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Synthesis of gallium phosphide nanowires *via* sublimation method

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Gallium phosphide nanowires were synthesized by sublimation of ball-milled powders and are straight, cylindrical, and smooth in surface, with mean diameter of 40 nm and length up to 300 μm; they have a single-crystalline zinc blende structure with [111] growth direction; X-ray diffraction and Raman spectroscopy reveal a high degree of crystallinity of the nanowires; photoluminescence, exciting with a 458 nm laser line, shows a broad donor–acceptor pair peak and its replicas in the energy range 2.05–2.20 eV.

Gallium phosphide (GaP) is a popular semiconductor material, due to its large energy band gap (E_g = 2.26 eV at 300 K) and good thermal stability. However, the indirect band gap usually limits applications in optoelectronic fields. Recently, one-dimensional nanostructures such as nanotubes and nanowires have attracted much attention because of their unique optical, electrical, mechanical and magnetic properties, distinctive from those of the bulk materials.[1–3] GaP nanowires would be ideally suited to investigate the role of dimensionality and size in the physical properties. Two methods have been developed to synthesize GaP nanowires. One is laser ablation of metal-containing GaP or gallium oxide (Ga_2O_3)–GaP mixture targets.[4,5] The other is to convert carbon nanotubes by reaction with a Ga/Ga_2O_3 powder mixture in a phosphorus vapor atmosphere.[6] Here we report a simple and efficient sublimation method to synthesize high-density GaP nanowires. We found that the use of ball-milled GaP powders gave rise to straight, cylindrical, and single-crystalline GaP nanowires. Furthermore, the photoluminescence (PL) emission of the GaP nanowires has been measured for the first time.

GaP (99.99%, Aldrich) pieces of size 2–5 mm were milled using a mechanical ball mill system (Spex 8000M) for 20 h. Then ball-milled GaP powder (or GaP pieces) were placed in a quartz boat located inside a quartz tube reactor. Transmission electron microscopy (TEM) microscopy of the ball-milled powder revealed that nearly amorphous particles aggregate with a size of 100–200 nm. Alumina substrates were coated with a 300 nm thickness film of a 0.01 M ethanol solution of $NiCl_2 \cdot 6H_2O$ (99.99%, Aldrich), leading to Ni nanoparticles deposited on the substrate. The substrate was placed at a distance of about 10 cm from the boat with argon introduced into the reactor at a rate of 500 sccm. The temperature of the GaP source was set at 1100 °C and that of the substrate was approximately 900 °C. The growth time was 10 min. The size and structure of the nanowires were examined by scanning electron microscopy (SEM, Hitachi S-4300), TEM (JEOL JEM-2010), electron diffraction (ED), energy dispersive X-ray spectroscopy (EDS), X-ray powder diffraction (XRD, Philips X'PERT MPD), and Raman spectroscopy (Renishaw RM1000) using a 514.5 nm argon ion laser. The PL was excited at 8 K by the 458 nm line from an argon ion laser. The wavelength was precisely calibrated using the atomic lines from an argon calibration lamp.

Greenish yellow wool-like product was deposited on the substrates. Fig. 1(a) shows the SEM image of the high-density nanowires homogeneously grown on a large area of the substrate. The nanowires are nearly aligned with a length up to 300 μm. High-magnification SEM observation reveals a clean surface without any particles. EDS analysis identifies Ga and P with an atomic ratio of nearly 1 : 1. The TEM image shows the general morphology of the GaP nanowires (Fig. 1(b)) which are straight, cylindrical and smooth in surface (Fig. 1(c)). There are negligible amorphous outerlayers and no catalytic particles exist at the tip. The diameters are 20–60 nm with an average value of 40 nm. A high-resolution TEM (HRTEM) image reveals that the nanowires consist of nearly perfect GaP single crystals (Fig. 1(d)). The [111] direction of the cubic unit cell is aligned to the wire axis. The (111) fringes perpendicular to the wire axis are separated by about 3.1 Å, which is consistent with that of bulk crystalline GaP (a = 5.4506 Å; JCPDS Card No. 32-0397). The selected-area ED (SAED) patterns further confirm that the nanowire is single-crystalline with a [111] growth direction (inset). The results show that the sublimation of the ball-milled powders produces straight single-crystalline GaP nanowires. However, when mm-sized GaP pieces were sublimed, curled polycrystalline nanowires are formed, as shown in the TEM image (Fig. 1(e)). Fig. 1(f) shows a HRTEM image revealing that the individual curled nanowires are made up of smaller crystalline grains with dimensions of a few nm. The corresponding SAED pattern also shows this polycrystalline nature (inset).

The XRD pattern of the straight GaP nanowires detached from the substrate is shown in Fig. 2(a) along with that of the microsized GaP crystals (GaP microcrystals) prepared by grinding GaP pieces. The peaks can be indexed to zinc blende structured GaP crystals. No other crystalline forms were detected. The position of each peak is the same for both

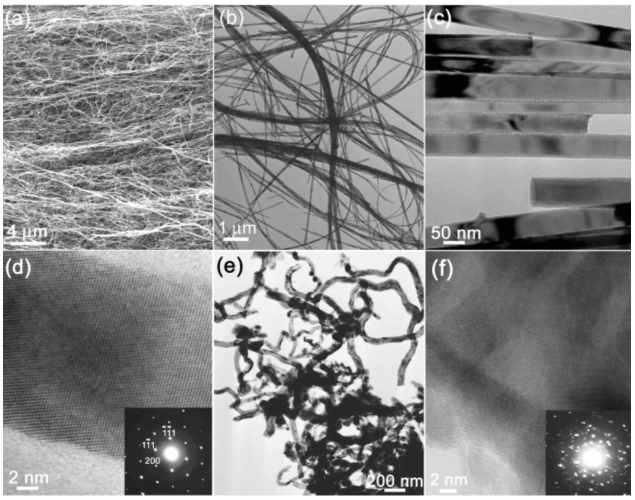

Fig. 1 (a) SEM micrograph of high-density GaP nanowires grown on a large area of Ni-deposited alumina substrates *via* the sublimation of the ball-milled GaP powders. (b) TEM image showing the general morphology of the GaP nanowires. (c) Higher magnification image showing all the nanowires to be straight and cylindrical. (d) HRTEM image of one GaP nanowire with its corresponding SAED pattern (inset), showing the single-crystalline zinc blende structure. (e) TEM image showing the curled GaP nanowires grown by sublimation of the GaP pieces. (f) HRTEM image of a polycrystalline nanowire with its corresponding SAED pattern (inset).

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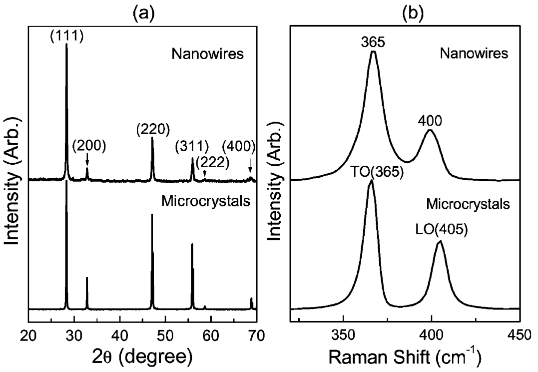

Fig. 2 (a) XRD patterns and (b) Raman spectra of GaP microcrystals and GaP nanowires. The excitation laser of Raman spectroscopy is a 514.5 nm argon ion laser.

samples, indicating no change of lattice constant for the nanowires. The sharpness of peaks is due to the high crystallinity of the nanowires. The room-temperature Raman spectra of GaP nanowires and GaP microcrystals are displayed in Fig. 2(b). In the spectrum of the GaP microcrystals, the first-order phonon frequencies of the transverse optical (TO) and longitudinal optical (LO) modes are at 365 and 405 cm^{-1}, respectively, which is consistent with the reported values, 365 and 402 cm^{-1}.[7] The corresponding peaks of the GaP nanowires appear at around 365 and 400 cm^{-1}, showing a downshift of the LO mode by about 5 cm^{-1}. The TO and LO peaks are somewhat broader than those of the microcrystals. The quantum confinement effect would be negligible for the nanowires having a diameter of 20–60 nm.[8] Since the nanowires possess an extremely large surface area, surface defects would play a role in shifting and broadening the Raman peaks.

The growth of GaP nanowires probably follows a typical vapor–liquid–solid mechanism.[3,4] The GaP vapor deposits on the Ni catalytic nanoparticles, forming miscible alloy nanoparticles. The GaP nanowires start to grow as the alloy particles are saturated with Ga and P. The ball-milled GaP powders are more volatile than the GaP pieces. A sufficient GaP vapor pressure from the powder would lead to continuous precipitation, producing straight nanowires. Under the lower vapor supply from the GaP pieces, the nanowires may not grow continuously, resulting in curled shapes. Therefore, the present GaP synthesis shows an unique example that the morphology of the nanowires can be controlled by the volatile properties of the reactants. The absence of catalytic particles at the tip suggests the base growth mechanism in which the GaP nanowires are grown out from the Ni nanoparticles deposited on the alumina substrate.

The PL spectrum of the GaP nanowires at 8 K is shown in Fig. 3 and exhibits two broad PL peaks at 2.13 and 2.175 eV with a shoulder at 2.08 eV. These are separated by about 45 and 50 meV, which are close to the energy of the LO mode of 48 meV. Therefore, the peaks can be assigned to the donor–acceptor pair (DAP, 0LO) peak and its replicas (1LO and 2LO). Impurities such as atomic vacancies, which probably occur on the surface, would determine the spectral position of the DAP peak. The present peaks are noticeably at lower energy than those of doped bulk GaP.[9,10] Low-intensity peaks appear at 2.215, 2.224 and 2.245 eV. For the identification of the origins of these PL peaks, the present PL spectrum is carefully compared with the well-known PL spectra of nitrogen (N)-doped bulk GaP reported elsewhere.[9,10] The positions are nearly identical to those of the isoelectronic exciton peaks NN_4, NN_5 and A, respectively, if all peaks are shifted to lower energy by 73 meV. Then, a small peak (at 2.188 eV) superimposed on the DAP peak would correspond to the NN_3 peak. The peak A originates from the recombination of isoelectronic excitons bound to isolated nitrogen atoms; peaks NN_3, NN_4 and NN_5 arise from the recombination of isoelectronic excitons bound to the N atom pairs. In order to confirm the identity of these peaks, we synthesized heavily doped GaP nanowires with N atoms at a concentration of $\sim 10^{18}$ cm^{-3}, and this showed increased intensity PL peaks at the same positions. This implies that N atoms are doped in the GaP nanowires. The appearance of the NN_4 and NN_5 peaks indicates that their concentration is above 10^{17} cm^{-3}. We suggest here that the N atoms would remain at the surface of nanowires due to the adsorption of air. Detailed studies will follow to elucidate the energy shift of the PL peaks.

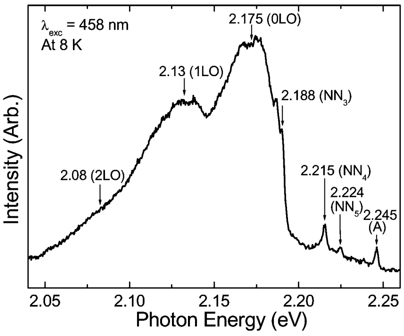

Fig. 3 PL spectrum of the GaP nanowires at 8 K. The excitation line is the 458 nm line from an argon ion laser.

In summary, we synthesized high-density GaP nanowires on a large area of Ni-deposited alumina substrates *via* the catalyst-assisted sublimation of ball-milled GaP powders under Ar flow. The diameters are uniformly 20–60 nm with an average value of 40 nm and the lengths are up to 300 μm. All nanowires are straight and consist of single-crystalline zinc blende structure with identical [111] growth direction. When mm-size pieces are sublimed instead of ball-milled powders, curled and polycrystalline nanowires are formed. This shows that the morphology of the GaP nanowires can be controlled by the volatility of the GaP source. XRD and Raman spectra confirm the synthesis of high-quality crystalline GaP nanowires. The surface defects would cause the downshift and broadening of the Raman peaks. The PL spectrum of the nanowires at 8 K shows a broad DAP peak and its replicas in the energy range 2.05–2.20 eV, for excitation at 458 nm. The typical N-bound isoelectronic exciton peaks appear probably due to the N-doping on the surface.

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