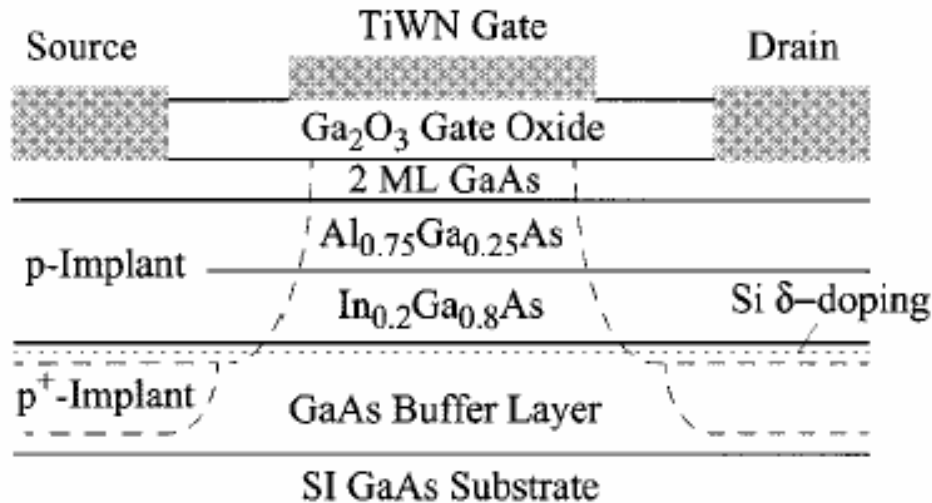


Gate Oxide-III/V Interfaces – Kummel UCSD



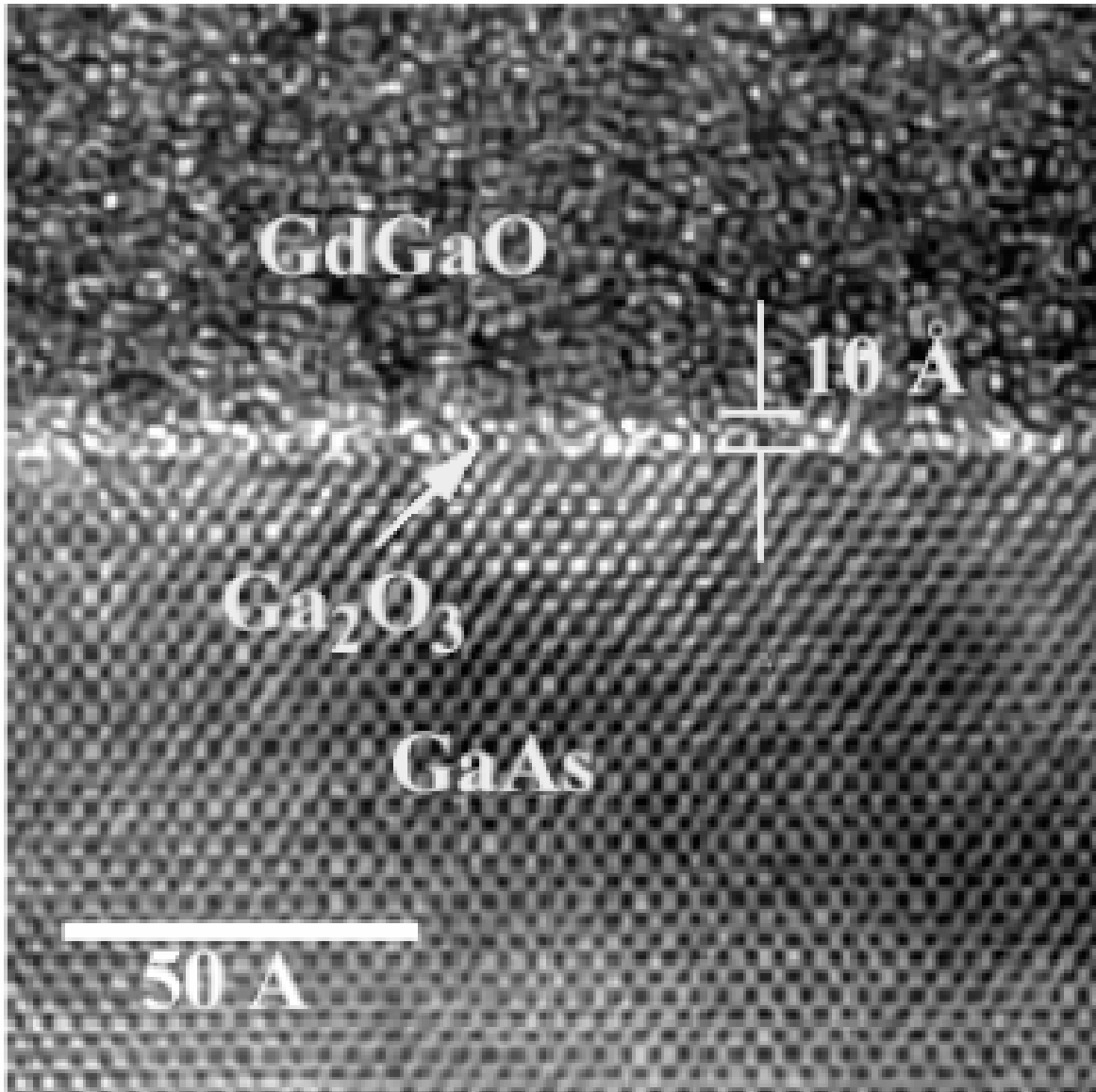
	Electron Mobility (cm ² V ⁻¹ s ⁻¹)	Hole Mobility (cm ² V ⁻¹ s ⁻¹)	Band Gap (eV)
Si	1,350	480	1.11
GaAs	8,000	300	1.43
InAs	30,000	450	0.36
In _{0.53} Ga _{0.47} As	15,000	300	0.75

Passlack *et al.* published the first working enhanced mode GaAs MOSFET device in 2002. However, the causes of Fermi level pinning/unpinning at oxide/III-V interfaces are still not well understood.

1. **Oxide/GaAs(100)-2x4 Pinning and Unpinning Mechanism**
2. **Oxide/InAs(100)-4x2 Bonding**
3. **Current Oxide/III-V or Oxide/Ge Projects**

Please do not distribute since some of the data has not yet been published

Amorphous Ga_2O_3 forms Ordered First Layer



- Ordered 1st layer reduces bond heterogeneity and probability of trap states.
- Only layer 1 is ordered. All other layers are amorphous.
- No reactions at the interface.
- Ga_2O_3 is weakly insulating thus limiting trap lifetimes.

Oxide/GaAs(100)-2x4 Study – STM/DFT Combo

Image Clean Surface



Image Surface with Adsorbates



Make Initial Guess on Bonding Geometries



Take STS Spectra to Identify the Electronic Properties of the System



Use DFT to Simulate Bonding Geometries

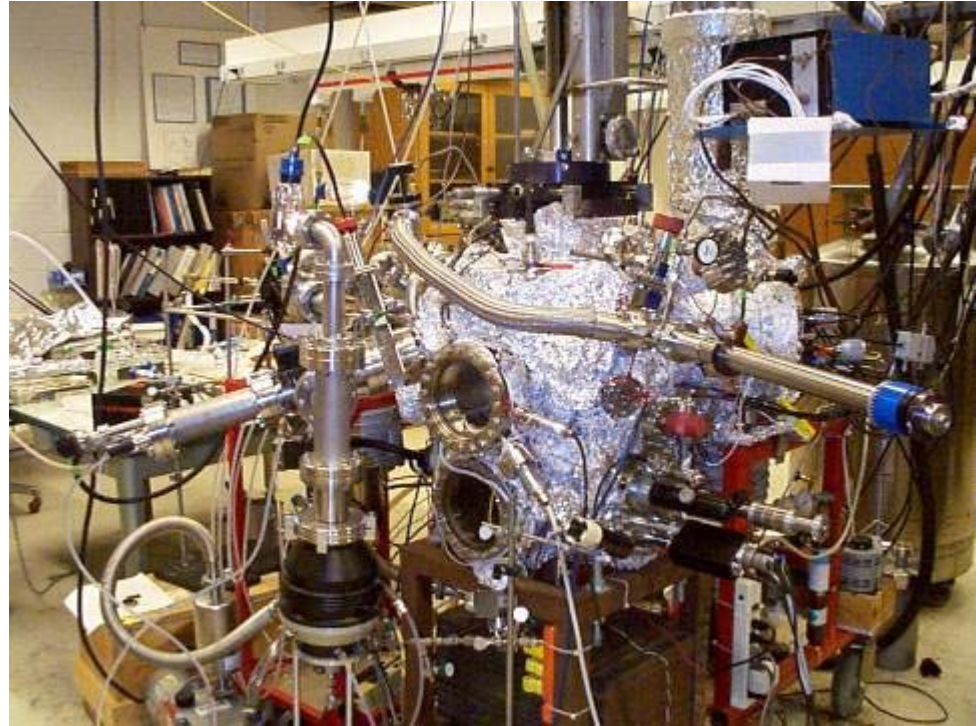


With the Help of DFT Identify how Bonding Geometries Effect the Electronic Properties of the System

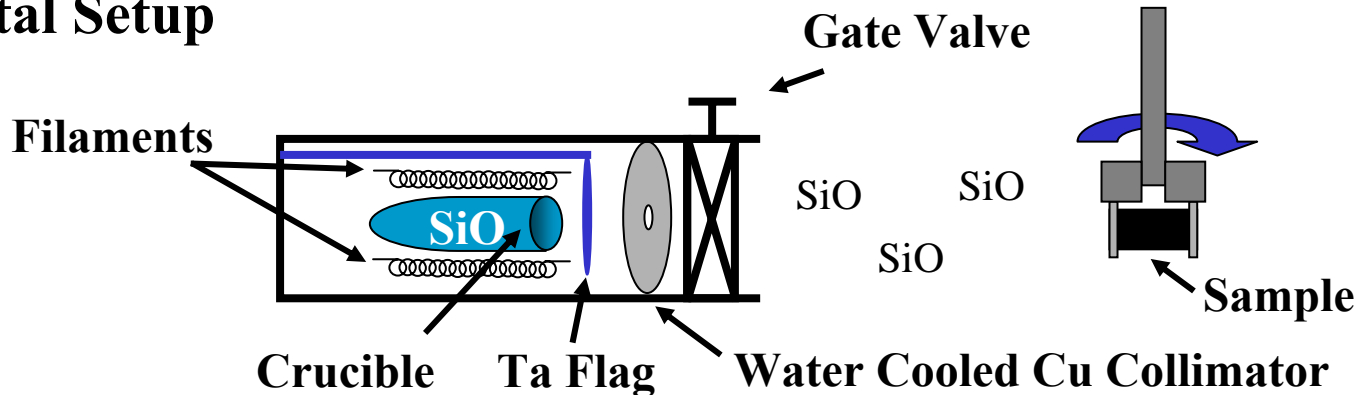
Experimental Apparatus

Chamber

- Low Energy Electron Diffraction (LEED)
- Scanning Tunneling Microscopy (STM)
- Scanning Tunneling Spectroscopy (STS)
- Auger Electron Spectroscopy (AES)
- Quadrupole Mass Spectroscopy (QMS)

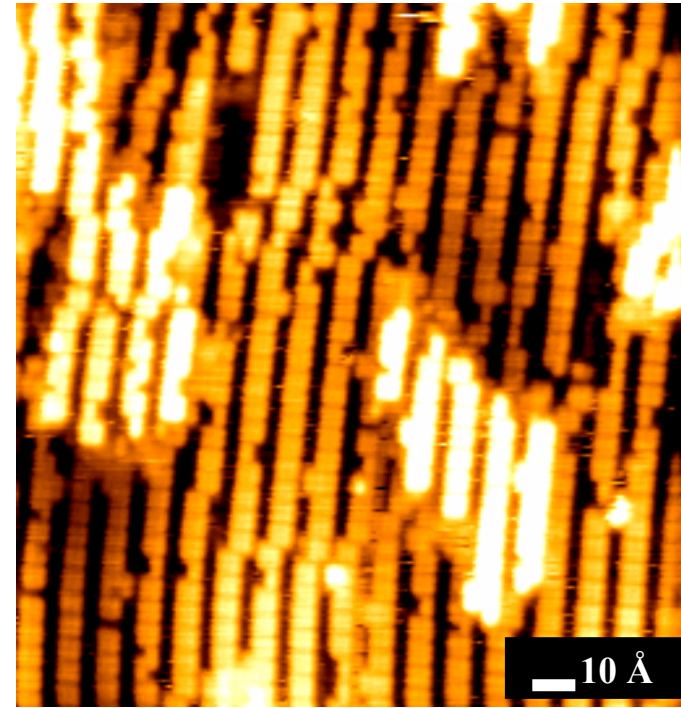
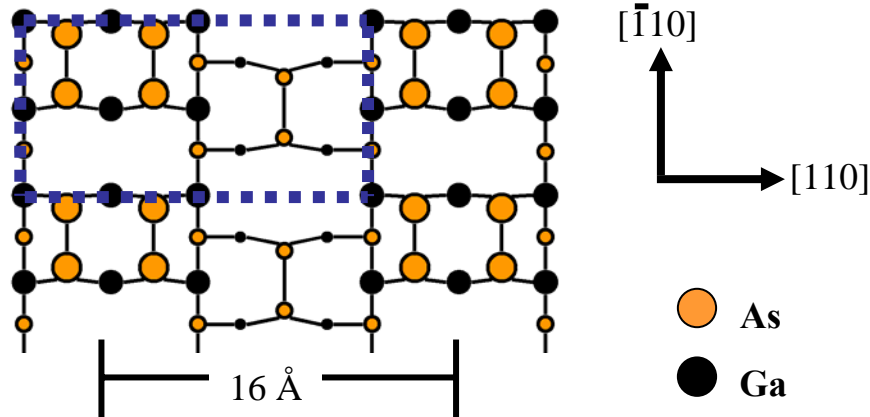


Experimental Setup

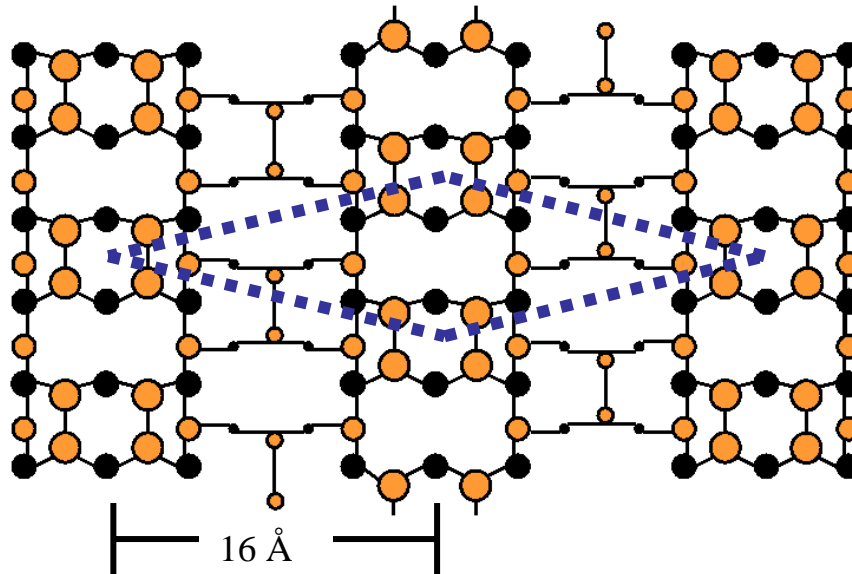


Clean GaAs(001)- $c(2\times 8)/(2\times 4)$

(2×4)

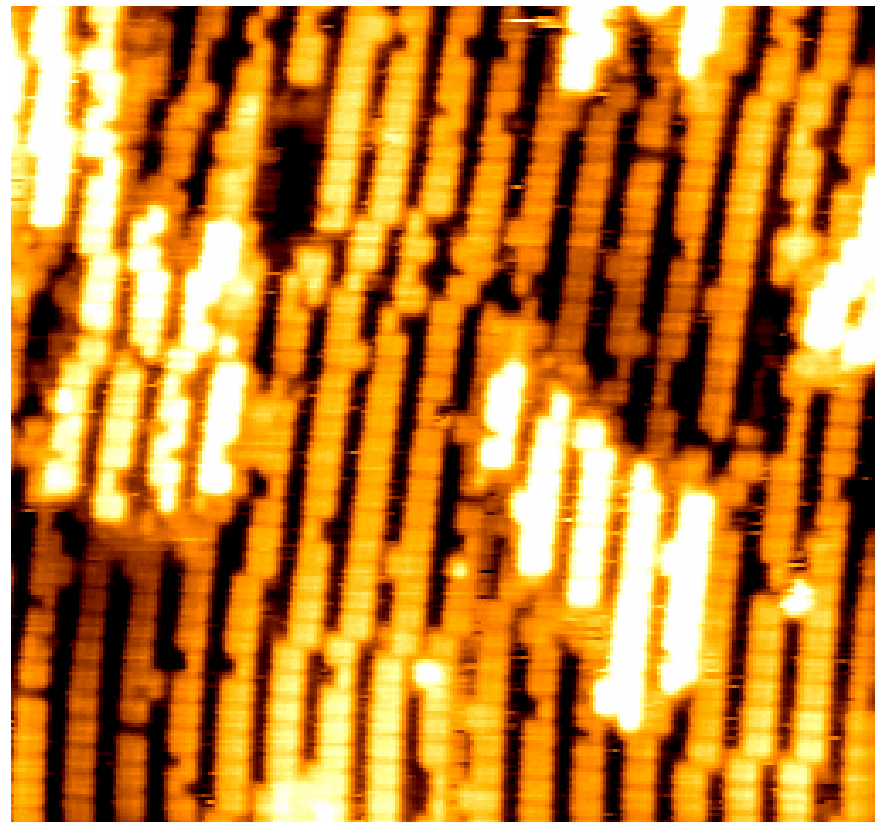
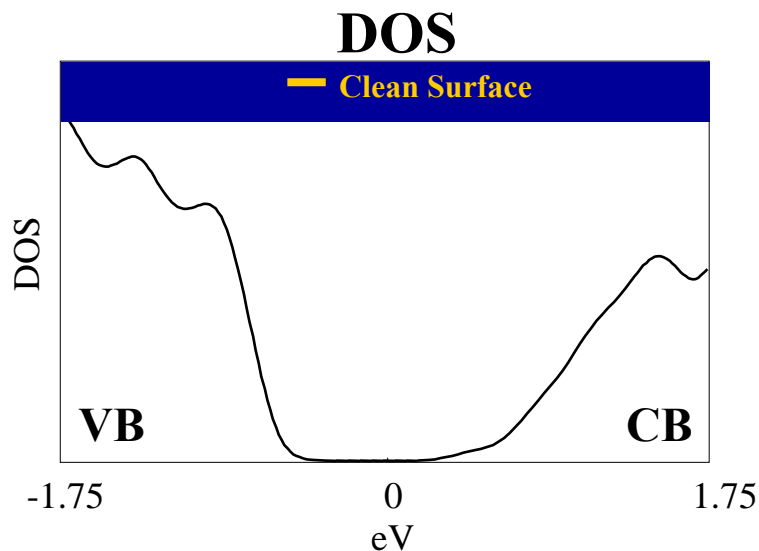
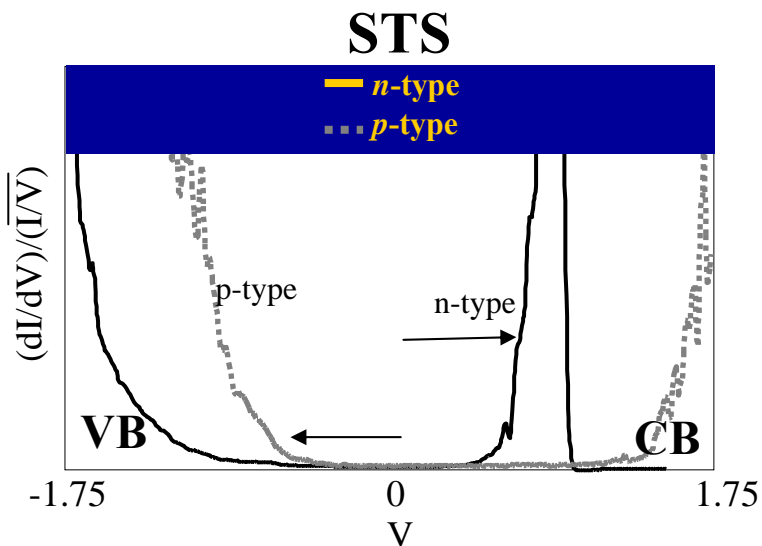


$c(2\times 8)$



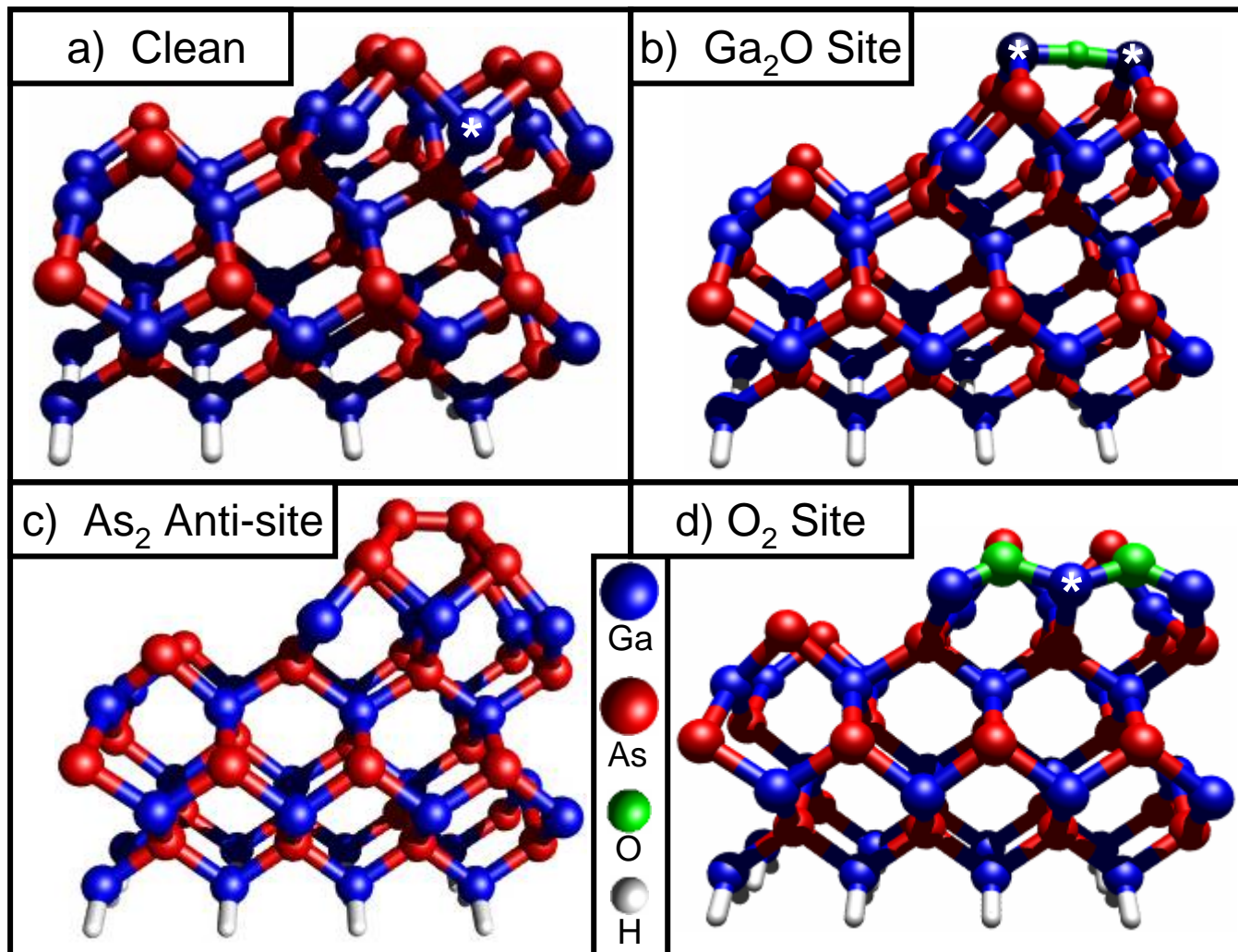
The clean surface is a combination of the two reconstructions. Both reconstructions have the same electronic properties.

Electronic Properties of Clean GaAs



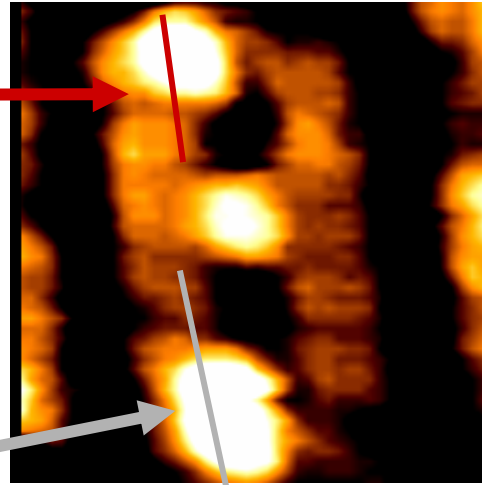
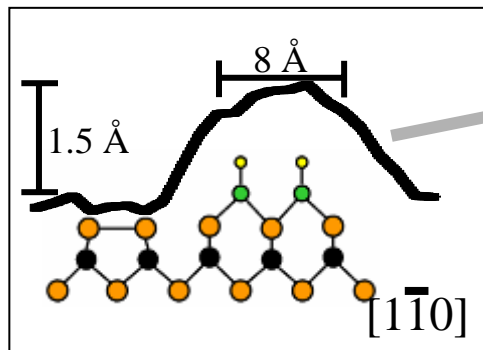
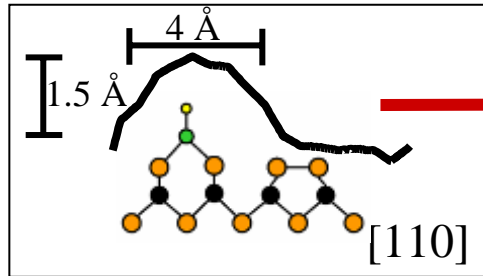
- In STS, for unpinned surfaces the Fermi level (0 V position) should shift from VB edge in *p*-type to CB edge in *n*-type.
- The clean GaAs(001)-*c*(2×8)/(2×4) surface is unpinned.

Calculation Techniques – Dr. Darby Winn



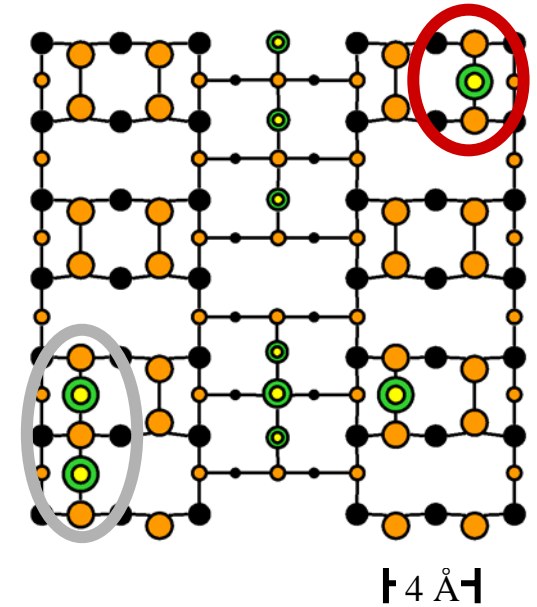
Vienna *Ab initio* Simulation Package (VASP) , Plane Waves, Periodic Boundary Conditions
Local Density Approximation (LDA), Ultrasoft Pseudopotentials, 4x4x1 Monkhorst-Pack k-points
Sampling in the First Brillouin Zone, 2 k-points, 8 Layer H Terminated Clean Slab (56 As, 60
Ga, and 32 H), (2x4) Reconstruction, ~18 Å (~11 Layers) of Vacuum, 300 eV Electron Kinetic
Energy Cut Off, Forces Less Than 0.05 eV/Å

SiO on GaAs(001)-c(2×8)/(2×4)



5 Å

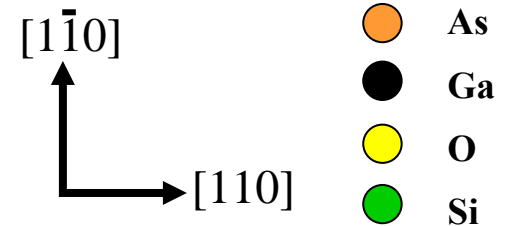
~5% of a Monolayer Coverage



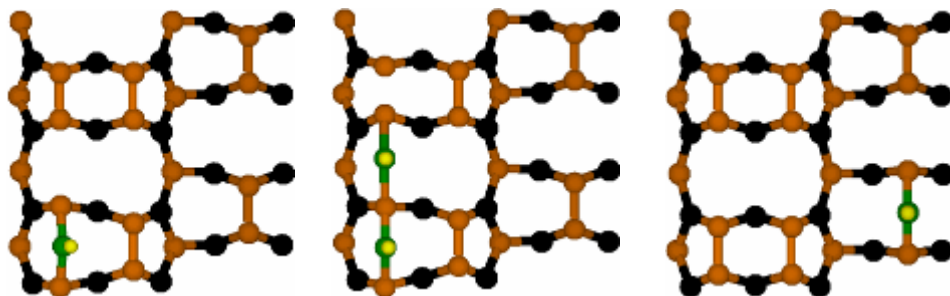
Row sites are single SiO molecules

At submonolayer coverage, SiO spontaneously forms sites in the trough which are as tall as the sites on the rows.

Trough sites are pyramids



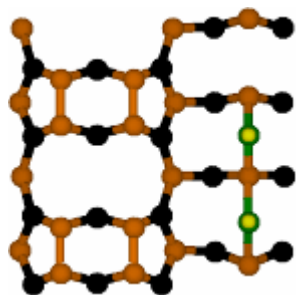
SiO on GaAs(001)-c(2×8)/(2×4)



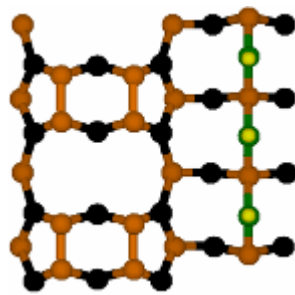
Row Single
(-1.08 eV/SiO)

Row Compact
Double
(-0.87 eV/SiO)*

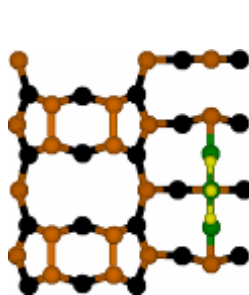
Trough Single
(-1.32 eV/SiO)



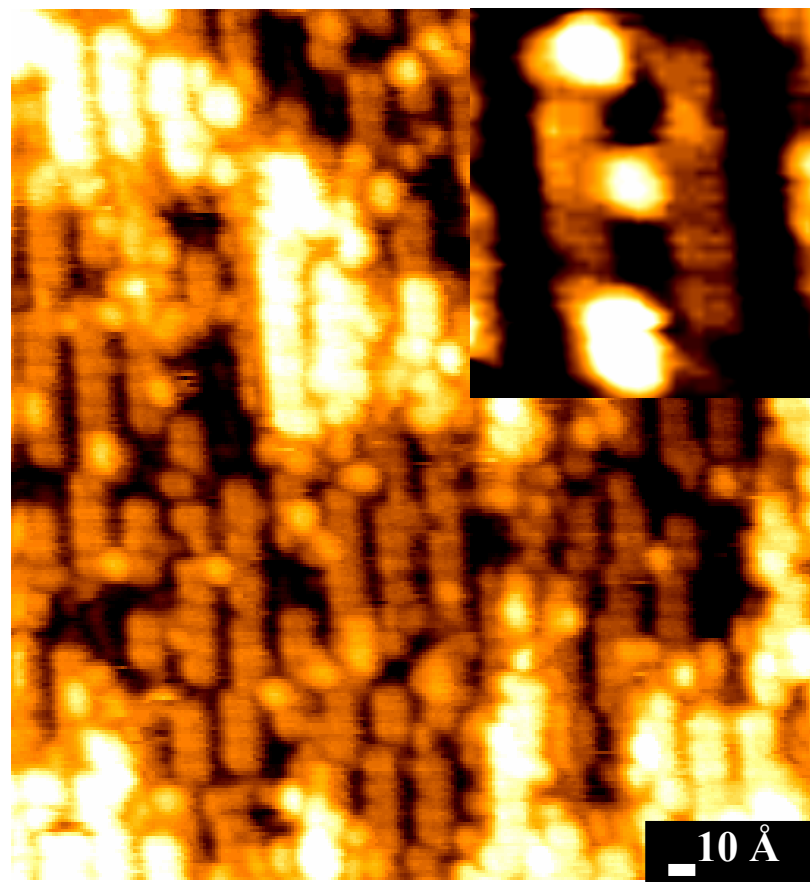
Trough Compact
Double
(-1.06 eV/SiO)*



Trough Triple
(-0.70 eV/SiO)



Trough Pyramid
(-0.94 eV/SiO)*

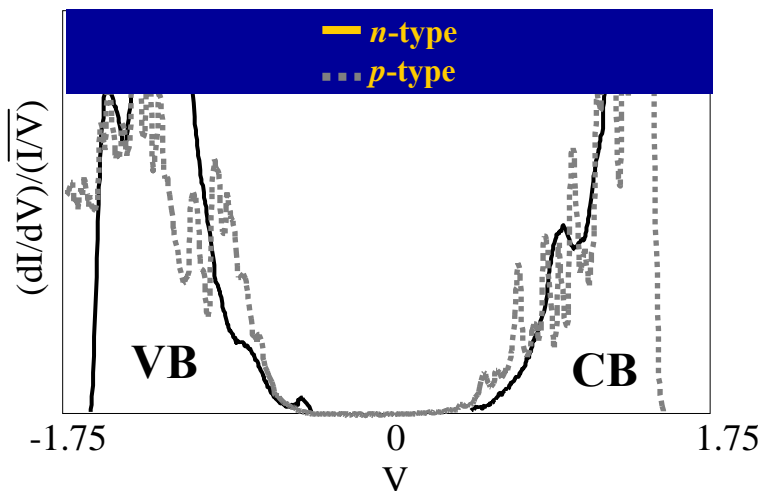


All of the SiO sites are observed even at low coverage consistent with the nearly degenerate DFT formation energies

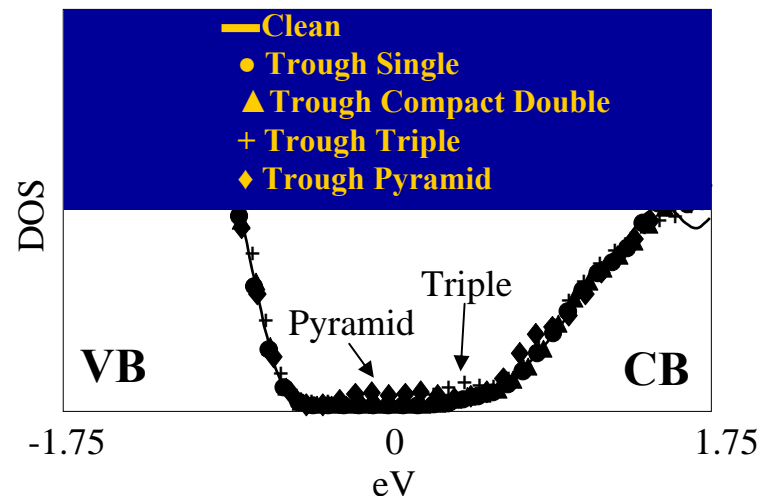
*Energies that have been corrected due to an undimerized As atom

Electronic Properties SiO on GaAs

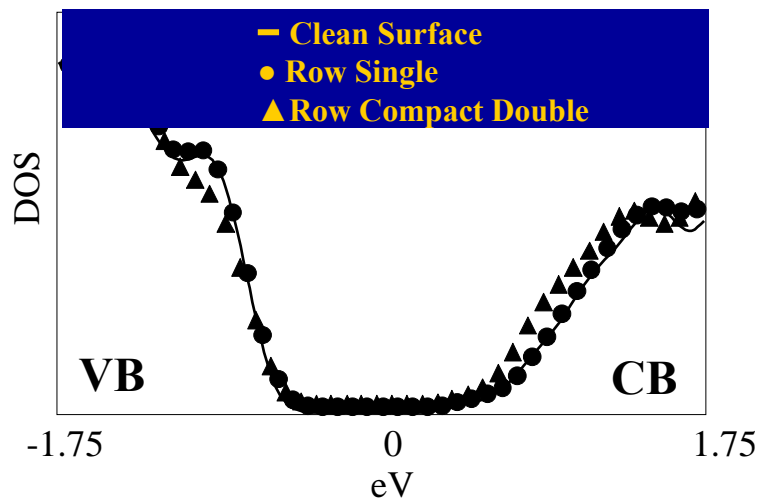
STS



DOS



DOS



- In STS, for unpinned surfaces, the Fermi level (0 V position) should shift from VB edge in p-type to CB edge in n-type.
- Experimental STS has a Fermi level (0V) at midgap for both n-type and p-type so it is pinned.
- The only SiO sites that pin the Fermi level are the trough triple and trough pyramid sites

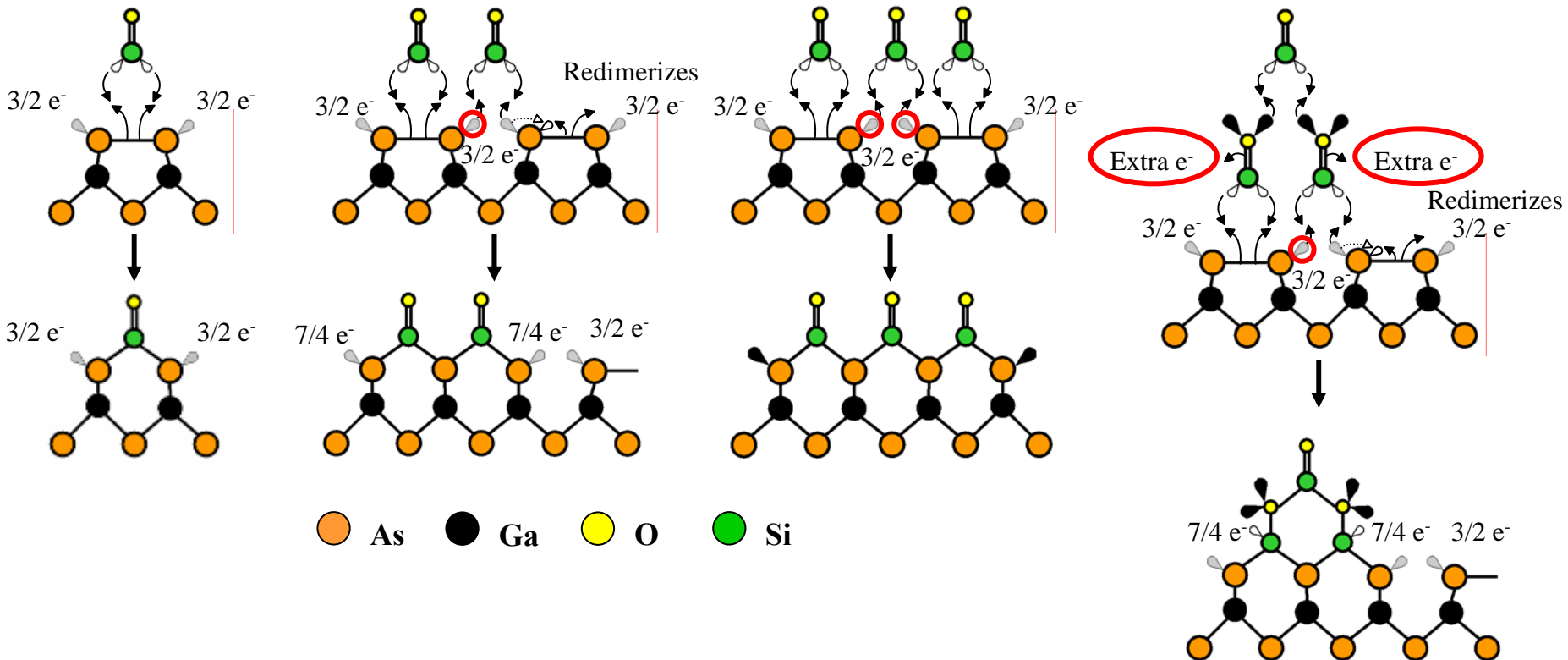
SiO Bonding Mechanisms

Single

Compact Double

Triple

Pyramid

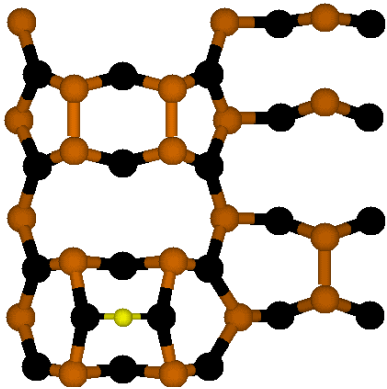


•Larger charge buildups occur on interior As atoms, involved in bonding, than on interior ones.

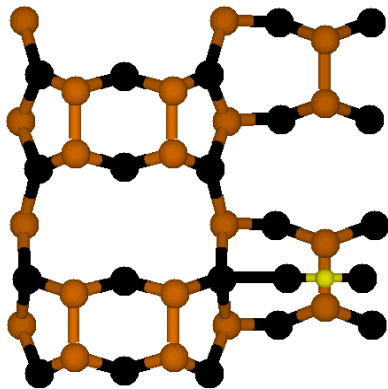
•The pyramid site also causes the generation of a partially filled dangling bond on the lower Si atoms.

- ◊ Dangling Bond with 1 e^-
- ◊ Dangling Bond with Charge Between $3/2 e^-$ and $2 e^-$ (As Marked)
- ◊ Dangling Bond with 2 e^-

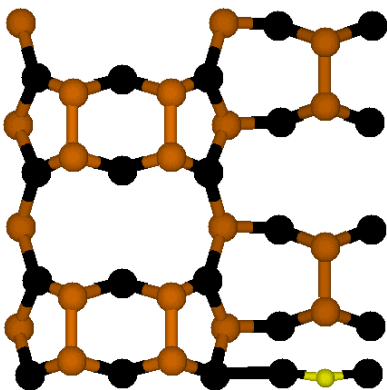
Ga₂O on GaAs(001)-c(2×8)/(2×4)



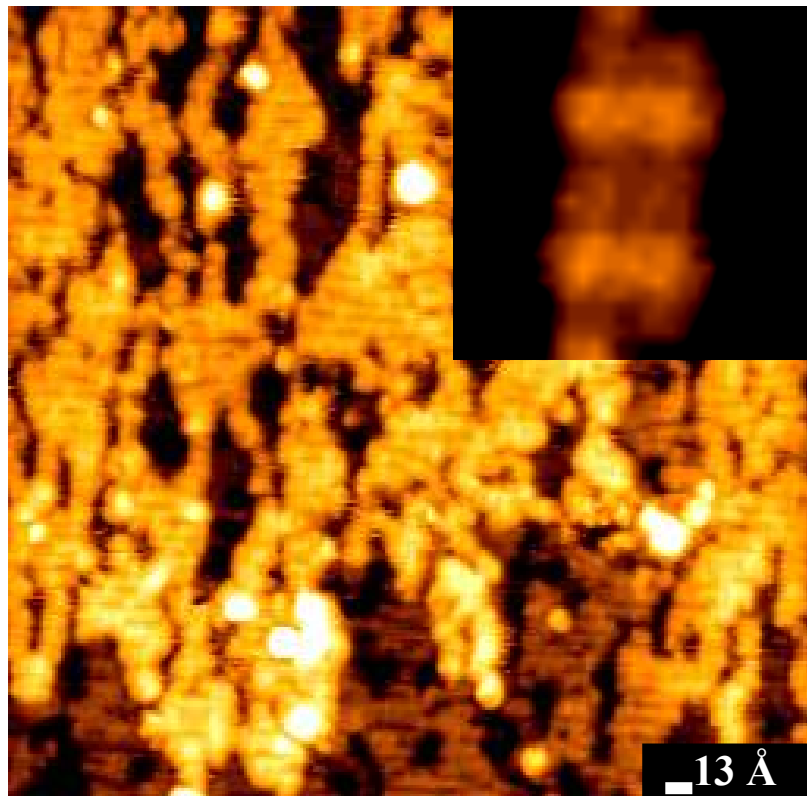
Insertion
(-1.87 eV/Ga₂O)



Over Dimer
(-1.06 eV/Ga₂O)



Between Dimer
(-0.69 eV/Ga₂O)



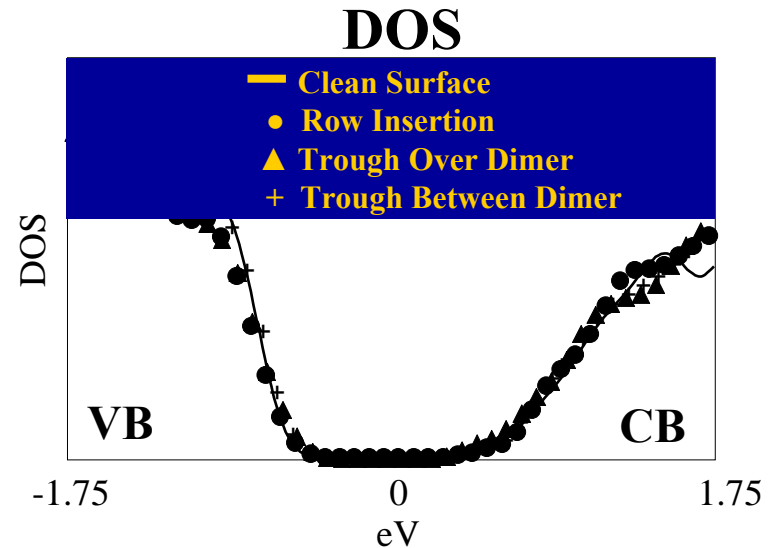
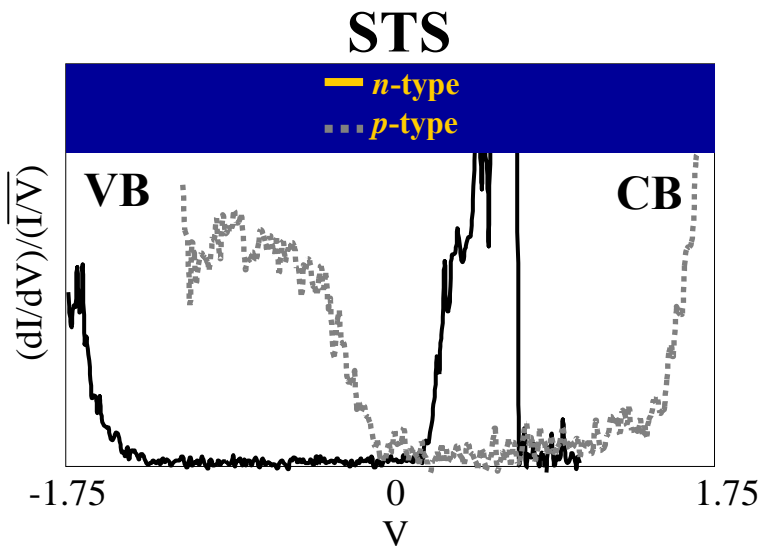
• Experimentally, only the row insertion site has been observed for Ga₂O on GaAs(001)-c(2×8)/(2×4) consistent with the DFT energies.

• The row site does not generate dangling bonds but restores As to a more bulk-like bonding environment



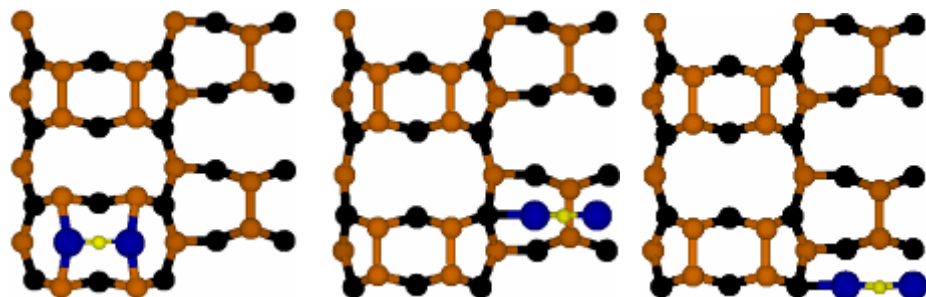
but only Ga₂O sticks to the surface

Electronic Properties Ga₂O on GaAs

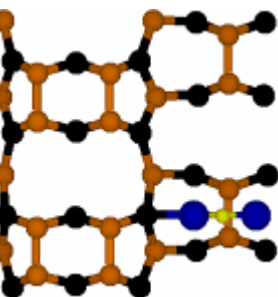


- In STS, for unpinned surface the Fermi level (0 V position) should shift from VB edge in *p*-type to CB edge in *n*-type.
- None of the Ga₂O sites generate states in the band gap region this is consistent with the Fermi level being unpinned.
- The unpinned Fermi level is consistent with Ga₂O inserting into As-As bonds without creating dangling bond or charge buildup

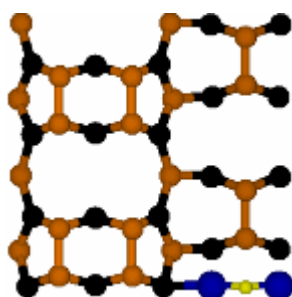
In₂O on GaAs(001)-c(2×8)/(2×4)



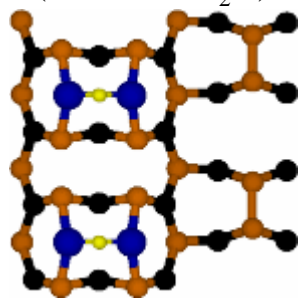
Insertion
(-1.18 eV/In₂O)



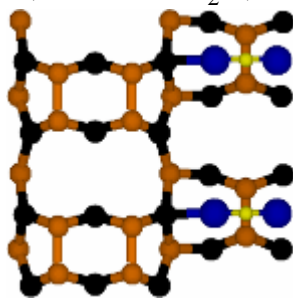
Over Dimer
(-1.26 eV/In₂O)



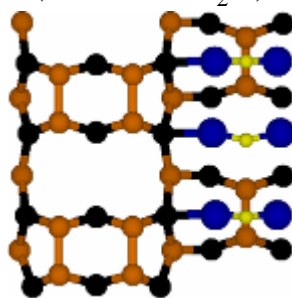
Between Dimer
(-0.86 eV/In₂O)



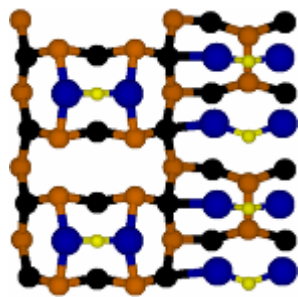
Full Coverage
Insertion
(-1.01 eV/In₂O)



Full Coverage
Over Dimers
(-1.25 eV/In₂O)



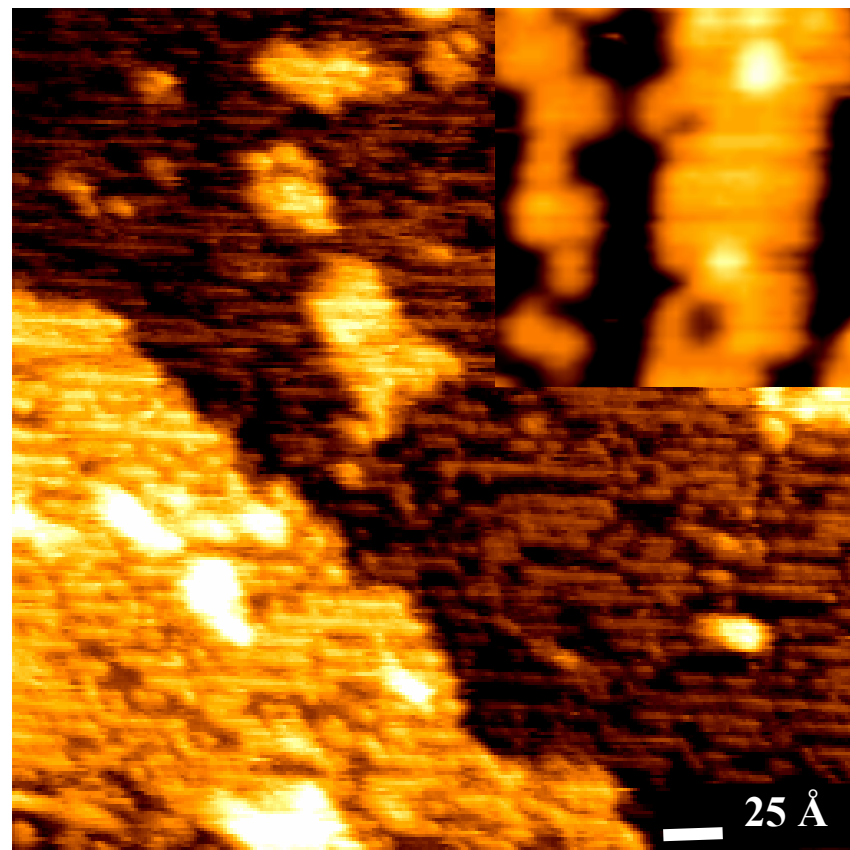
Triple
(-1.06 eV/In₂O)



Complete Coverage
(-1.05 eV/In₂O)



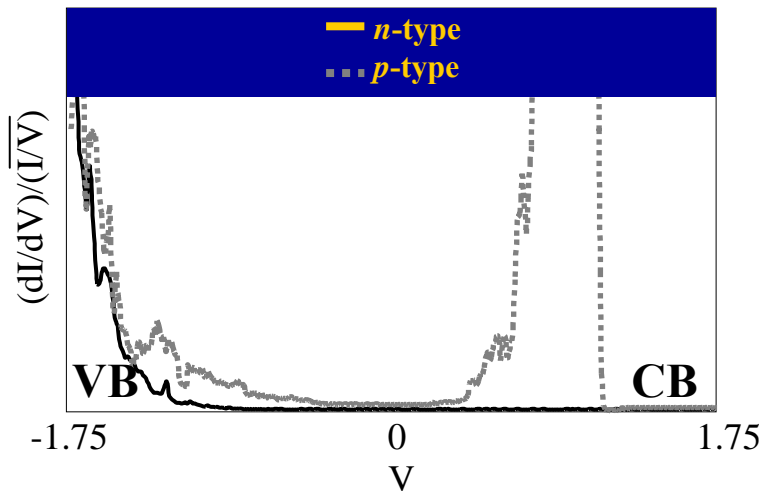
$\text{In}_2\text{O}_3(\text{s}) \rightarrow \text{In}_2\text{O}(\text{g}) + \text{O}_2(\text{g})$
but only In₂O sticks to the surface



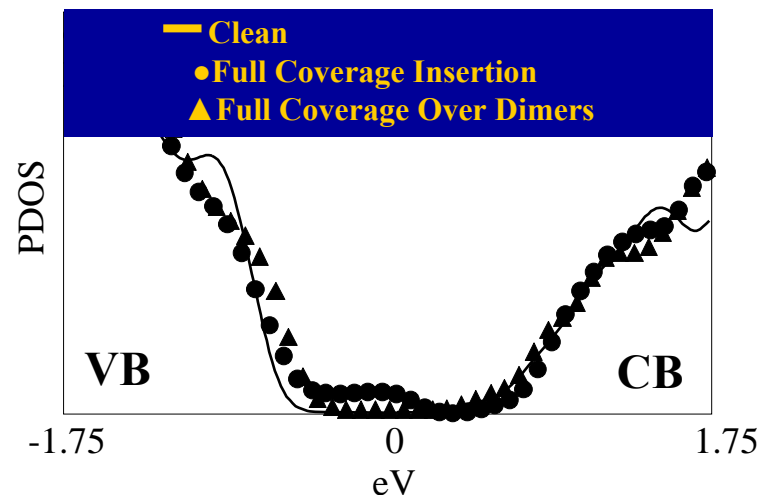
Experimentally the trough sites were seen to fill in prior to the formation of row sites consistent with the DFT energies and the lack of an activation barrier for trough sites.

Electronic Properties In₂O on GaAs

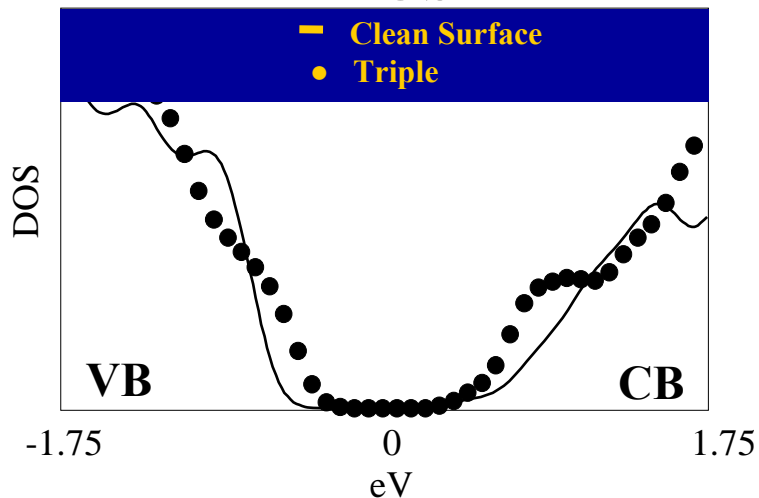
STS



DOS

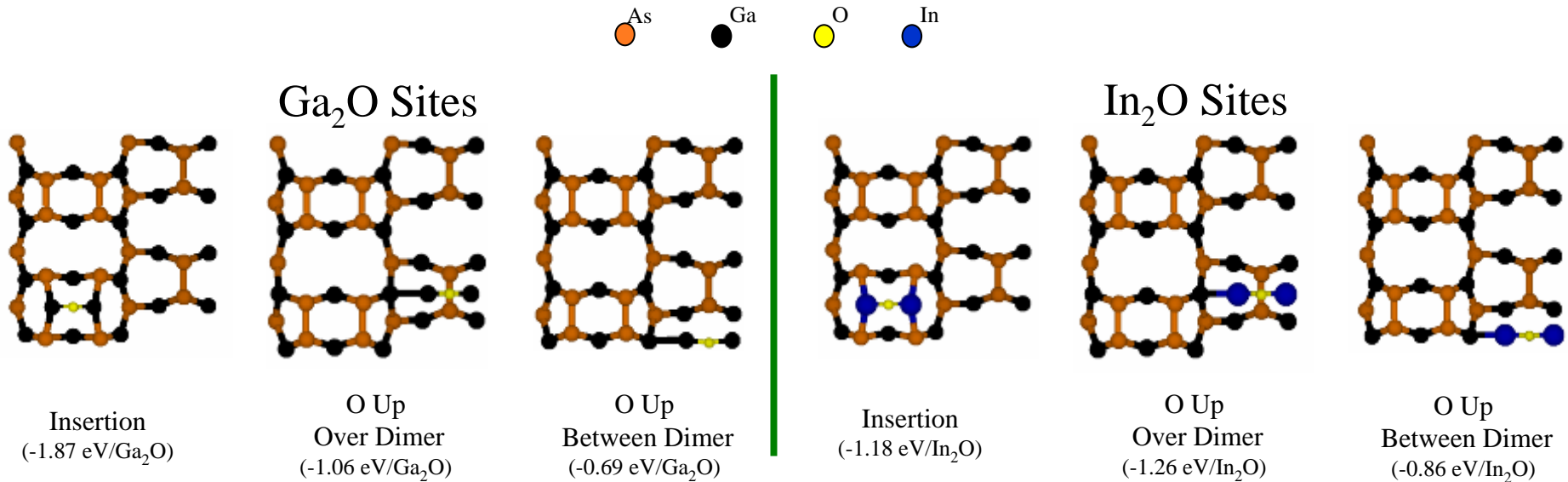


DOS



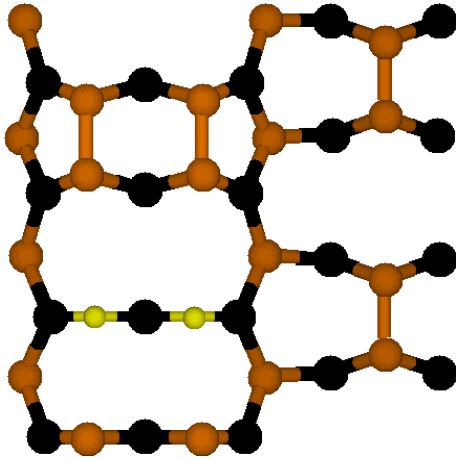
- In STS, for unpinned surfaces, the Fermi level (0 V position) should shift from VB edge in p -type to CB edge in n -type
- STS spectra reveal that In₂O pins the Fermi level near the CB edge.
- The DFT DOS shows that as the In₂O coverage increases so does the number of states in the band gap region.

Ga₂O and In₂O on GaAs(100)-(2x4)

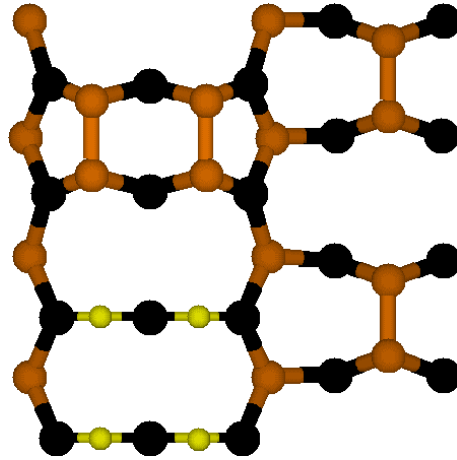


- Experimentally at low Ga₂O coverage Ga₂O is only inserts into the dimers
- Experimentally, all of the In₂O sites are seen at low coverage because the In₂O sites are nearly degenerate.
- The difference in energy between the Ga₂O and In₂O insertion sites comes from a difference in bond strength between Ga-As bond and the In-As bond.
- When either In₂O or Ga₂O bonds over dimers it is more stable than when it bonds between dimers because when the oxides bonds between the dimers the filled dangling bonds on the As dimers interact with the O atom.

O₂ on GaAs(001)-c(2×8)/(2×4)

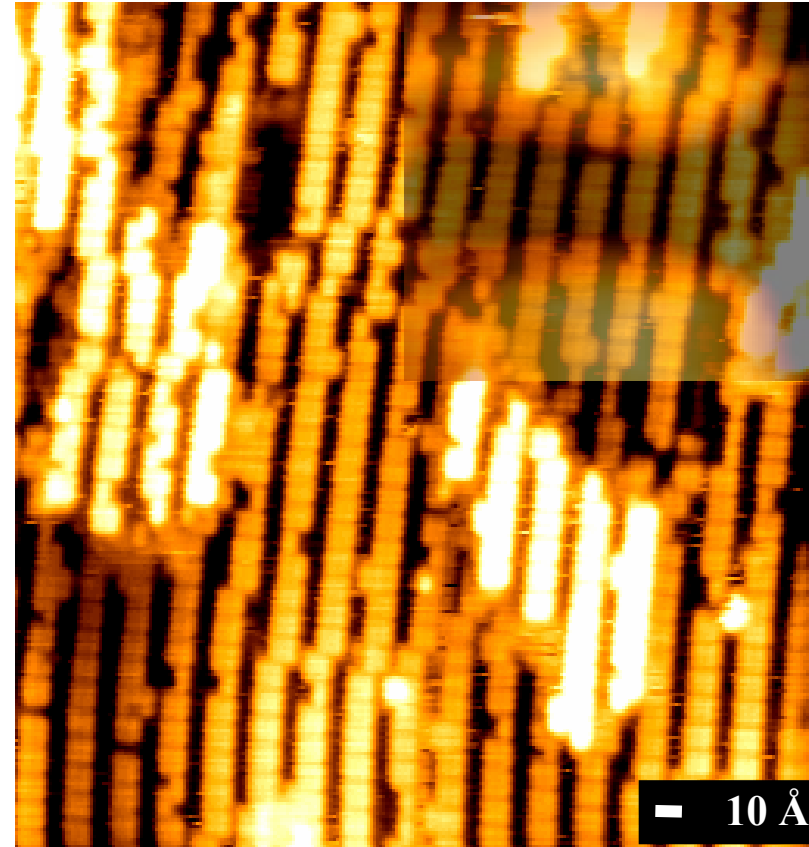


Single Dimer Displacement
(-1.73 eV/O²)*



Double Dimer Displacement
(-2.08 eV/O²)

● As ● Ga ● O

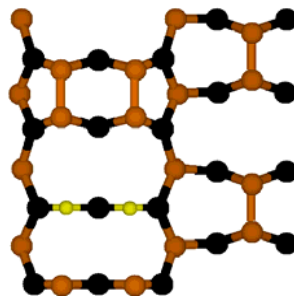
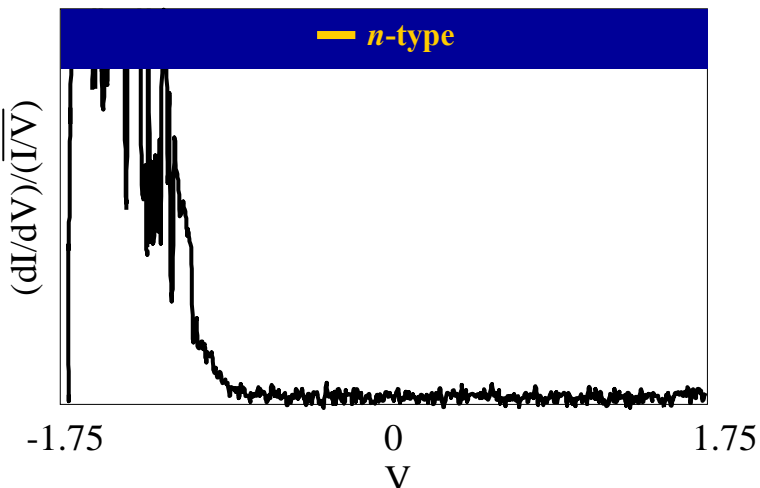


The adsorption energies reveal that the double dimer displacement site is only slightly more favorable than the single dimer displacement site. Both sites have been observed experimentally

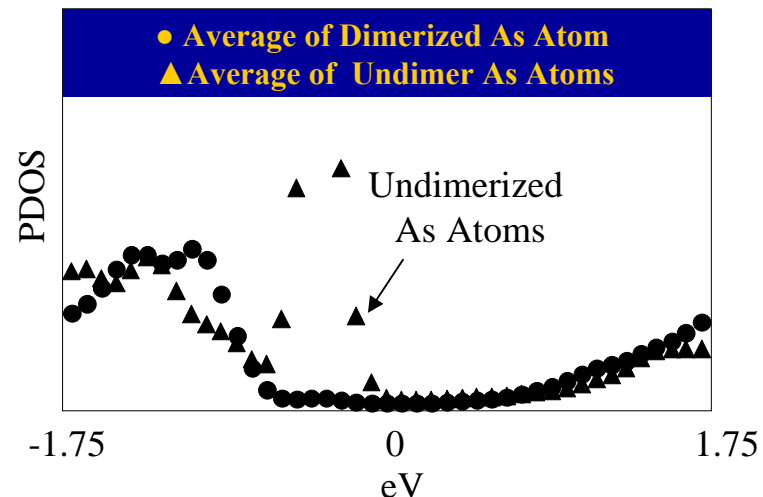
*Energies that have been corrected due to an undimerized As atom

Electronic Properties O₂ on GaAs

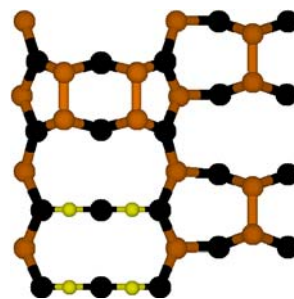
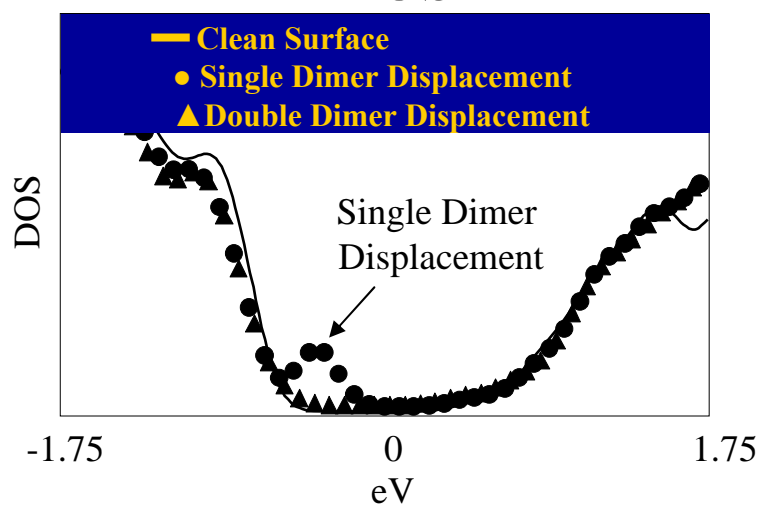
STS



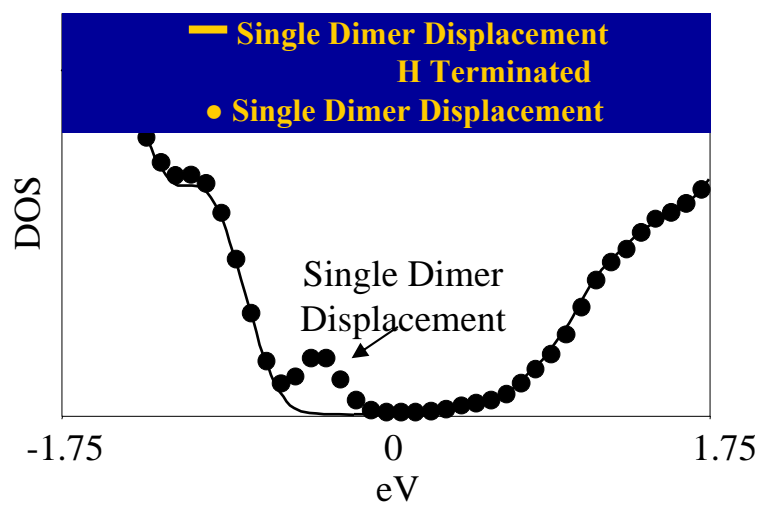
PDOS



DOS



DOS



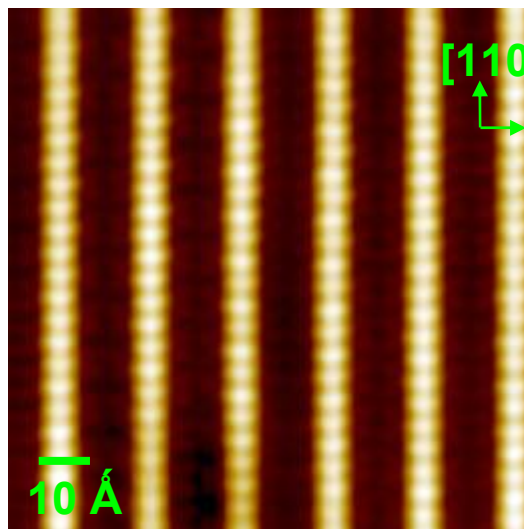
The undimerized As atoms in the single dimer displacement site are responsible for Fermi level pinning consistent with creation of new dangling bonds.

Adsorbates on GaAs Summary

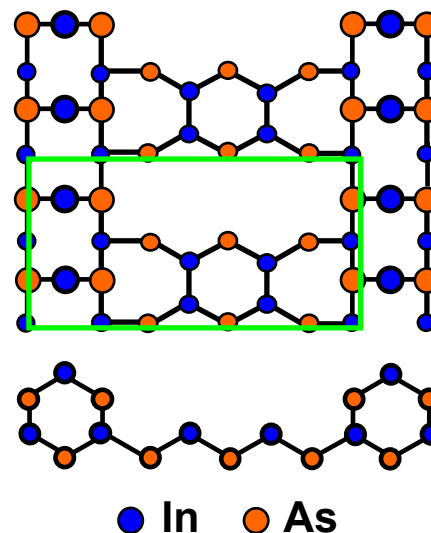
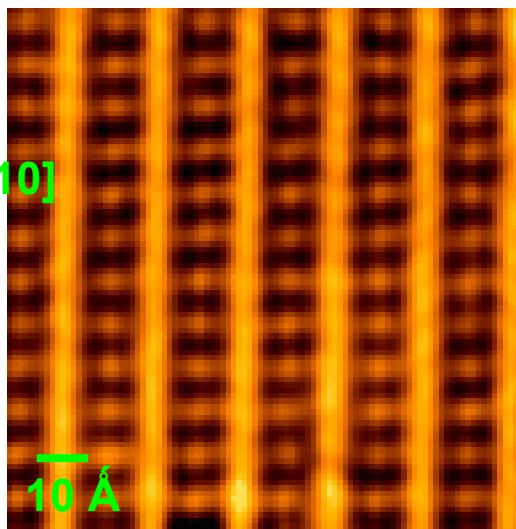
- **SiO on GaAs(001)-c(2×8)/(2×4)**
 - Pinned (Directly and Indirectly)
 - ❖ Buildup of local charge at the surface
 - ❖ Partially filled dangling bonds
 - ❖ Formation of undimerized As atoms
- **Ga₂O on GaAs(001)-c(2×8)/(2×4)**
 - Unpinned
- **In₂O on GaAs(001)-c(2×8)(2×4)**
 - Pinned (Directly)
- **O on GaAs(001)-c(2×8)/(2×4)**
 - Pinned (Indirectly)
 - ❖ Formation of undimerized As atoms

Clean InAs(001)-*c*(8x2)/(4x2) – Dr Winn and Jian Shen

Filled State STM

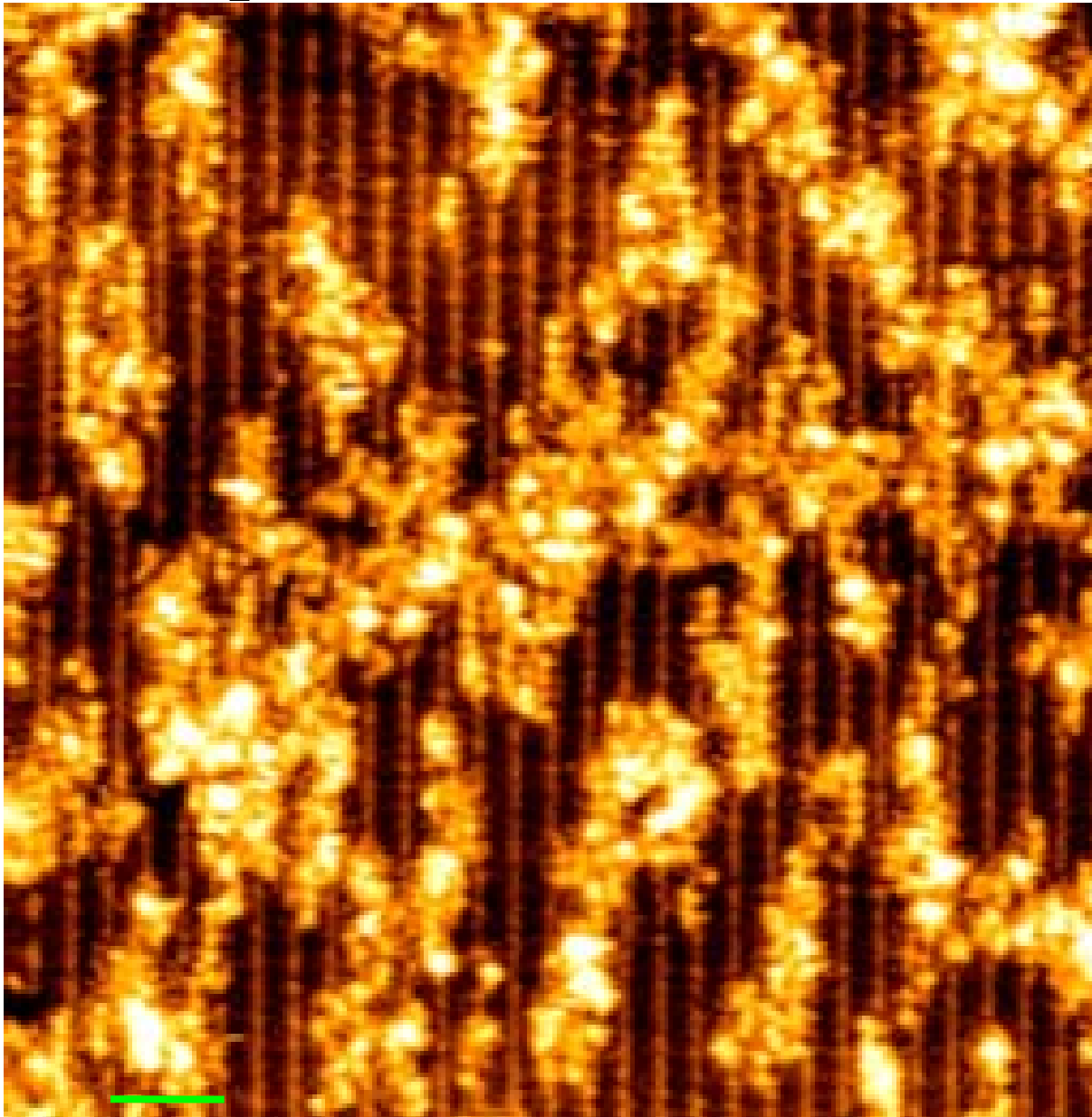


Empty State STM



- The As-rich pure 2x4 reconstruction of GaAs(100) does not exist on InGaAs or InAs so we need to change our approach for the high mobility III-V channels
- The group III reconstructions should have very low reactivity to oxygen so they should be favorable for ALD of gate oxides
- The In-rich InAs(001)-(4x2) surface structure is referred to as the $\beta 3'$ (4x2).

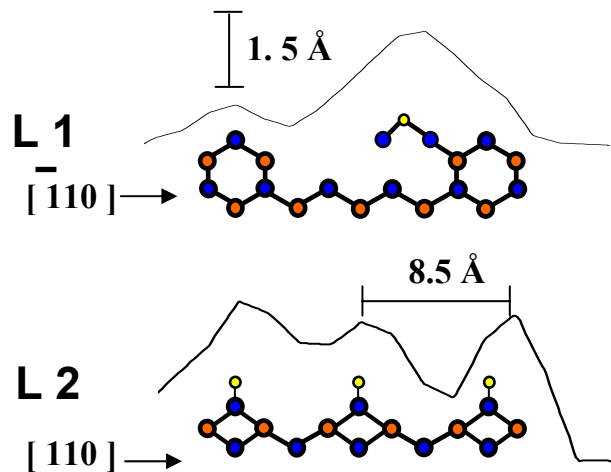
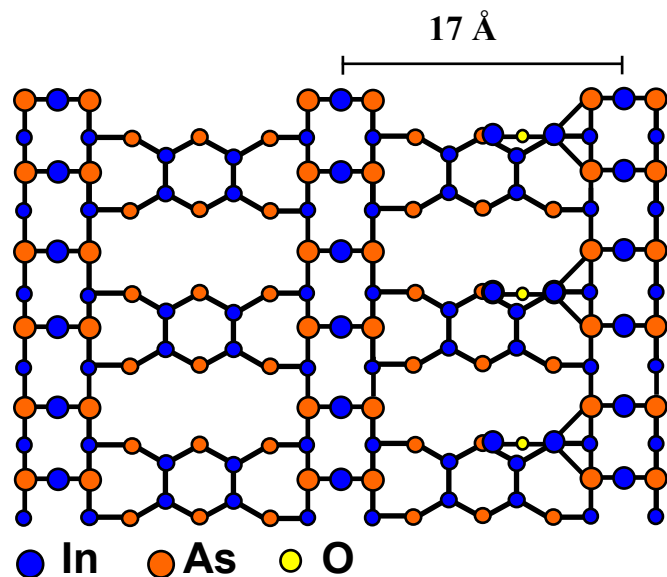
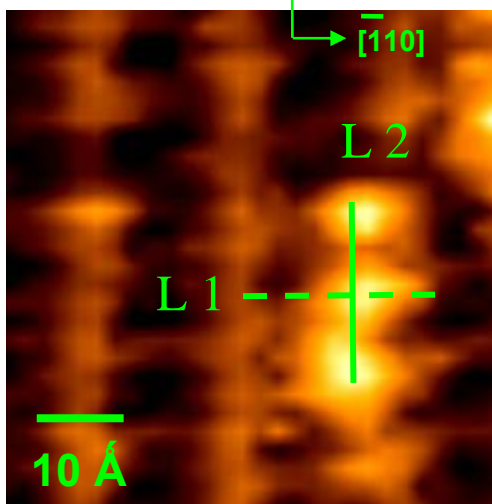
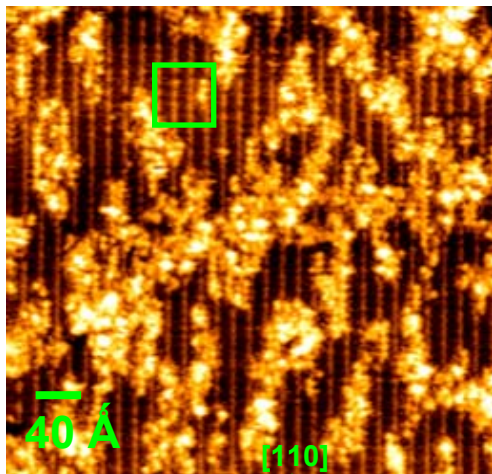
In_2O Deposited on $\text{InAs}(001)\text{-}c(8\times 2)/(4\times 2)$



50 Å

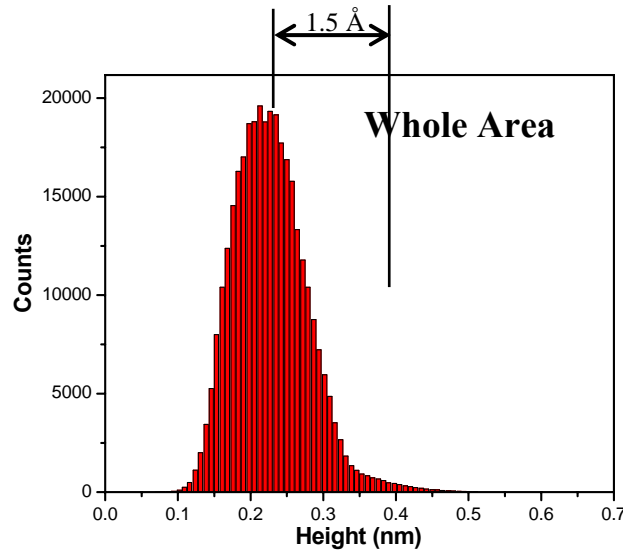
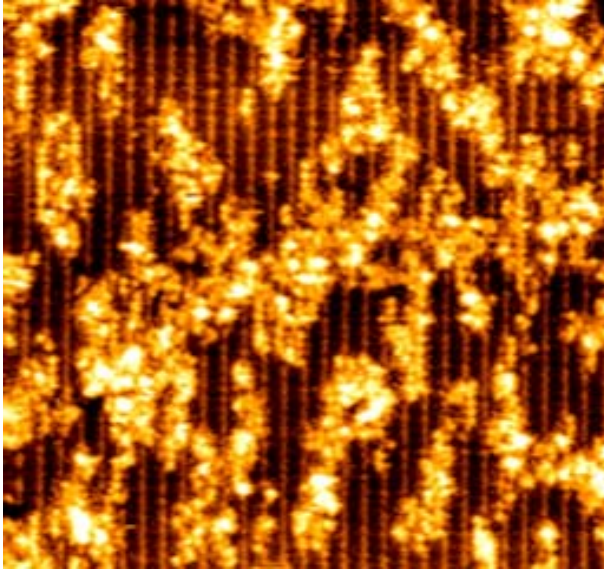
- In_2O forms order overlayer on $\text{InAs}(001)\text{-}c(8\times 2)/(4\times 2)$.
- Initial In_2O molecules only occupy specific site at the edge of row.

Bonding Model for $\text{In}_2\text{O}/\text{InAs}(001)\text{-}c(8\times 2)/(4\times 2)$

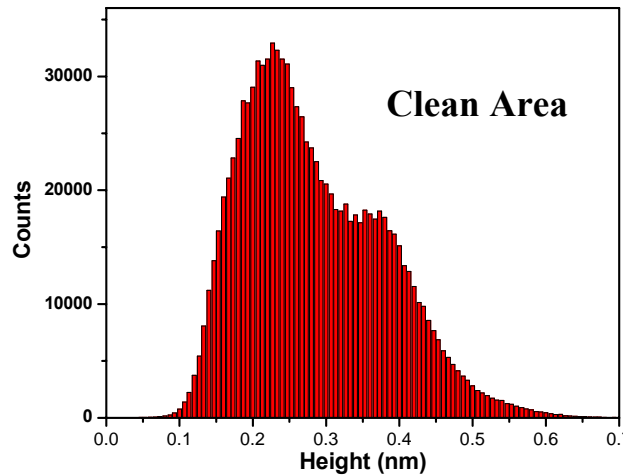
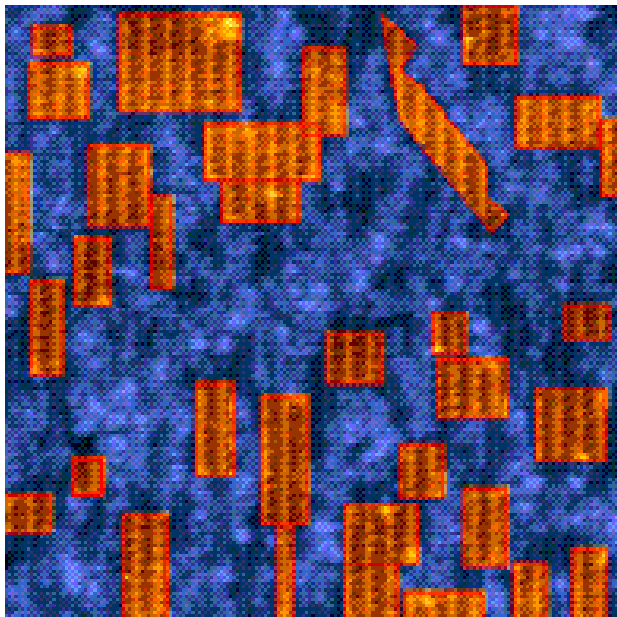


- In_2O most likely form new In-As bonds to surface
- The 1.5 Å spacing with the oxide and surface is consistent with height distribution analysis of single monolayer growth
- In_2O never causes the abstraction of any surface atoms.

Single Monolayer $\text{In}_2\text{O}/\text{InAs}(001)\text{-}c(8\times 2)/(4\times 2)$

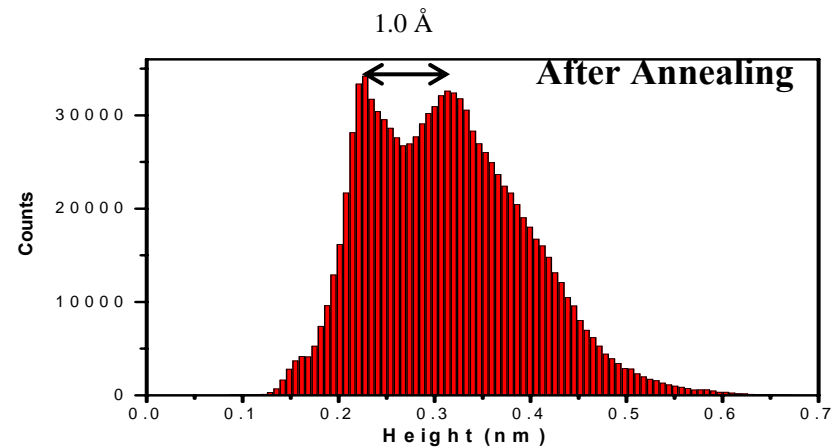
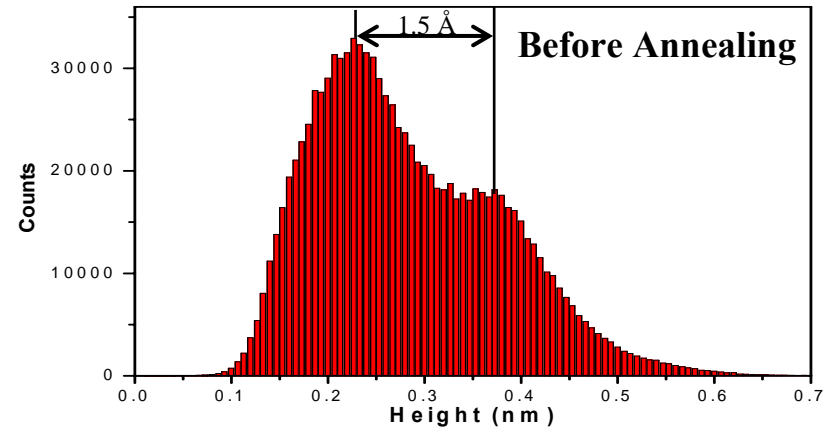
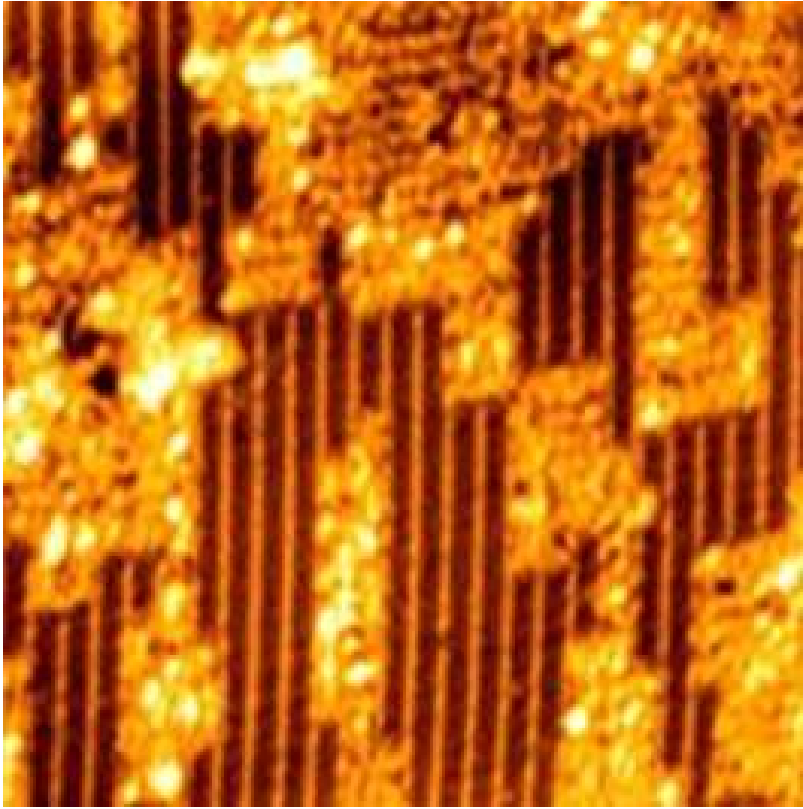


- The bimodal height analysis has a lower peak which is identical to the height distribution of the clean regions of the surface.



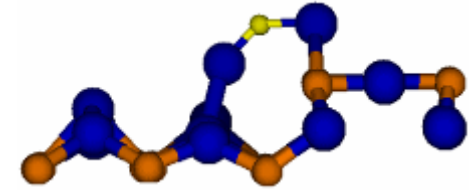
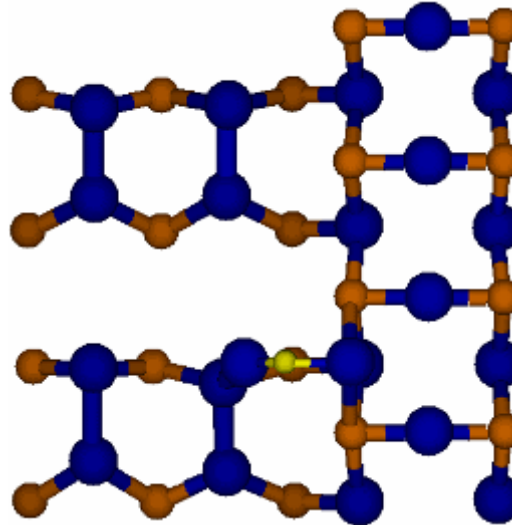
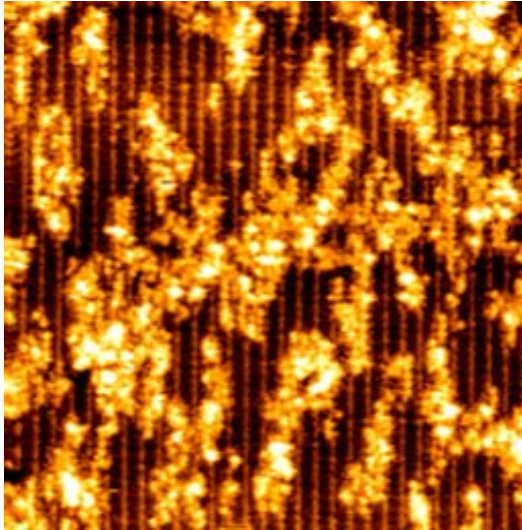
- The 1.5 Å spacing with the oxide and surface is consistent with single monolayer growth

The Effect of Annealing on In₂O/InAs(001)



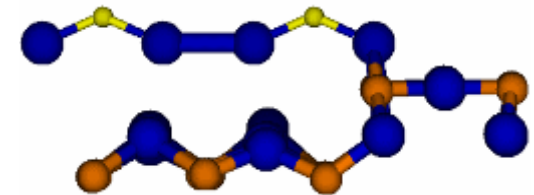
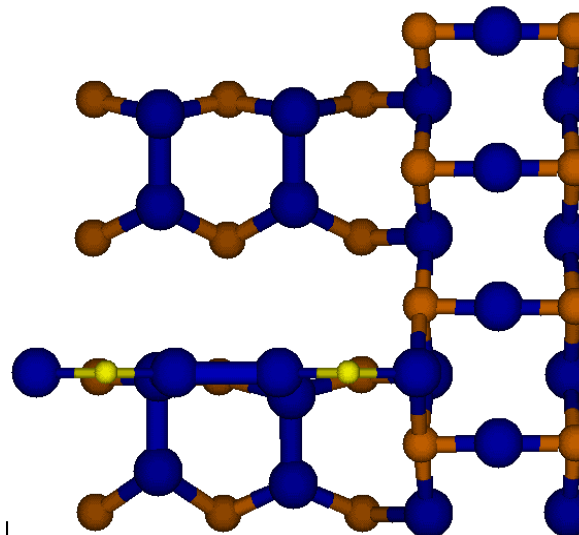
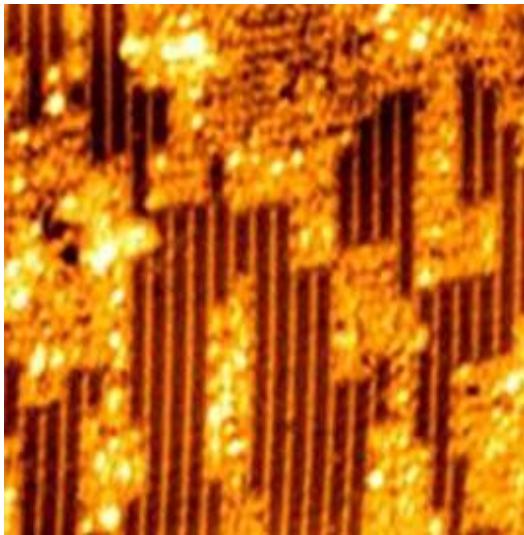
- Annealing the samples causes a more ordered reconstruction to form
- The ordered In₂O islands both fill in the troughs and form ordered rows perpendicular to the In-In dimers on the surface
- An order 1st oxide layer is favorable since it is easier to have 1 unpinned bonding sites than multiple unpinned bonding sites.

DFT of In_2O on In-rich $\text{InAs}(001)$



- Before annealing, In_2O form clusters sites on the side of the trough

○ As ● In ● O



- After annealing, perpendicular rows are observed.

Conclusions

- Undimerized $\beta 3-(4 \times 2)$ structure for indium-rich $\text{InAs}(001)-c(8 \times 2)/(4 \times 2)$.
- An ordered 1st In_2O oxide layer is favorable on $\text{InAs}(001)-c(8 \times 2)/(4 \times 2)$ surface.
- In_2O never causes the abstraction of any surface atoms.
- Annealing the sample post deposition causes a more ordered overlayer.

CURRENT PROJECTS ON OXIDE/III-V and Ge

MBE Oxides (In₂O and Ga₂O) on InGaAs/InP-4x2

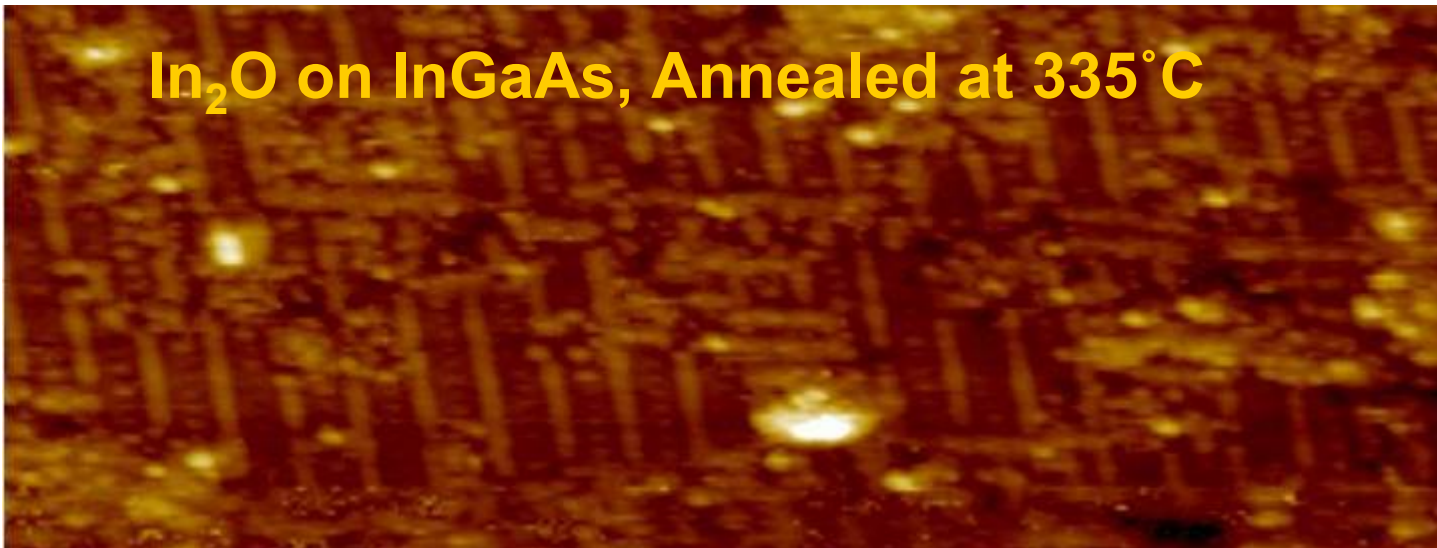
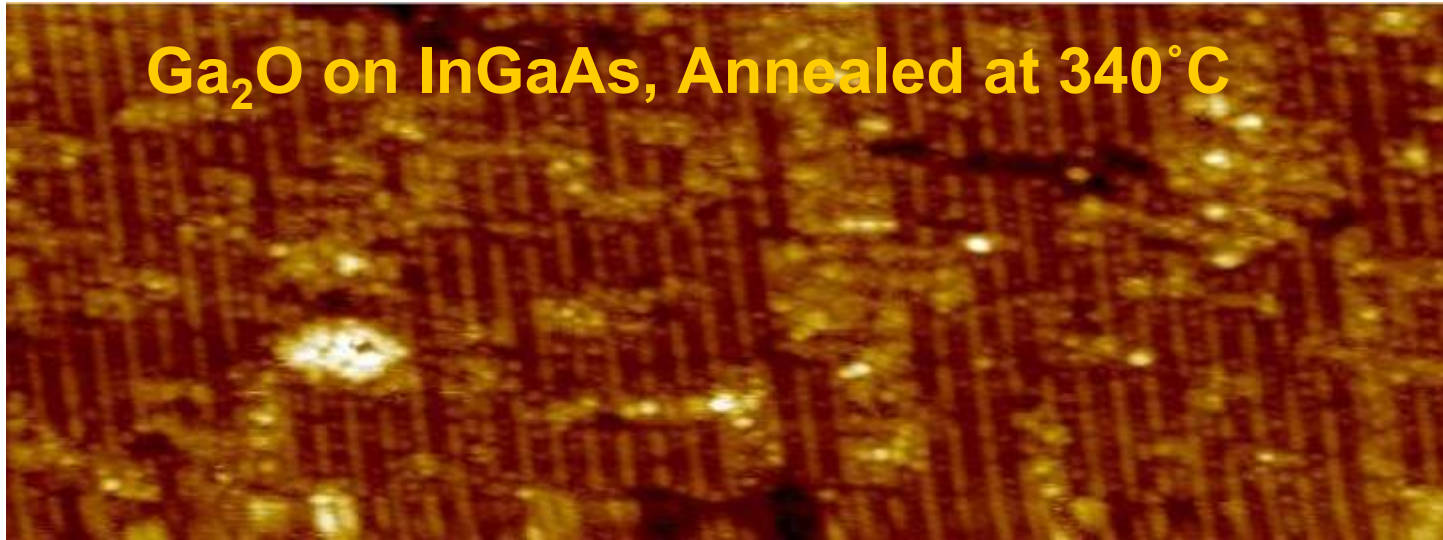
HfO₂ and ZrO₂ on InAs by reactive deposition and ebeam

Passivation of III-V for ALD oxide growth

DFT molecular dynamics of buried Oxide/III-V and Oxide/Ge Interface

Cross Sectional STM and SKPM of oxide/semiconductor interfaces in working MOSFET and MOSCAPs

MBE Oxide on $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}(001)-(4\times 2)$

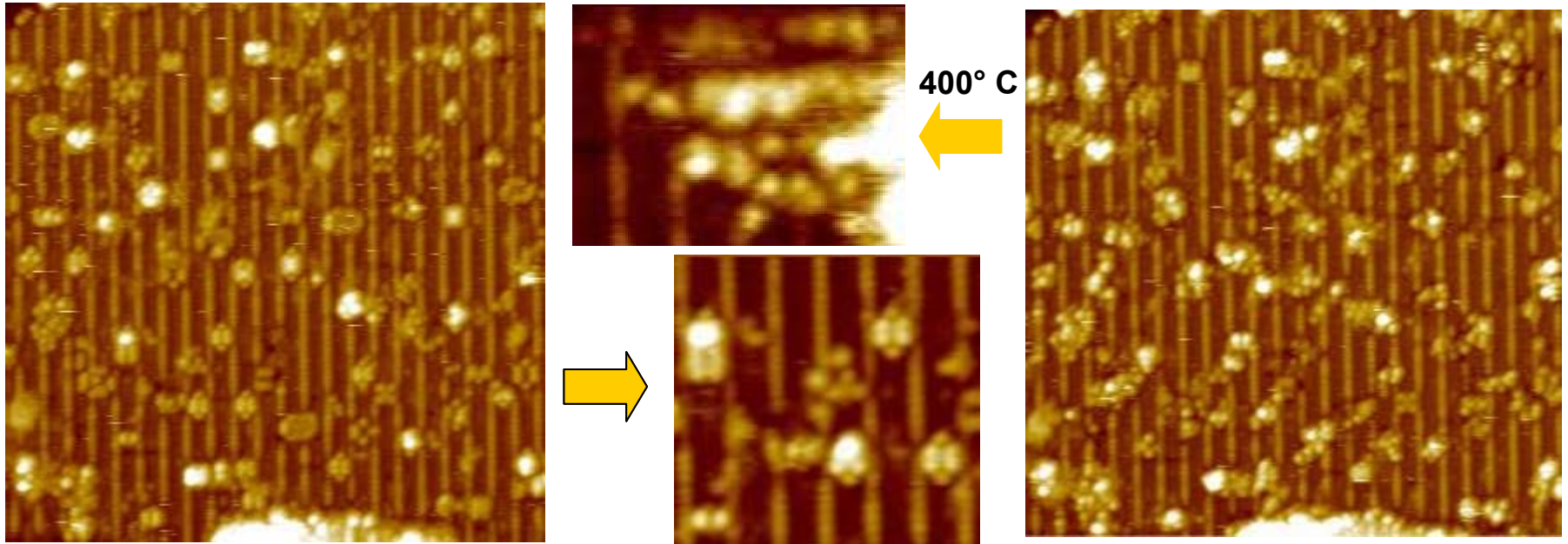


**Jian
Shen**

- Deposition occurs mainly at edge of rows with no substrate disruption
- Similar results on $\text{InAs}(001)-(4\times 2)$

Please do not distribute since some of the data has not yet been published

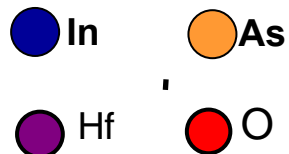
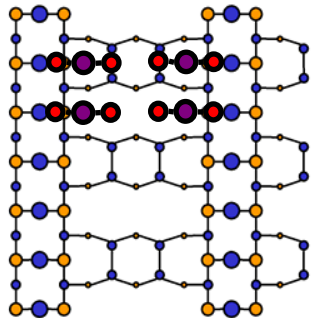
Growth of $\text{HfO}_2/\text{InAs}(001)$ -(4x2) by Oxidation



Hf deposited by e^- beam then annealed to 400°C for 5-15 minutes.

Smallest islands number ~ 6 Hf atoms.

Large islands show no order- typical of metals



Annealed $\text{Hf}/\text{InAs}(100)$ -(4x2), dosed at RT with O_2 .
Movies recorded.

Isolated Hf and small clusters unreactive to O_2 .

Large metallic clusters react with O_2 to form semi-ordered oxide after post-oxidation annealing to 400°C for ~ 10 min.

Preliminary bonding assignment is HfO_2 bonding in or over the trough but it could be sideways

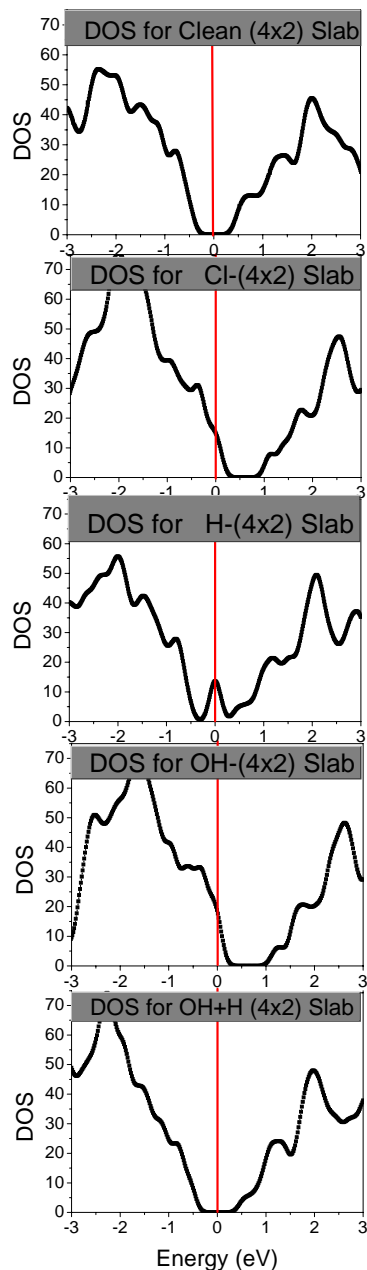
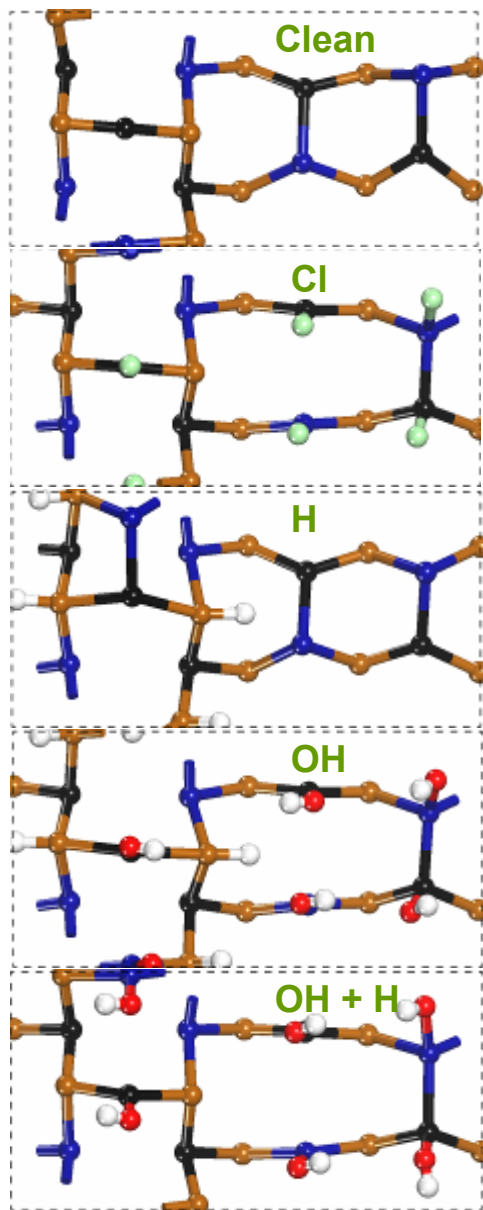
DFT calculations being performed.

Future: e^- beam HfO_2 deposition.

Please do not distribute since some of the data has not yet been published

Jon
Clemens

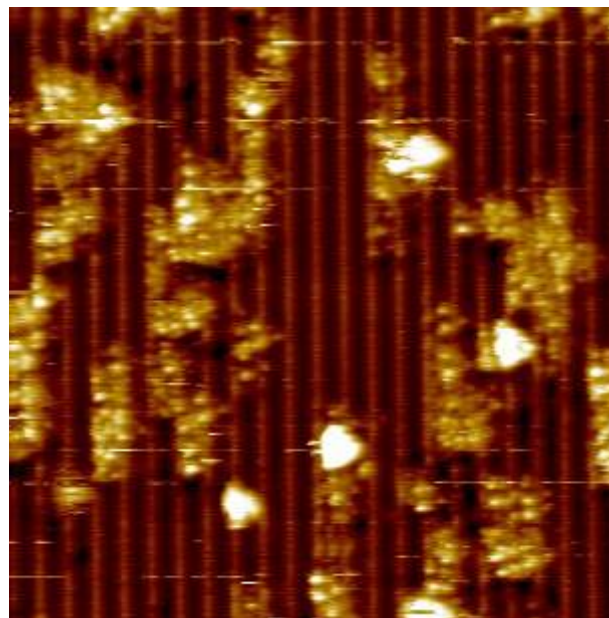
Cl, OH, H, OH+H Passivation for InGaAs(001)-(4x2)



● As ● In ● Ga ● O ● Cl ○ H

ALD gate oxide requires -OH termination for deposition of MCl_4 or Cl termination for the H_2O step.

We have a combined DFT STM project to determine which terminations are readily formed on InGaAs and InAs, thermally stable at ALD temperatures, and don't disrupt the substrate lattice.

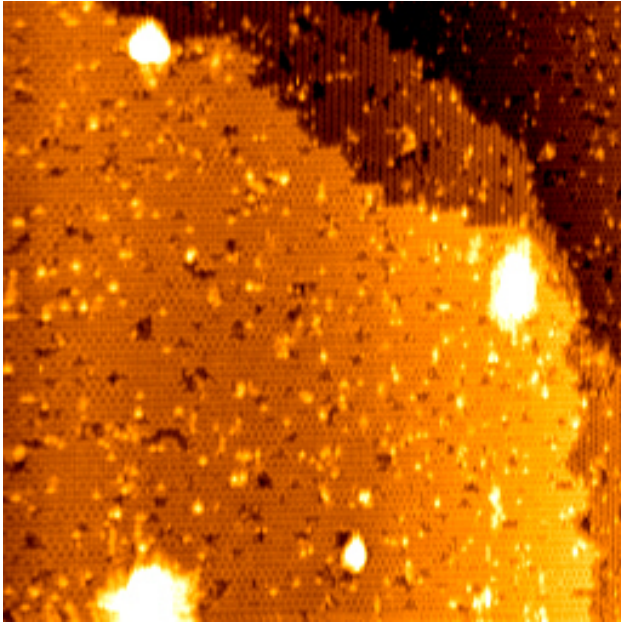


Dr. Tao Song

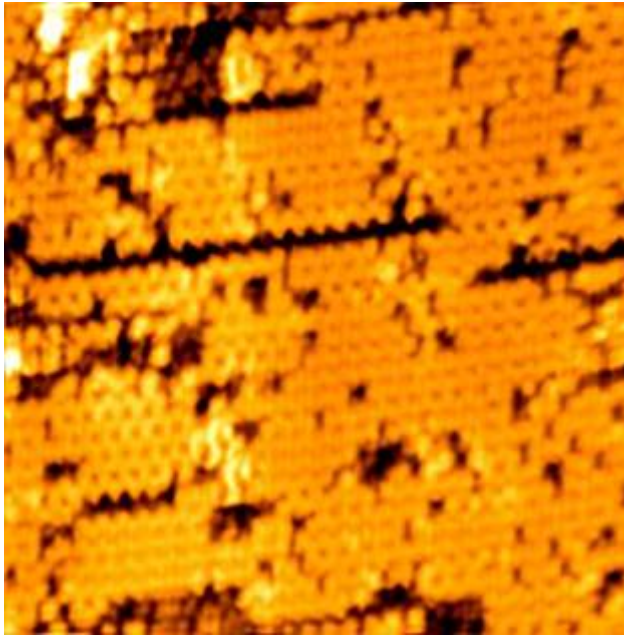
Please do not distribute since some of the data has not yet been published

Jon Clemens

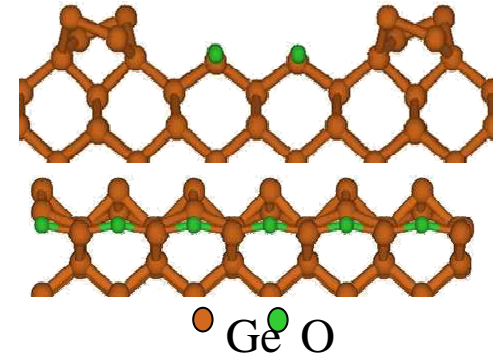
Plasma nitridation of Ge(100) - Joon Lee



Atomic N + 200C anneal

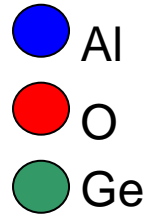


O₂ + 325C anneal



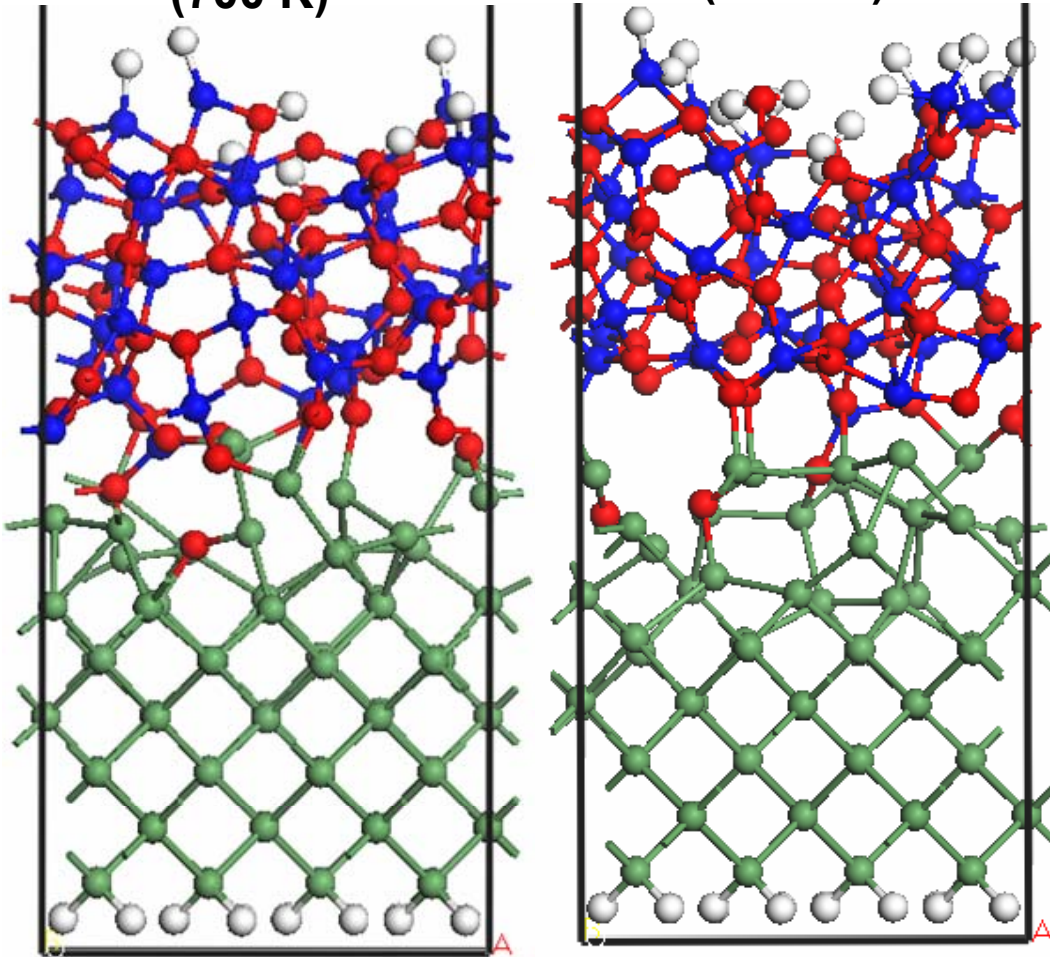
- Nitration of Ge is known to provide superior oxide/Ge electrical properties but reasons are not well understood. It is a challenge to form a nitride without oxide; O₂ dosing pins the Fermi level.
- STM performed at a sample bias of -2V, tunneling current of 0.2nA

a-Al₂O₃ on Ge(100) – Al-O-Ge Bonding – Dr. Chagarov



Final System
(700 K)

Final System
(1100 K)



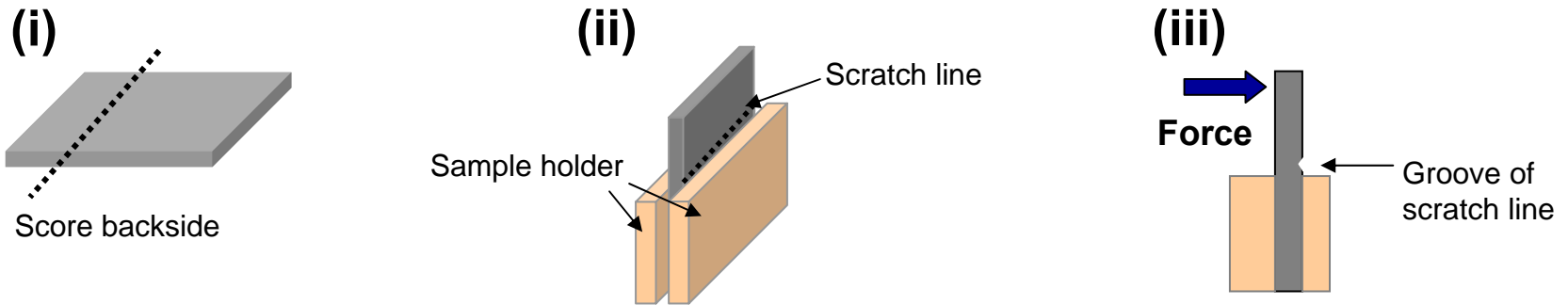
All useful high-k gate oxide are amorphous but nearly all DFT modeling is done with crystalline oxides. We use DFT molecular dynamics (DFT-MD) to model the real amorphous oxide-semiconductor buried interface structure

For a-Al₂O₃/Ge, the oxide-semi bonds are Al-O-Ge with no Al-Ge bonds causing a large interface dipole

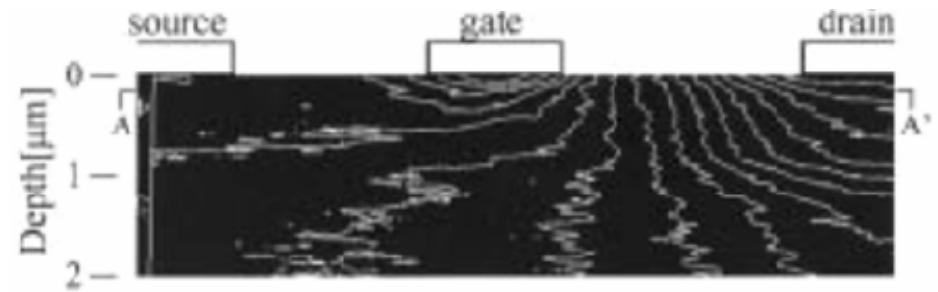
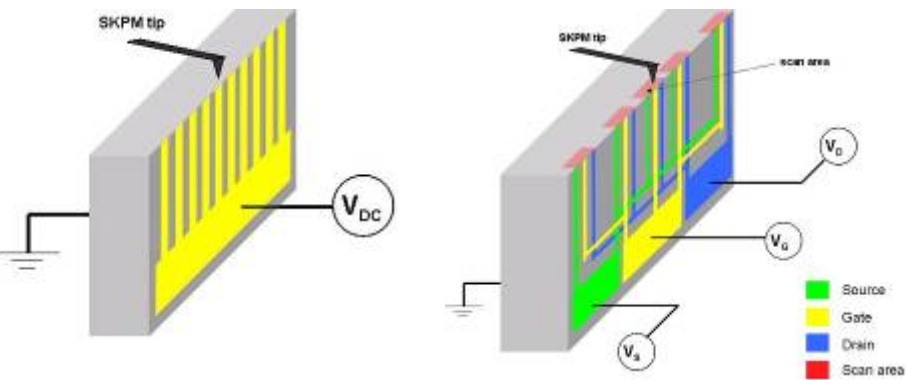
Similar work for
a-ZrO₂/Ge
a-Al₂O₃/InGaAs
a-Al₂O₃/InAlAs
a-HfO₂/InAlAs

Cross-sectional x-STM/SKPM – Joon Lee, Jian Shen

Sample cleaving is performed in the UHV chamber.



Diagrams of cross-sectional SKPM or STM experiments on MOSCAP and MOSFETs



Scanning Kelvin Probe Microscopy (SKPM) – This air SKPM image shows the contour lines of the potential profiles of a GaAs MESFET. The voltage step of contour line is 100 mV. Matsunami et al, Solid-State Electronics 43, pp. 1547-1553 (1999).

Cross section UHV SKPM (1 of only 2 in the USA) can be used to determine interfacial oxide/semiconductor electronic structure for MOSFET and MOSCAP fabricated off-site and shipped to UCSD for in-situ cleaving. Results can be compared to DFT-MD

UCSD team

DFT Calculation: Tyler Grassman, Darby Winn, Sarah Bishop, Tao Song

Amorphous Oxide DFT - Evgueni Chagarov, PhD

III-V STM – Darby Winn, Jian Shen, Jon Clemens, Wil Melitz

Ge STM – Joon Lee, Tyler Grassman,

Key External Collaborators/Contacts

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Niti Goel, Wilman Tsai, Matthew Metz, Wily Rachmady – Intel

Paul McIntyre (Stanford), Alex Demkov (UT Austin), Gene Fitzgerald (MIT),

Chris Palmstrom (UCSB), Susanne Stemmer (UCSD), Mark Rodman (UCSB),

Jesus del Alamo (MIT), Bob Wallace (UT Dallas), P. D. Ye (Perdue), Chi-On Chui

(UCLA), Jim Harris (Stanford)