



III-V nanostructured materials synthesized by MBE droplet epitaxy

E.A. Anyebe¹, C. C. Yu¹, Q. Zhuang^{1,*}, B. Robinson¹, O Kolosov¹, V. Fal'ko¹,
R. Young¹, M Hayne¹, A. Sanchez², D. Hynes², and F. Anderson³,

1 Physics Department, Lancaster University

2 Physics Department, Warwick University

3 Oxford Instrument

**q.zhuang@lancaster.ac.uk*

Outline

2

◆ Motivation

 Why droplet epitaxy

 GaAs/AlGaAs quantum dots

 In(As,Sb) Nanowires on Si (111) or graphite

◆ Structural properties

 SEM for geometry

 X-ray for phase and composition

◆ Optical properties

◆ Summary

Motivation: why droplet epitaxy

3

Droplet epitaxy –starts from metal droplets on substrate as the seeding followed by crystallization or spontaneous growth

A new approach to fabricate novel nanostructures:

◆ QDs in any material systems

📁 no strain is required

📁 No wetting layer present

◆ One-dimensional nanowires

📁 Free standing NWs on cheap Si substrates

📁 Widely tuneable composition

Motivation: why QDs & NWs

4

◆ Type-I GaAs/AlGaAs QDs

- ✓ Nearly strain-free in the QDs
- ✓ Easily tuneable confinement
- *Solar cells – intermediate transitions: 55% efficiency; strain!!*
- integrated quantum photonics, Kuroda et al. already demonstrated entangled photon emission (111A)! (PRB 88, 041306 '13)

◆ InAsSb NWs on Si and graphene

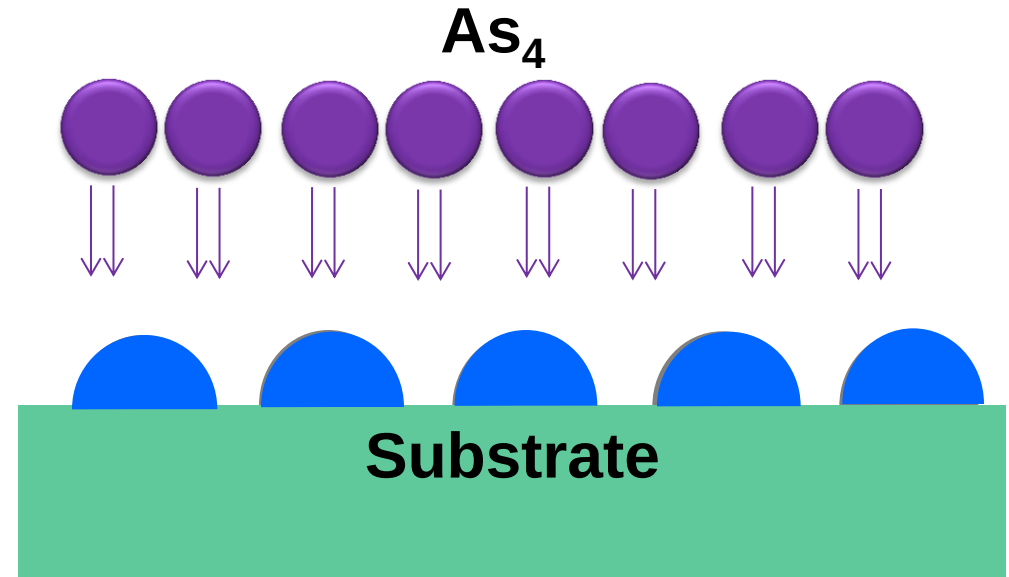
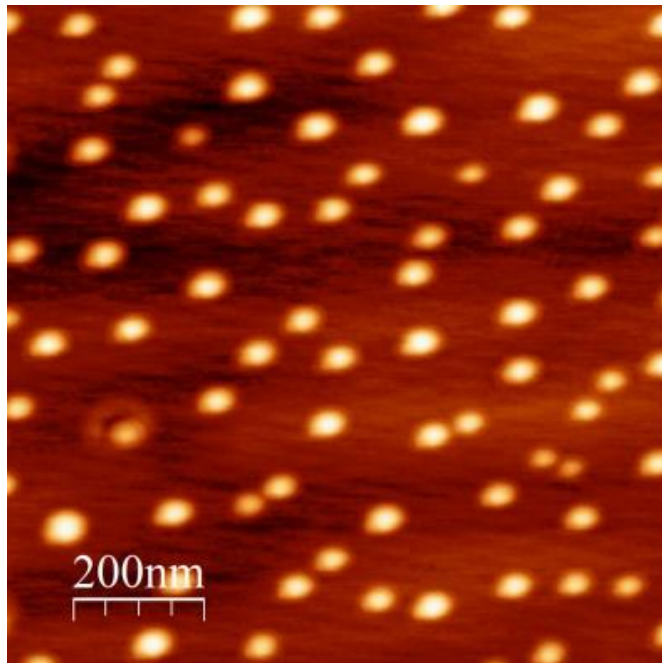
- ✓ Dislocation-free
- ✓ Tuneable bandgap 100-350 meV (2-12 um spectral range)
- Integrated optoelectronics on Si
- *Low-cost thermophotovoltaics*

Droplet epitaxy of QDs

5

Three-step growth (self-catalyst)

- ◆ Gallium droplets (3 ML)
- ◆ Crystallization under As_4
- ◆ Annealing



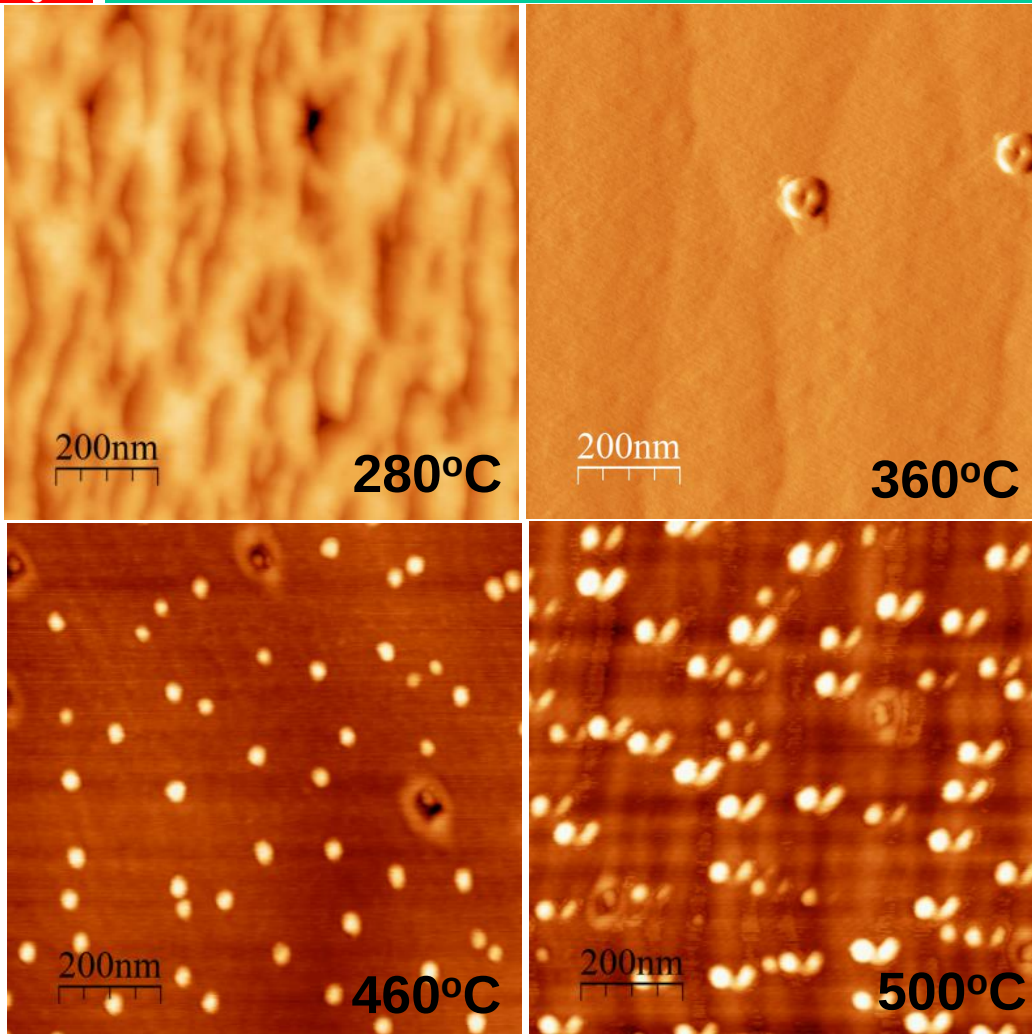
Ga droplets (1x1 μm AFM)

Density: $5.1 \times 10^9 \text{ cm}^{-2}$

Diameter: $80 \pm 3 \text{ nm}$; Height: $8 \pm 0.2 \text{ nm}$

Structural evolution of GaAs QDs

6



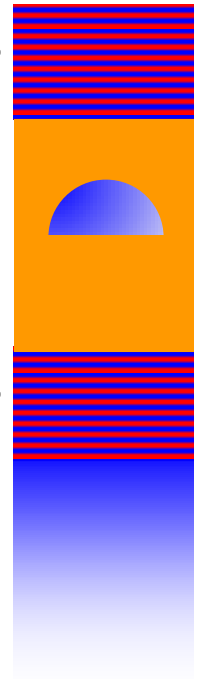
Single QD
characterisation

GaAs/AlAs SL
(28/28Å)

$\text{Al}_{0.35}\text{GaAs}$

GaAs/AlAs SL
(28/28Å)

GaAs
(100)

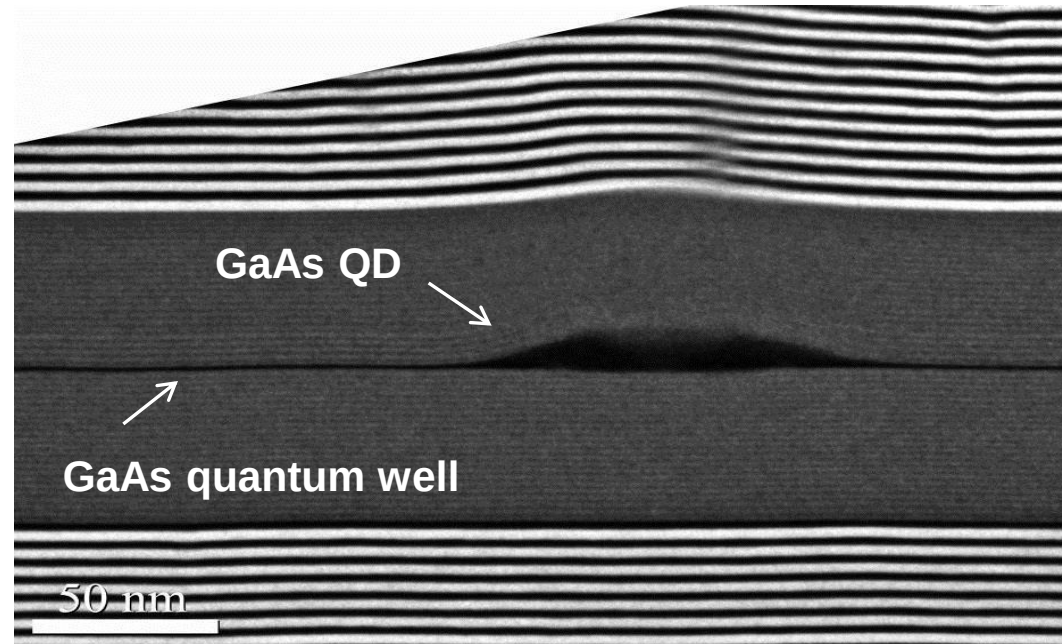
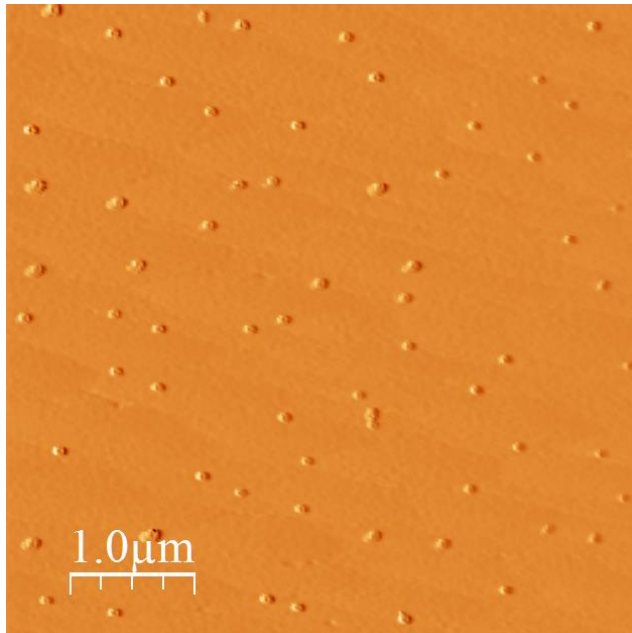


1x1 μm AFM of GaAs QDs
Crystallized at different temperatures

GaAs/AlGaAs QDs embedded in SL

7

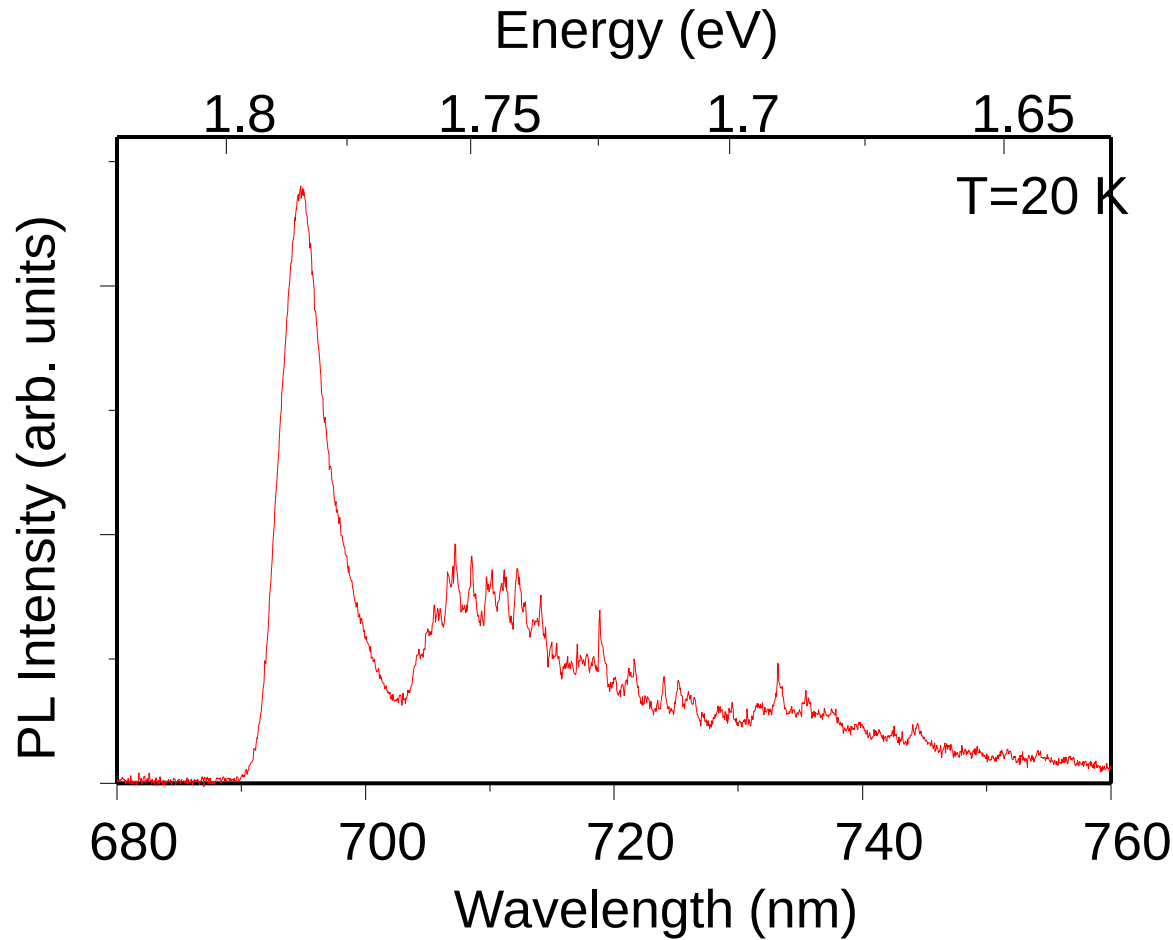
- QD density is $\sim 2 \times 10^8 / \text{cm}^2$
- Average diameter $\sim 100 \text{ nm}$
- Average height $\sim 8 \text{ nm}$
- A 'wetting layer' is clearly visible in TEM due to a specific recipe



The QD's are rather large,
but we observe clear 0D
confinement...

μ -PL

8

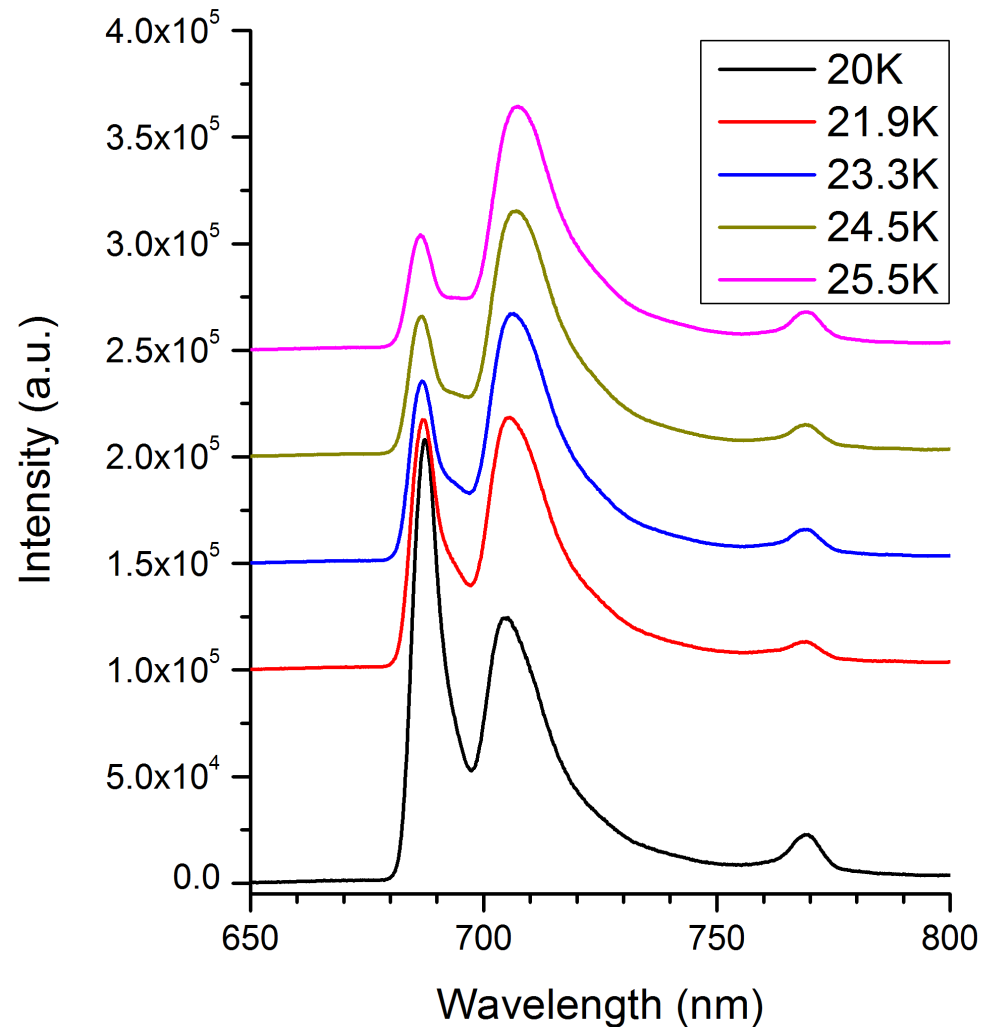


μ PL from the bulk sample reveals the classic signature of QD's and a wetting layer:

- A broad ensemble of dots with a FWHM of ~ 50 meV and a confinement of < 100 meV.
- Strong emission from a QW at 690 nm, in rough agreement with width and composition of the WL from TEM.

Temperature elevated PL

9



- Wetting layer emission quenches quickly
- QDs emission becomes dominant at above 23 K
- Good quantum confinement

Future work:

- *QDs without wetting layer*
- *Dense QDs*

Growth of NWs

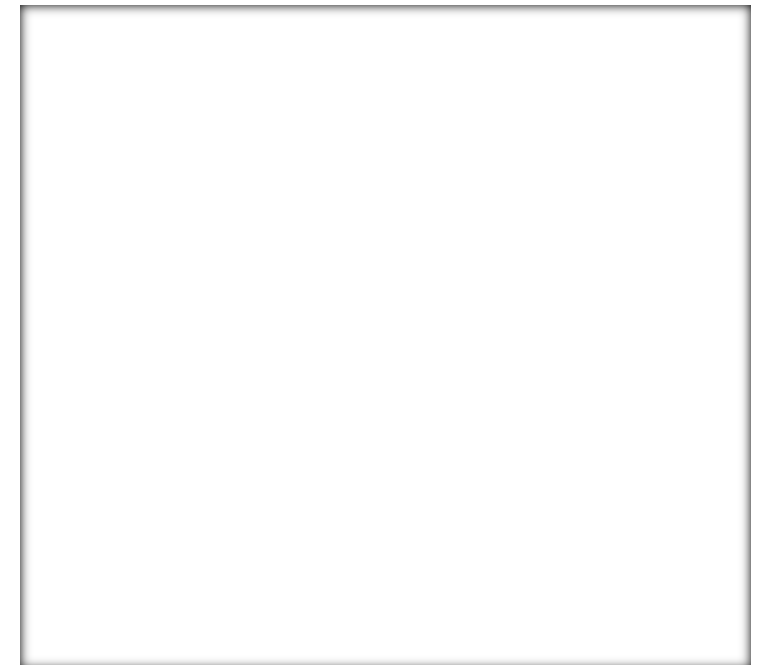
10

Challenging epitaxy on graphite due to the *weak van der Waals bonds*

Metal droplet self-catalyst growth

- ◆ Indium droplets (3 ML)
- ◆ Epitaxy of InAs
- ◆ Start from growth on Si (111)

Indium droplets:
Average Density: $3.6 \times 10^9 \text{ cm}^{-2}$
Average Diameter: 80 nm
Average Height: 22 nm



1x1 μm AFM image

InAs NWs on Si(111)

11

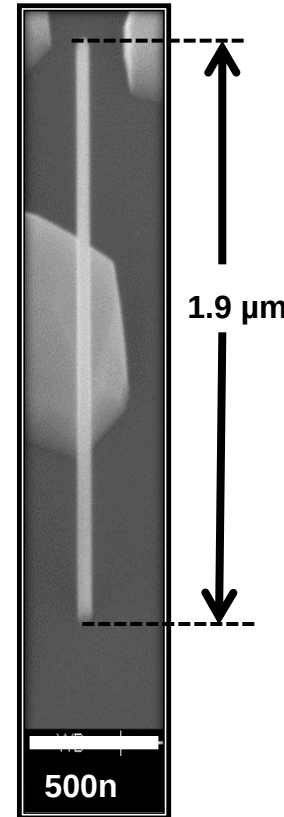
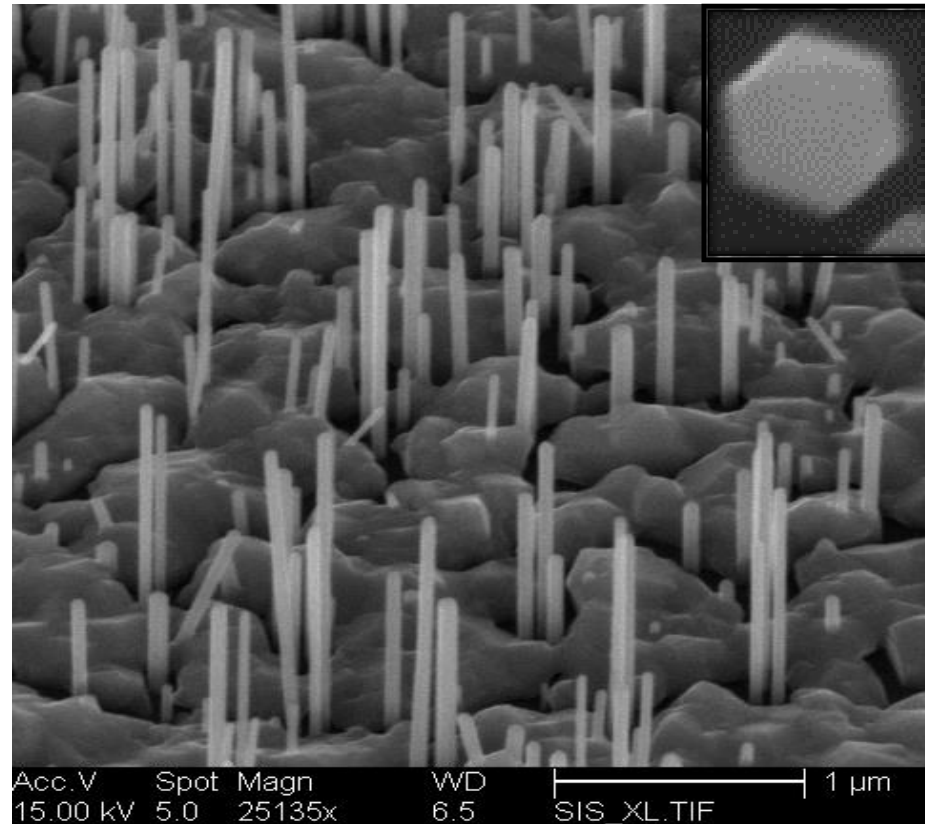
Geometrical properties:

- ◆ Height: $1.9 \pm 1.1 \mu\text{m}$
- ◆ Diameter: $62.5 \pm 3.0 \text{ nm}$
- ◆ Density: $1.0 \times 10^9 \text{ cm}^{-2}$

Parasite bumps on the surface

Highly uniform diameter along growth direction

Hexagonal cross-section –
zinc-blende or wurtzite?



45° SEM image of InAs NWs on Si(111)

InAsSb NWs on Si(111)

12

Growth conditions:

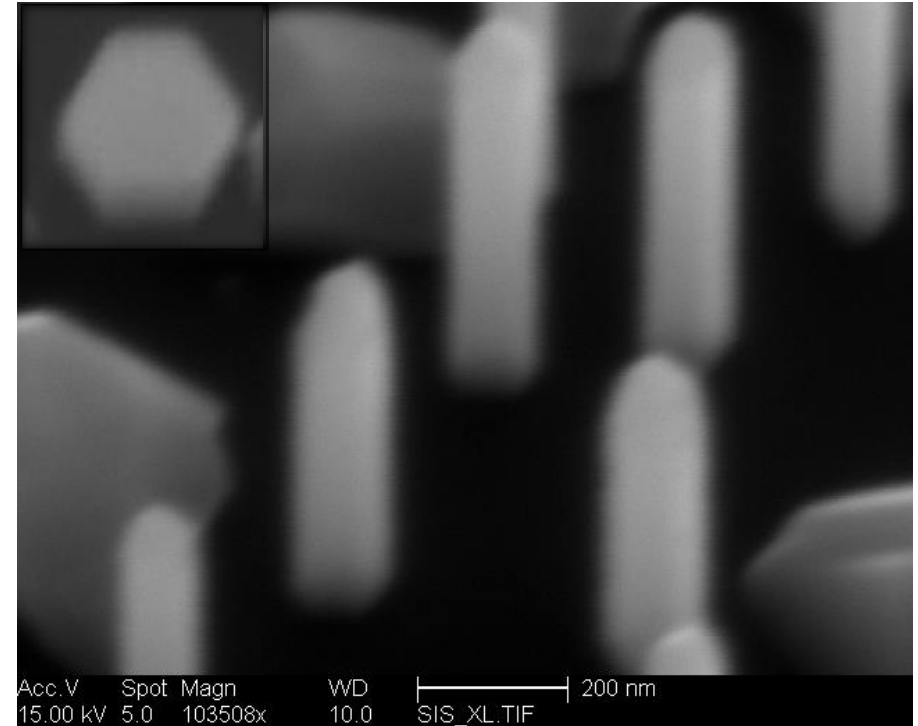
- ◆ Similar growth parameters to that of InAs
- ◆ Expose to Sb flux during the InAs growth

Geometrical properties:

- ◆ Height: $1.3 \pm 0.3 \mu\text{m}$
- ◆ Diameter: 95 nm
- ◆ Density $1.8 \times 10^{10} \text{ cm}^{-2}$

Comparison with InAs NWs:

- ◆ *Thicker & Shorter*
- ◆ *More dense & uniform*

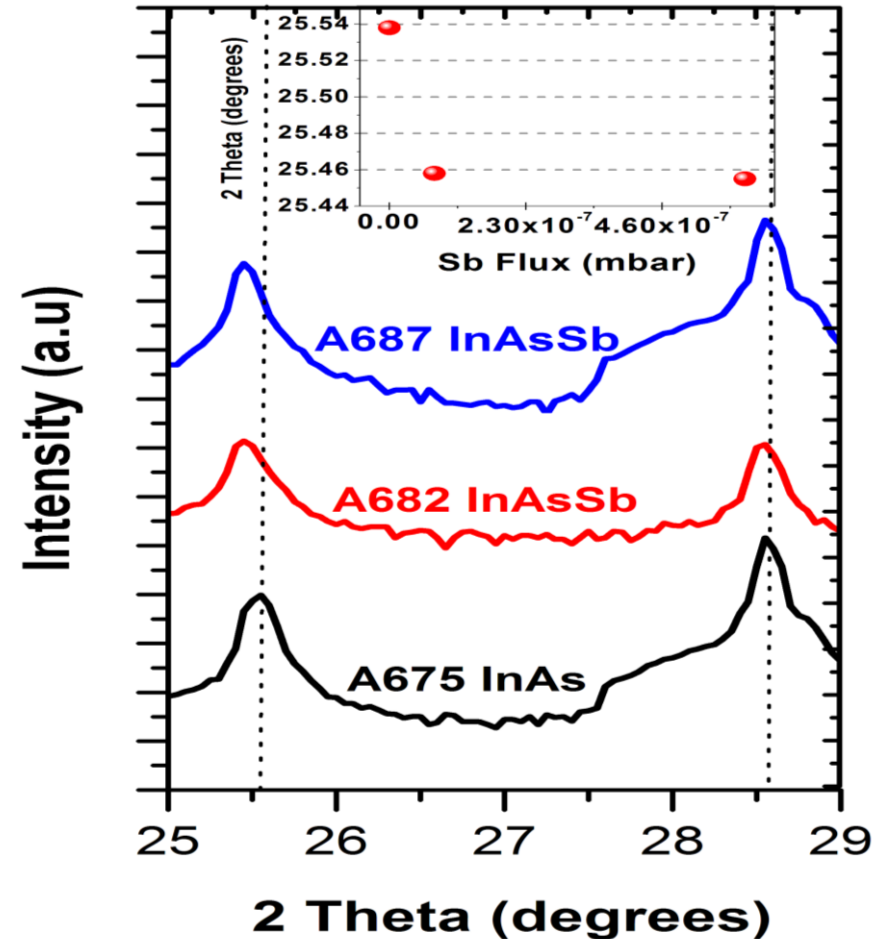


45° SEM image of the resulting InAsSb NWs on Si(111)

InAsSb NWs on Si(111) - XRD

13

- ◆ The InAs(Sb) peak (111) shifted to lower angle
 - 📁 Indicating the incorporation of Sb into the InAs NWs
 - 📁 4.2 and 4.5 % Sb
- ◆ The Sb flux has significant effect on the nucleation and the growth of NWs
 - 📁 Attributed to its well known surfactant effect
 - 📁 Method to modify the geometry of NWs

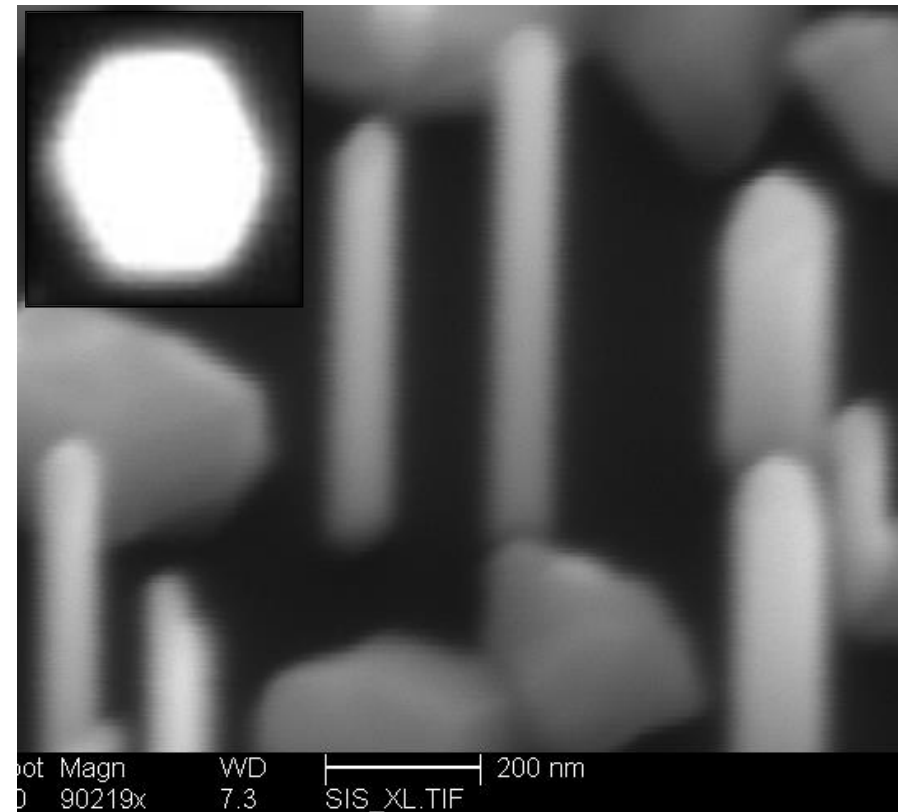


XRD curves of the InAsSb NWs on Si (111) grown at various Sb BEP fluxes

InAs NWs on HOPG - SEM

14

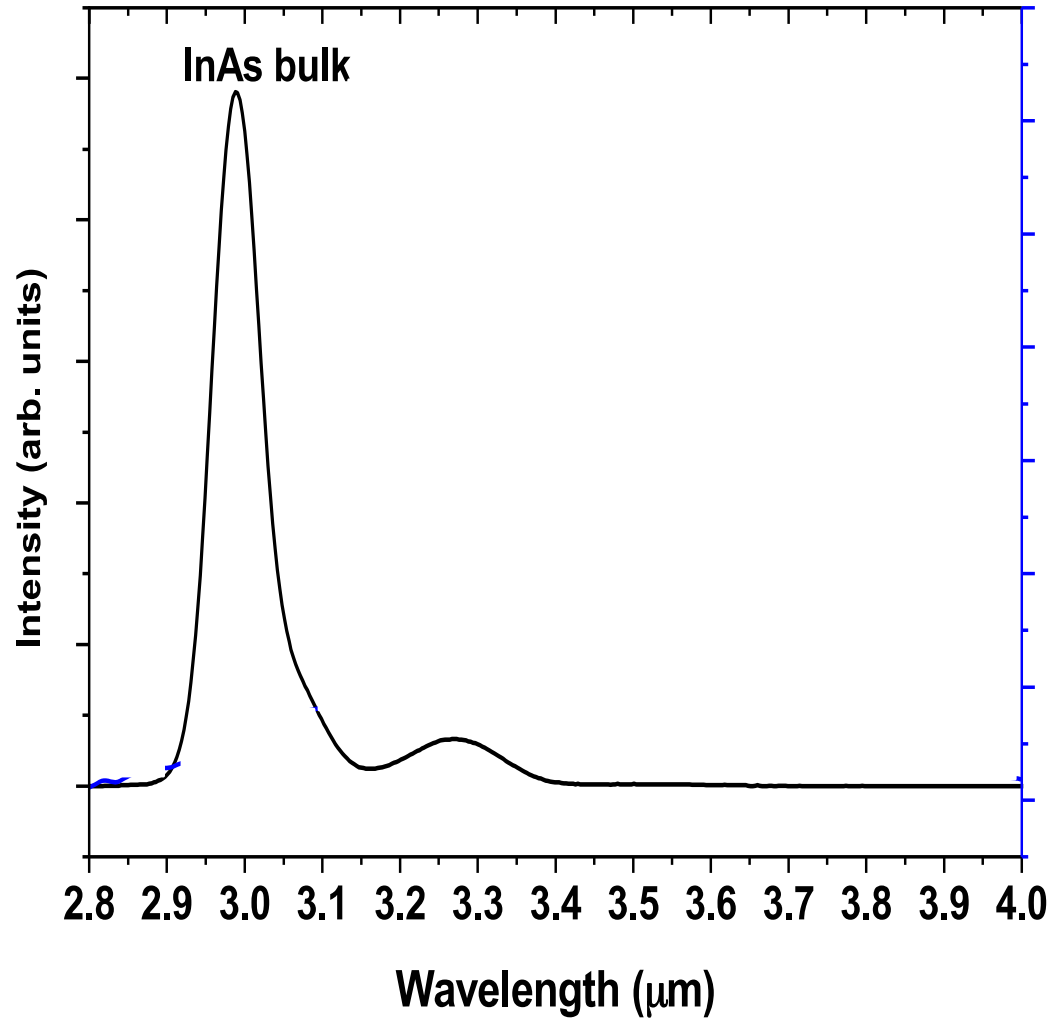
- ◆ InAs NWs on highly oriented polycrystalline graphite
- ◆ Geometrical properties
 - 📏 Diameter: 80nm
 - 📏 Height: 1.1μm
 - 📏 Density of $4.4 \times 10^9 \text{ cm}^{-2}$
- ◆ Compare with InAs NWs on Si(111): thicker, shorter and slightly more dense
 - 📏 Poor wettability
 - 📏 Poor chemical binding on the surface of HOPG



45° SEM image of InAs NWs on HOPG

PL of NWs on Si(111)

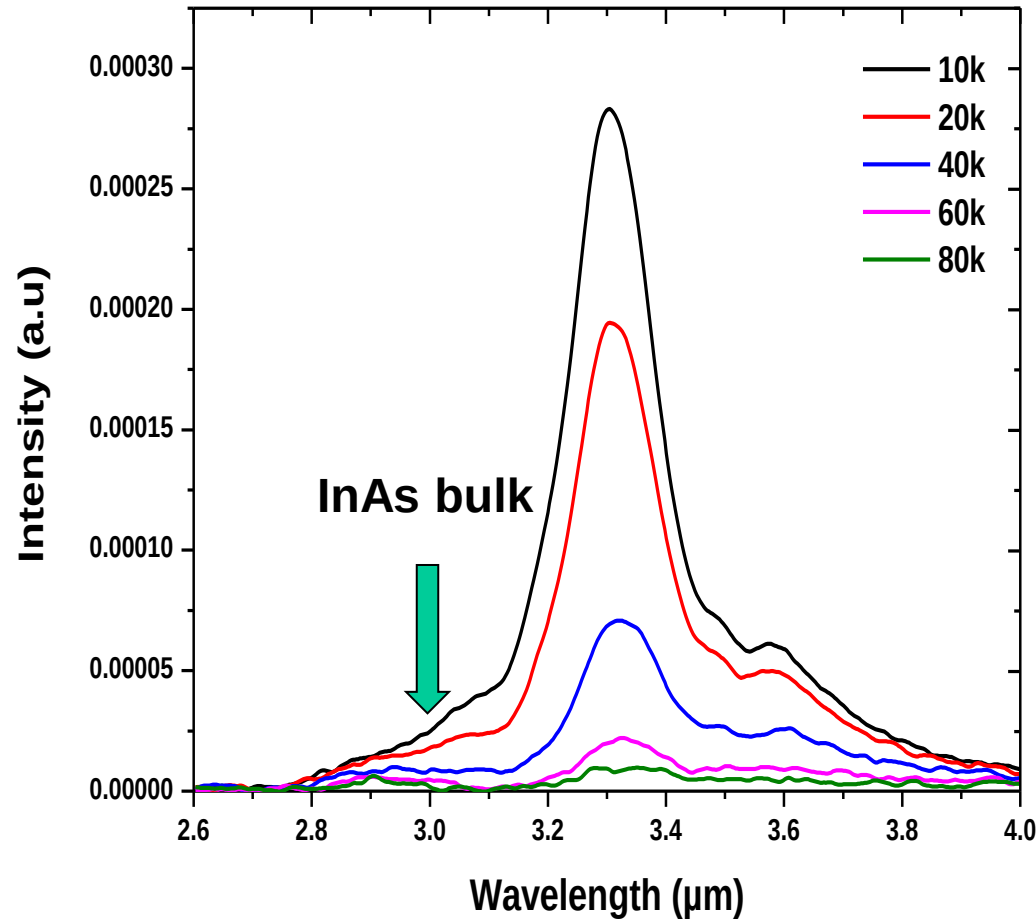
15



Typical 4 K PL of
bulk InAs

PL of InAs NWs on Si(111)

16

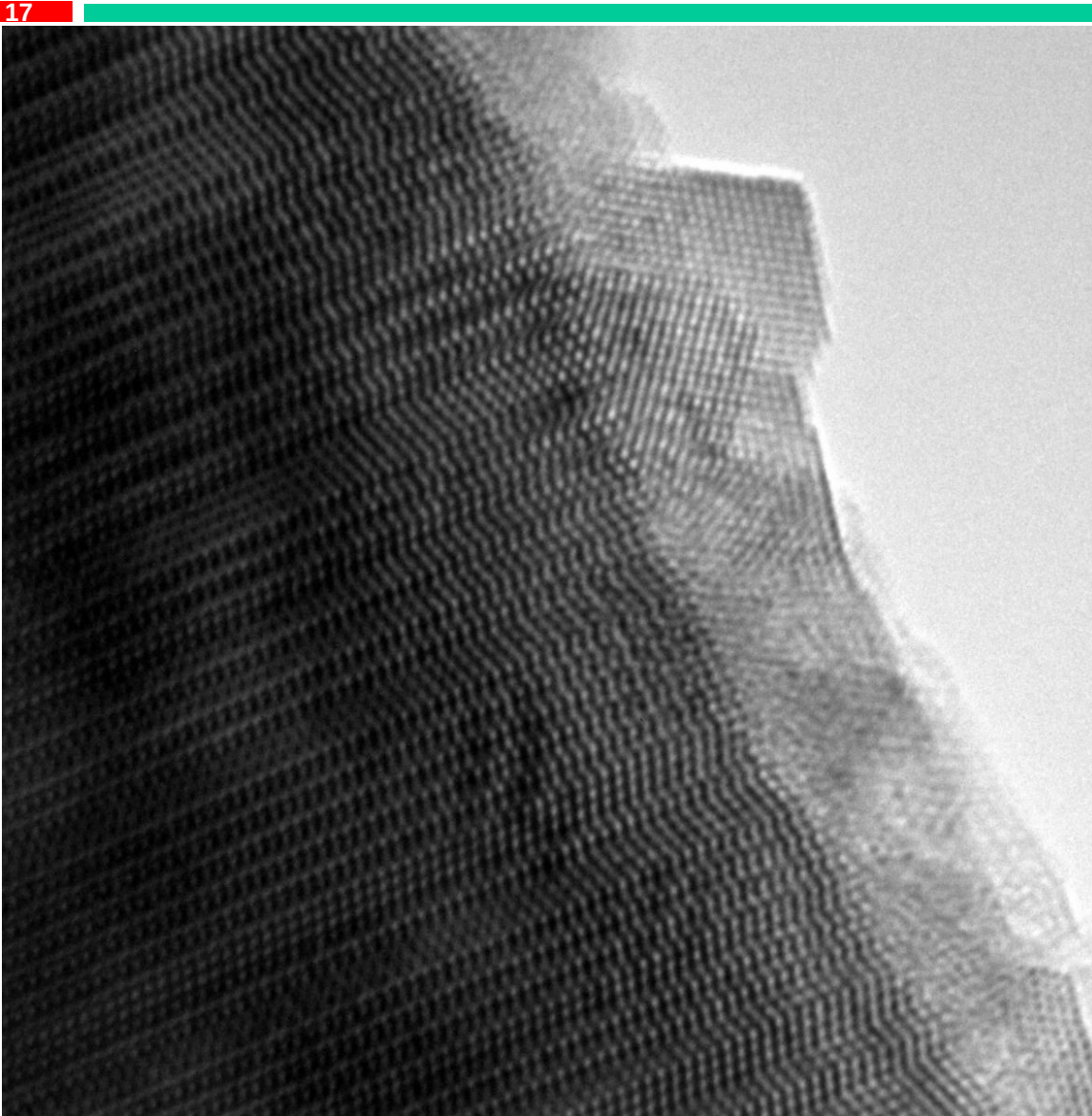


Temperature dependent PL at 0.5 W

Three peaks present

- ☞ Dominate 3.3 μm – acceptor related or WZ-ZB mixture?
- ☞ 2.9 μm – band-band
- ☞ 3.6 μm – acceptor-donor
- ☞ Short wavelength emission quenches slower

Crystal structure - TEM

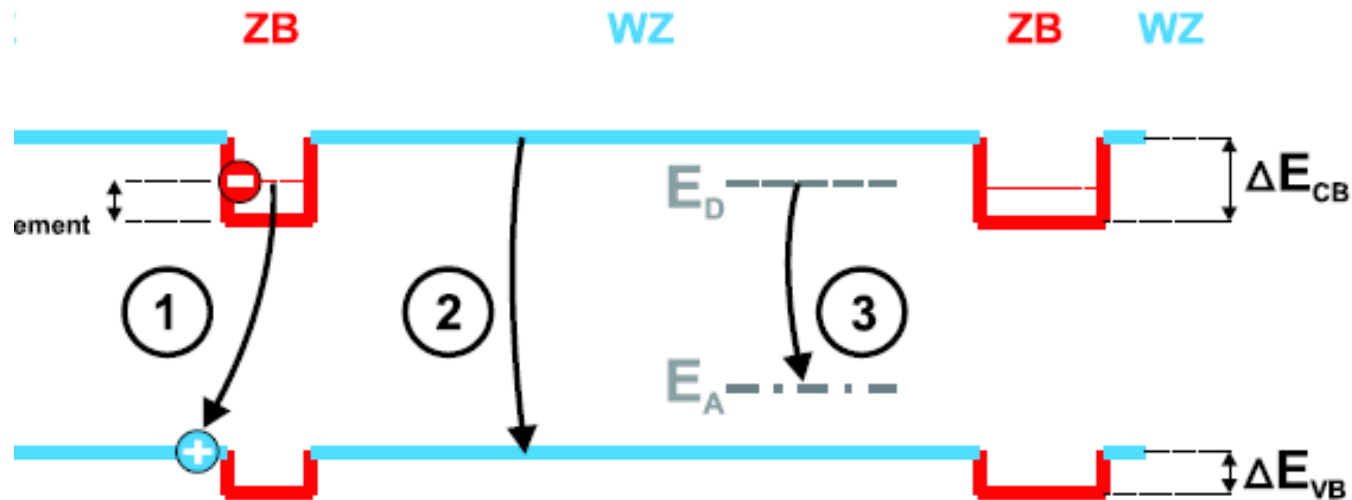


HRTEM image shows
the mixture of WZ and ZB!

Possible origin of the dominant PL emission

18

Confinement from the mixture of WZ-ZB?



Sun et al, Nano Lett. 12, 3378(2012)

Summary

19

GaAs QDs from droplet epitaxy:

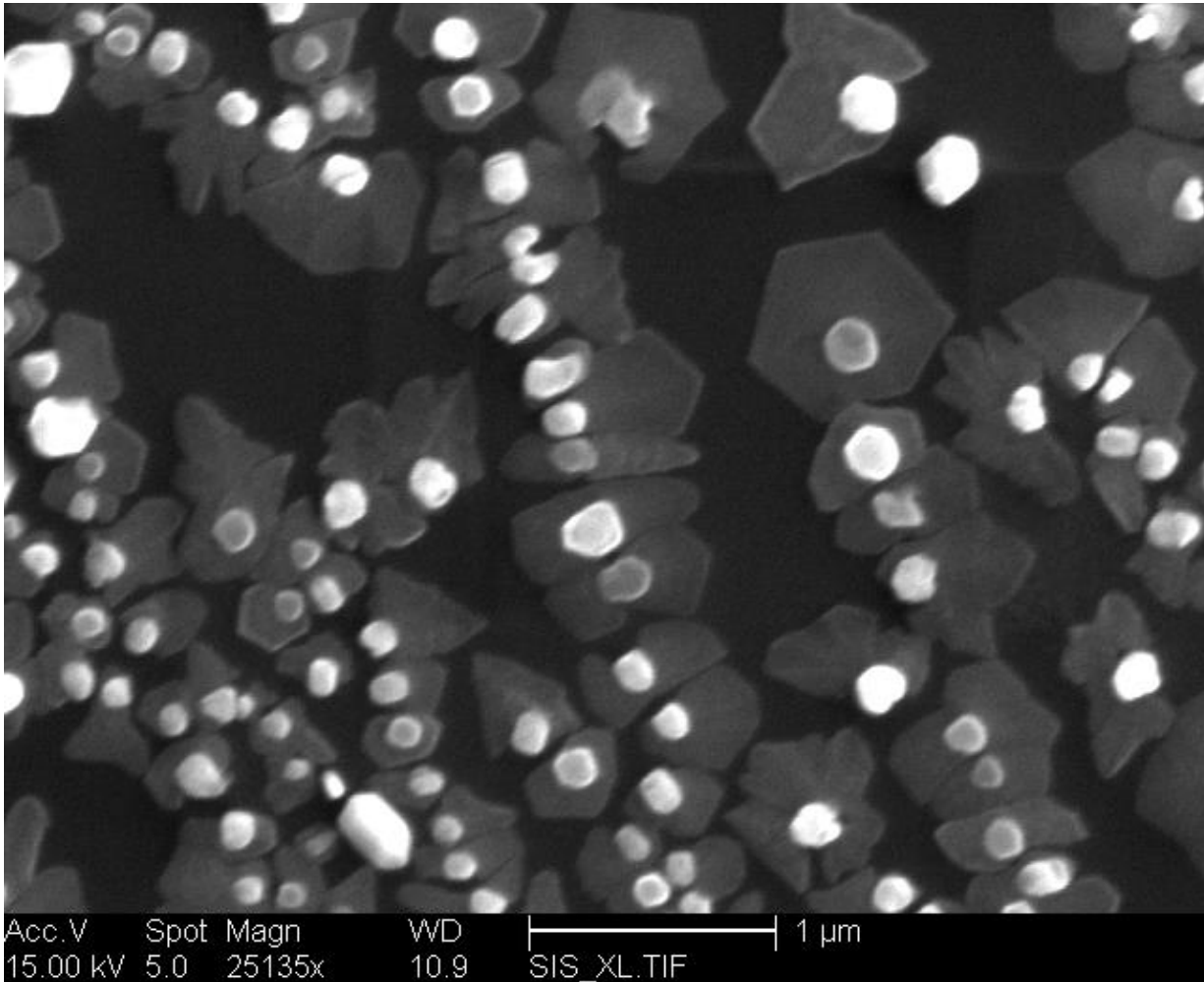
- ❖ Established control over the geometry of GaAs QDs
- ❖ Obtained high quality GaAs embedded in AlGaAs
- ✓ *QDs solar cells next!*

In(As,Sb) NWs from droplet epitaxy

- ❖ Demonstrated InAsSb NWs on Si(111) – Sb *modifies the geometry of the NWs*
 - ❖ Obtained InAs NWs on HOPG
 - ❖ Observed photoluminescence from the InAs NWs on Si(111)
- xFurther optimization*

2D epitaxial growth on HOPG?

20



- ◆ Start growth at 2D favorite growth conditions then change to 3D growth conditions
- ◆ Flakes with NWs on them
- ◆ Nucleation along terraces

Motivation

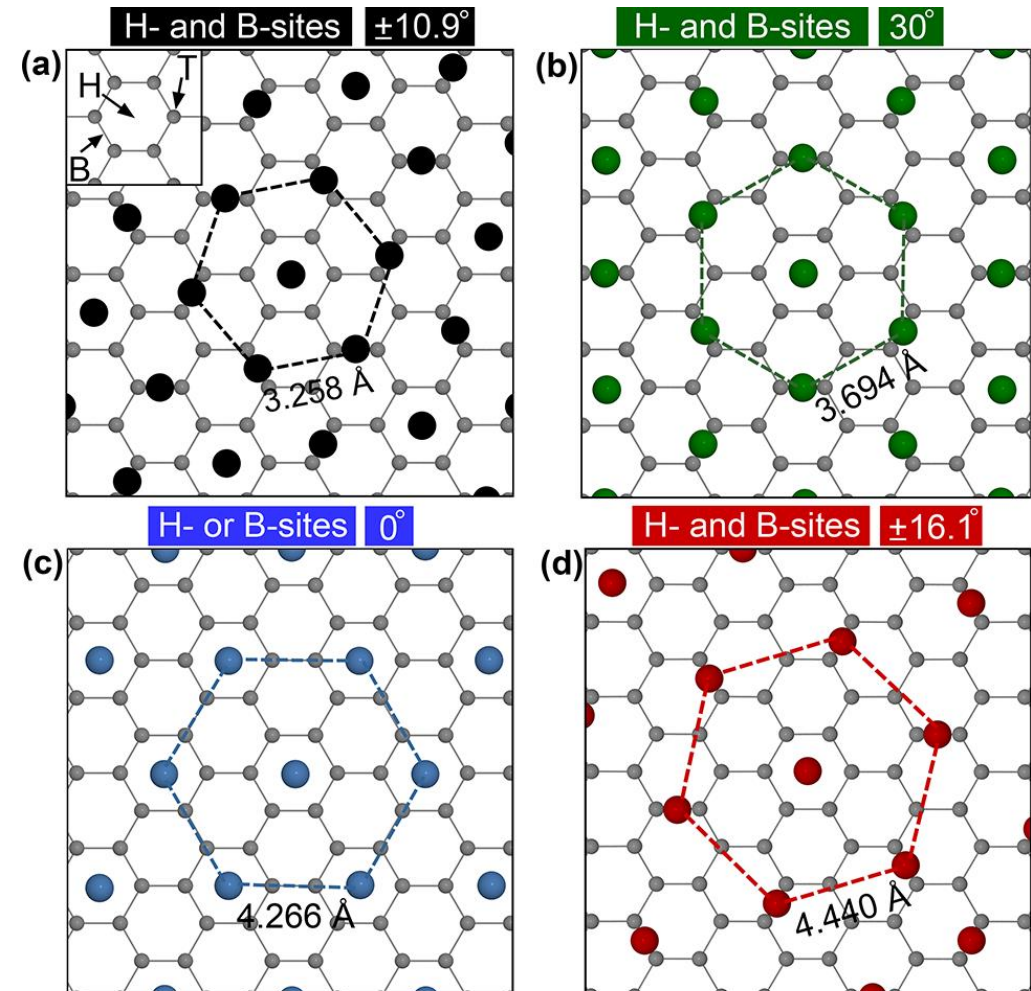
21

◆ InAs-based III-V family

- 📁 Various applications ✓
- 📁 Expensive & type II or III band alignment ✗

◆ New architecture for lost-cost and more tolerance to strain

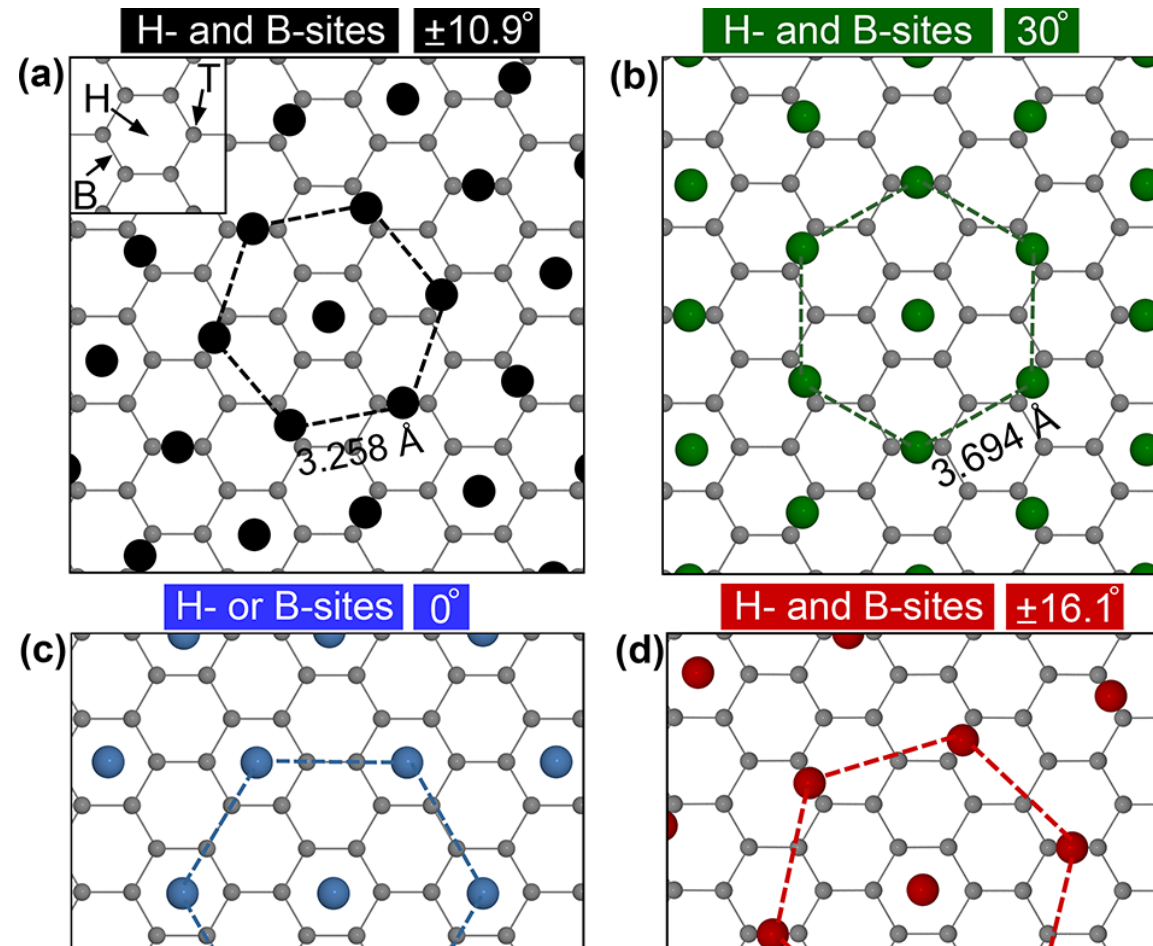
- 📁 1-D nanowires (Enhanced light absorption & dislocation free)
- 📁 Graphite (flexible substrate, super-cells for lattice match)



A. Munshi et al, Nano Lett. 12, 4570 (2012)

Motivation (cont'd)

- ◆ Lattice matched: GaN, ZnO & InAs – epilayer is possible
- ◆ *InAsSb NWs on HOPG and monolayer graphene* towards flexible and cost-effective optoelectronics
 - 📖 *InAs & InAsSb NWs on Si*
 - 📖 *InAs NWs on HOPG*
- ◆ Graphene/InAs hybrid structure for band tailoring



A. Munshi et al, Nano Lett. 12, 4570 (2012)

MBE growth – substrate preparation

23

◆ Growth on Si(111)

- 📁 Etch in dilute HF solution
- 📁 Repeated etching for smooth surface

◆ Growth on graphite

- 📁 Thin melt indium film Si (111)
- 📁 Mechanically exfoliate thin layer of HOPG (*monolayers of graphene as well*)
- 📁 Transfer onto Si wafer and cool down to RT

