

Synthesis of blue-light-emitting ZnGa₂O₄ nanowires using chemical vapor deposition

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A high-density array of vertically aligned ZnGa₂O₄ nanowires has been synthesized on Si substrates *via* CVD of ZnO–Ga at 1000 °C consisting of a single-crystalline cubic spinel structure grown in a [111] direction and exhibiting strong photoluminescence and cathodoluminescence in the blue wavelength region.

Zinc gallate (ZnGa₂O₄) has attracted much attention in recent years, because it is one of the most promising luminescence oxide materials for blue emission.^{1–12} Room-temperature resistivity has been reported at an order of 30 mΩ cm for polycrystalline ZnGa₂O₄.¹ Therefore it can be used for applications in vacuum fluorescent display and field emission display as a low-voltage cathodoluminescence phosphore. With a band gap of 4.4–4.7 eV, ZnGa₂O₄ is potentially useful as a transparent conducting oxide, particularly when transparency through the violet to near UV region is desired. It can also act as an excellent host material for multicolor emitting phosphor layers; manganese-activated ZnGa₂O₄ (ZnGa₂O₄:Mn) for green emission and ZnGa₂O₄:Cr for red emission.^{3,5} A polycrystalline ZnGa₂O₄ thin film has been synthesized using various methods such as a solid-state reaction, sputtering, sol–gel processing, combustion, electrophoresis, and pulsed laser deposition.^{1–11} Nanocrystalline ZnGa₂O₄ has been synthesized by a hydrothermal reaction.¹² However, the synthesis of ZnGa₂O₄ nanowires has not yet been reported. As stimulated by the novel properties of carbon nanotubes, one-dimensional nanostructures are currently the subject of intense research because of the potential for nanoscale electronic and optoelectronic applications.^{13,14} Here we present the synthesis of cubic spinel-structured ZnGa₂O₄ nanowires *via* chemical vapor deposition (CVD). The ZnGa₂O₄ nanowires are highly pure and singly-crystalline, so they exhibit strong blue photoluminescence (PL) and cathodoluminescence (CL).

Synthesis of ZnGa₂O₄ nanowires has been carried out using a tube furnace. ZnO (99.99%, Aldrich) powders and Ga metal (99.9999%, Aldrich) were placed in a quartz boat located inside a quartz tube reactor. The Si substrates were coated with HAuCl₄·3H₂O (98+%, Sigma) ethanol solution, forming the Au catalytic nanoparticles. The substrate was positioned on the quartz boat containing the reactant source. The temperature of the reactor was maintained at 800–1000 °C for 1 h. Argon flowed at a rate of 500 sccm. Blue tinted white film deposited on the whole substrate. The as-grown materials were characterized and analyzed by scanning electron microscopy (SEM, Hitachi, S-4300), transmission electron microscopy (TEM, Jeol JEM-2010, 200 kV), electron diffraction (ED), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS, PHI 5800), X-ray diffraction (XRD, Philips X'PERT MPD), and Raman spectroscopy (Renishaw) using a 514.5 nm argon ion laser. The PL measurement was conducted at 8 K and room temperature, with a 325 nm line from a helium–cadmium (He–Cd) laser. The laser power was about 1 kW cm⁻². Room temperature CL (Gatan MonoCL2) measurements were performed at an acceleration voltage of 10 kV.

We synthesized the nanowires over the temperature range 800–1000 °C. At 800 °C the products are pure ZnO nanowires. As the temperature increases, nanowires with a new crystal phase, spinel ZnGa₂O₄, appear. Fig. 1(a) shows a SEM image of the vertically aligned nanowires grown on a large area of the Si

substrate at 1000 °C. The length is about 5 μm. A magnified SEM reveals that the nanowires have an unique sharp tip and a virtually square cross-section (Fig. 1(b)). Some of the adjacent nanowires are connected by bridges. The TEM image shows that the nanowires are straight and that the diameter is uniformly 80 nm (Fig. 1(c)). A high-resolution TEM image for a nanowire whose tip is sharp and diameter is 80 nm is shown in Fig. 1(d). The surface is slightly bumpy. The selected-area ED (SAED) pattern shows that the nanowire consists of a singly-crystalline cubic ZnGa₂O₄ crystal with a [111] direction parallel to the long axis (inset). No amorphous phase or outer layers exist. An atom-resolved image reveals the cubic structure of the ZnGa₂O₄ nanowire (Fig. 1(e)). The (111) planes perpendicular to the growth direction are separated by a distance of 4.8 Å, which is consistent with that of cubic ZnGa₂O₄ crystal (*a* = 8.3349 Å; JCPDS Card No. 38–1240). No stacking faults are found in the lattice planes. We observed that all nanowires are composed of the cubic spinel-structured ZnGa₂O₄ crystals with a uniform [111] growth direction.

XPS was used to determine the composition of the nanowires. The whole scanning spectrum shows only Ga, Zn, and O peaks (Fig. 2(a)). The atomic ratio of Ga : Zn is estimated to be about 2 : 1 from several measurements. The fine XPS spectrum reveals Ga 2p_{3/2} and Ga 2p_{1/2} peaks at 1118.9 and 1145.8 eV (Fig. 2(b)). The gap between Ga 2p_{3/2} and Ga 2p_{1/2} is 26.9 eV, which agrees with the reference value of the element 26.84 eV.¹⁵ The fine XPS spectrum of Zn 2p_{3/2} and Zn 2p_{1/2} peaks at 1045.7 and 1022.7 eV are displayed in Fig. 2(c). The gap between these two peaks is 23.0 eV, which is nearly the same as the reference value of the element 22.97 eV.¹⁵ The fine XPS spectrum of O 1s at 531.8 eV is displayed in Fig. 2(d).

The XRD pattern is displayed in Fig. 3(a). The peaks are assigned to (200), (311), (222), (400), (422), and (511) of cubic

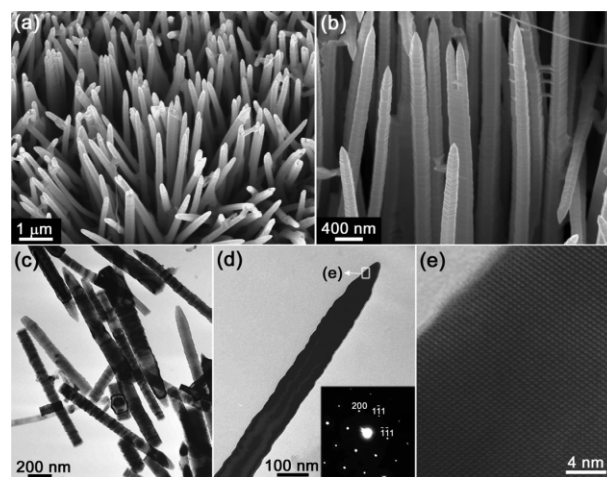


Fig. 1 (a) SEM micrograph shows the vertically aligned ZnGa₂O₄ nanowires on a large area of the Si substrate. (b) A magnified image shows the sharp tip of ZnGa₂O₄ nanowires. (c) TEM image showing the general morphology of the nanowires. The average diameter is 80 nm. (d) HRTEM image for a nanowire having a sharp tip. The SAED pattern reveals the [111] growth direction (inset). (e) Atom-resolved image for the marked area in (d) reveals the (111) planes separated by 4.8 Å.

ZnGa₂O₄ following JCPDS Card No. 38-1240. The Raman scattering spectrum is displayed in Fig. 3(b). The peaks at 473, 609, and 714 cm⁻¹ can be assigned to the T_{2g}(2), T_{2g}(1), and A_{1g} modes of the cubic spinel-structured ZnGa₂O₄, respectively, which is consistent with the reported ZnGa₂O₄ film.¹¹

A high-intensity PL spectrum measured at room temperature and 8 K is displayed in Fig. 4(a). The excitation photon energy is 3.815 eV obtained from a 325 nm-line of a He-Cd laser. Although the photon energy is below the band gap, a strong and broad emission band centered at 445 nm (2.79 eV) is observed from room-temperature PL. As the temperature decreases to 8 K, the peak position shifts to 437 nm (2.84 eV) and the intensity increases by a factor of 3. Fig. 4(b) shows the CL spectrum at room temperature. The strong emission occurs at 415 nm (2.99 eV), which is similar

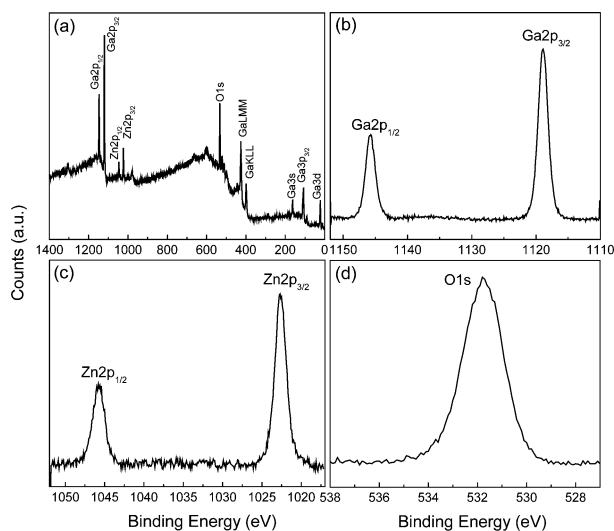


Fig. 2 (a) The XPS whole scanning spectrum and the fine spectra of (b) Ga 2p, (c) Zn 2p, and (d) O 1s.

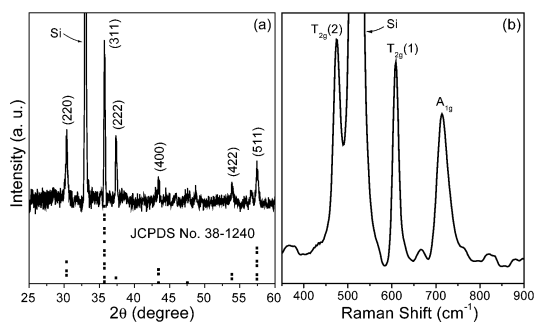


Fig. 3 (a) XRD pattern and (b) Raman spectrum of ZnGa₂O₄ nanowires. The excitation laser is a 514.5 nm argon ion laser.

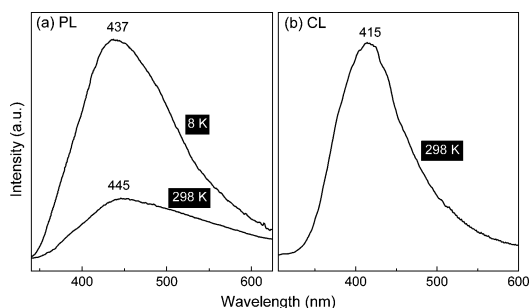


Fig. 4 (a) PL spectrum of ZnGa₂O₄ nanowires measured at 298 K (room temperature) and 8 K. The excitation wavelength is a 325 nm line from a He-Cd laser. (b) CL spectrum at room temperature.

to that of PL. A number of research groups reported that the PL and CL emission bands of the polycrystalline ZnGa₂O₄ film are centered at 440–450 nm, which is consistent with that of the nanowires.^{2,3,6–11,16} They suggested that the blue emission originated from the self-activation center of the octahedral Ga–O group in the spinel lattices. The Ga³⁺ ions combine with UV-generated free electrons produced in oxygen vacancies.

The growth of the ZnGa₂O₄ nanowires on the Au nanoparticles-deposited Si substrates would follow a typical vapor–liquid–solid growth mechanism. The Ga, Zn, and O dissolve into the Au nanoparticles and precipitate following saturation. The growth temperature of ZnGa₂O₄ nanowires is 900–1000 °C, a similar range to that of the growth of Ga₂O₃ nanowires.¹⁷ We were able to control the composition ratio of Ga–Zn simply by varying a condition such as growth temperature; the Ga–Zn ratio usually increases with the temperature.

In summary, we report the high-density arrays of vertically aligned ZnGa₂O₄ nanowires. They were synthesized on the Au nanoparticles-deposited Si substrates *via* the simple CVD of a ZnO–Ga mixture at 1000 °C. The average diameter of nanowires is 80 nm and the length is about 5 μm. The HRTEM images and SAED patterns reveal that the ZnGa₂O₄ nanowires consist of a singly-crystalline cubic structure grown in a [111] direction. The Ga : Zn = 2 : 1 ratio has been confirmed by XPS. The XRD and Raman data provide further evidence for the cubic spinel structure of ZnGa₂O₄ nanowires. The nanowires exhibit a strong PL and CL band centered around 450 nm, which is attributed to the Ga–O bonds. The ZnGa₂O₄ nanowires can be promising nanostructures in the application of high-performance LED devices operating at a blue wavelength.

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