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Understanding Surface Reconstruction Coexistence in III-V Alloys

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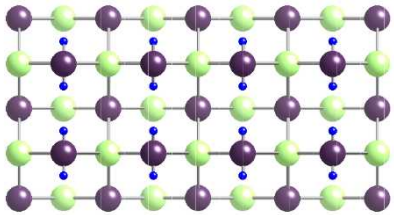
Semiconductor Surfaces Reconstruct to Lower Energy

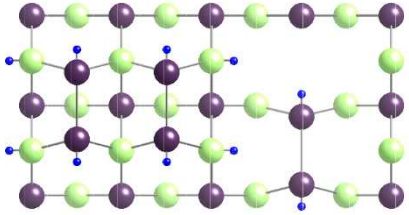
InAs (001)

Unreconstructed

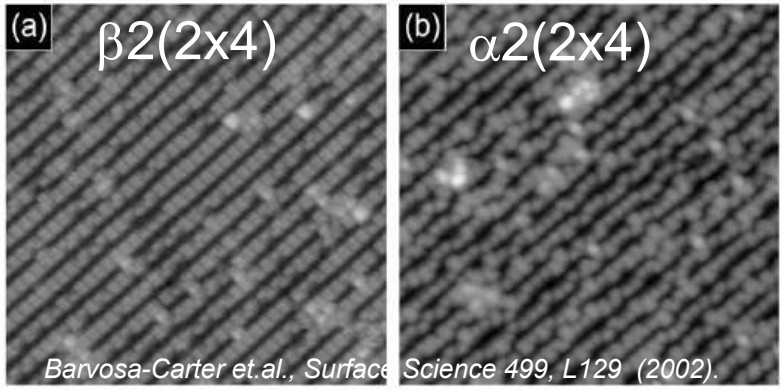
=Anion
=Cation
=Dangling Bond



β2(2x4)



Scanning Tunneling Microscopy (STM) Images



- When a surface is formed, the dangling bonds rearrange on the surface to minimize their energy
  - Competing Interactions
    - Local Chemistry
    - Long Range Electrostatics
    - Strain
- Surface reconstructions affect
  - Ordering in alloys
  - Interfaces
  - Self Assembly
  - Catalysis
  - Epitaxial Film Growth
- InAs (001) and GaAs (001)
  - Single Reconstruction Surface
  - Changes with Chemical Potential

Outline

Goal: Examine Atomic Surface Structure of III-V Alloys

- Ternary alloys exhibit reconstruction *coexistence*
- Understanding the Role of Strain
  - Atomic size mismatch strain
    - z(4x4) reconstruction
    - (4x3) reconstruction (?)
  - Lattice mismatch strain
    - Sb/GaAs reconstruction coexistence

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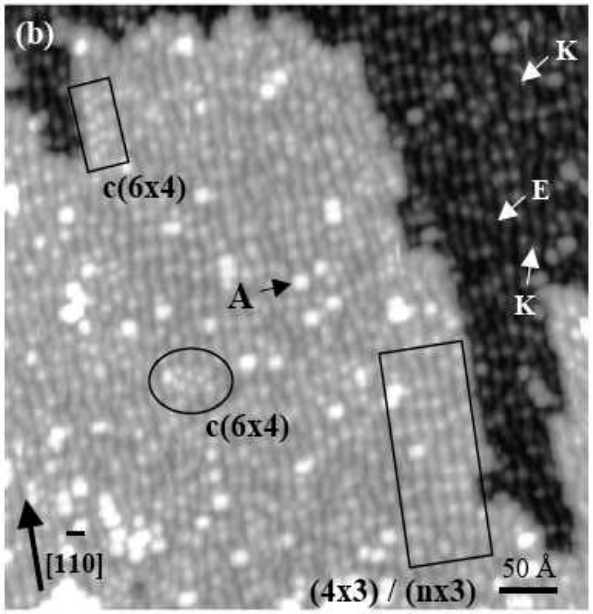
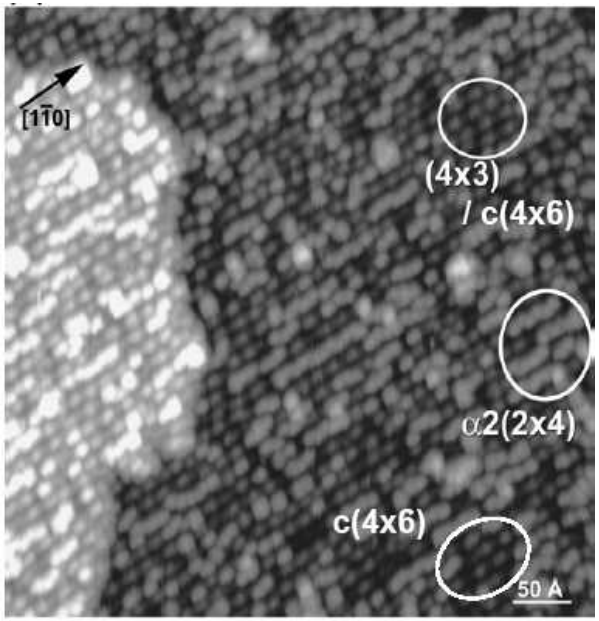
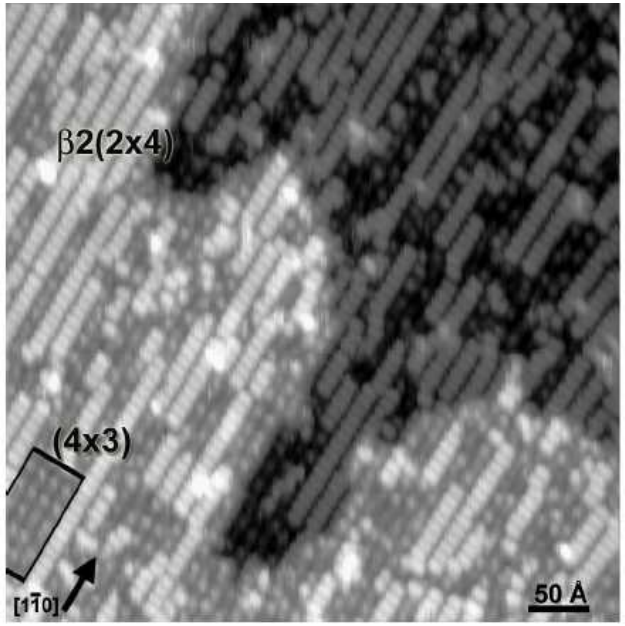
Alloy Reconstructions Distinct from Constituents



- $In_{0.53}Ga_{0.47}As/InP$
- Lattice Matched
- (4x3) reconstruction



- $In_{0.27}Ga_{0.73}As/GaAs$
- 2% compressive Strain
- (4x3) and α2(2x4) reconstructions

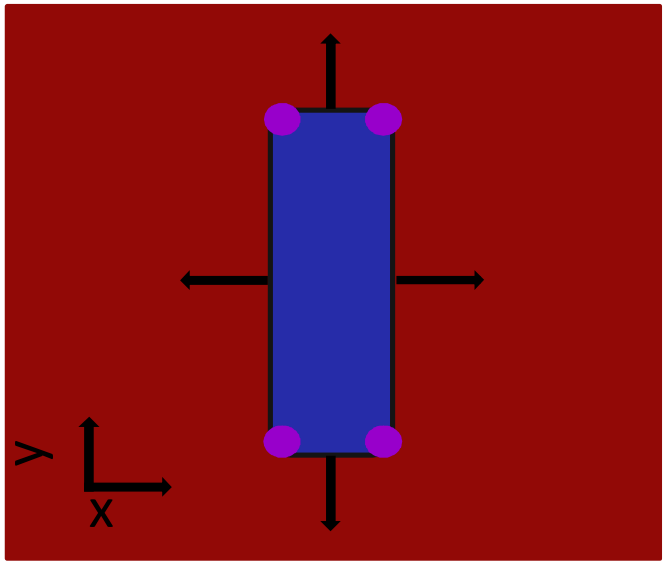


- $In_{0.81}Ga_{0.19}As/InP$
- 2% compressive Strain
- (4x3) and β2(2x4) reconstructions

Images courtesy of A. Riposan, PhD Dissertation, University of Michigan

Elastic Relaxation Drives Coexistence of Reconstructions

- Strained InGaAs films exhibit nanoscale domains of different reconstructions
- Well behaved distribution of anisotropic domains



- Thermodynamic model for reconstruction coexistence*

$$\Delta G = \underbrace{2(s+t)\beta}_{\text{Boundary Energy}} + \underbrace{st\Delta\gamma}_{\text{Surface Energy}} + \underbrace{U(s,t)}_{\text{Elastic Relaxation Energy}} + \underbrace{E_c}_{\text{Corner Energy}}$$

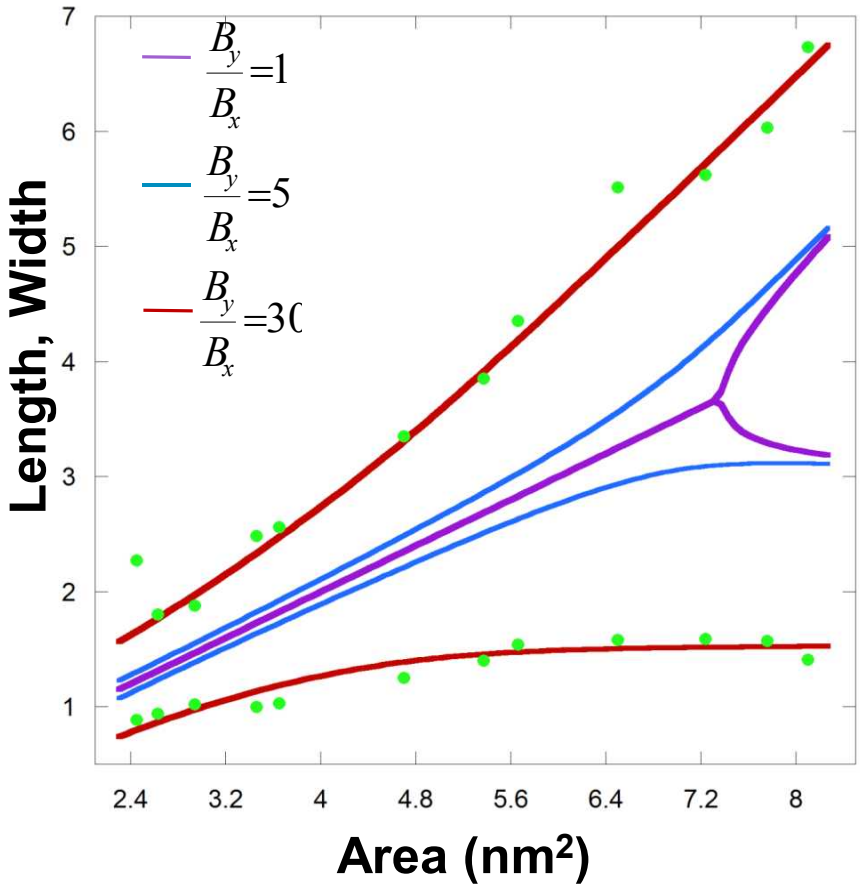
- Competing Interactions
  - Minimize surface energy
  - Maximize elastic relaxation
- Detailed evaluation of model requires knowledge of physical terms such as surface energy, surface tension, and boundary energy
  - Utilize DFT to determine values

*Tromp, Hannon, Surf. Rev. and Lett. v9, 1565 (2002)

Anisotropic Boundary Energy

- For an isotropic boundary energy the length and width are equal below a critical area.
  - Above critical area rectangular domains are stable
- Square domains are not stable at any size when boundary energy is anisotropic.
- Experimental Data is Consistent!!!

$$\Delta G = 2(s+t)\beta + st\Delta\gamma + U(s,t) + E_c$$



Sears, Pearson, Millunchick, *Appl. Phys. Lett.* (Submitted).

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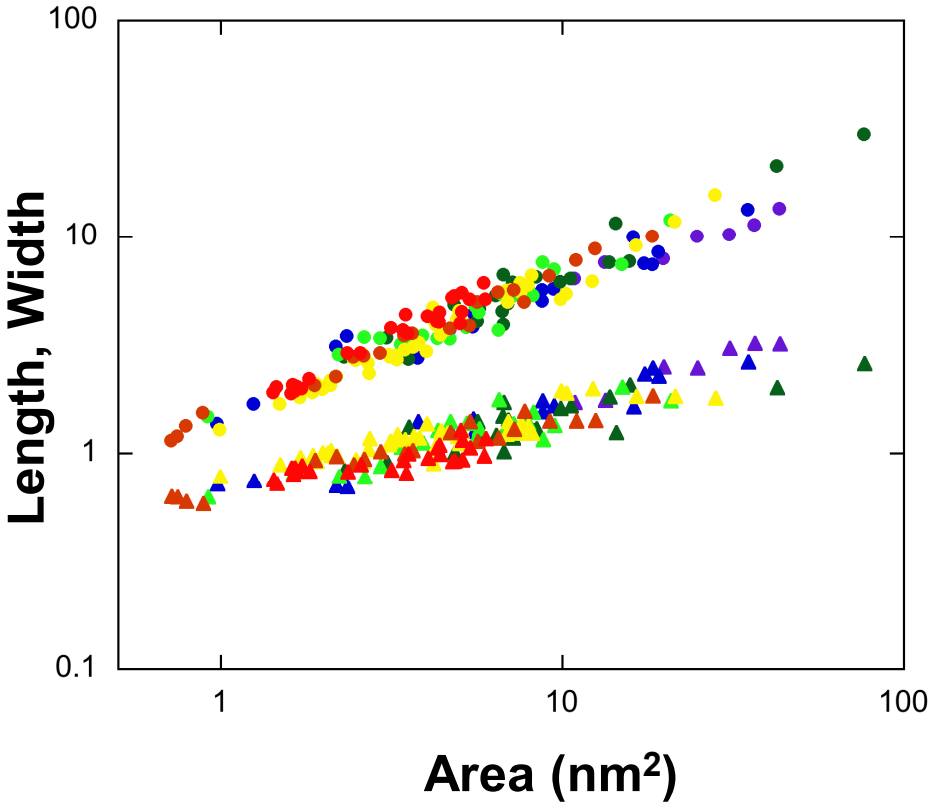

Sears, Pearson, Millunchick, *Appl. Phys. Lett.* (Submitted).

Outline

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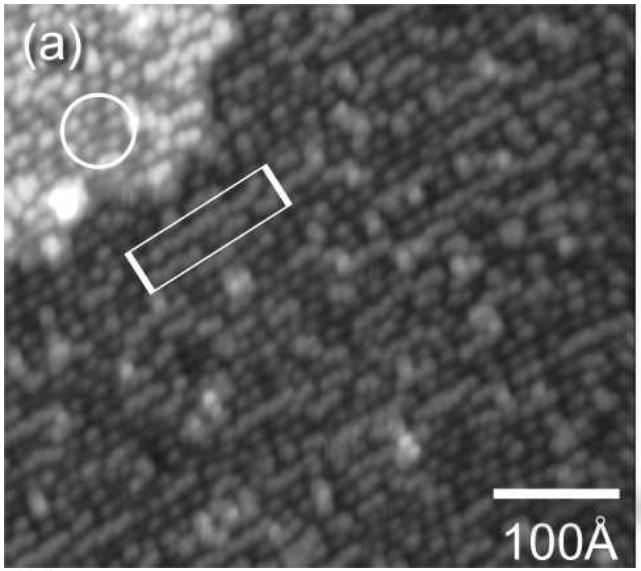
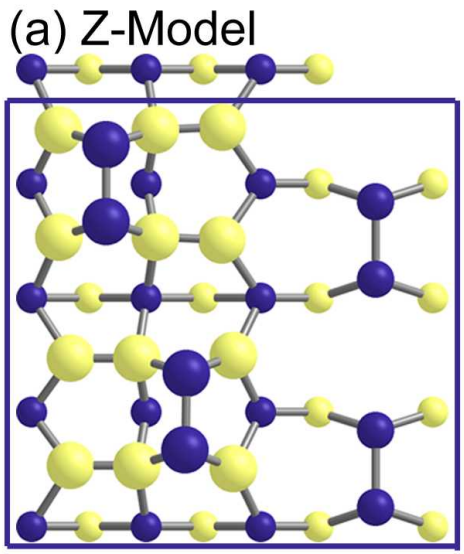
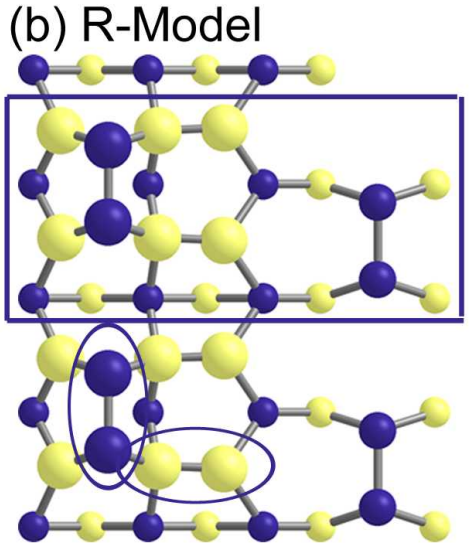
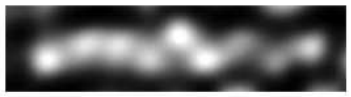
- Ternary alloys exhibit reconstruction *coexistence*
- Understanding the Role of Strain
  - Atomic size mismatch strain
    - z(4x4) reconstruction
    - (4x3) reconstruction (?)
  - Lattice mismatch strain
    - Sb/GaAs reconstruction coexistence

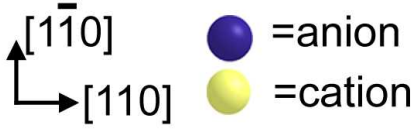
The Alternating Dimer Configuration





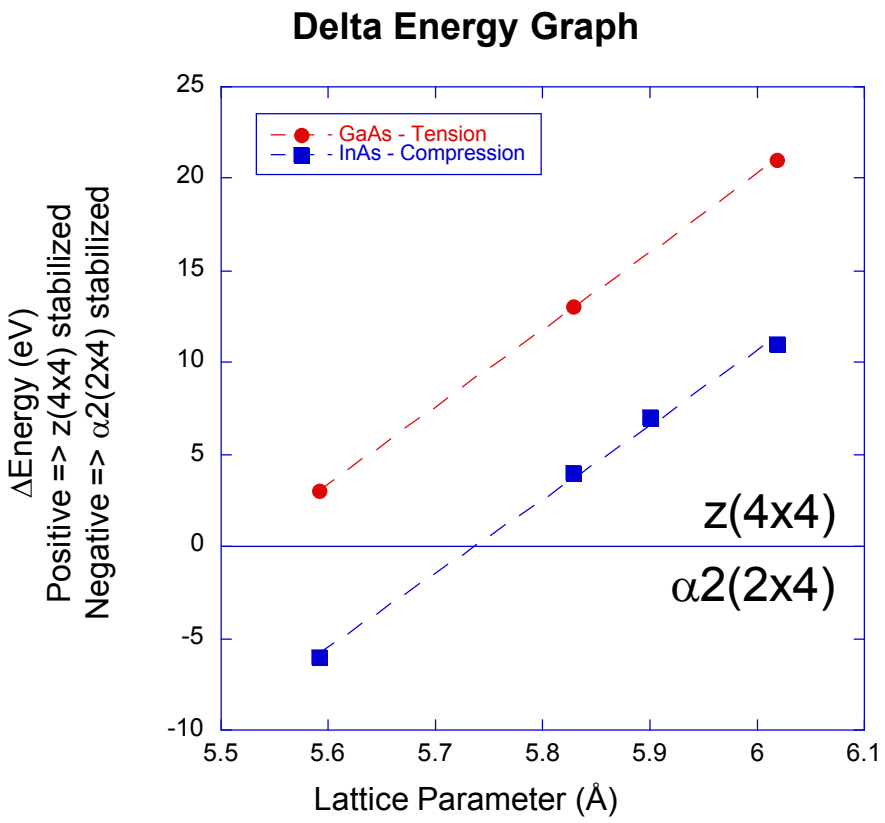






- $In_{0.27}Ga_{0.73}As$ experiment shows the surface dimer alternates position with an 80% incidence
  - z(4x4) reconstruction
- z(4x4) not seen in pure InAs or GaAs

Misfit Strain Does Not Explain z(4x4)

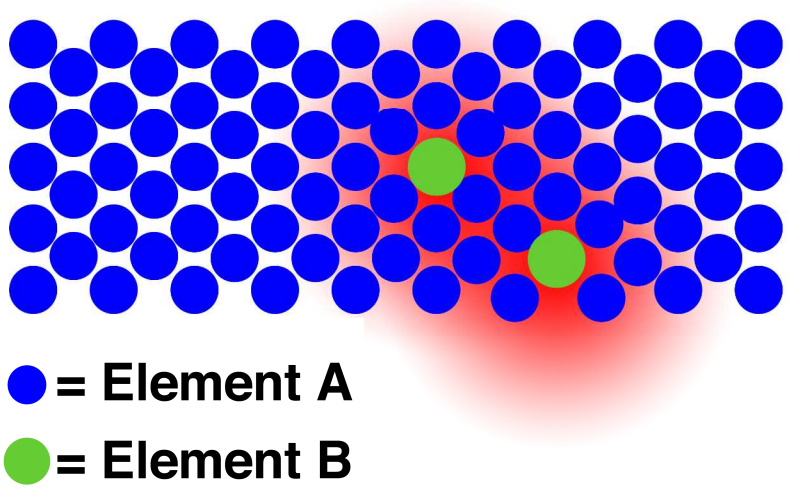


- Misfit Strain is

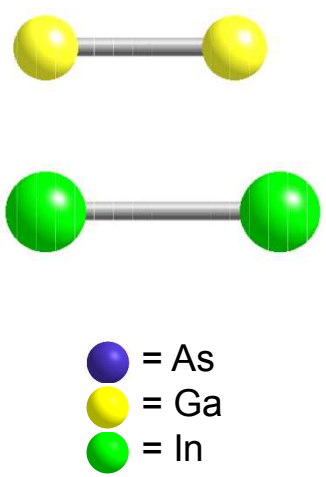
$$\varepsilon = \frac{a_{film} - a_{substrate}}{a_{substrate}}$$

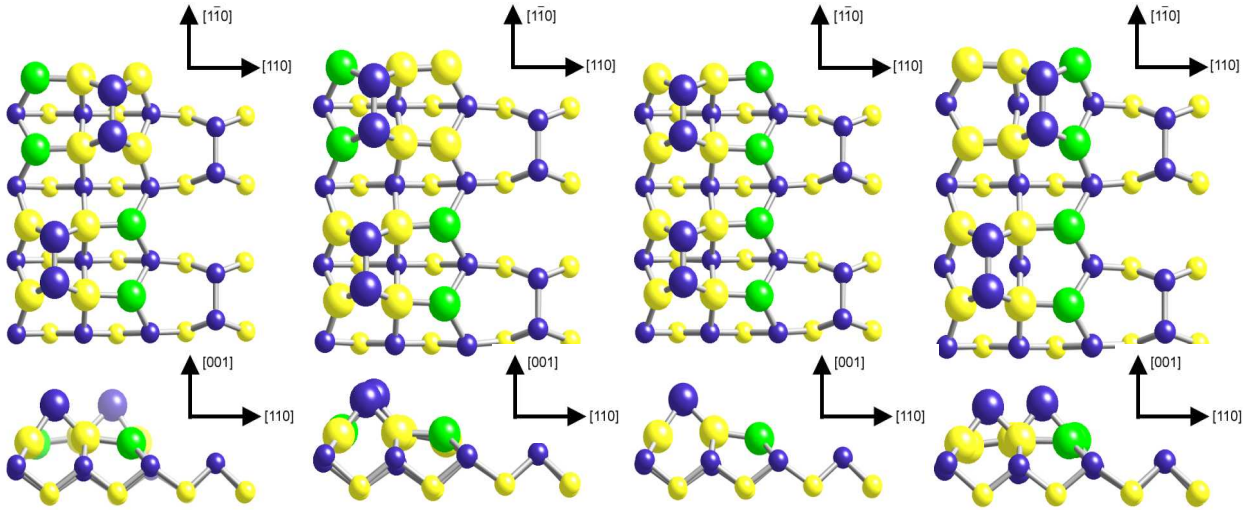
- Pure GaAs and InAs show slight z(4x4) stabilization
  - Not enough to overcome effects of temperature
- Misfit strain alone is not enough to stabilize z(4x4)

Atomic Size Mismatch Strain



Surface Alloying Stabilizes z(4x4)





• z(4x4)-zig In
-132meV

□ α2(2x4)-zig In
-40meV

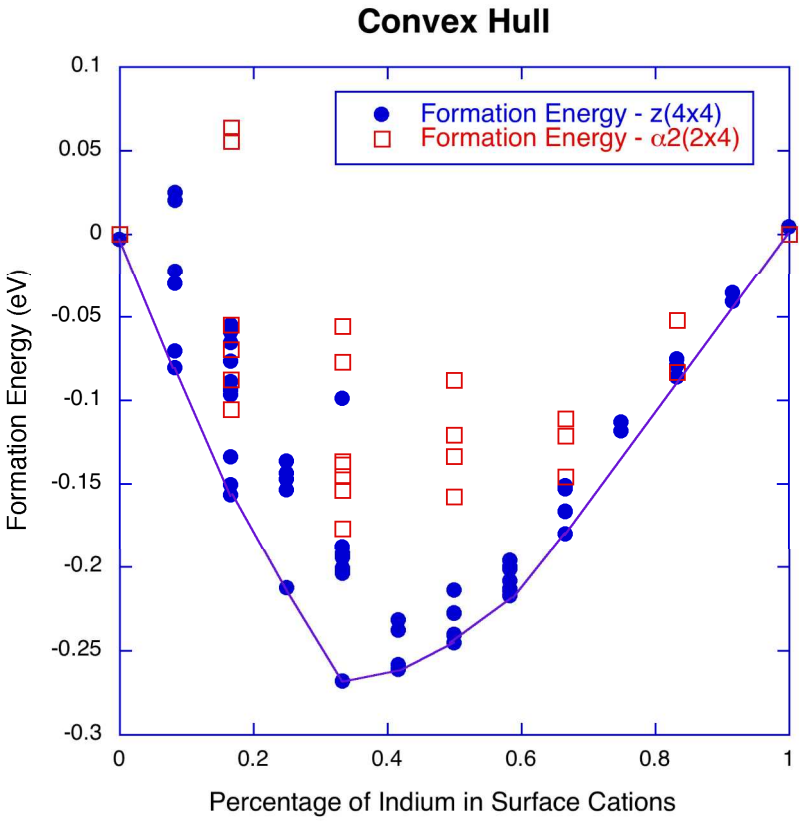
□ α2(2x4)-straight In
0meV

• z(4x4)-straight In
37meV

Increasing Energy

- Atomic size mismatch strain is induced by the size difference between two cations
- Placement of Indium in specific locations induces a surface solute strain and strongly stabilizes the z(4x4)
  - In atoms can relax the cation-cation bond
  - Large atoms can better relax in alternating pattern

The Role of Atomic Size Mismatch Strain



- Convex hull displays formation energy of multiple configurations on a single graph
- z(4x4) is more stable than the α2(2x4) for most surface percentages of In
- Approximately 100meV stabilization for X_{In}=0.33
- Atomic size mismatch strain stabilizes the surface reconstruction
- Suggests that the surface layer is most stable for a mixed composition

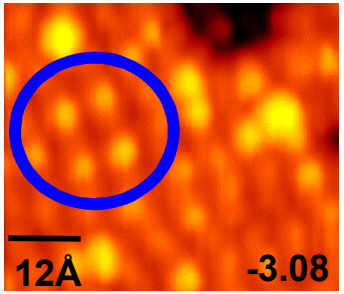
Bickel, Modine, Van der Ven, Millunchick, *Appl. Phys. Lett.* **92,** 062104 (2008)

(4x3) Surface Structure Still Unknown

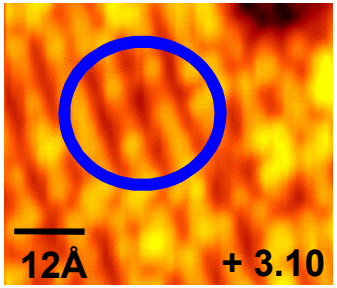
Experimental STM of the (4x3) Structure

- $In_{0.53}Ga_{0.47}As$
- Annealed 25 min at growth conditions

Filled state image



Empty state image

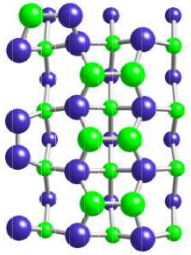


Filled State Image
- Bright spots on dim rows

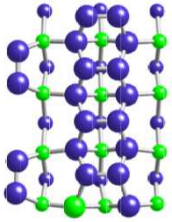
Empty State Image
- Bright spots and rows

DFT Simulated STM of the (4x3) Structure*

Model



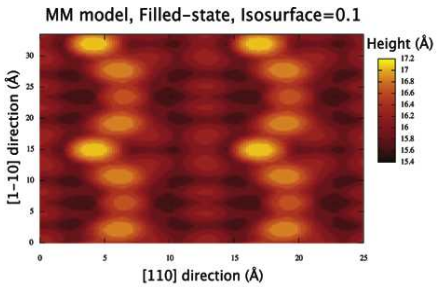
Millunchick et al

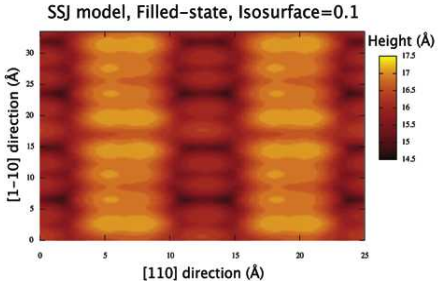


Jones et al

= As
= In

Filled state image





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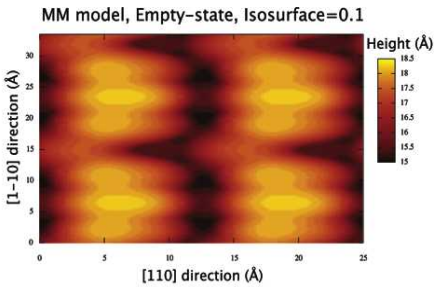
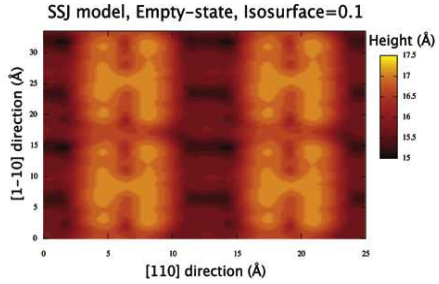




Cation Dimer Model
- Mixed Termination
- Anion Dimers
- Cation Dimers
- Hetero Dimers
- As coverage = 0.5ML

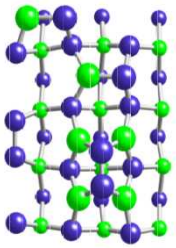
Millunchick et al. Surf. Sci. ***550*** *1 (2004)*

Anion Dimer Model
- Anion Termination
- Anion Dimers
- Excess Anion Dimer
- As coverage = 1.5ML

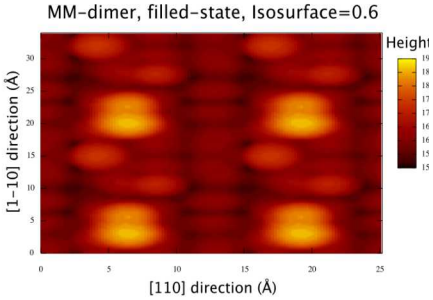
P.A. Bone et al., Surf. Sci. ***600*** *973 (2006)*

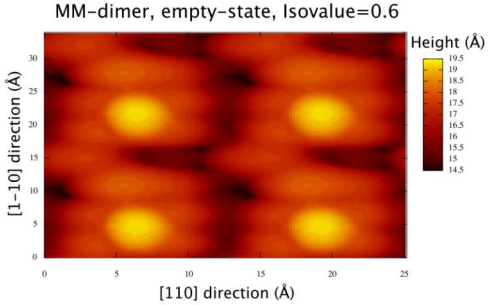
J. Tersoff, D.R. Hamann, Phys. Rev B,* ***50* *1998 (1983)*

(4x3) Likely Stabilized By Solute Strain



Riposan

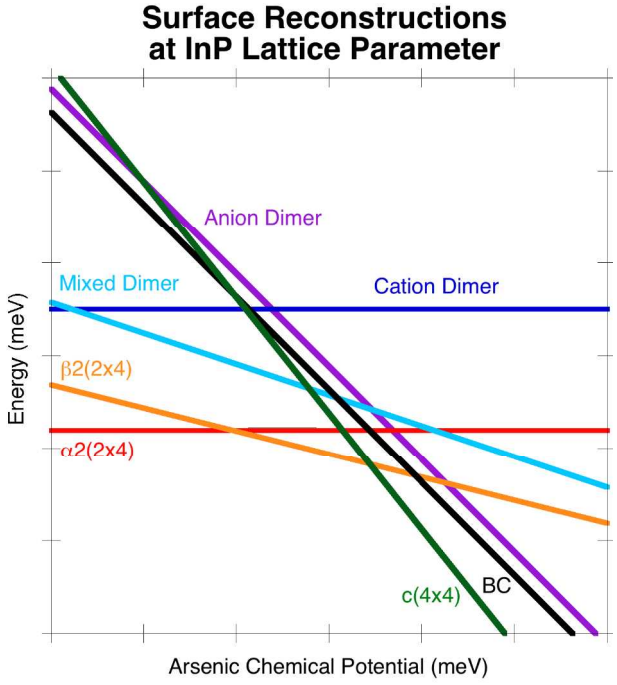




Mixed Dimer Model

- Mixed Termination
- Anion Dimers
- Hetero Dimers
- As coverage = 0.83ML

A. Riposan, (PhD dissertation) University of Michigan



Surface stability follows lowest energy line as a function of chemical potential

- Best experimental STM to DFT STM match is mixed dimer model
- Energy remains too high
- Misfit strain does not sufficiently lower energy
- Alloy induced solute strain may be the key

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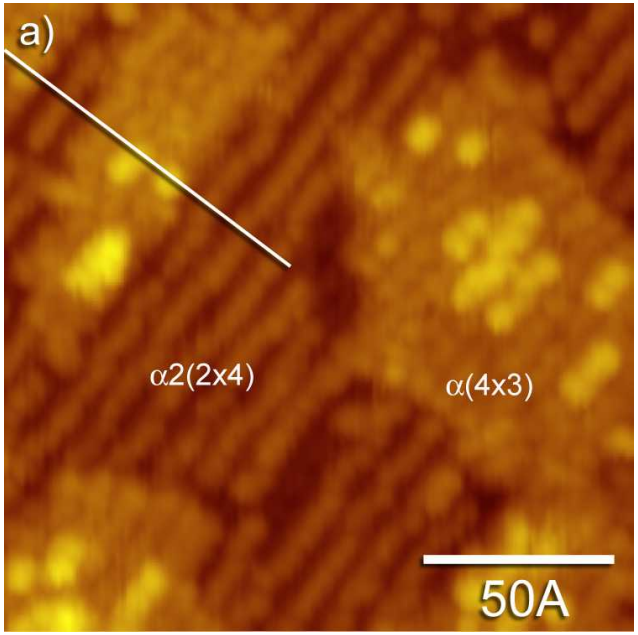
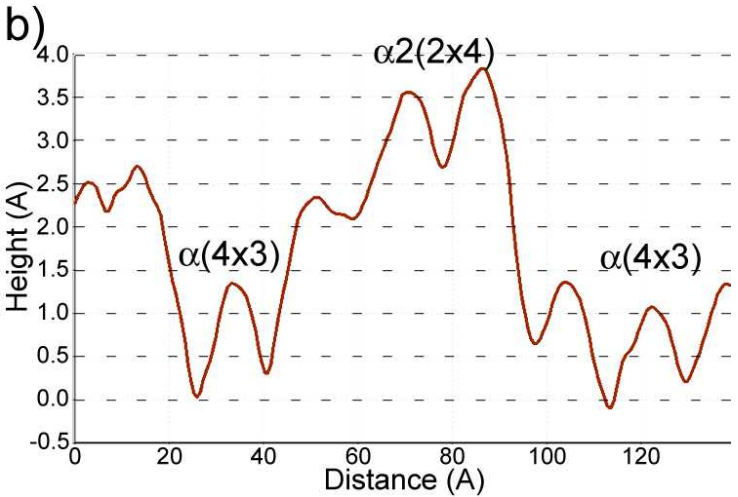
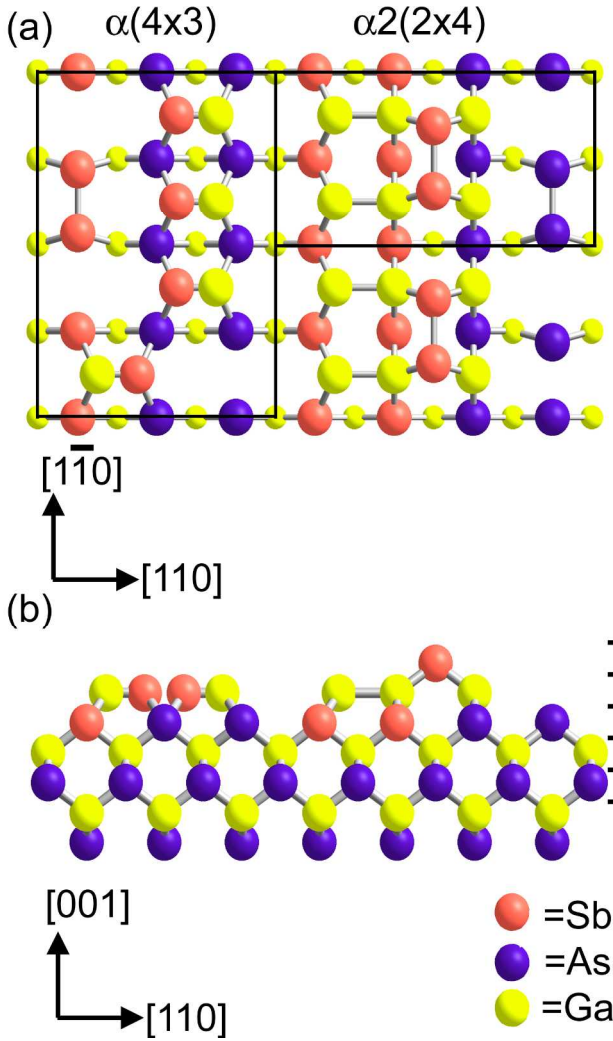
    - (4x3) reconstruction (?)
  - Lattice mismatch strain
    - Sb/GaAs reconstruction coexistence

Reconstructions on Sb/GaAs

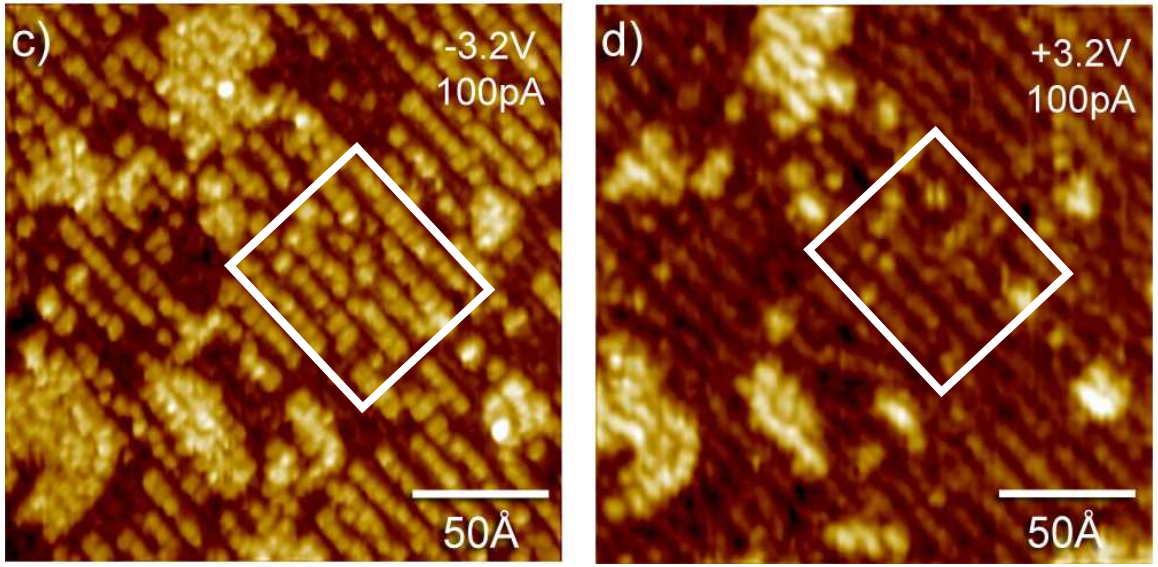




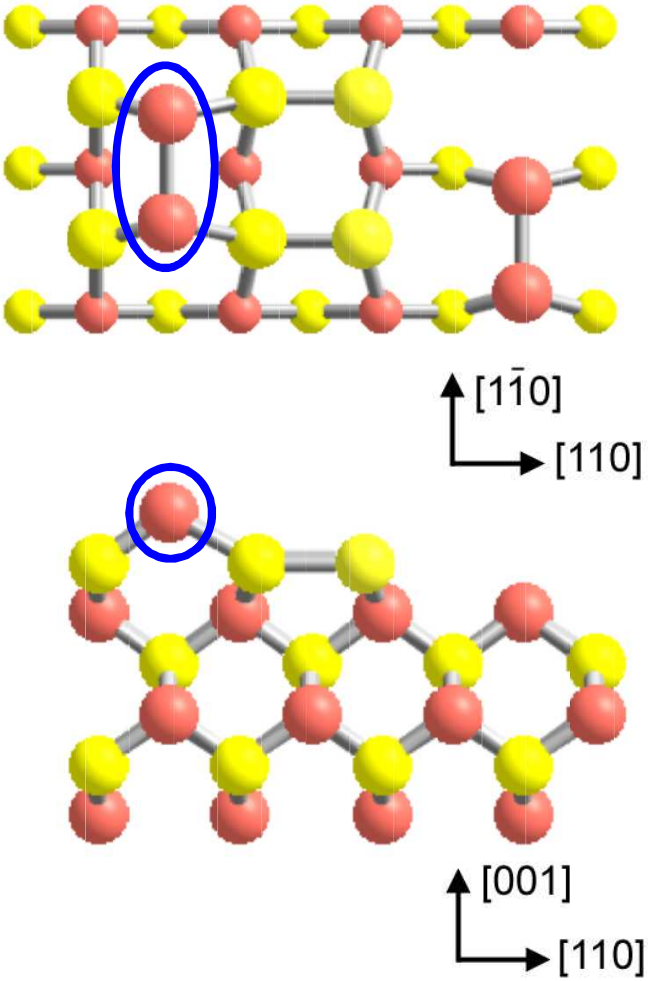


Surface Reconstruction of Sb/GaAs(001)

α2(2x4) reconstruction

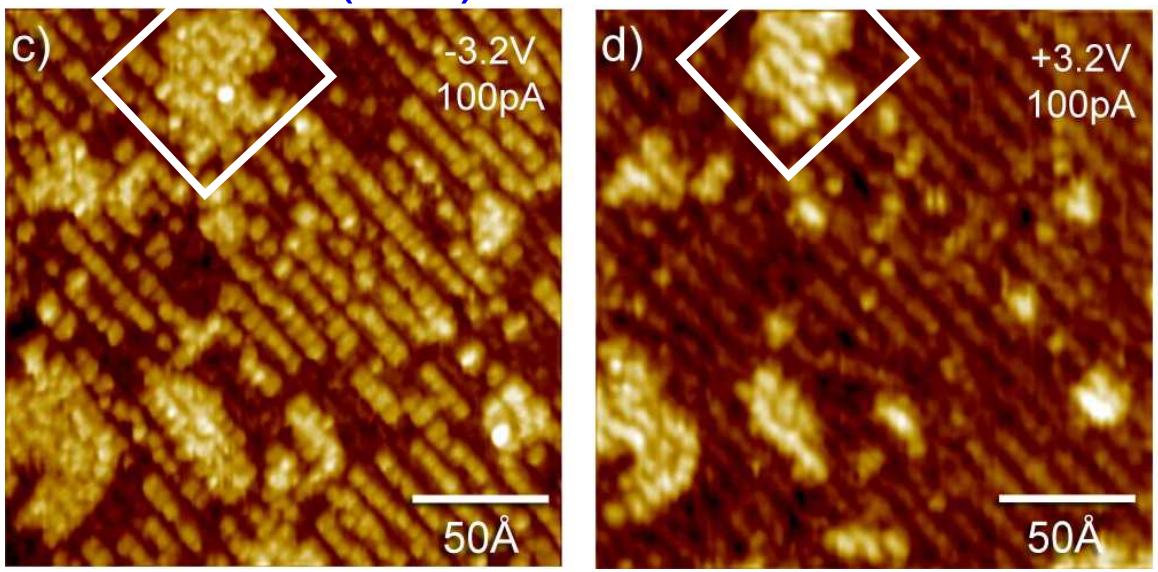


- α2(2x4)
  - Common to GaAs
  - Not common to bulk GaSb

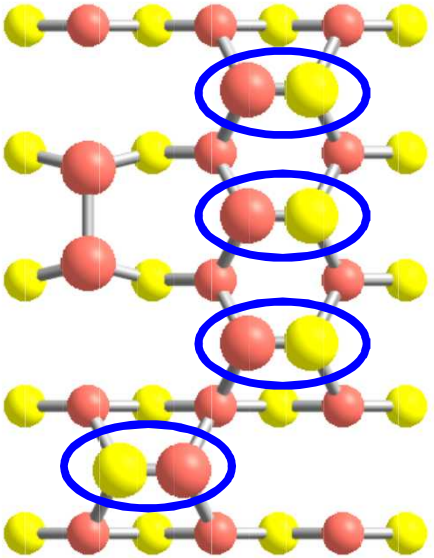


Surface Reconstruction of Sb/GaAs(001)

α(4x3) reconstruction

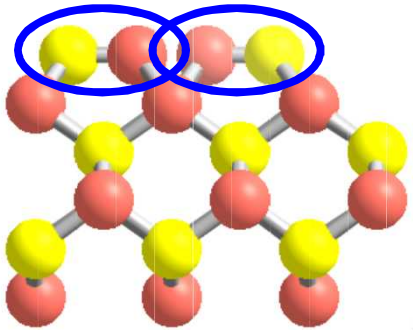


- α(4x3)
  - Bulk GaSb reconstruction
  - Not common to GaAs

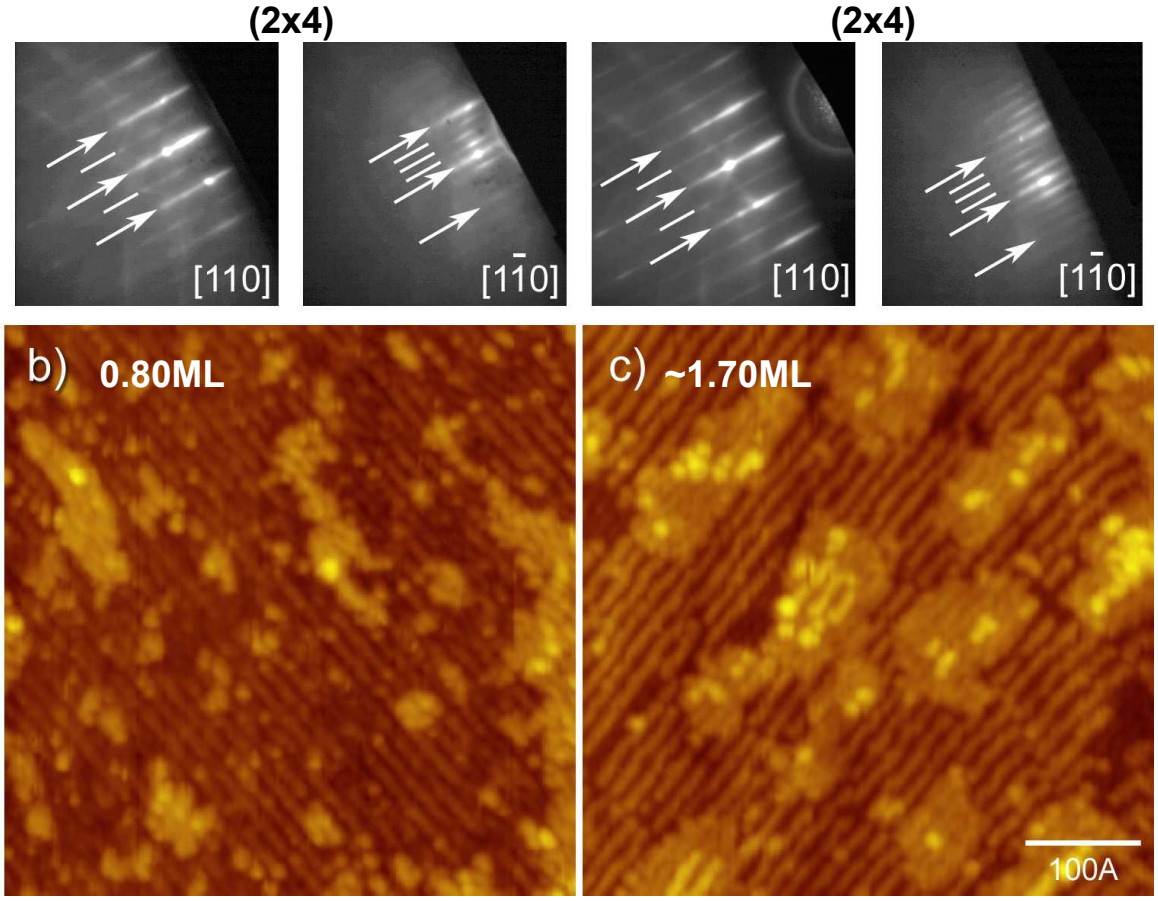


= Ga
= Sb

Some atoms omitted for clarity



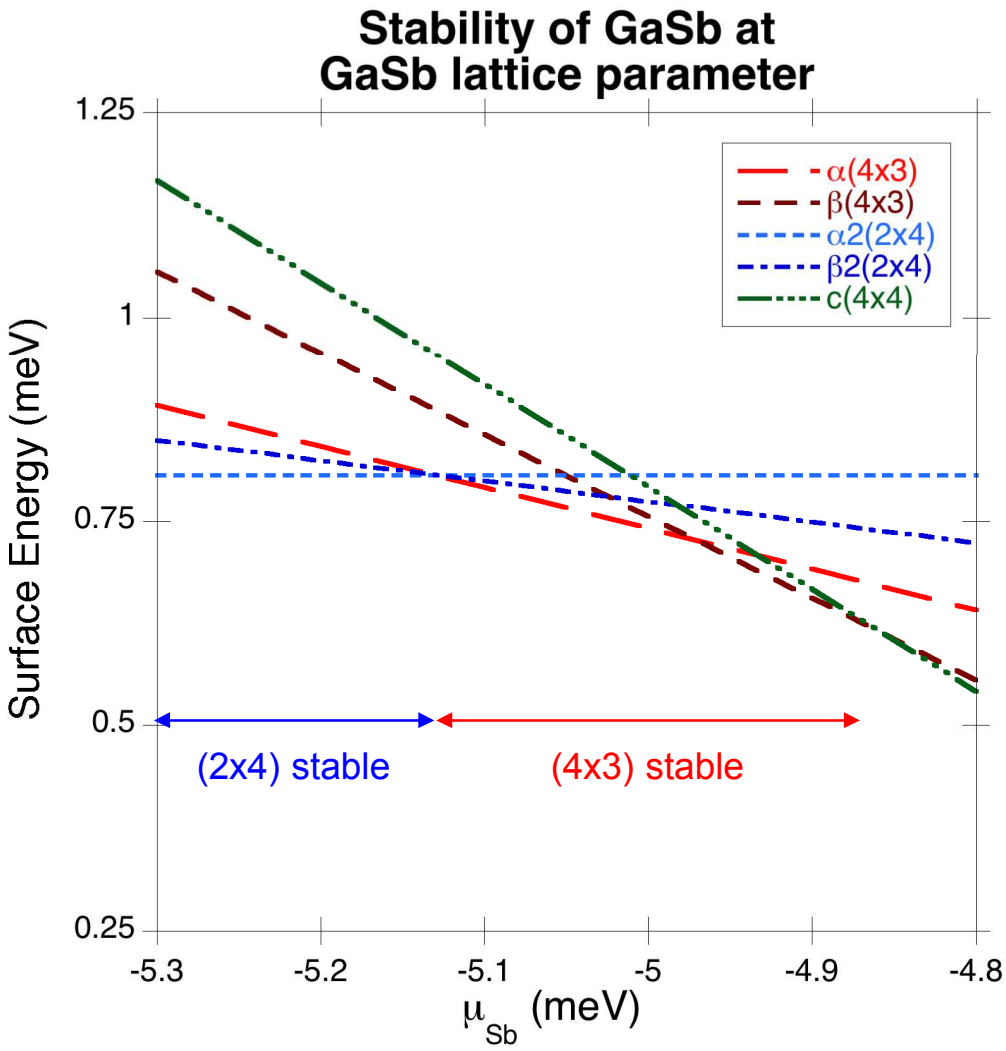
Mixed Reconstruction Stability



RHEED of the samples after quenching (top), and room temperature STM images (bottom) for increasing thickness of Sb/GaAs. b) 0.8ML, c) ~1.7ML. The box in (a) indicates an area of x3 rows within the disordered surface.

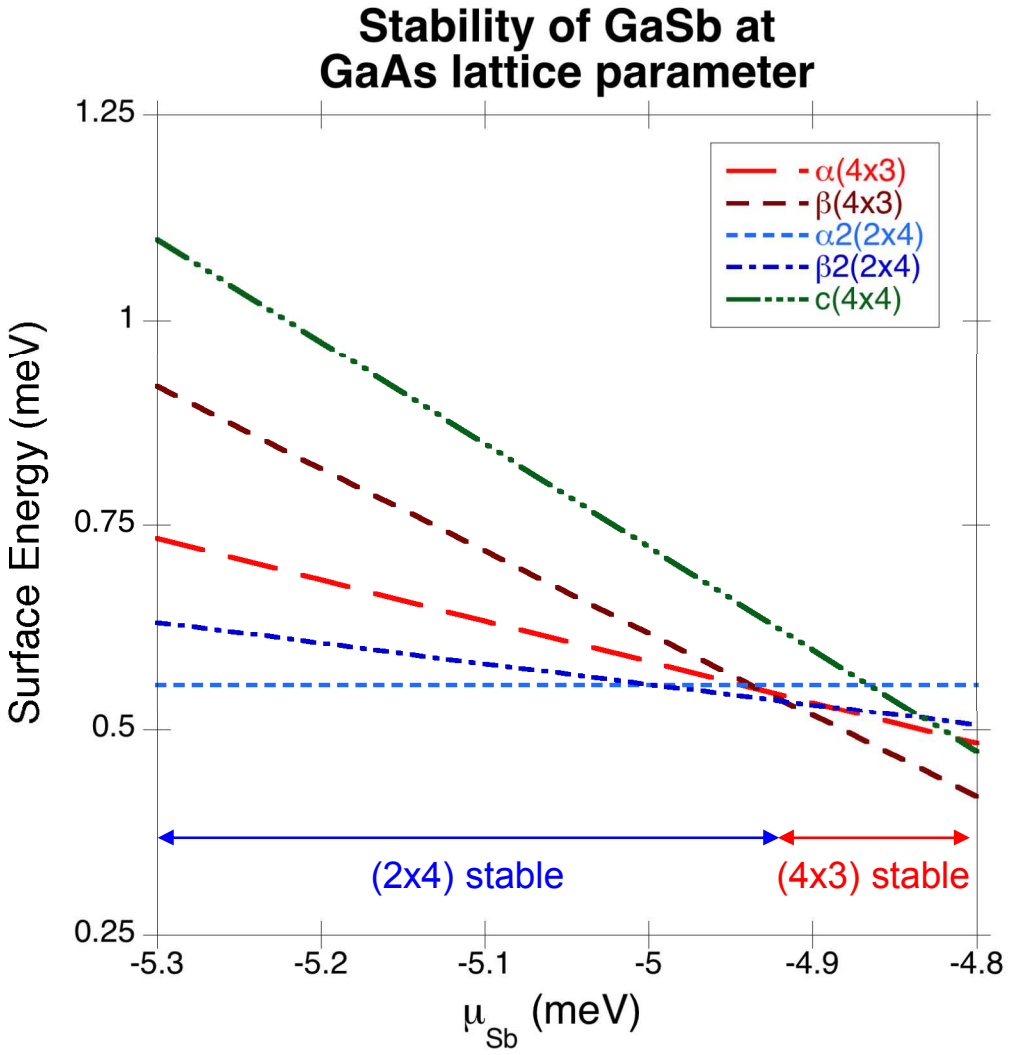
Elastic Relaxation

- GaSb Lattice Parameter
  - Lowest line = stable reconstruction
  - (4x3) reconstruction stable for much of μ_{Sb}
    - μ_{Sb} =chemical potential of Sb
  - Stability with decreasing μ_{Sb}
    - c(4x4)
    - β(4x3)
    - α(4x3)
    - α2(2x4)



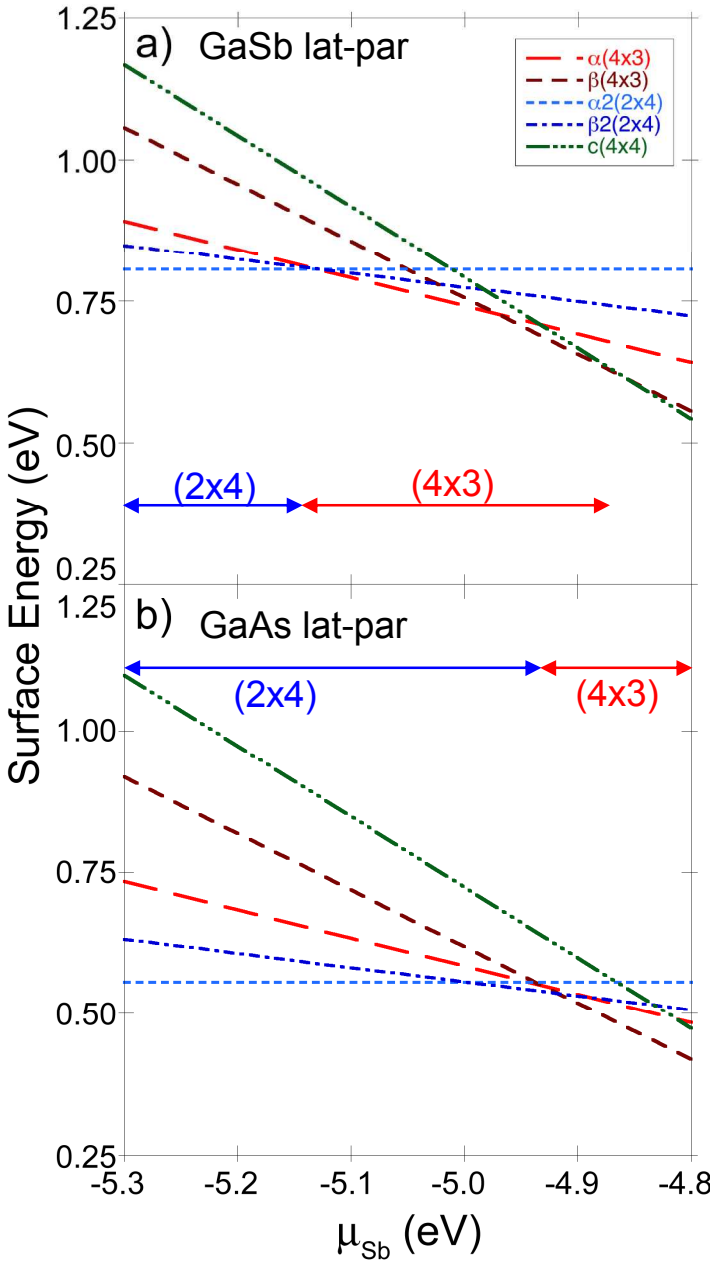
Elastic Relaxation

- GaAs Lattice Parameter
  - Lowest line = stable reconstruction
  - (2x4) reconstruction stable for much of μ_{Sb}
    - μ_{Sb} =chemical potential of Sb
  - Stability with decreasing μ_{Sb}
    - β(4x3)
    - β2(2x4)
    - α2(2x4)



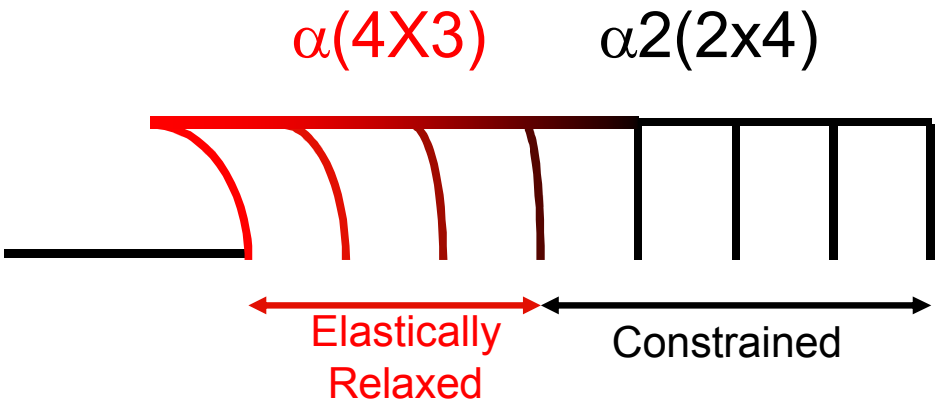
Elastic Relaxation

- Mixed Reconstruction in GaSb/GaAs (001)
  - Mixed Anion System
- α2(2x4)
  - Stable for smaller lattice parameters
  - Appears where lattice parameter is constrained
- α(4x3)
  - Stable at larger lattice parameters
  - Appears at terrace edges where lattice parameter can elastically relax



Elastic Relaxation

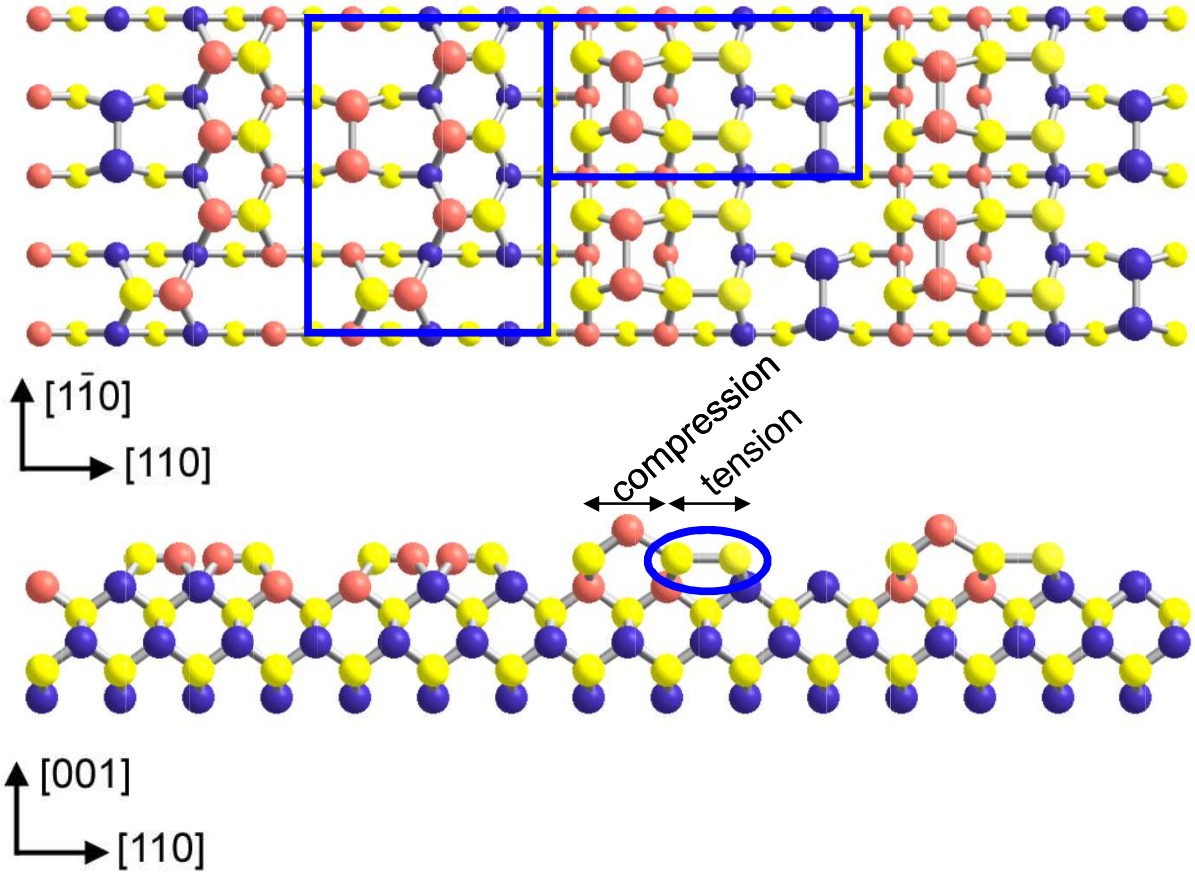
- Mixed Reconstruction in GaSb/GaAs (001)
  - Mixed Anion System
- α2(2x4)
  - Stable for smaller lattice parameters
  - Appears where lattice parameter is constrained
- α(4x3)
  - Stable at larger lattice parameters
  - Appears at terrace edges where lattice parameter can elastically relax



Bickel, Modine, Pearson, Millunchick, *Phys. Rev. B,* **77**, 1 (2008).

α2(2x4) Relieves Compressive Strain

α(4x3) α2(2x4)



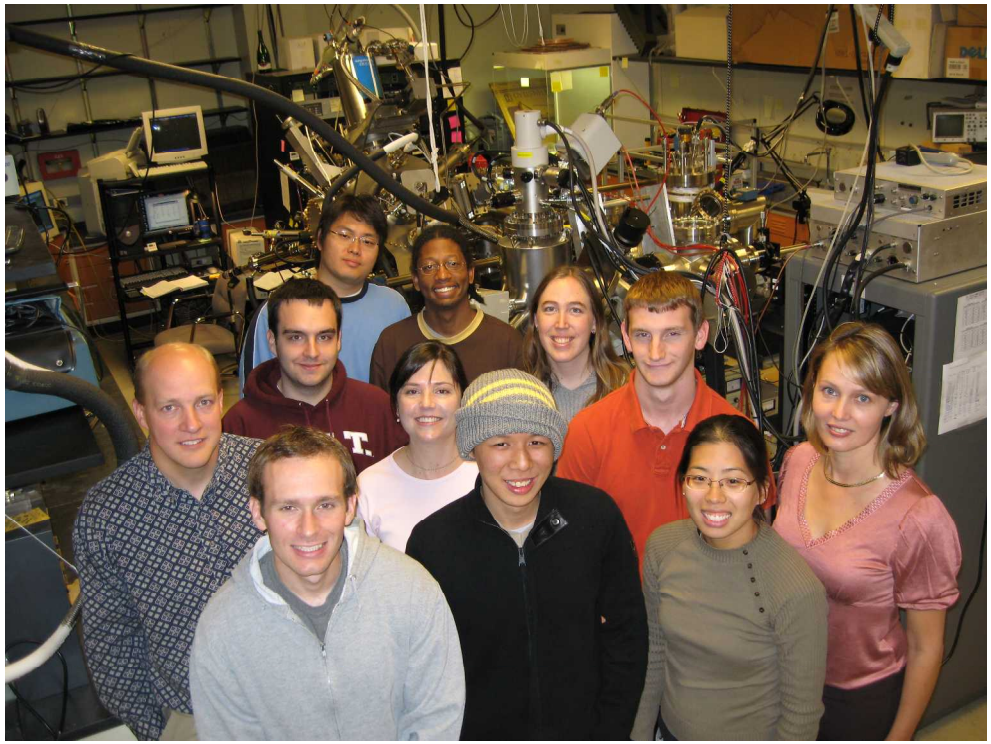
= As
= Ga
= Sb

Some atoms omitted for clarity

Conclusions

- Ternary alloys are complex than their binary counterparts
- *Thermodynamic* Coexistence Model
  - Fit to data suggests that this is not a kinetic effect
- Role of Strain
  - Atomic Size Mismatch Strain
    - Stabilizes the z(4x4) reconstruction
    - Mixed cation surface
    - Alloying necessary to DFT treatment
  - Lattice Mismatch Strain
    - Elastic relaxation at step edges => complex strain field on surface
    - May stabilize surface coexistence as for Sb/GaAs

Acknowledgements



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Joanna Mirecki Millunchick

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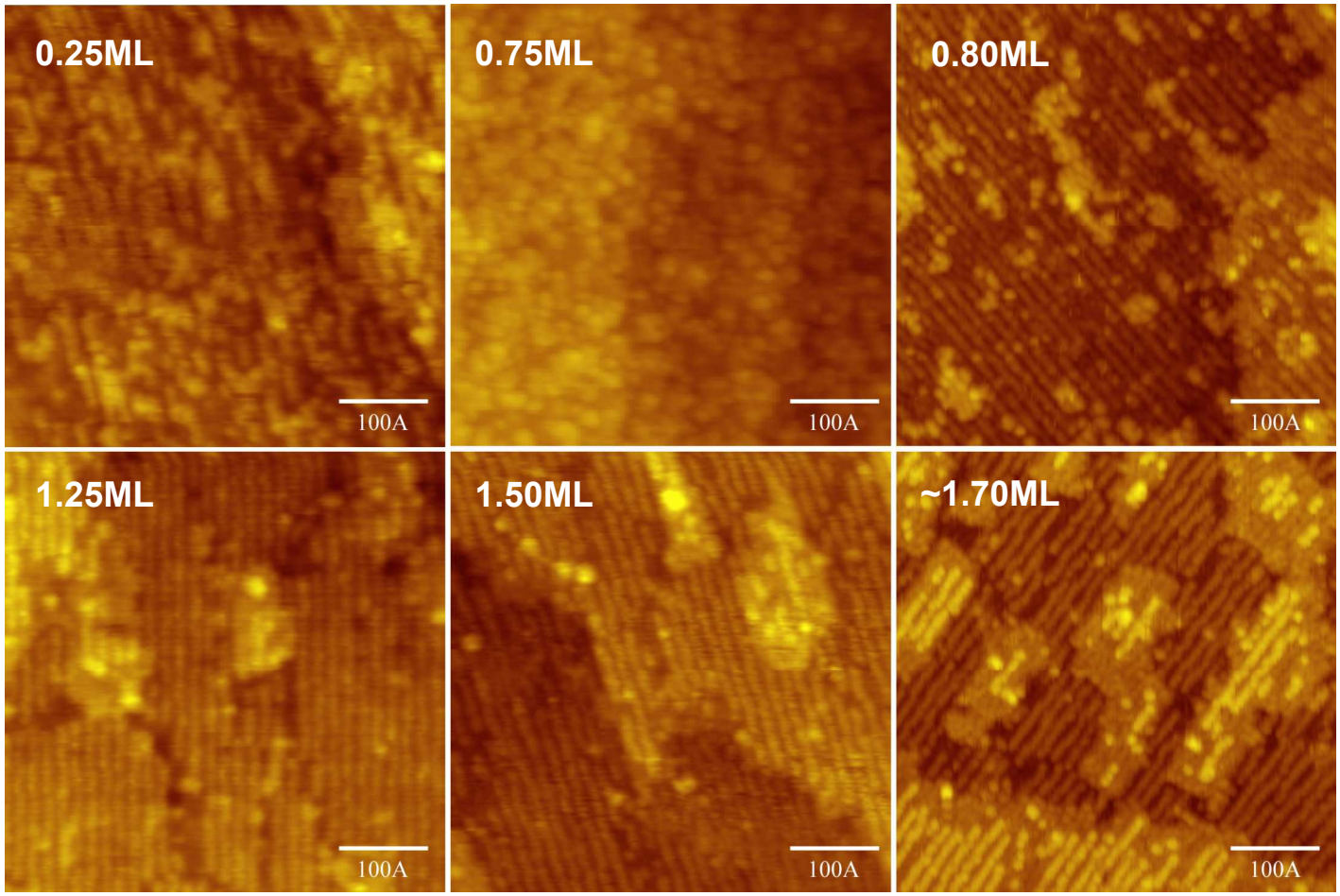
Supplemental Slides

Thickness Study



Thin layers of Sb/GaAs. Top left to right: 0.25ML, 0.75ML, 0.8ML.
Bottom left to right: 1.25ML, 1.5ML, ~1.7ML

Elastic Relaxation

$$U(s,t) = 2F_0 \left\{ \begin{array}{l} -s(1-\nu)\left[\ln\frac{s}{a} - 1\right] + u_1(a) \\ -t(1-\nu)\left[\ln\frac{t}{a} - 1\right] + u_1(a) \\ +2\nu\left(s + t - \sqrt{s^2+t^2}\right) + u_2(a) \\ +(1-2\nu)\left(s - \sqrt{s^2+t^2}\right) + t(1-\nu)\ln\frac{\sqrt{s^2+t^2}+t}{s^2+t^2-t} \\ +(1-2\nu)\left(t - \sqrt{s^2+t^2}\right) + s(1-\nu)\ln\frac{\sqrt{s^2+t^2}+s}{s^2+t^2-s} \end{array} \right.$$

Energy of Border s

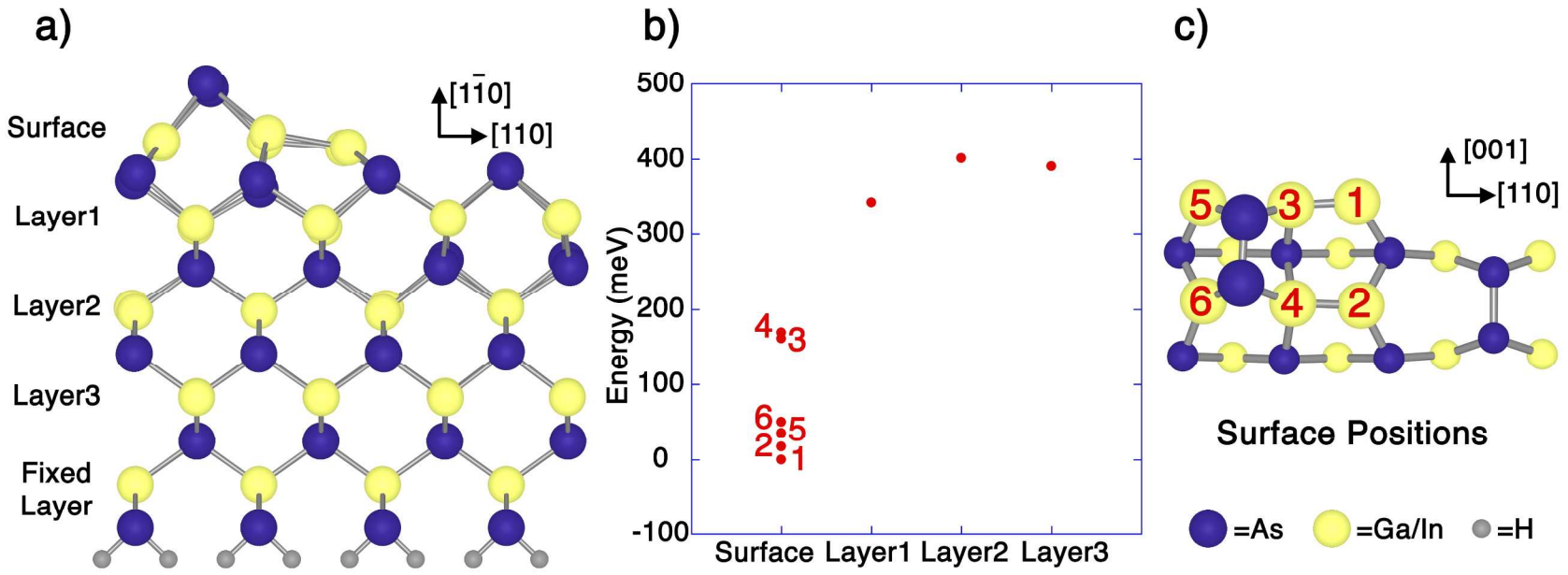
Energy of Border t

Energy of Interaction where s,t meet

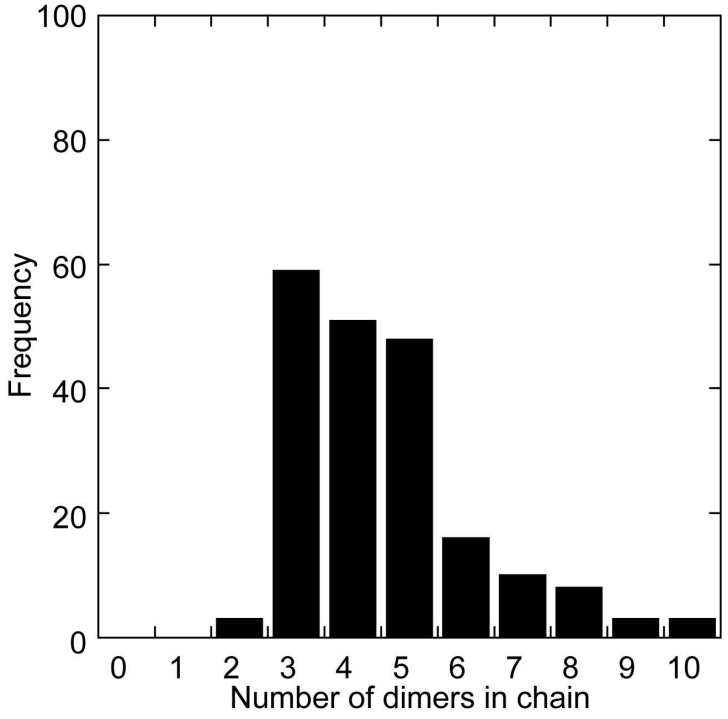
Interaction between parallel segments in s

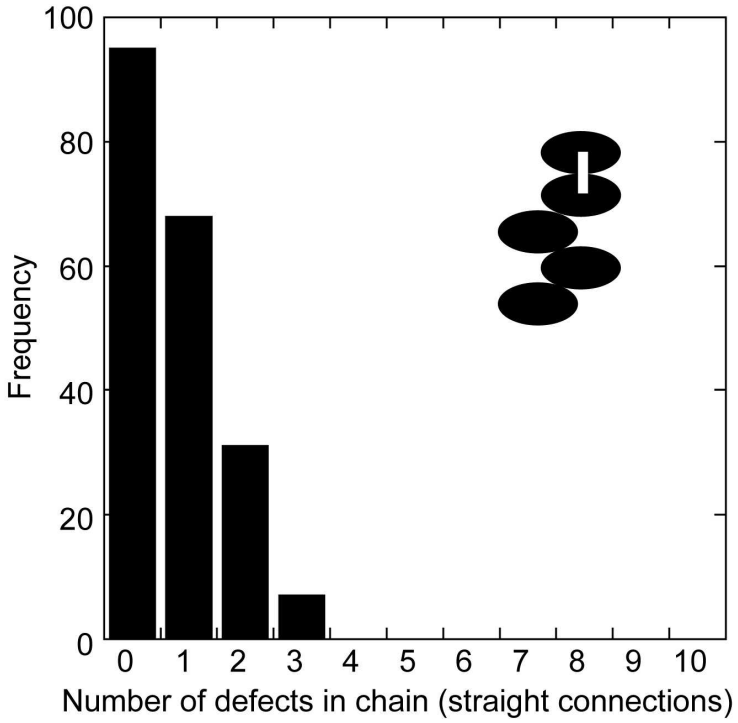
Interaction between parallel segments in t

Indium Surface Segregation

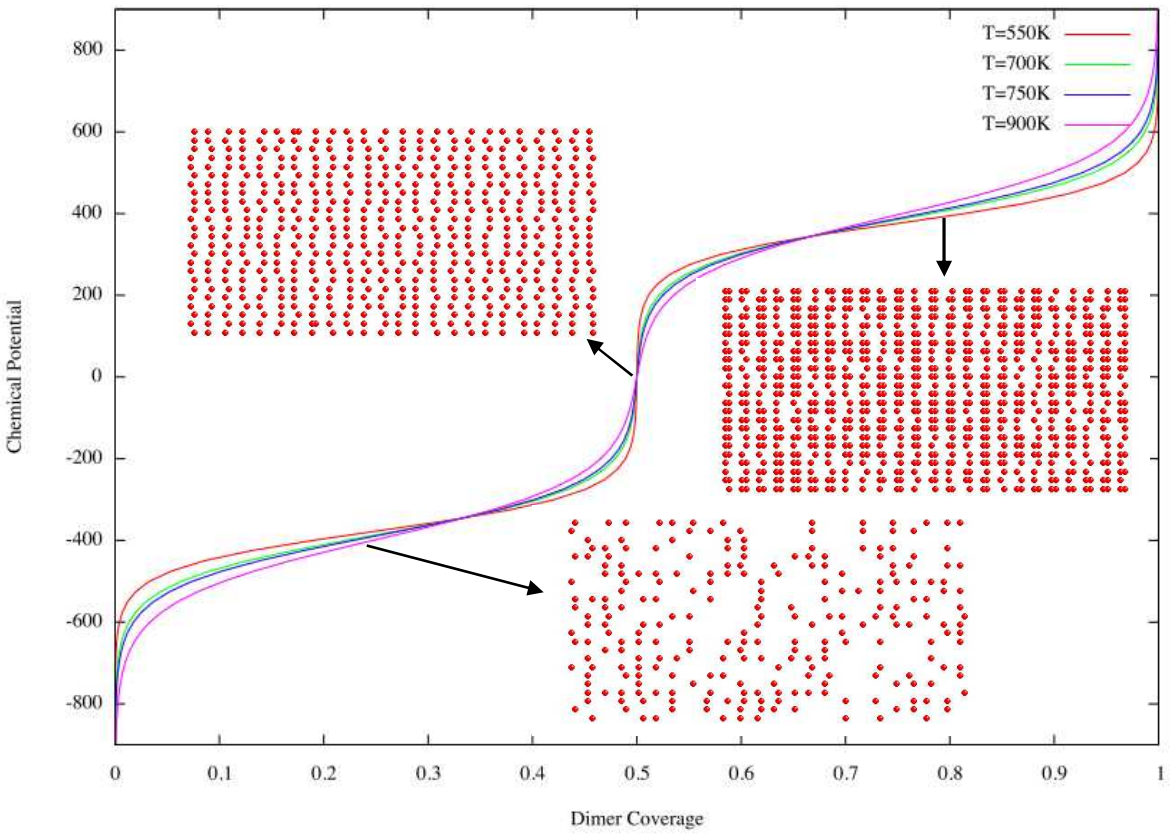


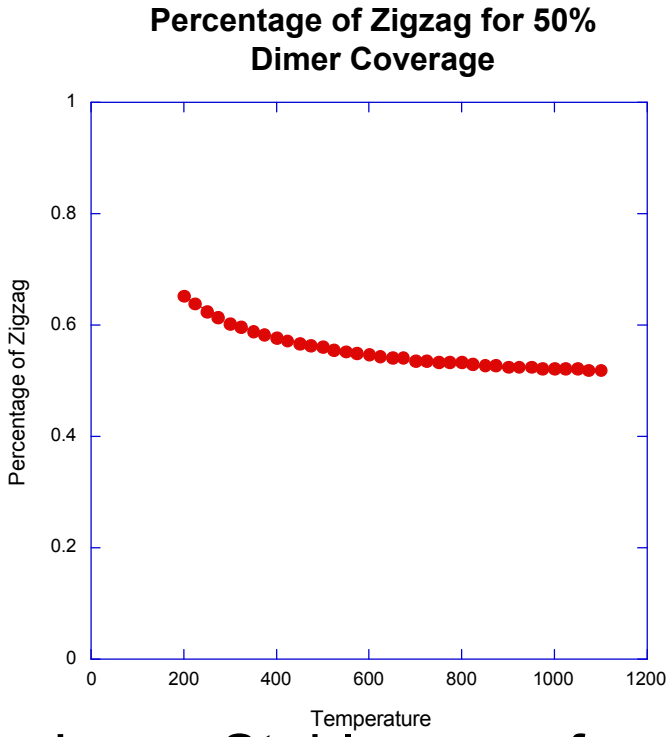
z(4x4) Statistics





Monte Carlo of Pure InAs

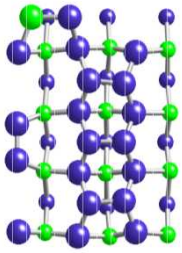




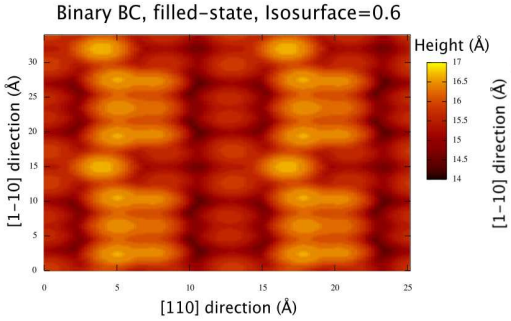
- Large Stable areas for 50% dimer coverage
- Do see a slight favoring of the z(4x4), particularly for lower temperatures

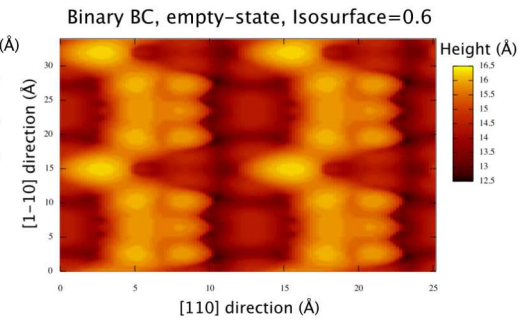
Reconstructions in (4x3) Energy Comparison

Model | Filled state image | Empty state image | Model Characteristics

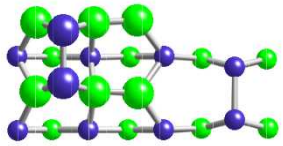


Barvosa-Carter et al
W. Barvosa-Carter, et al, Phys. Rev. Lett. ***84*** *4649 (2000)*

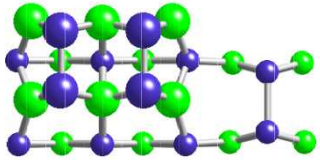




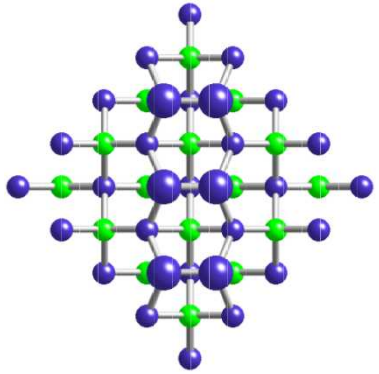
BC (4x3) model
- Mixed Termination
- Anion Dimers
- Hetero Dimers
- As coverage = 1.5ML



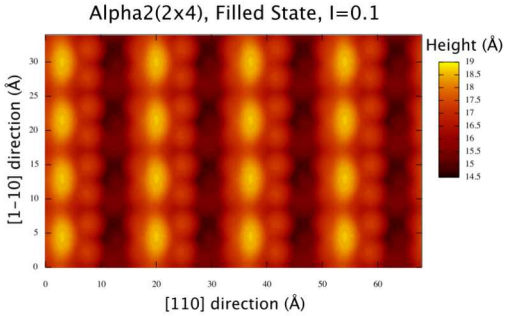
α2(2x4)

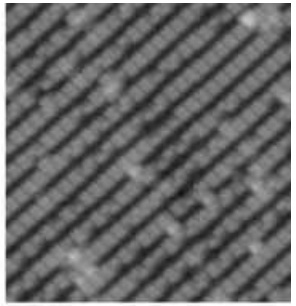


β2(2x4)



QuickTime™ and a
:(LZW) decompressor
ded to see this picture.



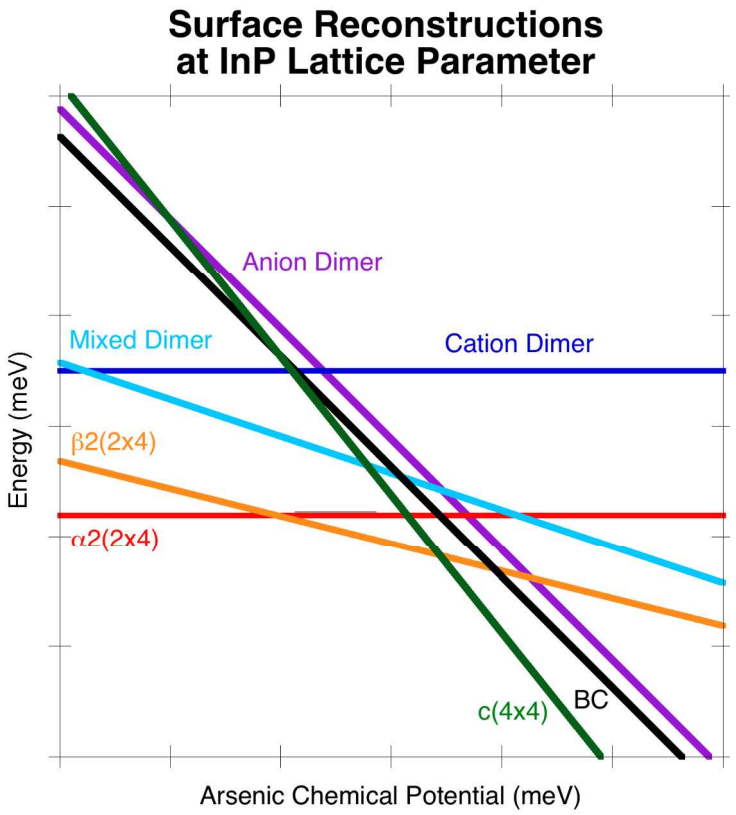


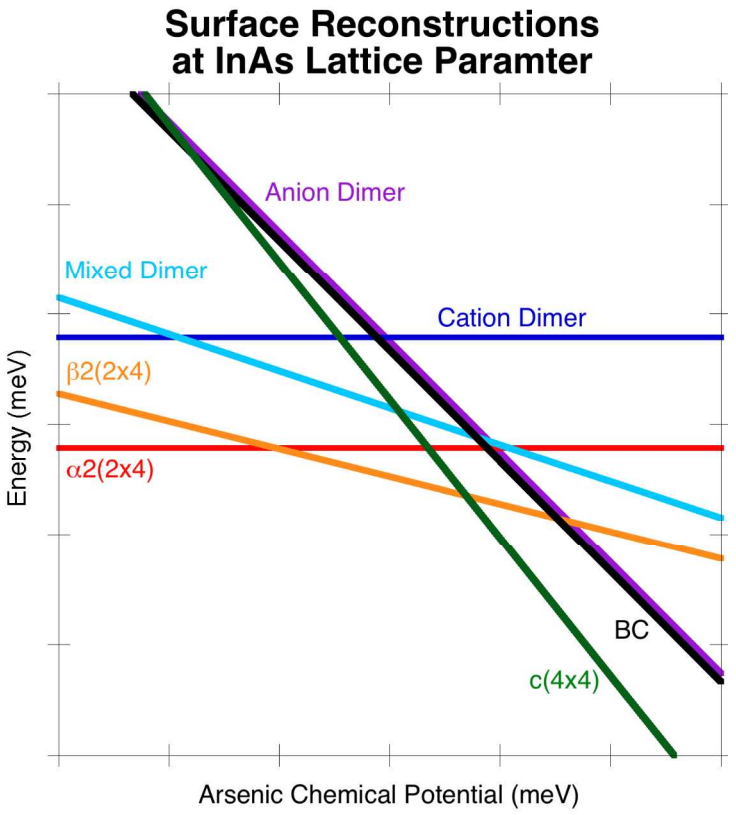
= As
= In

Barvosa-Carter et.al., Surface Science 499, L129 (2002).

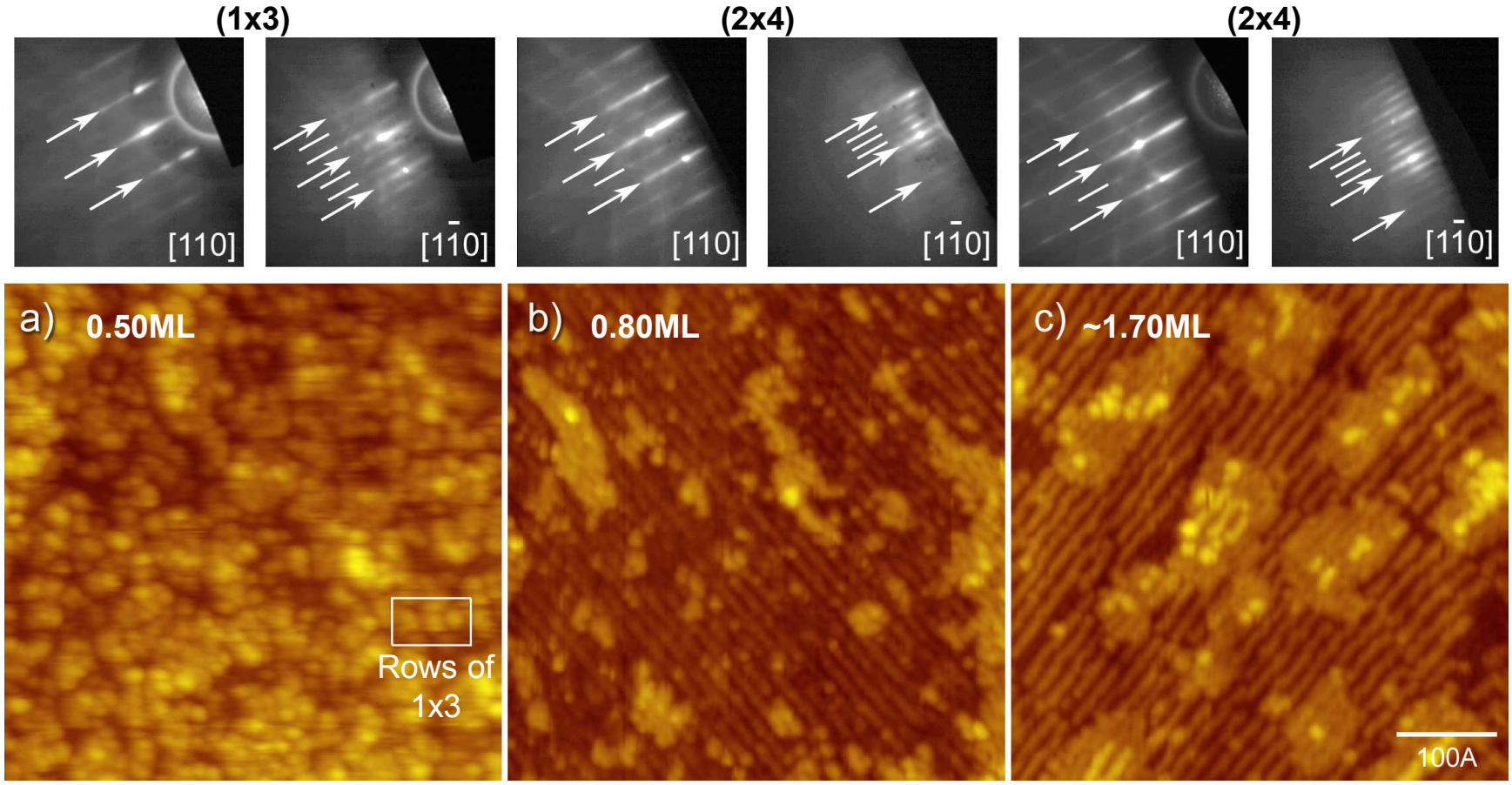
LaBella et.al., Surface Science 60, 1 (2005).

Effect of Misfit Strain on (4x3) Stability





Thickness Study



RHEED of the samples after quenching (top), and room temperature STM images (bottom) for increasing thickness of Sb/GaAs. a) 0.5ML, b) 0.8ML, c) ~1.7ML. The box in (a) indicates an area of x3 rows within the disordered surface.

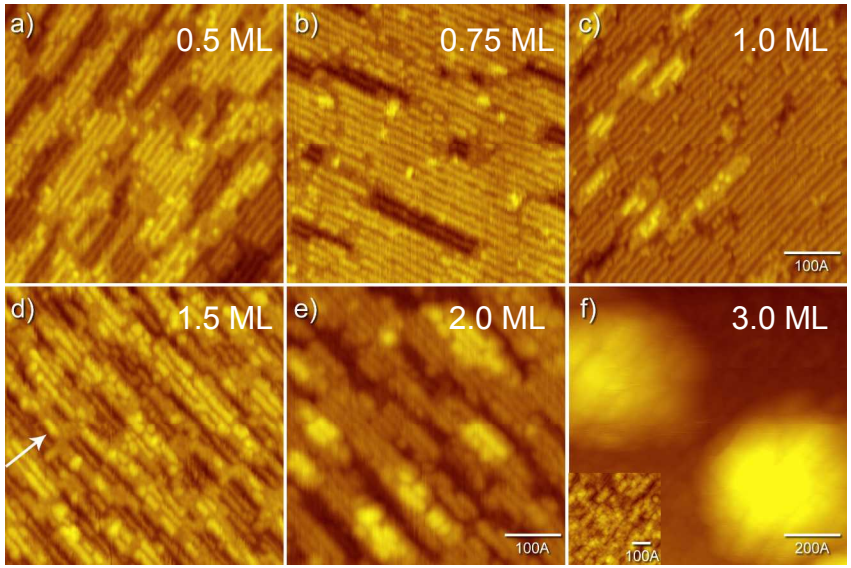
Growth Model

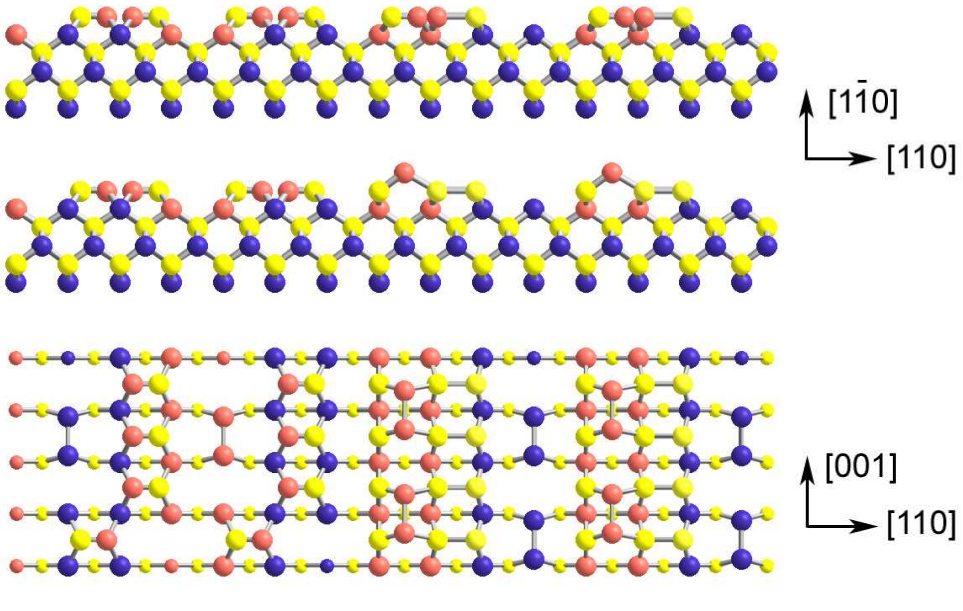
Flat α2(2x4) film

Sb nucleates on surface as α(4x3)

α(4x3) domains grow and transform into α2(2x4)

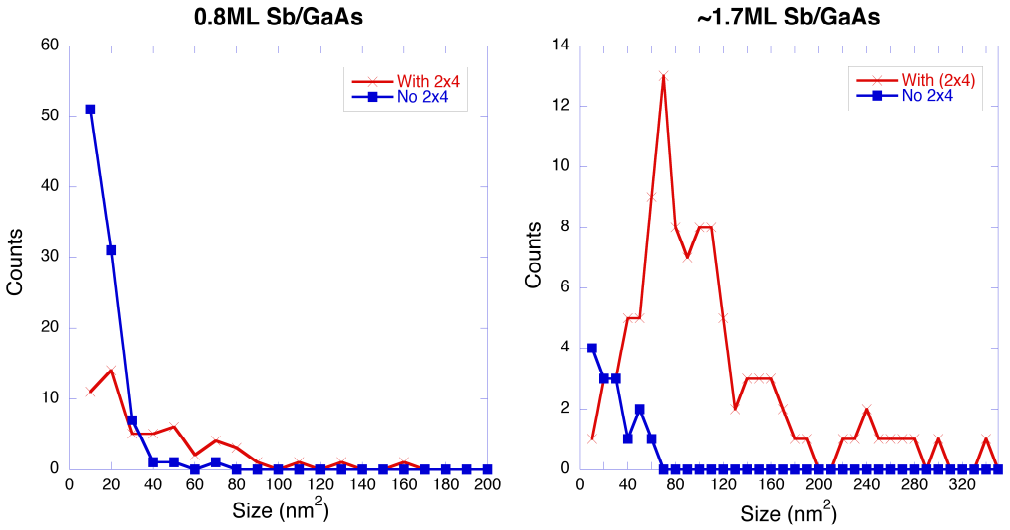
Layer fills in



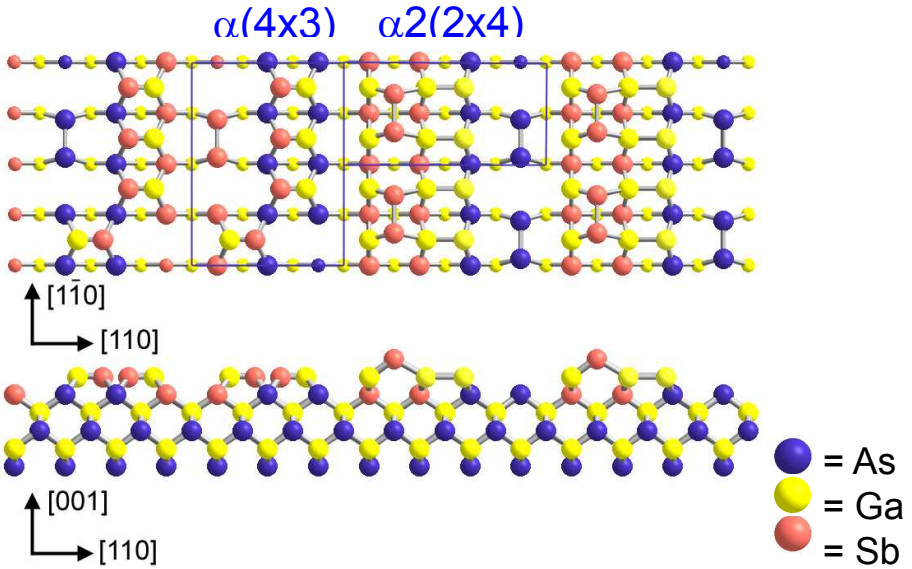


Critical Terrace Size

- Two types of terraces
  - α(4x3) only
  - α(4x3) at edge with α2(2x4) in center
- Maximal size of α(4x3) terrace = 30±10nm^2
- Suggests strain a factor in surface reconstruction stabilization



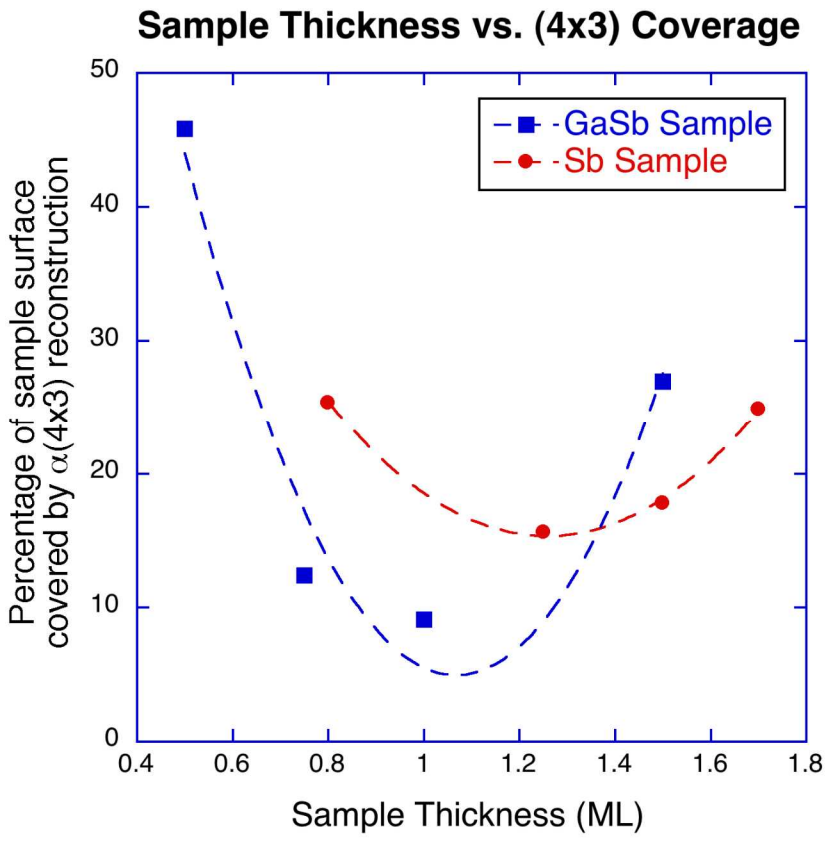
- The reconstructions are able to coexist next to each other
- Both have trench dimers which could help coexistence
- Notice the height difference



Role of Ga

The percentage of the sample surface covered by either reconstruction changes during growth due not only to strain but also to the availability of Ga.

- (2x4) requires 9 Ga per unit area
- (4x3) requires 4 Ga per unit area



GaSb growth

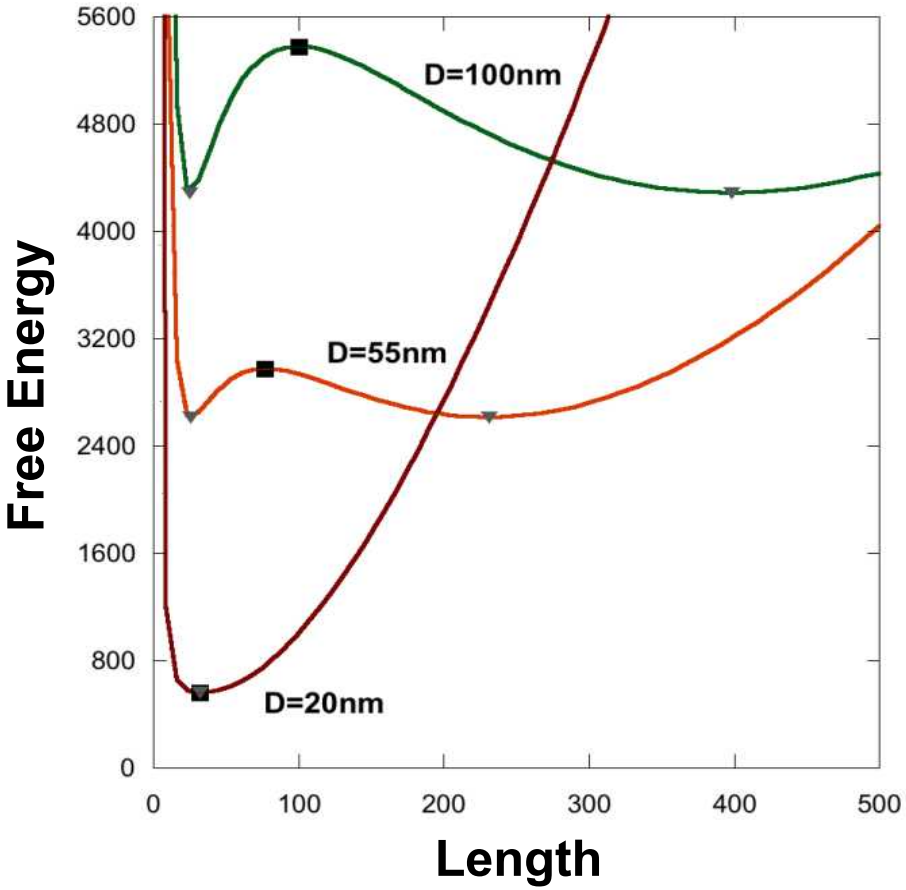
- Ga is present in the beam
- Transformation is easy
- Percentage of (4x3) on the surface varies dramatically
- Minimum percentage of Sb is ~1.05ML

Sb Growth

- Ga is present only via diffusion from step edges
- Transformation Ga-limited
- Percentage of (4x3) is much more constant
- Thickness at which transformation complete is higher, ~1.25ML

Low unit strain energy

- For small values of F the surface energy and boundary energy terms dominate
  - Above a critical size square domains are not energetically favored
  - Multiple rectangular shaped domains coexist
- But domains want to shrink to zero (i.e. disappear



High Unit Strain Energy

- For large values of F
  - Still a critical size above which square domains are not energetically favorable
  - Domains are now globally stable.
- The equilibrium reconstruction domain shape is a quantum wire.