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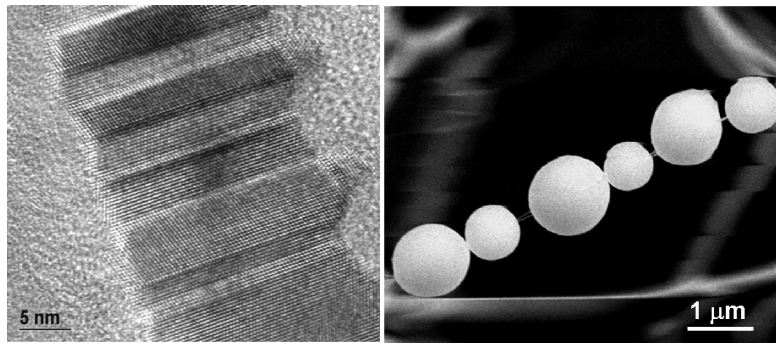

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Vapor-Phase Synthesis of Gallium Phosphide Nanowires

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ABSTRACT: Gallium phosphide (GaP) nanowires were synthesized in a high yield by vapor-phase reaction of gallium vapor and phosphorus vapor at 1150 °C in a tube furnace system. The nanowires have diameters in the range of 25−100 nm and lengths of up to tens of micrometers. Twinning growth occurs in GaP nanowires, and as a result most nanowires contain a high density of twinning faults. Novel necklacelike GaP nanostructures that were formed by stringing tens of amorphous Ga−P−O microbeads upon one crystalline GaP nanowires were also found in some synthesis runs. This simple vapor-phase approach may be applied to synthesize other important group III−V compound nanowires.

Introduction

As an important Group III−V phosphide semiconductor, GaP with an indirect band gap of 2.26 eV has been used as red, orange, and green light-emitting diodes since the 1960s.[1] In recent years, considerable efforts have been paid to the synthesis of GaP nanowires due to its potential applications in miniature optical and optoelectrical devices.[2–8] Several techniques have thus been developed to synthesize GaP nanowires including pulse laser ablation of a target of GaP powder and gold nanoparticles,[2,3] thermal evaporation of GaP powder,[4,5] metal-organic chemical vapor deposition (MOCVD) of single molecular tris(ditert-butylphosphino) gallane in a mixture of amine stabilizers,[6] hydrothermal synthesis in the presence of surfactant (CTAB),[7] supercritical fluid-liquid−solid synthesis by reacting $P(SiMe_3)_3$ and $(tBu)_3Ga$ in the presence of dodecanethiol-stabilized gold nanocrystals,[8] etc. Most of these syntheses involve gold nanocrystals which act as catalysts to direct the nanowires growth via a vapor−liquid−solid (VLS) growth mechanism.

In this paper, we report a simple vapor-phase approach to high-yield growth of GaP nanowires by using GaN and phosphorus powders as the source materials without using any catalysts. This research was motivated by our previous successes in using GaN powder as an efficient gallium catalyst source for growing SiO_2 nanowires.[9,10] One unique feature for this approach is that at the reaction temperature of ∼1150 °C, GaN powder can be efficiently decomposed into dense gallium vapor, which can mix uniformly and react efficiently with phosphorus vapor. The GaP nanowires thus synthesized have high-crystallinity and uniform diameter distribution.

Experimental Section

The growth was conducted inside a tube furnace system, as that shown in Figure 1. Commercial GaN powder (99.99%, Alfa Aesar) and red phosphorus powder (99%, Alfa Aesar) were used as the source materials. In a typical run, 1 g GaN powder was placed at the center of a 1.75 in. alumina tube that was inserted in a horizontal tube furnace, where the temperature, reaction chamber pressure, and carrier gas flow rate were well controlled. Considering the huge evaporation temperature difference of GaN and phosphorus powders (∼1000 °C for GaN versus ∼200 °C for phosphorus), a movable sample transfer rod was attached to the left end of the furnace tube to transfer the phosphorus powder to the desired temperature regions. During the temperature increase period, the phosphorus powder (0.5 g) was located at the leftmost end, where the temperature was at about room temperature. When the furnace temperature reached at 1150 °C (the efficient decomposition temperature for GaN powder), the phosphorus powder was immediately transferred to a region with temperature of ∼300 °C at which the phosphorus powder was efficiently evaporated. The phosphorus vapor thus generated was carried by 80 sccm (standard cubic centimeter per minute) argon gas to the downstream part, where it mixed and reacted efficiently with gallium vapor to form GaP nanowires. Several alumina plates (50 mm long and 10 mm wide) were placed downstream in a region with temperature of 500−700 °C to collect the nanowires. Through the quartz window located at the right end of the furnace tube, heavy smokelike vapor was visible during the entire reaction period. The reaction chamber pressure was kept at 300 Torr and the growth time varied from 10 to 30 min. The furnace was then cooled down naturally to room temperature.

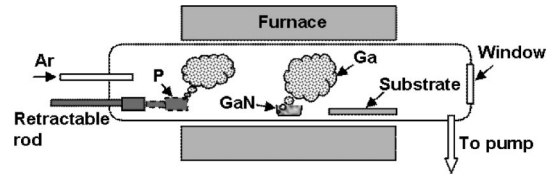

Figure 1. Schematic diagram of the experimental setup.

The morphology of the as-synthesized nanowires was examined with an Inspect F field emission gun (FEG) scanning electron microscope (SEM) operating at 15 kV. The microstructure was characterized with a Hitachi HF-2000 FEG transmission electron microscope (TEM) operating at 200 kV. The composition was analyzed by an energy-dispersive X-ray spectrometer (EDS) attached to the SEM and TEM. The crystallinity was investigated by a PANalytical X'Pert PRO diffractometer with CuKα radiation. The photoluminescence study was carried out at room temperature on a Horiba Fluorolog3−2iHR320 spectrofluorometer using a Xe lamp as the excitation source.

Results and Discussion

After the growth, a thick layer (can be up to 5 mm thick after 30 min growth) of light yellow color GaP nanowires were deposited on the alumina substrates, covering a substrate length of ∼50 mm. Checking with a sharp tweezers under a 50× optical microscope, we found that the nanowires were very dense and tangled together, and no apparent differences were

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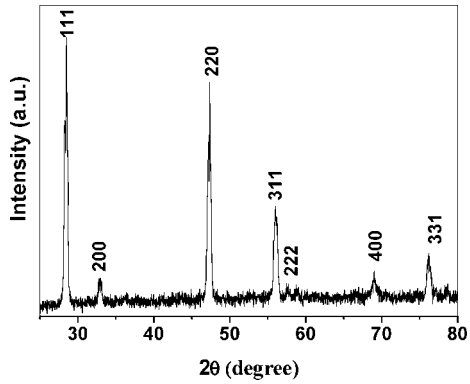

Figure 2. XRD pattern recorded from GaP nanowires.

observed through the millimeter-thick deposition layer. These phenomena, together with the dense smoke present in the deposition region, suggest that the nanowires may be nucleated and quickly (within several seconds) grown in the vapor[11] and then deposited on the substrates. This assumption is further supported by the fact that a small amount of GaP nanowires can also be collected on the inner wall of the processing alumina tube even at the room temperature part due to the transport of the carrier gas. We have actually observed similar phenomenon on other material systems, such as the growth of SnO_2 nanobelts by thermal evaporation of SnO powder.[12]

The XRD pattern recorded from the nanowire product (Figure 2) matches that of pure zinc-blende (cubic) GaP (JCPDS card 32-0397). No peaks related to phosphorus, GaN, or other impurities were detected. The strong intensity of the (111) peak indicates that the GaP nanowires have a preferential growth direction along <111> orientation.

SEM observations reveal that the GaP nanowires synthesized using our vapor-phase approach have very high purity (Figure 3a). The diameter of the nanowires is in the range of 25−100 nm, and the length can be up to tens of micrometers. Each nanowire has a uniform diameter along its entire length. Low-magnification TEM observations show that while some nanowires exhibit single crystalline nature without apparent faults, the majority of the GaP nanowires display dense twinning band contrast (Figure 3b). This is confirmed by high-resolution TEM (HRTEM) and electron diffraction analyses. Figure 3c is a lattice image of a GaP nanowire without twinning faults. The wire is a single crystal with a lattice spacing of about 0.31 nm, which is in good agreement with the expected (111) lattice spacing of bulk GaP (0.314 nm), suggesting that the GaP nanowires grow along <111> direction. Figure 3d is a high-magnification TEM image of a GaP nanowire with high density of twinning faults. The twins with random spacing are distributed orthogonally to the long axis of the nanowire. HRTEM imaging confirms that the twinning boundaries are perpendicular to the [111] axial direction of the nanowires (Figure 3e,f). Fast Fourier transform (FFT) diffraction patterns (insets in Figure 3e,f) associated with the twinning in Figure 3e,f display ambiguous streaking that is the character of a long-range twinning coherence, that is, they exhibit a series of additional distinct diffraction spots superimposed onto the [111] rotational twinning pattern.[3] In addition, the HRTEM images shown in Figure 3e,f clearly reveal that the twinning nanowire surfaces are composed of a series of zigzag facets, which are apparently correlated with the locations of the twin boundaries. These facets can be indexed as {111} surfaces, which possess the lowest free energy compared with other surfaces in the zinc-blende structure.[3]

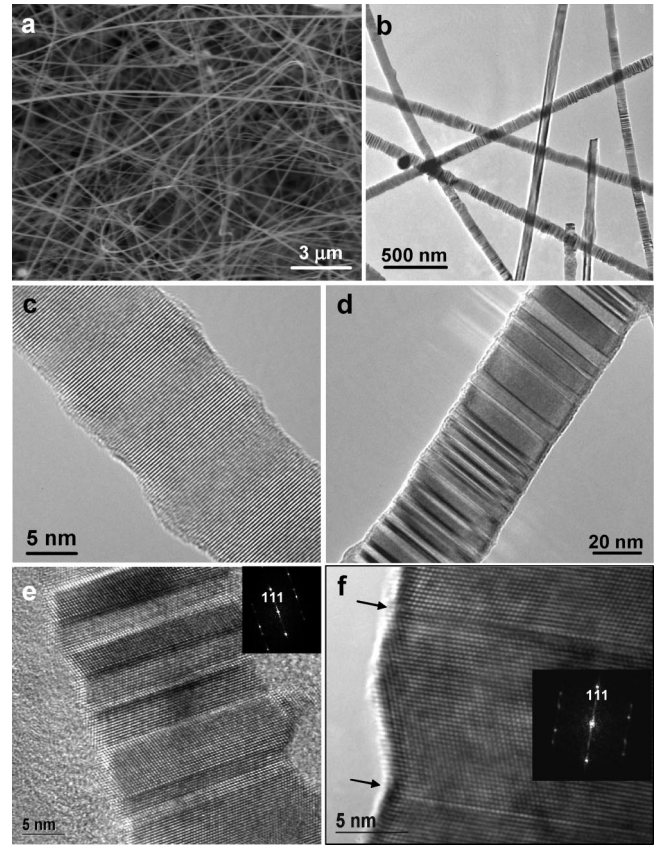

Figure 3. Electron microscope images of GaP nanowires. (a) SEM image of GaP nanowires. (b) TEM image of GaP nanowires. Dense twinning bands are visible for most nanowires. (c) Lattice image of one defect-free nanowire. (d) High-magnification TEM image of a GaP nanowire containing dense twinning faults. (e) HRTEM image of a twinning growth GaP nanowire. The inset is the FFT diffraction pattern associated with the HRTEM image. (f) HRTEM image of the edge of a twinning GaP nanowire. The twinning boundaries are highlighted by black arrows. The inset is the corresponding FFT diffraction pattern.

The twinning growth is a common feature for GaP nanowires, which has been recently reported on GaP nanowires synthesized by several techniques such as pulse laser ablation,[3] supercritical fluid-liquid−solid synthesis,[8] and thermal evaporation.[4] Even though these growth approaches are different, the formation of the twins are usually attributed to the oscillation (or fluctuations) existed in the reaction systems.[3,8] For our synthesis, the growth was believed to conduct in the vapor phase within a very short time (several seconds), during which the oscillations may not be responsible for the formation of the extremely high density of twins. Since we did not find the twinning growth phenomenon in many other nanowires that we synthesized using the same thermal evaporation technique,[12] the twinning growth might be related to the intrinsic growth habit of GaP compound. Further investigation is needed to explain this unique growth phenomenon.

Besides the smooth nanowires shown in Figure 3, in some runs we also obtained GaP necklaces as those shown in Figure 4a−d. The necklaces are actually tens of microbeads strung together by a thin GaP nanowire (Figure 4a). The diameters of the beads vary from 0.5 to 2 μm (Figure 4b), and the nanowire diameters are in the range of 50−200 nm. The relationship between the nanowires and the beads can be better shown with TEM imaging. The contrast of TEM imaging (Figure 4c,d) reveals that the nanowires are crystalline and the beads are amorphous and that the beads seem to attach to the nanowires after the wires were formed. Figure 4c also shows that the GaP

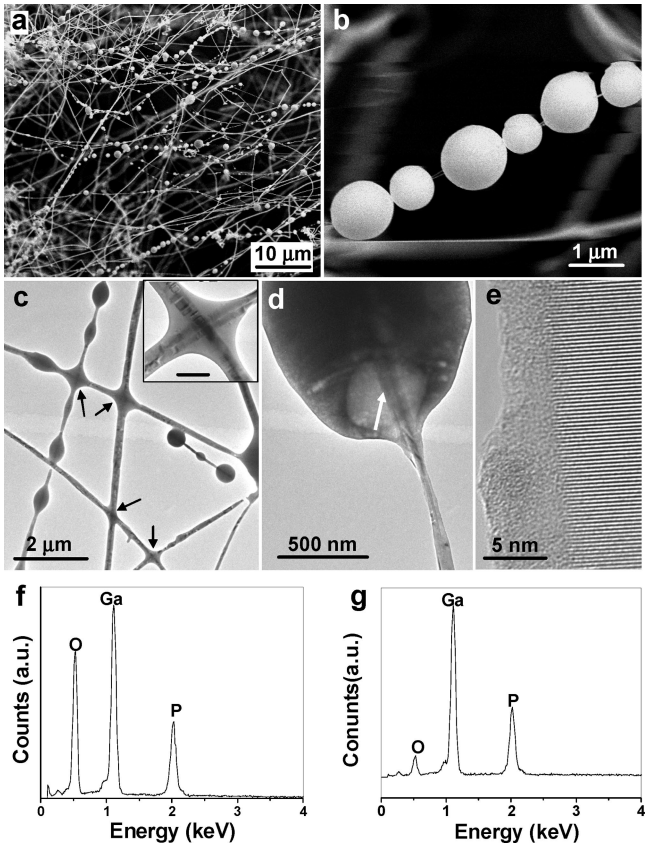

Figure 4. Electron microscope images and EDS spectra of GaP necklaces. (a) Low-magnification SEM image of GaP necklaces. (b) High-magnification SEM image of part of a GaP necklace, showing six Ga−P−O beads strung together by two parallel GaP nanowires. (c) Low-magnification TEM image of GaP necklaces. The black arrows indicate the welding positions of two nanowires by amorphous Ga−P−O glass. The inset is a high-magnification image showing four crystalline GaP nanowires are welded into a cross by amorphous Ga−P−O glass. Scale bar, 200 nm. (d) High-magnification TEM image showing a Ga−P−O bead strung by a GaP nanowire. The white arrow indicates the nanowire position inside the bead. (e) Lattice image of part of a GaP nanowire, showing an amorphous Ga−P−O layer coated on the crystalline GaP nanowire surface. (f) EDS spectrum recorded on the beads, showing the beads contain Ga, O, and P. (g) EDS spectrum taken from the nanowires, showing the oxygen concentration is much lower than that contained in the beads.

nanowires tend to be welded together by amorphous bead material (indicated by black arrows); the detailed structure of the joints is clearly displayed in the inset in Figure 4c. Moreover, as the HRTEM image shown in Figure 4e the nanowires grown in these runs are usually coated with a thin amorphous layer with thickness of up to 10 nm. EDS analyses (Figure 4f,g) show that the beads and the coating layers contain significant high oxygen and thus they are amorphous Ga−P−O glass. The formation of Ga−P−O glass is probably because of the system leaking in some runs. This glass is a viscous liquid at nanowire growth temperature and will solidify into amorphous microbeads or thin coating layers on nanowire surfaces when cooled.

The room-temperature photoluminescence (PL) spectra of the GaP nanowires were measured using a Xe lamp as the excitation source. A strong, broad blue emission that peaked at ~440 nm, which corresponds to GaP band gap,[6] is detected under 365 nm excitation (Figure 5). A small peak centered at 575 nm is also detected, which can be attributed to internal defect emission,

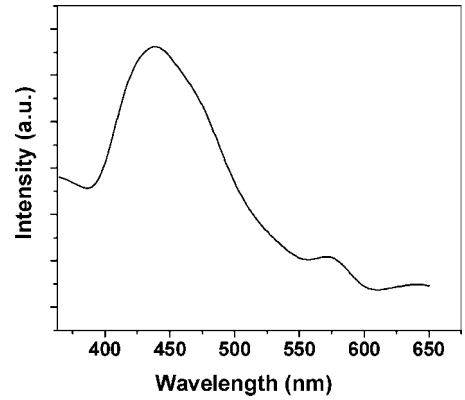

Figure 5. Photoluminescence spectrum of GaP nanowires under 365 nm wavelength excitation.

probably due to the substitution oxygen in GaP that exhibits some anomalous properties.

Conclusions

In summary, GaP nanowires were synthesized in a high yield by the reaction between gallium vapor and phosphorus vapor inside a tube furnace system. Most nanowires contain a high density of twinning faults, which may be related to the intrinsic growth habit of GaP compound. When a leak happens in the reaction system, necklacelike GaP nanostructures will be formed by stringing tens of amorphous Ga−P−O microbeads upon one crystalline GaP nanowire. The GaP nanowires might be used as building blocks to fabricate blue light-emitting LED devices. Our simple vapor-phase approach may be applied to synthesize other important III−V compound nanowires such as GaAs and InP.

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