Supporting Information to "Towards Defect-Free Thin Films of the Earth-Abundant Absorber Zinc Phosphide by Nano-Patterning"

Simon Escobar Steinvall,[a] Elias Z. Stutz,[a] Rajrupa Paul,[a] Mahdi Zamani,[a] Nelson Y. Dzade,[b] Valerio Piazza,[a] Martin Friedl,[a] Virginie de Mestral,[a] Jean-Baptiste Leran,[a] Reza R. Zamani,[c] and Anna Fontcuberta i Morral[a,d]*

[a] Laboratory of Semiconductor Materials, Institute of Materials École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
[b] School of Chemistry, Cardiff University, Main Building, Park Place, CF10 3AT, Cardiff, United Kingdom
[c] Centre Interdisciplinaire de Microscopie Électronique, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
[d] Institute of Physics, École Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland
* Corresponding Author: anna.fontcuberta-morral@epfl.ch

Methodology

Substrate Fabrication. Indium phosphide (100) substrates were prepared by depositing 30 nm of silicon dioxide (SiO_2) using plasma-enhanced chemical vapour deposition (PECVD) in an Oxford Plasmalab System 100. The samples were then spin-coated with 40 nm ZEP resist before they were exposed using a Raith EBPG5000+ electron beam lithography system operating at 100 kV. The samples were then cold developed using n-amylacetate which was kept at -18 °C for one minute followed by one minute in isopropanol. The resist was then descummed for 10 seconds at low power in a Tepla GiGAbatch oxygen plasma system, and subsequently the oxide was etched using SPTS APS Dielectic etcher for 30 seconds. The resist was then stripped using the previously mentioned oxygen plasma system for 10 minutes at a high power. Finally, a 10 second dip in a 1:39 BHF and deionised water solution was performed, and after a rinse the substrates were ready for introduction into the MBE system.

Growth. The growth was carried out in a Veeco GENxplor MBE system. First, the substrate was degassed for one and a half hours at 150 °C in the load lock, and then for 2 hours at 300 °C in the buffer module. The samples were then introduced to the growth module (base pressure ~1.5×10^{-10} Torr), where the native oxide was removed by degassing at a manipulator temperature of 580 °C for 10 minutes under a phosphorus atmosphere (phosphorus flux $> 1 \times 10^{-6}$ Torr), supplied by a MBE Komponenten GaP sublimation source. Fluxes are defined by the beam flux monitor (BFM) reading. The manipulator is then ramped to the growth temperature (280-300 °C for intrinsic substrates, 280 °C for doped substrates), and a five-minute zinc pre-deposition was performed (zinc flux of 3.4×10^{-7} Torr). Growth was then carried out for a time ranging from five minutes to six hours depending on the sample, using a zinc base pressure of 6.04×10^{-7} Torr whilst varying the phosphorus flux between 1.09×10^{-7}Torr and 4.35×10^{-7} Torr.

Electron Microscopy. SEM images were acquired in a Zeiss Merlin operating at 3 kV and 100 pA using an InLens detector. TEM lamellae were prepared by focused ion beam in a Zeiss NVision 40 CrossBeam FIB and SEM setup on a sample grown for 4 hours at 280 °C at a V/II ratio of 0.39 on a p-type indium phosphide substrate and a sample grown for 6 hours on intrinsic indium phosphide with a V/II ratio of 0.5 to observe coalescence. Conventional TEM and STEM analysis were performed in a FEI Talos TEM operating at 200 kV, while aberration-corrected STEM imaging was performed in a FEI Titan Themis operating at 200 kV, equipped with a cold field-emission gun, monochromator, and a CEOS aberration correctors (probe and image). GPA was done using the Gatan Digital Micrograph plugin GEM-GPA v10.1. The AC-HAADF-STEM images were treated using a radial Wiener filter.

Optical Characterisation. Room temperature PL was carried out on a sample grown for 4 hours at a V/II ratio of 0.5 and at 290°C using a 488 nm Ar^+ laser (25 µW) and Andor iDus DV420A-OE detector using 3s integration with 20 accumulations.

Atomic Force Microscopy. Normal AFM was done using a Bruker FastScan AFM equipped with an Si tip operating in contact mode. Conductive AFM was performed in an Asylum Research Cypher VRS AFM with a platinum−silicide (PtSi-FM) tip. Contact mode was used to acquire the I-V curves. The cantilever is grounded while a bias is applied across the sample. The tip is employed as the top contact and the bottom contact is made using silver paste to join the backside of the InP chip to the stage.

Atomic Models. The unit cell model was illustrated using VESTA using data from the Crystallography Open Database based on the report by Stackelberg and Paulus.[1] The 3D core-shell models were created using the Rhodius software package.[2]

Density Functional Theory. The electronic structure was calculated through density functional theory (DFT), using Vienna Ab initio Simulation Package (VASP) to implement the periodic boundary conditions.[3–5] Valence and core electron interactions were described with the projected augmented wave (PAW) method.[6,7] The GGA-PBE functional was used to calculate the electronic exchange-correlation potential, and the Grimme DFT-D3 method was use to account for the long-range dispersion forces.[8–10] To converge the total energy of the system a plane-wave basis with a kinetic energy cut-off of 600 eV was used. This allowed it to converge to within 10^{-6} eV and for the residual Hellmann-Feynman forces to reach 10^{-3} eV $Å^{-1}$ for the relaxed atoms. A 5×5×3 Monkhorst–Pack *K*-points mesh was used to sample the Brillouin zone of the bulk Zn_3P_2.[11] For the (001), (101), and (112) surfaces, *K*-points meshes of 5×3×1, 5×3×1, and 3×3×1 were used, respectively, to ensure electronic and ionic convergence. The $P4_2/nmc$ space group was used in the META-DISE code to generate the (001), (101), and (112) surfaces, ensuring zero dipole moment perpendicular to the surface plane.[1,12] The surface energies calculated and visualisations of the different surfaces are shown in Figure S1.

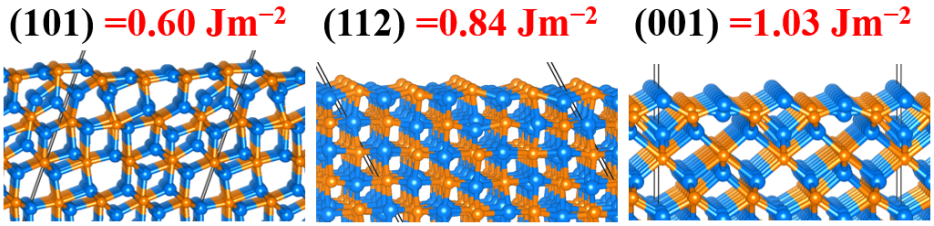

Figure S1. Surface energies for the different planes considered and an illustration of the structures used for the DFT calculations.

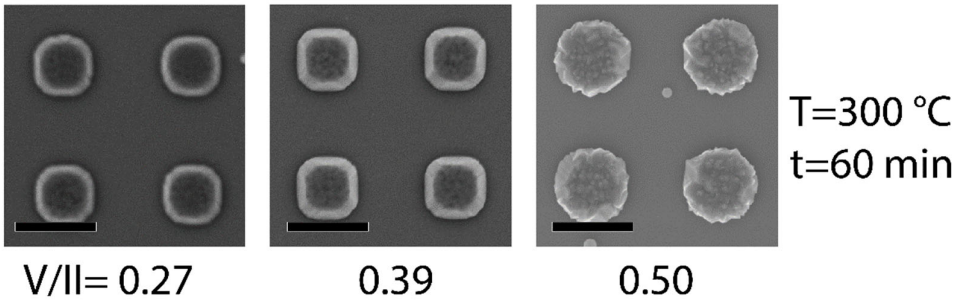

Figure S2. SEM images of a V/II series grown at a manipulator temperature of 300 °C, showing how the ideal growth conditions shift from a V/II ratio of 0.5-0.63 to 0.27-0.39 (500 nm scale bars).

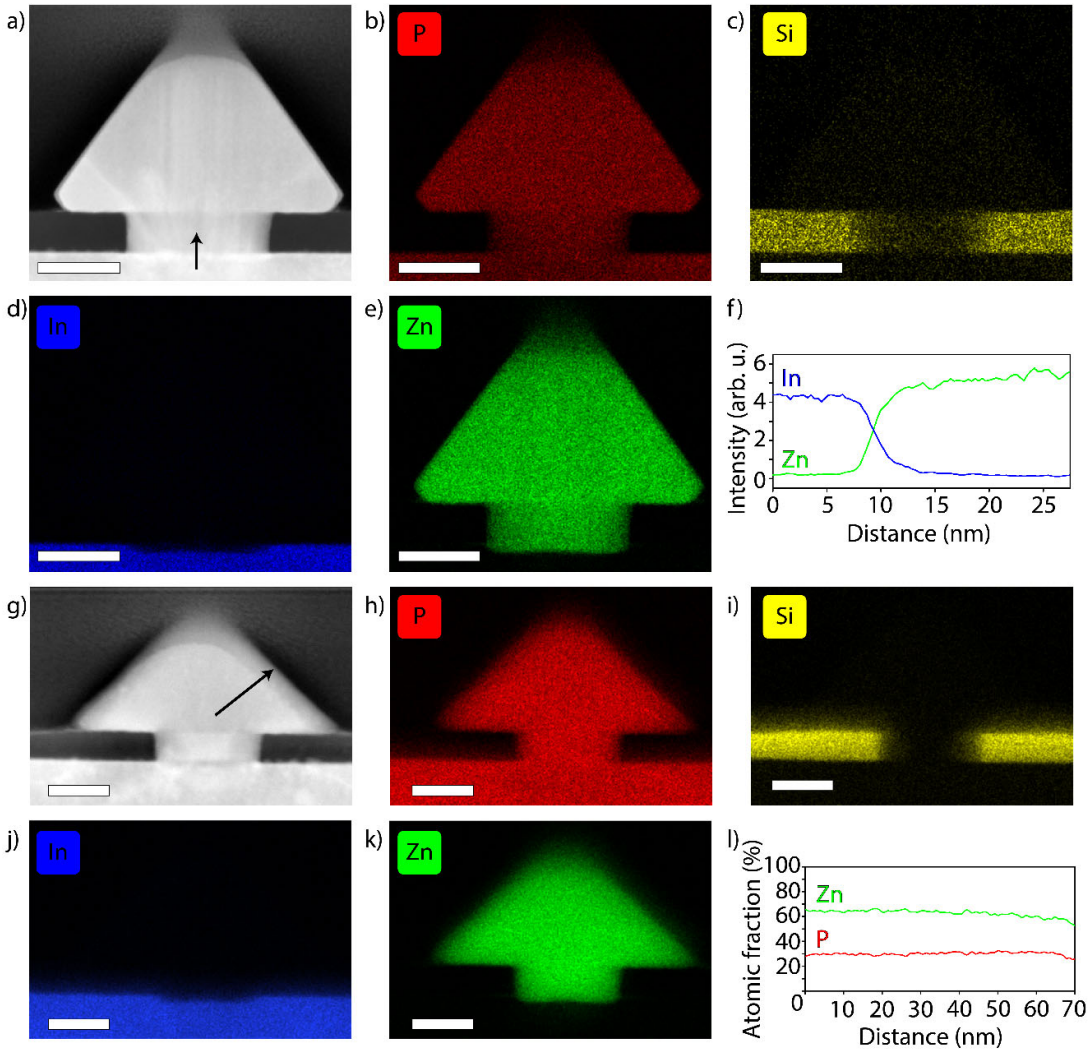

Figure S3. (a) HAADF image of pyramid grown in a 30 nm nominal hole along [100]. (b-e) EDX maps of P, Si, In, Zn of the pyramid. (f) Line-scan of the interface between the base and the pyramid showing a diffuse boundary between In and Zn in the area as indicated by the arrow in (a). (g) HAADF image of a pyramid grown in a 30 nm nominal hole along [110]. (h-k) EDX maps of P, Si, In, Zn of the pyramid. (l) Line-scan showing a homogeneous composition along the pyramid along the area indicated by the arrow in (g). (50 nm scale bars.)

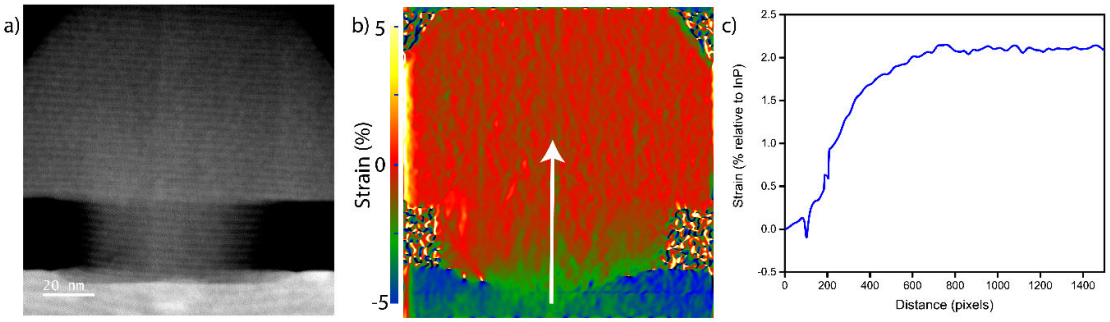

Figure S4. (a) AC-HAADF-STEM of a pyramid grown from a 30 nm nominal hole. (b) Strain map acquired through GPA in the in-plane (xx) direction, perpendicular to the surface normal. (c) Line-scan along the arrow in

(b) showing the strain relaxation of the zinc phosphide (right) in relationship to the indium phosphide (0) as it grows out from the hole.

References

1 M. V. Stackelberg and R. Paulus, *Z. phys. Chem*, 1935, **28**, 427–460.
2 S. Bernal, F. J. Botana, J. J. Calvino, C. López-Cartes, J. A. Pérez-Omil and J. M. Rodríguez-Izquierdo, *Ultramicroscopy*, 1998, **72**, 135–164.
3 G. Kresse and J. Hafner, *Phys. Rev. B*, 1993, **47**, 558–561.
4 G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251–14269.
5 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
6 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
7 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
8 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
9 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396–1396.
10 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
11 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188–5192.
12 G. W. Watson, E. T. Kelsey, N. H. de Leeuw, D. J. Harris and S. C. Parker, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 433–438.