Electronic Supplementary Material (ESI) for Nanoscale.

Seeding Layer Assisted Selective-area Growth of As-rich InAsP Nanowires on InP Substrates

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Supplementary Information

Growth of InAs nanowires on InP (111)B with InAs seeding layer

The growth parameters of InAs NWs on InAs (111)B substrates, *i.e.* fixed gas flow of TMIn at 4.54×10^{-2} sccm and V/III ratio of 8, were directly transferred to the growth on InP (111)B substrates. The growth temperature for InP substrates is 575°C, 15°C lower than 590°C which was normally used for selective-area InAs NWs on InAs substrates. Such temperature difference was to compensate the discrepancy of surface temperature on SiO_2 mask caused by different thermal conductivities of those two substrates[1]. Almost 100% vertical yield was achieved for both growths, and the NW dimensions, *i.e.* average diameter and height were similar in two cases, as shown in Figure S1(a) and (b).

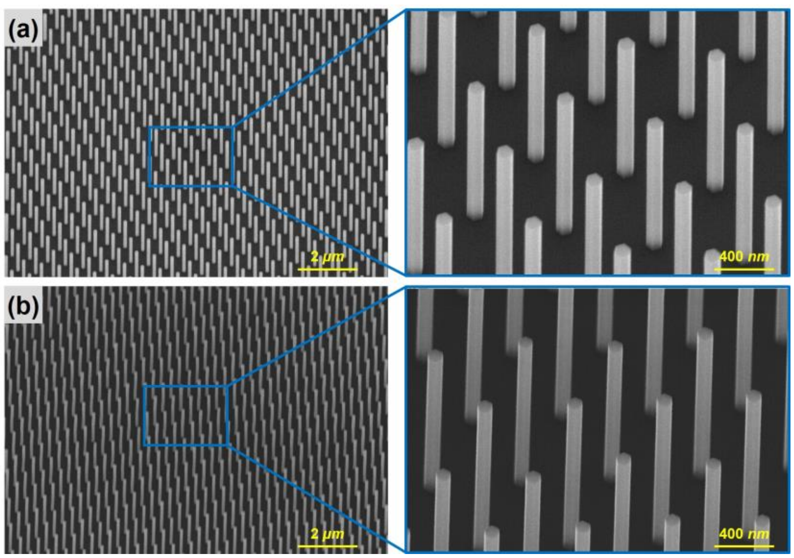

Figure S1. *Comparison of InAs NW growth on (a) InP (111)B and (b) InAs (111)B substrates. The nanohole patterns are the same, i.e. 40 nm in diameter and 600 nm in pitch. The growth time of vertical NW section is 2.5 mins. The average diameter and height in (a) are 96 nm and 1656 nm, respectively.*

Growth of InAsSb nanowires on InP (111)B with InAs seeding layer

Followed by the previous study of InAsSb NW on InAs (111)B[2], the same growth strategy was applied to obtain NW on InP (111)B with nearly 100% vertical yield, as shown in Figure S2(a). The outer rectangular trench, or ‘fence’, was used to accumulate excess antimony (Sb) from outside diffusion and avoid Sb condensation. The growth parameters are as follows: growth temperature of 530°C, vapor phase of 0.6 (x_v = *[TDMASb]/([TBAs]+[TDMASb])*) where TBAs flow was kept at 4.45×10^{-2} sccm, and a V/III ratio of 4.2. The equivalent growth temperature on InAs substrates was approximately 545°C with 15°C offset. Photoluminescence (PL) performed at 77 K is shown in Figure S2(b), giving peak energy of 0.427 eV and full-width-half-maximum of 60.6 meV. Compared with the calibrated relationship between Sb solid-phase and PL peak energy[1], the Sb composition is estimated between 0.039 and 0.046; however, InAsSb NWs grown at 540°C on InAs substrates resulted in a much higher composition of 0.128[2]. A higher V/III ratio leads to lower Sb corporation[2], and therefore the lower Sb composition in this growth is due to a higher nominal V/III ratio as well as even higher actual V/III resulting from adatom absorption by the trench.

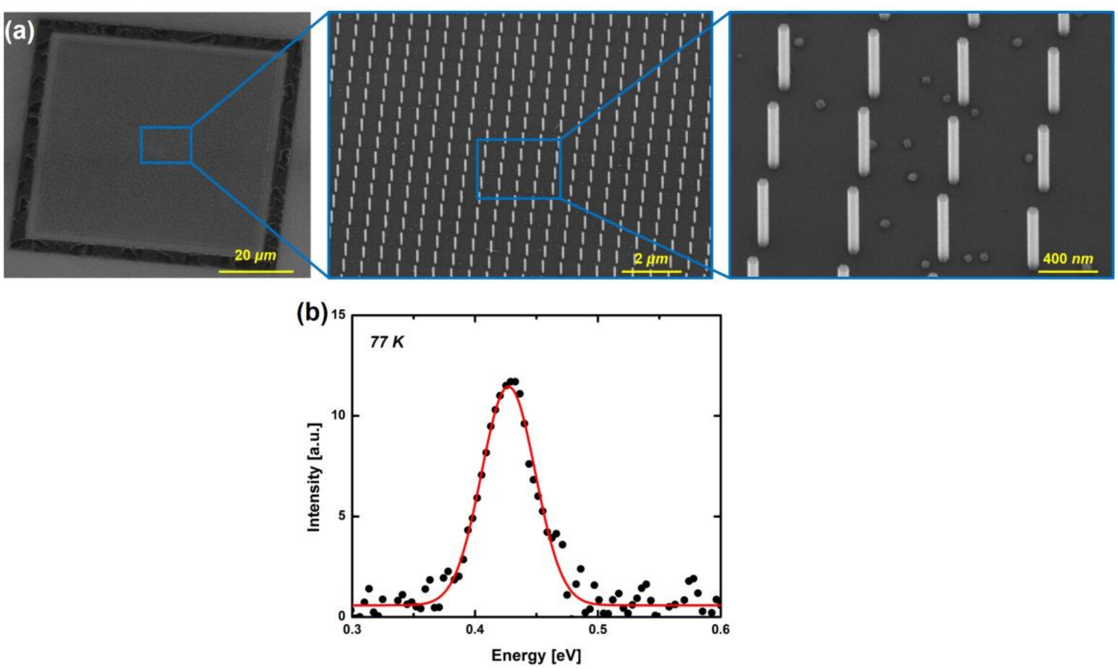

Figure S2. *(a) As-grown* $InAs_{1-x}Sb_x$ *(0.039 < x < 0.046) on InP (111)B substrates. (b) PL intensity as a function of energy at 77 K. The measured intensity is shown in black dots, and the fitted Gaussian function is given in solid red line.*

Growth of InAsP nanowires on InAs (111)B (without InAs seeding layer)

The growth of high-uniform InAsP nanowires were performed on InAs (111)B at 590°C with V/III ratio of 32, as shown in Figure S3(a). PL spectrum clearly shows two emission peaks – one from InAsP nanowires and one from InAs substrate. This is the first reported InAsP nanowire growth on InAs substrate by catalyst-free selective area epitaxy. The growth samples were compared in the same manner as InP substrates discussed in the main text.

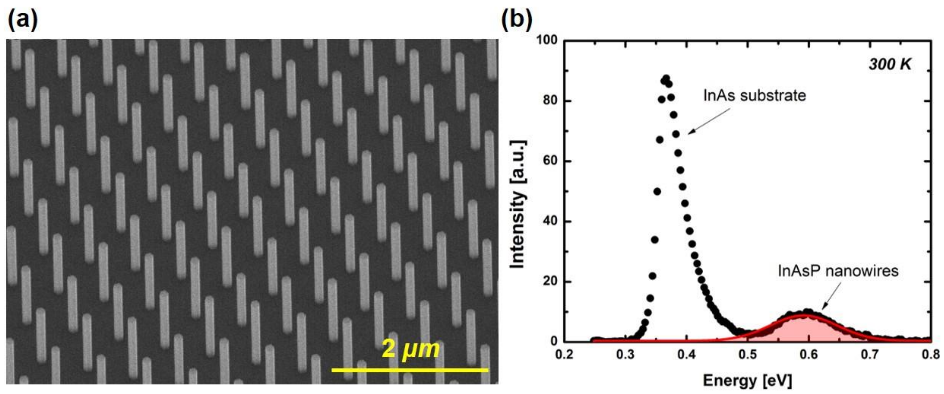

Figure S3. *(a) As-grown InAsP on InAs (111)B substrates. (b) PL intensity as a function of energy at 300 K. The measured intensity is shown in black dots, and the fitted emission from InAsP nanowires by Gaussian function is highlighted in solid red line.*

Growth of InP nanowires on InP (111)A

The growth of high-uniform InP nanowires on InP (111)A were performed at 660°C and V/III ratio of 37, as shown in Figure S4. The growth conditions were similar to the ones in literature[3].

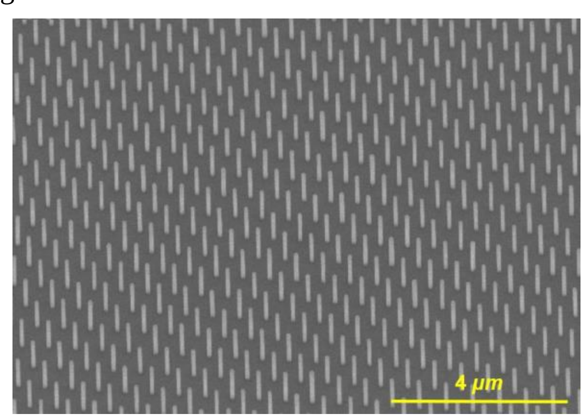

Figure S4. *As-grown InP on InP (111)A substrates.*

Hypothetical bowing relation between phosphorus solid phase and growth temperature

It is highly possible that there would be a bowing relation between the optimized temperature and phosphorus composition. To better explain the hypothesis, we fitted the optimized temperature as a function of phosphorus solid phase, as shown in Figure S5. Here, we define the optimized temperature as the temperature to achieve the maximized aspect ratio.

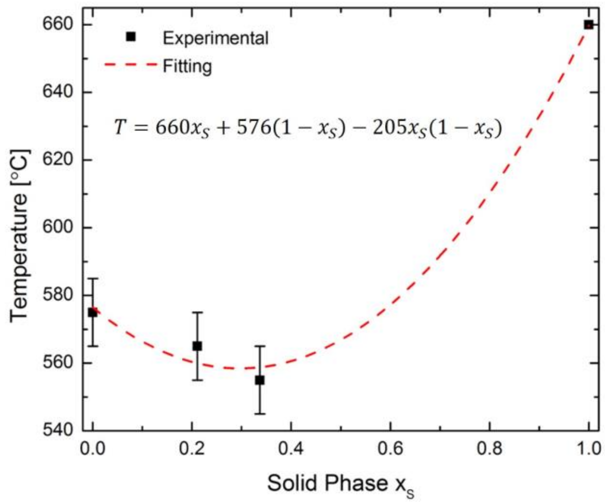

Figure S5. *Hypothetical bowing relation between phosphorus solid phase and optimized temperature grown by catalyst-free SAE mode.*

Uniformity of composition across nanowires

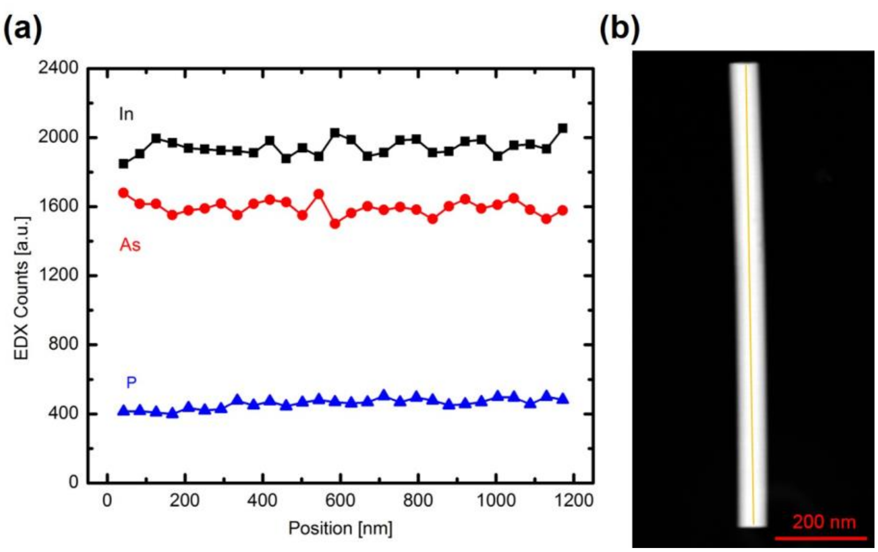

Figure S6. *(a) EDX composition profile along axial direction of nanowire. (b) STEM image of nanowire.*

The line-scan of EDX was performed to demonstrate the composition uniformity. The EDX profile shown below in Figure S5 was obtained from the nanowires grown at temperature of 555°C with vapor phase of 0.90.

Energy-gap fitting by photoluminescence

The energy-gap of $InAs_xP_{1-x}$ at room-temperature is described by[4]

$$E_g^{InAs_xP_{1-x}}(300K) = x \cdot E_g^{InAs}(300K) + (1-x) \cdot E_g^{InP}(300K) - 0.078x \cdot (1-x)$$

Since there have been no reported studies for temperature-dependent energy-gap of thin film As-rich InAsP, we assume that energy-gap at other temperature obeys to the same equation as well

$$E_g^{InAs_xP_{1-x}}(T) = x \cdot E_g^{InAs}(T) + (1-x) \cdot E_g^{InP}(T) - 0.078x \cdot (1-x)$$

where the energy-gap of InAs and InP follow Varshni equation written as

$$E_g^{InAs}(T) = E_g^{InAs}(0K) - \frac{\alpha_{InAs} \cdot T^2}{\beta_{InAs} + T}$$

$$E_g^{InP}(T) = E_g^{InP}(0K) - \frac{\alpha_{InP} \cdot T^2}{\beta_{InP} + T}$$

The values of *Eg (0K*), α, and β are experimentally determined.

References

1. Maycock P. D. "Thermal conductivity of silicon, germanium, III-V compounds and III-V alloys" *Solid State Electron.* **1967**, 10, 161-168.

2. Farrell A. C.; Lee W.-J.; Senanayake P.; Haddad M. A.; Prikhodko S. V.; Huffaker D. L. High-quality InAsSb nanowires grown by catalyst-free selective-area metal-organic chemical vapor deposition. *Nano Lett.* **2015**, 15, 6614-6619.

3. Mohan P.; Motohisa J.; Fukui T. "Controlled growth of highly uniform, axial/radial direction-defined, individually addressable InP nanowire arrays" *Nanotechnology* **2005**, 16, 2903-2907.

4. http://www.ioffe.ru/SVA/NSM/Semicond/GaInAsP/bandstr.html