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Synthesis and optical study of crystalline GaP nanoflowers

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GaP nanoflowers composed of numerous GaP nanowires are synthesized through heating InP and Ga₂O₃ powders. Crystalline GaP nanowires growing from Ga-rich particles have a cubic structure, uniform diameters of ~300 nm, and lengths from several to tens of micrometers. Typically, an individual GaP nanowire displays a hexagonal prism-like morphology with $\langle 111 \rangle$ as the preferential growth direction. Cathodoluminescence measurements show that GaP nanoflowers and GaP nanowires emit at ~600 and ~750 nm, respectively. Additional low-intensity emission peaks are observed for GaP nanoflowers at ~450 nm. © 2005 American Institute of Physics. [DOI: 10.1063/1.1875732]

Recently, nanostructural semiconducting materials with various structures and morphologies have received much attention due to their technological applications, intriguing properties, and quantum size effects.¹⁻³ It has been found that the nanostructure properties may have strong dependence on size, morphology, and shape.^{4,5} As an important semiconductor material, gallium phosphide (GaP), a wide band gap semiconductor ($E_g = 2.26$ eV at room temperature), is of special interest due to its excellent properties and potential applications in electrical and optical devices.^{1,6,7} To date, various GaP structures such as nanoparticles, nanowires, nanobelts, and "nanotrees" have been synthesized via different synthesis processes.⁸⁻¹¹ Another structure, a "nanoflower", has been observed in SiC, MoS₂, and NbS₂, etc.^{12–14} All these intriguing structures have stimulated us to focus on the synthesis for GaP nanoflowers and analysis of their morphologies. In this letter, the flower-like GaP nanomaterial has been synthesized and its structure, morphology, and optical properties are systemically investigated.

GaP nanoflowers were synthesized in a conventional resistance furnace through heating Ga₂O₃ and InP (1:1) starting reactants in a flow of NH₃. The starting materials were mixed completely and put into the center of a quartz tube, then the reactants were heated to 1000 °C under an Ar flow [200 standard cubic centimeters per minute (sccm)], and Ar was subsequently substituted by NH₃ (300 sccm) as the temperature increased to 1150 °C. After the whole system was maintained at 1150 °C for 1 h, dark-brown fibers deposited within the quartz tube (downstream). The as-synthesized products were examined by means of an x-ray diffractometer (RINT-2200V, 40 V/40 mA with Cu K_{α} radiation), a scanning electron microscope [(SEM) JEOL, JSM-6700F], and a high-resolution field emission transmission electron microscope [(TEM) JEOL, JEM-3000F] equipped with an x-ray energy dispersive spectrometer (EDS). The cathodoluminescence (CL) spectra were recorded in a charge-coupled device (spectra view 2D; Jobin Yvon, France).

The structure and crystallinity of as-synthesized products were examined by x-ray diffraction. As shown in Fig. 1, the product is well crystallized and may be indexed to a cubic GaP phase with the lattice constant of a=0.545 nm, matching that of a bulk material (see JCPDs Card No. 32-0397) within the experiment error.

SEM images reveal that the as-synthesized products are of flower-like morphology, as shown in Fig. 2(a). As an example, Fig. 2(b) presents a complete GaP nanoflower. Numerous individual GaP nanowires grew densely from its inner core. Generally, an individual GaP nanowire is straight and has a uniform diameter of ~ 300 nm and length ranging from several to tens of micrometers. High-magnification SEM image, shown in Fig. 2(c), reveals that each GaP nanowire possesses a hexagonal prism morphology with each hexagonal prism layer stacking along the axis direction. The



FIG. 1. XRD pattern of as-synthesized GaP nanoflowers.

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FIG. 2. (a,b) Low-magnification and (c) high-magnification SEM images of GaP nanoflowers.

inset of Fig. 2(c) shows that some GaP hexagonal prisms may intersect.

The structure and chemical composition of GaP nanoflowers were further examined by TEM and EDS. The typical TEM image of a GaP nanoflower is depicted in Fig. 3(a). The GaP nanoflower consists of a massive core of $\sim 4 \ \mu m$ and numerous nanowires as petals with lengths ranging from several to dozens of micrometers. Chemical composition analysis performed on the core verifies that the core is enriched in Ga and depleted in P, as displayed by EDS spectrum in Fig. 3(c). Surprisingly, no traces of In are detected in the core within the EDS resolution limit. However, it should be noted that the source InP material is thought to play a key role for the formation of GaP nanoflowers. Although the exact growth mechanism for the GaP nanoflowers has not yet been fully understood, a vaporliquid-solid process is assumed to cause the growth. When the temperature is increased above the melting point of InP (1060 °C), it starts to decompose into In and P atoms. Meanwhile, Ga₂O₃ transforms to a liquid Ga droplet at 1100 °C



FIG. 3. Representative TEM images of (a) a GaP nanoflower and (b) an individual GaP nanowire and (c,d) corresponding EDS spectra. (e) HRTEM image of a GaP nanowire.

(as indicated by DTA experiments, not shown here) and a large number of liquid Ga droplets are carried to a low temperature zone by the flowing gas and congregate into Ga-rich particles in an In-vapor atmosphere. The P atoms are absorbed onto the surface of Ga particles and bond with Ga atoms. This results in GaP nanowires densely protruding from the surface of Ga-rich particles. The absence of In in the Ga-rich particles and GaP nanowires is possibly due to the lattice mismatch between In, Ga, and GaP structures. TEM image of a representative GaP nanowire protruding from a GaP nanoflower is presented in Fig. 3(b). Typically, the GaP nanowires have a rough surface, a diameter of \sim 300 nm, and a length reaching several micrometers. EDS analysis, Fig. 3(d), confirms that the wires consist of P and Ga atoms in an atomic ratio $\sim 1:1$. They have a marginal content of O as a result of insurmountable surface oxidation during the growth process.

Figure 3(e) displays a representative high-resolution TEM (HRTEM) image of a GaP nanowire with a hexagonal prism-like morphology. HRTEM and electron diffraction (ED) analyses performed on an individual nanowire imply a face-centered-cubic structure. The intrafringe separations in the directions parallel and perpendicular to the wire axis are



FIG. 4. CL spectra of GaP nanoflowers and a nanowire measured at room temperature.

0.314 and 0.274 nm, respectively, being in a good agreement with the ED data. They correspond to the (111) and (220) planes of a GaP cubic structure. Further, based on the HR-TEM image and ED pattern, it could be concluded that the hexagonal prism structure observed in the SEM image [Fig. 2(c)] grows through stacking the {111} planes along the preferential $\langle 111 \rangle$ orientation and the six planes in the GaP prism correspond to the {220} planes.

Optical properties of the GaP nanoflowers were finally studied. Figure 4 shows room-temperature CL spectra taken from the GaP nanoflowers and an individual GaP nanowire. The characteristic emission peak at around 600 nm is detected for both GaP nanoflowers and the individual nanowire. This shows an obvious redshift compared to the bulk and porous GaP materials (\sim 550 nm).¹⁵ It should be noted that the redshift may possibly result from some impurity effects, e.g., atomic vacancies on the wire surface, rather than from the size effects (nanowire diameters are rather big \sim 300 nm). N-doped GaP nanobelts with a low N content have been reported to show a redshift.¹⁰ The present GaP nanoflowers were synthesized with the assistance of NH₃. There may be some N atoms absorbed on the surface, though no N traces were detected during the EDS analysis within its resolution limit. In addition, the similar emission peaks for nanoflowers and the nanowire were observed at \sim 750 nm. The peak intensity for the nanoflowers was higher compared with such characteristic peaks in an individual GaP nanowire. This broad peak was also observed during cathodoluminescence and photoluminescence studies at room temperature for standard GaP, which was attributed to radiative recombination by way of a donor-acceptor pair in the band gap.^{15,16} This interpretation also looks reasonable for the present nanoscale GaP materials. The difference in light emission intensity for GaP nanoflowers and nanowires $(\sim 750 \text{ nm})$ may result from the different Ga content, as revealed by EDS analysis. The low intensity peak in the visible range (~450 nm) was observed for GaP nanoflowers; this peak was not seen for the GaP nanowires though. A similar supra-band-gap emission has also been reported by van Driel *et al.*¹⁷ in porous GaP and Cullis *et al.*¹⁸ in porous Si. This emission was usually attributed to an oxide-originated defect rather than to a size confinement effect. The GaP nanoflowers, may be easily oxidized due to the high content of Ga in their inner cores. These oxide-originated defects could be eliminated by subsequent hydrogen passivation treatment.¹⁸

In summary, GaP nanoflowers have been synthesized by means of a simple evaporation of InP and Ga₂O₃ powders. The GaP nanoflowers are crystalline and possess a cubic structure. The growth is assumed to start from the surface of Ga-rich particles and controlled by a vapor-liquid-solid mechanism. An individual GaP petal has a hexagonal prism morphology with a diameter of ~ 300 nm and a length of several micrometers or more. TEM analysis implies that the GaP nanowires grow along the $\langle 111 \rangle$ direction. Optical measurements reveal a redshift at ~ 600 nm for both GaP nanoflowers and GaP nanowires due to impurity atoms absorbed on the wire surface. Additional emission peak at \sim 750 nm for GaP nanoflowers and nanowire has also been observed, possibly due to radiative recombination by way of a donoracceptor pair in the band gap. The authors envisage that the flower-like GaP structure may be valuable for future nanodevice design.

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