 3 J/cm^2, in a chamber filled with oxygen background gas. Ablated species was then deposited on a sapphire substrate which was mounted on a heater. The target- substrate distance was set from 20 to 70 mm and the chamber pressure was set to be relatively high of more than 1 Torr. The morphology and crystallinity of the as-deposited products were observed by a scanning electron microcopy (SEM) and an X-ray diffractometer (XRD), respectively.

After 30 min deposition, a white-colored product was found to cover the substrate surface. SEM analysis of the as-deposited product shows that ZnO nanorods could grow at substrate temperature of more than 600 °C. Figure 1a shows the SEM image of the top ZnO nanorods arrays grown on sapphire substrate at 700 °C and background gas pressure of 5 Torr. While, Fig. 1b shows the SEM image of single nanorods taken from the ZnO rods-arrays. Nanorods with a size range from 200 to 500 nm and a length of more than 6 μm can be observed. The nanorods have hexagon edge and are isolated each other. Crystallinity analysis shows that the nanorod arrays were well *c*-axis oriented.

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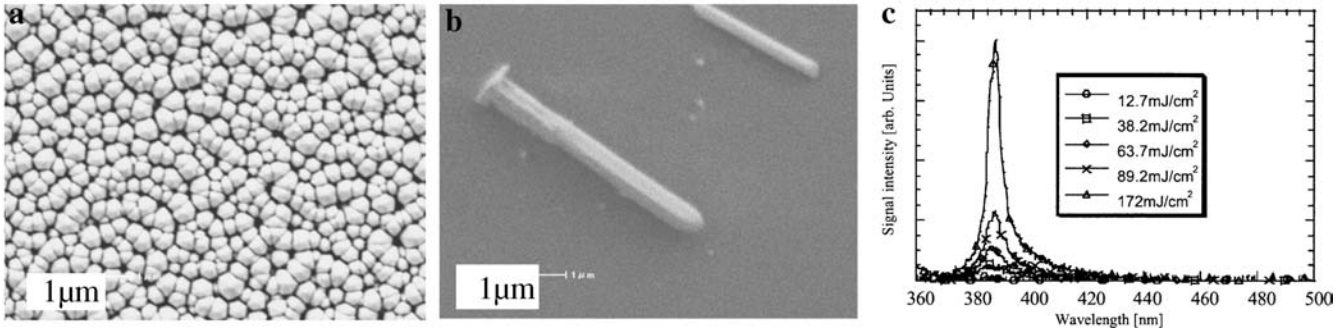

FIGURE 1 **a** Top view of the as-deposited ZnO film, **b** SEM image of single nanorods, **c** PL spectra from single nanorods

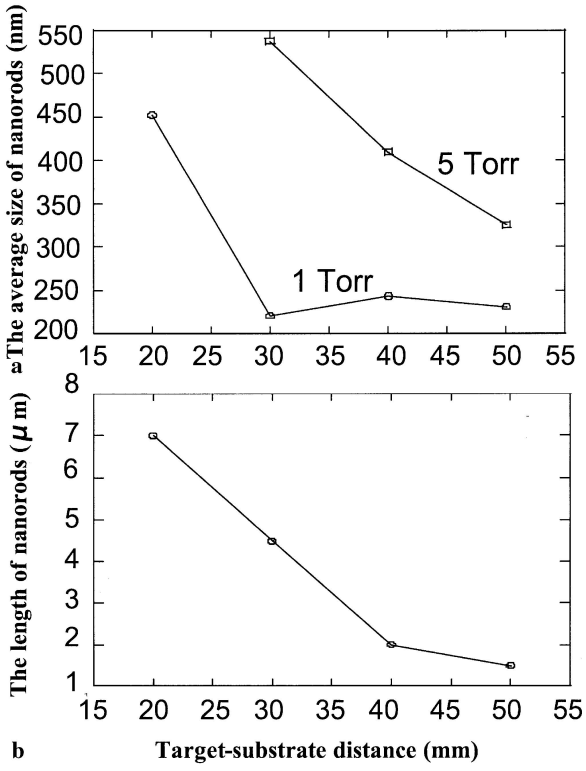

FIGURE 2 **a** The average size of nanorods and **b** the length of nanorods as the target-substrate distance changed

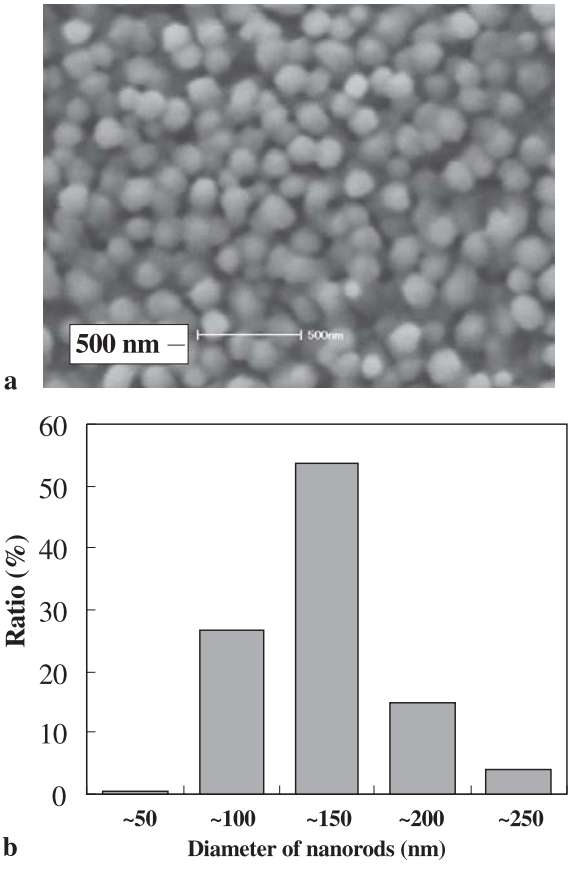

FIGURE 3 **a** SEM image of nanorods arrays, **b** Size distribution of the nanorods

Figure 1c shows the photoluminescence (PL) spectra from the nanorods optically pumped by the third harmonics (THG) of a Nd : YAG laser operating at 355 nm. Stimulated emission was observed at UV region of about 388 nm when the pump energy exceeds about 50 mJ/cm^2.

In the previous report [9] we showed a direct evidence that nanoparticles formed in the gas phase and reached onto the substrate surface became the source for the nanorods growth. We suggest that by controlling the size and the density of these nanoparticles, we can control the size of the as-grown nanorods.

The size and the density of nanoparticles were controlled by adjusting the chamber pressure and the target-substrate distance, as observed by Rayleigh scattering previously [8]. At the lower gas pressure, the smaller nanoparticles in the gas phase can be achieved. And, at the longer target-substrate distance, the lower nanoparticles density participates in the nanorods growth.

Figure 2a shows an evolution of the average size of nanorods deposited at 1 Torr and 5 Torr as the target-substrate distance changed. All the films were synthesized with 30 min deposition time. At both 1 and 5 Torr gas pressure condition, the nanorods' size became smaller when the the target-substrate distance was set longer. We can also confirm that the nanorods synthesized at 1 Torr have a smaller size compared with the one synthesized at 5 Torr. Under gas pressure of 1 Torr and target-substrate distance of more than 30 mm, nanorods with an average size of less than 250 nm can be achieved. On the other hand, as shown in Fig. 2b, the length of the nanorods become shorter as the target-substrate distance was set longer.

We suggest that the smaller nanorods can be achieved because at lower gas pressure the nanoparticles formed in the gas

phase become smaller and at longer target-substrate distance the density of nanoparticles participate in the nanorods growth become smaller.

To further support our suggestion, we tried to synthesize nanorods at a gas pressure of 3 Torr, a target-substrate distance of 70 cm vertically and 20 cm horizontally, a deposition time of 30 min, and a substrate temperature of 700 °C. Figure 3a shows the top view of the as-synthesized nanorod arrays, while Fig. 3b shows the size distribution of the nanorods. The nanorods have an average size of 122 nm and more than 30% of nanorods have a size of less than 100 nm.

3 Conclusion

ZnO nanorods have been synthesized by PLD without any catalyst. Stimulated emission at UV region was observed from as-synthesized nanorods under optical pumping. We have also demonstrated the size control of nanorods by controlling the size and the density of nanoparticles participating in nanorods growth. Nanorods with an average size of about 122 nm were successfully achieved.

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