Available online at www.sciencedirect.com
ScienceDirect
Journal of Physics and Chemistry of Solids 69 (2008) 1491–1494
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS
www.elsevier.com/locate/jpcs

# Composite nanowires with MgO/ZnO core–sheath structures: Study of thin ZnO shell layers

Hyoun Woo Kim*, Jong Woo Lee, Seung Hyun Shim

*School of Materials Science and Engineering, Inha University, Incheon 402-751, Republic of Korea*

Received 30 June 2007; received in revised form 25 October 2007; accepted 30 October 2007

**Abstract**

Coaxial nanowires of magnesium oxide (MgO) core with zinc oxide (ZnO) shells were synthesized with the assistance of atomic layer deposition method. The diameters of these composite nanowires varied from 50 to 110 nm, with sheath thickness in the range of 15–25 nm. The sheath layer comprised a hexagonal ZnO phase. We found that the overall shape and peak positions of PL emission spectrum were almost unchanged by the sheath coating with a thin enough ZnO layer.


*Keywords:* A. Inorganic compounds; B. Crystal growth; C. Electron microscopy; D. Crystal structure

## 1. Introduction

After the successful synthesis of various nanotubes and nanowires, there has been great interest in the realization of multilayer coaxial nanostructures [1,2]. It is anticipated that by combining the different types of nanotubes and nanowires in a radial direction, nanoscale electronic devices possessing various interesting functions might be realized [3]. Magnesium oxide (MgO) is a typical wide-band-gap insulator. It has found many important applications for use in catalysis, refractory material industry, toxic waste remediation, paint, superconductors and substrates for thin film growth [4–8]. In addition, the MgO nanowires can display a unique capability to pin the magnetic flux lines within a high-temperature superconductor [9]. On the other hand, zinc oxide (ZnO) is of much interest because of their attractive optical functions based on large binding energy of excitons and biexcitons as well as their multifunctional physical properties. In this paper, we report the fabrication of MgO/ZnO core–sheath nanowires. To the best of our knowledge, this is the first report on the synthesis of MgO/ZnO core–sheath nanowires with continuous and layered sheath successfully being deposited. Since both MgO and ZnO are important oxides for industrial applications and scientific interests, this novel approach to fabricate the nanowire heterostructures will be a step toward the potential applications of composite nanowires to nanodevices.

## 2. Experimental

The synthesis process of MgO core nanowires, being carried out in a 100 cm-long horizontal quartz tube with an inner diameter of 50 mm, was similar to the previous experiments [10]. The Au-coated (3 nm thick) Si substrates were annealed at 700 °C prior to MgO deposition, in a flow of nitrogen ($N_2$) gas (flow rate 500 standard $cm^3$/min) for 30 min. While the pure $MgB_2$ powders were situated in the ceramic boat in the middle of the quartz tube, the substrates were placed on the top of the source powders with the Au-coated side facing downwards. At 900 °C, the ambient gas ($Ar+O_2$) was flowed at a constant total pressure of 2 Torr, with the typical percentage of $O_2$ and Ar partial pressure being set to approximately 3% and 97%, respectively. After 2 h of typical heating process, the substrate was cooled down and then removed from the furnace for analysis. Subsequently, ZnO was deposited on the synthesized MgO nanowires by using atomic layer deposition (ALD) technique, with the system being

*Corresponding author. Tel.: +82 32 860 7544; fax: +82 32 862 5546.
*E-mail address:* hwkim@inha.ac.kr (H.W. Kim).

0022-3697/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jpcs.2007.10.094

previously outlined [11]. Diethylzinc (DEZn) and $H_2O$ were kept in bubblers at 10 °C. These source gases were alternately fed into the chamber though separate inlet lines and nozzles. The typical pulse lengths were 0.2 s for DEZn dosing, 2 s for Ar purging, 0.2 s for the $H_2O$ dosing and 2 s for Ar purging. The number of ALD cycles was optimized and set to 50. The substrate temperature and the pressure in the chamber were set to 150 °C and 0.3 Torr, respectively. The crystal structure of the product was examined by means of glancing angle (0.5°) X-ray diffraction (XRD; X'pert MPD-Philips) with the contribution from the substrate minimized. The morphologies of the samples were checked by scanning electron microscopy (SEM; Hitachi S-4200) and transmission electron microscopy (TEM; Philips CM-200). Energy-dispersive X-ray spectroscopy (EDX), which was attached to TEM, was employed for identifying the elemental compositions of the product. The PL spectra were measured at 298 K by using a 325 nm He–Cd laser (Kimon, 1K, Japan).

## 3. Results and discussion

Fig. 1 shows the XRD pattern of the ZnO-coated MgO nanowires. While some diffraction peaks can be indexed to the tetragonal rutile structure of MgO with lattice constants of $a = 4.738$ Å and $c = 3.187$ Å (JCPDS File No. 41-1445) presumably from the core nanowires, other reflection peaks are readily indexed as hexagonal lattice of ZnO, which are in agreement with JCPDS File No. 05-0664. Accordingly, XRD analysis reveals not only that the ZnO was successfully deposited on the core MgO nanowires, but also that the deposited ZnO comprises a crystalline phase. Fig. 2 depicts the SEM image of the coated product, indicating that dense wire-like nanostructures were observed. Statistical analysis of many SEM images indicated that the average diameter of the produced 1D structures was in the range of 50–110 nm. The inset of Fig. 2 shows a typical closer-view SEM image of

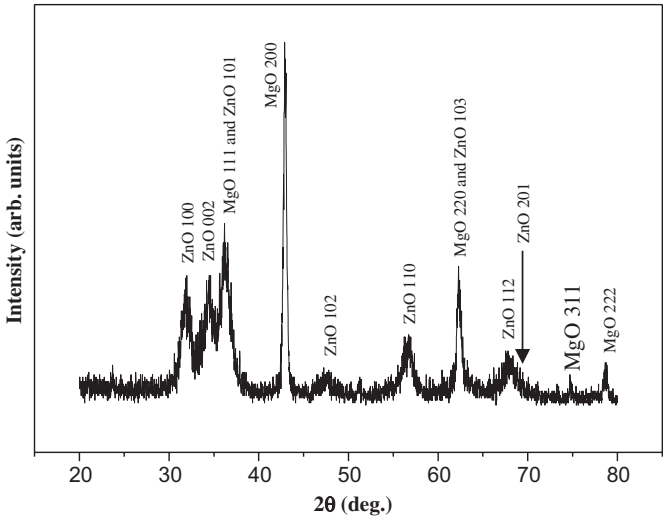


Fig. 1. XRD spectrum of the ZnO-coated MgO nanowires.

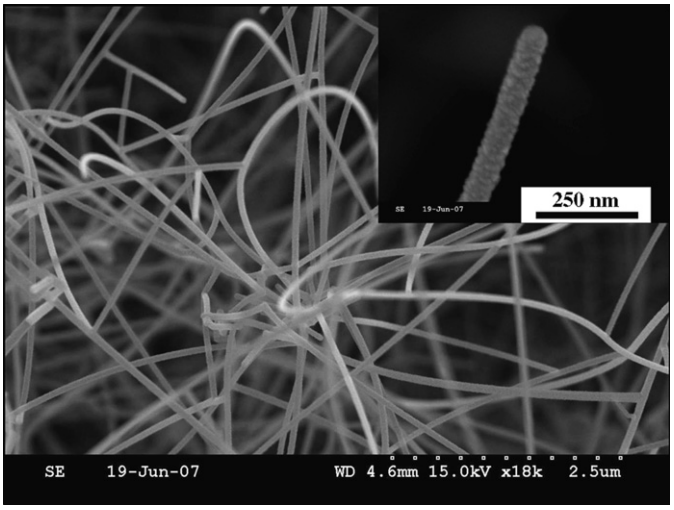


Fig. 2. SEM image of coated product (inset: typical closer-view SEM image of a ZnO-coated MgO nanowire).

ZnO-coated MgO nanowires. It is noteworthy that the surface of the ZnO-coated nanowire is not perfectly smooth.

Fig. 3a shows a low-magnification TEM image of coated product, revealing that the coated nanowires are indeed a core–sheath structure with a sheath thickness in the range of 15–25 nm. A clear interface is found between the MgO core and ZnO sheath from the TEM images. Although the thickness of the sheath is not perfectly uniform, they are continuous along the length direction of nanowires. Fig. 3b shows a TEM image of a coated nanowire and an associated selected area electron diffraction (SAED) pattern. The pattern shows weak diffraction rings possibly from the poly-crystalline sheath, suggesting that the ZnO sheath layer contains crystalline phases in (1 0 0), (1 0 1), (1 0 2) and (1 1 0). Fig. 3c shows a lattice-resolved TEM image enlarging an area enclosed by dotted square in Fig. 3b. The observed interplanar spacing is about 0.25 nm, which belong to the (1 0 1) plane of hexagonal ZnO. Fig. 3c also reveals that the shell layer of the coated nanowire is crystalline. Fig. 3d shows a TEM–EDX spectrum, indicating that the coated nanowire consists of Mg, Zn and O elements, whereas C and Cu signals were generated from the TEM microgrid mesh supporting the nanowires.

Fig. 3b clearly shows that the surface of the ZnO sheath layer is rougher than that of the MgO core nanowire, indicating that the surface roughness of the sheath layer is not originated from underlying MgO surface, but is associated with the ALD process. In our preliminary work on the deposition of ZnO on MgO nanowires [12], we obtained irregularly shaped structures comprising ZnO amorphous nanoparticles. After systematic investigation, we reveal that unoptimized number of ALD cycles (i.e., $>100$) contributed to the uneven (i.e., island-type or three-dimensional) growth, possibly because a homogeneous distribution of the active species was not attained

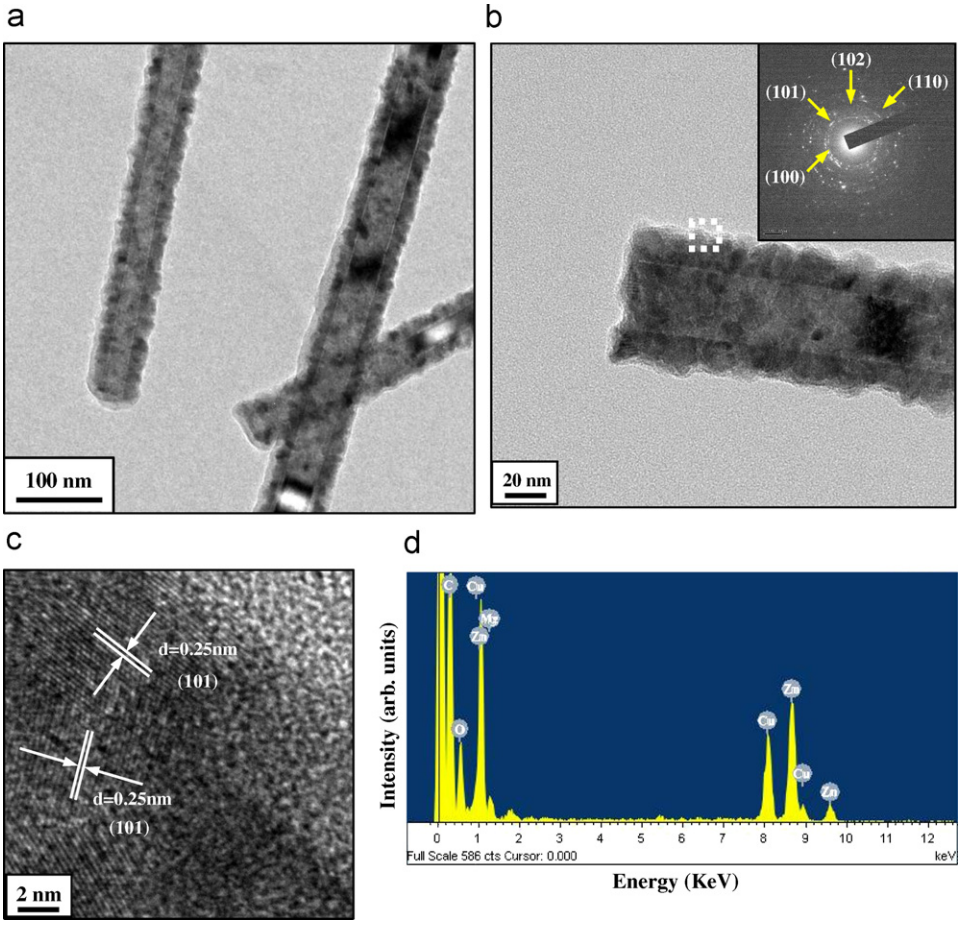


Fig. 3. (a) Low-magnification TEM image of coated product. (b) TEM image of a coated nanowire (inset: associated SAED pattern). (c) Lattice-resolved TEM image taken at the area marked with the dotted box in part (b). (d) Typical EDX spectrum from the coated nanowire.

throughout the surface area. By reducing the numbers down to 50 in the present study, we deposited a relatively smooth and continuous sheath layer, resulting in the MgO/ZnO core–sheath structures. Fig. 4a shows the EDX concentration profile of Zn, along the line drawing in a typical coated nanowire (Fig. 4b). Since the highest peaks are in the sheath region (indicated by arrowheads), Fig. 4a suggests that Zn elements mainly reside in the shell region.

Fig. 5a and b show the PL spectra of uncoated and ZnO-coated products, respectively. We found that the line shape of normalized PL spectrum, which is characteristic of MgO PL emissions, was almost unchanged by the sufficiently thin ZnO coating. After multi-peak Gaussian fitting to two major bands in the PL spectrum, we found that the Gaussian curves fit the original curves almost perfectly. Therefore, the PL spectrum mainly consists of two bands, which peaks at approximately 2.30 eV in the green region and 2.86 eV in the blue region, respectively. Rosenblatt et al. reported the green light emission in bulk MgO [13], whereas Hao et al. observed the blue emission from MgO nanostructures [14]. Since blue and green emissions originate from defects in MgO [13,14], we surmise that those defects were generated during the high-temperature fabrication process of MgO core nanowires In our previous experiments, we observed that the thicker ZnO shell structures contributed PL emissions (not shown here), suggesting that sufficiently thin sheath layer helps to preserve the PL characteristics of the uncoated samples. Since thin ZnO shell layer does not degrade the intrinsic properties of core MgO nanowires, it can be used as a protecting layer for preventing surface contamination or degradation, in MgO-based nanodevices for optoelectronics, catalyst and superconductor applications. Furthermore, with the insulating MgO core, thin semiconducting ZnO will be efficient active layers for nanoelectronic devices.

## 4. Conclusions

We successfully prepared MgO nanowires with crystalline ZnO wrapping layers by using an ALD technique. XRD spectrum, lattice-resolved TEM image and SAED pattern coincidentally reveal that the coating generated a hexagonal ZnO phase, whereas SEM image shows that the coated product consists of a large quantity of nanowires. The PL measurement of the thin ZnO-coated sample

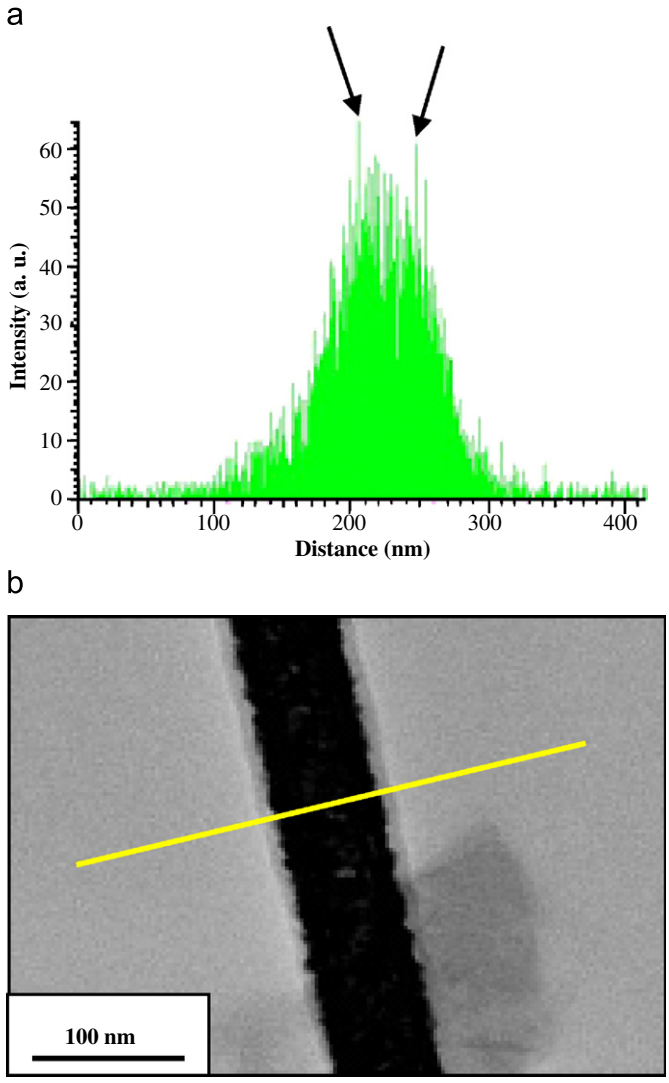


Fig. 4. EDX concentration profile of (a) Zn along the line drawing in a coated nanowire shown in part (b).

(50 ALD cycles) with the Gaussian fitting exhibits apparent visible light emission bands centered at 2.34 and 2.88 eV, being similar to an uncoated one but being contrary to thick ZnO-coated one (>100 ALD cycles). This method could be applied to a wide range of materials and result in various heterostructures, which may serve as potential building blocks in various nanodevices.

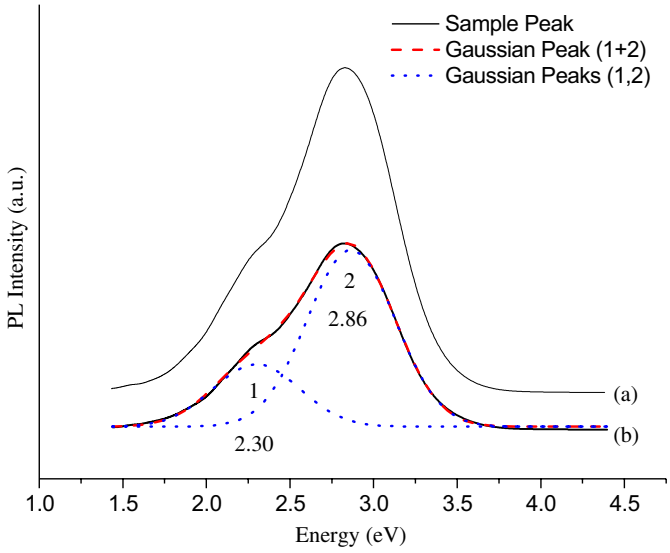


Fig. 5. PL spectra of uncoated (a) and ZnO-coated (b) MgO nanowires.

## Acknowledgment

This work was supported by an Inha University research grant.

## References

[1] R. Tenne, M. Homyonfer, Y. Feldman, Chem. Mater. 10 (1998) 3225.
[2] X. Blasé, J.-C. Charlier, A. De Vita, R. Car, Appl. Phys. A 68 (1999) 293.
[3] J. Hu, T.W. Odom, C.M. Lieber, Acc. Chem. Res. 32 (1999) 435.
[4] Y. Kawaguchi, Solid State Commun. 117 (2000) 17.
[5] S.H.C. Liang, I.D. Gay, J. Catal. 101 (1986) 293.
[6] A.N. Copp, Am. Ceram. Soc. Bull. 74 (1995) 135.
[7] R.Z. Ma, Y. Bando, Chem. Phys. Lett. 370 (2003) 770.
[8] Y.Q. Zhu, W.K. Hsu, W.Z. Zhou, M. Terrones, H.W. Kroto, D.R.M. Walton, Chem. Phys. Lett. 347 (2001) 337.
[9] P. Yang, C.M. Lieber, Science 273 (1996) 1836.
[10] H.W. Kim, S.H. Shim, Chem. Phys. Lett. 422 (2006) 165.
[11] J. Lim, K. Shin, H. Kim, C. Lee, Thin Solid Films 475 (2005) 256.
[12] H.W. Kim, S.H. Shim, J. Korean Phys. Soc. 49 (2006) 241.
[13] G.H. Rosenblatt, M.W. Rowe, G.P. Williams Jr., R.T. Williams, Y. Chen, Phys. Rev. B 39 (1989) 10309.
[14] Y. Hao, G. Meng, C. Ye, X. Zhang, L. Zhang, J. Phys. Chem. B 109 (2005) 11204.