

Low Temperature Synthesis of Zn₃P₂ Nanowire

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Zn₃P₂ is an important II-V group semiconductor for optoelectronic applications since it has a direct bandgap in the range of 1.4-1.6 eV that corresponds to the optimum range for solar energy conversion [1-3]. In addition, abundance of its constituent atoms leads to increased feasibility of large scale development of devices, such as solar cells, infrared and/or ultraviolet sensors [4]. Syntheses of one-dimensional (1-D) nanostructures, such as tubes, wires, belts and ribbons, have drawn considerable attention because of potential applications in nanosize devices with various functionalities. A number of studies have reported synthesis of 1-D Zn₃P₂ nanostructures using various synthesis methods including thermochemical processes [5], thermal-assisted pulsed laser ablation [2], and chemical vapor deposition [6]. From the perspectives of technology, however, the synthesis temperatures in those reports are rather high ranging from 850 to 1400 °C [2, 4-7].

In this study, we report low temperature synthesis of Zn₃P₂ nanowires using a chemical reflux method.

Triethylphosphine (TOP) is supplied to a glass vessel, and a pre-cleaned Zn foil is placed on the top of a fritted glass in the glass vessel. When heated, the Zn foil is exposed to vapors of TOP. The vapors of TOP are refluxed back to the bottom of the glass vessel due to the cooling water at the top of the vessel. The heating was maintained at 350 °C for 2 h, and followed by air cooling to room temperature. Nitrogen gas is introduced throughout the synthesis process to prevent undesirable oxidation. The synthesized Zn₃P₂ nanowires were examined with Zeiss Supra 55 VP FE-SEM at 5 kV for overall morphology. Then, the Zn₃P₂ nanowires were carefully exfoliated from the Zn foil and dispersed on a Cu grid coated with lacey carbon film for TEM examination. TEM analysis was performed using JEOL JEM-2100F field emission TEM equipped with EDS at 200kV.

Figure 1 shows plan-views of FE-SEM image of the as-prepared sample. A lower magnification image of Fig. 1(a) shows that Zn₃P₂ nanowires are grown on the Zn foil in a highly homogeneous way, while a magnified image of Fig. 1(b) reveals that straight nanowires mixed with some of curly ones have a diameter distribution ranging from ~15 to ~70 nm. Transmission electron diffraction pattern (TED) shown in Fig. 2 turned out to match well with [111] net pattern of tetragonal α -Zn₃P₂ ($a=0.8095$ nm, $c=1.147$ nm and space group= $P4_2/nmc$), indicating that Zn₃P₂ nanowires are successfully synthesized by current method. High-resolution TEM (HRTEM) image combined with a FFT pattern shown in Figure 3 reveals that growth direction of the nanowires is along [101], which is in good agreement with previous results on a Zn₃P₂ nanowires synthesis [8]. In addition, the angle between growth direction and growth front (i.e., growth surface) is measured ~66°. Note that the angle between [101] direction and (101) plane in α -Zn₃P₂ is ~71° since α -Zn₃P₂ has tetragonal structure. This indicates that growth front structure may be very similar to that of (101) surface. A previous first-principle simulation study on β -tetragonal boron crystal showed that the highest surface energy plane is (101). Given that β -tetragonal boron has similar tetragonal structure, it can be presumed that α -Zn₃P₂ in this study grows on the highest surface energy plane along [101] direction [9].

References

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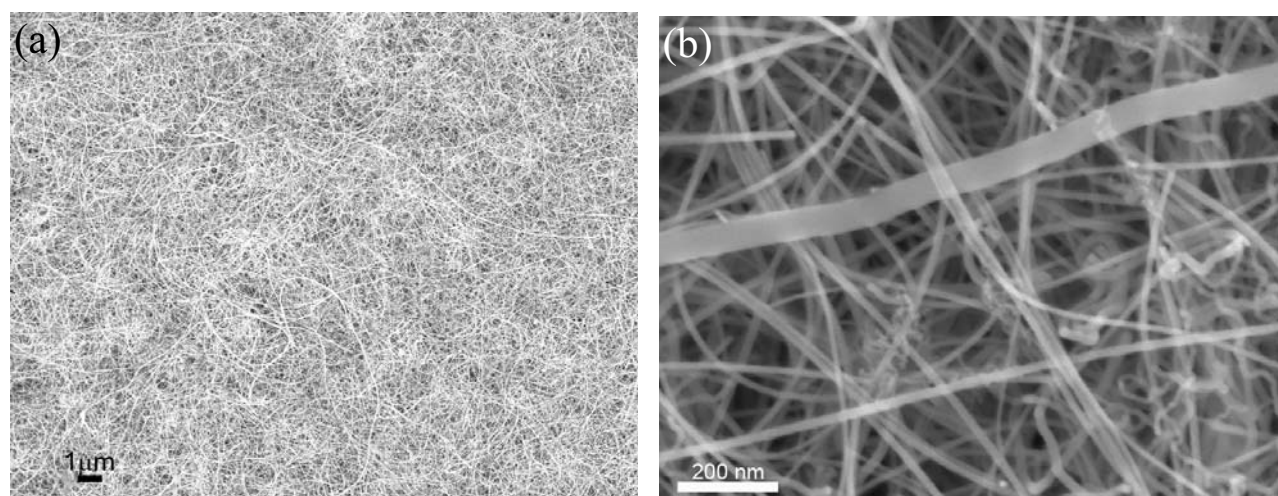


FIG. 1 Plan-view FE-SEM images of Zn_3P_2 nanowires at low magnification (a), and high magnification

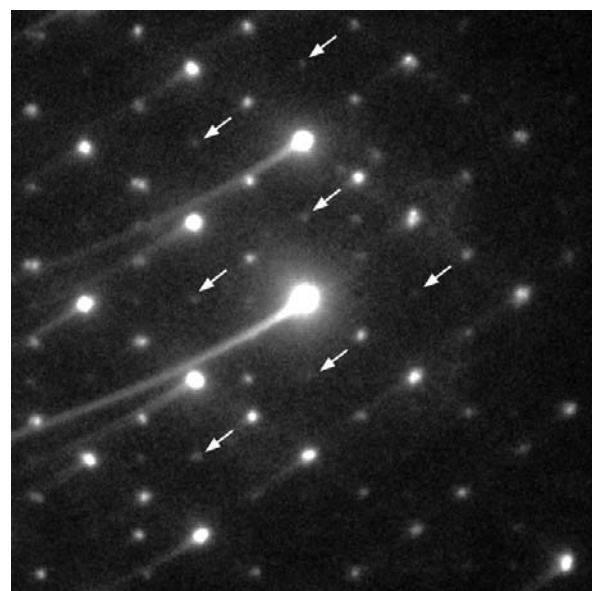


FIG. 2 TED pattern from a nanowire corresponding to [111] zone axis of tetragonal Zn_3P_3

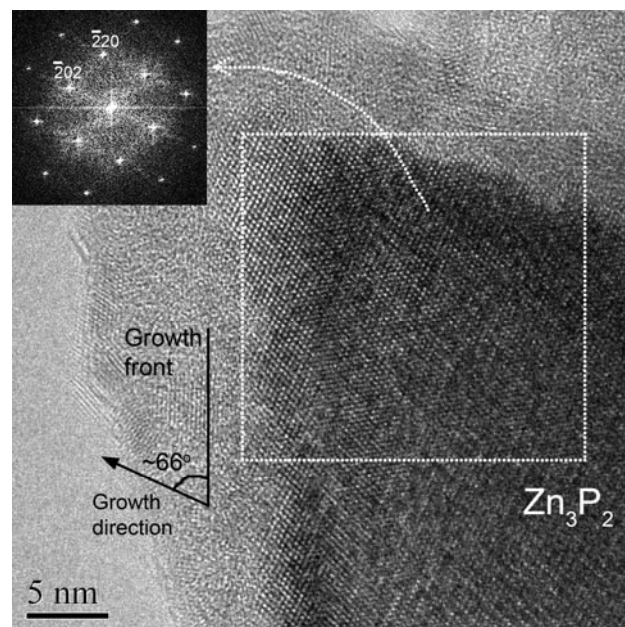


FIG. 3 HRTEM image from a Zn_3P_2 nanowire with a FFT pattern