

# Synthesis of Core/Shell Nanowires Using Doped ZnO Targets

Daisuke NAKAMURA, Kota OKAZAKI, Kazuki KUBO, Koji TSUTA, Mitsuhiro HIGASHIHATA and Tatsuo OKADA

Graduate School of Information Science and Electrical Engineering, Kyushu University,  
744 Motoooka, Nishi-ku, Fukuoka 819-0395, Japan  
E-mail: dnakamura@ees.kyushu-u.ac.jp

ZnO nanowires have attracted a great attention as building blocks for the optoelectronic devices. For the practical optoelectronic applications based on the ZnO nanowires, synthesis technique of ZnO nanowire with layered structures is significantly important in order to achieve a *p-n* junction, a core/shell structure, and a multiple quantum well structure. We have been succeeded in growing nanowires on the pre-deposited ZnO film and core/shell structure by a newly developed nanoparticle-assisted pulsed-laser deposition (NAPLD) using multi-target changer. In this paper, recent progresses of synthesis of layer-structured ZnO nanowires using doped ZnO target, such as a Li-Ni codoped ZnO, are described.

DOI:10.2961/jlmn.2012.01.0021

**Keywords:** ZnO, Pulsed laser deposition, Nanowire, Core/shell structure

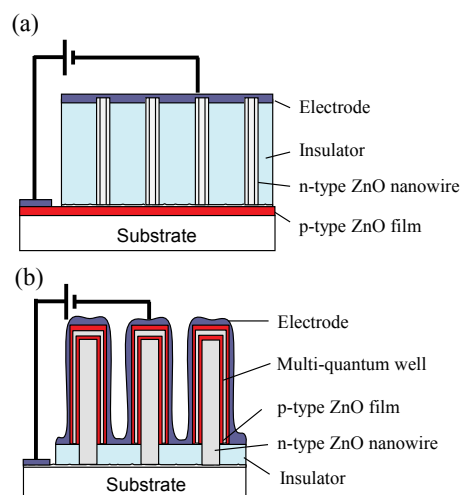
## 1. Introduction

Zinc oxide (ZnO) is one of the promising materials in UV optoelectronic applications such as a light-emitting diode (LED) and a laser diode (LD) because of a direct wide band-gap of 3.37 eV at room temperature and a relatively large exciton binding energy of 60 meV [1]. Especially, ZnO nanowire has attracted a great attention for building blocks of nanodevices such as an UV-LD[2], an UV-LED [3], an UV photodetector [4], and a gas sensor [5], because it has superior crystalline quality, better electrical/optical quality, and large surface area to volume ratio. Furthermore, ZnO nanowires have no need for a lattice matched substrate for the overgrowth [6]. Those ZnO nanostructures are able to be synthesized using several methods such as a molecular beam epitaxy [7], sputtering [8], a chemical vapor deposition [9], solution method [10] etc.

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, a core-shell structure, and a multiple quantum well structure, as shown in Fig.1. In our study, we have succeeded in synthesizing various nanostructures, such as nanorods [11], nanowalls [12], the vertically and horizontally aligned ZnO nanowires [13] by nanoparticle-assisted pulsed-laser deposition (NAPLD) without any catalyst. Furthermore, we have been also succeeded in growing ZnO nanowires with layered structures, such as a film-wire layered structure and core/shell structure in one NAPLD chamber using the multi-target changer [14]. In this paper, we describe progresses of synthesis and photoluminescence of the layer-structured ZnO nanowires by NAPLD using doped ZnO target, such as a Li-Ni codoped ZnO, are described.

## 2. Experiments

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



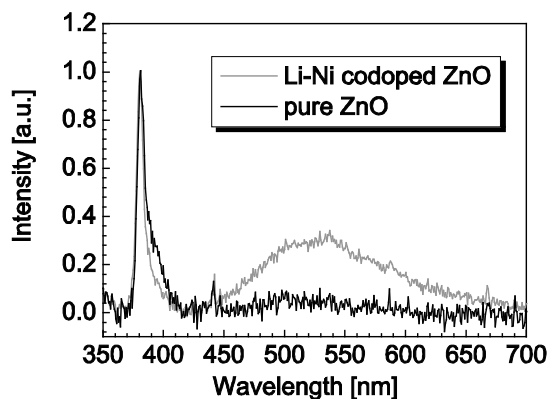
**Fig. 1** Schematic of the layer-structured ZnO nanowires, (a) film-wire structure and (b) core/shell quantum well.

a vacuum chamber and the target-substrate distance was set to 40 mm. The substrate was heated to 400-800 °C in the vacuum chamber filled with a background gas of argon or oxygen. The ZnO target was ablated with the third harmonics 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<sup>2</sup>. 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 a He-Cd laser.

## 3. Results and Discussion

### 3.1 Film-Wire Layer-Structured ZnO Nanowires

We have succeeded in growing the layer-structured ZnO nanowire consisting of different materials of a pure ZnO and a Li-Ni codoped ZnO target [14]. Li-Ni codoped ZnO is one of the promising targets for *p*-type ZnO thin film [15,16]. ZnO nanowires were synthesized using the



**Fig. 2** PL spectrum of the ZnO nanowires on the ZnO and the Li-Ni codoped ZnO thin film.

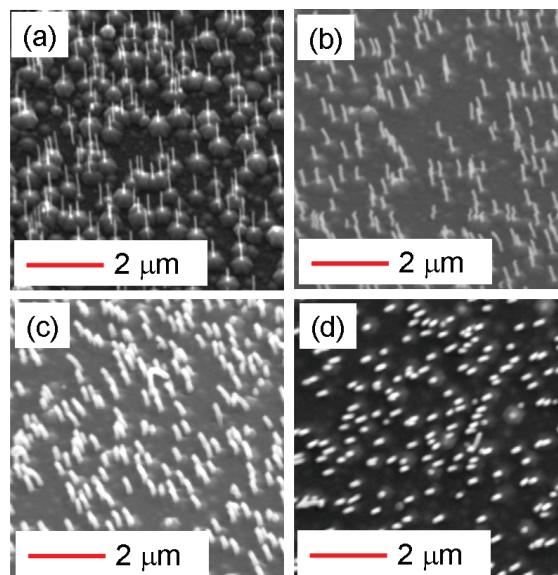
pure ZnO target after deposition of the Li-Ni codoped ZnO film. The Li-Ni codoped ZnO film was deposited on a *c*-plane sapphire substrate temperature of 400 °C and oxygen gas pressure of 26 mTorr. After deposition of the film for 5 minutes, the nanowires were subsequently synthesized on the film at the temperature of 750 °C and argon gas of 200 Torr in the same chamber. The growth time of the ZnO nanowires was 15 min. The vertically-aligned low density ZnO nanowires with the diameter of 50-100 nm and the length of around 2  $\mu\text{m}$  were formed. Most nanowires were grown on hexagonal cone-shape cores. The cores have not been seen in samples without the pre-deposition of the ZnO film. Besides, most of the cores are formed in the same size using a Sb doped ZnO target [17]. Thus the ZnO film layer probably contributes to the formation of the cores. Although the more detail mechanism should be investigated, an interaction between the buffer film and the depositing nanoparticles occurred.

The optical property of the ZnO nanowires was characterized with PL spectra measurement at room temperature by a spectrometer (multi-channel analyzer C10027, HAMAMATSU photonics). Fig.2 shows the PL spectra from the ZnO nanowires synthesized on the Li-Ni codoped ZnO and the pure ZnO thin film. The spectra are normalized at the UV peak for easy comparison. A strong UV peak centered at 380 nm and a weak broad visible emission with a peak at about 500 nm were observed from the ZnO nanowires of the pure ZnO film. The UV emission band is due to a near-band-edge (NBE) recombination of ZnO, which is the emission of excitons through an electron-hole recombination process [18]. The broad green emission peak of ZnO is a typical defect-related emission, which is usually attributed to the deep-level oxygen vacancy in the surface and subsurface lattices of ZnO materials [19]. The intensity of the broad visible emission from the nanowires grown on the Li-Ni codoped ZnO film is higher than that on the pure ZnO film. The results show that the Li-Ni thin film might cause an increase of deep-level defects inside ZnO lattices [20]. However, as an intensity ratio of green emission to NBE from the ZnO nanowires is less than 0.4, evident strong UV exciton emission and weaker defect emission show the good crystal quality both of ZnO nanowires on the pure and Li-Ni codoped films.

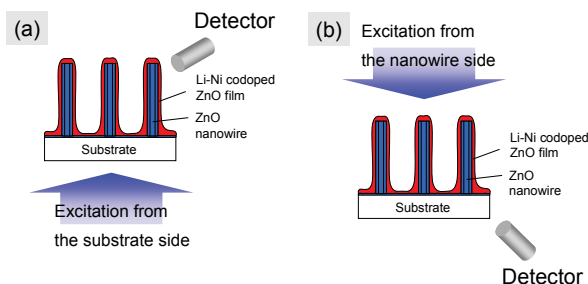
### 3.2 Core/Shell Structured ZnO Nanowires

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 [21]. We have demonstrated the core/shell structured ZnO nanowires by NAPLD using pure ZnO target [14]. After growth of low density ZnO nanowires at a typical growth condition of the nanowire, the shells were subsequently synthesized under the film deposition condition. It was found that ZnO shell coats homogeneously the entire nanowire, and thickness of the shell could be controlled by the deposition time.

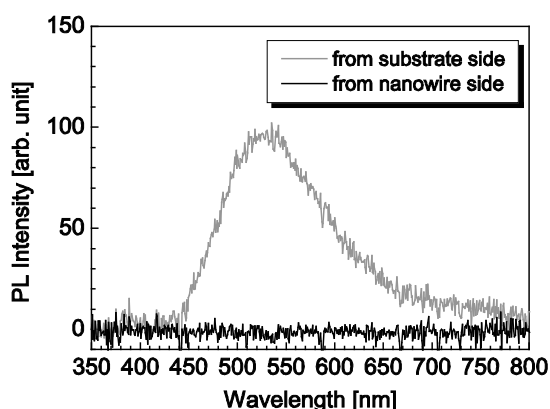
In this study, core/shell structured ZnO nanowires consisting of different material layers also could be synthesized using the pure and the Li-Ni codoped ZnO targets. Fig.3(a) shows the SEM image of the pure ZnO nanowires synthesized after deposition of the ZnO film. Fig.3(b) shows the SEM image of the ZnO/Li-Ni codoped ZnO core/shell structured ZnO nanowires after growth the shell for 10 minutes at the temperature of 400 °C and oxygen gas pressure of 26 mTorr. Fig. 3(c),(d) shows the 45° tilted view and top view SEM image of the ZnO nanowires after growth of the ZnO shell for 20 minutes. The diameter of the ZnO nanowires increased uniformly with increasing the deposition time of the shell. On the other hand, the hexagonal cone-shape cores, as seen in Fig.3(a), were buried in the Li-Ni codoped ZnO film as shown in Fig.3(b),(c). Thus, the incoming Li-Ni codoped ZnO seems to incorporate much more effectively into the ZnO buffer film layer than the nanowires. These results show the core/shell structure consisting of different ZnO targets is able to be fabricated by the multi-target changer system in the simple experimental setup.



**Fig. 3** SEM images of (a) ZnO nanowires on the film and the ZnO/Li-Ni codoped ZnO core/shell structured ZnO nanowires, where the growth time of the Li-Ni codoped ZnO shell layer were (b) 10 min. and 20 min. ((c) 45° tilted view, (d) top view).



**Fig. 4** Schematic of the PL measurement from the ZnO/Li-Ni codoped ZnO core/shell structured ZnO nanowires



**Fig. 5** PL spectrum of the core/shell structured ZnO nanowire.

The photoluminescence characteristic of the ZnO/Li-Ni codoped ZnO core/shell structured ZnO nanowires was also investigated. In the PL measurement, the nanowires were excited from the substrate side or the nanowire side, as shown in Fig.4. Fig.5 shows the PL spectra of the core/shell structured ZnO nanowires. A visible light emission at green emission band and very low UV emission were observed. On the other hand, no PL spectrum was detected under excitation from the nanowire side, as shown in Fig.5(b). The results indicate the Li-Ni codoped ZnO film absorbs the short wavelength region less than 450 nm. Thus, an intrinsic layer is inevitably required between the *p-n* junction, which is a PIN (*p*-type-Intrinsic-*n*-type) diode structure, to fabricate a ZnO-based homo-junction LED using the Li-Ni codoped ZnO as a *p*-type material in order to prevent absorption of the UV emission around the Li-Ni codoped ZnO.

## Conclusions

To summarize, we have succeeded in synthesizing layer-structured ZnO nanowires on *c*-plane sapphire substrates by NAPLD in the single chamber. Vertically-aligned low density ZnO nanowires were synthesized on the pure and the Li-Ni codoped ZnO film. In addition, core/shell structured ZnO nanowires consisting of different materials were also fabricated. Furthermore, PL characteristics of the layer-structured ZnO nanowires were observed under the He-Cd laser excitation.

## Acknowledgments

A part of this study has been financially supported by Special Coordination Funds for Promoting Science and Technology from Japan Science and Technology Agency and a Grant-in Aid for Scientific Research from the Japan Society of Promotion of Science.

## References

- [1] Y. Chen, D. M. Bagnall, H-J. Koh, K-T. Park, K. Hiraga, Z. Zhu, and T. Yao: J. Appl. Phys., 84, 3912 (1998).
- [2] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang: Science, 292, 1897 (2001).
- [3] M.-C. Jeong, B.-Y. Oh, M.-H. Ham, J.-M. Myoung: Appl. Phys. Lett., 88, 202105 (2006).
- [4] Y. Li, F. D. Valle, M. Simonnet, I. Yamada, J.-J. Delaunay: Nanotechnology, 20, 045501 (2009).
- [5] Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li, and C. L. Lin: Appl. Phys. Lett., 84, 3654 (2004).
- [6] M. Willander, L. L. Yang, A. Wadeasa, S. U. Ali, M. H. Asif, Q. X. Zhao and O. Nur: J. Mater. Chem. 19, 1006 (2009).
- [7] I.C. Robin, P. Marotel, A.H. El-Shaer, V. Petukhov, A. Bakin, A. Waag, M. Lafossas, J. Garcia, M. Rosina, A. Ribeaud, S. Brochen, P. Ferret, G. Feuillet: J. Cryst. Growth, 311, 2172 (2009).
- [8] Z. Guo, D.X. Zhao, Y. Liu, D. Shen, J. Zhang, B. Liu: Appl. Phys. Lett., 93, 163501 (2008).
- [9] J.-J. Wu, S.-C. Liu: Adv. Mater., 14, 215 (2002).
- [10] C. H. Ahn, W.S. Han, B. H. Kong, H. K. Cho: Nanotechnology, 20, 015601 (2009).
- [11] M. Kawakami, A. B. Hartanto, Y. Nakata, T. Okada: Jpn. J. Appl. Phys., 42, L33 (2003).
- [12] B. Q. Cao, T. Matsumoto, M. Matsumoto, M. Higashihata, D. Nakamura, T. Okada: J. Phys. Chem. C, 113, 10975 (2009).
- [13] R. Guo, M. Matsumoto, T. Matsumoto, M. Higashihata, D. Nakamura, T. Okada: Appl. Sur. Sci., 255, 9671 (2009).
- [14] D. Nakamura, T. Matsumoto, A. Kumeda, K. Toya, K. Okazaki, M. Higashihata, T. Okada: J. Laser Micro/Nanoeng., 6, 23 (2010).
- [15] E. S. Kumar, S. Venkatesh, M. S. R. Rao: Appl. Phys. Lett., 96, 232504 (2010).
- [16] E. S. Kumar, J. Chatterjee, N. Rama, N. DasGupta, and M. S. R. Rao: Appl. Mater. Interfaces, 3, 1974 (2011).
- [17] D. Nakamura, K. Okazaki, I. A. Palani, M. Higashihata, T. Okada, Appl. Phys. A, 103, 959 (2011).
- [18] B. Q. Cao, W. P. Cai, H. B. Zeng, Appl. Phys. Lett., 88, 161101 (2006).
- [19] S. B. Zhang, S.-H. Wei, and A. Zunger: Phys. Rev. B 63, 075205 (2001).
- [20] X. Liu, X. Wu, H. Cao, R. P. H. Chang: J. Appl. Phys., 95, 3141 (2004).
- [21] B. Q. Cao, J. Zúñiga-Pérez, N. Boukos, C. Czekalla, H. Hilmer, J. Lenzner, A. Travlos, M. Lorenz, M. Grundmann: Nanotechnology, 20, 305701 (2009).

(Received: June 6, 2011, Accepted: January 22, 2012)