Controlled polytypic and twin-plane superlattices in III–V nanowires

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Introduction

- Semiconductor nanowires show promise for use in nanoelectronics, fundamental electron transport studies, quantum optics and biological sensing.

- Such applications require a high degree of nanowire growth control, right down to the atomic level.

- However, many binary semiconductor nanowires exhibit a high density of randomly distributed twin defects and stacking faults, which results in an uncontrolled, or polytypic, crystal structure.

- Nanowires made from III–V materials, such as GaAs, GaP, InP and InAs often show randomly distributed rotational twin planes and stacking faults.

- A closely related problem is that of polytypism: most III–V nanowires will be composed of a mixture of wurtzite (WZ) and zinc-blende (ZB) segments.

- These effects have an impact on the nanowires optical properties and may pose problems in future nanoelectronic devices due to electron scattering at stacking faults or twin planes.

In this paper…

- *InAs nanowires have superior properties for both high-speed and low-power nanoelectronics, as well as for fundamental electron transport studies, spintronics and quantum computations.*

- *Full control of the crystal structure of InAs nanowires by varying nanowire diameter and growth temperature.*

- *Selectively tuning the crystal structure, fabricated highly reproducible polytypic and twin-plane superlattices within single nanowires.*

Terminology

Polytypic: Mixture of wurtzite (WZ) and zinc-blende (ZB) segments.

Wurtzite and Zinc-blende: Explained in the next slide.

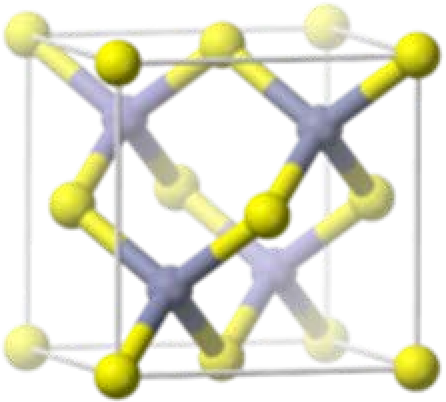
Twin-plane and Stacking faults: Wurtzite, ABABABAB...
Zinc-blende, ABCABCABC...each letter represents a bilayer)

WZ, ABABABAB... $\xrightarrow{\text{misplacement}}$ $ABA\underline{B|C}BCB$...(defined as stacking fault), single unit of ZB
ZB, ABCABCA... $\xrightarrow{\text{misplacement}}$ $ABC\underline{A}CBA$... (twin plane, $\underline{A}$), no WZ segment
$AB\underline{CA|C|A}$... (two twin plane, 4 bilayers), smallest segment of WZ

For InAs, the smallest WZ segment in ZB phase has a length of 2.8 nm (ABAB),
and the smallest ZB segment in the WZ phase has a length of 2.1 nm (ABC)

Wurtzite and Zinc blende

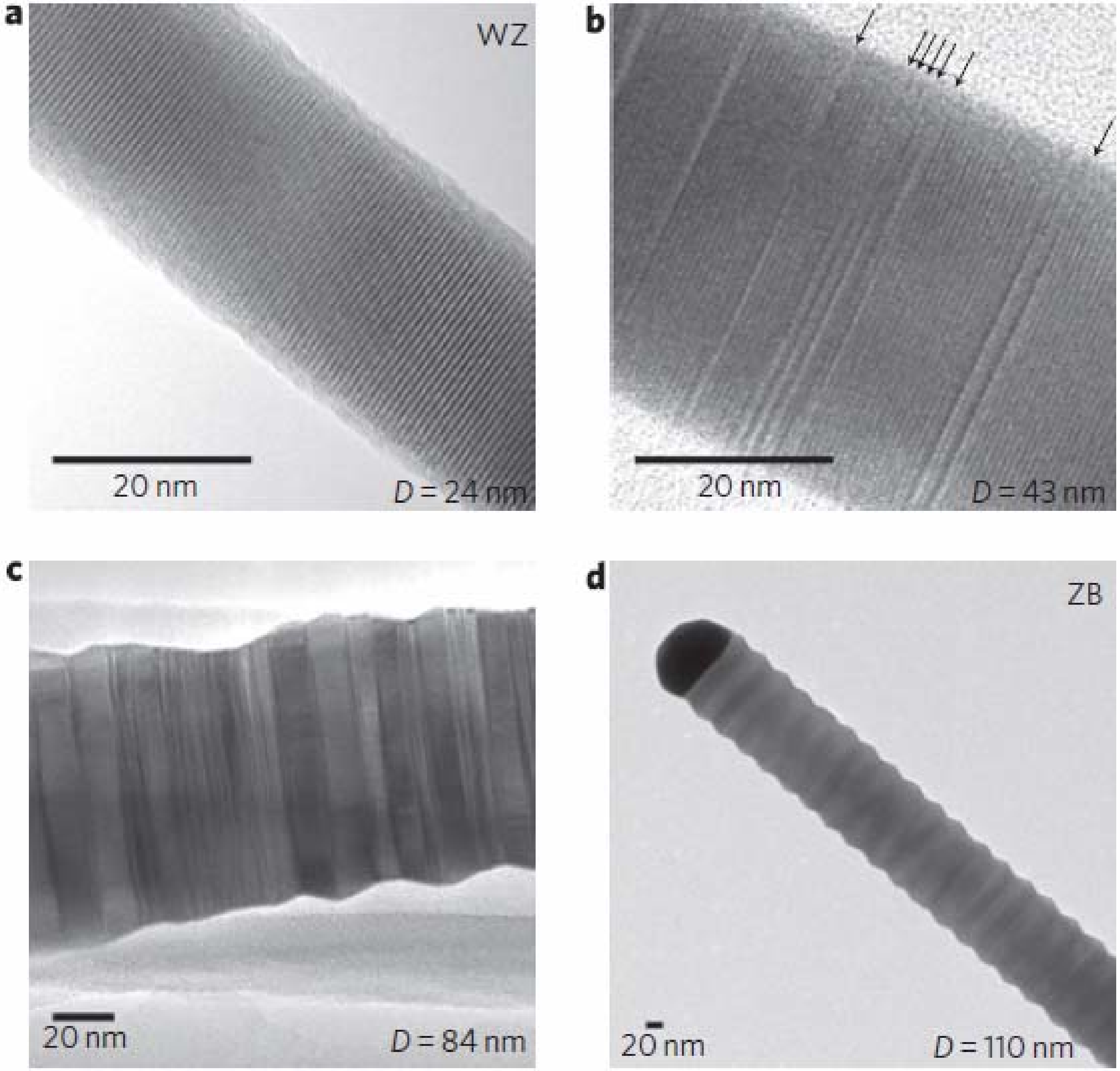
It is an example of a hexagonal crystal system and consists of tetrahedrally coordinated zinc and sulfur atoms that are stacked in an ABABAB pattern



It is an example of a face centered cubic lattices and are stacked in an ABCABCABC pattern

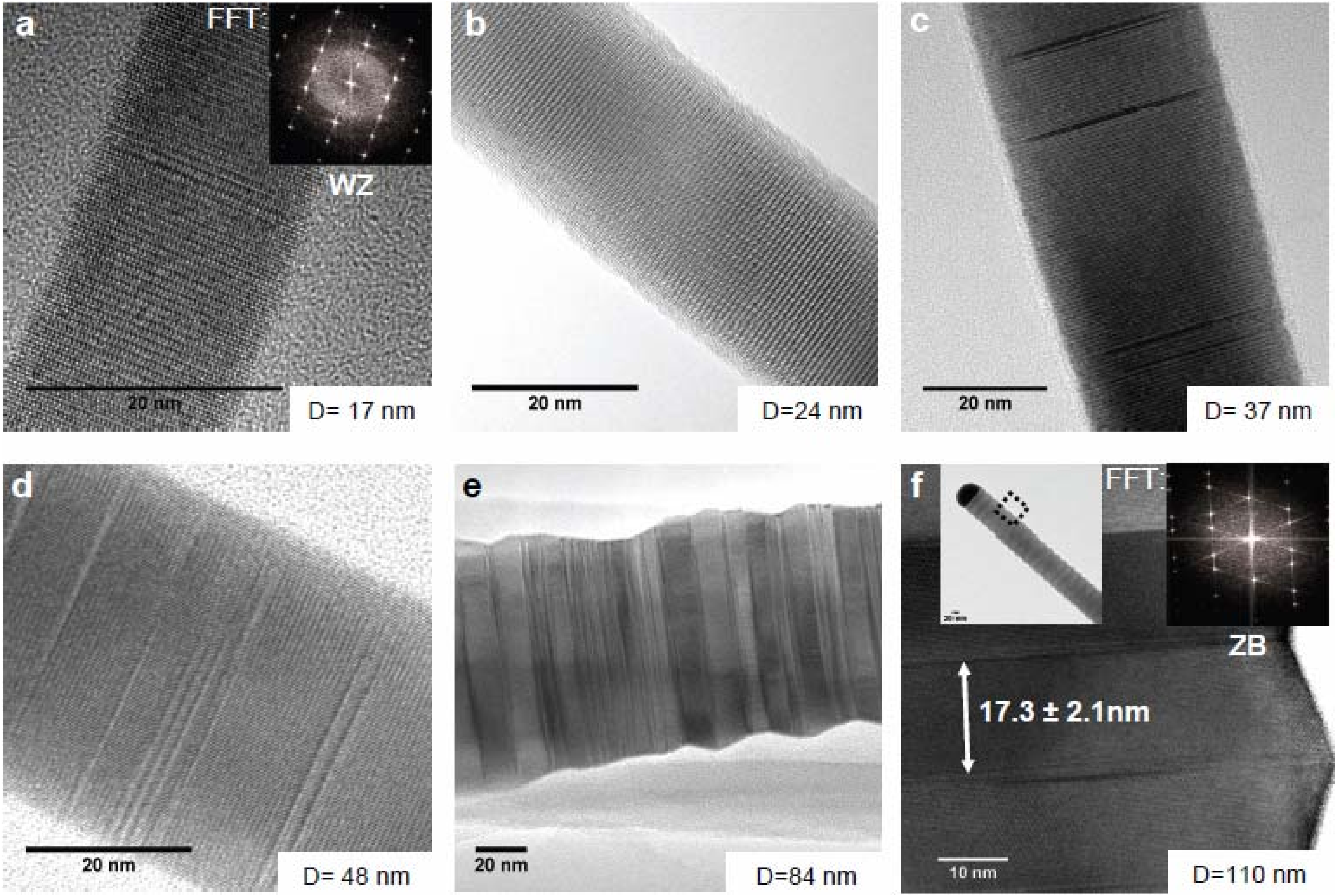
- *Zincblende/sphalerite is based on a fcc lattice of anions whereas wurtzite is derived from an hcp array of anions*
- *In both structures, the cations occupy one of the two types of tetrahedral holes present*
- *In either structure, the nearest neighbor connections are similar, but the distances and angles to further neighbors differs.*
- *Zincblende has 4 asymmetric units in its unit cell whereas wurtzite has 2.*

Dependence of InAs nanowire crystal structure on diameter



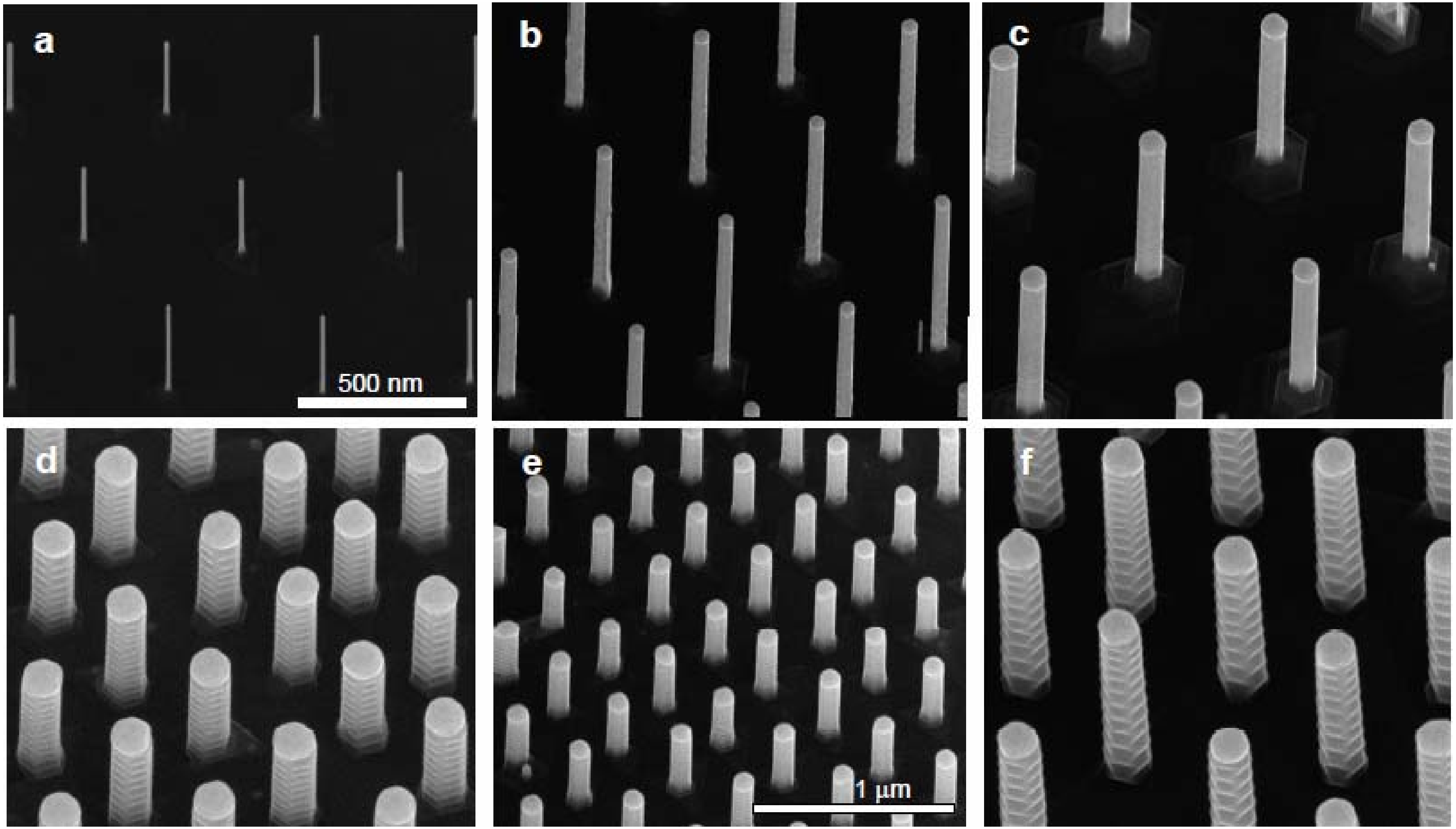
a–d, TEM images viewed along (110) zone axis, showing the influence of nanowire diameter on the InAs nanowire crystal structure, with diameter increasing from a to d. With increased diameter, the crystal structure changes progressively from pure WZ (a), to WZ with single stacking faults (b), to a mixed WZ–ZB structure (c) and finally to pure ZB (d).

Dependence of InAs nanowire crystal structure on diameter



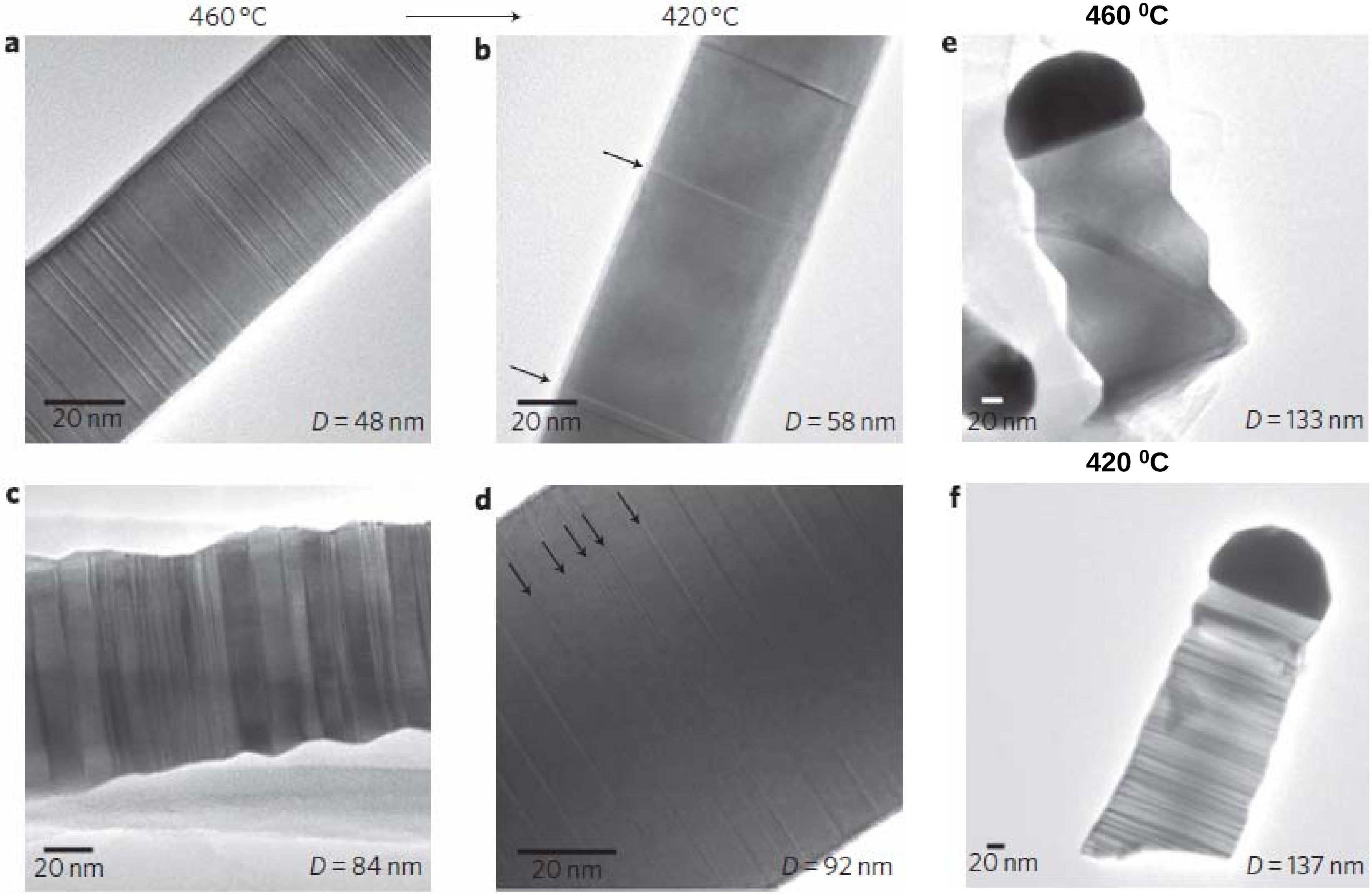
HRTEM images along the (-110) zone axis showing the influence of diameter on the crystal structure of InAs nanowire grown at 460°C. Characteristic diffraction patterns (FFT of the images) of pure WZ (a) and periodically twinned ZB are included in insets; low magnification image of the complete nanowire corresponding to figure (f) is included in inset.

InAs nanowires show diameter and structure control



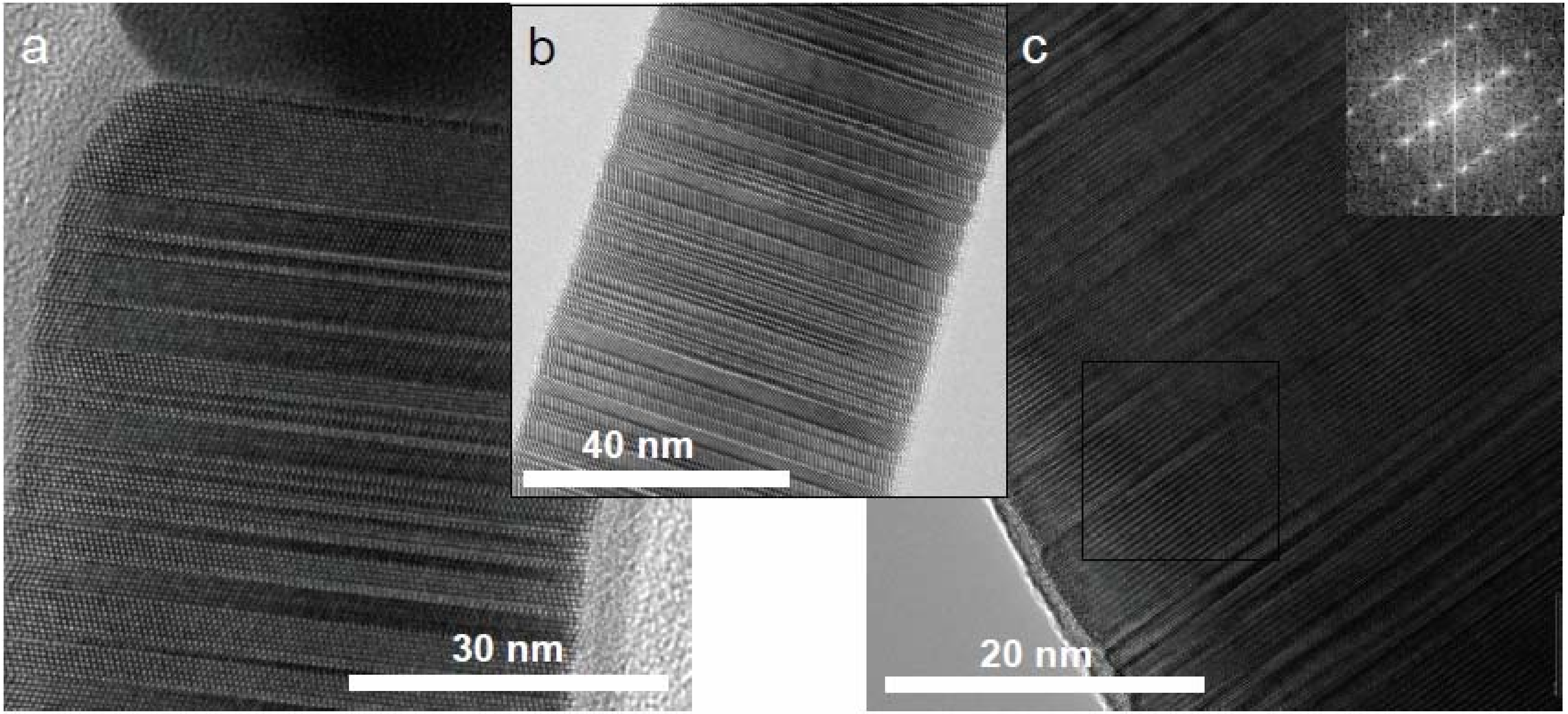
SEM images of ordered arrays of InAs nanowires produced by EBL positioning of Au particles. Nanowires shown in (a) to (e) are grown at 460 °C; nanowires shown in (f) are grown at 480°C. For all images tilt = 52°. (a) Nanowires with 22 nm diameter; these wires are hexagonal with flat side facets. (b) 60 nm diameter; side facets are somewhat “rough”. (c) 85 nm diameter; stacking faults become visible. (d) 115 nm diameter; nanowires shown periodic side facet modulation. (e) larger-area view of wires as in (d), showing the controlled diameter. (f) 120 nm diameter wires grown at 480 °C.

Dependence of InAs nanowire crystal structure on temperature



HRTEM images along the (110) zone axis of nanowires grown at 460 ^{0}C (left) and 420^{0}C (right) are shown. For all diameters, the proportion of the WZ phase is significantly higher at low temperature.

Temperature dependence of GaAs crystal structure – higher temperatures



TEM images of GaAs nanowires grown at higher temperatures. (a) GaAs nanowire grown at 415°C. The nanowire is ZB with a high density of twin planes, and occasional small WZ segments. (b) GaAs nanowire grown at 460°C. This nanowire shows a mixed WZ and ZB structure with very short segment length. (c) GaAs nanowire grown at 500°C. This nanowire has a predominantly WZ structure with a high density of stacking faults. The inset FFT (taken from the region shown in the box) shows a characteristic WZ pattern in the <11-20> zone axis. There is some streaking in the FFT due to the stacking faults in the selected region.

Structural studies

- *In the bulk, stability for ZB or WZ can be explained on the basis of ionicity of chemical bonds.*

- *The energy difference between WZ and ZB arises from an electrostatic interaction between third-nearest-neighbour atoms, which are closer together in the WZ structure.*

- *Materials with high ionicity favour a WZ configuration, but in materials with low ionicity ZB is favoured because steric hindrance prevents the closer WZ configuration in this case.*

- *For example that GaN (large ionicity of 0.557) nanowires crystallize mostly in a WZ structure, whereas GaSb (low ionicity of 0.108/0.246) and InSb (0.303/0.321) nanowires grow in a pure ZB phase, without any stacking fault or twin plane.*

- *The standard III–V semiconductors (GaAs, GaP, InAs and InP) have ionicity values between these extremes and all show polytypism in nanowires*

Formation of WZ and ZB structures

- The prevalence of twin planes in nanowires was explained by nucleation kinetics.

- Nanowires grow in a layer-by-layer mode with a single nucleation event at the edge of the particle–wire interface.

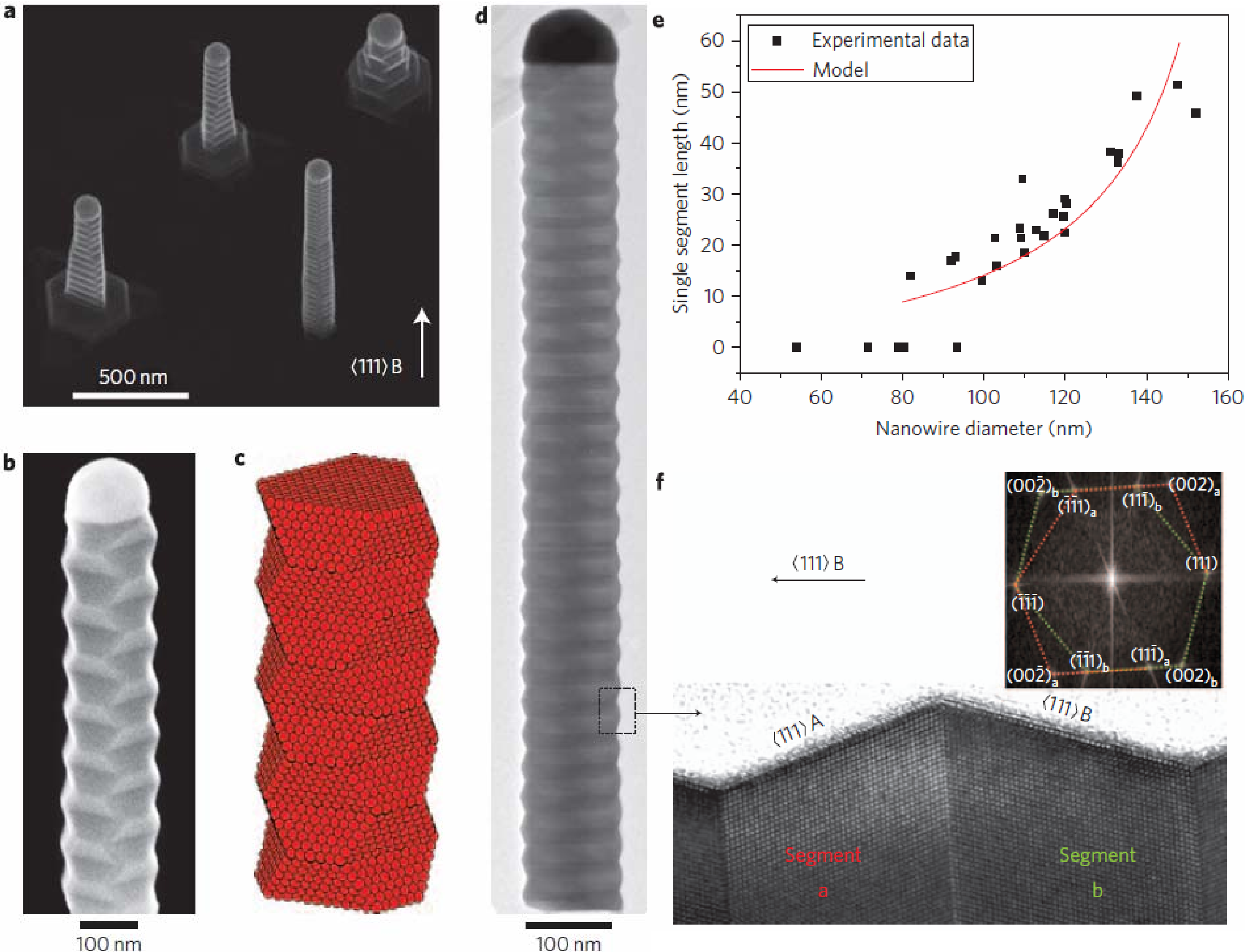
- The orientation of each critical nucleus determines whether a normal or a twin plane will form.

- The energy difference between the normal and twin nuclei is small, so small energy fluctuations during growth could give rise to randomly distributed twin planes.

- Nucleation specifically at the three-phase line allows for the possibility that twin plane nucleation can be more favourable than normal nucleation if the edge energy of the twinned nucleus is lower than for the normal nucleus.

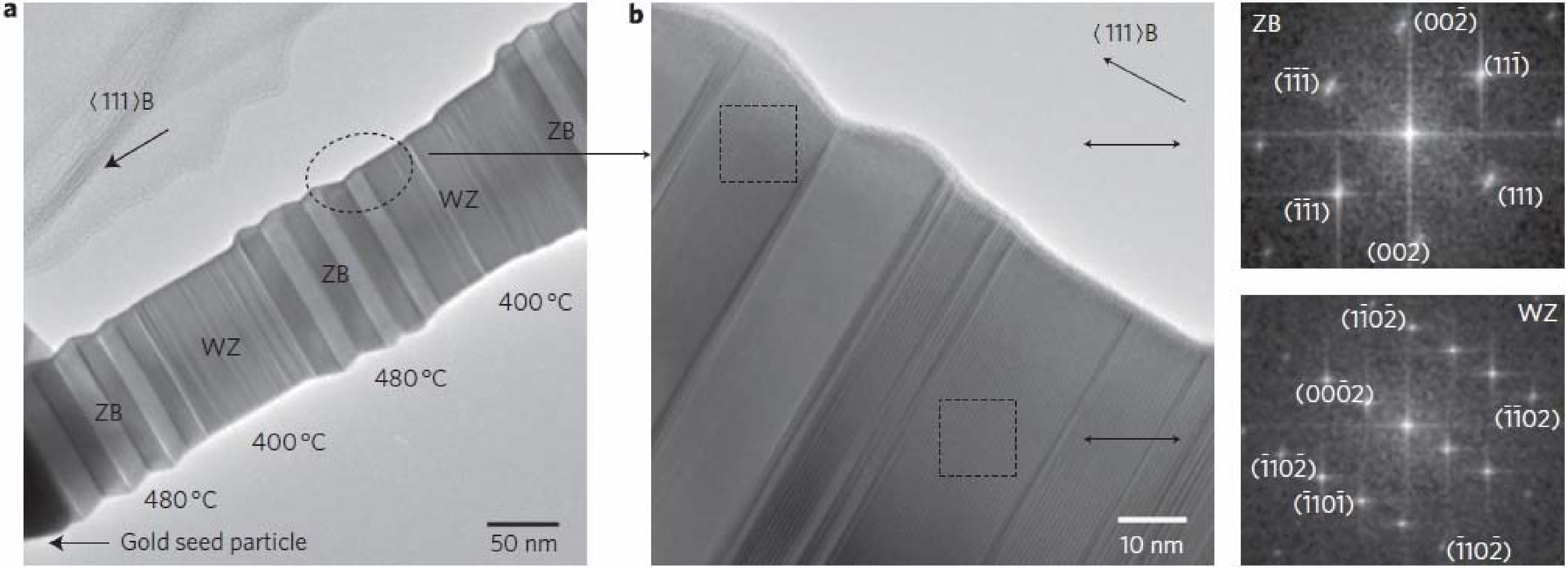
- It follows that significant amounts of the WZ phase may form in a nominally ZB nanowire.

Investigation of InAs coherent twin-plane superlattices



a, SEM image (tilt angle 30^0) of the periodic coherent twin superlattice in InAs nanowires for a wide range of diameters. b,c, SEM image of a slightly tilted broken-off nanowire (b) revealing the complex shape of the nanowires and the associated three-dimensional atomic model (c). d, TEM image of a similar nanowire to that shown in a and b, illustrating the perfect regularity of the twin boundaries. e, Average single ZB segment length versus nanowire diameter for nanowires grown at 460 ^{0}C, from high-resolution TEM measurements. f, High-resolution TEM image of two ZB segments separated by two single twin planes and the associated FFT image (inset) showing an indexed characteristic double-spot pattern.

Realization of a WZ–ZB polytypic superlattice



a, TEM image of the top of a WZ–ZB superlattice nanowire, where the seed particle is visible at the bottom left corner. The growth temperature sequence and associated crystal phases of the segments are indicated in the figure. The axial positioning and length of these segments are directly controlled by the growth sequence (see Supplementary Information for details on the growth procedure). b, High-resolution TEM image along the k110l zone axis of a smaller area of a and associated FFT images of the two different areas.

Material and Methods

- The nanowires were grown in a standard commercial metal organic vapour phase epitaxy (MOVPE) reactor at 10 kPa using gold as seed particles.
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- TMIn and AsH_3 as source precursor materials, and hydrogen as carrier gas. An aerosol deposition system was used to achieve the desired size selection of pure gold particles.

- Electron-beam lithography (EBL), followed by gold film deposition and liftoff, was used instead to produce patterned gold particles for the samples.

- Samples were grown at temperatures from 400 to 480 ^{0}C without special annealing steps, using particles with diameters ranging from 10 to 140 nm.

- Seed particles of all sizes were deposited on the same InAs substrates and nanowires were grown in a single growth run for each temperature, to allow for direct comparison between the resulting nanowires.

- Optimal low molar fractions were in the range of $4x10^{-4}$ and $3x10^{-6}$ for AsH_3 and TMIn, respectively, giving a V/III ratio of 130.

Conclusions

- *Careful tuning of the growth parameters, the crystal structure of InAs nanowires can be controllably varied between pure ZB and pure WZ.*

- *In particular, It is demonstrated experimentally that the crystal structure varies strongly with diameter, and that this effect, coupled with making using different temperatures.*

- *For the pure ZB case, the preferred morphology is a periodically twinned superlattice, an effect arising from the overall geometry of the stable side facets and particle–wire interface energy.*

- *The control over the nanowire structure to alternate between WZ and ZB structures within a single nanowire, opening the door to carefully tuned WZ–ZB polytypic superlattices within a single material.*

- *The results cannot be fully explained by the existing literature, and we expect these results to inspire the development of new theoretical models.*

Thank You