Crystal Oxides On Silicon

Jim Reiner

Kevin Garrity, Alexie Kolpak, Yaron Segal,
Fred Walker, Sohrab Ismail-Begi, Charles Ahn
Yale University

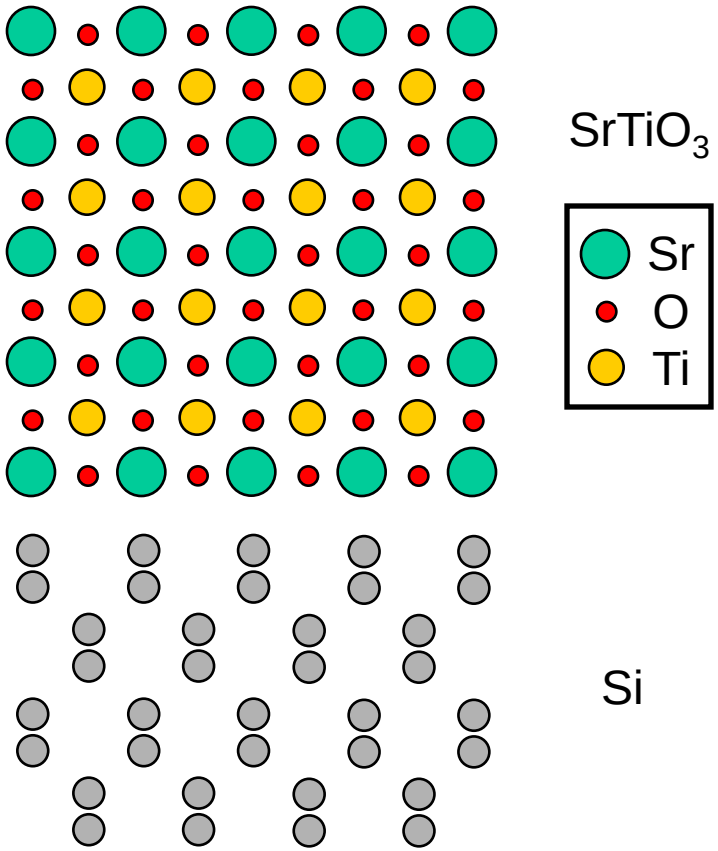
Zhan Zhang, Hawoong Hong
Advanced Photon Source
Argonne National Laboratory

Monica Sawicki, Christine Broadbridge
Southern Connecticut State University

Dong Su
Brookhaven National Laboratory

Motivation

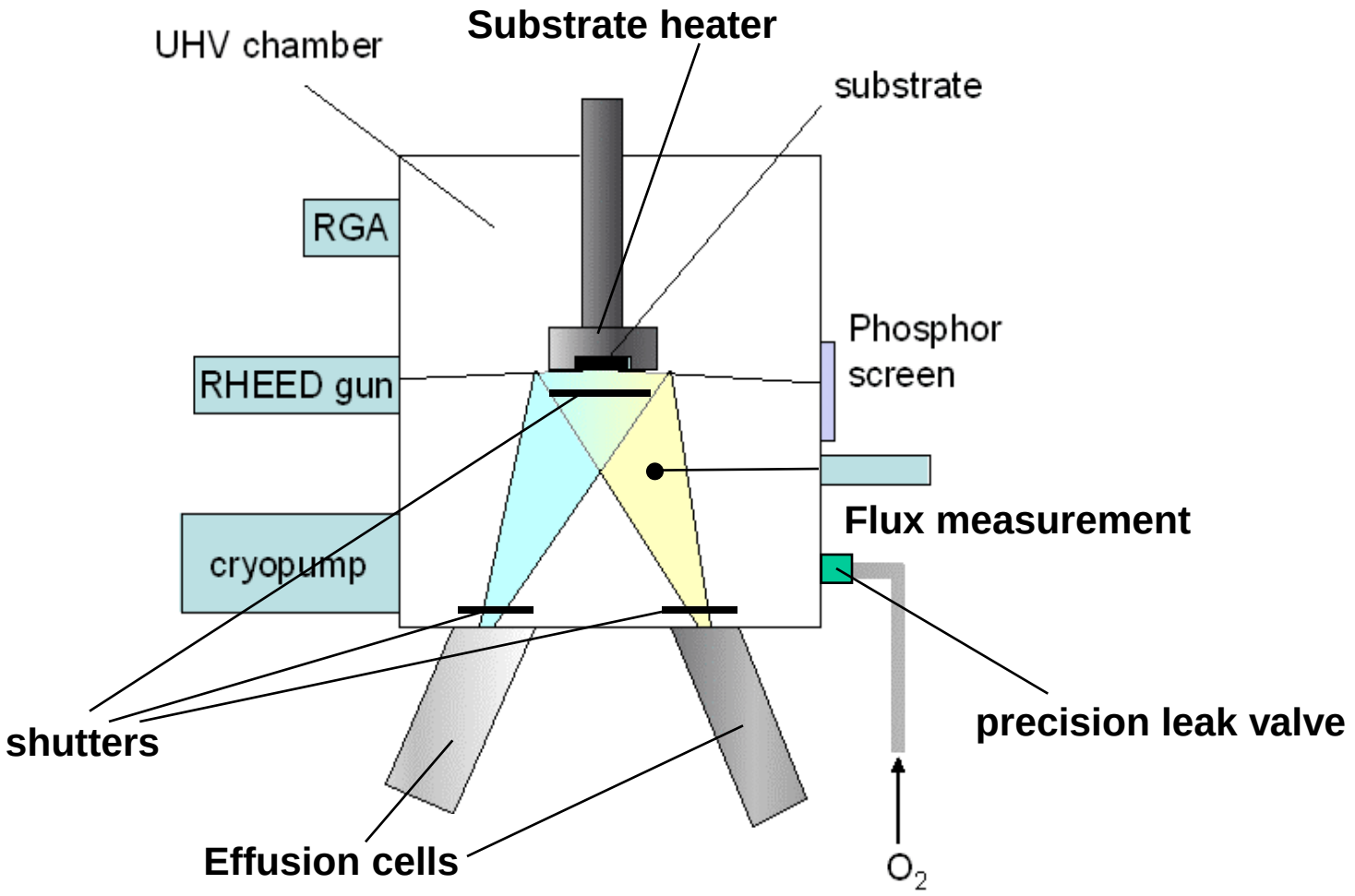
- Complex oxides exhibit wide range of phenomena
  - Ferroelectric: $PbTiO_3$
  - Magnetic: $La_{0.7}Sr_{0.3}MnO_3$
  - High-k: $SrTiO_3$, $LaAlO_3$
- Oxide heterostructures on Si (001) bring this functionality to an advanced device platform
- Creating fully crystalline structures with atomically abrupt interfaces a challenge



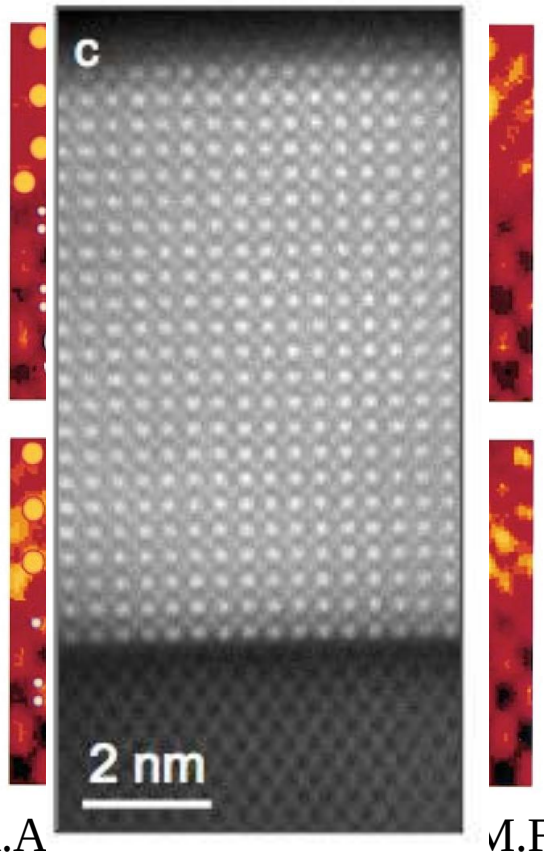
Outline

1. Interface between crystalline oxides and silicon
   - Reaction of strontium with silicon surface
   - XRD and DFT determination of interface
2. $SrTiO_3$ on silicon
   - Ferroelectric FET?
   - Influence of heteroepitaxial interface
3. $LaAlO_3$ growth on $SrTiO_3$/Si wafers

Oxide MBE system

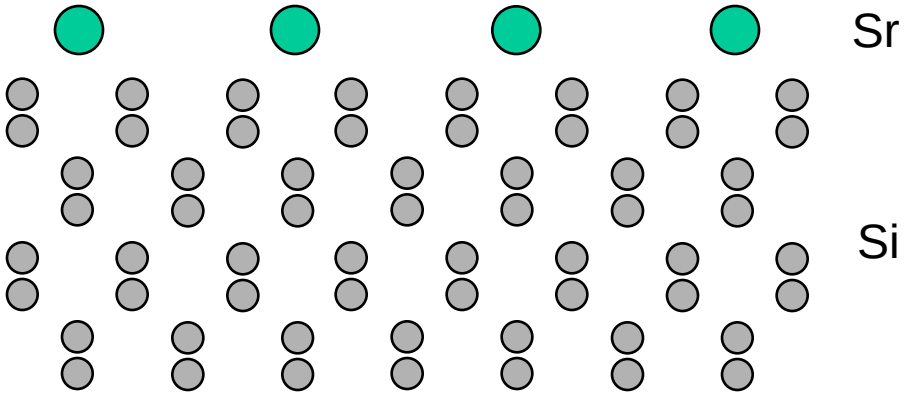


Complex Crystal Oxides on Si (001)

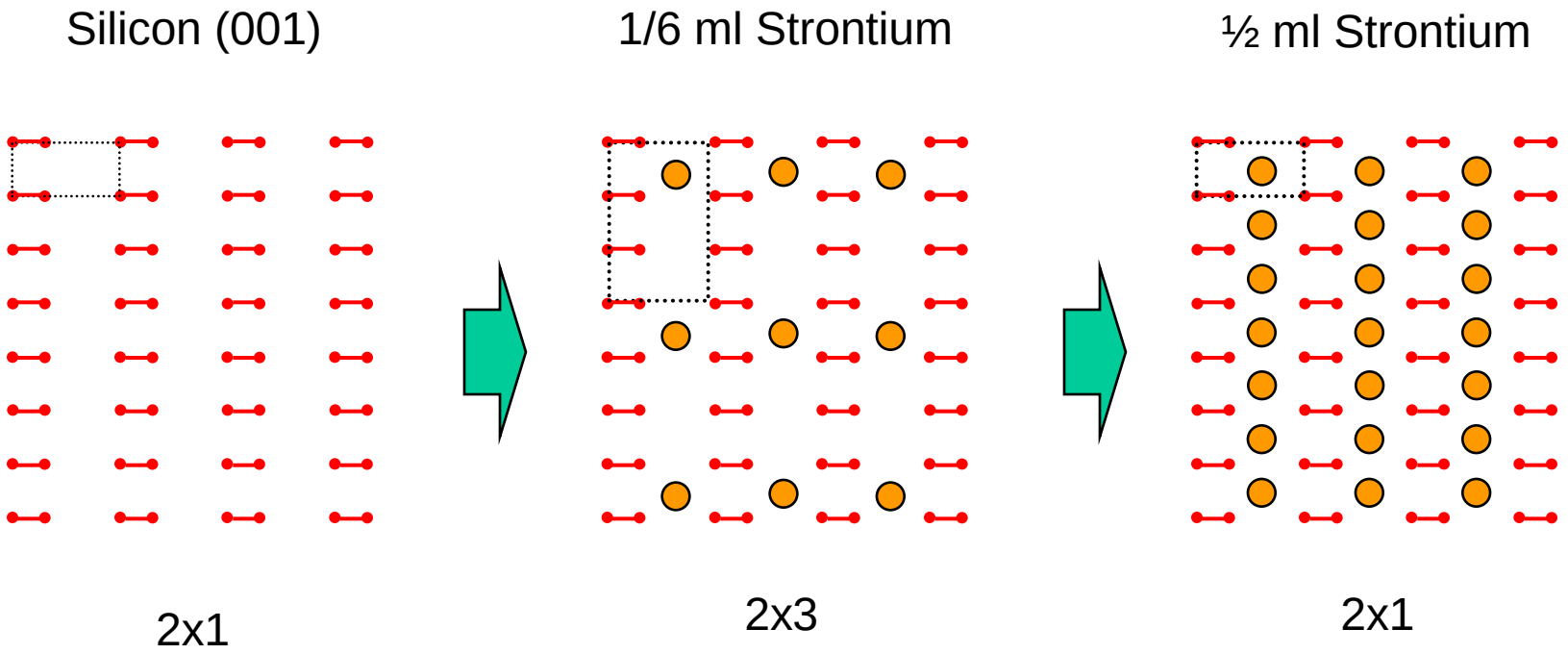


R.A M.F. Chisholm, PRL **81**, 3014 (1998).
Maitri et al., Science, last week

- $SrTiO_3$ was the first complex oxide epitaxially grown on Si
- Only a small number of crystalline oxides have been grown on Si (001)

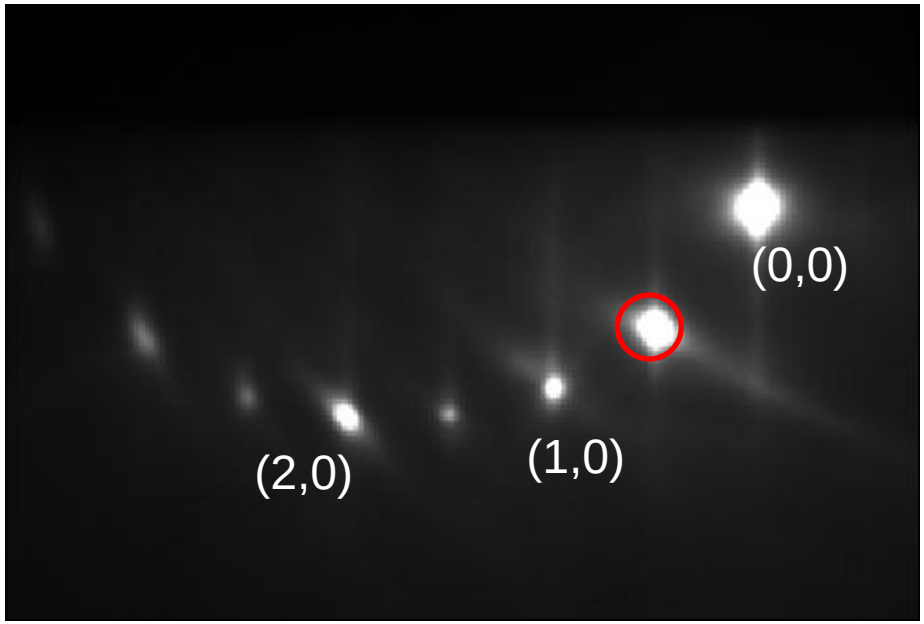


Strontium sub-monolayer structures?



RHEED Studies of Sr Deposition

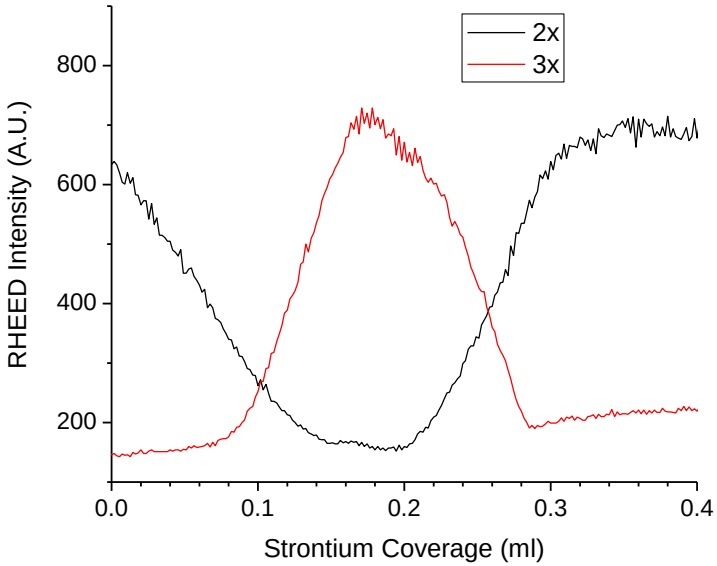
RHEED during ½ ml deposition of Sr



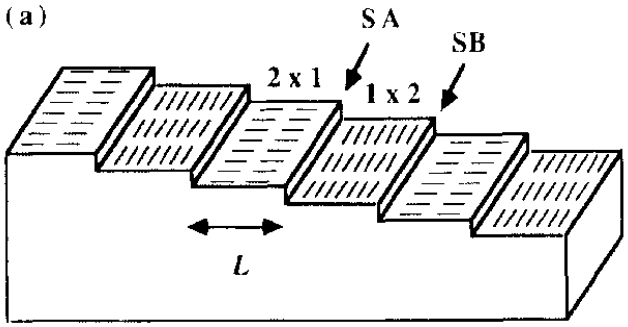
650 C

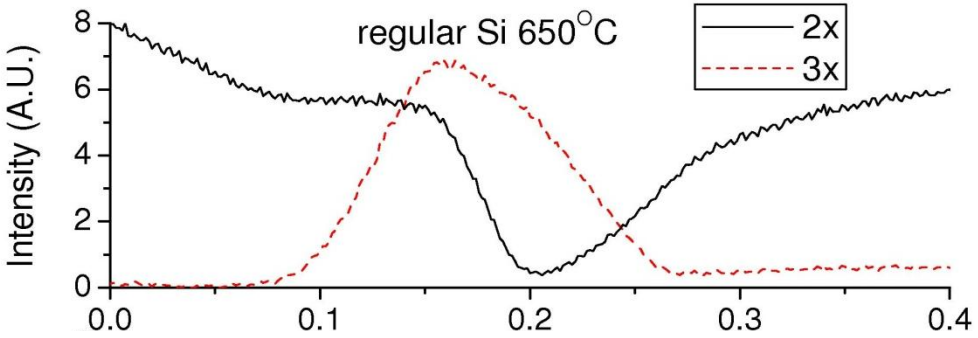
We see: 2x → 3x → 2x

See the same movie if the Si is at 0 , 90 , 180 , or 270



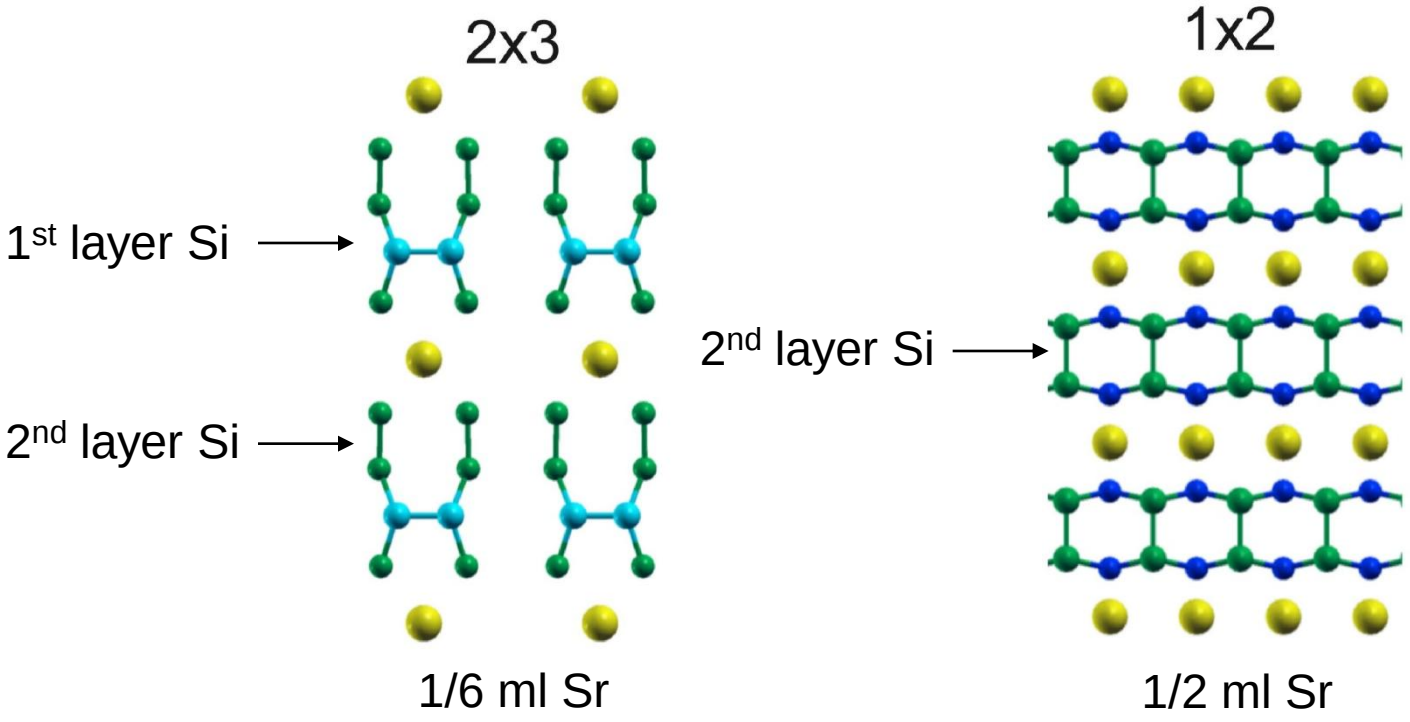
RHEED of Sr on flat and miscut Si (001)





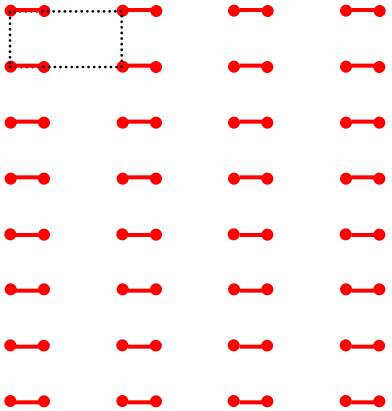
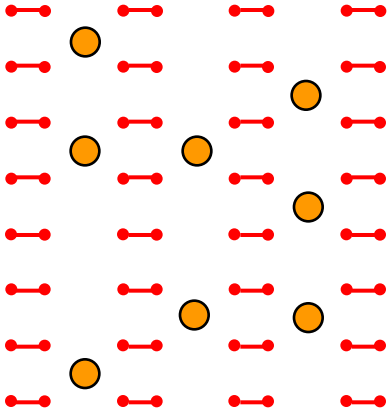
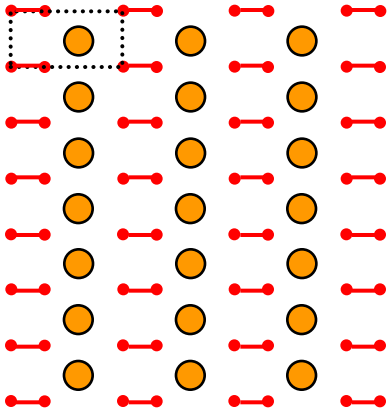
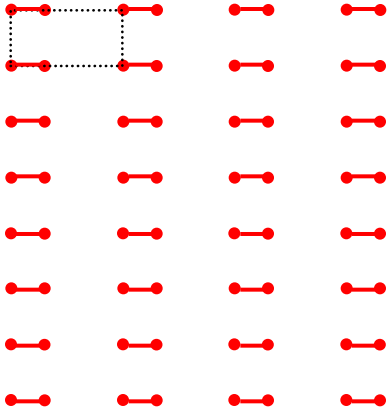
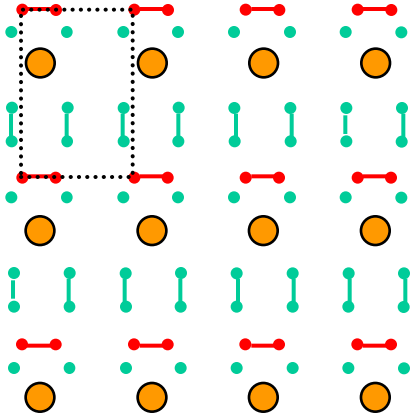
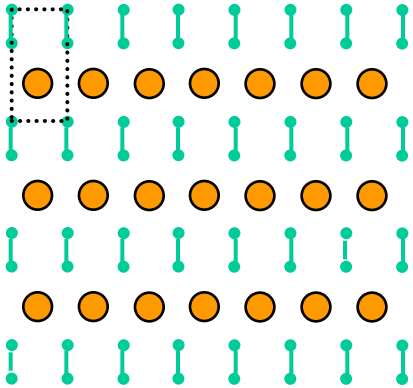
First Principles Theory

DFT calculations at 1/6 ml Sr coverage find the lowest energy state formed replaces two Si dimers with each Sr.

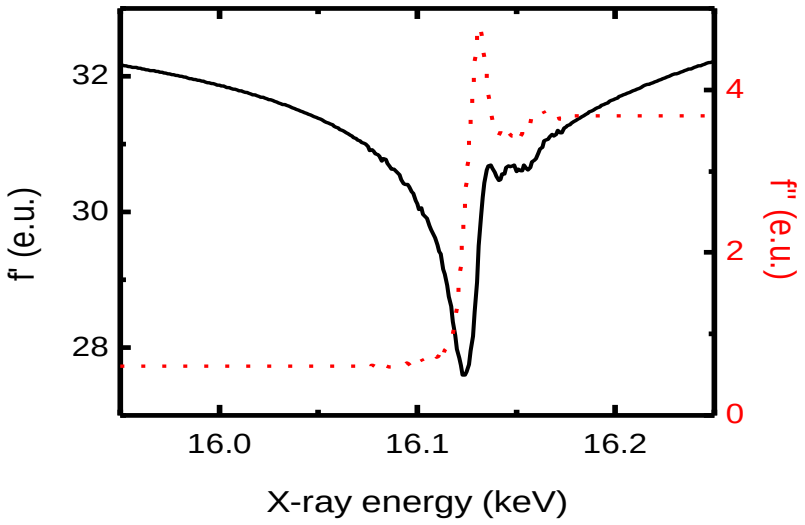


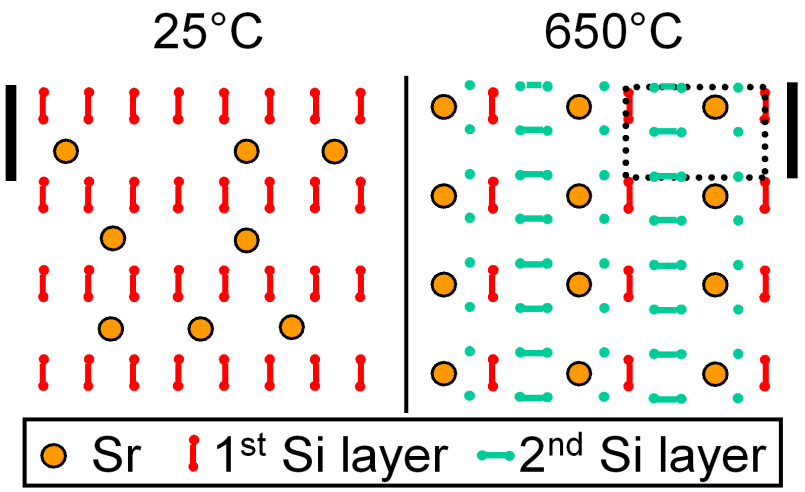
Reiner et al, Phys. Rev. Lett. **101**, 105503 (2008).

Strontium sub-monolayer structures

Temperature	Silicon (001)	1/6 ml Strontium	½ ml Strontium
25 C			
650 C			

Anomalous X-ray Diffraction





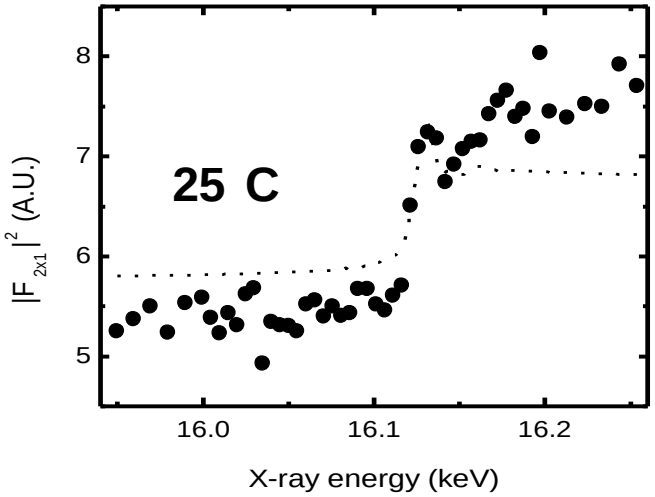
By scanning x-ray energy through a Sr absorption edge, we dramatically change how the Sr atoms scatter.

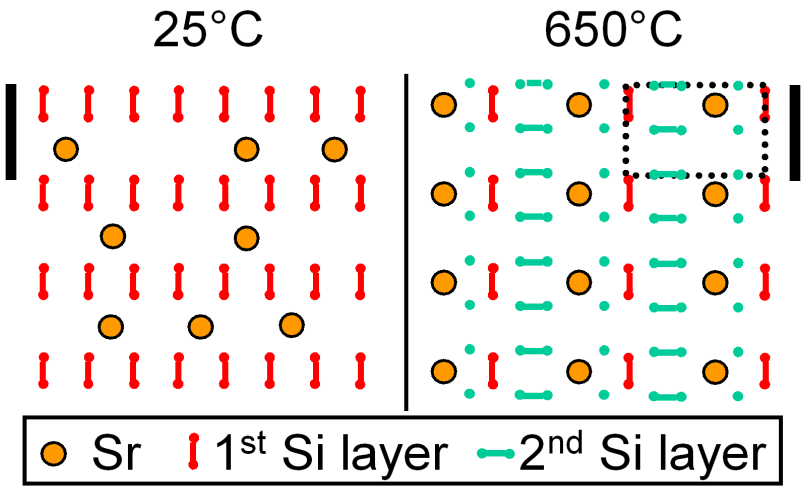
The energy dependence of the total diffraction will be different for the two structures because of how the Sr and Si scattering interfere.

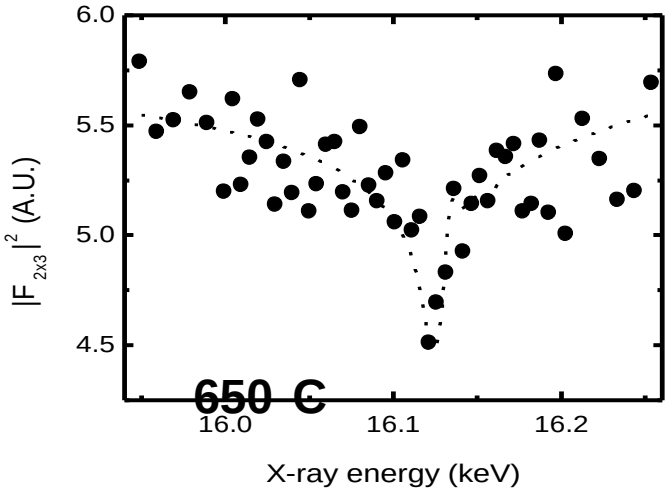
Anomalous X-ray Diffraction

We measured the diffraction from 1/6 ML Sr surfaces formed at 25 C and 650 C.

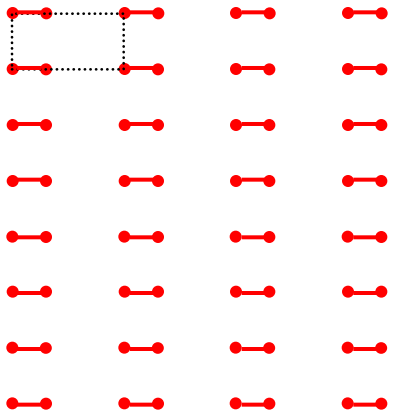
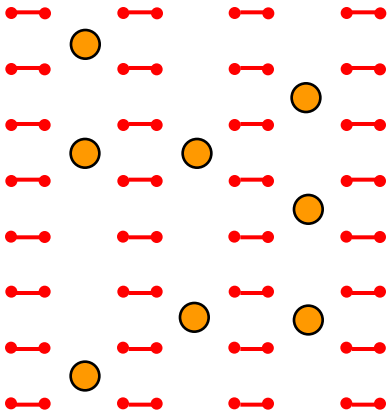
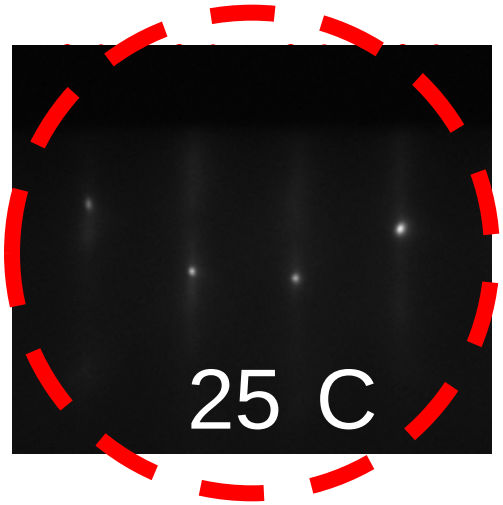
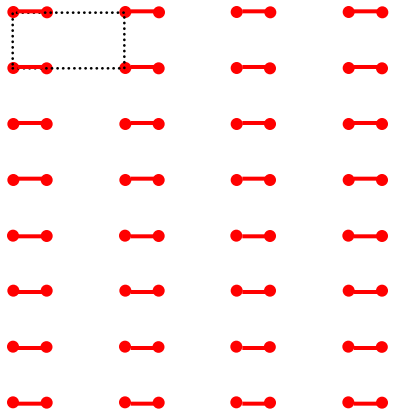
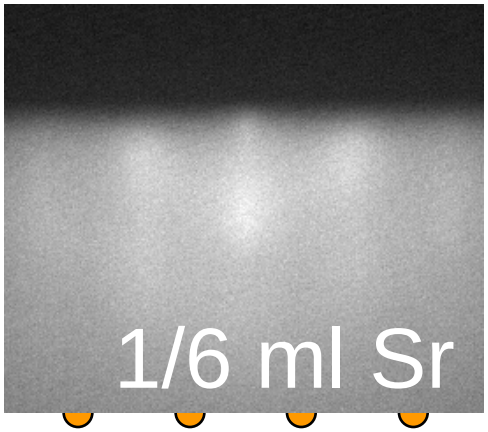
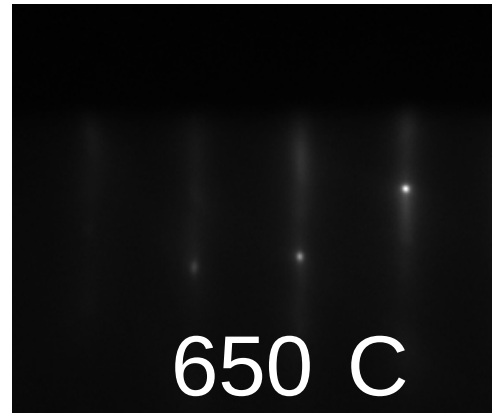
Based on the DFT structures, we have predicted the expected scattering, shown as the dotted lines.



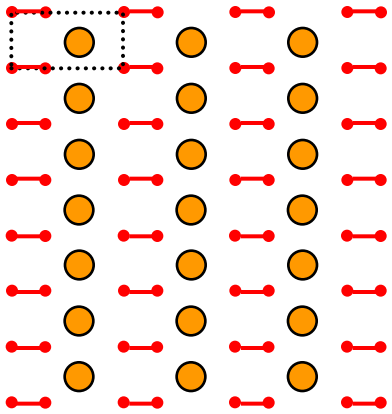




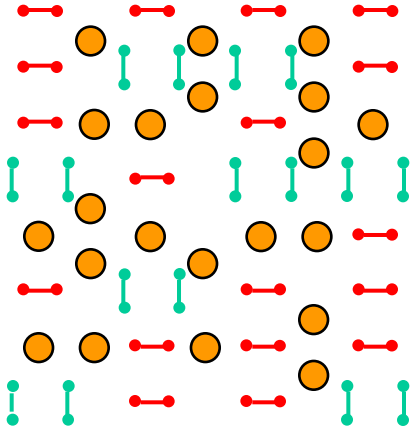
BaO Growth on Sr:Si (001) surfaces

Temperature	Silicon (001)	1/6 ml Strontium	½ ml Strontium
25 C			
650 C			

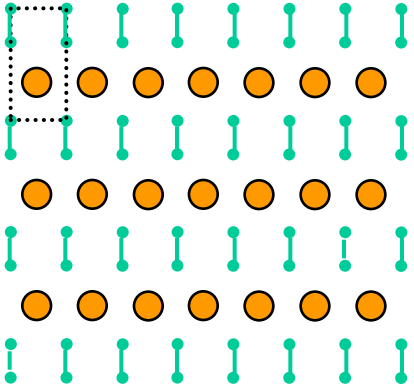
Effect of ½ ml Sr Temperature on BaO Epitaxy



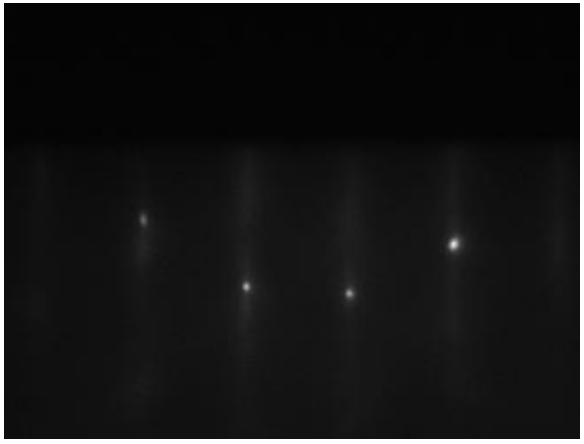
25 C

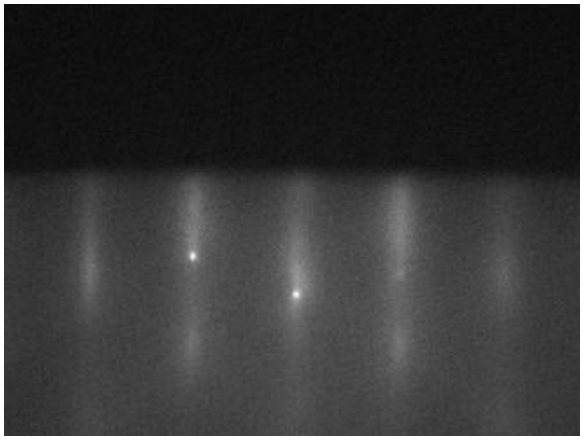


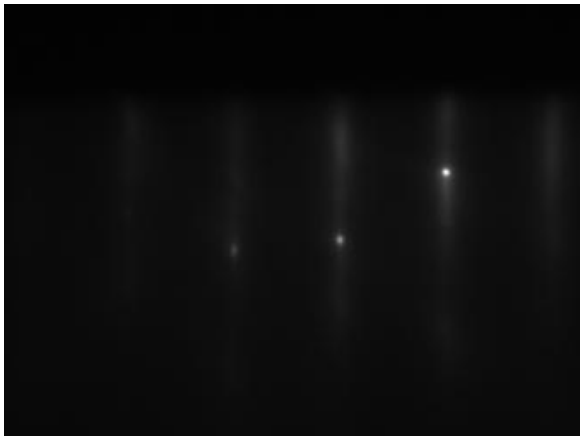
250 C



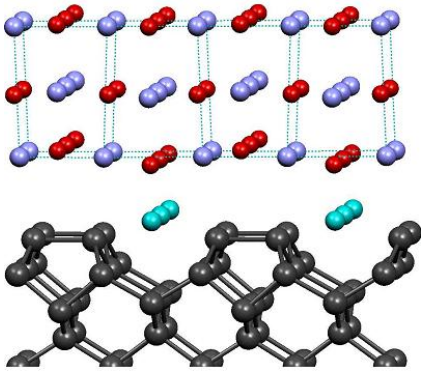
650 C



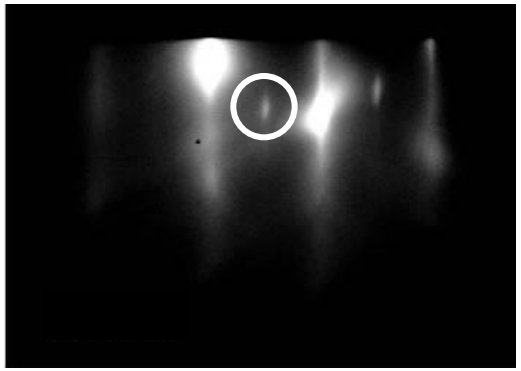




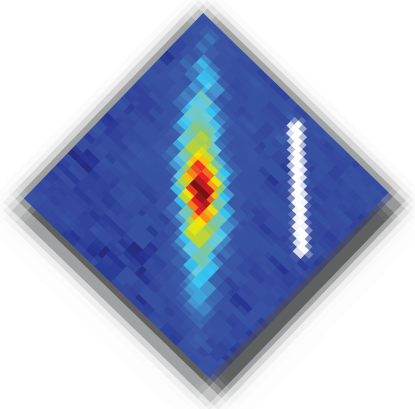
BaO epitaxy: 2 1 symmetry of first layer



Real space



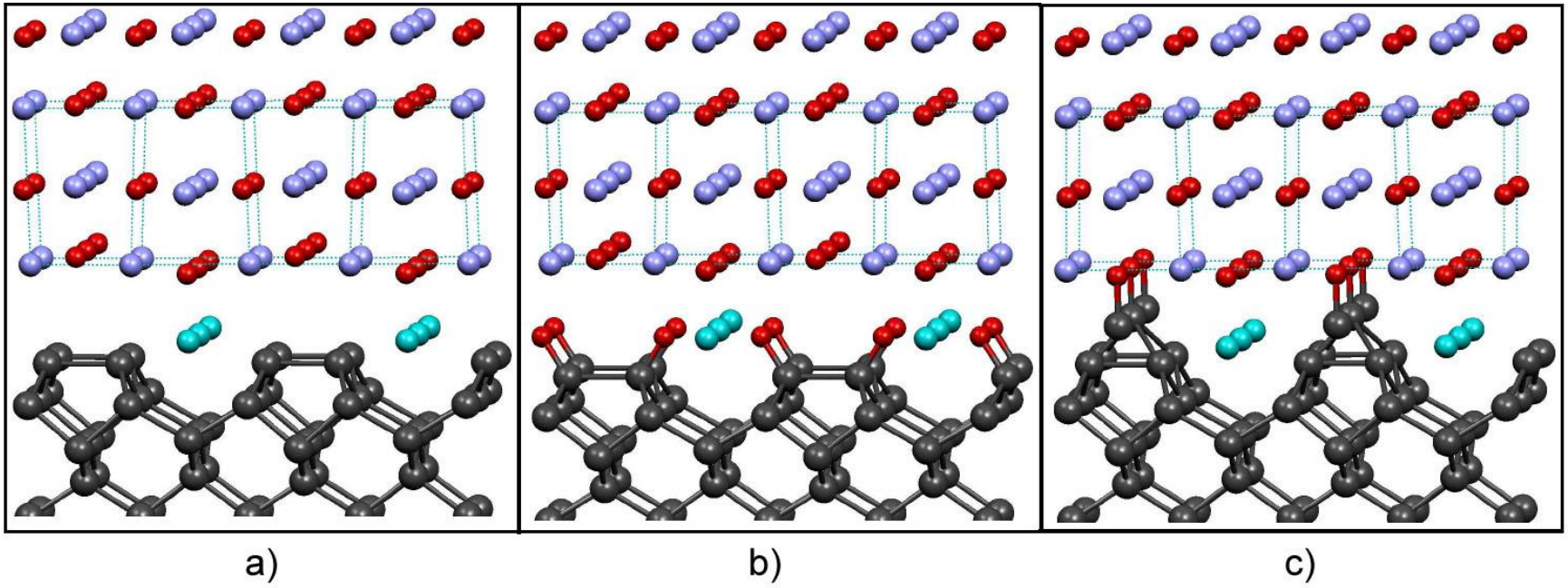
RHEED



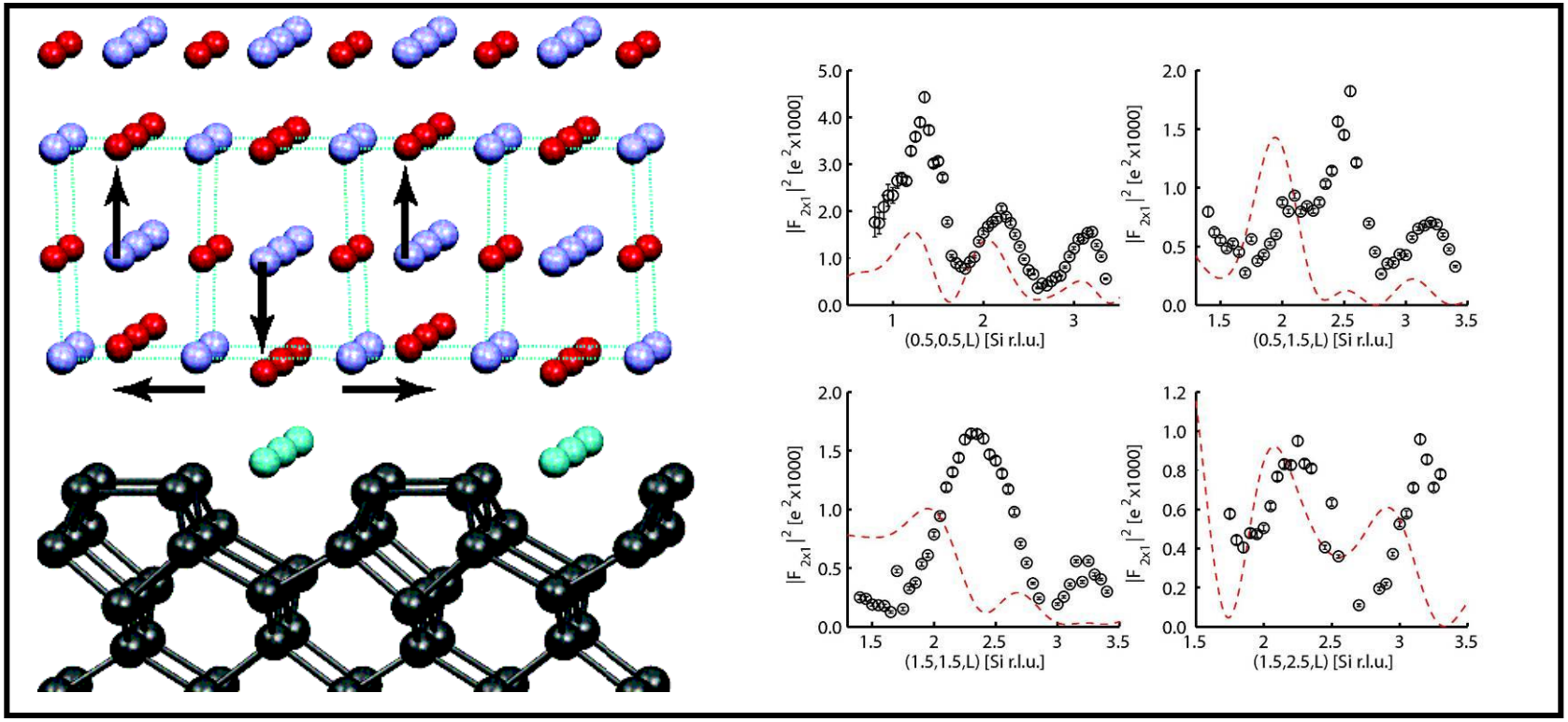
Synchrotron XRD

- 2 1 of Sr:Si(001) surface persists into BaO
- In RHEED, see 2 1 for ~ 1 unit cell BaO
- After BaO/Si interface is buried, still see 2 1 structure by synchrotron XRD

Possible structure of BaO/Si Interface

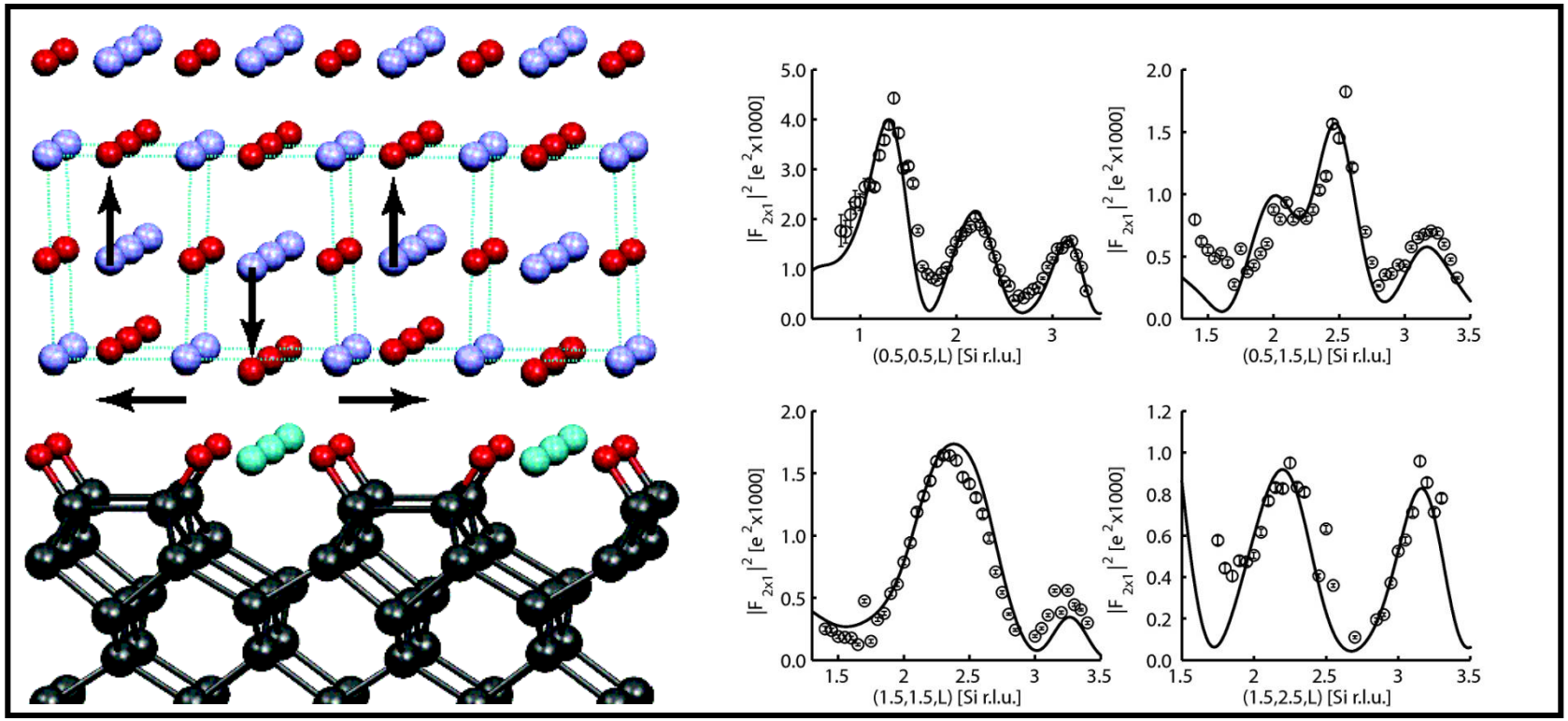


First principles calculation and XRD data



- Only look at diffraction associated with interface (2 1 symmetry)
- Compare predicted diffraction based of theoretical structure with actual diffraction from sample

First principles calculation and XRD data

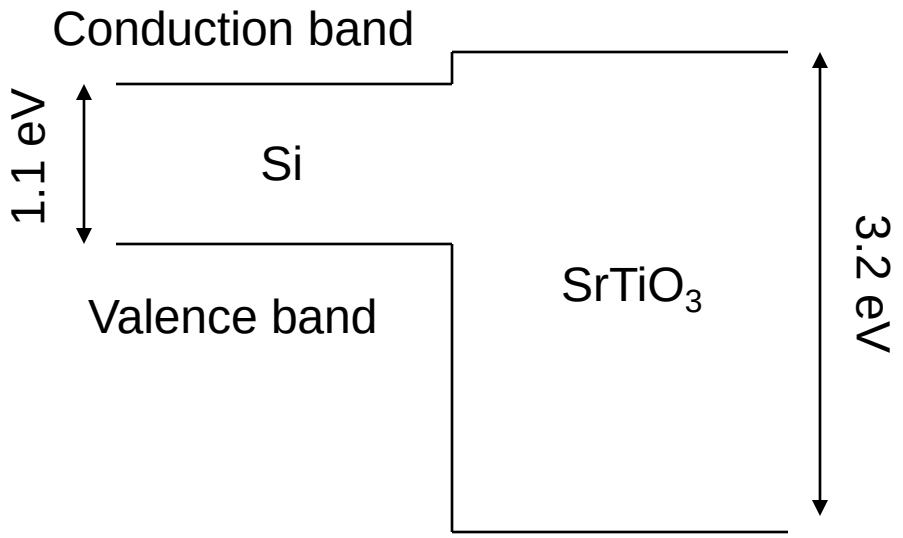


- Structure with 1 ml oxygen leads to best fit
- XRD predictions from theoretical structure only have two parameters:
  - Debye Waller Factor = 0.5 Å rms
  - 3 % expansion of BaO

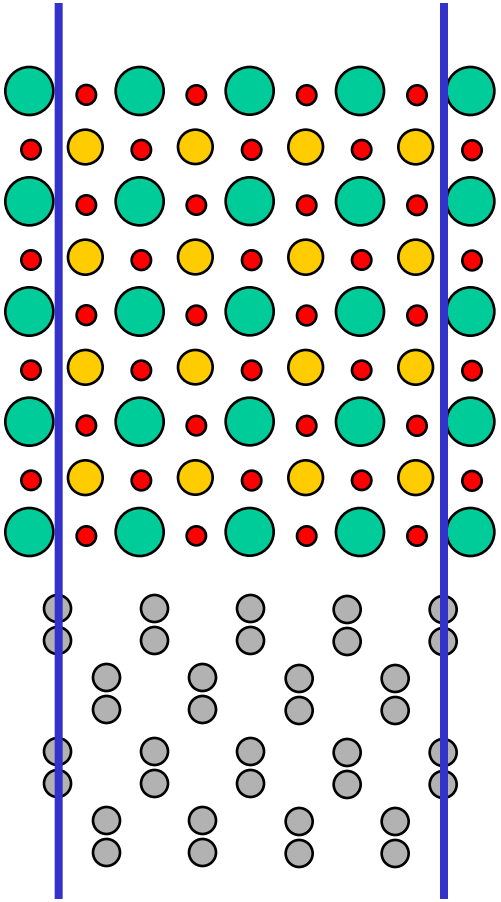
Y. Segal et al., Phys. Rev. Lett. **102**, 116101 (2009).

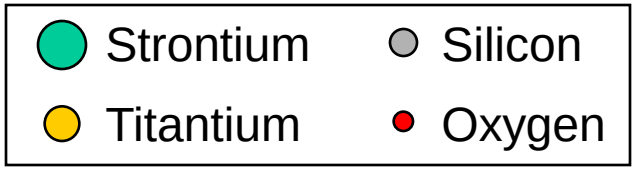
$SrTiO_3$ as a gate dielectric

- Dielectric constant is fantastic (~ 300)
- Band gap is less fantastic 3.2 eV
- Conduction band offset with silicon is small (1 eV is the minimum allowable)



Is $SrTiO_3$ Grown on Silicon Ferroelectric?





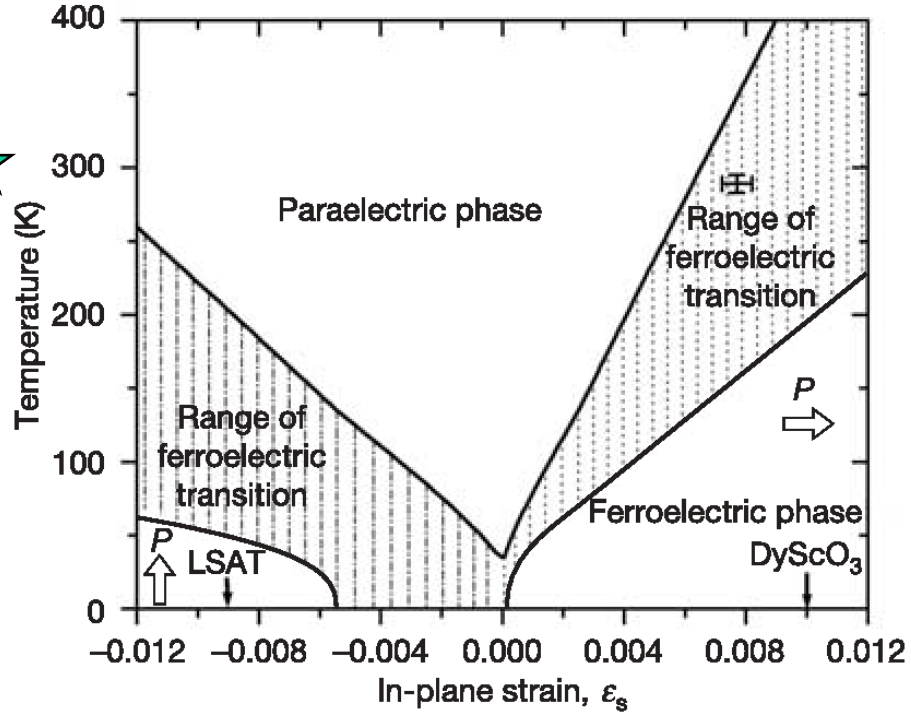
Start with bulk $SrTiO_3$ on Si (not ferroelectric)

In-plane lattice constant of $SrTiO_3$ shrinks to Si value

Out-of-plane lattice constant of $SrTiO_3$ expands because of compressive stress

Out-of-plane expansion triggers ferroelectric transition

Phase Diagram of Strained $SrTiO_3$



J.H. Haeni *et al*, Nature **430**, 758 (2004).
Woicik, *et al.* PRB **73**, 24112 (2006).

$SrTiO_3$ strain on silicon:

$\varepsilon_s = -0.017$

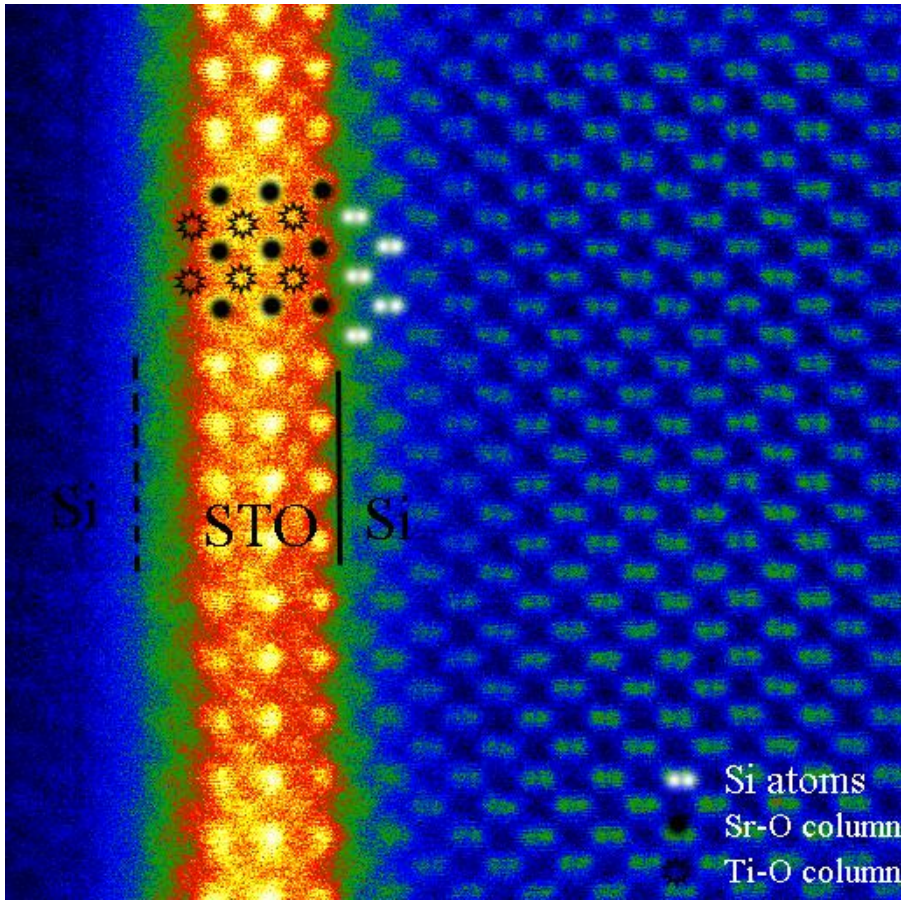
We expect out-of-plane polarization.

$SrTiO_3$ relaxes above 40Å

With $SrTiO_3$ on Si, the interface has 3 effects:

1. Coherent strain
2. Interface dipole
3. Electrical screening

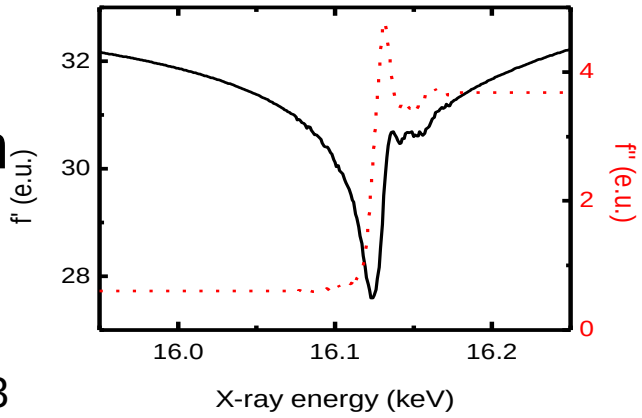
TEM of the $SrTiO_3$/Si Interface

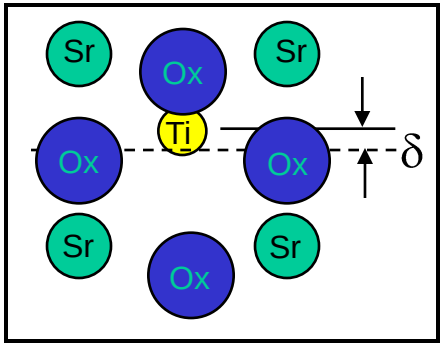


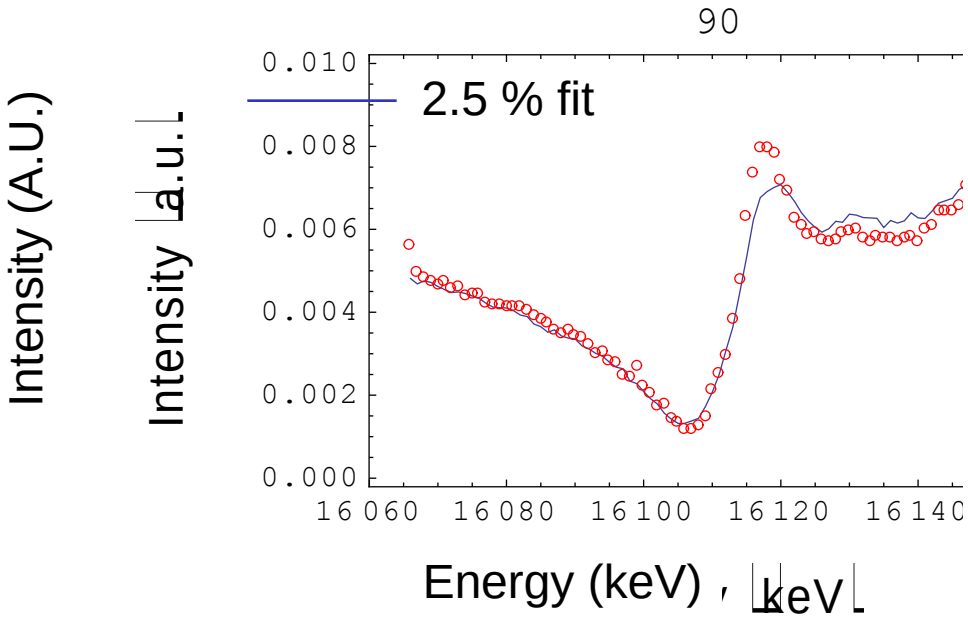
- Applying the same techniques to the $SrTiO_3$/Si interface
- Initial results indicate that the $SrTiO_3$/Si interface is significantly different
- No 2x1 structure seen in either XRD or TEM

Energy XRD from $SrTiO_3$ (2,0,1) peak

- 20Å strained $SrTiO_3$ film
- (2,0,1) strained $SrTiO_3$ peak, same as (2,2,1.4) Si, is sensitive to $SrTiO_3$ polarization
- $SrTiO_3$ is polarized 2.5%
- Ti pushed away from Si
- Can polarization be reversed?
- Can we see displacive temperature phase transition?

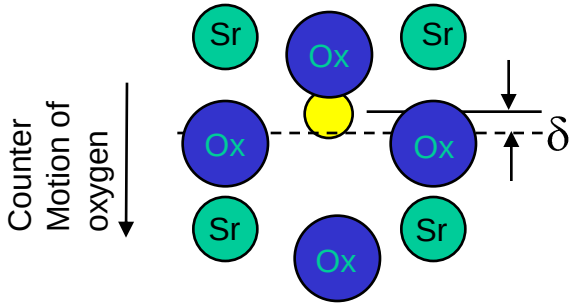


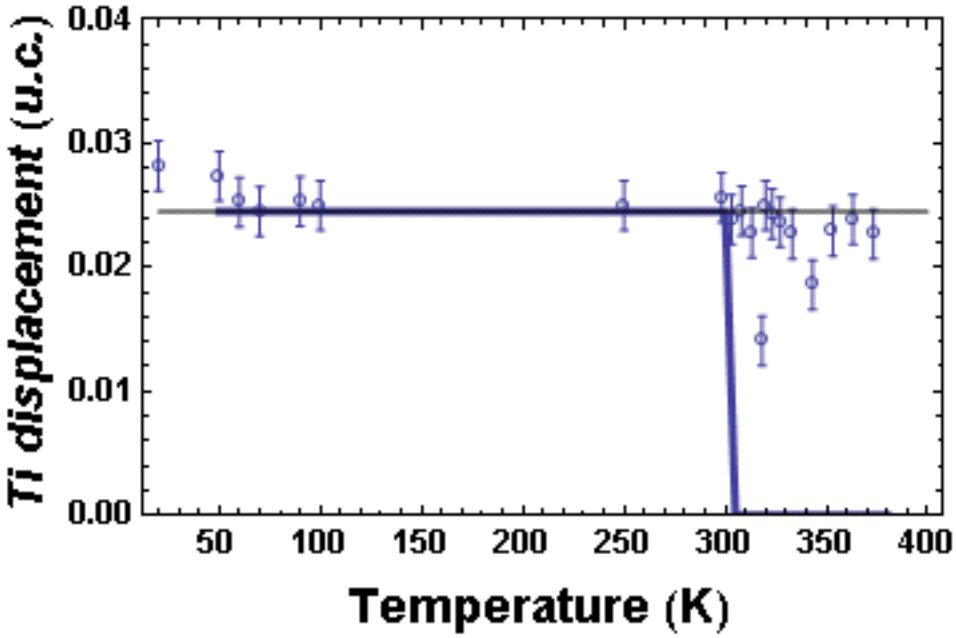




Temperature dependence of polarization

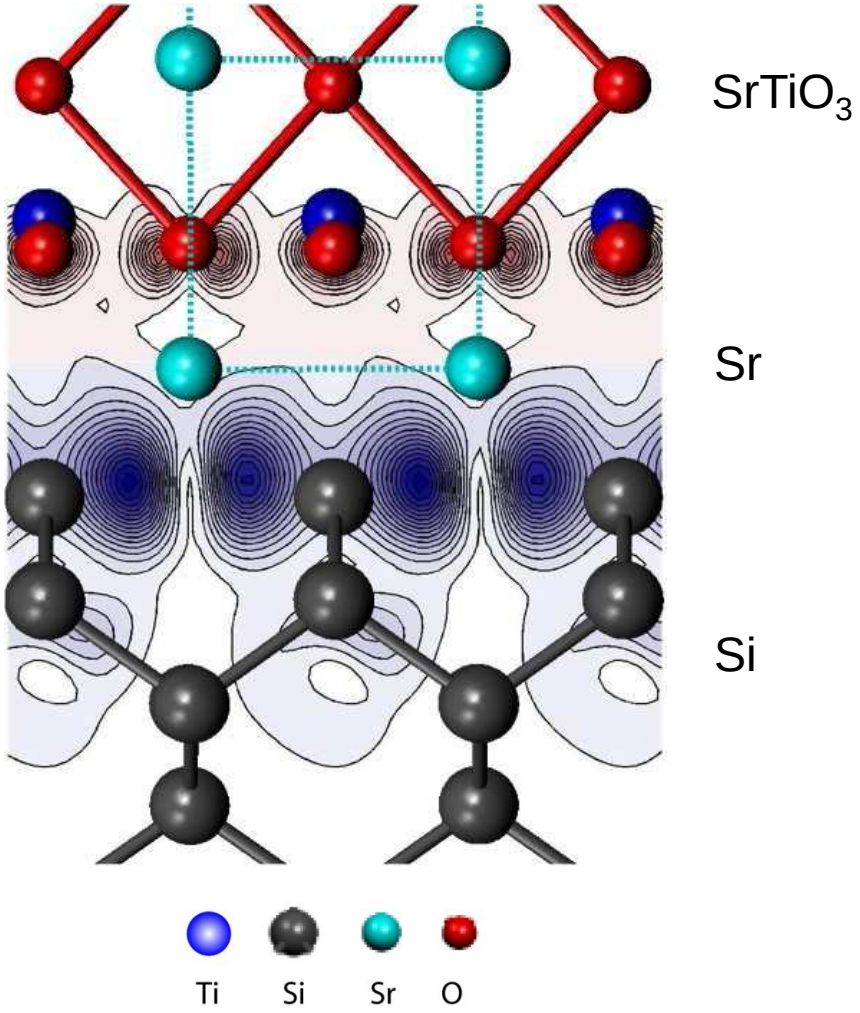
- A polar film is not necessarily ferroelectric
- Therefore, look for displacive phase transition.
- Polarization without displacive phase transition (20K-380K)





Polarization and the $SrTiO_3$/Si interface

- Ground state structure from first principles theory
- Net positive polarization
- Interface dipole created by charge transfer between $SrTiO_3$ and Sr:Si
- Dipole couples to soft phonon mode of $SrTiO_3$

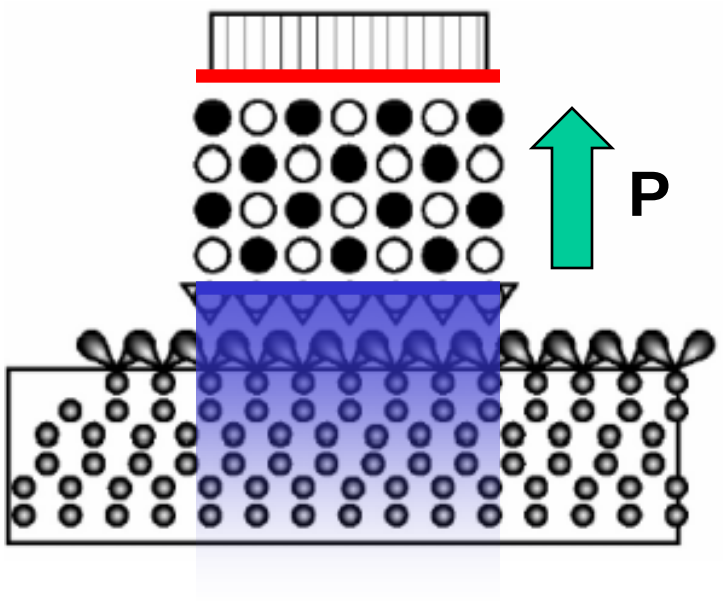


Screening and the $SrTiO_3$/Si interface

If the screening length is not short compared to the ferroelectric film thickness,

"Depolarization energy" = **E**· **P**

becomes important. For $SrTiO_3$/Si, if Si band bending is providing screening charge, screening length is large compared to 20Å.



Reiner et al., Phys. Stat. Sol. B **241**, 2287 (2004).

$LaAlO_3$ as high-κ dielectric: properties

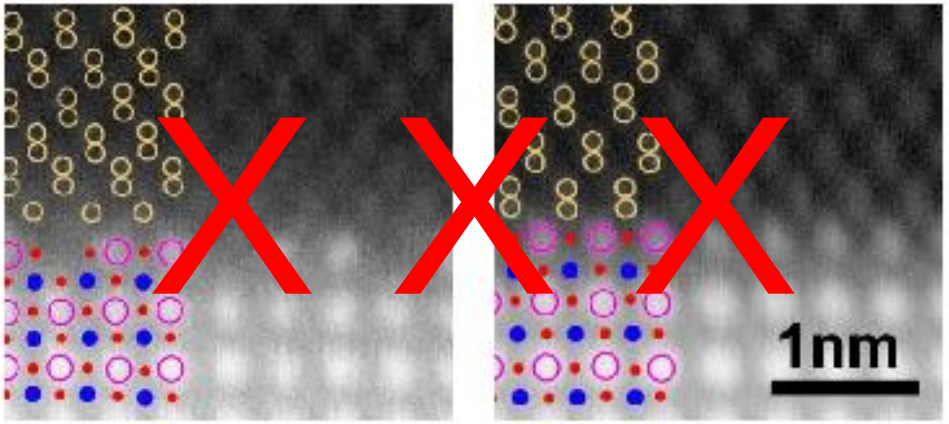
Favorable properties of $LaAlO_3$ for high-κ

- Dielectric constant 24
- Band gap 5.5 eV
- Large band offsets with Si

International Technology Roadmap for Semiconductors (ITRS)

$LaAlO_3$ – Si interface

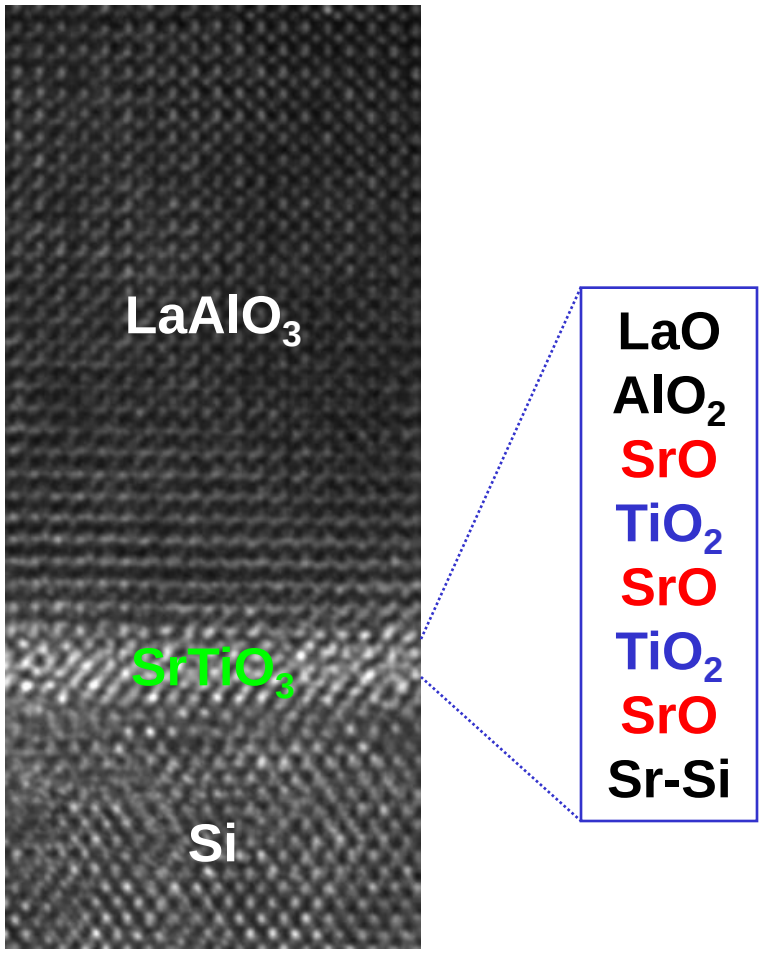
1. Amorphous $LaAlO_3$ grown on Si appears to form an abrupt interface
2. Crystalline Si has been grown on single crystals of $LaAlO_3$
3. Crystalline $LaAlO_3$ has **not** be grown in direct contact with Si



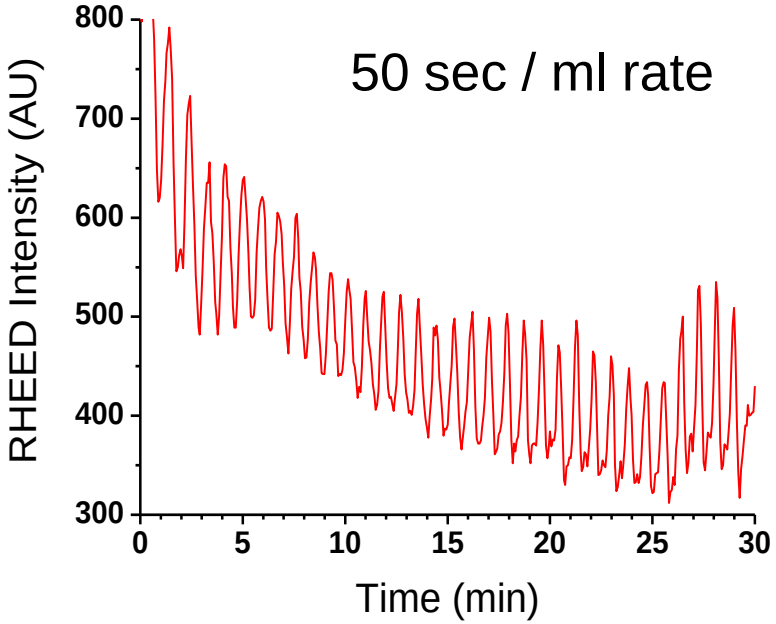
C.J. Först, K. Schwarz, P.E. Blöchl, Phys. Rev. Lett. **95**, 137602 (2005).

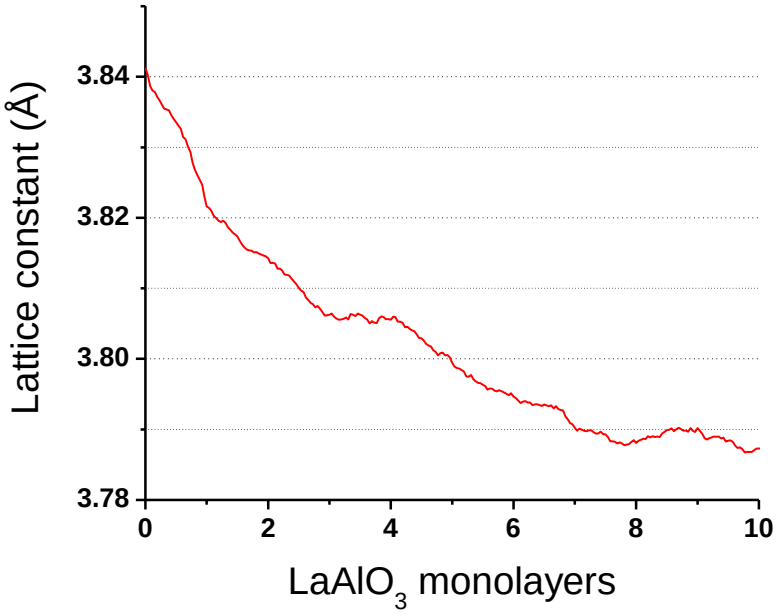
Approach to Epitaxial $LaAlO_3$ on Si

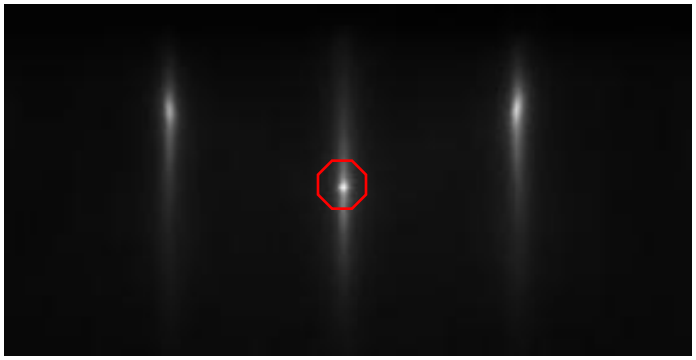
- $LaAlO_3$ can be grown on $SrTiO_3$ single crystals
- First grow a thin epitaxial $SrTiO_3$ film on Si, then grow $LaAlO_3$
  - Is epitaxial growth of $LaAlO_3$ compatible with a stable $SrTiO_3$/Si interface?
  - What is the minimum $SrTiO_3$ thickness required?
- Theory finds $SrTiO_3$ on Si buckles if less than 2½ ml

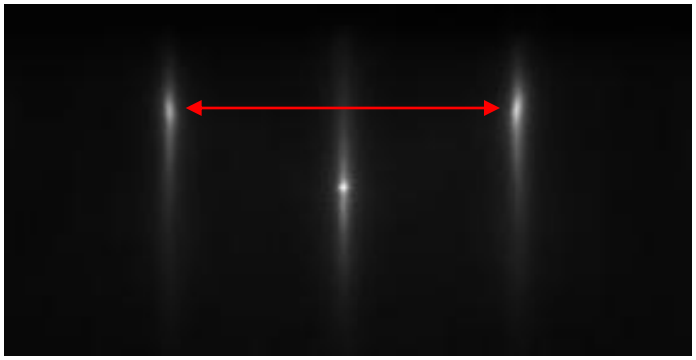


RHEED study of $LaAlO_3$ growth



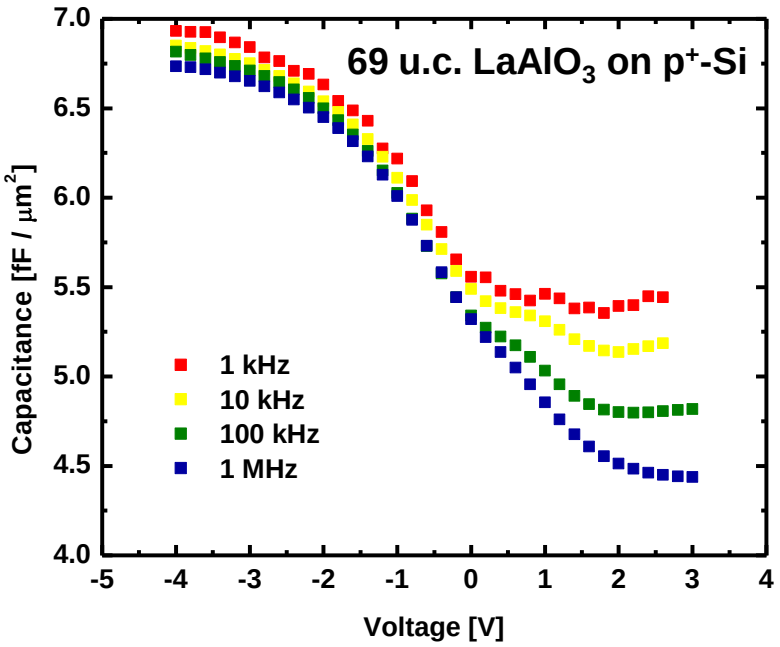


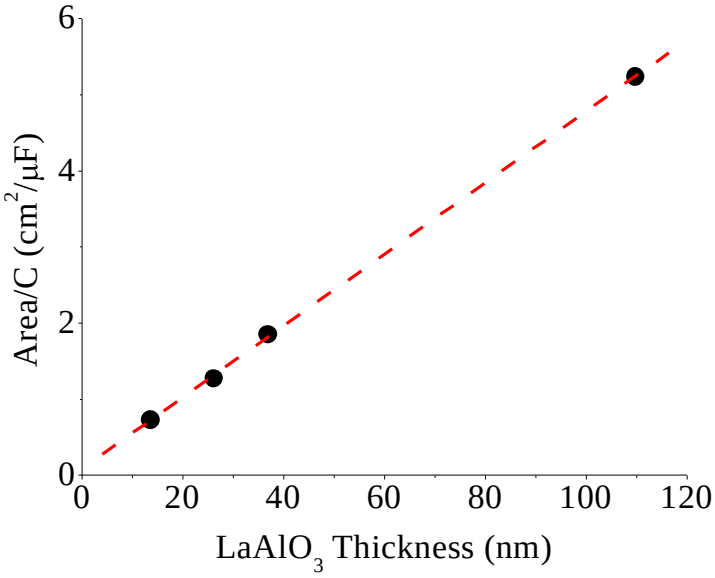




$LaAlO_3$ Capacitance vs. Voltage

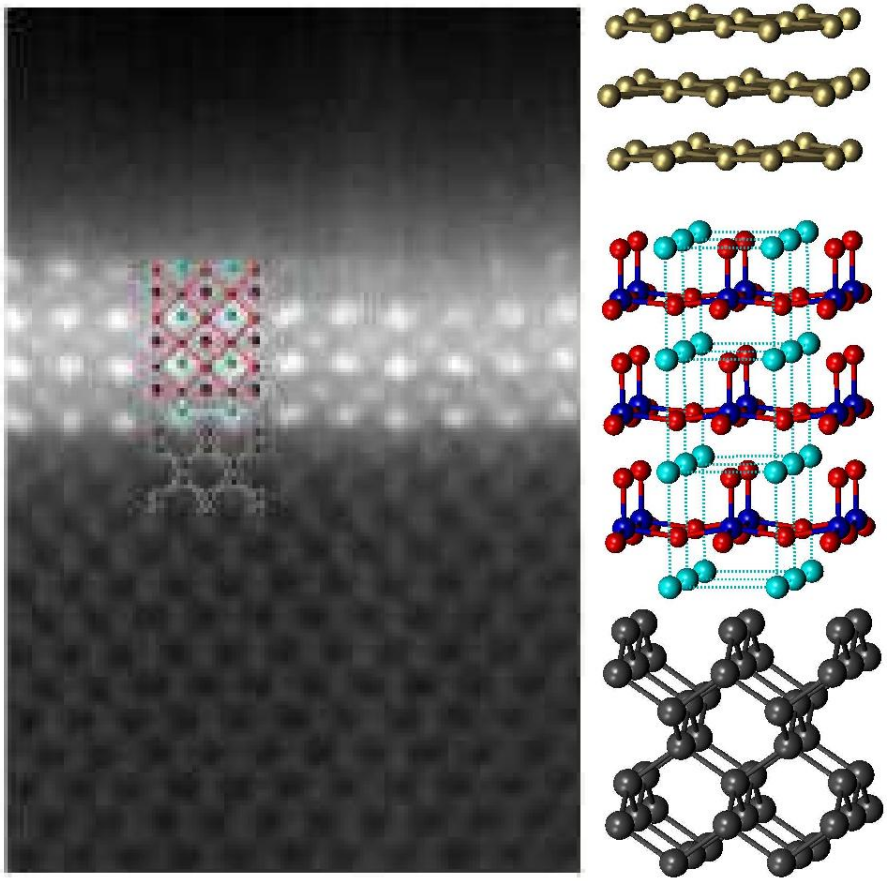
- Dielectric constant = 24 2
- Similar to bulk $LaAlO_3$ value





- Annealed in wet oxygen for 30 min at 350 C
- 10^{11} eV^{-1} cm^{-2} interface trap density
- $\kappa = 22$

Conclusions



With fully crystalline epitaxial systems,

- X-ray diffraction
- First principles theory
- TEM

can be combined to understand structure.

The crystal oxide-silicon interface stands out

- Technology
- Strong heteroepitaxy