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<td><strong>Author(s)</strong></td>
<td>Li, Shaozhou; Gan, Chee Lip; Cai, Hui; Yuan, C. L.; Guo, Jun; Lee, Pooi See; Ma, Jan</td>
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Enhanced photoluminescence of ZnO/Er$_2$O$_3$ core-shell structure nanorods synthesized by pulsed laser deposition

S. Z. Li, C. L. Gan,$^{a}$ H. Cai, C. L. Yuan, J. Guo, P. S. Lee, and J. Ma

School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

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A narrow size distribution of ZnO nanorod array has been synthesized on silicon substrate by pulsed laser deposition (PLD) in argon ambient. ZnO/Er$_2$O$_3$ core-shell nanostructures were then formed through PLD of a thin Er$_2$O$_3$ layer onto the fabricated ZnO nanorod surface. Transmission electron microscopy analysis shows that both the ZnO core and Er$_2$O$_3$ 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, as well as biosensors in life-science applications. 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. Moreover, ZnO is a biosafe and biocompatible material which may be used in biomedical applications without additional coating. Besides fabrication of ZnO nanostructures, engineering of ZnO properties through surface modification is another important aspect in creating optoelectronic devices. ZnO nanorod/CdS nanoparticle composites and ZnO/ZnGa$_2$O$_4$ core-shell nanostructures have been synthesized, and modification of their optical properties was reported. However, a study on ZnO/Er$_2$O$_3$ core-shell nanostructure has not yet been reported. This structure is attractive because Er$_2$O$_3$, 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/Er$_2$O$_3$ 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. After postgrowth annealing in air for 30 min at 350 °C, an approximately 10-nm-thick Er$_2$O$_3$ layer was then deposited on the nanorod array surface by PLD in argon atmosphere (10 mTorr) at room temperature. 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 (diameter 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.
Figure 2 shows the XRD patterns of pure ZnO and Er$_2$O$_3$-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/Er$_2$O$_3$ indicates that the Er$_2$O$_3$ was crystalline after annealing. However, this may be due to either the Er$_2$O$_3$ layer coated on the ZnO nanorod surface was crystalline or a crystalline Er$_2$O$_3$ layer that had formed simultaneously on the silicon substrate during the deposition of the Er$_2$O$_3$ 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 Er$_2$O$_3$ shell around the 50-nm-thick ZnO core. Selected area diffraction pattern shown in Fig. 3(b) confirms the compositions, with both ZnO and Er$_2$O$_3$ 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 Er$_2$O$_3$ is crystalline (space group IA 3-) after annealing. Due to the polycrystalline structure of Er$_2$O$_3$, no Moiré pattern was observed in the electron microscopy.

Photoluminescences (PLs) of the ZnO nanorod array before and after deposition of the Er$_2$O$_3$ shell were measured at room temperature to investigate the optical properties of this core-shell nanorod structure (Fig. 4). The ZnO nanorod array with Er$_2$O$_3$ 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/Er$_2$O$_3$ 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. The electron affinity of ZnO is 4.35 eV (Ref. 12) and that of Er$_2$O$_3$ is estimated about 2.4 eV. The energies of both the conduction and valence bands of Er$_2$O$_3$ (shell) are higher than those of ZnO (core). 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 structure 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/Er$_2$O$_3$ interfaces during the annealing step, leading to the formation of localized band edge state due to structural relaxation and charge exchange.

Figure 2. (Color online) XRD patterns of ZnO and ZnO/Er$_2$O$_3$ nanostructures grown on silicon substrates.

Figure 3. (Color online) (a) TEM image of ZnO/Er$_2$O$_3$ core-shell structure, (b) selected area diffraction pattern of ZnO/Er$_2$O$_3$ 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.

Figure 4. (Color online) Photoluminescence spectra of the ZnO nanorods array and ZnO/Er$_2$O$_3$ core-shell nanostructures.
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 Er$_2$O$_3$ on the surface to form core-shell structures. PL measurement indicated that the core-shell structures have enhanced UV emission compared to pure ZnO nanorods. The band diagram analysis shows that the ZnO/Er$_2$O$_3$ 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.