

Formation of Well-Aligned ZnGa₂O₄ Nanowires from Ga₂O₃/ZnO Core–Shell Nanowires via a Ga₂O₃/ZnGa₂O₄ Epitaxial Relationship

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Formation of well-aligned and single-crystalline ZnGa₂O₄ nanowires on sapphire (0001) substrates has been achieved via annealing of the Ga₂O₃/ZnO core–shell nanowires. Ga₂O₃/ZnO core–shell nanowires were prepared using a two-step method. The thickness of the original ZnO shell and the thermal budget of the annealing process play crucial roles for preparing single-crystalline ZnGa₂O₄ nanowires. Structural analyses of the annealed nanowires reveal the existence of an epitaxial relationship between ZnGa₂O₄ and Ga₂O₃ phases during the solid-state reaction. A strong CL emission band centered at 360 nm and a small tail at 680 nm are obtained at room temperature from the single-crystalline ZnGa₂O₄ nanowires.

Introduction

Given its good cathode luminescence (CL) characteristics at low voltages and stability in high vacuum in comparison with sulfide-based phosphors, ZnGa₂O₄ has attracted considerable attention for use as a blue phosphor in flat-panel displays in the past decade.^{1–8} ZnGa₂O₄ exhibits a spinel structure, in which Zn²⁺ and Ga³⁺ ions occupy the tetrahedrally and octahedrally coordinated sites, respectively.⁹ The origin of a self-activated blue emission band around 430 nm has been reported to correspond to an octahedrally coordinated Ga–O group.^{10,11} Green and red emissions have also been demonstrated in ZnGa₂O₄/Cr and ZnGa₂O₄/Mn phosphors, respectively.^{3,12,13} In addition, with a band gap of 4.4 eV, ZnGa₂O₄ is a promising transparent-conducting-oxide material as well.^{14–16} Recently, the synthesis of one-dimensional (1D) nanostructures has been of growing interest owing to their contributions to the understanding of fundamental concepts and their promising applications in nanoscale devices.¹⁷ Synthesis of ZnGa₂O₄ nanowires using a vapor–liquid–solid method has been reported recently.¹⁸ We have demonstrated syntheses of well-aligned Ga₂O₃ nanowires and ZnO nanorods using the vapor–liquid–solid (VLS) method and catalyst-free chemical vapor deposition (CVD) method, respectively.^{19,20} In the present work, Ga₂O₃/ZnO core–shell nanowires were prepared using a two-step method, and then a solid-state reaction was conducted to synthesize the ZnGa₂O₄ nanowires. Ga₂O₃/ZnGa₂O₄ core–shell nanowires, single-crystalline ZnGa₂O₄ nanowires, and ZnGa₂O₄ nanowires inlaid with ZnO nanocrystals were formed via annealing of Ga₂O₃/ZnO core–shell nanowires with various ZnO shell thicknesses at 1000 °C. Structural analyses reveal an epitaxial relationship existing between ZnGa₂O₄ and Ga₂O₃ phases during the solid-state reaction for the formation of the ZnGa₂O₄ nanowires. The room-temperature CL characteristics of the ZnGa₂O₄ nanowires are also demonstrated here.

Experimental Section

Ga₂O₃/ZnO core–shell nanowires were prepared using a two-step method, and then a solid-state reaction was conducted to

synthesize the ZnGa₂O₄ nanowires. Briefly, well-aligned β -Ga₂O₃ nanowires were synthesized on Au-precoated sapphire (0001) substrates via the VLS method, as described in detail elsewhere.¹⁹ Deposition of the conformal ZnO shell onto the surfaces of the as-synthesized Ga₂O₃ nanowires was conducted using metal organic CVD. Zinc metal organic precursor, zinc acetylacetonate hydrate (Zn(C₅H₇O₂)₂·xH₂O, Lancaster, 98%), placed on a Pyrex glass container was loaded into the low-temperature zone of the furnace, which was controlled to be at 100 °C to vaporize the solid reactant. The vapor was carried by a 200-sccm O₂ flow into the high-temperature zone of the furnace in which substrates were located. In this study, the ZnO shells were formed under a temperature of 400 °C and a pressure of 5 Torr for various deposition times of 10, 15, and 20 min. Ga₂O₃/ZnGa₂O₄ core–shell nanowires, single-crystalline ZnGa₂O₄ nanowires, and ZnGa₂O₄ nanowires inlaid with ZnO nanocrystals were formed via the annealing of Ga₂O₃/ZnO core–shell nanowires with various ZnO shell thicknesses under 200-sccm O₂ flow at 1000 °C and 5 Torr for 1 h.

The morphology of the as-deposited material was examined using scanning electron microscopy (FE-SEM, JEOL JSM-7000F). The crystal structures of the nanowires were investigated using transmission electron microscopy (TEM, JEOL 2010 and JEOL 3010 operating at 200 kV). Spatial-resolved energy-dispersive X-ray spectroscopy (EDS) analyses were also performed using scanning transmission electron microscopy (FEG-TEM, FEI Tecnai). Optical properties of the as-deposited material were characterized by CL measurements on a SEM (FE-SEM, JEOL JSM-7000F) at room temperature. Samples were excited with an electron beam with an energy of 8 kV.

Results and Discussion

Ga₂O₃/ZnO core–shell nanowires were synthesized via a two-step process. Catalytic growth of well-aligned β -Ga₂O₃ nanowires was first performed on Au-precoated sapphire (0001) substrates using gallium acetylacetonate.¹⁹ The ZnO shells were then deposited on the well-aligned β -Ga₂O₃ nanowires using zinc acetylacetonate under O₂ flow at a temperature of 400 °C. Figure 1a shows the typical SEM image of the Ga₂O₃/ZnO core–shell nanowires. It reveals that the well-aligned feature is maintained after forming the core–shell structure. Figures

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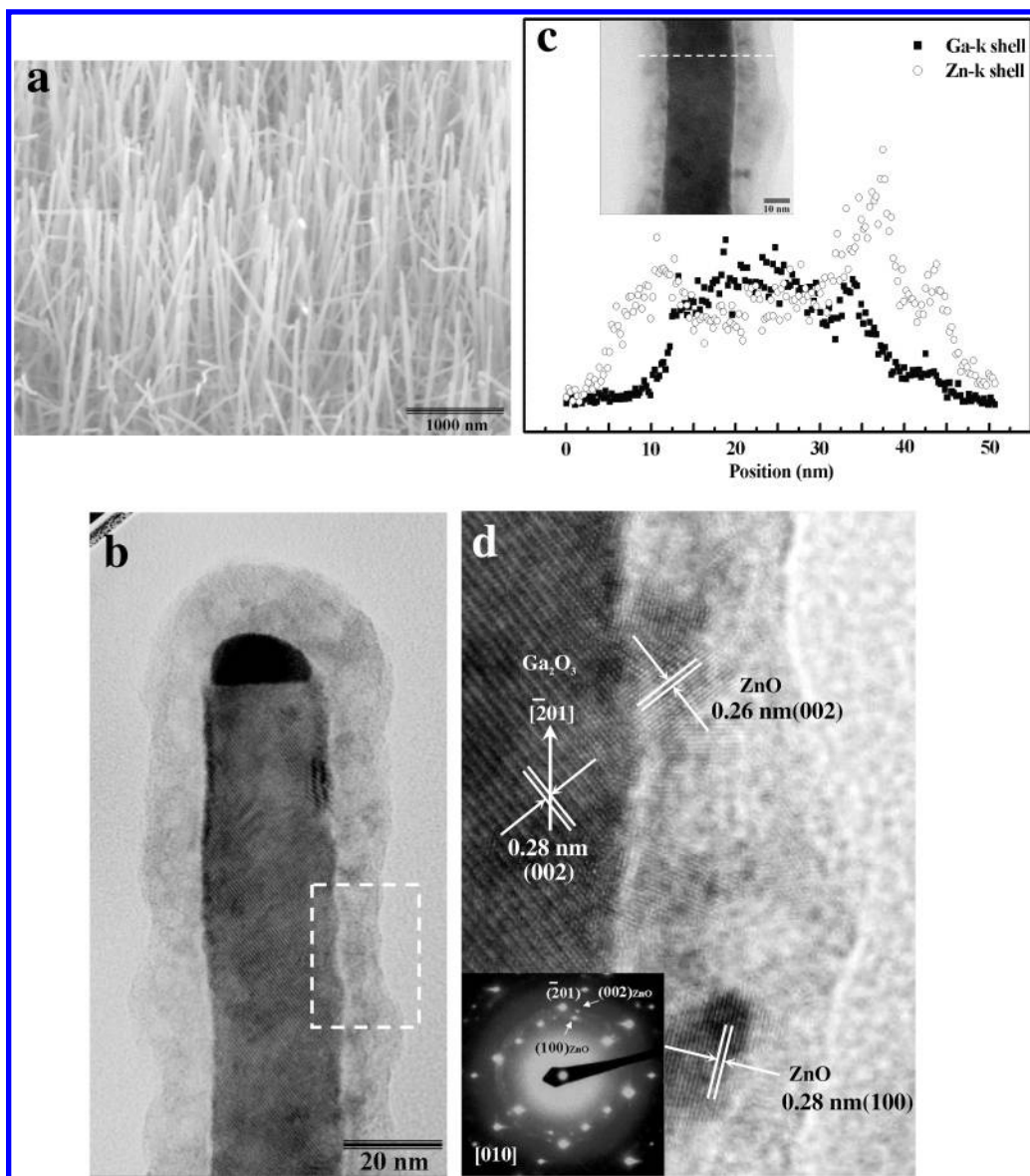


Figure 1. (a) SEM image of the Ga₂O₃/ZnO core-shell nanowires. (b) Low-magnification TEM image of an individual core-shell nanowire. (c) Line scanning Ga and Zn K-shell EDS spectra taken across an individual core-shell nanowire as illustrated in its inset. (d) HRTEM image and the corresponding electron diffraction pattern (inset) of the interfacial region of the core-shell nanowire.

1b–d show the TEM analyses of the Ga₂O₃/ZnO core-shell nanowires in which the ZnO shell were deposited for 15 min. In Figure 1b, a low-magnification TEM image of an individual nanowire reveals that a conformal sheath is formed on the surface of the nanowire. Compositional analysis of the core-shell nanowire was performed using energy-dispersive spectrometry (EDS) in the scanning transmission electron microscopy (STEM). Figure 1c shows the line scanning Ga and Zn K-shell EDS spectra taken across an individual core-shell nanowire as illustrated in its inset. A shell containing the Zn element was deposited on the Ga₂O₃ nanowire, confirming the formation of the core-shell nanowire structure using the two-step method. A high-resolution (HR) TEM image, Figure 1d, shows that the core possesses the single-crystal structure and the lattice spacing of around 0.28 nm corresponds to the *d* spacing of (002) crystal planes of monoclinic Ga₂O₃. Furthermore, it illustrates that nanocrystals embed in the amorphous matrix of the shell portion. The average grain size of the ZnO nanocrystals is around 2–10 nm. The corresponding selected-area electron diffraction (SAED) pattern is illustrated in the inset of Figure 1d. It shows a set of sharp diffraction spots and several

discrete diffraction rings that are ascribed to the single-crystalline Ga₂O₃ core and nanocrystalline ZnO shell, respectively.

The Ga₂O₃/ZnO core-shell nanowires were further annealed for the ZnGa₂O₄ nanowire formation. To obtain the stoichiometric ZnGa₂O₄ nanowire, the Ga₂O₃/ZnO core-shell nanowires with various shell thicknesses, which were prepared through ZnO shell deposition times of 10, 15, and 20 min, were annealed at 800 °C for 1 h. The glancing-angle-mode XRD patterns of the nanowires annealed at 800 °C are shown in Figure 2a. According to the XRD analyses, the cubic ZnGa₂O₄ phase is formed in all of the nanowires with various original Ga₂O₃/ZnO core-shell ratios after 800 °C annealing, which indicates the successful solid-state reaction of the core and shell along the radial direction. However, the Ga₂O₃ and/or ZnO phase still remained in the nanowires in the three cases. In addition to those of the ZnGa₂O₄, as shown in pattern I, the Ga₂O₃ diffraction peaks appear in the XRD pattern of those with original 10-min-grown ZnO shells. It suggests that the 10-min-grown ZnO shells are too thin to form uniform ZnGa₂O₄ nanowires, resulting in remaining the Ga₂O₃ cores within the annealed nanowires. On the contrary, pattern III shows the ZnO and ZnGa₂O₄

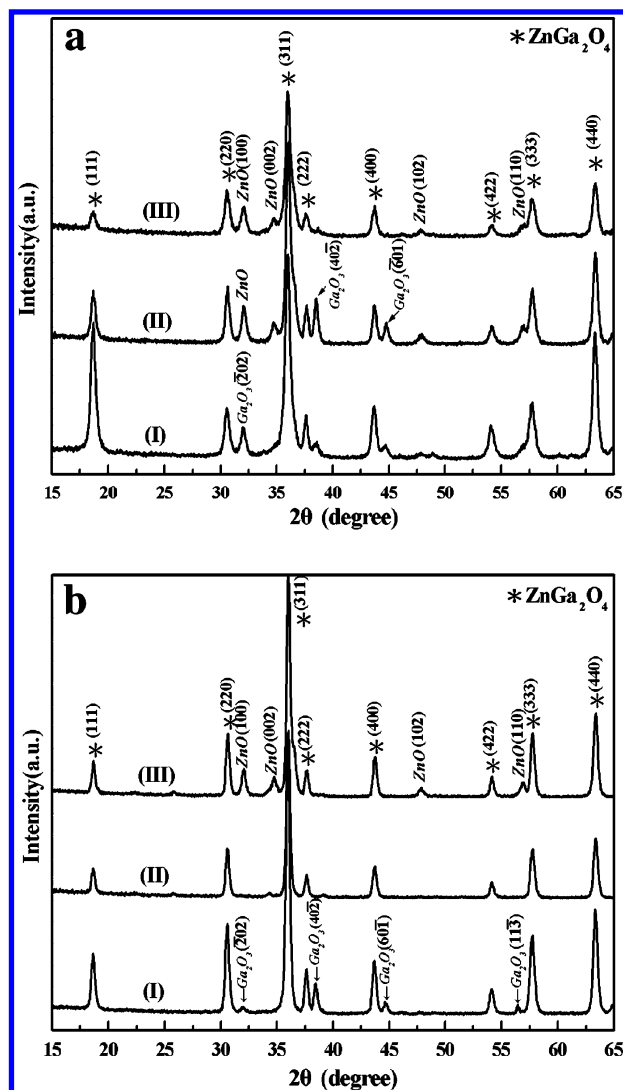


Figure 2. Glancing-angle-mode XRD patterns of the nanowires with various shell thickness annealed at (a) 800 °C and (b) 1000 °C. The original nanowires possess various ZnO shell thicknesses prepared through shell deposition times of 10 (pattern I), 15 (pattern II), and 20 min (pattern III).

structures coexisting in the nanowires with the original 20-min-grown ZnO shells, suggesting their ZnO shells are too thick to obtain single-phase ZnGa₂O₄ nanowires. In the case of the 15-min-grown ZnO shell, ZnO, ZnGa₂O₄, and Ga₂O₃ structures all exist in the nanowires after 800 °C annealing for 1 h, as shown in pattern II. It implies that the thermal budget of the annealing process, i.e., at 800 °C for 1 h, is not enough to complete the solid-state diffusion along the radial direction for the Ga₂O₃/ZnO core–shell nanowires with the original 15-min-grown ZnO shells.

To increase the thermal budget of the annealing process, the annealing of the Ga₂O₃/ZnO core–shell nanowires was conducted at a temperature of 1000 °C for 1 h. Figure 2b shows the glancing-angle-mode XRD patterns of the annealed nanowires. In the cases of the 10- and 20-min-grown ZnO shells, the same as the 800 °C annealing process, the diffraction peaks of ZnGa₂O₄ as well as Ga₂O₃ and ZnO structures are present in the XRD patterns of the annealed nanowires as illustrated in patterns I and III, respectively, due to an inappropriate ZnO/Ga₂O₃ ratio in the original core–shell nanowires. However, only diffraction peaks of the ZnGa₂O₄ phase appear in pattern II, indicating the successful formation of the single-phase ZnGa₂O₄

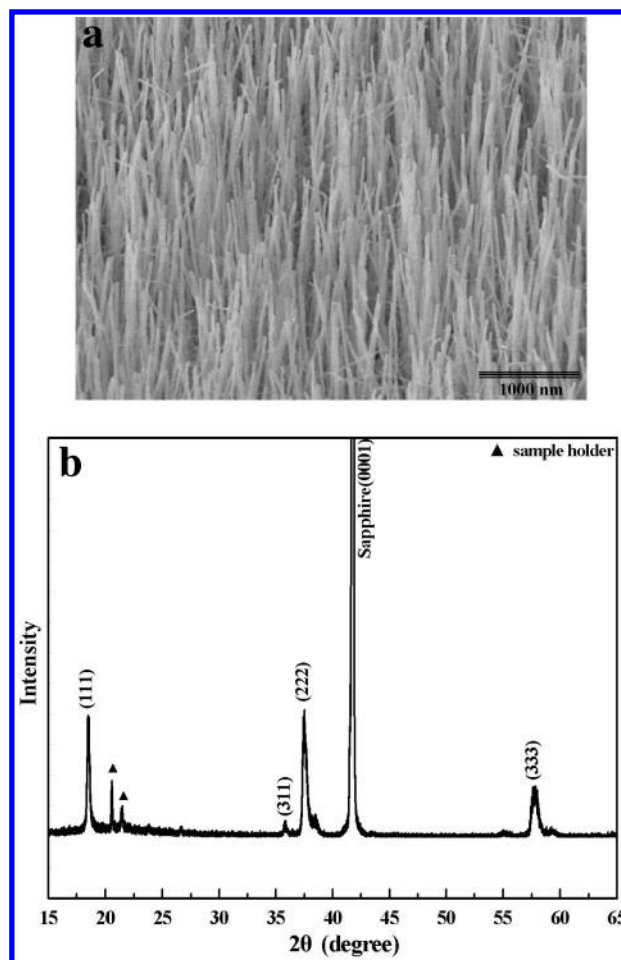


Figure 3. (a) SEM image of the single-phase ZnGa₂O₄ nanowires. (b) Powder-diffraction-mode XRD pattern of the ZnGa₂O₄ nanowires.

after annealing of the Ga₂O₃/ZnO core–shell nanowires with 15-min-grown ZnO shells. Figure 3a shows the SEM image of the single-phase ZnGa₂O₄ nanowires formed by annealing the Ga₂O₃/ZnO core–shell nanowires. It illustrates that the nanowires still possess the well-aligned feature after 1000 °C annealing. A powder-diffraction-mode XRD pattern of the ZnGa₂O₄ nanowires, as shown in Figure 3b, was further taken for examining the well-aligned characteristic of the ZnGa₂O₄ nanowires. Apart from the diffraction peaks attributed to the sapphire substrate and the sample holder for XRD analyses, the other peaks appearing here correspond to the diffraction peaks of the ZnGa₂O₄ crystal. In comparison with the ZnGa₂O₄ power diffraction, Joint Committee on Powder Diffraction Standards Card No. 86-0413, the XRD pattern in Figure 3b indeed reveals the (111) preferential orientation of the ZnGa₂O₄ nanowires.

TEM analyses of the annealed nanowires shown in Figure 2b are further carried out to investigate the formation mechanism of the ZnGa₂O₄ nanowires from 1D core–shell nanostructures. Figures 4a–e show the TEM analyses of the nanowire formed via annealing the Ga₂O₃ core/10-min-grown ZnO shell nanowire at 1000 °C for 1 h. A typical bright-field image of an individual nanowire reveals that the core–shell 1D nanostructure is preserved, as shown in Figure 4a. Nevertheless, the corresponding dark-field image illustrated in Figure 4b indicates that instead of nanocrystals embedding in the amorphous matrix before annealing a single-crystal structure is formed in the shell portion of the annealed nanowire after being treated at 1000 °C for 1 h. Figure 4c shows the line scanning Ga and Zn K-shell EDS spectra taken across an individual core–shell nanowire as

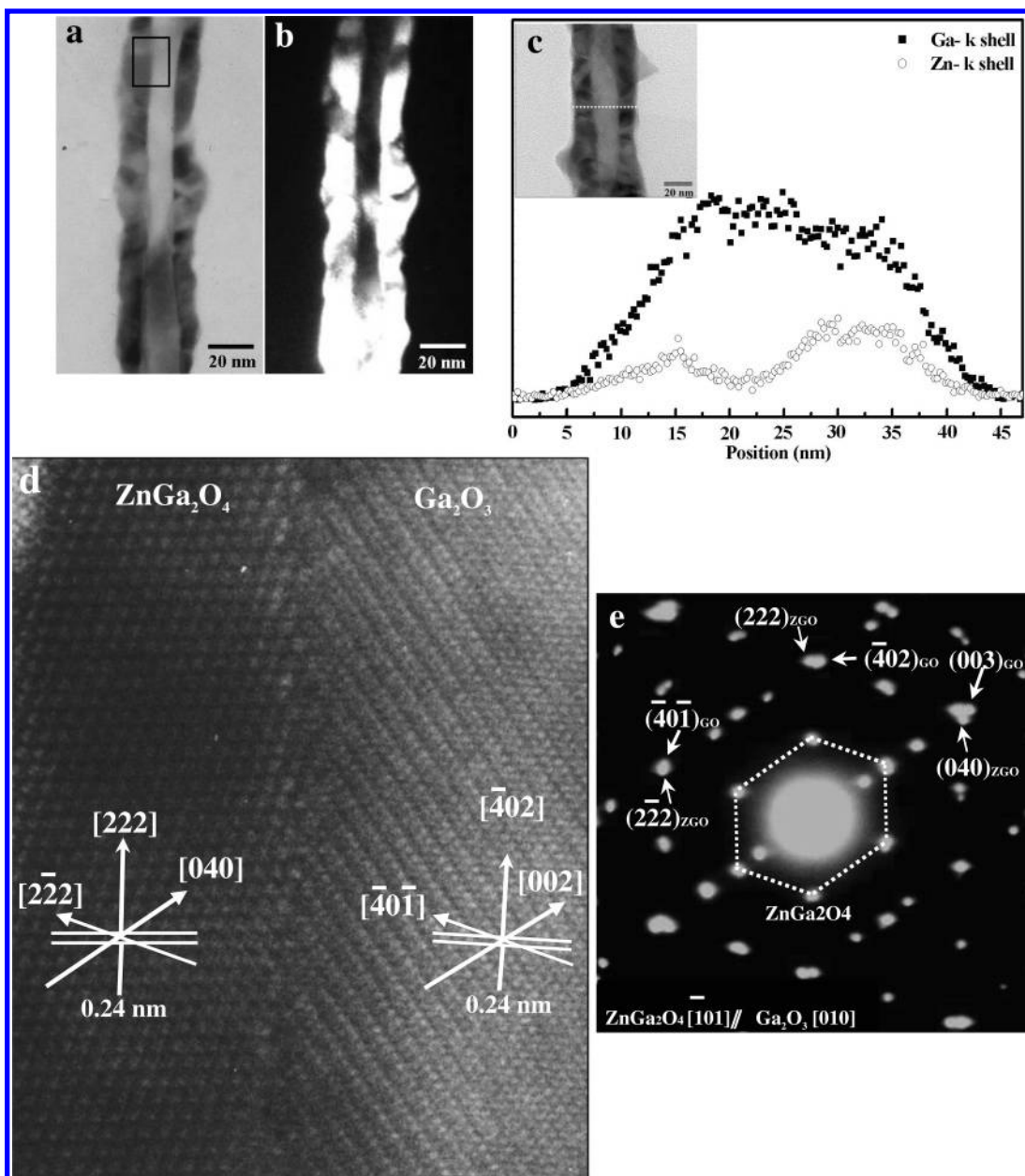


Figure 4. (a) Typical bright-field and (b) dark-field image of an individual nanowire formed via annealing the Ga₂O₃ core/10-min-grown ZnO shell nanowire at 1000 °C for 1 h. (c) Line scanning Ga and Zn K-shell EDS spectra taken across an individual annealed core-shell nanowire as illustrated in its inset. (d) HRTEM image of the interfacial region of the annealed core-shell 1D nanostructure. (e) Corresponding diffraction pattern of the annealed core-shell nanowire.

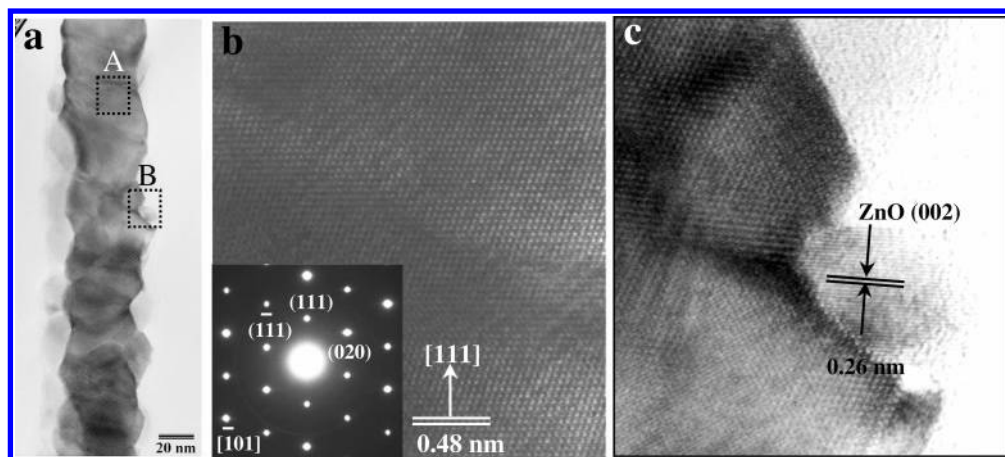


Figure 5. (a) Low-magnification TEM image of the nanowire formed via annealing the Ga₂O₃ core/20-min-grown ZnO shell nanowire at 1000 °C for 1 h. (b) HRTEM image and the corresponding SAED pattern of the core portion of the nanowire (region A in part a). (c) HRTEM image of the surface region of the nanowire (region B in part a).

illustrated in its inset. It reveals that the shell region is composed of both Zn and Ga elements whereas Ga is the major metallic element in the core region. Figure 4d shows the HRTEM image of the interfacial region of the core-shell 1D nanostructure, as denoted in Figure 4a. Crystalline structures of both the shell and the core are demonstrated in this HR image. The parallel fringes with spacings of 0.24 nm along the longitudinal axis direction of the nanowire are observed in both regions. The corresponding diffraction pattern, as shown in Figure 4e, indicates two sets of single-crystalline diffraction dots with an epitaxial relationship. According to the EDS result in Figure 4c, the diffraction patterns are assigned to be ascribed to the ZnGa_2O_4 shell and Ga_2O_3 core. With the zone axis of $[\bar{1}01]$ and $[010]$ for ZnGa_2O_4 and Ga_2O_3 , respectively, the epitaxial relationship of the ZnGa_2O_4 shell and Ga_2O_3 core is identified: The $[111]$ of the ZnGa_2O_4 shell aligns with the $[\bar{2}01]$ direction of the Ga_2O_3 core, and the $[040]$ of the ZnGa_2O_4 shell aligns with the $[003]$ direction of the Ga_2O_3 core. To the best of our knowledge, this is the first time that the existence of an epitaxial relationship of the ZnGa_2O_4 and Ga_2O_3 structures for the formation of the ZnGa_2O_4 crystals has been demonstrated during a solid-state reaction of Ga_2O_3 and ZnO phases.

Figures 5a–c illustrate the TEM images of the nanowire formed via annealing the Ga_2O_3 core/20-min-grown ZnO shell nanowire at 1000 °C for 1 h. A low-magnification TEM image reveals that the nanowire became twisted and was inlaid with nanocrystals on the surface, as shown in Figure 5a. The HRTEM image of the core portion of the nanowire (region A in Figure 5a) is shown in Figure 5b. It reveals that the core possesses the single-crystal structure and the lattice spacing of around 0.48 nm corresponds to the d spacing of (111) crystal planes of cubic ZnGa_2O_4 . The corresponding SAED pattern is illustrated in the inset of Figure 5b. In the surface region (B in Figure 5a), as shown in Figure 5c, the HRTEM image illustrates the inlaid nanocrystal possesses the ZnO structure, confirming the XRD analysis that the coexistence of the ZnGa_2O_4 and ZnO phases of the annealed nanowires, as shown in pattern III of Figure 2b.

In the case of the Ga_2O_3 core/15-min-grown ZnO shell nanowire, the slightly twisted nanowires with clear surfaces were formed after 1000 °C annealing for 1 h, as shown in Figure 6a. There is no nanocrystal inlaid on the surfaces of the annealed nanowires. The HRTEM image of the nanowire (denoted in Figure 6a) is shown in Figure 6b. It reveals that the nanowire possesses the single-crystal structure and the lattice spacing of around 0.48 nm along the longitudinal axis direction corresponds to the d spacing of (111) crystal planes of cubic ZnGa_2O_4 , confirming the XRD analysis of the formation of the (111) preferentially orientated ZnGa_2O_4 nanowires. The corresponding SAED pattern is illustrated in the inset of Figure 6b.

The phase diagram of the bulk $\text{Ga}_2\text{O}_3/\text{ZnO}$ system shows that ZnGa_2O_4 forms above 400 °C when the molar ratio of $\text{Ga}_2\text{O}_3/\text{ZnO}$ is unity.²¹ A solid-state reaction of Ga_2O_3 and ZnO at high temperatures has been employed to prepare ZnGa_2O_4 .^{4,6,11,14,22} On the basis of the XRD and TEM analyses in this study, the $\text{Ga}_2\text{O}_3/\text{ZnGa}_2\text{O}_4$ core-shell nanowires, the single-crystalline ZnGa_2O_4 nanowires, and the ZnGa_2O_4 nanowires inlaid with ZnO nanocrystals were obtained via annealing the $\text{Ga}_2\text{O}_3/\text{ZnO}$ core-shell nanowires with various ZnO shell thicknesses. It demonstrates that the formation of single-crystalline ZnGa_2O_4 nanowires has been achieved through the solid-state reaction of the $\text{Ga}_2\text{O}_3/\text{ZnO}$ core-shell nanowires along the radial direction. The thickness of the original ZnO shell and the thermal budget of the annealing process play crucial roles for preparing

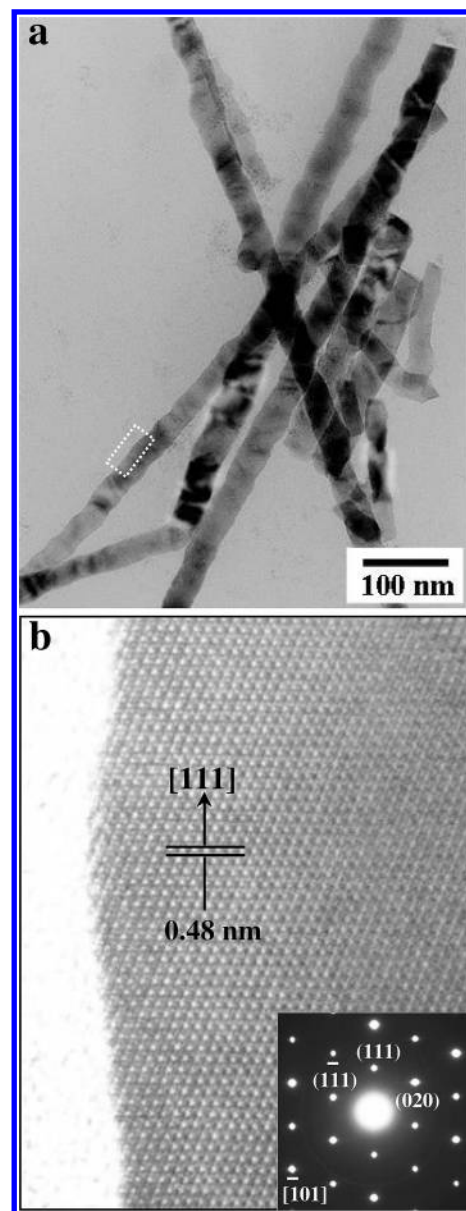


Figure 6. (a) Low-magnification TEM image of the nanowire formed via annealing the Ga_2O_3 core/15-min-grown ZnO shell nanowire. (b) HRTEM image and the corresponding SAED pattern of the nanowire (denoted in Figure 6a).

the single-crystalline ZnGa_2O_4 nanowires. Moreover, as shown in Figure 4, TEM analyses reveal that ZnGa_2O_4 and Ga_2O_3 phases exhibit an epitaxial relationship during the solid-state reaction.

Figure 7 shows the room-temperature CL spectra of the single-crystalline ZnGa_2O_4 nanowires. In contrast to the absence of any emission peak in the spectrum of the as-grown $\text{Ga}_2\text{O}_3/\text{ZnO}$ core-shell nanowires, a strong emission band centered at 360 nm and a small tail at 680 nm appear in the CL spectrum of the single-crystalline ZnGa_2O_4 nanowires. The emission peaks at 360 and 680 nm have been observed from the ZnGa_2O_4 after being annealed in a reducing atmosphere.²³ Formation of single oxygen vacancies after annealing in a reducing atmosphere has been demonstrated to relate to those emissions.²³ In this study, although the single-crystalline ZnGa_2O_4 nanowires are formed via annealing of the $\text{Ga}_2\text{O}_3/\text{ZnO}_2$ core-shell nanowires in an oxidizing environment, the appearances of the peaks at 360 and 680 nm in the CL spectrum suggest the existence of the oxygen vacancies within the ZnGa_2O_4 nanowires. In contrast to the

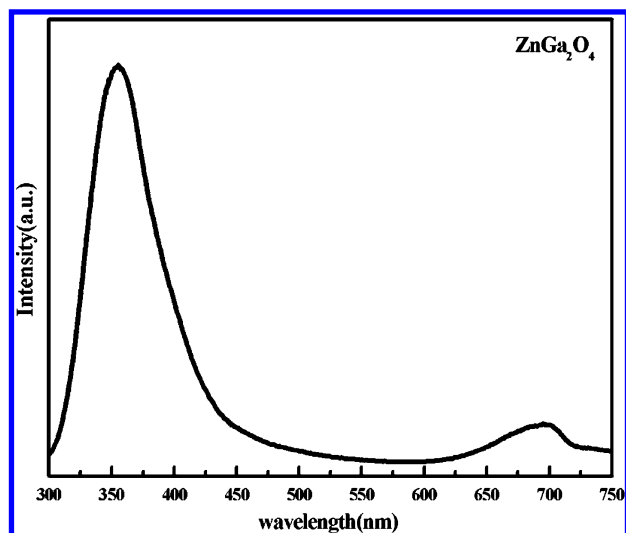


Figure 7. Room-temperature CL spectra of the single-crystalline ZnGa₂O₄ nanowires.

observation of a blue-shift UV emission from the original Ga₂O₃ nanowires,¹⁹ a blue shift is insignificant in the CL spectrum of the ZnGa₂O₄ nanowires compared with that of the ZnGa₂O₄ phosphors.²³ A blue-shift emission as a result of size reduction is mainly ascribed to a quantum confinement effect when the size of the crystal is smaller than its Bohr radius.²⁴ The absence of blue-shift emission in this study suggests that the diameter of the ZnGa₂O₄ nanowires is not small enough.

Conclusions

Well-aligned and single-crystalline ZnGa₂O₄ nanowires have been formed on sapphire (0001) substrates via annealing of Ga₂O₃/ZnO core-shell nanowires. Ga₂O₃/ZnO core-shell nanowires were prepared using a two-step method. Ga₂O₃/ZnGa₂O₄ core-shell nanowires, single-crystalline ZnGa₂O₄ nanowires, and ZnGa₂O₄ nanowires inlaid with ZnO nanocrystals were formed via annealing of Ga₂O₃/ZnO core-shell nanowires with various ZnO shell thicknesses at 1000 °C. The thickness of the original ZnO shell and the thermal budget of the annealing process play crucial roles for preparing the single-crystalline ZnGa₂O₄ nanowires. Furthermore, an epitaxial relationship between ZnGa₂O₄ and Ga₂O₃ phases during the solid-state reaction for the formation of the ZnGa₂O₄ nanowires was observed from TEM analyses. CL emission peaks centered at 360 nm 680 nm are obtained at room temperature from the

single-crystalline ZnGa₂O₄ nanowires, suggesting the existence of the oxygen vacancies within them.

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