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Annealing behavior of TiO_2-sheathed Ga_2O_3 nanowires

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Abstract TiO_2-sheathed Ga_2O_3 one-dimensional (1D) nanostructures were synthesized by thermal evaporation of GaN powders and then sputter-deposition of TiO_2. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) analysis results indicate that the Ga_2O_3 cores are of a single crystal nature with a monoclinic structure while the TiO_2 shells are amorphous. Photoluminescence (PL) emission is slightly decreased in intensity by TiO_2 coating, but it is significantly increased by thermal annealing in an oxygen atmosphere. The emission peak is also shifted from ~500 to ~550 nm by oxygen annealing. The increase in the green emission is due to the increase in the concentration of the Ga vacancies in the cores by the inflow of oxygen during oxygen annealing. On the other hand, annealing in a nitrogen atmosphere leads to a red shift of the emission to ~700 nm originating from nitrogen doping.

1 Introduction

In recent years, extensive research into coaxial one-dimensional (1D) nanostructures consisting of different materials in the radial direction has been carried out due to their potential applications in electronic and optoelectronic device applications. The coaxial 1D nanostructures can realize various tailor-made functions by fabricating heterojunction nanodevices or depositing multilayers with different chemical compositions in the radial direction as well as can protect them from oxidation or contamination [1]. Much more work has been done for the latter purpose in the synthesis of the radial heterostructures by coating the semiconductor cores with oxide materials. Here in this work we will focus on the former purpose, i.e. Ga_2O_3-core/TiO_2-shell coaxial 1D nanostructures are investigated to give an insight in tailoring the optical properties of Ga_2O_3 nanowires.

β-Ga_2O_3 is a wide band-gap semiconductor ($E_g \approx 4.9$ eV) with a monoclinic structure [1]. This material has potential applications in high temperature gas sensors as well as optoelectronic devices owing to its conductive and luminescence properties [2]. Various forms of 1D β-Ga_2O_3 nanostructures have been synthesized by using various methods such as direct current (dc) arc discharge of GaN powders with catalyst [3], thermal evaporation of Ga powders [4], thermal annealing of GaN powders [5], thermal annealing of GaAs in an oxygen atmosphere [6], thermal reaction of Ga_2O_3 powders with graphite of active carbon/carbon-nanotubes [4], silica-assisted Fe catalytic growth [7], metal organic chemical vapor deposition [8], etc. In this work we chose the thermal evaporation technique of GaN powders for synthesis of Ga_2O_3 nanowires since it is the easiest and offers nanowires with a relatively good quality.

Various techniques have been reported to be used to form shell layers on the 1D nanowire cores. These techniques include sol–gel process, thermal heating, solution-based method, and chemical vapor deposition (CVD) [9–14]. In this work, we used a RF magnetron sputtering technique to form TiO_2 shells on Ga_2O_3 cores. Sputtering is generally known to offer thickness uniformity worse than CVD, although the sputtering process is much simpler than that of CVD process. Nevertheless, we found that the thickness uniformity of the TiO_2 shell layers formed on the Ga_2O_3 cores by sputtering was much better than we anticipated.

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2 Experimental

First, gold (Au)-coated Al_2O_3 were used as substrates for synthesis of 1D Ga_2O_3 structures. Au was deposited on the (0001) Al_2O_3 substrate by dc magnetron sputtering. A quartz tube was mounted horizontally inside a tube furnace. The 99.99% pure GaN powders were placed on the lower holder at the center of the quartz tube. The Au-coated Al_2O_3 substrate was placed on the upper holder about 5 mm apart from the GaN powders. The furnace was heated up to 1050°C and maintained at the temperature for 1 h in N_2/3 mol% O_2 atmosphere with constant flow rates of oxygen (O_2) (15 standard cubic centimeter per min (sccm)) and N_2 (485 sccm). The total pressure was set to 1.5 Torr. Secondly, the substrates were transferred to a radio frequency (RF) magnetron sputtering system for TiO_2 coating. The sputtering was performed at room temperature for 12 min using a 99.95% TiO_2 target. The sputtering process parameters for TiO_2 deposition used in the sputtering process are as follows: RF power = 100 W, base vacuum = 1.0×10^{-6} Torr, chamber pressure = 1.2×10^{-2} Torr, Ar gas flow rate = 30 sccm, and substrate temperature = room temperature. After TiO_2 coating, the products were annealed at 650°C for 30 min in an O_2 or nitrogen (N_2) atmosphere. The process parameters for the annealing were as follows: (O_2 annealing) O_2 flow rate = 500 sccm, base pressure: 2.5×10^{-2} Torr, and chamber pressure = 1.7 Torr; (N_2 annealing) N_2 flow rate = 500 sccm, base pressure: 2.5×10^{-2} Torr, and chamber pressure = 1.1 Torr.

The samples were then characterized using glancing angle (0.5°) XRD (X'pert MPD-Philips with Cu-K_α radiation), scanning electron microscopy (SEM, Hitachi S-4200), and TEM (Phillips CM-200). The high resolution TEM (HRTEM) images and the selected area electron diffraction (SAED) patterns were also taken on the same systems. A PL measurements were performed at room temperature in a SPEC-1403 PL spectrometer with a He-Cd laser line of 325 nm as the excitation source (Kimon, 1K, Japan). The compositions across the diameter of the 1D coaxial nanostructure samples annealed in different atmospheres were investigated by using energy dispersive X-ray spectroscopy (EDS).

3 Results and discussion

Figure 1 shows the SEM image of the β-Ga_2O_3 1D nanostructures synthesized in this work. Most of the 1D nanostructures have a rod-like morphology but some have a belt-like morphology. The rod-like nanostructures are quite straight and very uniform in diameter. Most nanowires have diameters of a few tens to a few hundreds of

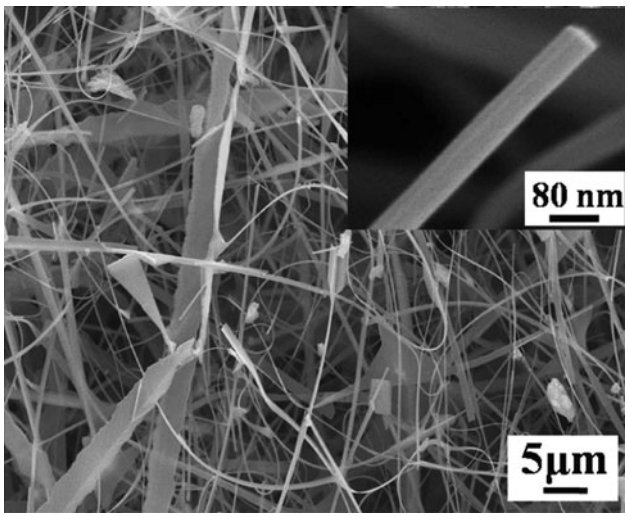

Fig. 1 SEM image of Ga_2O_3-core/TiO_2-shell nanowires synthesized by thermal evaporation of GaN powders on Au-coated the Al_2O_3 substrate

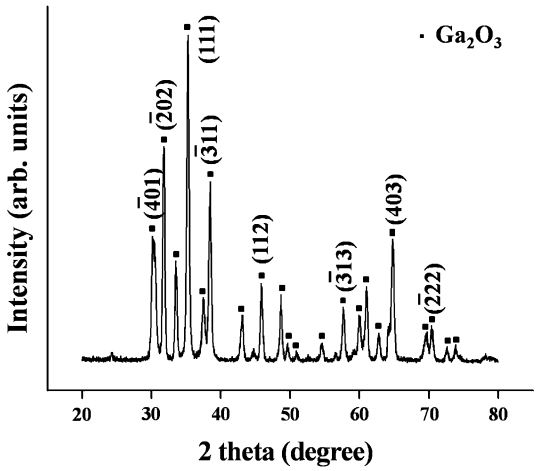

Fig. 2 XRD pattern of the Ga_2O_3-core/TiO_2-shell nanowires

nanometers as can be seen in a typical nanowire in the inset of Fig. 1 and lengths of a few micrometers. Most nanowires end up with round particles with diameters larger than those of other parts of the nanowires, which suggests that the growth mechanism of the nanomaterials can be regarded as a vapor liquid solid (VLS) mechanism. Figure 2 shows the XRD pattern of the nanowires. The main diffraction peaks in the pattern can be indexed to a monoclinic structure, in good agreement with the reported data of bulk β-Ga_2O_3 crystals (JCPDS card No. 43-1012, a = 12.23 Å, b = 3.04 Å, c = 5.80 Å, β = 103.7°) indicating that the nanomaterial is β-Ga_2O_3. In contrast, no appreciable diffraction peaks for a TiO_2 phase are observed, suggesting that as-sputtered TiO_2 is amorphous.

Figure 3a shows a low-magnification TEM image of a typical TiO_2-sheathed Ga_2O_3 nanowire, revealing that

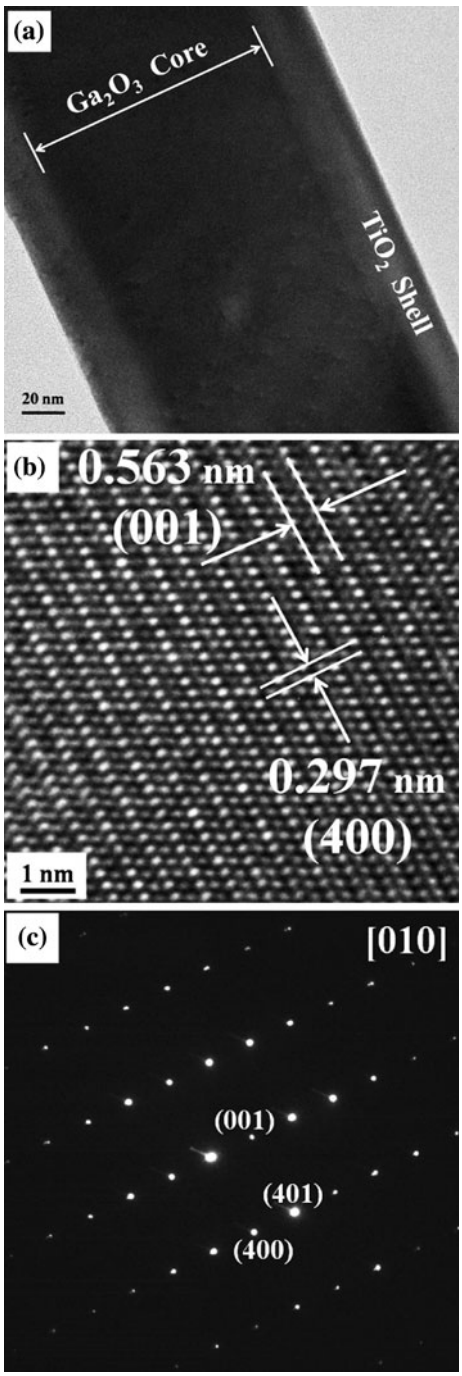

Fig. 3 **a** Low-magnification TEM image of a typical Ga_2O_3-core/TiO_2-shell nanowire. **b** Local HRTEM image of the nanostructure at the core–shell interface region. **c** SAED pattern of the [010] zone axis of the nanomaterial at the same region as in (**b**)

indeed a core–shell structure with a shell thickness of ~25 nm, indicating that the thickness uniformity of the TiO_2 shell is quite good in spite that it was formed by sputter-deposition which is a typical physical vapor deposition technique. A local high resolution TEM (HRTEM) image enlarging the core–shell interface area of the nanowire is given in Fig. 3b. The interplanar spacings are about 0.563 and 0.297 nm corresponding to β-Ga_2O_3 (001) and (400) planes, respectively. The associated selected area of electron diffraction (SAED) pattern (Fig. 3c), recorded perpendicular to the long axis, can be indexed for the [010] zone axis of β-Ga_2O_3. Not only the TEM image but also the SAED pattern indicate that the β-Ga_2O_3 core is monocrystalline. While the core of the sheathed nanowire structure is monocrystalline evidenced by the SAED pattern and clearly visible lattice fringes in the HRTEM image, the TiO_2 shell may be amorphous since no appreciable spotty pattern for crystalline TiO_2 is found in the SAED pattern.

Figure 4 displays the PL spectra, measured at room temperature, of the Ga_2O_3-core/TiO_2-shell nanowires annealed in different annealing atmospheres along with unannealed Ga_2O_3 nanowires (as-synthesized Ga_2O_3 nanowires) and Ga_2O_3-core/TiO_2-shell nanowires (TiO_2-sheathed Ga_2O_3 nanowires). The PL spectra of both the as-synthesized and TiO_2-sheathed Ga_2O_3 nanowires are characterized by an emission band centered at around 500 nm. This emission was reported to be associated with the vacancies in the Ga_2O_3 cores, such as gallium (Ga) vacancies, oxygen (O) vacancies [15] and Ga–O vacancy pairs [16]. Binet and Courier [17] reported that this emission could be produced by a tunnel recombination of an electron on a donor with a hole on an acceptor which could be either a Ga vacancy (V_{Ga}) or a charged Ga or O vacancy. Vacancies seem to be easily generated as the Ga_2O_3 nanowires were synthesized by thermal evaporation of GaN powders at a temperature as high as 1050°C in this work. The intensity of the PL emission of Ga_2O_3 nanowires has been slightly decreased by TiO_2 coating. This decrease in the emission intensity may be caused by absorption of

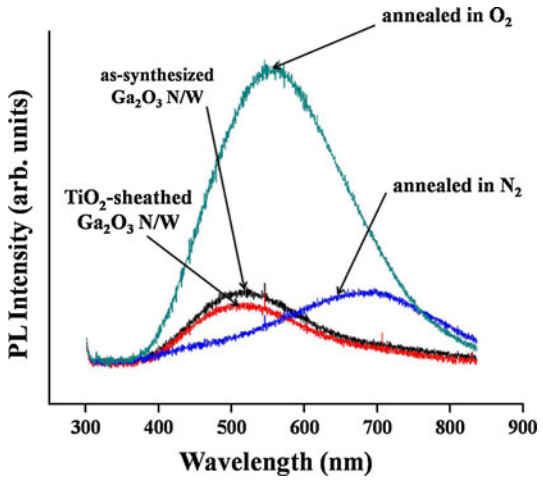

Fig. 4 Room temperature-PL spectra of the TiO_2-sheathed Ga_2O_3 1D nanostructures annealed at 650°C for 30 min in different atmospheres along with as-synthesized Ga_2O_3 and TiO_2-sheathed Ga_2O_3 1D nanostructures

the light, emitted from the Ga_2O_3 core, by the TiO_2 shell before it reaches our eyes since the TiO_2 shell layer is not so highly transparent.

On the other hand, the PL emission of the Ga_2O_3-core/TiO_2-shell nanowires is significantly enhanced and the emission peak is shifted from ~500 to ~550 nm by thermal annealing in an O_2 atmosphere. We performed EDXS analysis to investigate the origin of the PL enhancement and the red shift. Comparison of the EDXS concentration profile of the Ga_2O_3-core/TiO_2-shell nanowires annealed in an O_2 atmosphere (Fig. 5b) with that of the unannealed nanowires (Fig. 5a) reveals that the O concentration in the Ga_2O_3 core region respectively has significantly increased after O_2 annealing. The increase in the oxygen (O) concentration in the cores, in turn, leads to the increase in the concentrations of Ga vacancies resulting in enhancement in the green emission. It is well known that oxygen vacancies are formed in Ga_2O_3 under reduction growth conditions, forming an n-type semiconductor. Harwig. et al. [15] showed that samples annealed in a reduction atmosphere is in favor of formation of O vacancies and blue emission was enhanced, while samples heated in an O_2 atmosphere is in favor of formation of Ga vacancies, which shows a dominant green emission. Villora et al. [18] reported that with the decease of the O_2 partial pressure, the cathodoluminescence (CL) emission decreased in intensity, and shifted from green to blue. Our results are in good agreement with the previous reports in that the PL emission is increased in intensity and is shifted to the green region, i.e. the larger wavelength region by O_2 annealing.

On the other hand, the PL emission of the Ga_2O_3-core/TiO_2-shell nanowires annealed in an N_2 atmosphere is less enhanced. The PL emission enhancement by the N_2 annealing is also attributed to the increase in the O concentration in the core regions as can be clearly seen by comparison of Fig. 5c with a. However, the increase in the O concentration in the cores by N_2 annealing is less significant than that by O_2 annealing since a far smaller amount of oxygen is supplied by N_2 annealing than by O_2 annealing, resulting in the generation of a far smaller amount of O vacancies in the cores. One thing worth to note regarding the N_2 annealing is the red shift in the emission to ~700 nm. The red light shift may originate from the recombination of electrons trapped on acceptors due to the nitrogen dopants, presumably replacing oxygen atoms in the lattice. The N atoms for the *n*-type doping must be provided by the N_2 atmosphere during the thermal annealing process. A similar emission band centered at ~706 nm was recently reported by Kim et al. [19].

Figure 6a, b show that the SEM images of a typical ALD SnO_2-sheathed ZnSe nanowire and a typical CVD TiO_2-sheathed ZnS nanowire, respectively. As regards the shell layer thickness uniformity, comparison of the SEM image of a typical Ga_2O_3 nanowire sheathed with TiO_2 by sputtering (Fig. 3a) with those of a typical ALD SnO_2-sheathed ZnSe nanowire (Fig. 6a) and a typical CVD TiO_2-sheathed ZnS nanowire (Fig. 6b) clearly indicates that the shell layer of the former is as uniform as that of the typical ALD SnO_2-sheathed ZnSe nanowire and rather uniformer than that of the typical CVD TiO_2-sheathed ZnS nanowire.

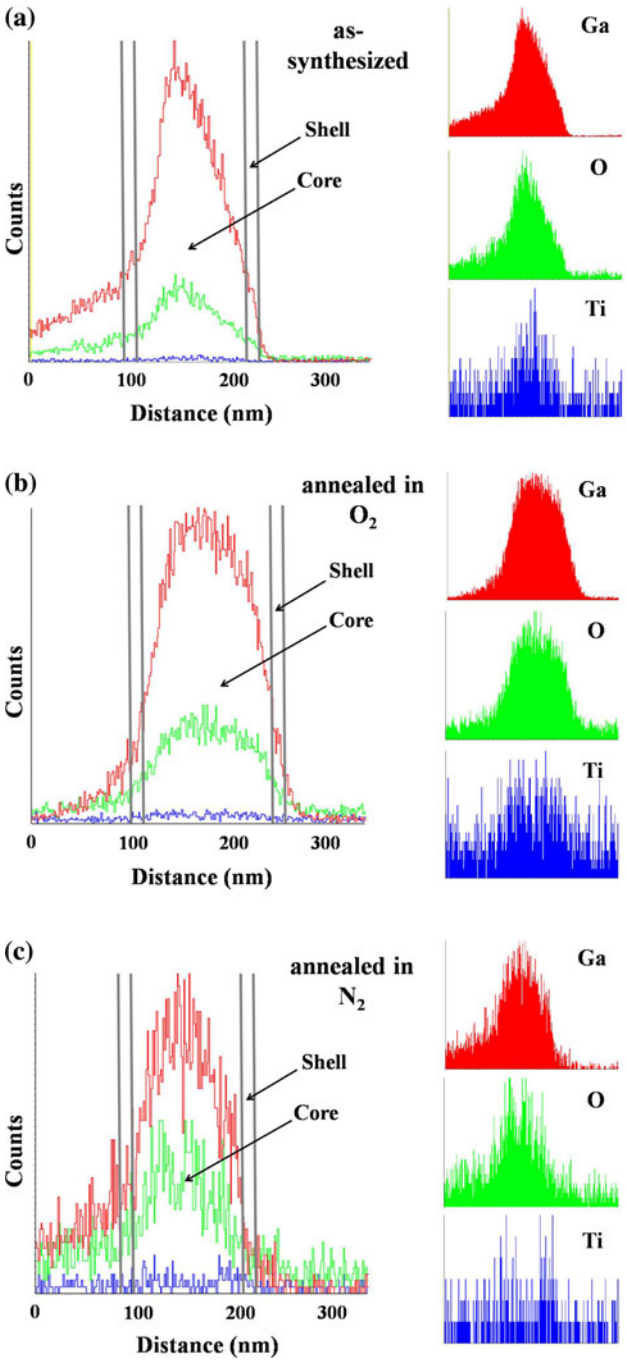

Fig. 5 EDX line scanning concentration profiles of the TiO_2-sheathed Ga_2O_3 1D nanostructures **a** as-synthesized (unannealed), **b** annealed in an O_2 atmosphere, and **c** annealed in an N_2 atmosphere

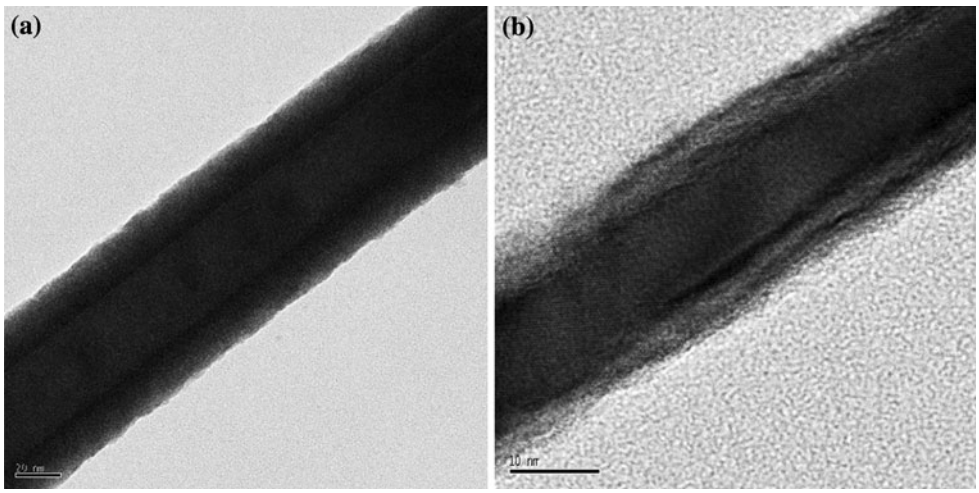

Fig. 6 Shell layer thickness uniformity of **a** a typical ALD-SnO_2 sheathed ZnSe nanowire and **b** a typical CVD-TiO_2 sheathed ZnS nanowire

The Ga_2O_3 nanowires can be quite uniformly coated with TiO_2 by sputtering as shown in Fig. 3a, since the synthesized Ga_2O_3 nanowires do not directly contact with the Au-coated Al_2O_3 substrate but stand freely in the space above the Au-coated Al_2O_3 substrate as shown in Fig. 1.

4 Conclusions

The Ga_2O_3-core/TiO_2-shell nanowires prepared by using thermal evaporation of GaN powders on Au-coated Al_2O_3 substrates and then RF-magnetron sputter-deposition of TiO_2 consist of the Ga_2O_3 cores of a single crystal nature with a monoclinic structure and the amorphous TiO_2 shells. Uniform coating of nanowires can be achieved by using a sputtering technique despite that sputtering is a typical physical vapor deposition deposition technique. The PL properties of Ga_2O_3 nanowires can be significantly increased by annealing in an O_2 atmosphere. The O concentration in the Ga_2O_3 core regions increases significantly during O_2 annealing. The increase in the O concentration in the cores, in turn, leads to an increase in the concentration of Ga vacancies, resulting in the enhancement in the green emission. On the other hand, annealing in a N_2 atmosphere leads to a red shift of the emission to $\sim$700 nm as well as a slight increase in the emission intensity. This red shift originates from the recombination of electrons trapped on acceptors due to the nitrogen dopants replacing oxygen atoms in the lattice. The results obtained in this work will give an insight in tailoring the optical properties of semiconductor nanostructures by means of coating and thermal annealing.

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