Supporting Information for:

Solution Phase Synthesis of Indium Gallium Phosphide Alloy Nanowires

Nikolay Kornienko¹, Desiré D. Whitmore¹, Yi Yu¹, Stephen R. Leone¹,²,⁴, Peidong Yang*¹,³,⁵,⁶

¹Department of Chemistry, ²Department of Physics and ³Department of Materials Science Engineering, University of California, Berkeley 94720, United States
⁴Chemical Sciences Division and ⁵Materials Sciences Division, Lawrence Berkeley National Lab, Berkeley CA 94720, United States
⁶Kavli Energy Nanosciences Institute, Berkeley, California 94720, United States

*Correspondence to: p_yang@berkeley.edu

Table of Contents:

Figure S1. TEM In/Ga growth seeds................................................................. 2
Figure S2. TEM of InP and GaP NWs................................................................. 2
Figure S3. Composition and diameter control.................................................. 3
Figure S4. XRD of InₓGa₁₋ₓP NWs ................................................................. 4
Figure S5. Electron diffraction of InₓGa₁₋ₓP NWs .............................................. 5
Figure S6. Raman spectra of InP and GaP .......................................................... 6
Figure S7. UV-Vis absorption of InₓGa₁₋ₓP NWs .............................................. 7
Figure S8. EELS analysis .............................................................................. 8
Figure S9. EELS data fitting ......................................................................... 9
Figure S10. Individual NW PL ........................................................................ 10
Figure S11. Normalized PL Intensity .............................................................. 11
**Figure S1.** STEM image of In/Ga alloy seeds (A) and their corresponding EDS elemental maps (B, C).

**Figure S2.** TEM analysis of products when In, Ga, and P precursors were mixed together in one step before heating reveals that separate InP and GaP NW’s form. EDS analysis of wires A and B shows pure InP while corresponding analysis of wires D and C indicates pure GaP.
Figure S3. Composition of the resulting NWs is controlled by the precursor ratio of TMIn and TEGa (A) and the diameter is controlled by the total precursor concentration (B). TEM images of NWs of increasing diameter (C-F).
Figure S4. XRD of InP, In$_x$Ga$_{1-x}$P, and GaP (A-D) indicate that the NWs all consist of primarily the zincblende crystal structure.
**Figure S5.** Electron diffraction of InP, In$_x$Ga$_{1-x}$P and GaP NWs rotated perpendicular to the [011] planes with composition indicated (A-E) reveals that the NWs grow in the [111] direction. Simulated electron diffraction pattern (F) for zincblende InP viewed perpendicular to the [011] planes matches the experimental data. A simple structural model (G) shows several low Miller index planes of the zincblende crystal structure.
Figure S6. Raman spectra of (A) InP NWs and wafer and (B) GaP NWs and wafer show consistent phonon modes positions and line shapes.
**Figure S7.** UV-Vis absorption spectrum for indirect band gap NWs (A) shows a below band gap absorption and only a sharp rise in absorption at energies greater than the direct band gap of the material. In contrast, direct band gap NWs (B) feature a sharp rise in absorption at the band edge.
Figure S8. EELS analysis of the NWs was performed using a monochromated ZLP with a FWHM of 0.17 eV (A). For power law fitting (B,C) the background was subtracted from the raw data and the inelastic signal was extracted. Band gap extraction using the inflection point from raw data (D) gave slightly different results but the trend of band gap vs. composition was consistent (E).
Figure S9. EELS onset fitting of GaP (A), In$_x$Ga$_{1-x}$P (B-D) and InP (E) NWs. GaP and InP EELS spectra can be well fitted with indirect band gap (E$^{3/2}$) and direct band gap (E$^{1/2}$) models while In$_x$Ga$_{1-x}$P have contributions from both direct and indirect band gaps. As the indium composition is increased, the EELS data resembles more the E$^{1/2}$ model, indicating a greater contribution from the direct band gap. The $E_g$ describes the extracted band gap value.
Figure S10. PL measurements correlating to the composition of individual NWs were taken to obtain an exact composition-band gap relation. The SEM image of an individual NW (A) was matched with the optical image of the same NW on a silicon substrate (B) to correlate its EDS spectrum (C) and elemental composition to the PL energy (D). The comprehensive measurements are summarized in (E) and follow the same trend as figure 5 in the main text.
Figure S11. PL intensity, normalized to the NW volume, was used as another method to pinpoint the direct-indirect band gap transition. SEM images (A) were used to measure volume and correlated to the optical image of the NW on a silicon substrate (B) and the PL intensity (C). The PL intensity, acquired under identical conditions for all samples, was divided by the NW volume to generate the normalized PL intensity vs. PL energy diagram (D). The yellow dotted line represents the expected PL intensity as the $\Gamma$ valley moves higher in energy than the X valley, which scales as: $\frac{1}{1+Be^{(E_{\Gamma}(x)-E_{X}(x))/kT}}$, where B is a constant and $E_{\Gamma}(x)$ and $E_{X}(x)$ are the band minima as a function of composition.