

Crystal Oxides On Silicon

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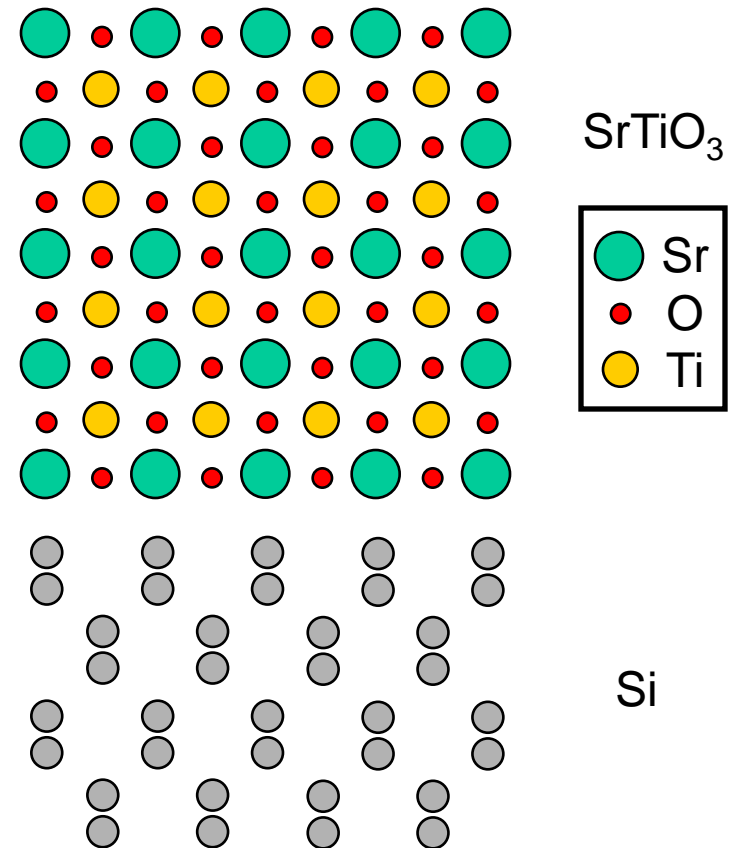
Zhan Zhang, Hawoong Hong
Advanced Photon Source
Argonne National Laboratory

Monica Sawicki, Christine Broadbridge
Southern Connecticut State University

Dong Su
Brookhaven National Laboratory

Motivation

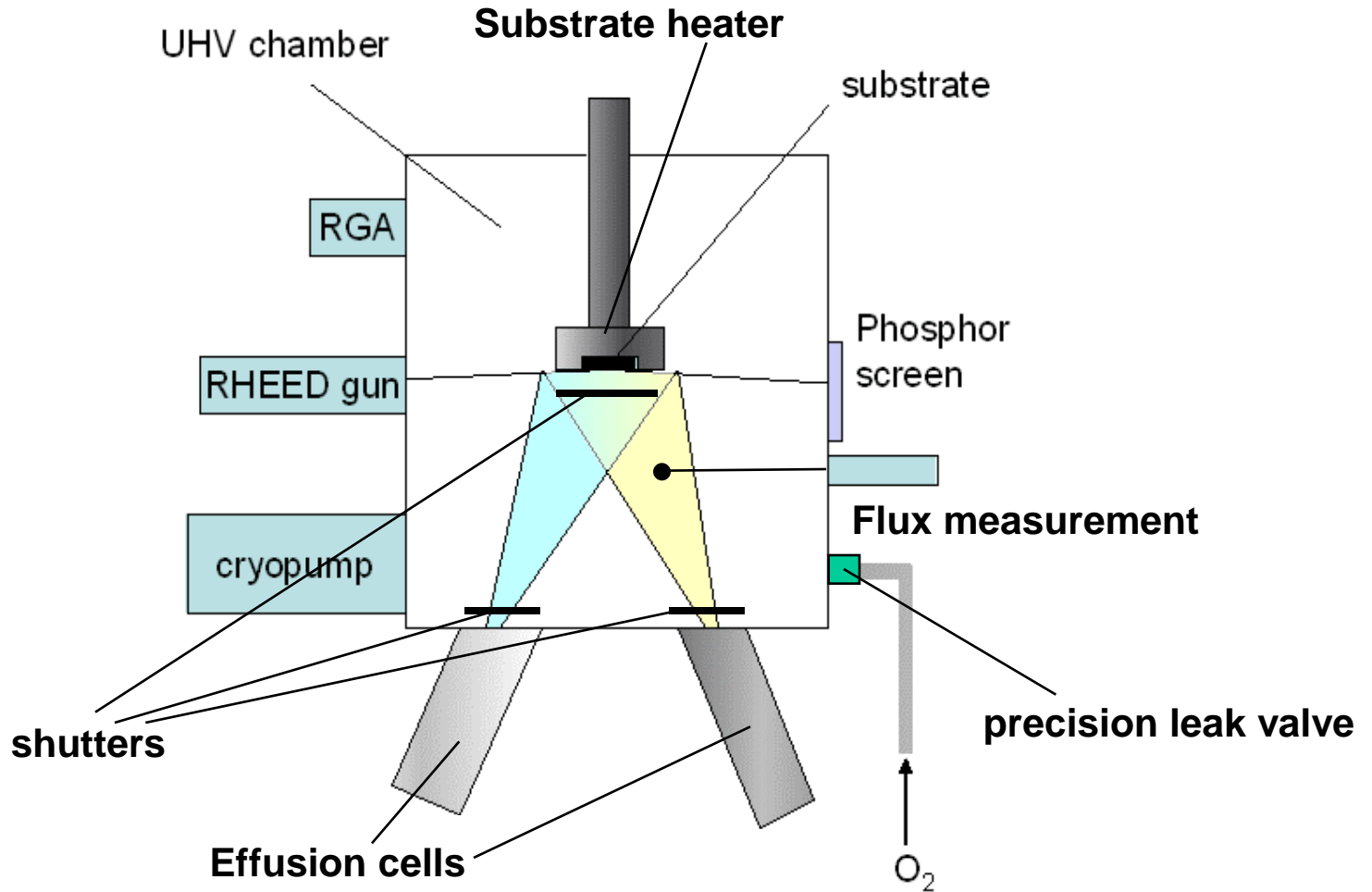
- Complex oxides exhibit wide range of phenomena
 - Ferroelectric: PbTiO_3
 - Magnetic: $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$
 - High-k: SrTiO_3 , LaAlO_3
- Oxide heterostructures on Si (001) bring this functionality to an advanced device platform
- Creating fully crystalline structures with atomically abrupt interfaces a challenge



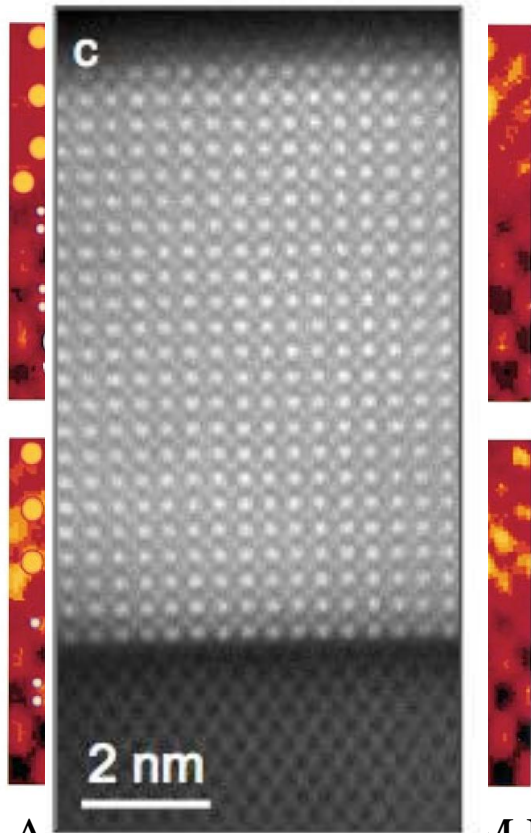
Outline

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

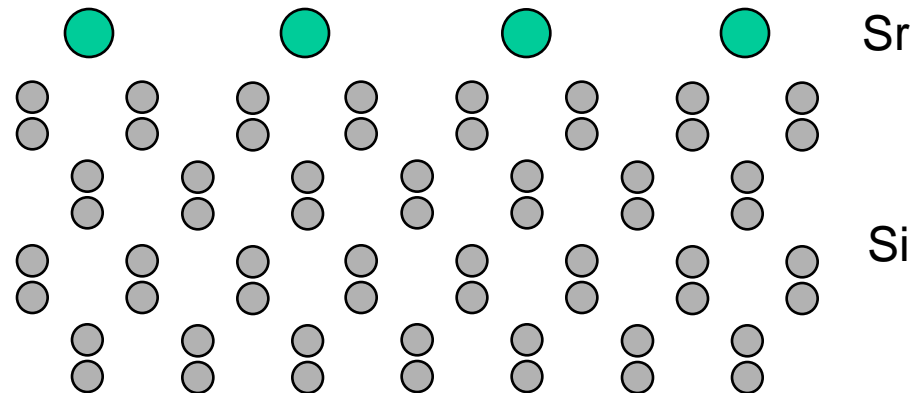


Complex Crystal Oxides on Si (001)



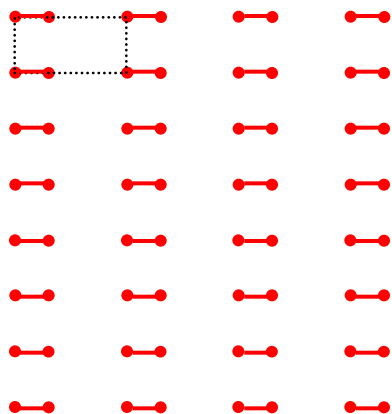
R.A. Chisholm, PRL **81**, 3014 (1998).
M.F. Maitri et al., Science, last week

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



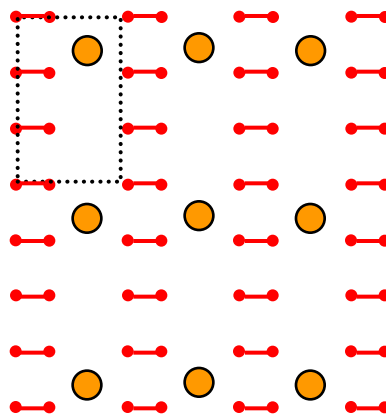
Strontium sub-monolayer structures?

Silicon (001)



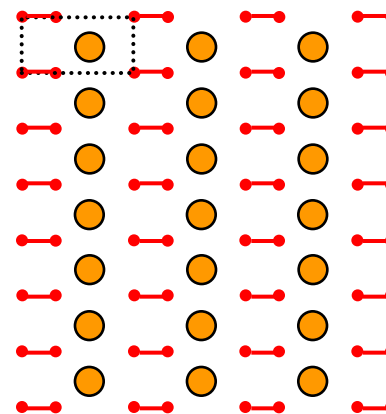
2x1

1/6 ml Strontium



2x3

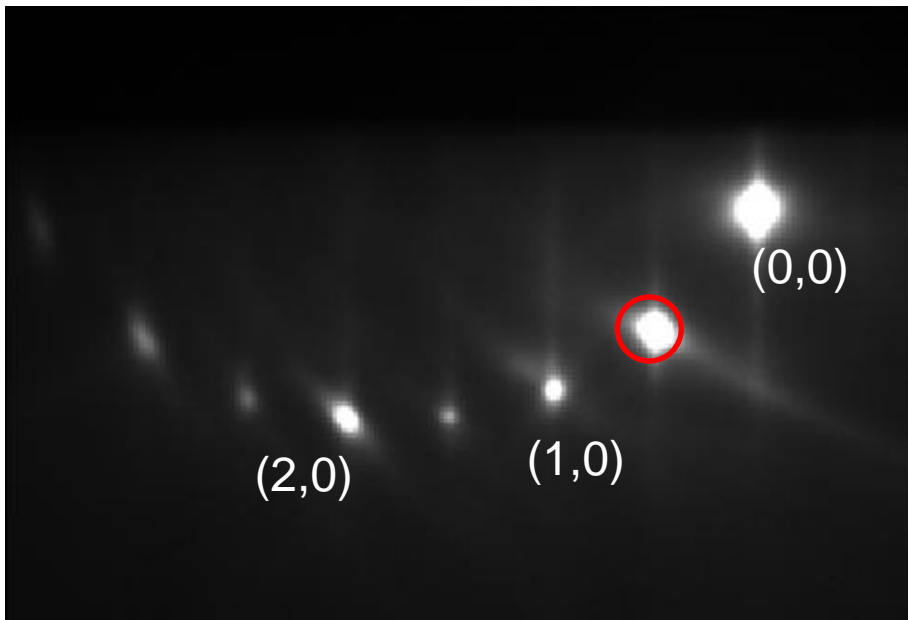
1/2 ml Strontium



2x1

RHEED Studies of Sr Deposition

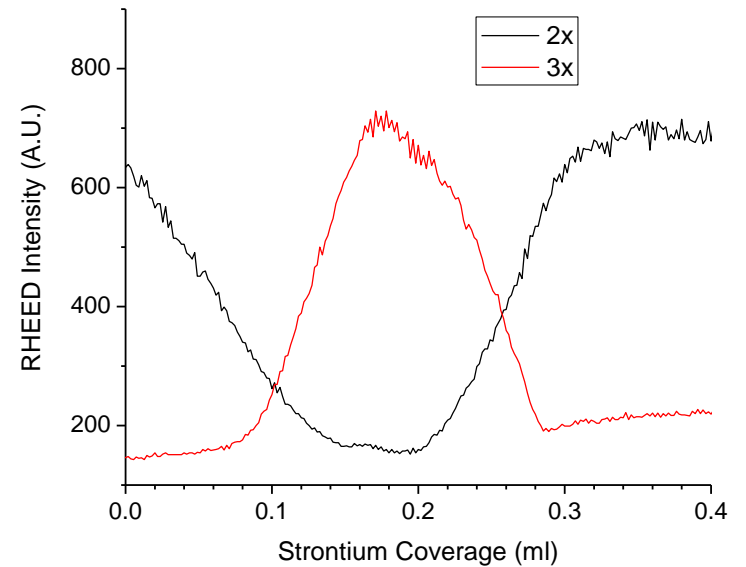
RHEED during $\frac{1}{2}$ ml deposition of Sr



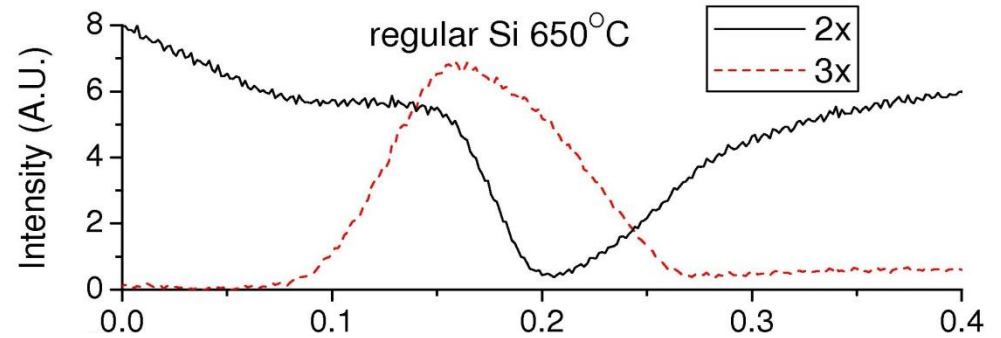
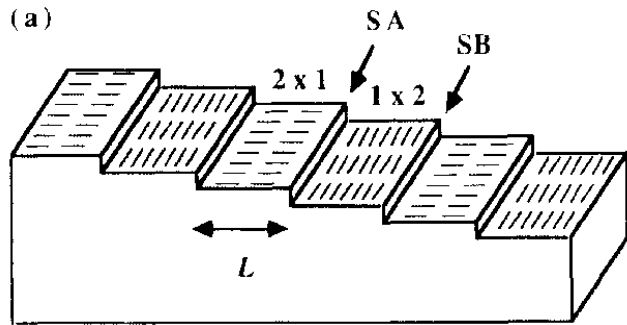
650 C

We see: 2x \rightarrow 3x \rightarrow 2x

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

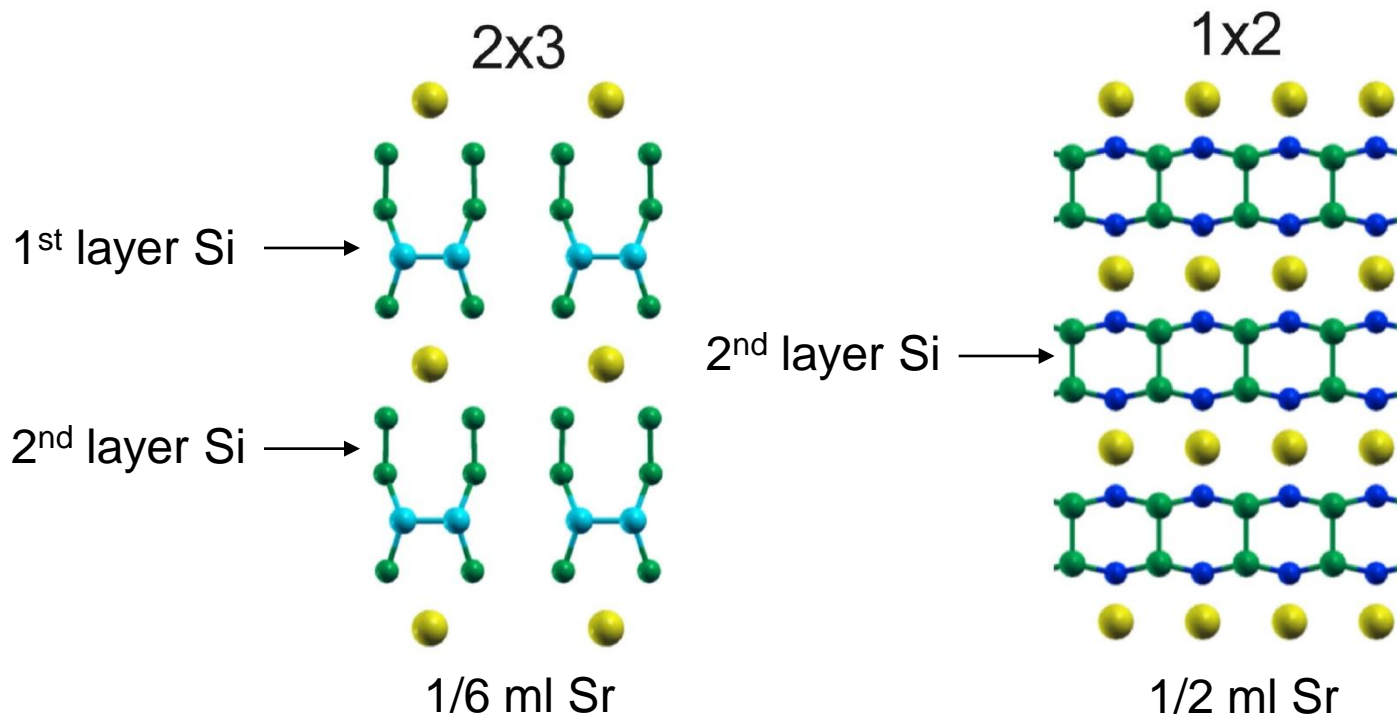


RHEED of Sr on flat and miscut Si (001)



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

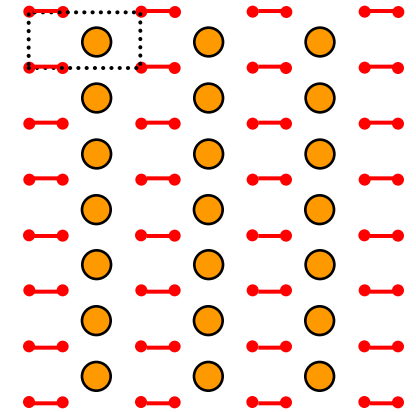
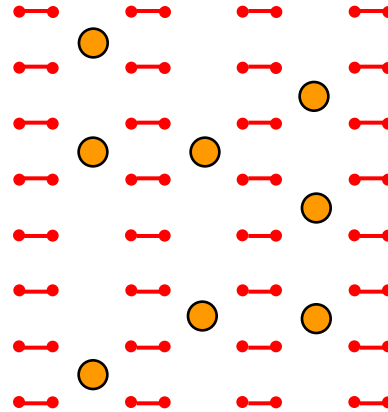
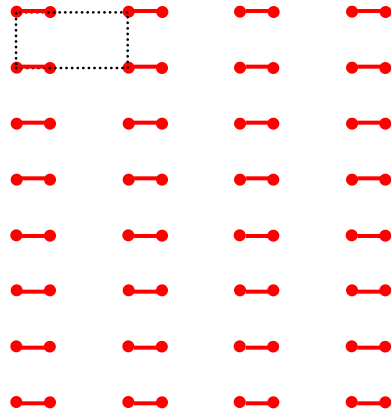
Temperature

Silicon (001)

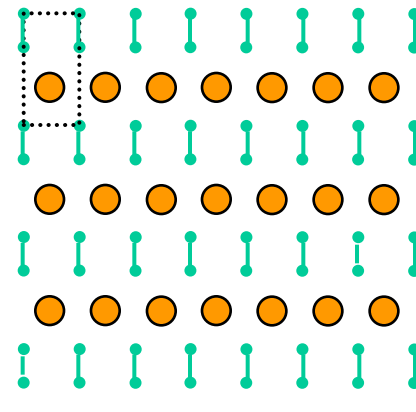
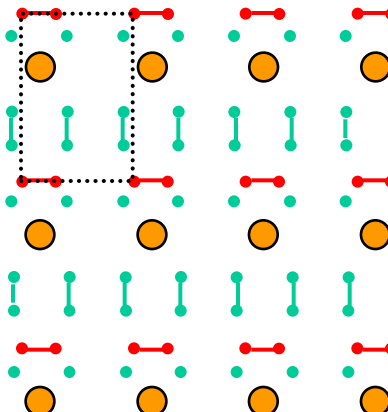
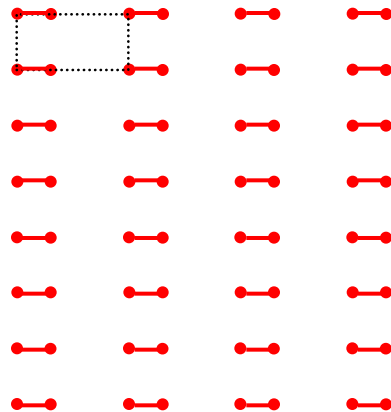
1/6 ml Strontium

1/2 ml Strontium

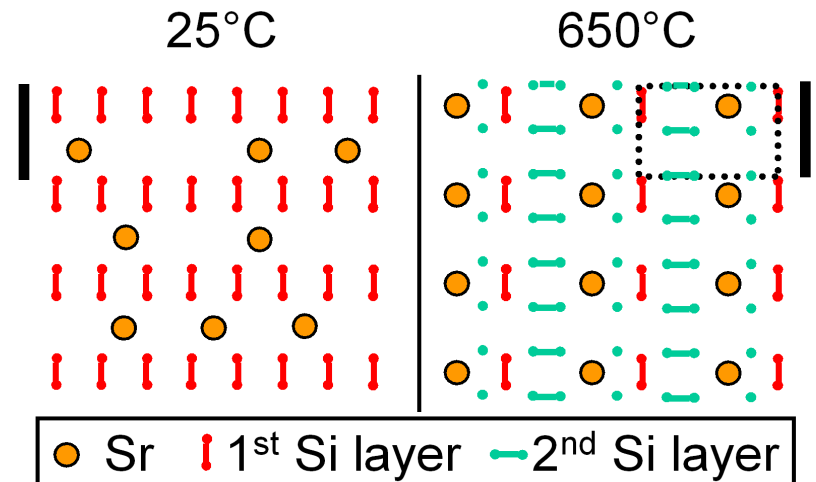
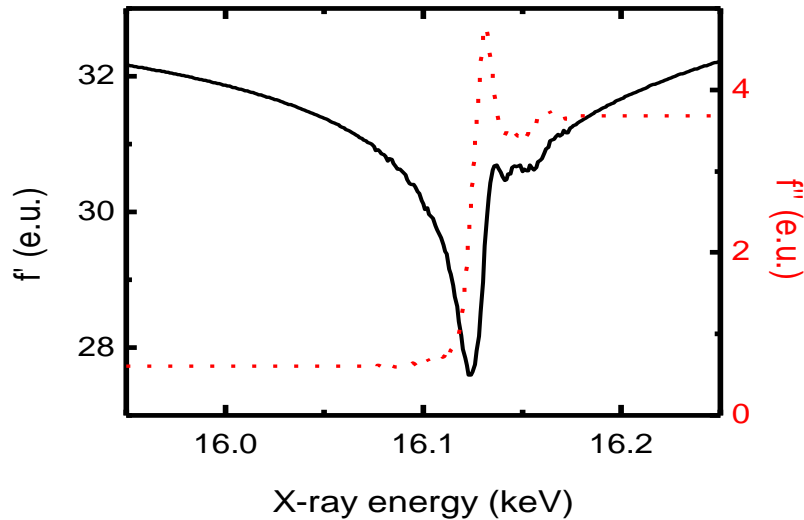
25 C



650 C



Anomalous X-ray Diffraction



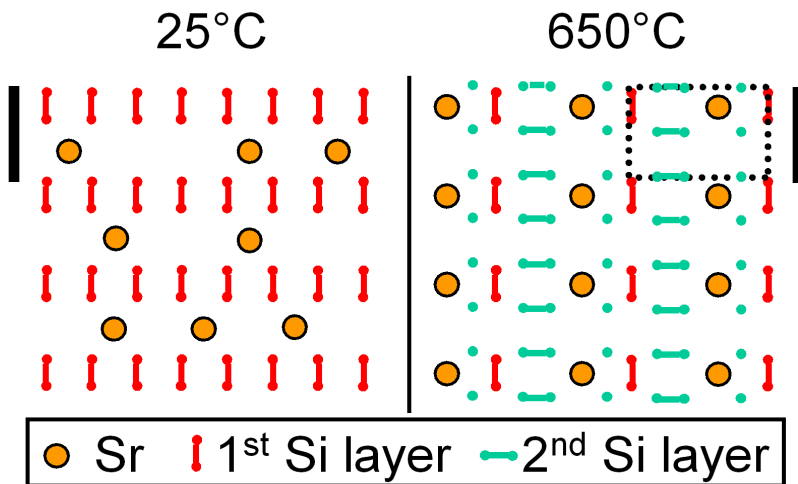
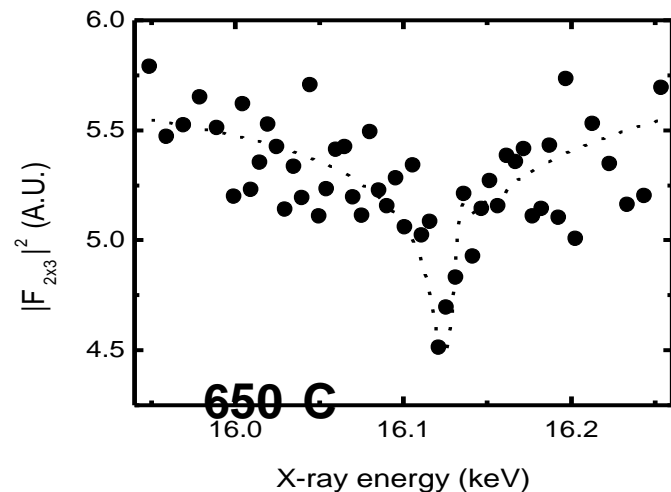
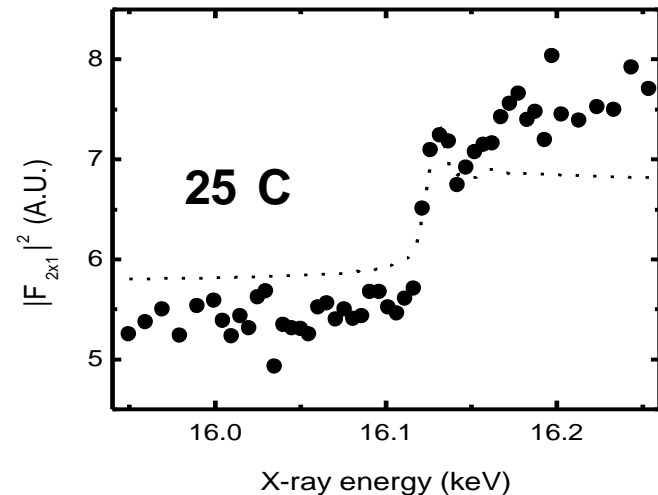
By scanning x-ray energy through a Sr absorption edge, we dramatically change how the Sr atoms scatter.

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

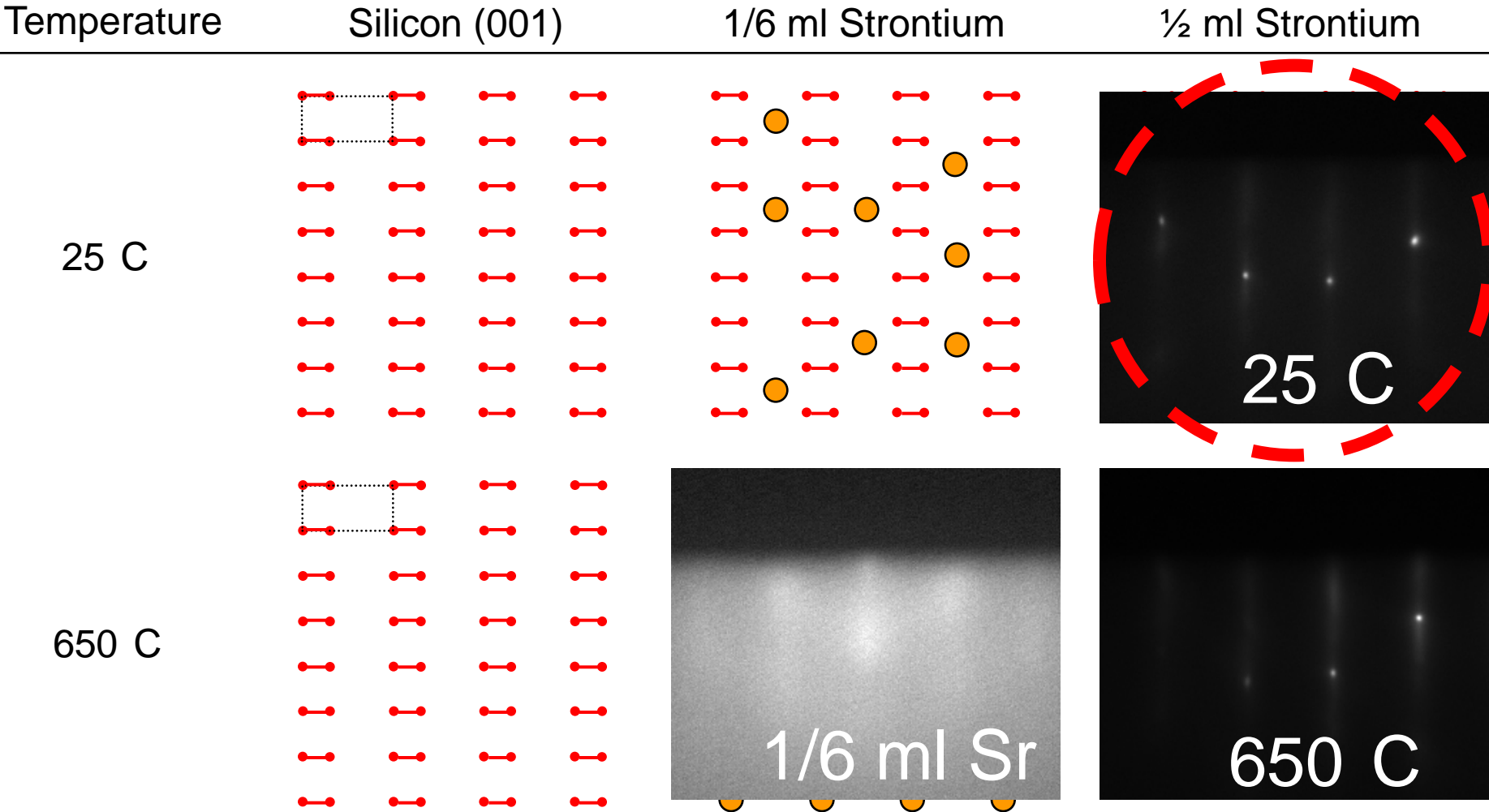
Anomalous X-ray Diffraction

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

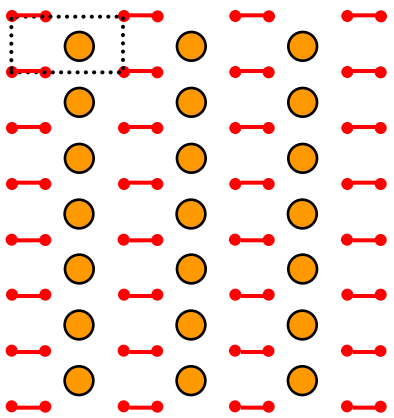
Based on the DFT structures, we have predicted the expected scattering, shown as the dotted lines.



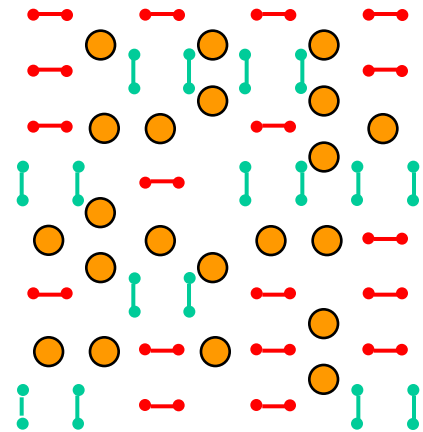
BaO Growth on Sr:Si (001) surfaces



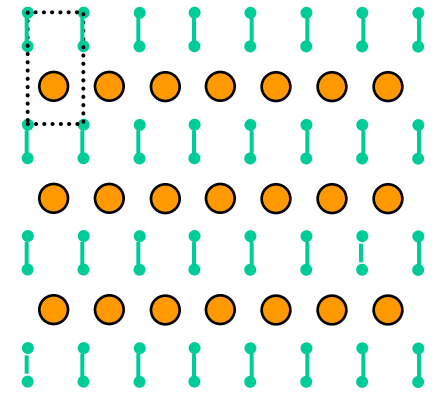
Effect of 1/2 ml Sr Temperature on BaO Epitaxy



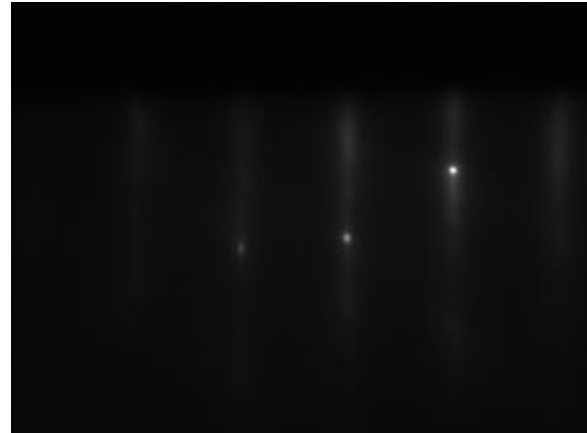
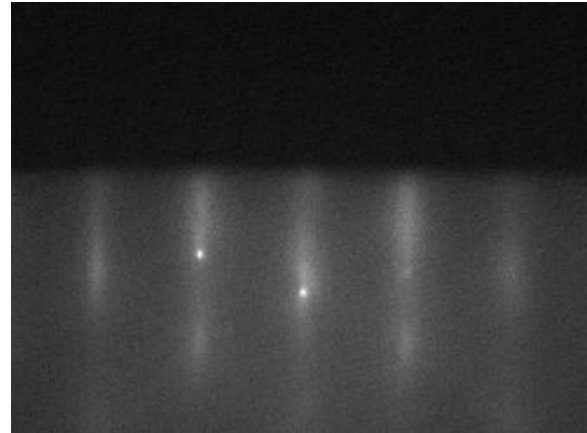
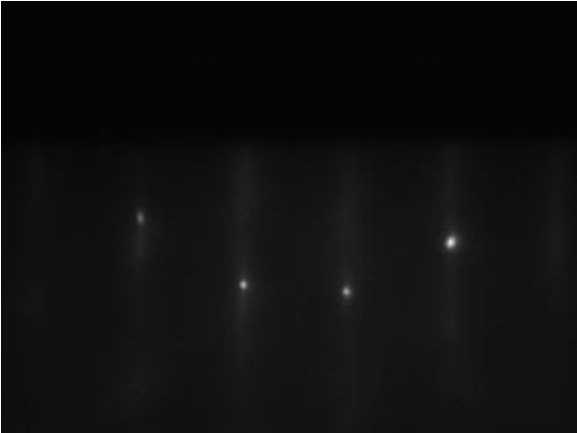
25 C



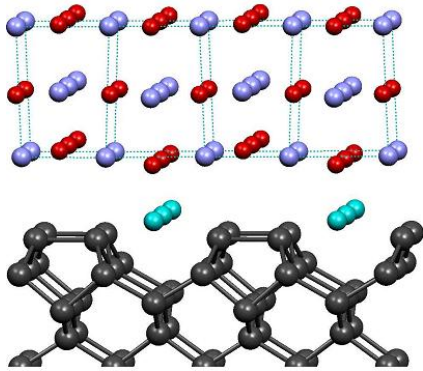
250 C



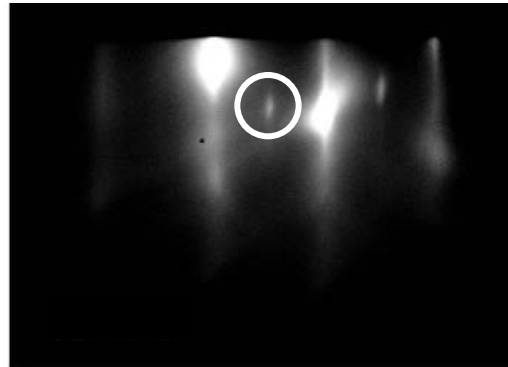
650 C



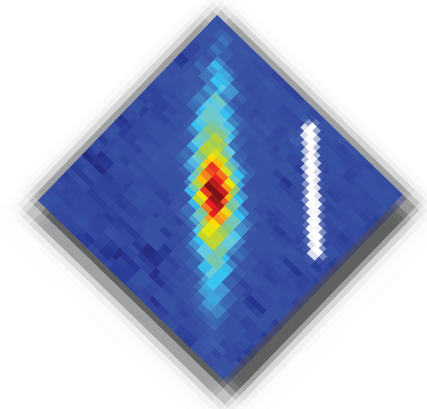
BaO epitaxy: 2×1 symmetry of first layer



Real space



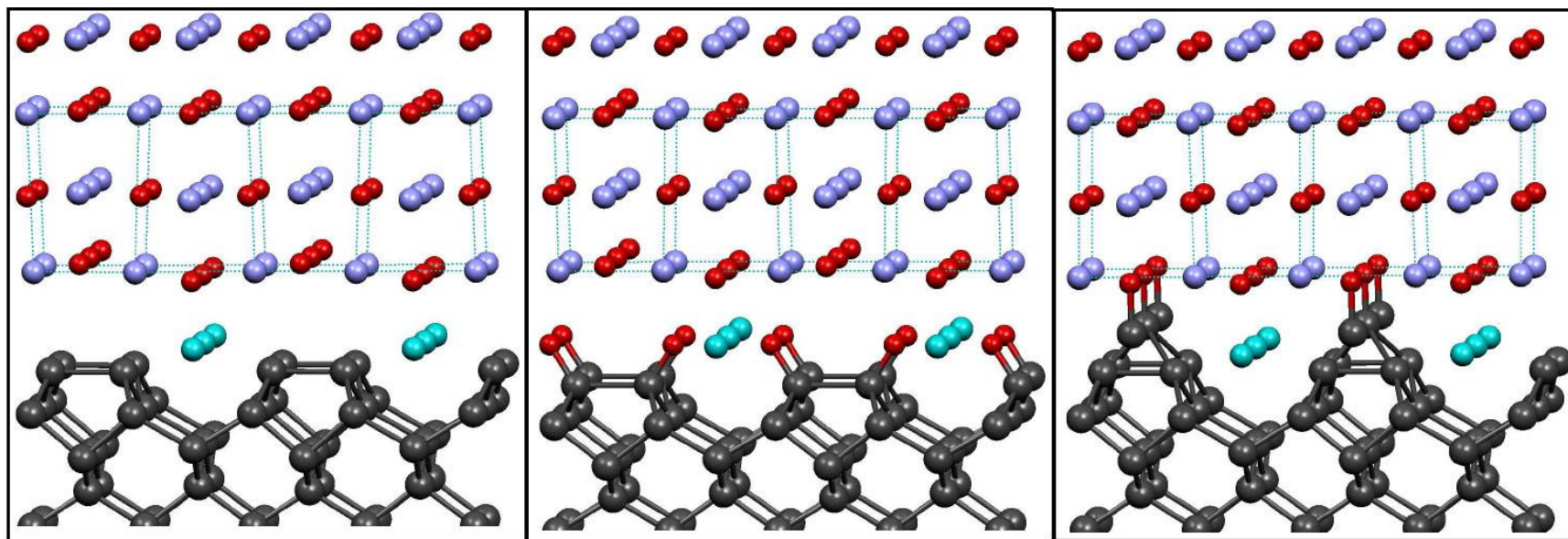
RHEED



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



a)

b)

c)



Sr

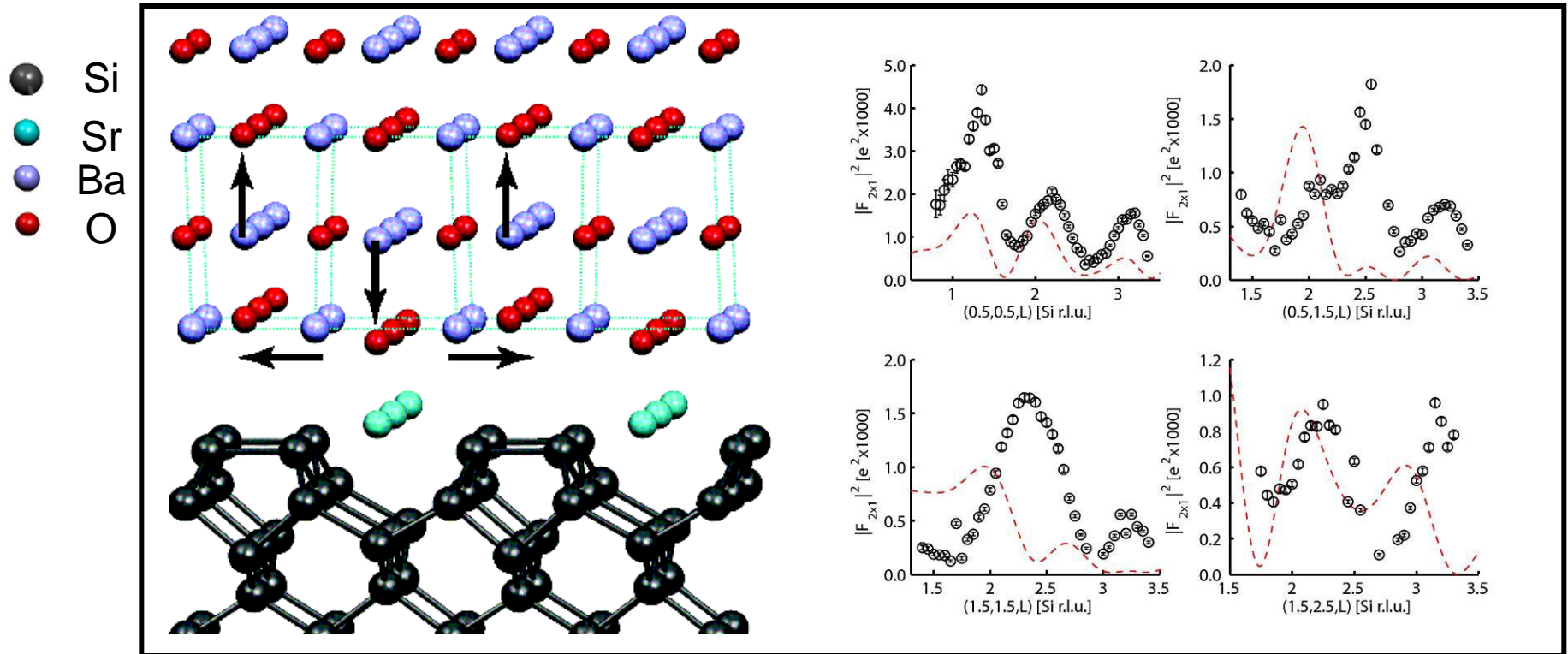


O



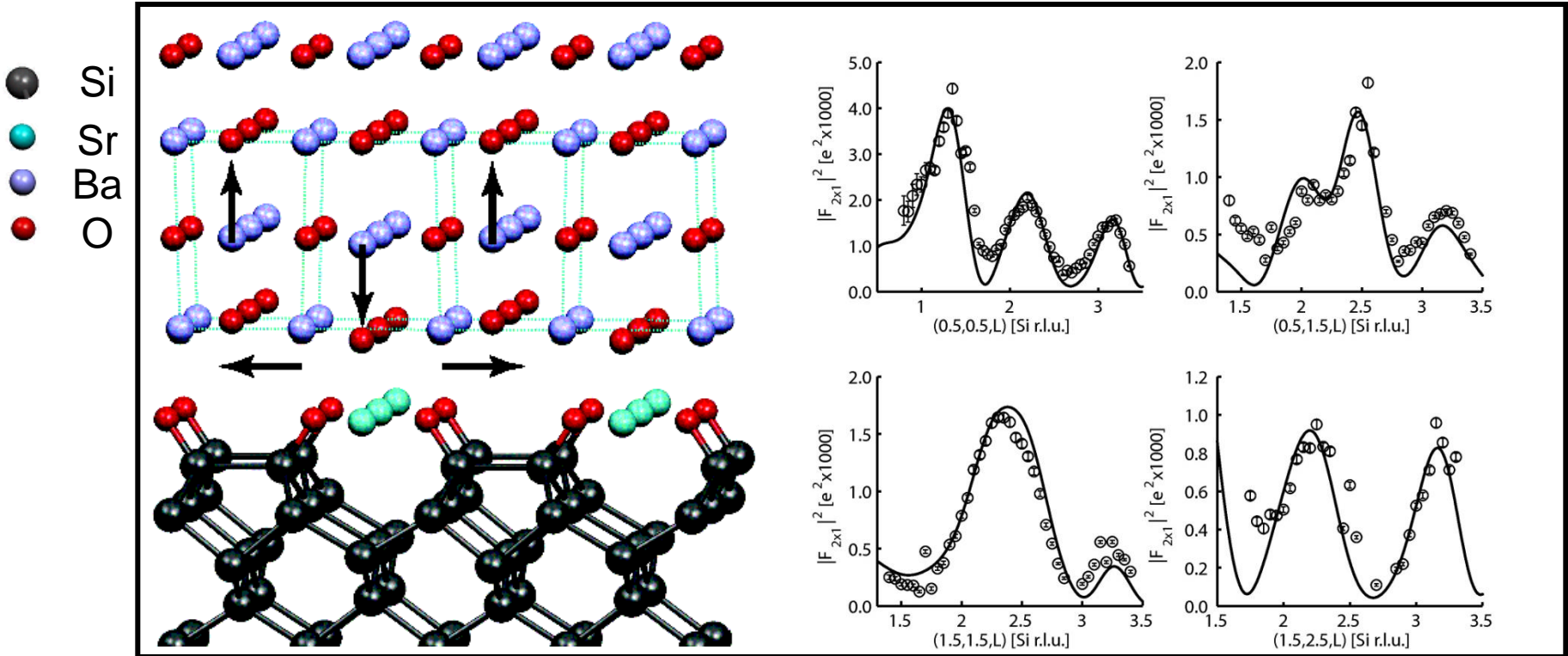
Ba

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 \AA rms
 - 3 % expansion of BaO

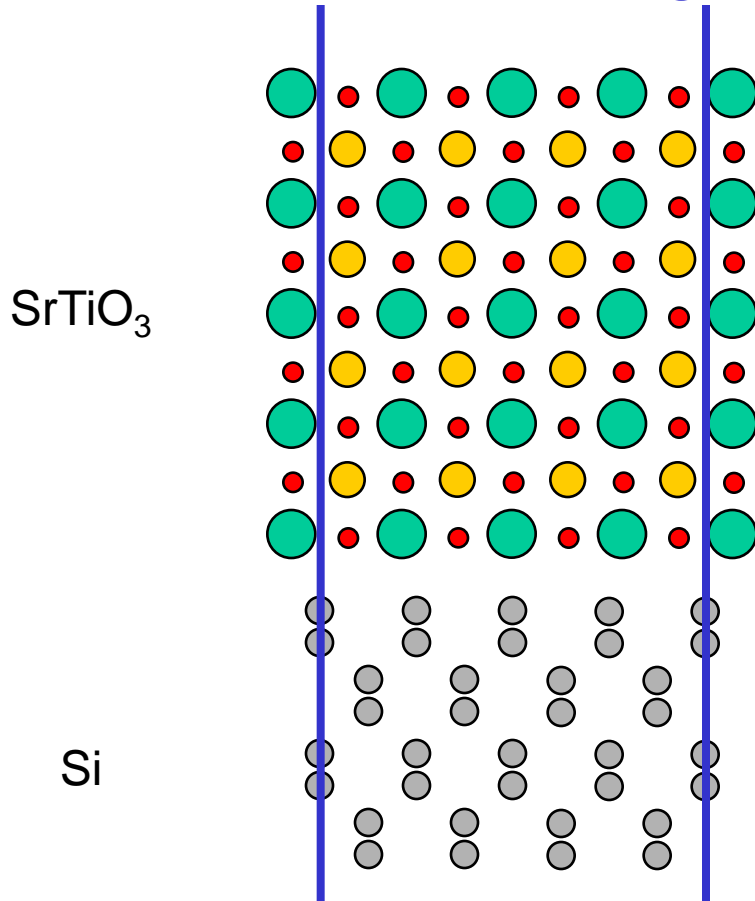
Y. Segal et al., Phys. Rev. Lett. **102**, 116101 (2009).





SrTiO₃ 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 SrTiO₃ Grown on Silicon Ferroelectric?



 Strontium	 Silicon
 Titanium	 Oxygen

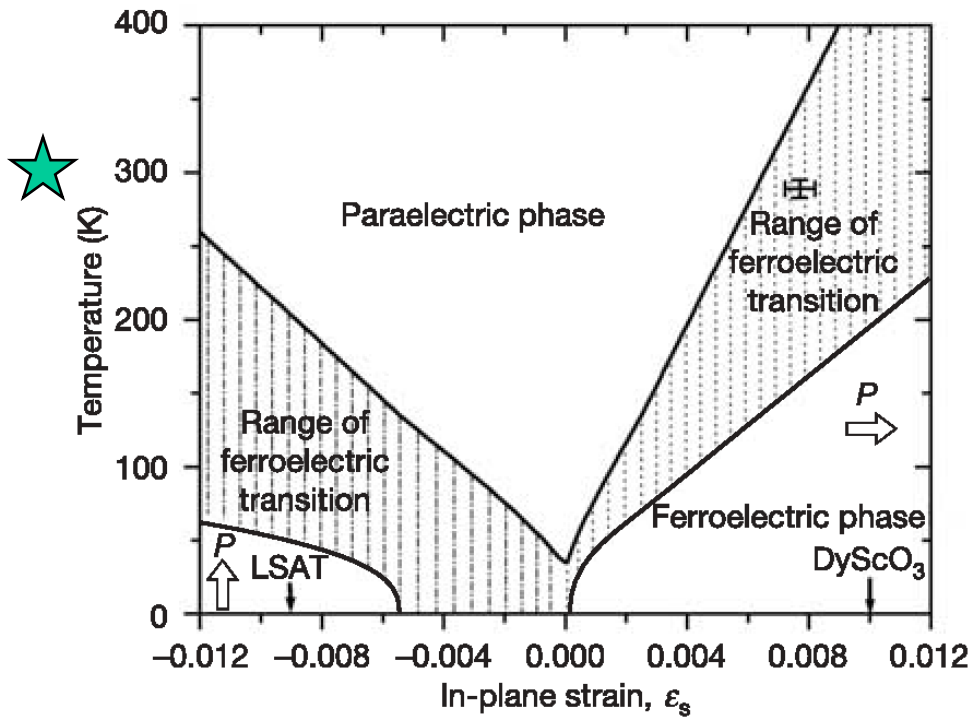
Start with bulk SrTiO₃ on Si
(not ferroelectric)

In-plane lattice constant of
SrTiO₃ shrinks to Si value

Out-of-plane lattice constant
of SrTiO₃ expands because of
compressive stress

Out-of-plane expansion triggers
ferroelectric transition

Phase Diagram of Strained SrTiO₃



SrTiO₃ strain on silicon:

$$\epsilon_s = -0.017$$

We expect out-of-plane polarization.

SrTiO₃ relaxes above 40Å

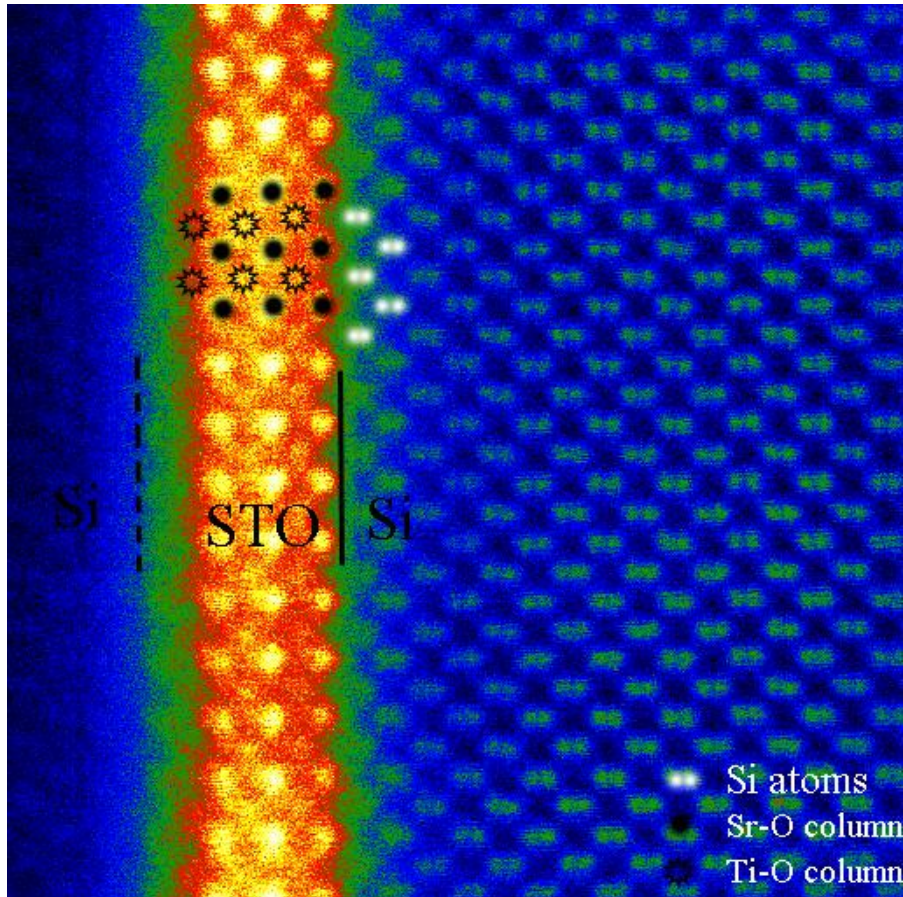
With SrTiO₃ on Si, the interface has 3 effects:

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

J.H. Haeni *et al*, Nature **430**, 758 (2004).

Woicik, *et al*. PRB **73**, 24112 (2006).

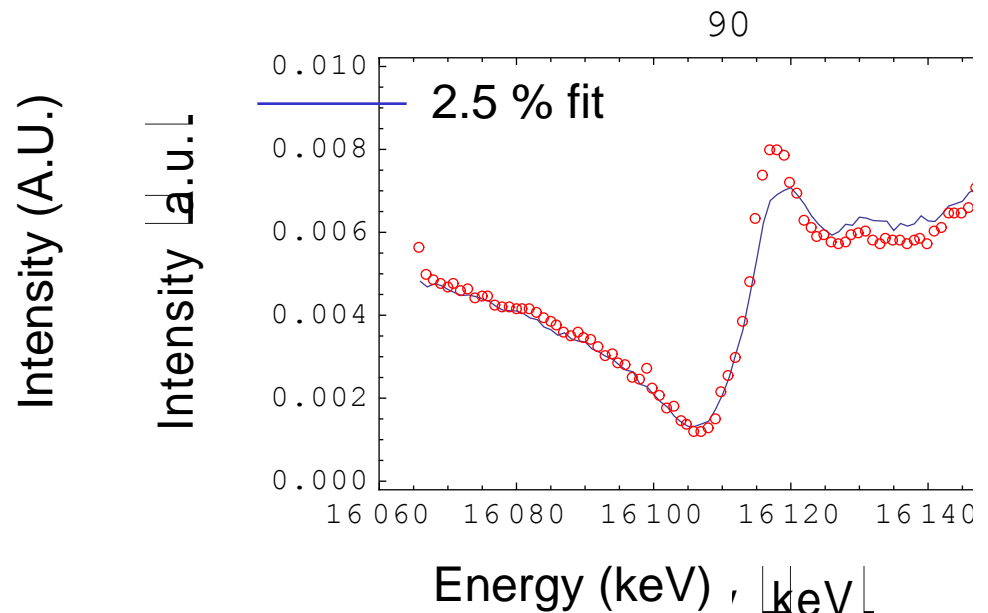
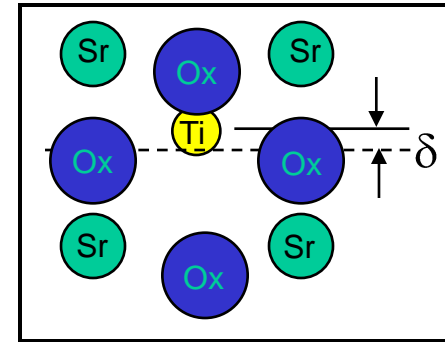
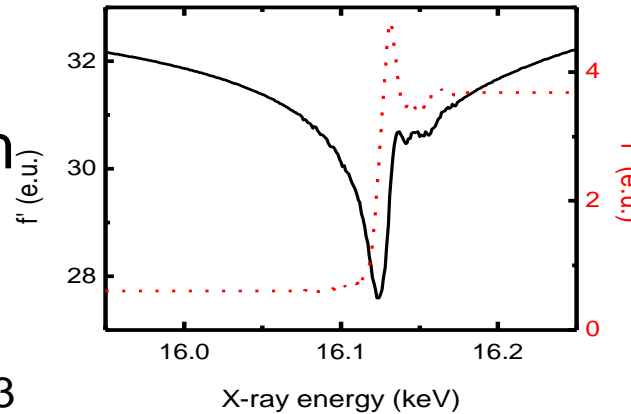
TEM of the SrTiO₃/Si Interface



- Applying the same techniques to the SrTiO₃/Si interface
- Initial results indicate that the SrTiO₃/Si interface is significantly different
- No 2x1 structure seen in either XRD or TEM

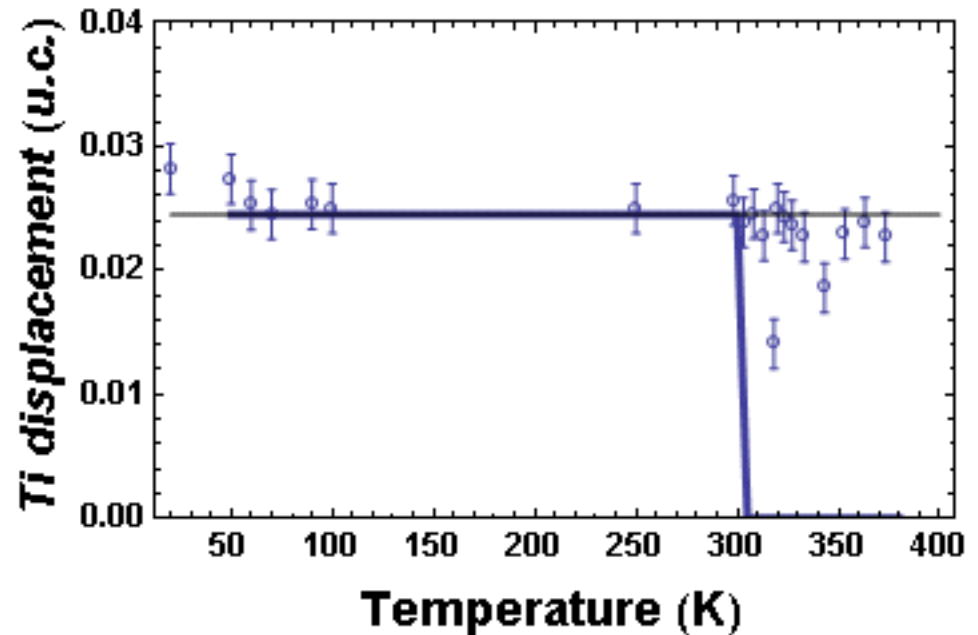
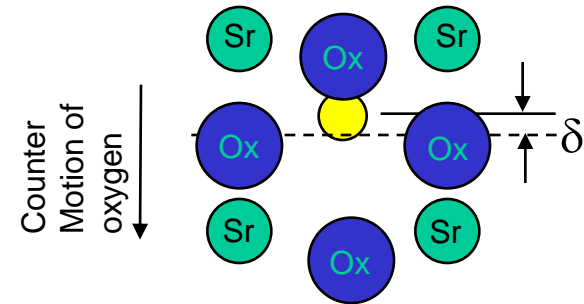
Energy XRD from SrTiO₃ (2,0,1) peak

- 20Å strained SrTiO₃ film
- (2,0,1) strained SrTiO₃ peak, same as (2,2,1.4) Si, is sensitive to SrTiO₃ polarization
- SrTiO₃ is polarized 2.5%
- Ti pushed away from Si
- Can polarization be reversed?
- Can we see displacive temperature phase transition?



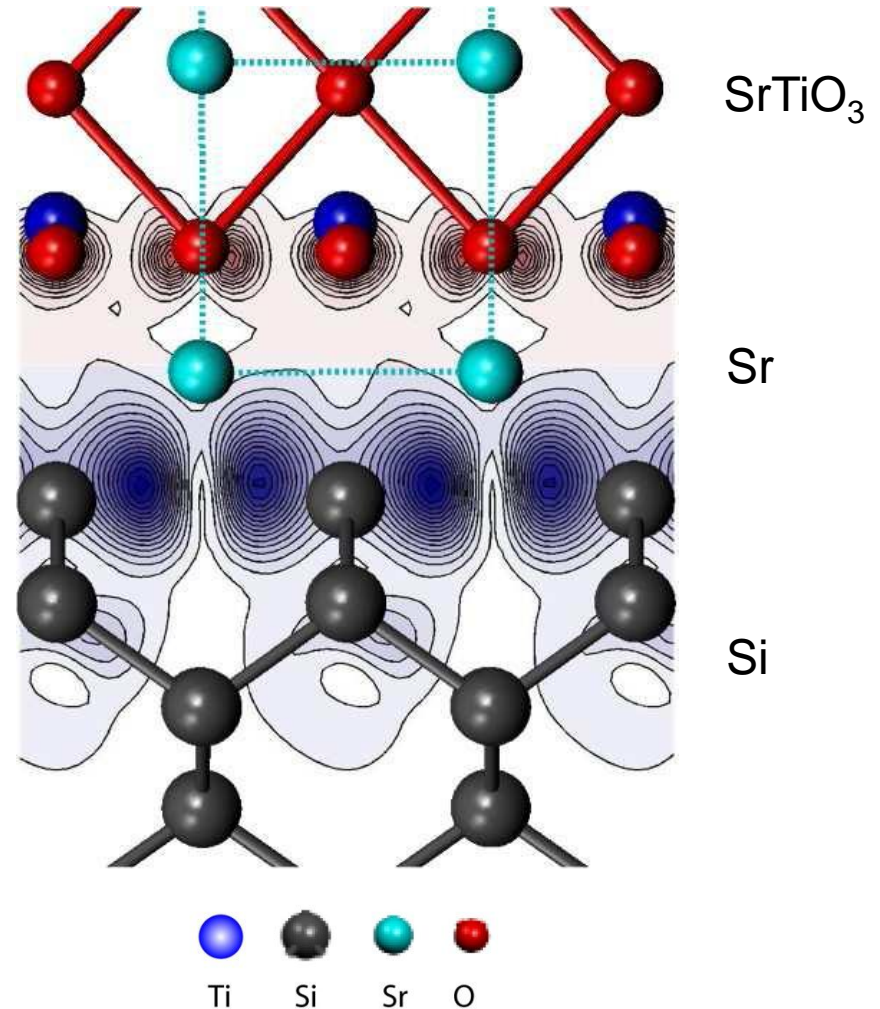
Temperature dependence of polarization

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



Polarization and the SrTiO₃/Si interface

- Ground state structure from first principles theory
- Net positive polarization
- **Interface dipole** created by charge transfer between SrTiO₃ and Sr:Si
- Dipole couples to soft phonon mode of SrTiO₃

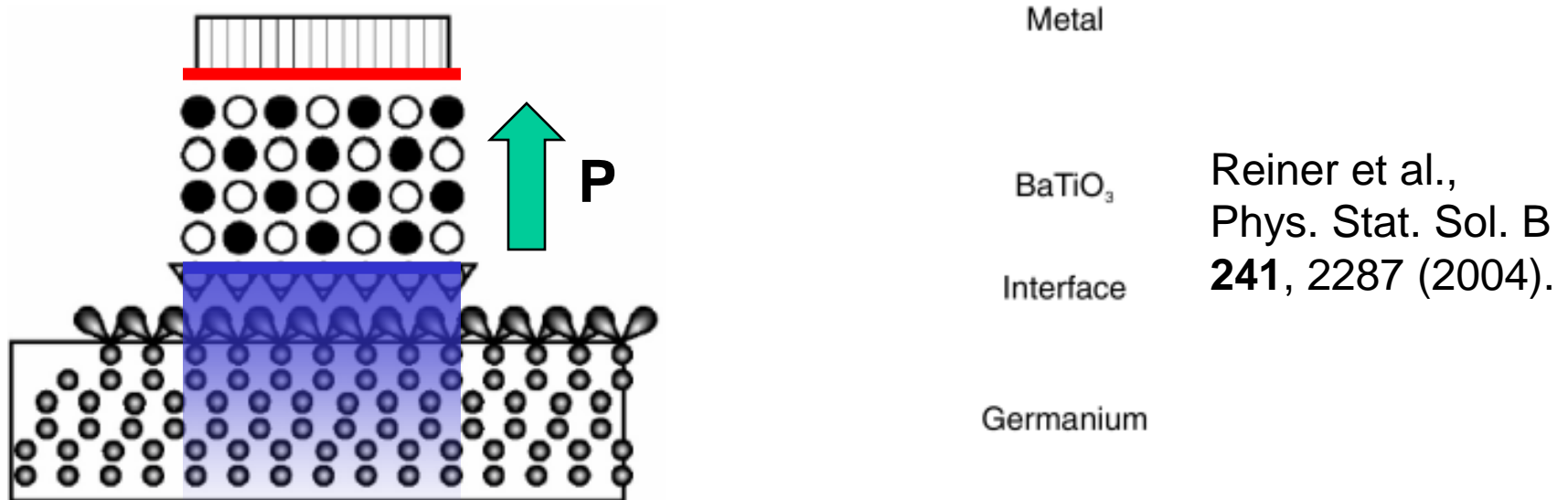


Screening and the SrTiO₃/Si interface

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

$$\text{“Depolarization energy”} = \mathbf{E} \cdot \mathbf{P}$$

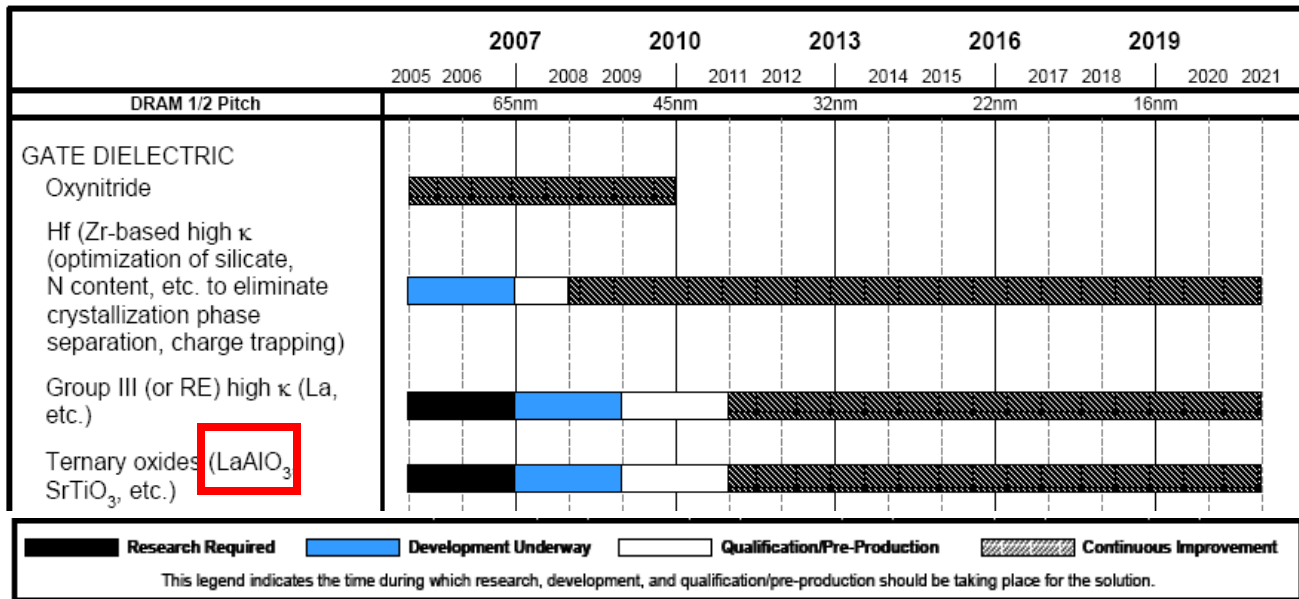
becomes important. For SrTiO₃/Si, if Si band bending is providing screening charge, screening length is large compared to 20Å.



LaAlO₃ as high-κ dielectric: properties

Favorable properties of LaAlO₃ for high-κ

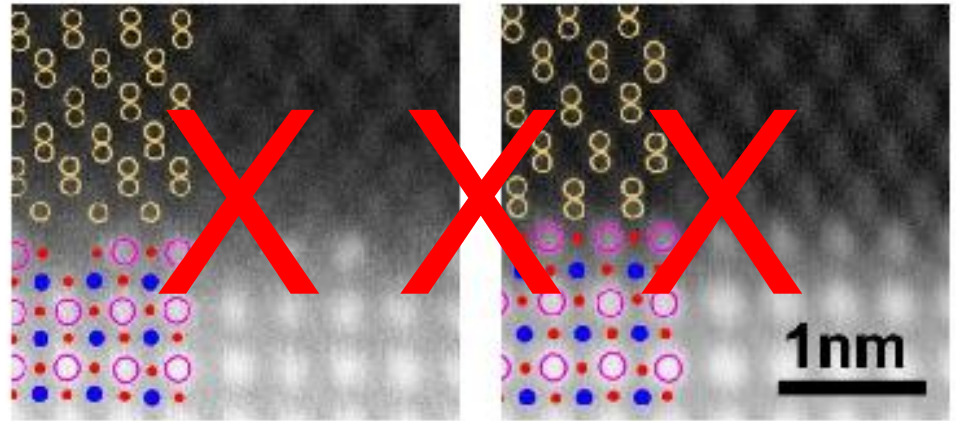
- Dielectric constant 24
- Band gap 5.5 eV
- Large band offsets with Si



International
Technology
Roadmap for
Semiconductors
(ITRS)

LaAlO₃ – Si interface

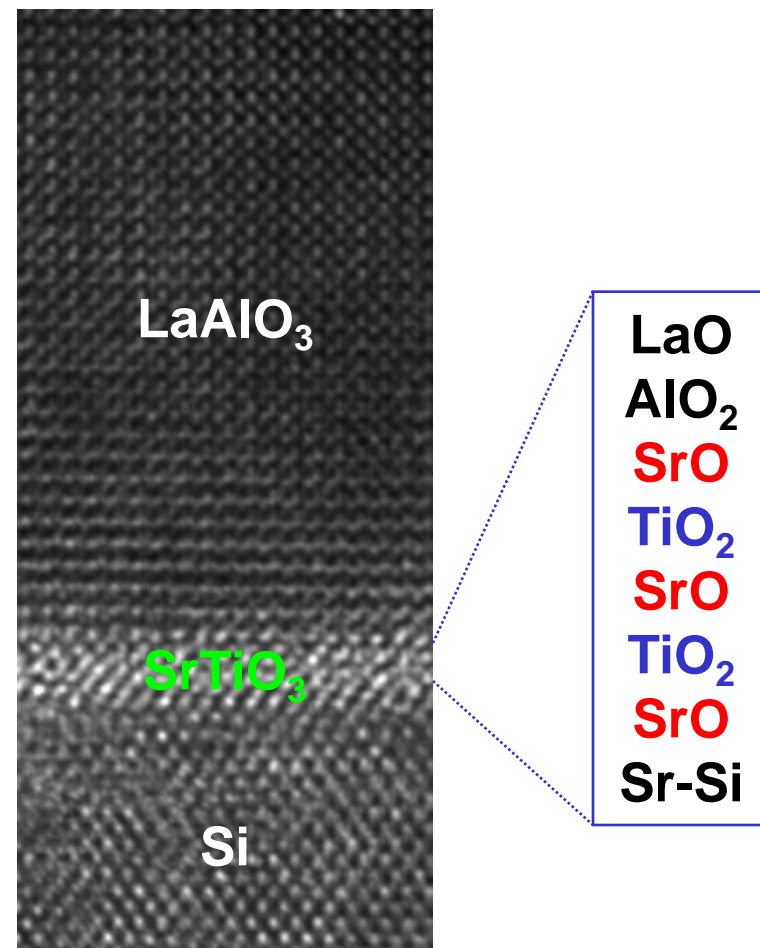
1. Amorphous LaAlO₃ grown on Si appears to form an abrupt interface
2. Crystalline Si has been grown on single crystals of LaAlO₃
3. Crystalline LaAlO₃ has **not** be grown in direct contact with Si



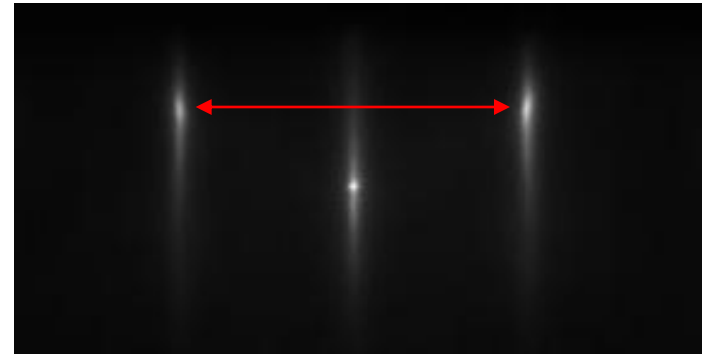
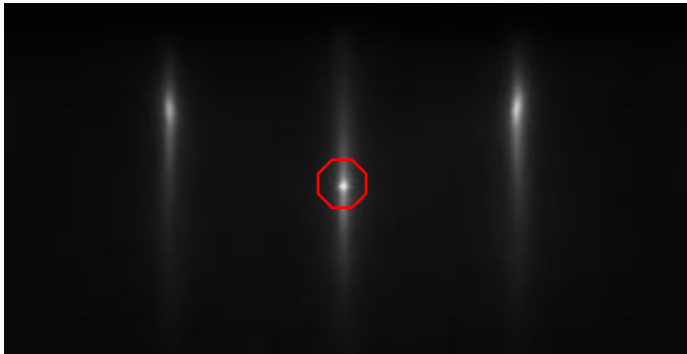
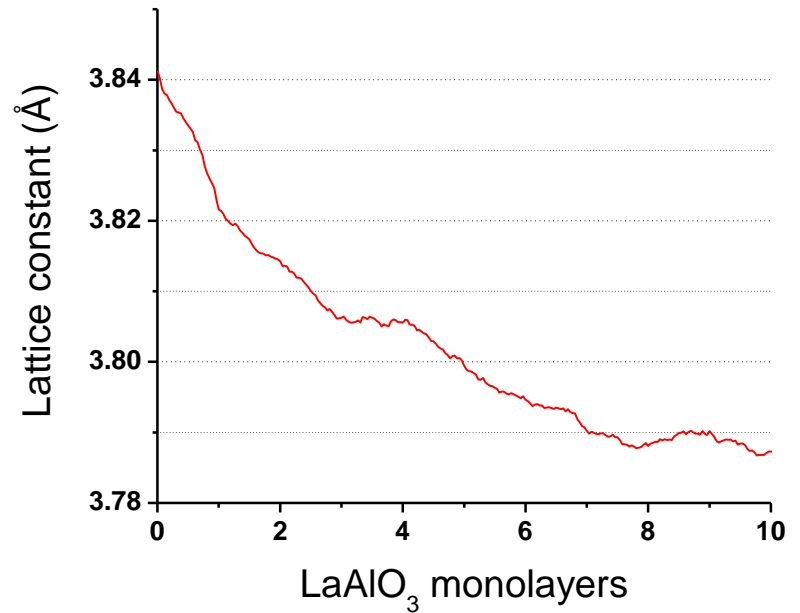
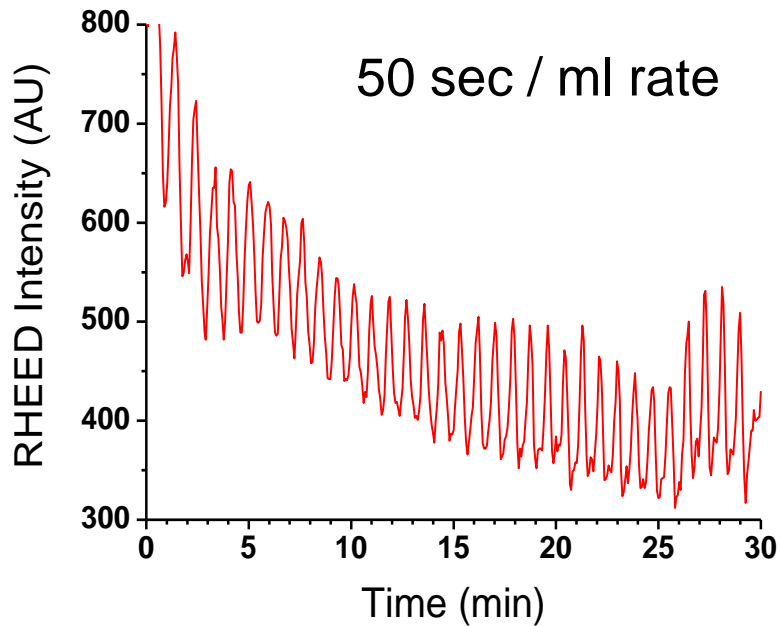
C.J. Först, K. Schwarz, P.E. Blöchl, Phys. Rev. Lett. **95**, 137602 (2005).

Approach to Epitaxial LaAlO₃ on Si

- LaAlO₃ can be grown on SrTiO₃ single crystals
- First grow a thin epitaxial SrTiO₃ film on Si, then grow LaAlO₃
 - Is epitaxial growth of LaAlO₃ compatible with a stable SrTiO₃/Si interface?
 - What is the minimum SrTiO₃ thickness required?
- Theory finds SrTiO₃ on Si buckles if less than 2½ ml

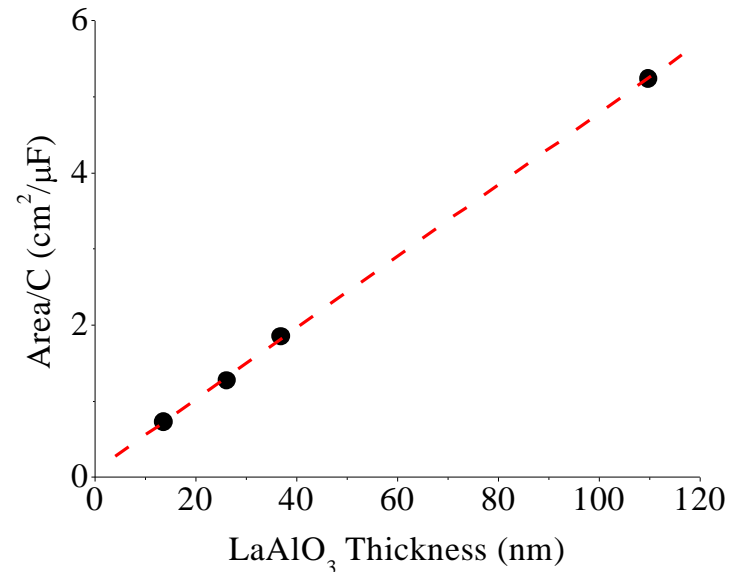
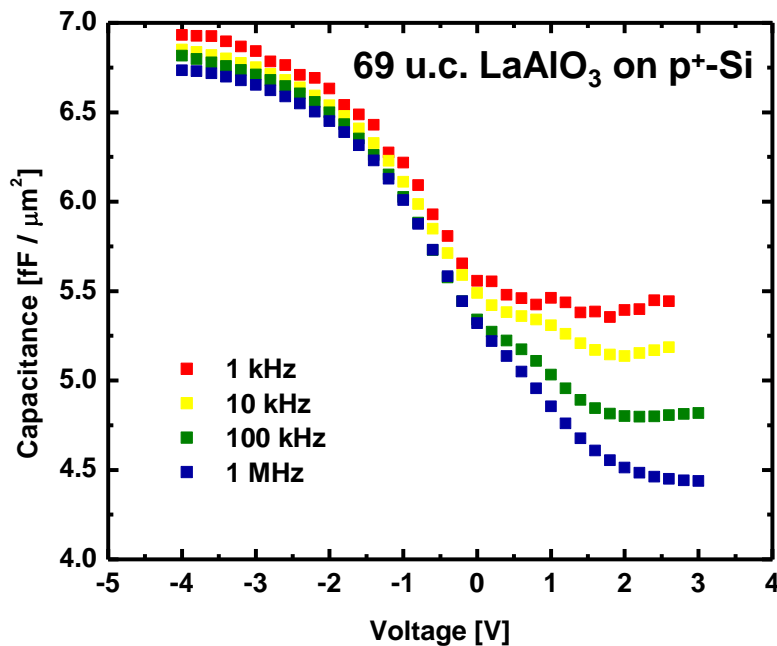


RHEED study of LaAlO_3 growth



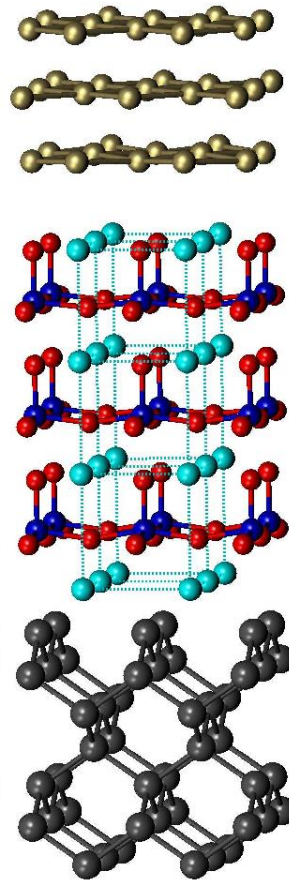
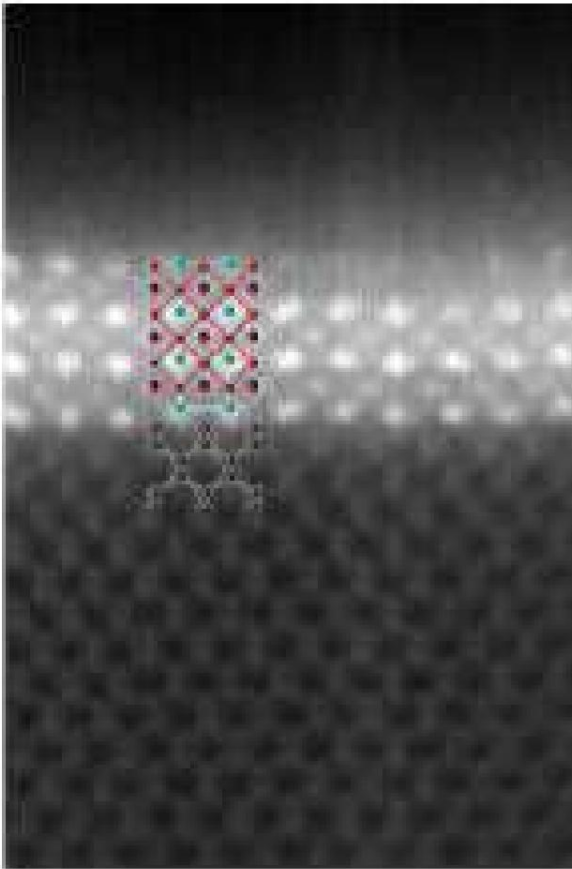
LaAlO₃ Capacitance vs. Voltage

- Dielectric constant = 24
- Similar to bulk LaAlO₃ value



- Annealed in wet oxygen for 30 min at 350 C
- $10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ 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