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Synthesis of high-purity GaP nanowires using a vapor deposition method

S.C. Lyu [a], Y. Zhang [a], H. Ruh [b], H.J. Lee [b], C.J. Lee [a,*]

[a] Department of Nanotechnology, Hanyang University, 17 Haengdang-dong Seongdong-gu, Seoul 133-791, Korea
[b] Microstructure Analysis Laboratory, Korea Research Institute of Standards and Science, Daejon 305-600, Korea

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Abstract

High-purity gallium phosphide (GaP) nanowires were successfully synthesized on the nickel monoxide (NiO) or the cobalt monoxide (CoO) catalyzed alumina substrate by a simple vapor deposition method. To synthesize the high-purity GaP nanowires, the mixture source of gallium (Ga) and GaP powder was directly vaporized in the range of 850–1000 °C for 60 min under argon ambient. The diameter of GaP nanowires was about 38–105 nm and the length was up to several hundreds of micrometers. The GaP nanowires have a single-crystalline zinc blend structure and reveal the core-shell structure, which consists of the GaP core and the $GaPO_4/Ga_2O_3$ outer layers. We demonstrate that the mixture of Ga/GaP is an ideal source for the high-yield GaP nanowires.

1. Introduction

The synthesis of wide bandgap semiconductor nanowires has attracted much attention because of their novel optical, electrical, and mechanical properties [1–14]. Among the wide bandgap semiconductor nanowires, the gallium phosphide (GaP) nanowires can promise many applications to electronic, optoelectronic, and magneto-optical devices [15]. Nevertheless, there were rare reports on the synthesis of GaP nanowires compared with gallium nitride (GaN) nanowires or zinc oxide (ZnO) nanowires. Duan and Lieber [16] synthesized GaP nanowires using a laser-assisted catalytic growth method, in which a pulsed laser is used to vaporize a solid target containing a catalyst/GaP mixture. Shi et al. [17] also reported the synthesis of GaP nanowires using laser-ablation method involving an oxide-assisted VLS growth mechanism. To synthesize GaP nanowires, the mixture target of GaP powders with 25 mol% gallium oxide (Ga_2O_3) was ablated by KrF pulsed excimer laser at a substrate temperature of 750 °C for 4 h. Tang et al. successfully synthesized GaP nanowires by reacting carbon nanotubes (CNTs) with the volatile metal oxide Ga_2O in a phosphorus vapor atmosphere. In their method, GaP nanowires were synthesized by loading appropriate amounts of Ga_2O, P, and CNTs inside a vacuum-sealed quartz capsule,

* Corresponding author.
E-mail address: cjlee@hanyang.ac.kr (C.J. Lee).

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which was heated to 1000 °C for 1 h in a furnace [18].

In this Letter, we report synthesis and specific core-shell structure of high-purity GaP nanowires by a simple vapor deposition method, in which the mixture source of Ga and GaP powders was directly vaporized in the range of 850–1000 °C under argon ambient in a furnace. We demonstrate that the metal-oxide nanoparticles play a key role in the growth of GaP nanowires and the mixture of Ga and GaP powder could act as an ideal source for the high-yield GaP nanowires with a single-crystalline structure.

2. Experimental

An alumina slice (10×5 mm in size), on which NiO or CoO catalyst nanoparticles were evenly distributed, was used as a substrate for the synthesis of GaP nanowires. In a typical process, a nickel (or cobalt) nitrate/ethanol solution (concentration 0.01 M) was dropped onto the surface of the alumina substrate. After drying the substrate at 400 °C in air ambient, the catalyzed alumina substrate was put on the top of a quartz boat filled with the mixture of the Ga/GaP powder (Ga: 99.999%, GaP: 99.99%, Sigma–Aldrich, Ga:GaP = 1:1 (volume ratio)). The vertical distance between the Ga/GaP source and the catalyzed alumina substrate was about 3–5 mm. The quartz boat was then transferred into a quartz tube of furnace system, which had been evacuated by rotary pump and purged by 1000 sccm argon flow. The temperature was increased to preset a reaction temperature at a rate of 35 °C/min. The nanowires were synthesized in the temperature range of 850–1000 °C for 60 min under a constant flow of argon (flow rate: 500 sccm). After the reaction the surface of alumina substrate appeared a white-colored material. The deposited products were characterized by scanning electron microscopy (SEM) [Hitachi S-4700], transmission electron microscopy (TEM) [Hitachi H-9000 NAR], energy-dispersive X-ray spectroscopy (EDX) [Hitachi S-4700], and X-ray diffraction (XRD) [Rigaku DMAX PSPC MDG 2000].

3. Results and discussion

The wire-like products observed on the substrate are almost exclusively slightly curved nanowires with random orientation as shown in Fig. 1. The nanowires have diameters in the range of 38–105 nm and lengths up to several hundreds of micrometers. The nanowires show a very clean surface without any nanoparticles and indicate nearly uniform diameters in SEM images. As shown in Fig. 1a–c, the average diameters of nanowires grown on NiO catalyst particles are about 38–45, 56–64, and 94–105 nm at the growth temperatures of 850, 950, and 1000 °C, respectively. The nanowires synthesized on CoO catalyst have a similar morphology but indicate a larger diameter of 74–82 nm at the same growth temperature (850 °C) as shown in Fig. 1d. Gudiksen and Lieber [19] reported that the diameter of nanowires is mainly dependent on the size of catalyst particle. In our experiment, the diameter of nanowires increases with increasing growth temperature because agglomeration of catalyst particles more actively progresses at a higher reaction temperature. By substituting CoO catalyst for NiO catalyst, the diameter of nanowires also increases at the same growth condition. It is assumed that Co catalyst can make a larger particle size compared with Ni catalyst during the reaction process. We found that Ga or GaP only as powder leads to amorphous materials on the substrate but the mixture source of Ga/GaP always induces high-purity nanowires.

Fig. 2 indicates SEM images for a typical nanowire, in which the catalyst particle does not appear at the tip of nanowires but seemed to have existed at the bottom of the nanowire. Inset shows TEM observation of the nanowire without catalyst at the tip. Zettl and Han [12] reported that Fe catalyst particles, attached to a substrate, existed at the bottom of nanowires while there are no catalyst particles at the tip of nanowires.

To evaluate the structure and compositions of nanowires, we performed EDX and XRD analysis. EDX analysis indicates that the nanowires are composed of Ga, P, and O elements as shown in Fig. 3a. XRD spectra also show that the nanowires consisted of single-crystalline zinc blend GaP and

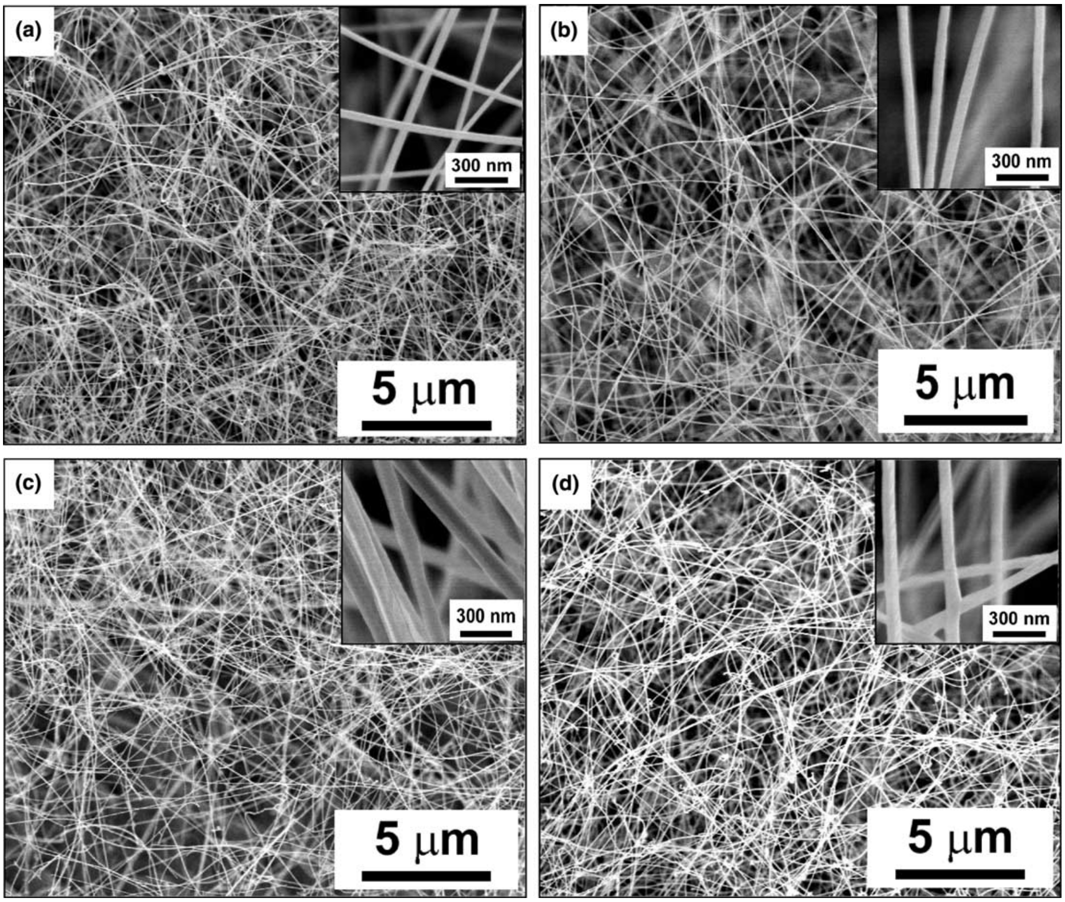

Fig. 1. SEM images of nanowires synthesized on the NiO catalyst nanoparticles (a–c) and CoO catalyst nanoparticles (d). Inset shows a magnified SEM image of nanowire.

orthorhombic $GaPO_4$ as shown in Fig. 3b. It reveals that the synthesized nanowires are organized by both the single-crystalline GaP and the gallium oxide phases.

We investigated TEM analysis to obtain more detailed information about the structure of nanowires. Fig. 4a shows that the GaP nanowires have a fairly straight shape in a short range without attached amorphous materials. A magnified TEM image of one GaP nanowire indicates that the nanowire consists of a typical core-shell structure with a single-crystalline GaP core and an outer gallium oxide layer as shown in Fig. 4b. Fig. 4c shows high-resolution TEM (HRTEM) indicating the microstructure of the core and outer oxide layer. HRTEM and selected area electron diffraction (SAED) clearly demonstrate that the core is zinc blend structured GaP and the outer oxide layer is a double layer of orthorhombic structured $GaPO_4$ and amorphous Ga_2O_3 layers. We presume that the $GaPO_4$ and Ga_2O_3 layers are formed on the surface of GaP nanowire during reaction process in the quartz tube. There were some reports that the outer oxide layer had appeared on the surface of nanowire after synthesizing nanowires [17,20]. But in our experiment, we suggest that the oxygen element, which contributes to the outer oxide layer, might originate from the oxide-catalyst not only from the residual oxygen in the apparatus at a high-growth temperature.

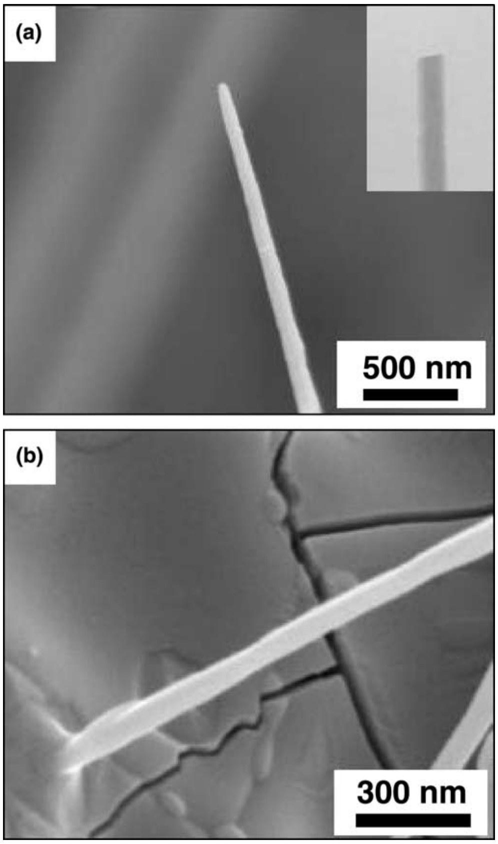

Fig. 2. SEM images of the tip (a) and the bottom (b) of nanowire synthesized on the NiO catalyst nanoparticles. Inset of (a) shows the TEM image of a typical nanowire tip without catalyst particles.

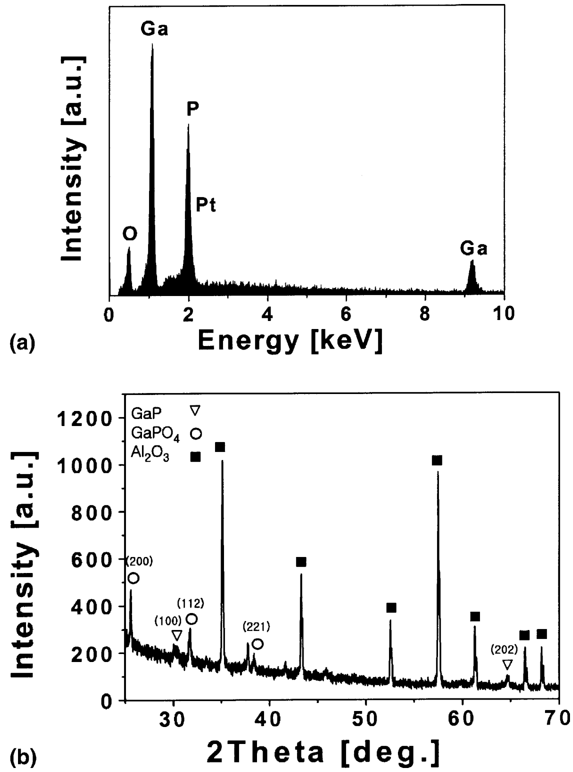

Fig. 3. EDX analysis (a) and XRD spectra (b) of GaP nanowires synthesized on the alumina substrate.

Our result indicates that the synthesis of GaP nanowire follows VLS growth mechanism. The growth of semiconductor nanowires has been explained by a vapor–liquid–solid (VLS) mechanism [16,17]. In our experiments, without catalyst nanoparticles, there were no GaP nanowires on the substrate but amorphous material only appeared. The fact indicates that metal-oxide nanoparticles play a key role in the growth of GaP nanowires. It is well known that transition metal-oxide nanoparticles have a catalytic effect on the nanowire produced by the VLS process, which is similar to metal catalysts [21]. For the synthesis of GaP nanowires, the metal-oxide (NiO) nanoparticles would be in a quasi-liquid state due to small-size effect at a reaction temperature (850–1000 °C). The quasi-liquid metal-oxide nanoparticles are surrounded by Ga, P, and GaP species inside a reaction tube. Subsequently, the Ga and P species dissolve into the metal-oxide particles and form a complex Ga–P–Ni–O alloy. Continuous feeding of Ga and P into the quasi-liquid nanoparticles leads to one-dimensional growth of GaP single crystal.

In summary, high-purity single-crystalline GaP nanowires were successfully synthesized on the NiO or CoO nanoparticle deposited alumina substrate by a simple vapor deposition method. The metal-oxide nanoparticles play a key role in the growth of GaP nanowires. The mixture source of Ga and GaP powders proves to be an ideal source for the high-yield fabrication of high-purity GaP nanowires. The synthesized nanowires consists of GaP core and $GaPO_4/Ga_2O_3$ shell. The synthesis of GaP nanowire follows the VLS growth mechanism.

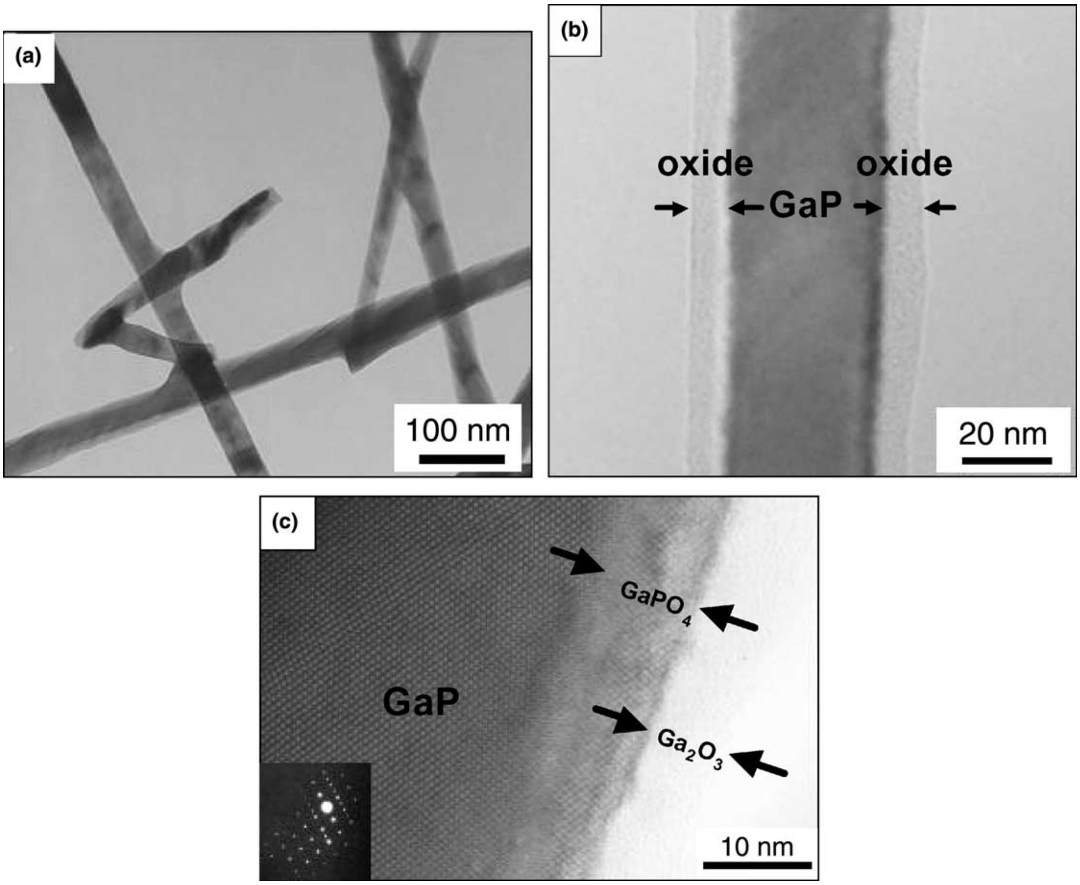

Fig. 4. (a) A low-dimensional TEM image of GaP nanowires. (b) A magnified TEM image of a typical GaP nanowire consisting of the core and the outer oxide layer. (c) HRTEM image of the microstructure of the core (GaP) and the outer shell-layer ($GaPO_4$ and Ga_2O_3). Inset shows the SAED pattern.

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