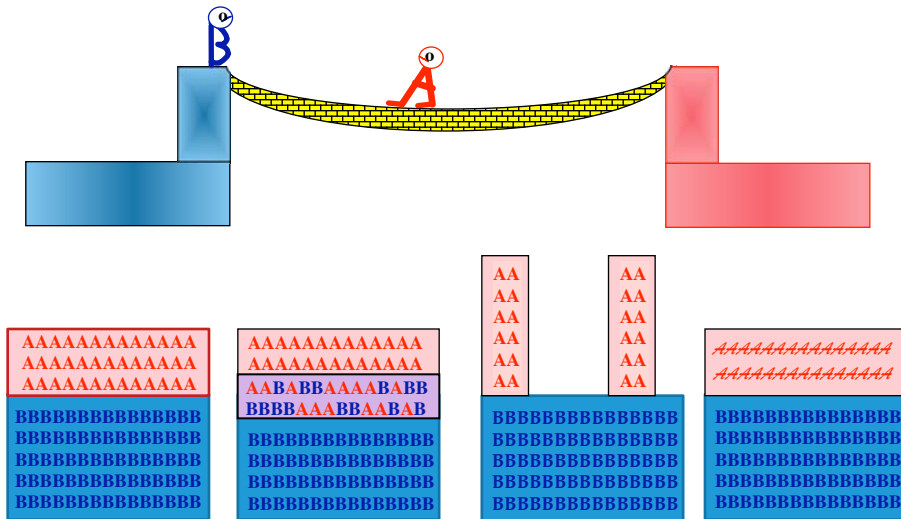


Building Atomic Bridges Between Dissimilar Materials



Professor Marjorie Olmstead, Department of Physics olmstd@uw.edu

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Miniaturization

1930's Victrola	1960's Tabletop Turntable	1990's Walkman	2020's
Vacuum Tube L ~ 5 mm	Transistor L ~ 5 μm	Heterostructure Laser L ~ 5 nm	

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Inside your I-Pod ...



Flash Memory

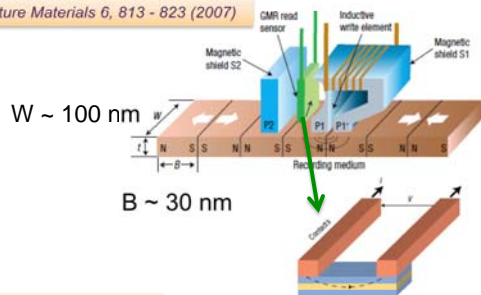
http://www.micron.com/innovations/process_tech/index

Rapid Advancements in NAND Process Technology



GMR Read Head

Nature Materials 6, 813 - 823 (2007)



Field Effect Transistors



Intel Press Release on cnet.com

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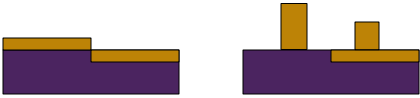
Future Devices – Interfaces Matter

- Silicon Based Nanoelectronics:
 - Join Silicon with things that do what Silicon doesn't do
 - Increase speed:
 - ✧ Strain electron channel by adding Germanium
- Islands and Interdiffusion
- Modulate Light:
 - ✧ Add layers of compound materials
- Interface Compounds and Crystal Symmetry
- Add Magnetic Effects
 - ✧ Transition-metal doped oxides and semiconductors
- Unwanted Reactions and Phase Segregation

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Questions to Answer

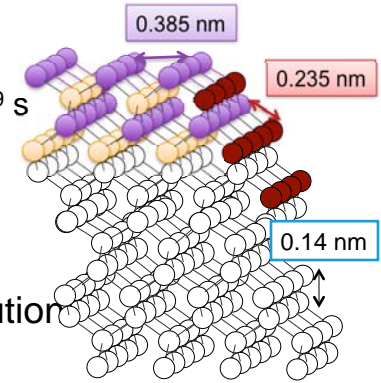
When you grow A on B ...

- Is there intermixing? 
- How does B's structure influence A's? 
- Does A form a flat film (laminar) or form islands? 
- Does A have new properties?

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How can we answer these questions?

- Ultrahigh Vacuum
 - Atmospheric pressure: Surface atoms hit once each 10^{-9} s
 - 1 layer/second = 1 micron/hour
 - Work at $\sim 10^{-13}$ atmospheres, grow \sim few layers / minute
- Microscopy with sub-nm resolution
 - Atomic spacing $\sim 0.2 - 0.4$ nm
- Atom-specific structural information
 - Elemental distribution perpendicular to growth direction

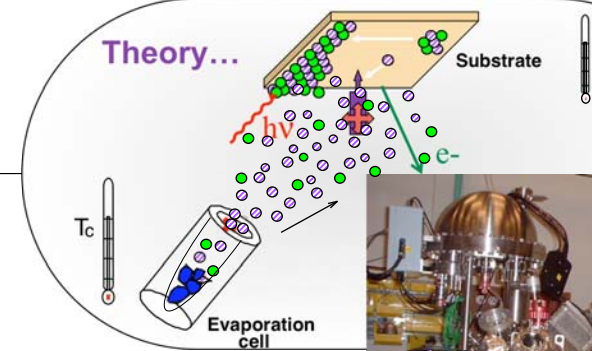


Silicon Lattice

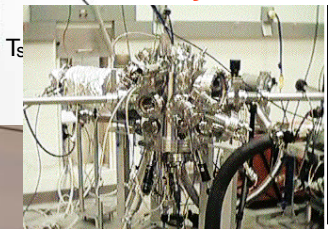
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How it's done ...


Theory...



Reality:



B049



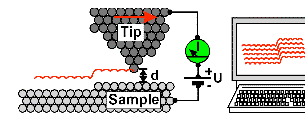
B009

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Synchrotron Source-Berkeley

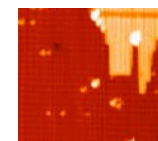
Experimental tools: Microscopy

- Scanning tunneling microscopy (STM):
 - Electrons tunnel between tip and sample
 - Measure electronic state corrugation

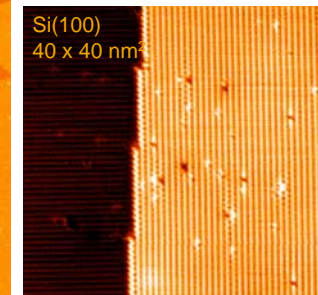
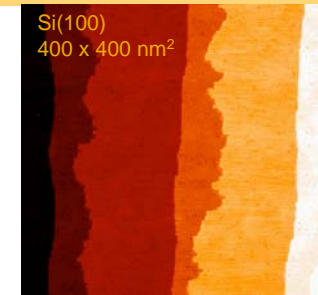


http://www.nanoscience.de/group_r/stm-spstm/stm/

- Real space information
- No direct information of the elements

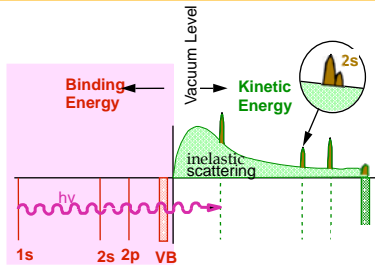


Si(100)+ 1 ML Arsenic
400 x 400 nm²

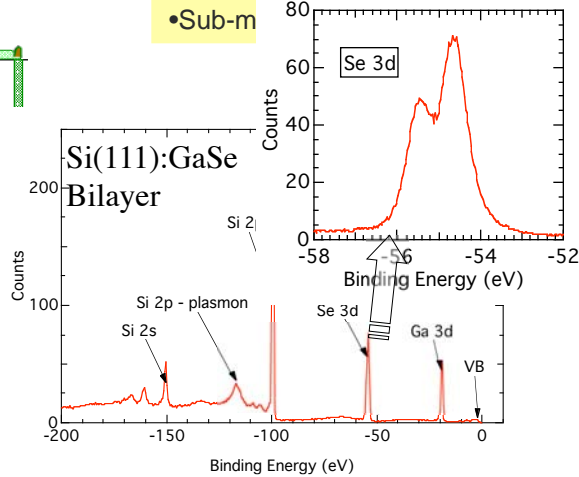


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Experimental Tool: Photoemission Spectroscopy



- Element-specific
- Environment-specific
- Sub-m



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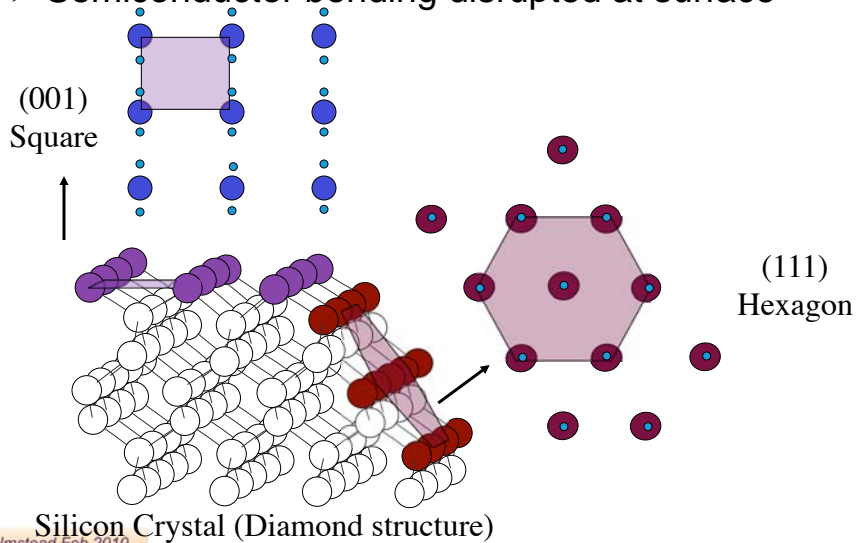
A Few Intrinsic Factors in Heteroepitaxy

- **Surface Structure** -- Symmetry, Defects
 - **GaSe vs Ga₂Se₃/Si**: Substrate control of crystal structure
- **Chemical Reaction** – Interface Compound Formation
 - **TiO₂/Si**: Buffer layer inhibition of interface reaction
- **Impurity Incorporation** – Solubility Limits, Phase segregation
 - **Cr and Mn-doped Ga₂Se₃/Si**: Concentration-dependent structure

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Surface Symmetry

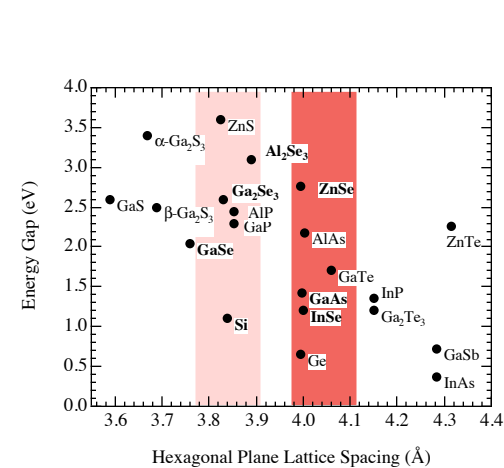
- Semiconductor bonding disrupted at surface



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Optoelectronics Heteroepitaxy

- Optical Band Gap vs. Lattice Parameter



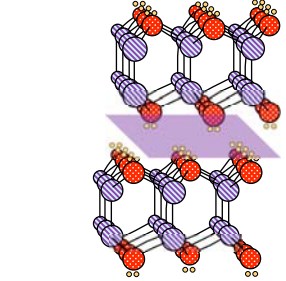
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- GaSe, Ga₂Se₃, Al₂Se₃
 - Matched to Si
 - Non-linear optics
 - Direct band gap
 - Anisotropic
 - Cool growth physics
 - Useful material??

2	3	4	5	6	7	8
B	C	N	O	F	Ne	
Al	Si	P	S	Cl	Ar	
Zn	Ga	Ge	As	Se	Br	Kr
Cd	In	Sn	Sb	Te	I	Xe

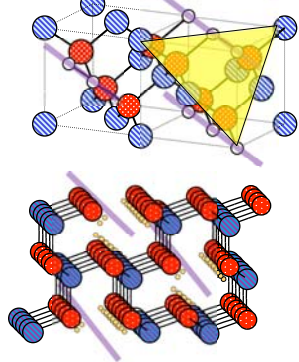
Gallium Selenide Crystal Structure

Hexagonal GaSe Layered
 $a_{\text{hex}} = 0.97 a_{\text{Si-111}}$



Planes

Cubic Ga₂Se₃ Zincblende
 $a_{\text{cube}} = 1.01 a_{\text{Si-cube}}$



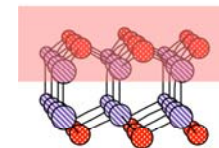
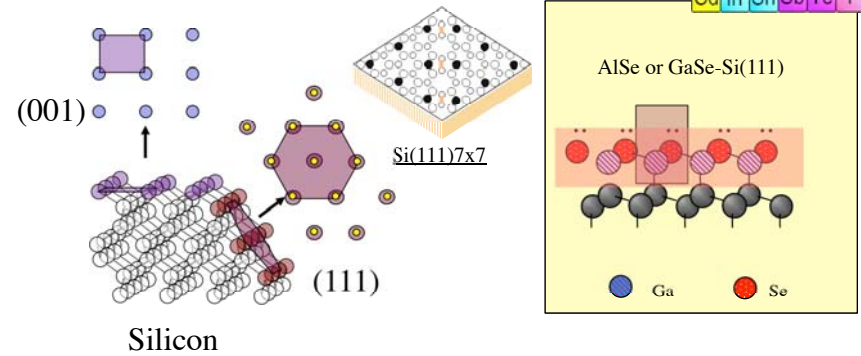
Lines

Flexible Bonding Configuration: Vacancies and Lone Pairs

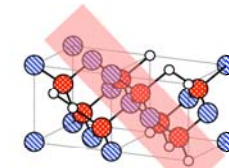
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Si(111): Passivate Dangling Bonds

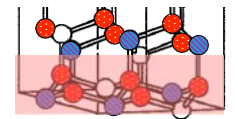
2	3	4	5	6	7	8
B	C	N	O	F	Ne	
Al	Si	P	S	Cl	Ar	
Zn	Ga	Ge	As	Se	Br	Kr
Cd	In	Sn	Sb	Te	I	Xe



Layered GaSe



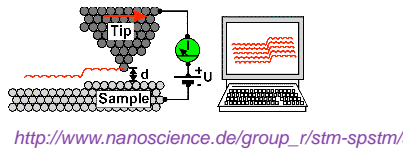
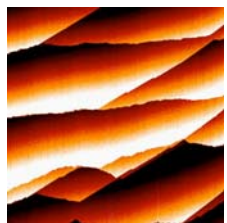
Cubic Ga₂Se₃



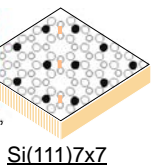
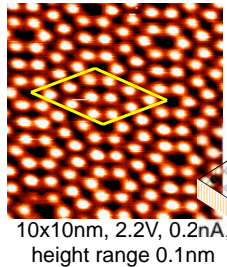
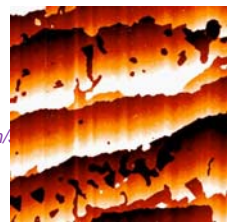
Wurtzite Al₂Se₃

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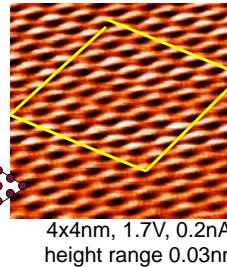
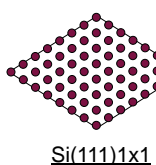
GaSe Bilayer on Si(111)7x7



+ GaSe at ~ 525°C



1x1 smooth structure

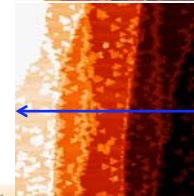
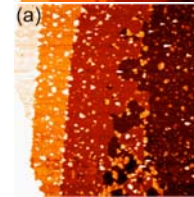


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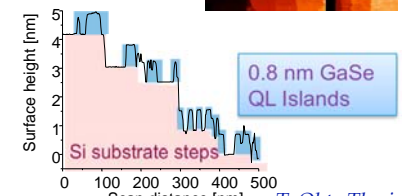
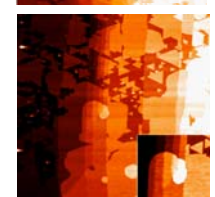
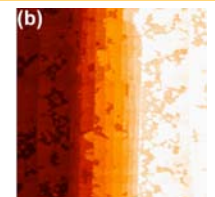
PRB Feb 2004

GaSe Nucleation and Growth on Si(111)

500 x 500 nm²



6.5 HBL
(1 HBL + 2.7 QL)

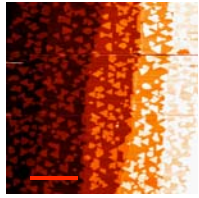


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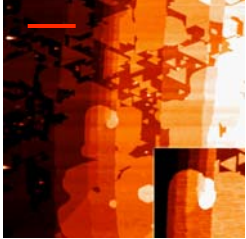
T. Ohta Thesis (UIW) 2004.

Nucleation on Si(111):GaSe Hexagonal, Layered GaSe

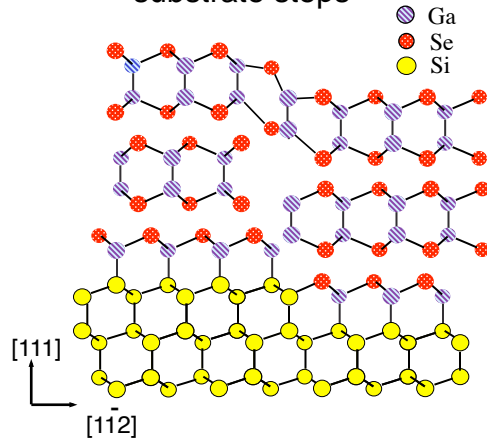
1.1QL on bilayer
(3.2HBL coverage)



2.7QL on bilayer
(6.5HBL coverage)



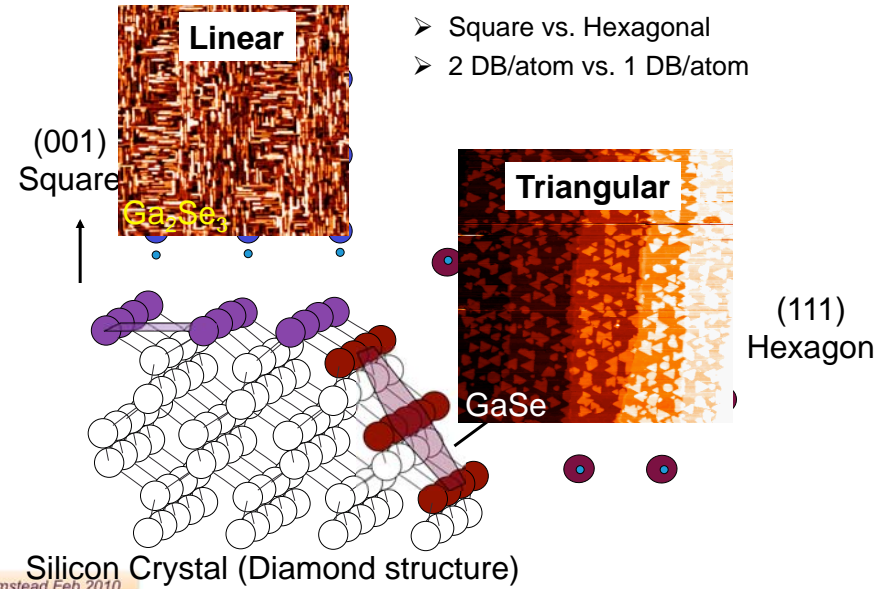
- Triangular Islands
- 1 QL high (0.8 nm)
- "Carpet on steps" over substrate steps



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Scale bar 100 nm

Change Symmetry: Si(001) vs. Si(111)

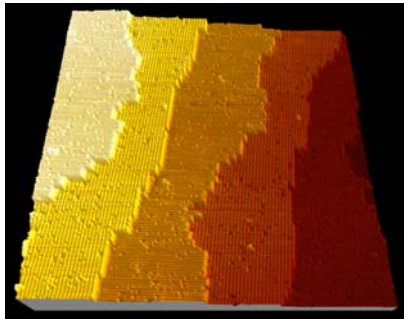
- Square vs. Hexagonal
- 2 DB/atom vs. 1 DB/atom



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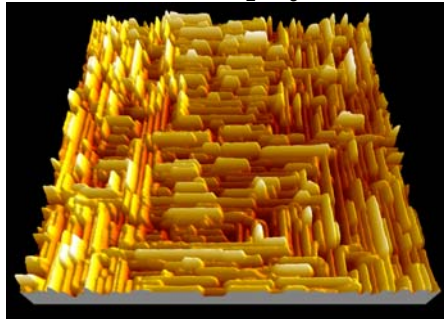
Growth on Si(001)

bare Si(100)

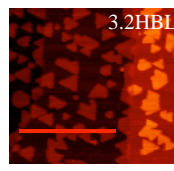
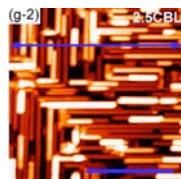
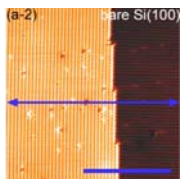
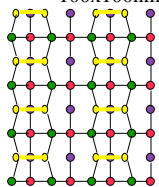


100x100nm², -2V, 0.1nA

Zinc-blende Ga₂Se₃ (2.5CBL)



100x100nm², 5.4V, 0.09nA



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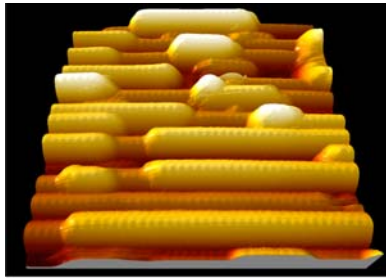
on Si(111)

Nanorod Nucleation and Growth

Large scale 500x500 nm² Scale Bar 25 nm

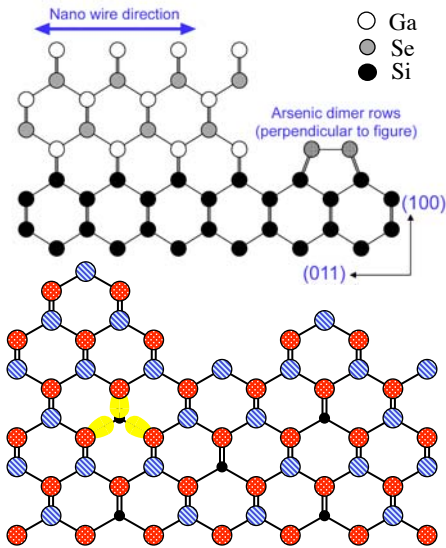
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Ga₂Se₃ Nanoridge Structure ↔ Growth



-5.4 V, 0.09 nA, 20x20nm²

- 1 Ga-Se bilayer high
- Corrugation = Ga-Ga distance
- Rods perp. to As dimer rows
- Lateral shift between layers

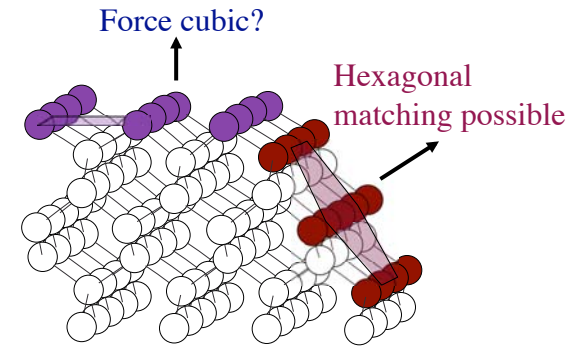


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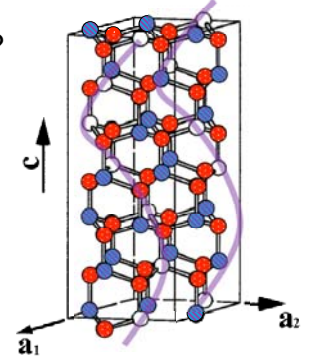
T. Ohta et al, PRL 2005.

Al₂Se₃ on Si(001):As

- Bulk Al₂Se₃ is hexagonal
 - Can we induce cubic?
 - Does intermixing still occur?
 - Do vacancies align for nanoridges?



Hexagonal Al₂Se₃ Wurtzite



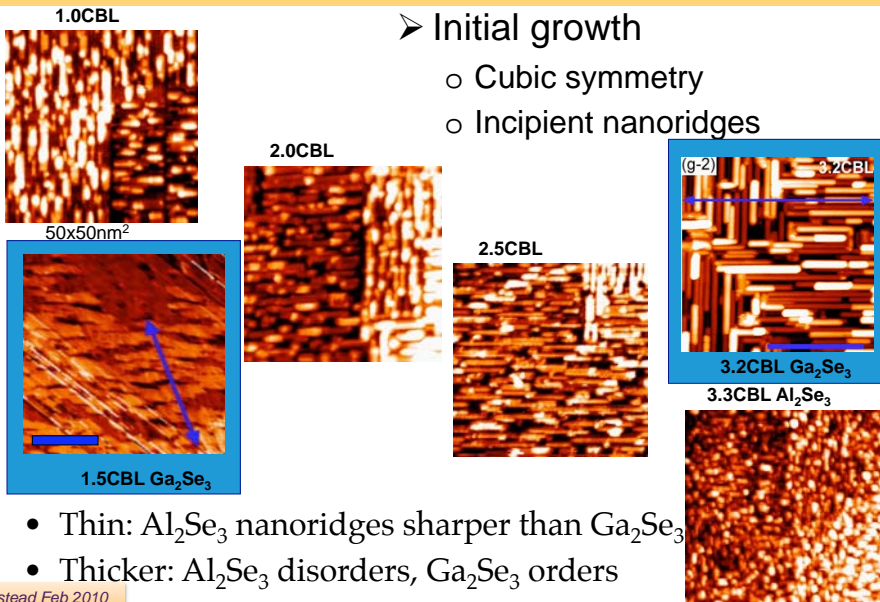
Helices

C. Lu thesis

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Al₂Se₃ Growth on Si(001):As

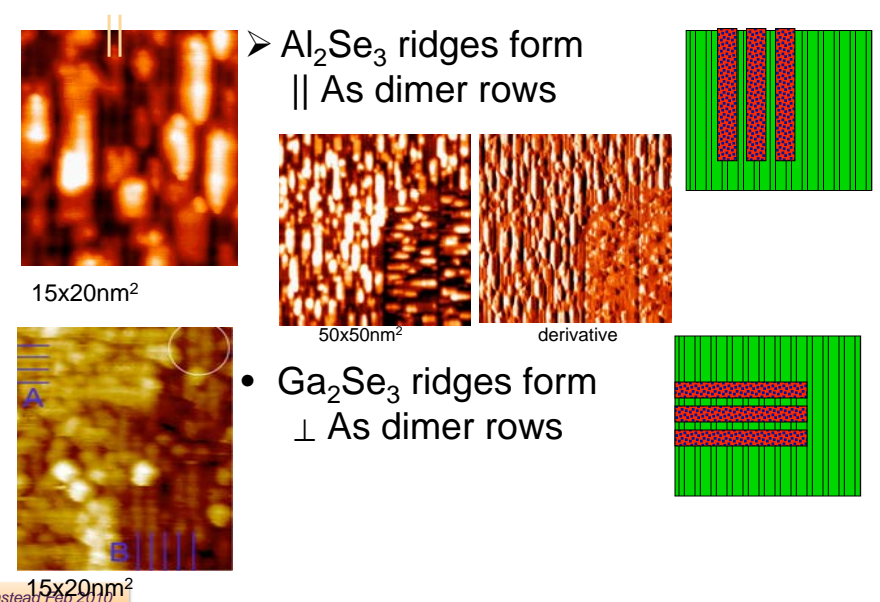
- Initial growth
 - Cubic symmetry
 - Incipient nanoridges



- Thin: Al₂Se₃ nanoridges sharper than Ga₂Se₃
- Thicker: Al₂Se₃ disorders, Ga₂Se₃ orders

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Interface Structure and Orientation



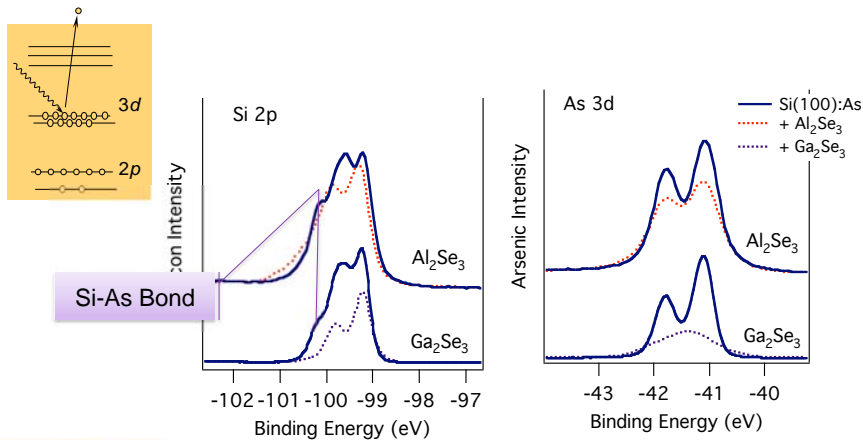
- Al₂Se₃ ridges form || As dimer rows

- Ga₂Se₃ ridges form ⊥ As dimer rows

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Why? Different Reactivity

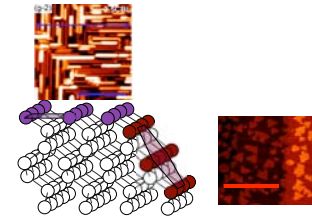
- Ga_2Se_3 : As interdiffuses into Ga_2Se_3
- Al_2Se_3 : As stays bonded to Si



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A Few Intrinsic Factors in Heteroepitaxy

- **Surface Structure** – Symmetry, Defects



- **Chemical Reaction** – Interface Compound Formation
 - TiO_2/Si : Buffer layer inhibition of interface reaction
- **Impurity Incorporation** – Solubility Limits, Phase segregation
 - **Cr** and **Mn**-doped $\text{Ga}_2\text{Se}_3/\text{Si}$: Concentration-dependent structure

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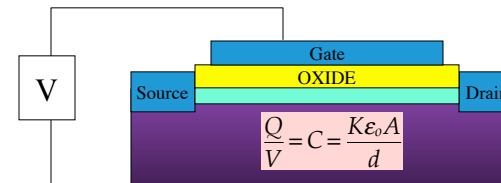
Chemical Reactions: Good or Bad?

- **Bad**
 - Wrong properties for desired application
 - Passivate to the point nothing wets the surface
- **Good**
 - Unzip surface reconstruction
 - Satisfy electron counting at interface
 - Special properties of unique material

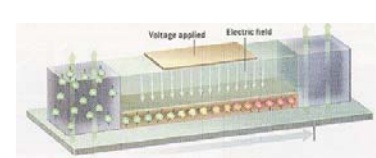
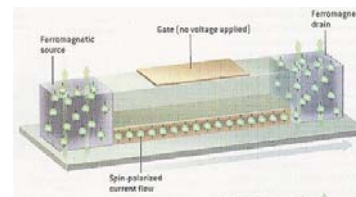
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TiO_2 : Heteroepitaxial Oxide on Silicon

- High K dielectric for transistor as area shrinks



- Ferromagnetic semiconductor for spin-transistor

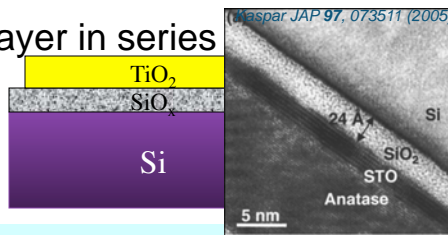


Rashbah effect: Voltage rotates spin

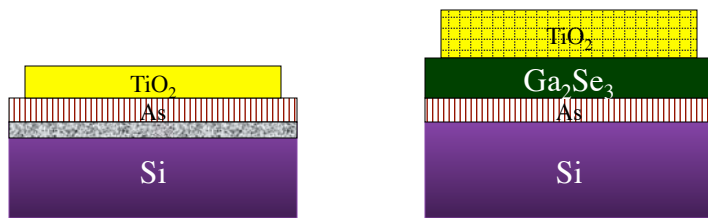
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TiO₂ Problem: Unwanted SiO₂

- Low dielectric constant layer in series
 - Large capacitance
- Amorphous interface
 - scatters spin-polarization



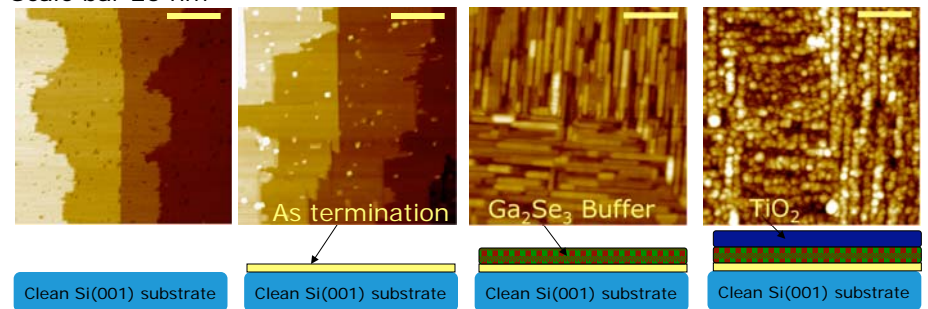
Solution: Nanoscale Buffer Layer



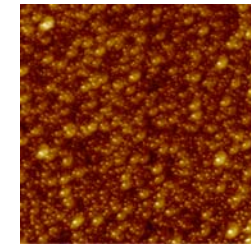
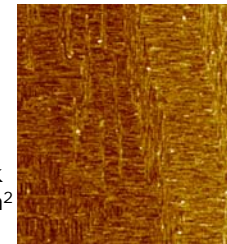
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Scanning Tunneling Microscopy

Scale bar 25 nm



Co:TiO₂
0.2 nm thick
500x500 nm²

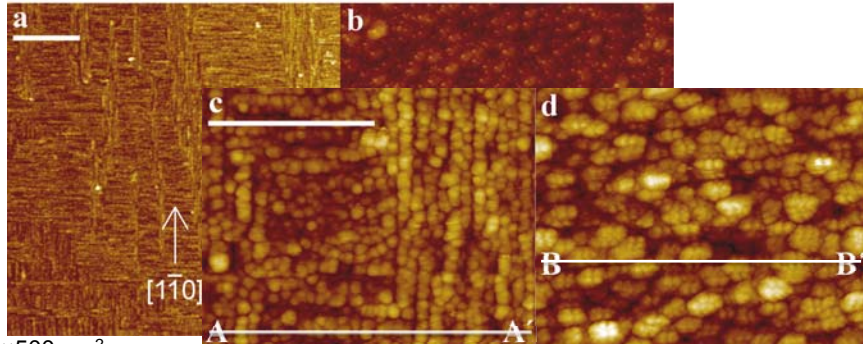


Co:TiO₂
4 nm thick
500x500 nm²

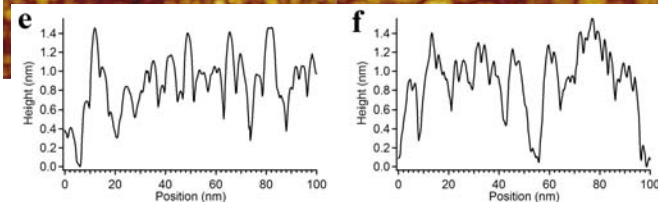
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Co:TiO₂/Ga₂Se₃/As/Si(001)

~0.3 nm Co:TiO₂/Ga₂Se₃ ≥3.5 nm Co:TiO₂/Ga₂Se₃

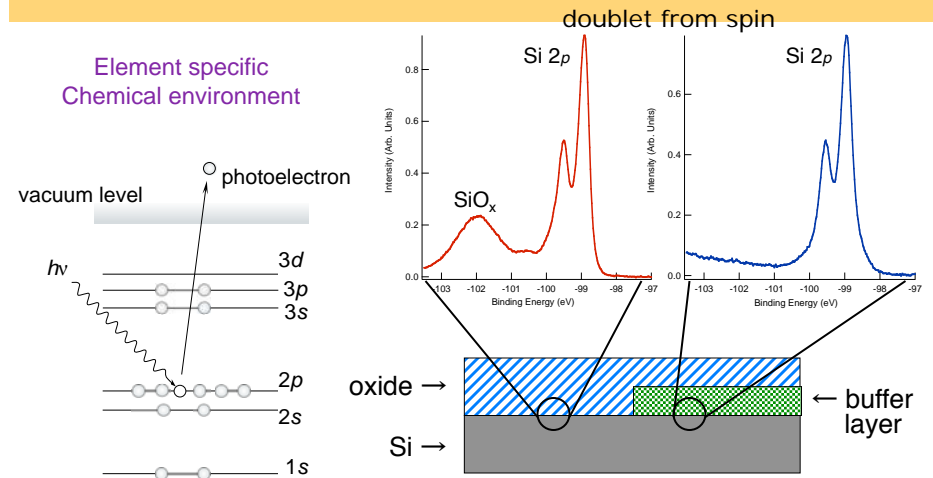


500x500 nm²
2.8 V, 0.09 nA



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Photoemission - Si Chemistry



Lend valence electrons to Oxygen --
Remaining electrons are more tightly bound

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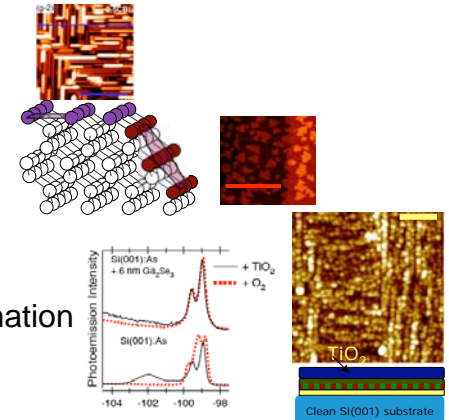
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A Few Intrinsic Factors in Heteroepitaxy

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- **Chemical Reaction** – Interface Compound Formation



- **Impurity Incorporation** – Solubility Limits
 - **Cr and Mn-doped Ga₂Se₃/Si**: Phase segregation

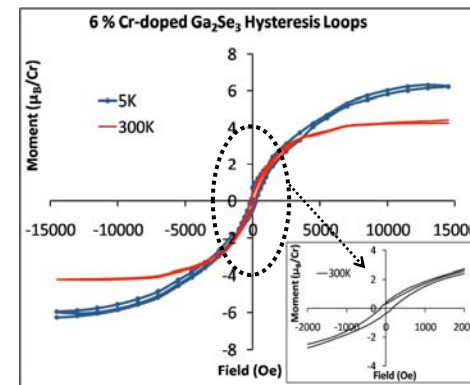
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Can we Make the Buffer Layer Magnetic?

- Doping with transition metals
 - Mn-doped GaAs
 - Ferromagnetic below $-100\text{ }^{\circ}\text{C}$
 - Cr-doped GaN or TiO₂
 - Ferromagnetic at room temperature
 - Needs defects to work – impurity phases?

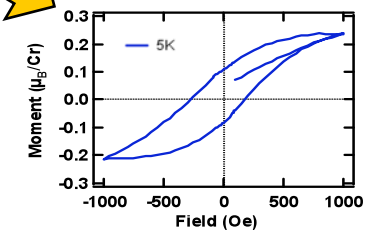
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Ferromagnetism in Cr-doped Ga₂Se₃



❖ Adding Chromium to Ga₂Se₃ makes it a ferromagnet at room temperature

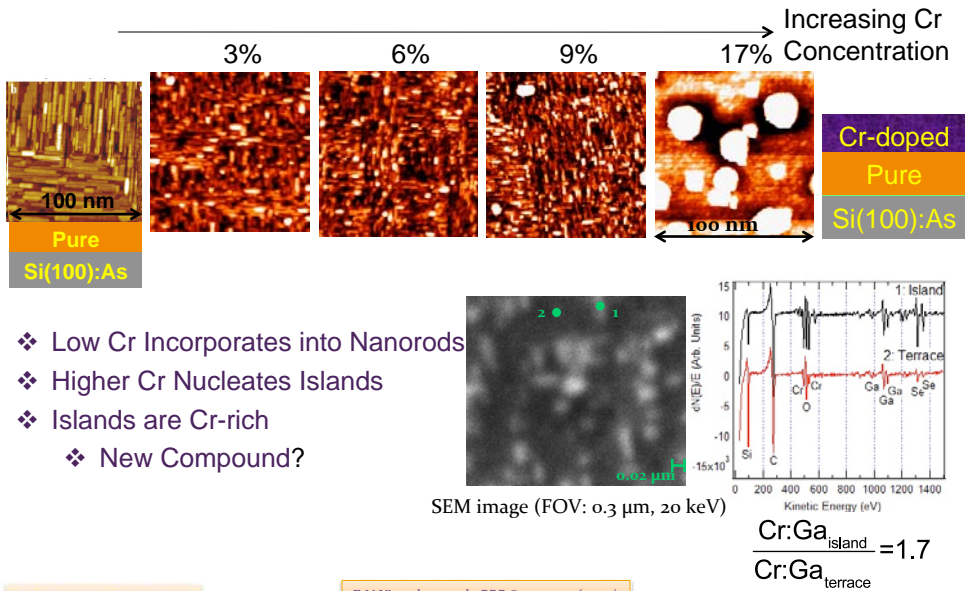
Cr-doped
Pure
Si(100):As



36 Olmstead Feb 2010

E.N.Yitamben et al., submitted to PRL 2010

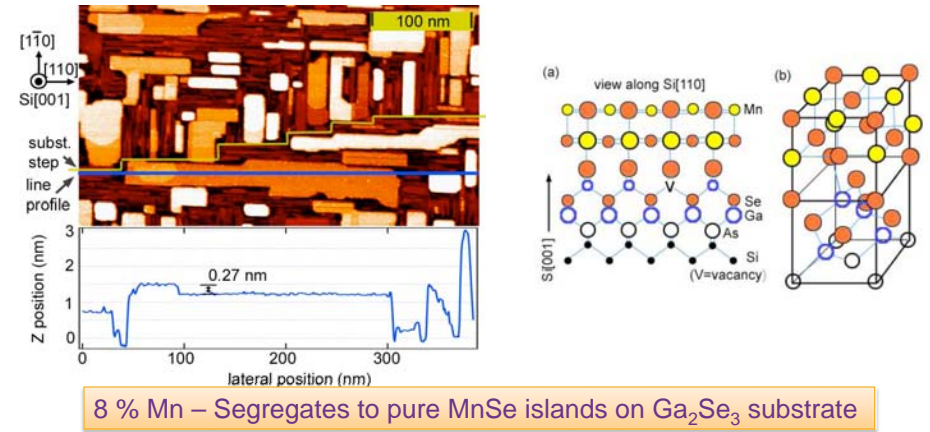
Surface morphology (solubility limit?)



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E.N.Yitamben et al., PRB 80, 075314 (2009)

Mn doping – leads to MnSe

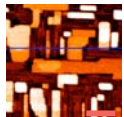
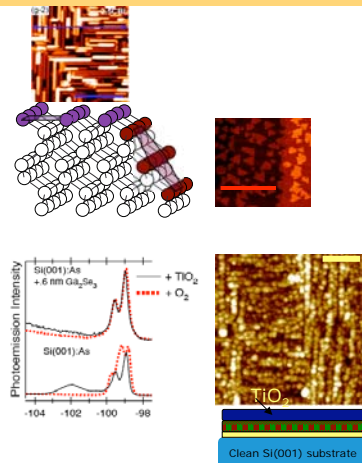


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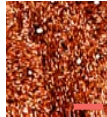
T. Lovejoy, et al APL 95 (2009) 241907

A Few Intrinsic Factors in Heteroepitaxy

- **Surface Structure** -- Symmetry, Defects
- **Chemical Reaction** – Interface Compound Formation
- **Impurity Incorporation** – Phase Segregation



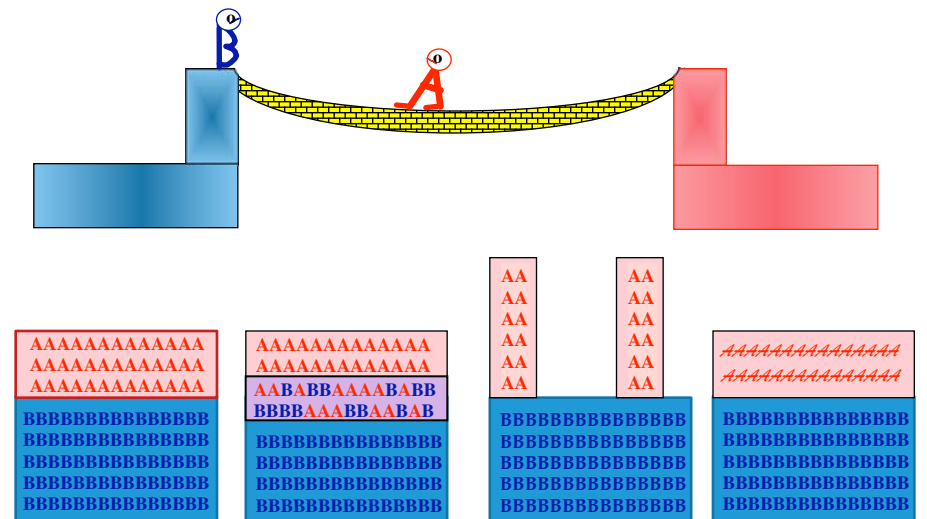
9 % Mn



9 % Cr

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Building Atomic Bridges Between Dissimilar Materials



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