自己組織化による半導体ナノワイヤ立体ナノ構造
Self-assembled semiconductor nanowire hierarchical nanostructures

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Hierarchical nanostructures are gaining much interest due to their high surface areas and electrical properties. They have shown high potential in energy generation devices (solar cells, fuel cells, etc.), energy storage devices (secondary batteries, super capacitor, etc.) and in energy efficient electronics [1]. Semiconductor-nanowire-based hierarchical nanostructures have attracted much attention due to their potential applications in energy generation devices [1]. However, a general synthesis approach of semiconductor-nanowire-based hierarchical nanostructures with high material purity, high scalability and high controllability still remains challenging. For compound semiconductor nanowires, high material purity can be realized by bottom up self-catalyzed vapor-liquid-solid (VLS) synthesis approach [2]. On the other hand, the self-assembly approach has shown high potential for high scalability and controllability [3-5]. Here we report self-assembled semiconductor nanowire hierarchical nanostructures realized by two-time self-catalyzed VLS nanowire growth from self-assembled nanoparticles.

We synthesized the InP nanowires in a metalorganic vapor phase epitaxy (MOVPE) system in the self-catalyzed VLS mode [2-6]. Indium particles were formed by self-aggregation of indium atoms resulting from decomposition of TMIn material absorbed on the surface. To form indium nanoparticles on the nanowire side faces, we supplied only indium source material (TMIn) after the InP nanowire growth for 5 min. at 320 °C [6]. Indium nanoparticles were formed on nanowire side faces (Fig. 1a). The indium nanoparticles were then used for the second growth of InP nanowires via the self-catalyzed VLS mode to form InP nanowire branches (Fig. 1b). These nanotrees exhibit six nanowire branches along six equivalent <112> directions. By the multi VLS growth process from self-assembled nanoparticles, InP nanotree hierarchical nanostructures were formed (Fig. 1c). There are indium nanoparticles at tips of InP nanowire branches (Fig. 1d).

The synthesis approach is also applicable for other nanoparticles. We have shown that Bi nanoparticles could be formed on InP nanowire side faces in a self-assembly way [6]. The Bi nanoparticles were used for the second growth of InP nanowire branches via Bi-particle-catalyzed VLS mode (Fig. 2). We have confirmed the presence of Bi nanoparticles at tips of InP nanowire branches by compositional analysis. We have also clarified the structural property of both of InP-nanowire-based hierarchical nanostructures by TEM analysis. In contrast to the <111> growth direction of backbone nanowires, nanowire branches are oriented along <112> direction.

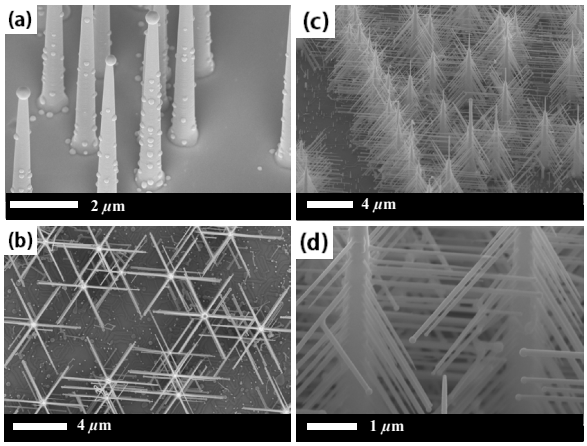

Fig. 1. (a) SEM image (tilt: 38º) of InP nanowires with indium nanoparticles on side faces. (b) Top view of InP nanotrees after the second growth of InP nanowire branches. (c) and (d) Side view (tilt: 38º) of InP nanotrees.

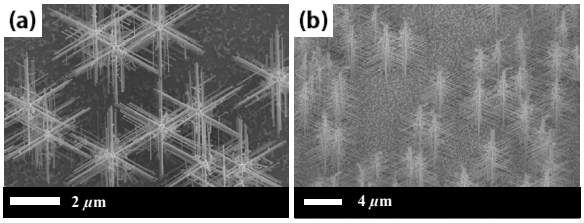

Fig. 2. SEM images (a) top view and (b) side view (tilt: 38º) of InP nanotrees after second growth of InP branches from Bi nanoparticles self-assembled on the side faces.

In conclusion, we have developed a general synthesis approach for self-assembled semiconductor nanowire hierarchical nanostructures with high material purity, high scalability and controllability. This work opens up new opportunities for development of novel applications by semiconductor-nanowire-based hierarchical nanostructures in energy generation and energy efficient device (solar cells, fuel cells, etc.) research field.

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References: [1] Hierarchical Nanostructures for Energy Devices, Edited by Seung H Ko and Costas P Grigoropoulos, Royal Society of Chemistry, 2014. [2] Zhang et al., Sci. Adv. **5** (2019) eaat8896. [3] Zhang, et al. Appl. Phys. Express **5** (2012) 055201 [4] Zhang, et al. ACS Nano **9** (2015) 10580. [5] Zhang, et al. Nanotechnology **29** (2018) 155202. [6] Zhang et al., 2019秋応用物理会議, 19p-E317-3.