

Supplementary Information for “Monolithic integration of InP on Si by molten alloy driven selective area epitaxial growth”

Dmitrii V. Viazmitinov^{a,‡}, Yury Berdnikov^{b,‡}, Shima Kadkhodazadeh^c, Anna Dragunova^d, Nickolay Sibirev^b, Natalia Kryzhanovskaya^d, Ilya Radko^e, Alexander Huck^e, Kresten Yvind^a and Elizaveta Semenova^a

^a DTU Fotonik, Technical University of Denmark, Kongens Lyngby DK-2800, Denmark.

^b ITMO University, Kronverkskiy 49, 197101 St. Petersburg, Russia.

^c DTU Nanolab—National Centre for Nano Fabrication and Characterization, Technical University of Denmark, Kongens Lyngby DK-2800, Denmark.

^d National Research University Higher School of Economics, 16 Soyuza Pechatnikov, St Petersburg 190008, Russia.

^e Center for Macroscopic Quantum States (bigQ), Department of Physics, Technical University of Denmark, Kongens Lyngby DK-2800, Denmark.

S1. Mask fabrication

First, a 50 nm stoichiometric silicon nitride (Si_3N_4) film was grown on a Si (100) wafer using low pressure chemical vapor deposition (Fig. S1(a)). The pattern formed by deep UV lithography (Fig. 1(b)) was transferred into Si_3N_4 film by inductively coupled plasma reactive ion etching (ICP RIE) (Fig. S1(c)). The resulting mask pattern consists of an openings array with diameter of around 200 nm and alternating pitch size 400-800 nm. Subsequent KOH wet chemical etch was implemented to release a family of four equivalent Si {111} planes in the mask openings forming inverted pyramidal shaped holes (Fig. S1(e)). The results for different pitch sizes are similar, and only structures with pitch 800 nm (corresponding to 5% open area) are discussed in the manuscript.

S2. Epitaxial growth

The epitaxial growth was performed in a low-pressure (80 mbar) MOVPE system Turbodisc® Discovery 125 with H_2 as a carrier gas. Wafer temperature was precalibrated using a Realtemp® pyrometer on a bare silicon wafer. Trimethylindium (TMIn) and phosphine (PH_3) were used as IIIrd and Vth group precursors respectively. Prior the growth the Si wafer covered with mask were cleaned using standard RCA process and annealed for 15 minutes *in-situ* in the MOVPE reactor at 750 °C in H_2 ambient. The MADSAG process implies two main steps. The first step was the formation of an In-P melt in the V-shaped holes in Si, defined by the {111} planes inside Si_3N_4 mask openings. For the melt deposition TMIn and PH_3 were used with fluxes 3.7×10^{-6} mol/min and 4×10^{-3} mol/min respectively. The second step was annealing of the sample under PH_3 flow to crystallize the In melt into the cubic InP. For the samples with ramped PH_3 flow it was increasing linearly up with the slope 2.7×10^{-4} mol/min per minute.

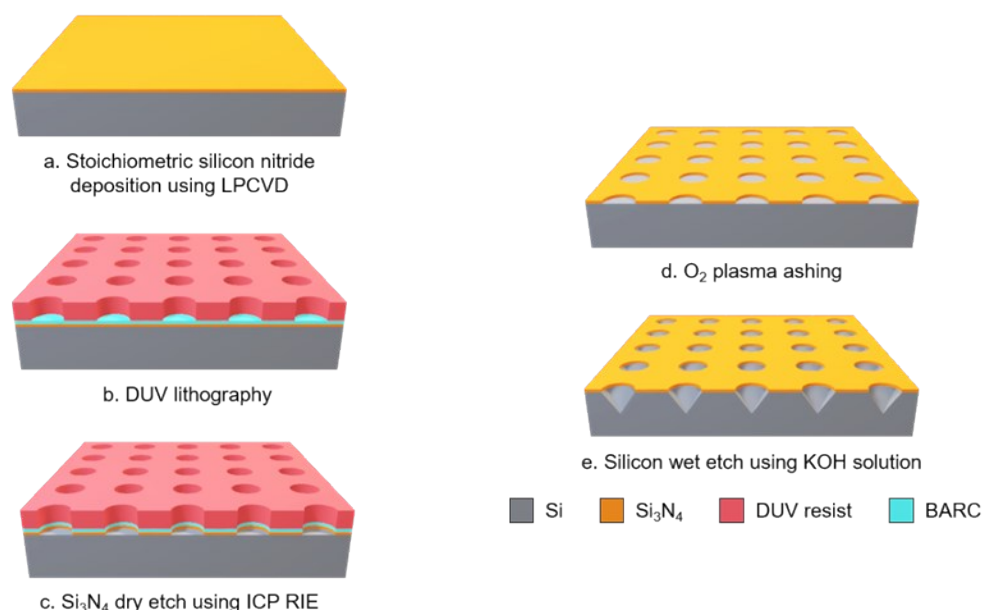


Fig. S1. Si_3N_4 mask fabrication process

S3 STEM investigations

TEM and STEM images were recorded using an FEI TEM instrument equipped with a field emission electron gun and aberration correction on the probe forming lenses. The microscope was operated at 300 kV. In STEM, the probe size and convergence angle were $\sim 1.0 \text{ \AA}$ and 18 mrad, respectively. High-angle annular dark-field STEM images were acquired with a collection angle of 48 mrad. Thin film specimens in the cross-section geometry were prepared by focused ion beam milling (FIB). Cross-sections with approximate dimensions of $15 \mu\text{m} \times 5 \mu\text{m} \times 1 \mu\text{m}$ from the samples were cut, lifted out and mounted on TEM compatible grids, followed by additional thinning of the samples to electron transparency ($\sim 100 \text{ nm}$ in thickness). The FIB milling was carried out at 30 kV. The FIB current used during the rough milling and cutting stage was $\sim 1 \text{ nA}$. The beam current was reduced gradually during the thinning stage from 1 nA to $\sim 20 \text{ pA}$, followed by a final cleaning of the thin films at 5.0 kV beam energy and 50 pA beam current.

S4. STEM and FFT investigations

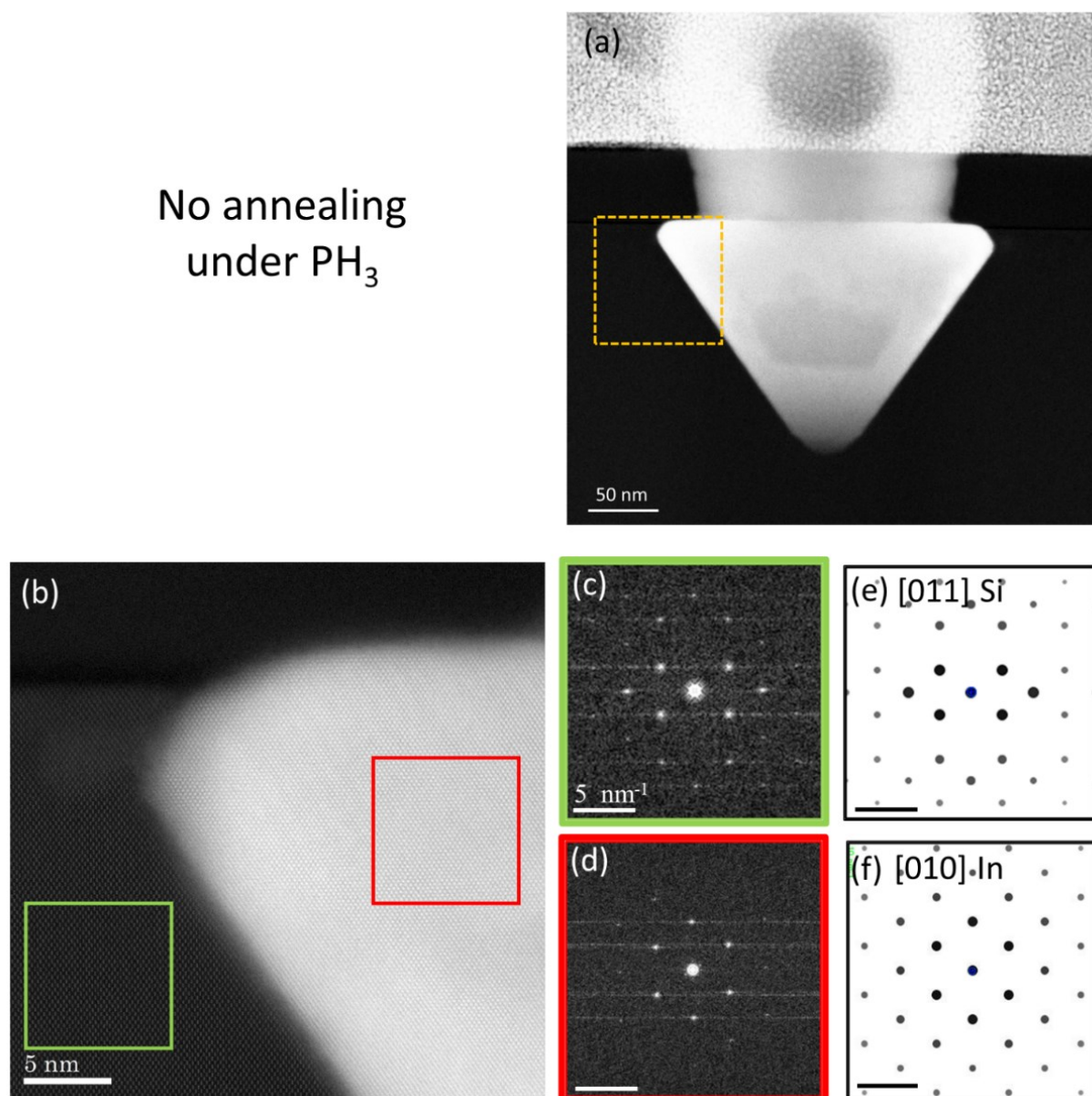


Fig. S2. (a) STEM and (b) high resolution HAADF STEM image of the cross-section of sample obtained without annealing under PH_3 flux. FFT patterns of the marked areas of the Si and inverted pyramid regions in (b) are shown in (c) and (d). Simulated electron diffraction patterns (using commercial software JEMS) from an fcc Si crystal along the $[110]$ orientation is shown in (e) and that for a body centred tetragonal (bct) In crystal along the $[010]$ orientation is shown in (f). Comparing (b) and (d) confirms that the Si region is viewed along the $[110]$ zone axis, and that the pyramid region is metallic In with a bct crystal structure, viewed close to a $[010]$ zone axis.

Annealing
under PH_3
flux of
 1.2×10^{-2}
mol/min

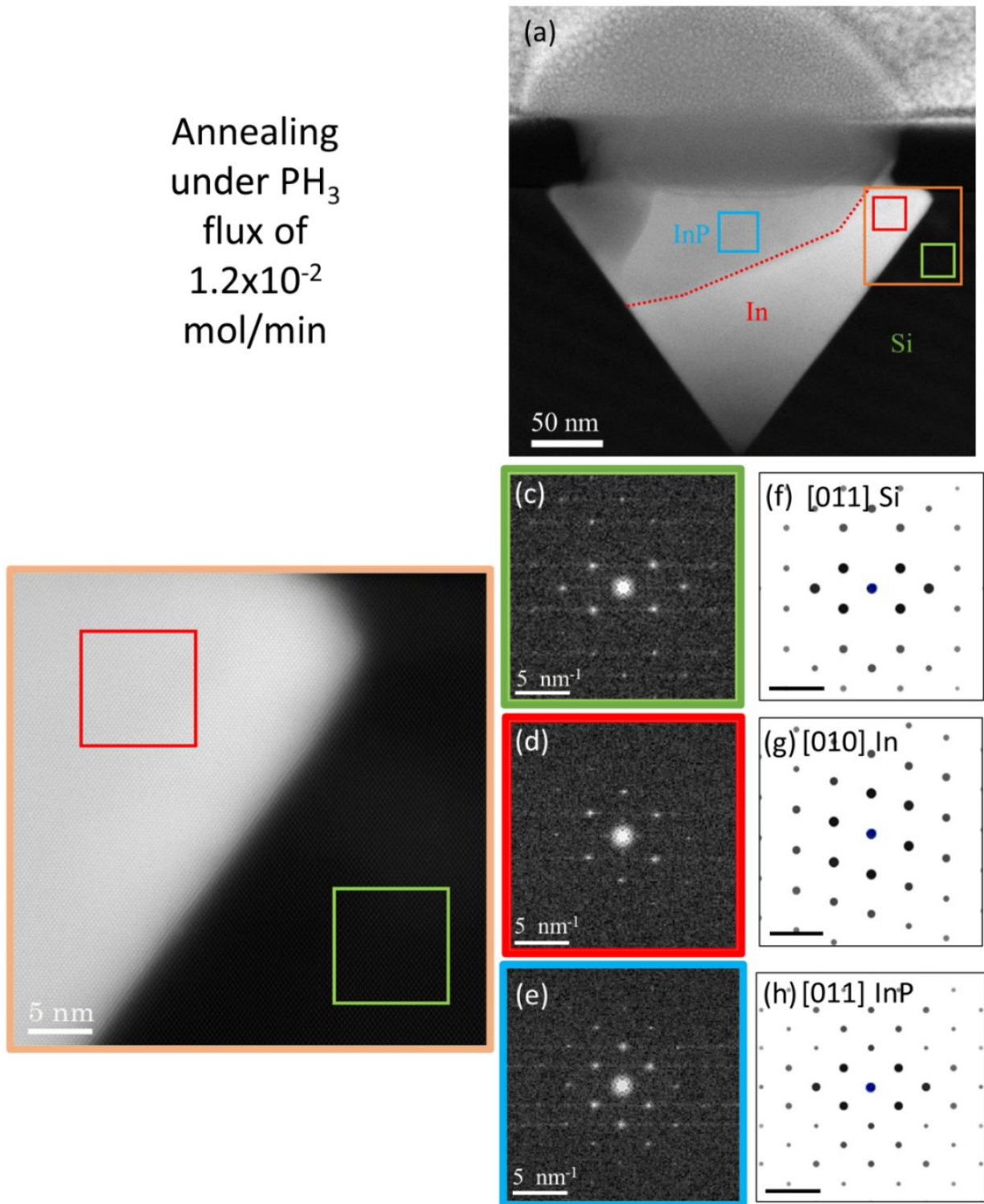


Fig. S3. (a) STEM and (b) high resolution HAADF STEM image of the cross-section of sample obtained after annealing under PH_3 flux of 1.2×10^{-2} mol/min. FFT patterns of the marked areas of the Si and inverted pyramid regions in (b) are shown in (c-e). Simulated electron diffraction patterns from an fcc Si crystal along the [011] orientation is shown in (f), that for a bct In [010] is in (g) and that for fcc InP [011] is in (h). Comparing (c) and (d) confirms that the Si region is viewed along the [011] zone axis, and that the pyramid region contains both metallic bct In viewed close to a [010] zone axis and fcc InP viewed along the [011] zone axis.

Annealing
under PH_3
flux of
 2.2×10^{-2}
mol/min

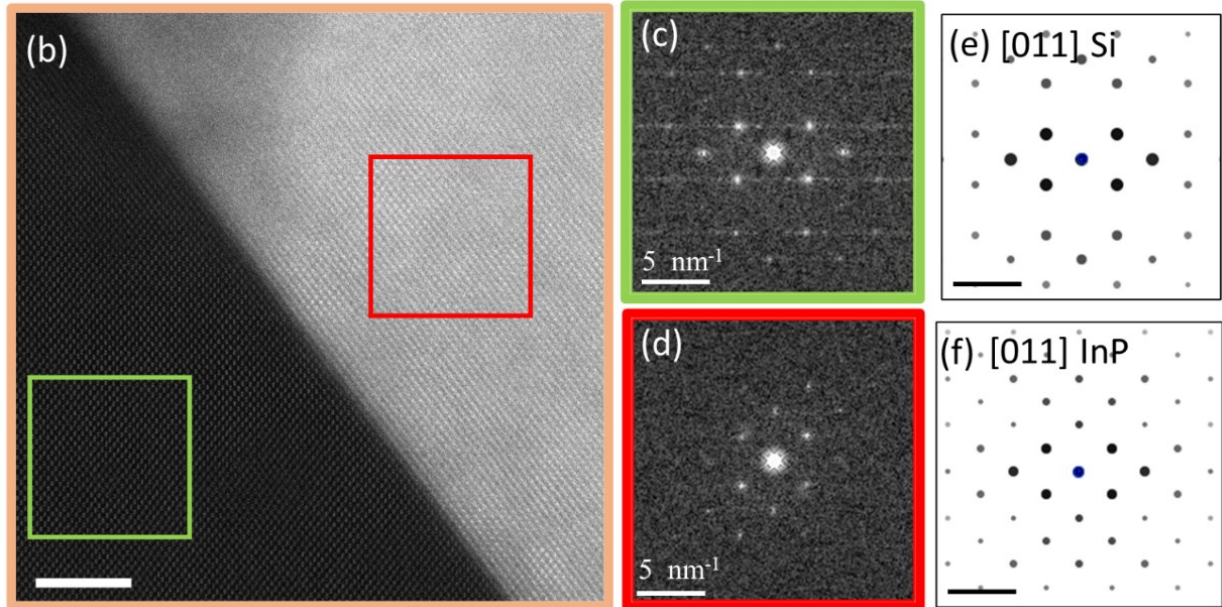
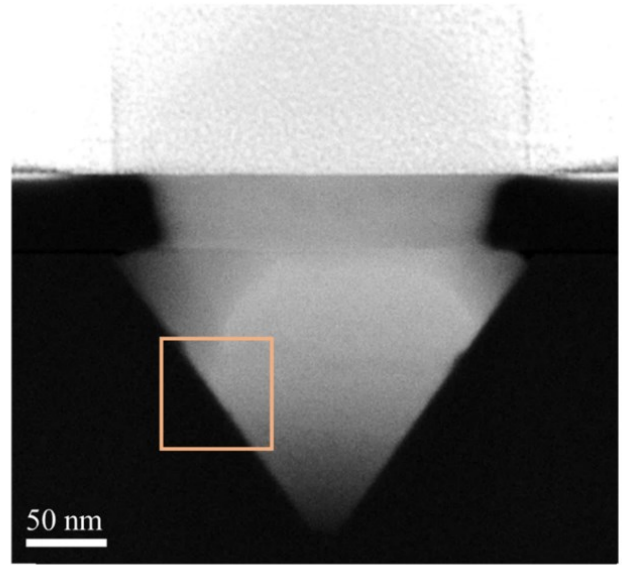


Fig. S4. (a) STEM and (b) high resolution HAADF STEM image of the cross-section of sample obtained after annealing under PH_3 flux of 2.2×10^{-2} mol/min. FFT patterns of the marked areas of the Si and inverted pyramid regions in (b) are shown in (c) and (d). Simulated electron diffraction patterns from an fcc Si crystal along the $[011]$ orientation is shown in (e) and that for fcc InP crystal along the $[011]$ orientation is shown in (f). Comparing (c) and (e) confirms that the Si region is viewed along the $[011]$ zone axis, and that the pyramid region is InP with a fcc crystal structure, viewed close to a $[011]$ zone axis.

S5 Optical characterization

For the temperature dependent PL measurements, the samples were mounted in a flow cryostat Janis ST-500. PL was excited by the second harmonic of a continuous wave operating Nd:YLF laser with a wavelength of 527 nm. An exciting laser spot (normal incidence) was focused on the array of InP nanoinsertions by a 10x microscope objective (Olympus, NIR). The emitted light was collected from the sample by the same objective, directed by mirror optics into a grating monochromator (Spectral Products DK480) and detected by a cooled Si single-channel detector.

Fig. S5a shows the evolution of the PL spectra from a broad peak at 290 K to a narrow peak at 78 K obtained from the optimized samples annealed at 600 °C. A small shoulder at higher energies is observed only at low temperatures, which may be related to signal from strained InP. We observe that the integrated peak intensity at 78 K is about 12 times higher than of the corresponding value at 290 K. The obtained PL signals for each acquisition temperatures can be fitted by sum of two peaks. Fig. S5b shows the example for PL spectra obtained at 200 K. The peak positions obtained from the best fit correspond well to zincblende(ZB) and type-II band alignment peaks observed in previous works¹⁻³. In optimized samples, we observe only ZB and Type-II peaks and no signal corresponding to InP in wurtzite phase (WZ), as marked by arrows in Fig. S5b. Fig. S5c shows the peak positions as functions of acquisition temperatures obtained in our measurements (filled symbols). Our results correlate well with the observations on PL spectra obtained from mostly ZB InP nanoneedles¹ shown with open symbols in Fig. S5c. The ZB peak energy fits well the Varshni temperature dependence $1.417 - 4.9 \times 10^{-4} T^2 / (T + 327)$ (shown by solid line in Fig. S5c) for ZB InP¹ with the bandgap energy at 0K of 1.417 eV. Thus the observed PL signal demonstrate the high crystalline quality of ZB InP insertions.

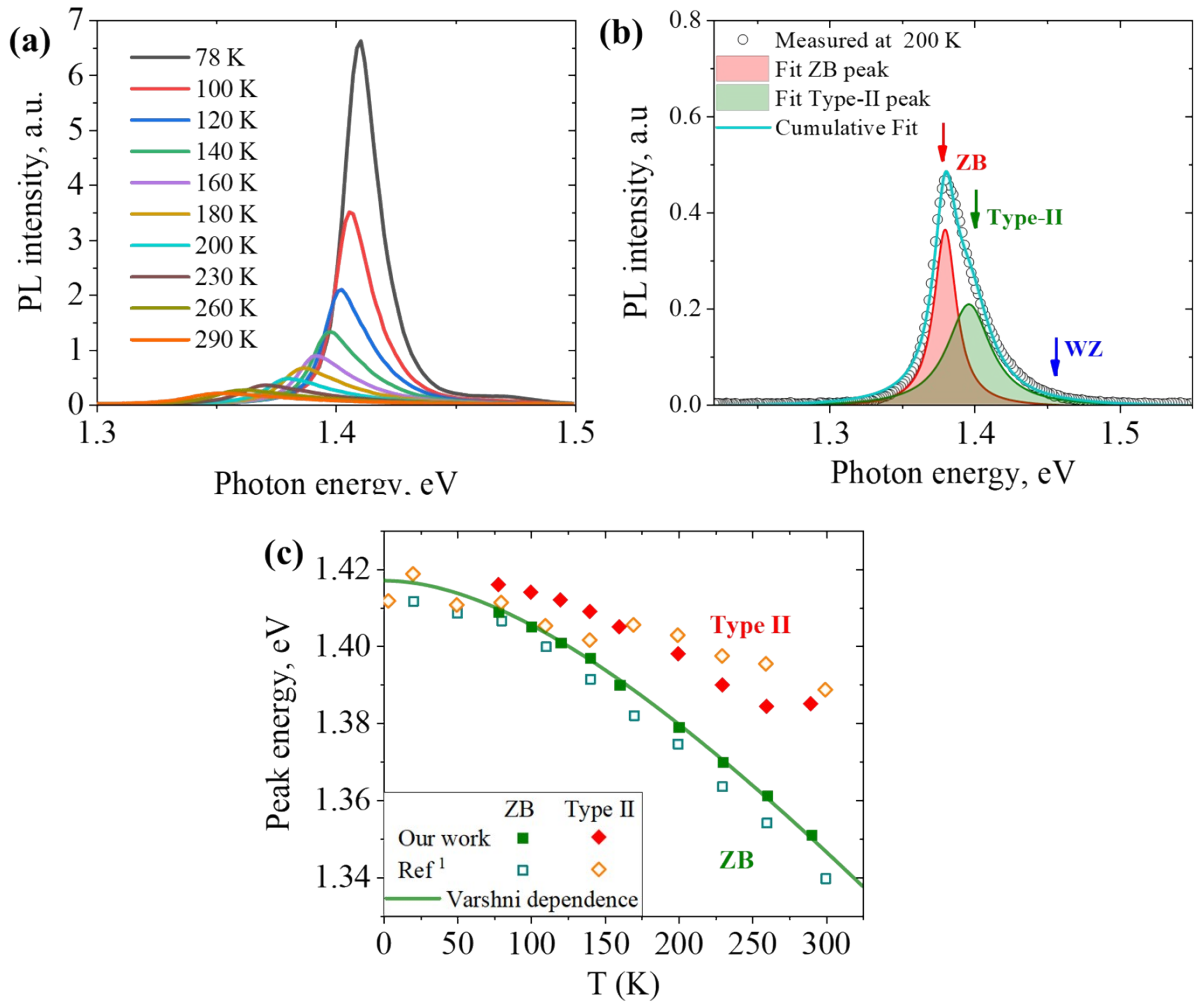


Fig. S5. (a) PL spectra obtained at 78-290 K from optimized MADSAG InP/Si structures. (b) Sample plot of two-peak fit of the PL signal acquired at 200 K. The arrows indicate the expected peak positions for InP in zincblende(ZB), type-II and wurtzite (WZ) crystal phases. (c) Temperature dependence of ZB (squares) and Type-II (diamonds) peak energies at different temperatures. We present our data (filled symbols) in comparison with the results of Ref. ¹ (open symbols). Solid line shows the Varshni dependence for ZB InP.

S6. XRD pole figures

Structural properties were investigated by high resolution x-ray diffractometry (XRD) using a Rigaku SmartLab diffractometer, equipped with a Ge(220) $\times$ 2 monochromator. The measurements were taken in pole figure geometry using Cu $K\alpha_1$ line.

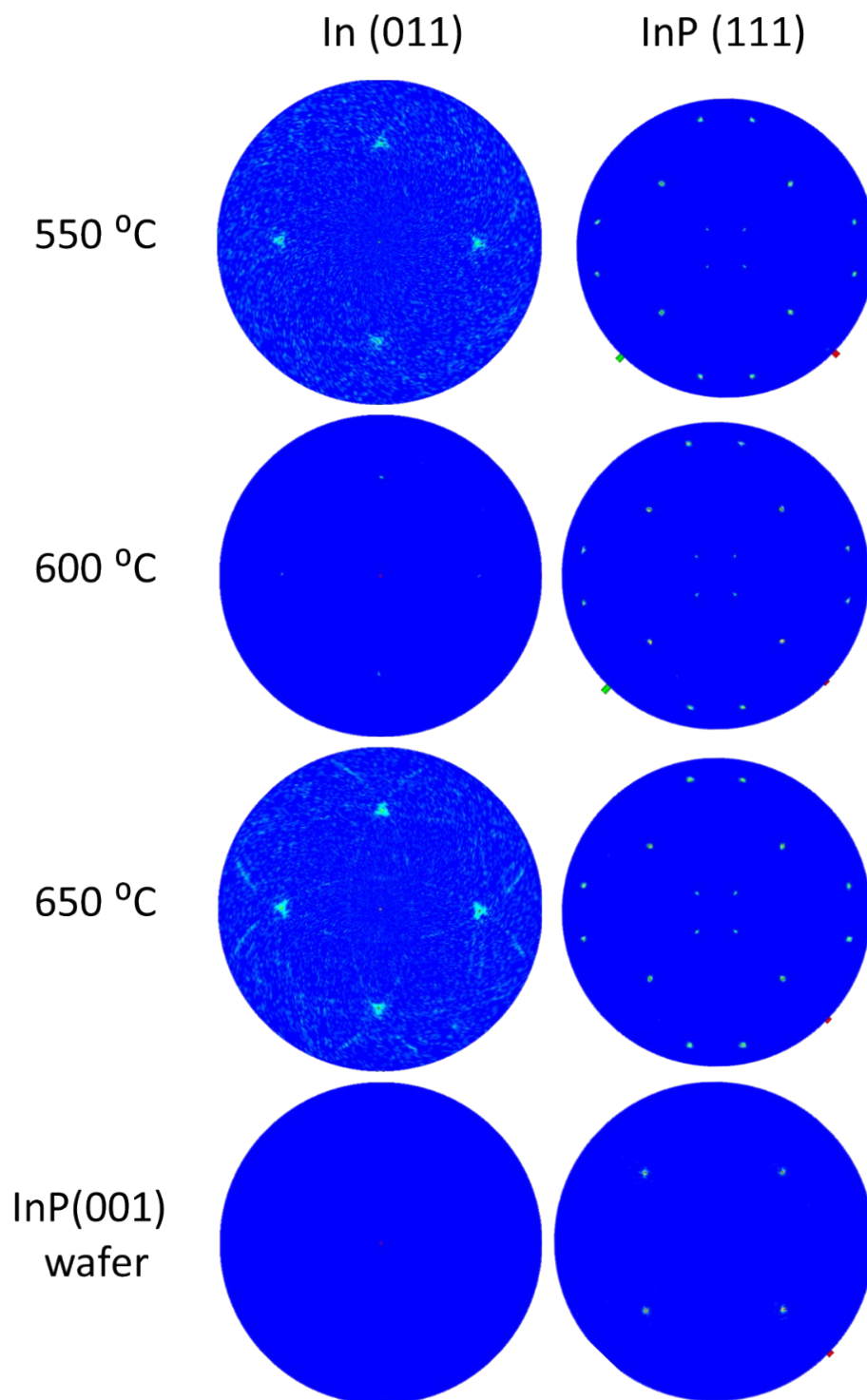


Fig. S6. XRD measurement of InP insertions into Si(100) substrate and InP wafer for the reference in pole figure configuration.

S7. Growth modeling

Within the first-order approximation, N_P^{cryst} , given by Eq. (2), of the main text, is proportional to the duration of crystallization t_{cryst} and pore area A . The duration of the process t_{cryst} can be evaluated in the analysis of the temporal evolution of the crystallization stage. We assume that InP crystallization rate v is limited by P transport from the vapor phase and proportional to P concentration in the liquid $v \approx \alpha C$, where $\alpha = D/\sigma'$ is the ratio of the diffusion coefficient D of P in the liquid In to the surface area per atom σ' . Dynamics of P concentration can be described as

$$N_{In} dC/dt = AF - \alpha \eta C, \quad (S1)$$

where η is a geometric coefficient. Therefore, P concentration after nucleation decreases exponentially to the saturated value C_f :

$$C(t) = \exp(-\alpha \eta t)(C_0 - C_f) + C_f, \quad (S2)$$

and thus, the contribution of P desorption can be neglected. $\int_0^{t_{cryst}} \alpha C(t') dt' = \sqrt{2}a/h$. The duration of crystallization stage can be found from $\int_0^{t_{cryst}} \alpha C(t') dt' = \sqrt{2}a/h$, where h is the InP monolayer height and a is the opening size. In the estimation of t_{cryst} we neglect the exponential term assuming that $\alpha t_{cryst} \gg 1$ and $C_f \ll C_0$, and thus, obtain

$$t_{cryst} \approx \frac{\sqrt{2}a/h - C_0}{C_f \alpha}. \quad (S3)$$

Next, we insert the expressions for t_{cryst} from Eq. (S3) and $C(t)$ from Eq. (S2) into Eq. (1) of the main text to obtain

$$N_{In}^{res} = N_{In} - N_P^0 - AF \frac{\sqrt{2}a/h}{C_f \alpha} + AF \frac{C_0}{C_f \alpha} + A \frac{\sqrt{2}a/h}{\tau \alpha}. \quad (S4)$$

N_P^0 is proportional to the steady-state P concentration in the first stage $N_P^0 \approx N_{In} C_0 \sim F \tau$ assuming that most of the alloy consists of In. The characteristic time of evaporation τ can be estimated by considering the equilibrium between liquid and vapor phases at concentration of P in liquid In C_{eq} . In this case the evaporation rate is proportional to P vapor partial pressure P_p . Thus the detailed balance implies $P_p \sim C_{eq}/\tau$ or $\tau \sim C_{eq}/P_p$. Both C_{eq} and P_p are exponential functions of temperature: $C_{eq} \sim \exp[-T_{eq}/T]$ with $T_{eq} = 11411 \text{ K}^4$ and $P_p \sim \exp[-T_{ev}/T]$ with $T_{ev} = 10800 \text{ K}^5$. Therefore $\tau \sim C_{eq}/P_p \sim \exp[-T_{vap}/T]$ with $T_{vap} = 611 \text{ K}$. And thus, $C_0 \sim \tau$ increases with the substrate temperature.

The temperature dependence of α is characterized by the intensity of diffusion in the melt $\alpha \sim \exp[-T_D/T]$ with $T_D = 3838 \text{ K}^6$. Saturated crystallization rate $v_f = \alpha C_f$ is limited by the rate of P influx F and considered temperature-independent due to complete decomposition of phosphine in liquid phase. Therefore, I as the function of T can be written as

$$I_{In(011)} = I_0 + I_1 \exp\left[-\frac{T_{vap}}{T}\right] + I_2 \exp\left[\frac{T_{vap} + T_D}{T}\right] \quad (S5)$$

with temperature-independent term $I_0 \sim (N_{In} - FA\sqrt{2}a/(\alpha C_f h))$, and increasing and decreasing exponential functions of the

$$I_1 \sim \left(AF \frac{1}{C_f \alpha} - N_{In} \right) \quad \text{and} \quad I_2 \sim \left(A \frac{\sqrt{2}a/h}{\tau \alpha} \right).$$

growth temperature with the corresponding prefactors

The three main processes contribute to the nonmonotonic temperature dependence of the residual amount of In and thus intensity of In(011) XRD signal: i. motion of the growth front which affects the crystallization duration t_{cryst} ; ii. P supersaturation in liquid In before nucleation given by N_P^0 ; iii. evaporation of P after the nucleation during InP crystallization.

The temperature dependence of t_{cryst} is represented by the term $AF C_0 / C_f \alpha$ in the right hand side of Eq. (S4) and contributes to increasing exponent $I_1 \exp[-T_{vap}/T]$ in Eq. (S5). The amount of P before nucleation N_P^0 reduces the prefactor of the increasing exponent. The evaporation of P is represented by the term $A\sqrt{2}a/h\tau\alpha$ in Eq. (S4) and obviously more intensive at higher temperatures. Hence, it constitutes the decreasing exponent $I_2 \exp[(T_{vap} + T_D)/T]$ in Eq. (S5).

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