Synthesis of ZnO Nanowire Heterostructures by Laser Ablation and Their Photoluminescence

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ZnO nano-crystals have been paid a great attention as building blocks for the optoelectronic devices, such as an UV-LED. We have been succeeded in growing ZnO nanostructures, such as vertically-aligned ZnO nanowires and nanowalls, by a newly developed nanoparticle-assisted pulsed-laser deposition without using any catalyst. Depending on the growth condition a film-wire layer-structured ZnO and core/shell structured ZnO nanowires were synthesized on sapphire substrates. The room temperature photoluminescence spectrum of synthesized ZnO nanostructures exhibited an intrinsic UV emission and a defect-related visible emission.

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1. Introduction

Zinc oxide (ZnO), which has a direct wide band-gap of 3.37 eV at room temperature and a relatively large exciton binding energy of 60 meV, is one of the promising materials in UV optoelectronic applications such as a light-emitting diode (LED) and a laser diode (LD). In addition, since ZnO has a strong tendency for self-organized growth, ZnO nanostructures could be synthesized using some such methods as a chemical vapor deposition [1] and a nanoparticle-assisted pulsed-laser deposition (NAPLD) [2,3]. Especially, ZnO nanowire has attracted a great attention for building blocks of nanodevices such as an UV-LD, an UV-LED [4-8], and an UV gas sensor [9,10], because it has superior crystalline quality, better electrical/optical quality, freedom to choose substrate and large surface area to volume ratio. Furthermore, ZnO nanowires have no need for a lattice matched substrate for the overgrowth [11].

For the practical optoelectronic applications based on the ZnO nanowires, however, three important issues are essentially required: p-type doping, growth control and fabrication of layered structures for p-n junction and core-shell structure. In our study, we have succeeded in synthesizing various nanostructures, such as nanorods [12-15], nanowalls [16], the vertically and horizontally aligned ZnO nanowires [17,18] by NAPLD without any catalyst. Recently, we found that ZnO film and nanowires were synthesized in one chamber with changing the deposition condition. This predicts the ZnO nanowire layered structures, such as film-wire structure and core/shell structure, can be fabricated in a simple experimental setup. In this paper, we describe progresses of synthesis of layer-structured ZnO nanowires by NAPLD using a multi-target changer system. In the use of the multi-target changer system, ZnO source targets can be changed without disturbing chamber condition during synthesis of ZnO nanowires.

2. Experiments

Fig.1 shows the schematic of the experimental setup for synthesis of layer-structured ZnO nanowires by NAPLD. In the experiment, sintered cylindrical ZnO source targets were used in synthesizing ZnO nanowires. A c-plane sapphire substrate (1 cm×1 cm) was put on a SiC heater in a vacuum chamber and the target-substrate distance was set to 40 mm. The substrate was heated to 400-800 ºC in the vacuum chamber filled with a background gas of argon or

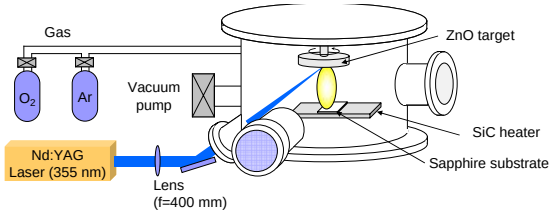

Fig. 1 Schematic of the experimental setup for synthesis of layer-structured ZnO nanowires by NAPLD.

oxygen. The ZnO target was ablated with third harmonic generation (THG) of a Q-switched Nd:YAG laser at 355 nm with a repetition rate of 10 Hz and a fluence of about 1.3 J/cm^2. The morphology of the as-deposited products was analyzed by scanning electron microscopy (SEM). The optical properties of the ZnO nanowires were investigated by observing the photoluminescence (PL) with THG of other Q-switched Nd:YAG laser.

3. Results and Discussion

3.1 Synthesis of ZnO nanowires

In NAPLD, ZnO nanostructures are synthesized at a higher background gas pressure. A sintered ZnO target with 99.99% purity was used as source material in synthesizing ZnO nanowires. Fig.2 shows the SEM image of the ZnO nanowires on the c-plane sapphire substrate at 800 ºC and

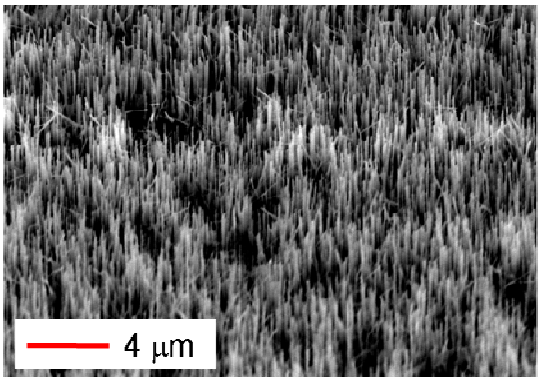

Fig. 2 SEM image (45° tilted view) of ZnO nanowires.

background argon gas pressure of 200 Torr. In NAPLD, the ablated species were perfectly confined in a small volume with a stoichiometric composition of ZnO, and then ZnO nanoparticles are formed in the gas phase during the transport of the ablated species to the substrate. Nanoparticles deposited on the substrate form thin buffer layer and some nucleation. Then nanowires grow on them. It can be seen the vertically-aligned thin ZnO nanowires with average length of about 2 μm.

3.2 Film-Wire Layer-Structured ZnO Nanowires

As an initial demonstration of fabricating the film-wire layered structure, ZnO nanowires were synthesized after deposit a ZnO film. The film was deposited on a c-plane sapphire substrate temperature of 650 ºC and oxygen gas pressure of 26 mTorr. After deposition of the ZnO film for 5 minutes, the nanowires were subsequently synthesized on the film at the temperature of 750 ºC and argon gas of 200 Torr in the same chamber. The growth time of the ZnO nanowires was 15 min. Fig.3 shows the SEM image of the ZnO nanowires on the film. It was found that the vertically-aligned low density ZnO nanowires with the diameter of 50-100 nm and the length of around 1.5 μm. Most nanowires were grown on the hexagonal pyramid. This result is similar to that of Cao et al. [19]. They say that ZnO buffer film seems to prevent nanowire nucleation and growth since the incoming ZnO incorporates much more effectively into the ZnO buffer film. Although the more detail mechanism should be investigated, an interaction between the buffer film and the depositing nanoparticles occurred.

Furthermore, layer-structured ZnO nanowires consisting of different material layers also could be synthesized using a non-doped and a Li-Ni codoped ZnO targets. Fig.4 shows the SEM image of the ZnO nanowires synthesized on the Li-Ni codoped ZnO film. The growth condition was the same as in Fig. 3. The vertically-aligned low density ZnO nanowires were also synthesized on the Li-Ni codoped ZnO film. This indicates the film-wire layered structure consisting of different ZnO targets is fabricated by the multi-target changer system in the simple experimental setup.

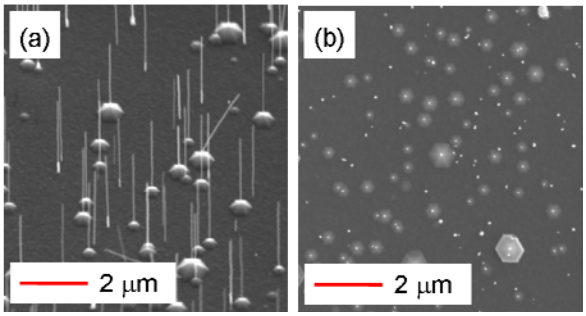

Fig. 3 SEM images of ZnO nanowires synthesized on the ZnO film, (a) 45° tilted view and (b) top view.

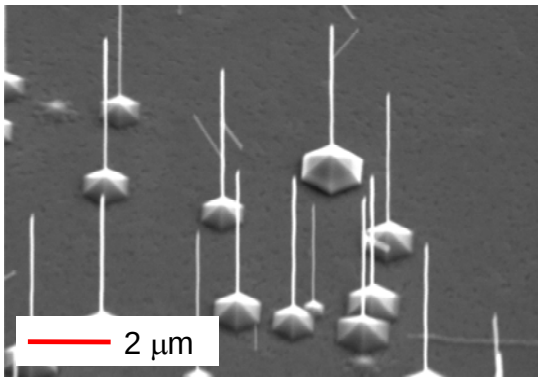

Fig. 4 SEM image of the ZnO nanowires synthesized on the Li-Ni codoped ZnO film.

3.3 Core/Shell Structured ZnO Nanowires

It is important to fabricate layered structure in not only the nanowire axial direction but also the radial direction, because core/shell nanowires are expected to be more efficient in emitting due to low thermal quenching and large surface effect.

Fig.5(a) shows the SEM image of the ZnO nanowires on the film after growth of the ZnO core at the same deposition condition as Fig.3 and 4. Fig. 5(b),(c) show the top view and 45° tilted view SEM images of ZnO nanowires

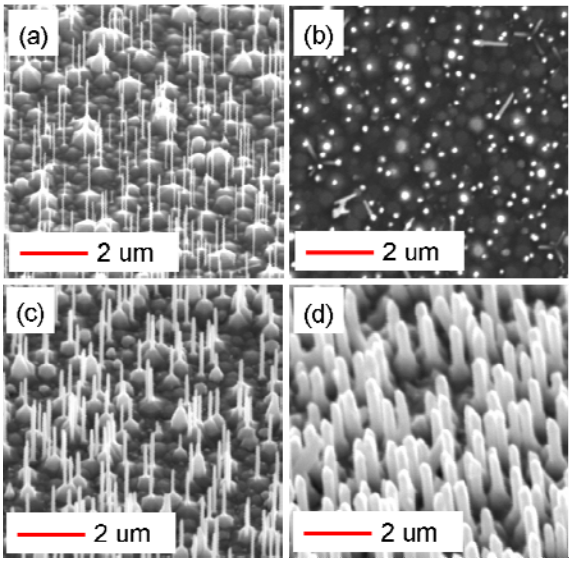

Fig. 5 SEM images of (a) ZnO nanowires on the film and core/shell structued ZnO nanowires, where the growth time of the shell layer were 5 min ((a) top view, (c) 45° tilted view), and (d) 20 min.

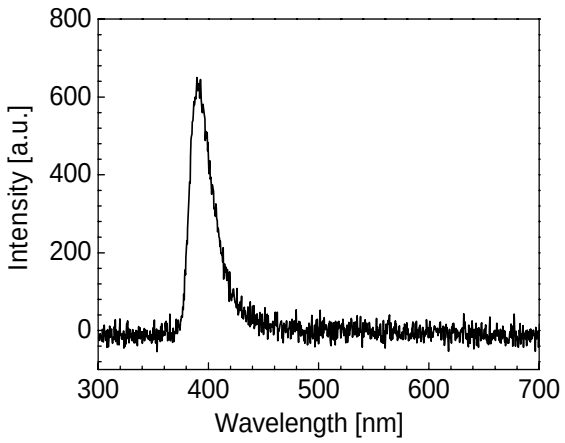

Fig. 6 PL spectrum of the ZnO nanowires on the ZnO film.

after growth the shell for 5 minutes at the temperature of 650 ºC and oxygen gas pressure of 26 mTorr. The ZnO nanowires grew uniformly in the radial direction, indicating that ZnO shell coats homogeneously the entire nanowire. Fig. 5(d) shows the SEM image of the ZnO nanowires after growth of the ZnO shell for 20 minutes. The diameter of the ZnO nanowire increased uniformly with increasing the deposition time. Thus, it was found that thickness of the shell could be controlled by the deposition time and expected that core/shell structure consisting of different material layers could be fabricated using different kinds of targets.

3.4 Photoluminescence of the ZnO nanowires

The photoluminescence characteristic of the as-deposited products was also investigated. Fig. 6 shows the PL spectrum of the ZnO nanowires on the ZnO film shown in Fig. 3 by spectrometer (Lambda Vision, LVM200-KS), where the power of the excitation laser was 90 kW/cm^2 and the exposure time was 2 sec. The UV emission centered at around 390 nm, which is the contribution of the near band edge emission of the wide band-gap ZnO, and no visible light emission at green emission band attributed to the deep-level defects inside ZnO lattices were observed. The deep-level luminescence is related to the oxygen vacancies in the grown ZnO crystals. This indicates a very low concentration of deep-level defects inside ZnO lattices.

Conclusions

To summarize, we have succeeded in synthesizing vertically aligned ZnO nanorods, nanowires on c-plane sapphire substrates by NAPLD in the same chamber. In this study, the film-wire layer-structured ZnO nanowires were synthesized. Vertically-aligned low density ZnO nanowires with were synthesized on the ZnO film. In addition, synthesis of the film-wire layered structure ZnO nanowires consisting of different ZnO targets were demonstrated. Core/shell structured ZnO nanowires were also fabricated in the single chamber. Furthermore, near band edge emission of ZnO was observed from synthesized ZnO nanowires.

Acknowledgments

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