



# Versatile self-catalyzed growth of freestanding zinc blende/wurtzite InP nanowires on an aerographite substrate for single-nanowire light detection

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## Impact statement

Semiconductor nanowires gain wider application in light and gas sensors, memory and memristive devices. In this article, we describe a fast and rather simple approach of fabricating catalyst-free InP nanowires with aspect ratio of 200. Important benefits of this method are stoichiometric chemical composition and freestanding arrangement of wires on the aerographite substrate. We demonstrate the development of a robust IR single-nanowire sensor stable at 20–300 K both in the air and vacuum atmosphere, with  $I_{ph}/I_{dark}$  ratio in the range 4–1.7.

The self-catalyzed growth of InP nanowires on an aerographite substrate is demonstrated in this study by using high growth rate hydride vapor-phase epitaxy technology. Nanowires with aspect ratios higher than 200 and diameters of 0.2–2  $\mu\text{m}$  were analyzed by scanning electron microscopy, transmission electron microscopy, energy-dispersive x-ray analysis, Raman spectroscopy, and photoelectrical characterization. The nanowires were found to be of constant diameter over their length, except for a well-faceted hexagonal tapered end. The novel growth process results in formation of self-catalyzed nanowires compatible with integrated circuit technology. Single-wire InP photodetectors with predominant sensitivity in the infrared spectral range have been prepared and characterized.

## Introduction

Semiconductor nanowires (NWs) find multiple applications in photonics, nanoelectronics, and thermoelectrics.<sup>1</sup> InP NW are promising candidates for nanoscale on-chip optoelectronic integration applications, exhibit poor absorption, and strong light polarization dependence due to their inherent anisotropic geometry.<sup>2</sup>

In this study, InP NWs were fabricated by means of hydride vapor-phase epitaxy (HVPE) on the aerographite (AG) substrates. AG is a carbon-based three-dimensional (3D) aero-material exhibiting structure composed of interconnected hollow tetrapods.<sup>3</sup> A series of new semiconductor-based aero-materials have emerged in recent years, many of which are related to nanocomposite

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doi:10.1557/s43577-023-00524-5



materials prepared on AG templates. AG templates decorated by semiconductor nanocrystals and microcrystals, such as GaN,<sup>4</sup> ZnO,<sup>5</sup> InP,<sup>6</sup> and CdS,<sup>7</sup> have been demonstrated for strain sensors, pressure sensors, and specific electromechanical applications.

Most commonly, vapor–liquid–solid (VLS) growth of NWs is stimulated by catalytic metal as golden nanoparticles, where solid NW precipitate from liquid droplets, supersaturated with the vapor-phase precursors.<sup>8</sup> However, catalyst residue is incompatible in certain applications. InP NWs, as well as NWs of other non-nitride III–V compounds, are usually grown by catalyst-assisted metal–organic chemical vapor deposition (MOCVD) or metal–organic vapor-phase epitaxy (MOVPE).<sup>8–22</sup> Among other technologies for producing InP NWs are chemical beam epitaxy (CBE),<sup>23</sup> chemical vapor deposition (CVD),<sup>24–30</sup> laser-assisted catalytic growth (LCG),<sup>31,32</sup> and molecular beam epitaxy (MBE).<sup>33,34</sup> We have shown in a previous study<sup>6</sup> successful formation of InP microrods and nanowires on an AG surface with golden nanoparticles as the catalyst via HVPE growth. Small NWs grown by using Au catalysts,<sup>6</sup> however, were immediately oxidized into In<sub>2</sub>O<sub>3</sub>.

Alternatively, self-catalyzed (or self-assisted) growth arises as the gold-free method. In the same way as golden nanoparticles induce growth of microrods and nanowires, the other metal nanoparticles, including In, could promote nanostructuring of InP.<sup>35</sup> A well-known example of self-catalyzed VLS method is gallium-assisted fabrication of GaAs nanowires by MBE. Here, a gallium nanodroplet is used instead of a gold one to gather arsenic precursors to precipitate GaAs underneath.<sup>36</sup>

InP crystallizes in two structures of zinc blende (ZB) and wurtzite (WZ) types with direct bandgaps of 1.42 and 1.35 eV at room temperature, respectively. It was suggested that small-radius NWs are produced with the WZ structure, while larger NWs are of the ZB structure, corresponding to the thermodynamically most stable bulk crystals. This was explained by the larger contribution of lateral surfaces to the total free energy of small radius fully formed NWs. It was found that InP NWs with diameters up to 40 nm are of the WZ structure, while for NWs larger than 40 nm in diameter, the intergrowth of WZ and ZB phases becomes more frequent.<sup>11</sup> Theoretical modeling suggested that the critical diameter for producing WZ InP NWs is approximately 60 nm.<sup>8</sup> According to other first-principles calculations with an empirical interatomic potential, the estimated phase transition threshold diameter for InP NWs is 32 nm.<sup>9</sup>

Up-to-date various results on InP NW fabrication were obtained. Most of them follow a catalyst-assisted route<sup>6,8–22,24,26–28,30,32</sup> and are produced by means of more hazardous methods as MOCVD and MOVPE.<sup>8–22</sup> In this work, we demonstrate the possibility to use a less complicated and hazardous HVPE method, which has important advantages of cheaper source materials, reduced capital equipment costs, and a higher growth rate compared to other technologies. We also demonstrate a single-step self-catalyzed process, excluding

impact of extrinsic catalysts. InP NWs often adopt a wurtzite lattice structure only below the diameter of 125 nm.<sup>12</sup> Low diameters and irregular shapes of InP NW in most of the known research represent an obstacle on the way of NW transfer and chip integration. Large-diameter NWs are required in many applications, such as single-NW photodetectors and photonic lasers, for better confinement of the photonic mode to the gain region.<sup>17</sup> In the current study, we demonstrate the fabrication method of freestanding InP NW via HVPE, having regular geometry and suitable for chip integration.



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