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2007

Li, S. Z., Gan, C. L., Cai, H., Yuan, C. L., Guo, J., Lee, P. S., et al. (2007). Enhanced photoluminescence of ZnO/Er₂O₃ core-shell structure nanorods synthesized by pulsed laser deposition. *Applied Physics Letters*, 90(26).

<https://hdl.handle.net/10356/95029>

<https://doi.org/10.1063/1.2752020>

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Enhanced photoluminescence of ZnO/Er₂O₃ core-shell structure nanorods synthesized by pulsed laser deposition

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(Received 31 March 2007; accepted 4 June 2007; published online 26 June 2007)

A narrow size distribution of ZnO nanorod array has been synthesized on silicon substrate by pulsed laser deposition (PLD) in argon ambient. ZnO/Er₂O₃ core-shell nanostructures were then formed through PLD of a thin Er₂O₃ layer onto the fabricated ZnO nanorod surface. Transmission electron microscopy analysis shows that both the ZnO core and Er₂O₃ shell are polycrystalline. Photoluminescence measurement was carried out to characterize the optical properties of the core-shell nanostructures. The band diagram of the core-shell structure shows that a type-II nanostructure may have formed, which explains the ultraviolet emission enhancement of the core-shell structure over pure ZnO nanorods. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2752020]

In recent years, one-dimensional nanostructures have attracted much attention due to their potential as building blocks for electronics and photonics devices,^{1,2} as well as biosensors in life-science applications.³ Much effort has been devoted to developing various nanostructures, especially ZnO nanostructures because of their unique properties such as large excitation binding energy (60 meV), near ultraviolet (UV) emission, transparent conductivity, and piezoelectricity.⁴ Moreover, ZnO is a biosafe and biocompatible material which may be used in biomedical applications without additional coating.⁴ Besides fabrication of ZnO nanostructures, engineering of ZnO properties through surface modification is another important aspect in creating optoelectronic devices.⁵ ZnO nanorod/CdS nanoparticle composites⁶ and ZnO/ZnGa₂O₄ core-shell nanostructures⁷ have been synthesized, and modification of their optical properties was reported. However, a study on ZnO/Er₂O₃ core-shell nanostructure has not yet been reported. This structure is attractive because Er₂O₃, being a high-*k* dielectric material, may also act as the gate dielectric of ZnO nanowire transistors.

In this letter, we report the fabrication of ZnO/Er₂O₃ core-shell nanostructures and their optical property. The core-shell structures were characterized by field emission scanning electron microscope (FESEM), x-ray diffractometer (XRD), and transmission electron microscopy (TEM). The optical property was measured by a spectrophotometer with a He–Cd as the excitation source.

ZnO nanorods were fabricated by pulsed laser deposition (PLD) under argon atmosphere with the aid of Au catalysts.⁸ After postgrowth annealing in air for 30 min at 350 °C, an approximately 10-nm-thick Er₂O₃ layer was then deposited on the nanorod array surface by PLD in argon atmosphere (10 mTorr) at room temperature.⁹ The sample was again annealed in the same condition before further characterizations were carried out.

Figure 1 illustrates the top view and cross-sectional view of the ZnO nanorod array grown in argon atmosphere. Figure 1(a) shows a high density and narrow size distribution (di-

ameter is approximately 60 nm) of ZnO nanorod array. The wetting layer between the silicon substrate and ZnO nanorods array [Fig. 1(b)] indicates that Stranski-Krastanov nucleation had taken place before the formation of ZnO nanorods. The selective area energy dispersive x-ray spectroscopy (EDS) measurement shows the absence of gold nanoparticles on the surface and tip of the ZnO nanorods.

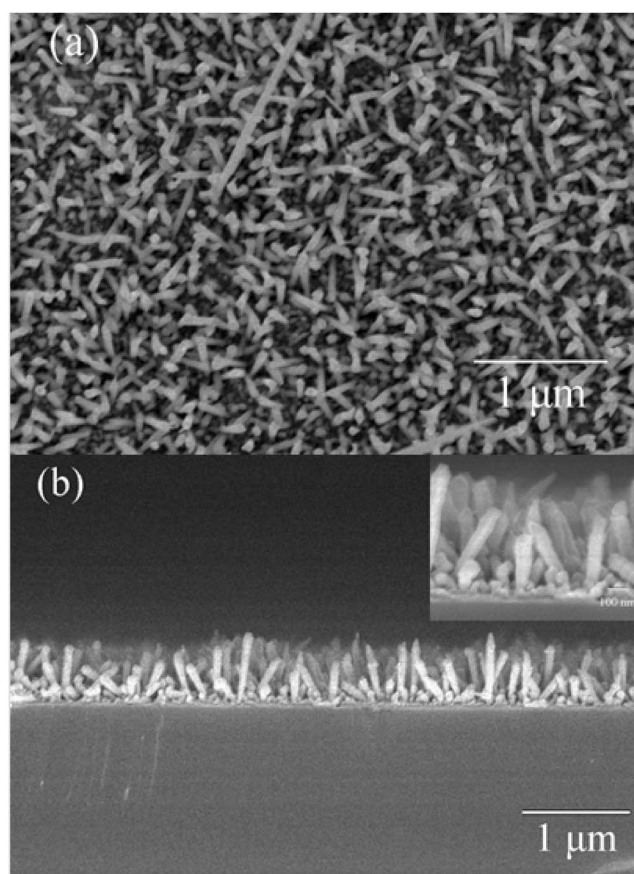


FIG. 1. FESEM images of (a) top view and (b) cross-sectional image of ZnO nanorod array grown in argon ambient at 800 °C. The inset shows a high magnification of the ZnO nanorods and the scale bar is 100 nm.

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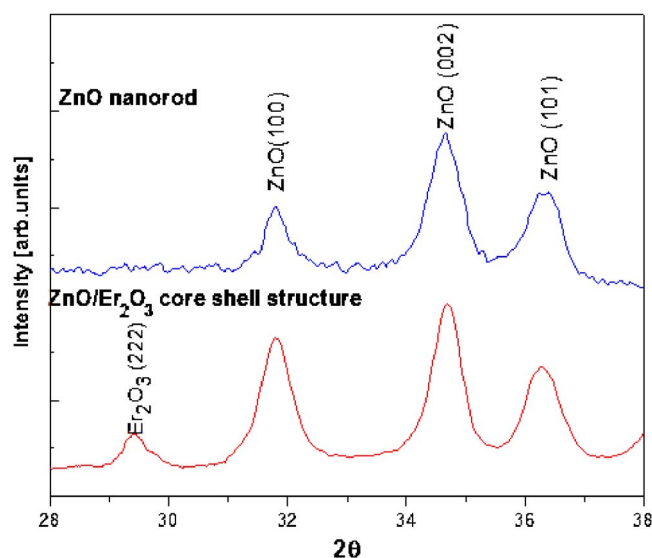


FIG. 2. (Color online) XRD patterns of ZnO and ZnO/Er₂O₃ nanostructures grown on silicon substrates.

Figure 2 shows the XRD patterns of pure ZnO and Er₂O₃-coated ZnO nanorod arrays grown on silicon substrates. The pure ZnO XRD pattern indicates that the nanorods were polycrystalline. A high intensity of (002) peak also reveals that most of the ZnO nanorods were aligned with *c*-axis orientation. The XRD pattern of ZnO/Er₂O₃ indicates that the Er₂O₃ was crystalline after annealing. However, this may be due to either the Er₂O₃ layer coated on the ZnO nanorod surface was crystalline or a crystalline Er₂O₃ layer that had formed simultaneously on the silicon substrate during the deposition of the Er₂O₃ shell layer.

To further analyze the core-shell structure, TEM characterization was carried out. The TEM sample was prepared by scraping some of the nanorods off the top surface of the substrate onto a TEM grid. The details of the core-shell structure were studied using a low magnification TEM, as shown in Fig. 3(a). An EDS cross-section line scan was carried out to indicate the Er and Zn distribution profiles across the core-shell nanorods, as shown in Fig. 3(c). The scans clearly show an approximately 10-nm-thick Er₂O₃ shell around the 50-nm-thick ZnO core. Selected area diffraction pattern shown in Fig. 3(b) confirms the compositions, with both ZnO and Er₂O₃ diffraction patterns observed. It can be seen that the ZnO has a wurtzite structure (hexagonal phase, space group P6 3mc). It also confirms that the Er₂O₃ is crystalline (space group IA 3-) after annealing. Due to the polycrystalline structure of Er₂O₃, no Moiré pattern was observed in the electron microscopy.

Photoluminescences (PLs) of the ZnO nanorod array before and after deposition of the Er₂O₃ shell were measured at room temperature to investigate the optical properties of this core-shell nanorod structure (Fig. 4). The ZnO nanorod array with Er₂O₃ coating exhibits a distinct enhanced UV emission. The full width at half maximum of the PL spectra decreases from 165 meV (ZnO nanorod) to 102 meV (ZnO/Er₂O₃ core shell), accompanied by an intensity increase. In addition, as compared to the photoemission of pure ZnO nanorod array, a redshift of core-shell structure was observed (about 10 meV). The PL enhancement may be explained by the formation of a type-II nanostructure.¹⁰ Based on the electron affinity model,¹¹ the schematic band diagram

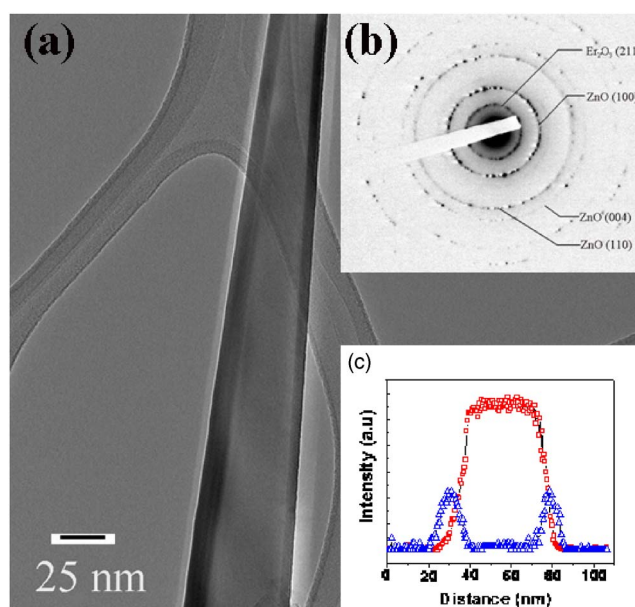


FIG. 3. (Color online) (a) TEM image of ZnO/Er₂O₃ core-shell structure, (b) selected area diffraction pattern of ZnO/Er₂O₃ core-shell nanorods, and (c) EDS cross-sectional line scan of a nanorod, highlighting the distribution profiles of Zn (□) and Er (△) across the core-shell nanorod.

of ZnO/Er₂O₃ core-shell structure is shown in Fig. 5. The electron affinity of ZnO is 4.35 eV (Ref. 12) and that of Er₂O₃ is estimated about 2.4 eV.¹³ The energies of both the conduction and valence bands of Er₂O₃ (shell) are higher than those of ZnO (core).¹⁴ Consequently, the core-shell structure confines the photogenerated electrons inside the ZnO core since the high band gap of the shell material suppresses tunneling between them, which enhances the UV emission of ZnO. A tiny redshift of about 5 meV was also reported in ZnO/ZnS core-shell structure¹⁵ and the shift in energy is also much lower than the redshift induced by type-II structures. This shift may be due to the diffusion of elements between ZnO/Er₂O₃ interfaces during the annealing step, leading to the formation of localized band edge state due to structural relaxation and charge exchange.¹⁶

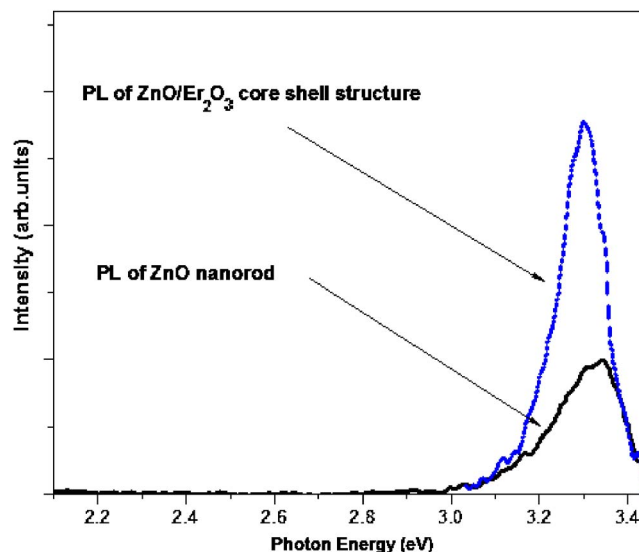


FIG. 4. (Color online) Photoluminescence spectra of the ZnO nanorods array and ZnO/Er₂O₃ core-shell nanostructures.

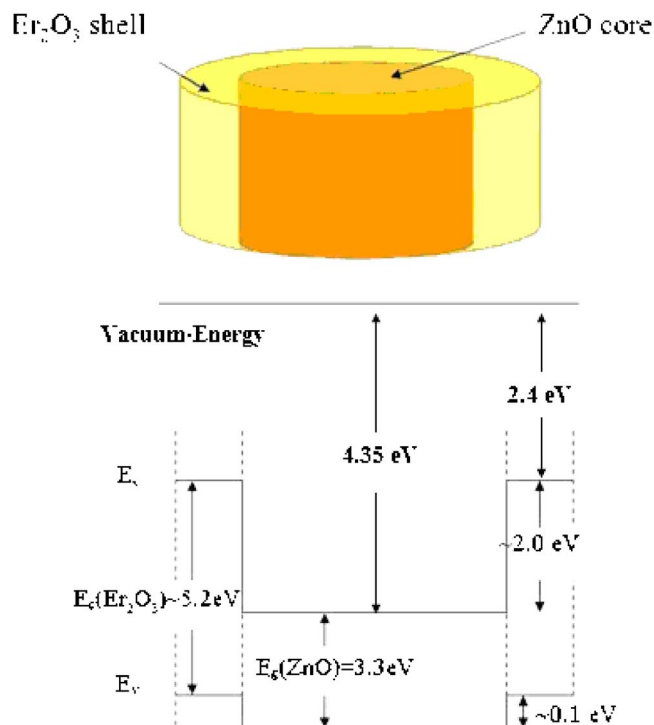


FIG. 5. (Color online) Schematic band diagram of ZnO/Er₂O₃ core-shell nanostructure.

In summary, a self-assembled ZnO nanorod array on silicon substrate has been fabricated by PLD in argon atmosphere. The ZnO nanorods were then coated with a layer of Er₂O₃ on the surface to form core-shell structures. PL mea-

surement indicated that the core-shell structures have enhanced UV emission compared to pure ZnO nanorods. The band diagram analysis shows that the ZnO/Er₂O₃ core shell has a type-II nanostructure, which confines the electrons in the ZnO core and thus results in an emission enhancement. Our experiment and results have shown that the optical properties of ZnO nanostructures can be enhanced by choosing suitable shell materials.

¹D. Appell, *Nature (London)* **419**, 553 (2002).

²X. F. Duan, Y. Huang, Y. Cui, J. F. Wang, and C. M. Lieber, *Nature (London)* **409**, 66 (2001).

³Y. Cui, Q. Wei, H. Park, and C. M. Lieber, *Science* **293**, 1289 (2001).

⁴G. Yi, C. Wang, and W. I. Park, *Semicond. Sci. Technol.* **20**, S22 (2005).

⁵L. Guo, J. X. Cheng, X.-Y. Li, Y. J. Yan, S. H. Yang, C. L. Yang, J. N. Wang, and W. K. Ge, *Mater. Sci. Eng., C* **16**, 123 (2001).

⁶T. Gao, Q. Li, and T. Wang, *Chem. Mater.* **17**, 887 (2005).

⁷C. Hsu, Y. Lin, S. Chang, T. Lin, S. Tsai, and I. Chen, *Chem. Phys. Lett.* **411**, 221 (2005).

⁸S. Choopun, H. Tabata, and T. Kawai, *J. Cryst. Growth* **274**, 167 (2005).

⁹O. Hayden, A. B. Greytak, and D. C. Bell, *Adv. Mater. (Weinheim, Ger.)* **17**, 701 (2005).

¹⁰K. Yu, B. Zaman, S. Romanova, D. Wang, and J. A. Ripmeester, *Small* **1**, 332 (2005).

¹¹R. L. Andersen, *Solid-State Electron.* **5**, 341 (1962).

¹²Y. I. Alivov, E. V. Kalinina, A. E. Cherenkov, D. C. Look, B. M. Ataev, A. K. Omaev, M. V. Chukichev, and D. M. Bagnall, *Appl. Phys. Lett.* **83**, 4719 (2003).

¹³S. Sugunan and K. B. Sherly, *React. Kinet. Catal. Lett.* **51**, 533 (2005).

¹⁴Y. Y. Zhu, R. Xu, S. Chen, Z. B. Fang, F. Xue, Y. L. Fan, X. J. Yang, and Z. M. Jiang, *Thin Solid Films* **508**, 86 (2006).

¹⁵J. Li, D. Zhao, X. Meng, Z. Zhang, J. Zhang, D. Shen, Y. Lu, and X. Fan, *J. Phys. Chem. B* **110**, 14685 (2006).

¹⁶Y.-Z. Yoo, Zheng-Wu Jin, T. Chikyow, T. Fukumura, M. Kawasaki, and H. Koinuma, *Appl. Phys. Lett.* **81**, 3798 (2002).