Physics as a Journey

and

Integration of Ferroelectric Oxides on Semiconductors

Alex Demkov
The University of Texas at Austin

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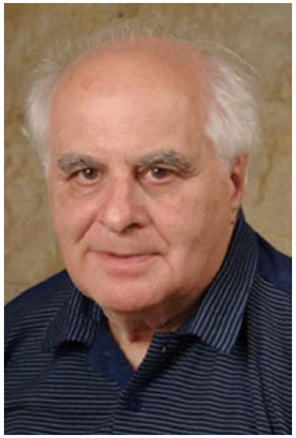
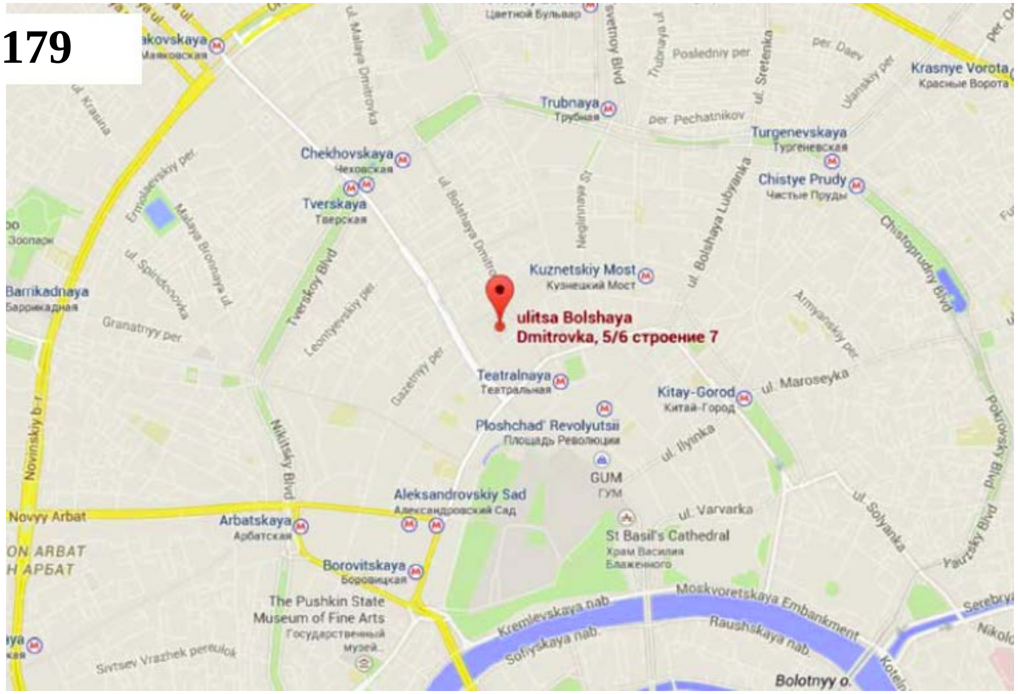


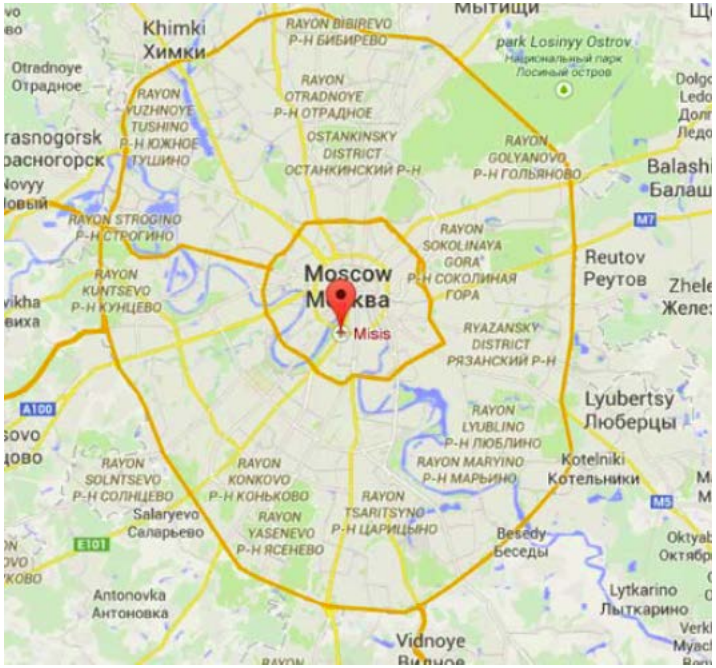
Viulen Veniaminovich (Vladimir Vladimirovich) Bronfman*
09.03.1925-16.09.2009

My high school physics teacher

Moscow Public School 179



*Physics - Uspekhi **52** (12) 1285 ± 1286 (2009)*



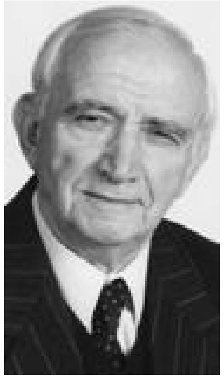
Moscow Institute for Steel and Alloys

Website http://www.misis.ru

National University of Science and Technology "MISIS“ was established in 1918 as part of the Mining Academy. In 1930, it became independent and was known as Stalin Moscow Institute of Steel. In 1962 it united with the Institute of Nonferrous Metals and Gold and assumed its current name. The Technological University status was awarded in 1993.

M. P. Shaskolskaya

L. G. Aslamazov

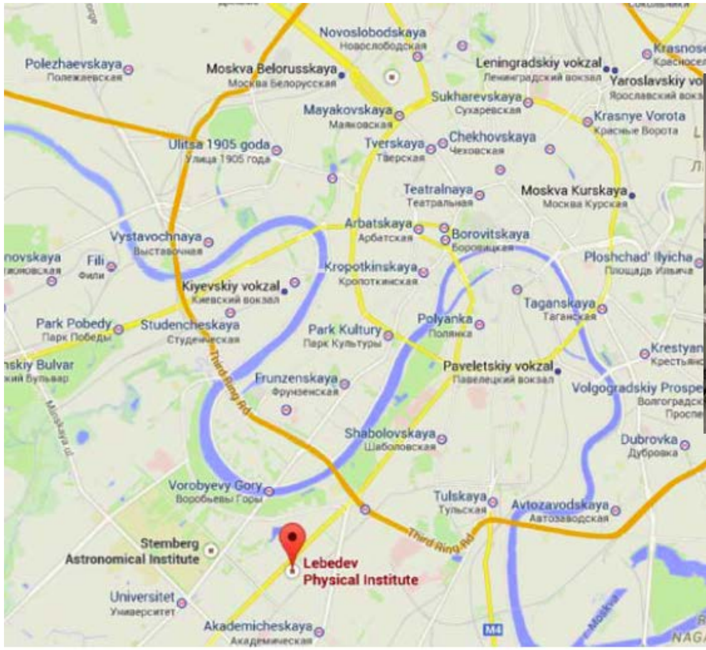


S. S. Gorelik

My college professors

P.N. Lebedev Physical Institute of the Russian Academy of Sciences

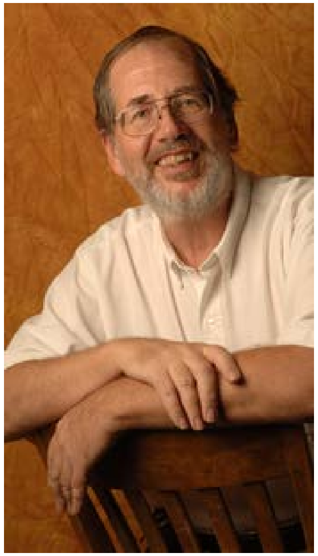
My first physics job



The history of LPI begins from the collection of scientific devices and instruments in the Kunstkamera founded by the decision of Tsar Peter the Great in 1714. Based on the use of collected instruments the first studies at the Physics Cabinet of the Kunstkamera are dated by 1724 when the Saint Petersburg Academy of Sciences has been established. The Cabinet of Physics was well recognized by the activity of prominent scientists of that time as D. Bernoulli, L. Euler, M.V. Lomonosov. LPI moved to Moscow in1934.

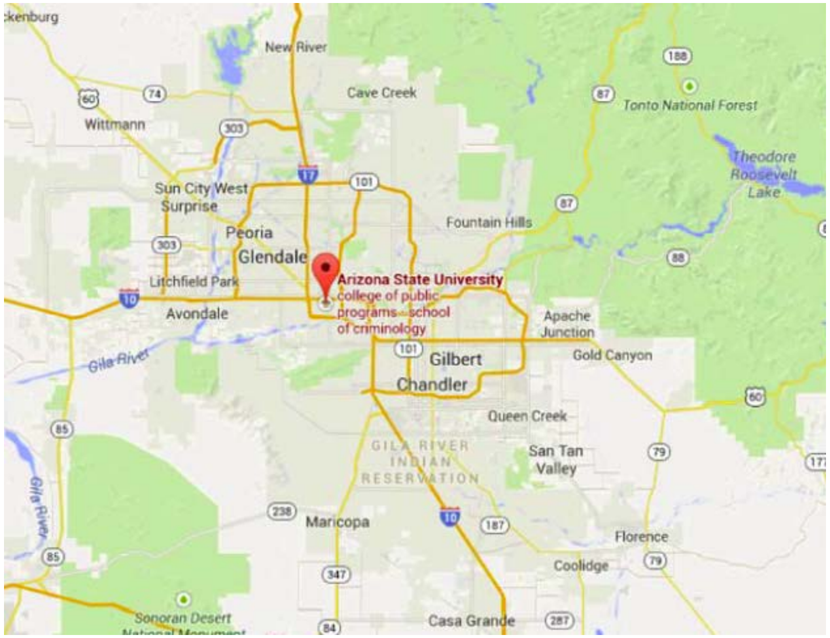
ASU
ARIZONA STATE UNIVERSITY

Graduate School

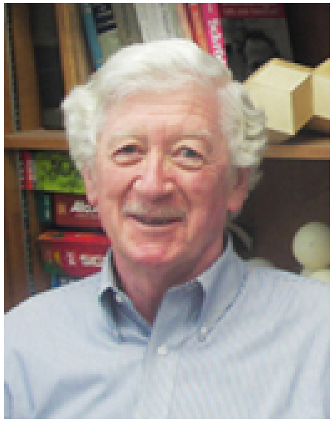


My advisor: Otto Sankey

John Page



Kevin Schmidt



Mike O'Keefe

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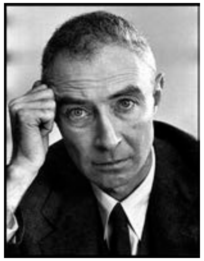
Electronic Structure Theory

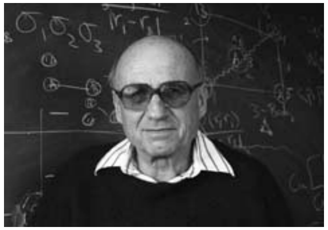
$$\left(-\frac{\hbar^2\nabla^2}{2m}+V\left(r\right)\right)\psi_i\left(r\right)=\varepsilon_i\psi_i\left(r\right)$$



$$\Psi(\mathbf{R},\mathbf{r})=\sum_{k=1}^{K}\chi_k(\mathbf{r};\mathbf{R})\phi_k(\mathbf{R}),$$

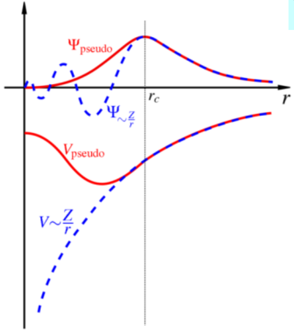
$$H_{\mathrm{e}}\;\chi(\mathbf{r})=E_{\mathrm{e}}\;\chi(\mathbf{r})$$

$$\left[T_{\mathrm{n}}+E_{\mathrm{e}}(\mathbf{R})\right]\phi(\mathbf{R})=E\phi(\mathbf{R})$$

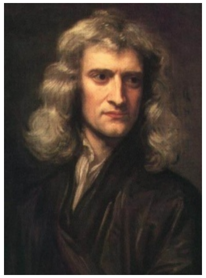


$$E_{KS}[n]=\left\langle\Psi\middle|\hat{H}\middle|\Psi\right\rangle=E_{K.E}[n]+E_{Hartree}[n]+E_{elec-ion}[n]+E_{ion-ion}+E_{XC}[n]$$

$$\left(-\frac{\hbar^2\nabla^2}{2m}+V_{KS}(r)\right)\psi_i(r)=\varepsilon_i\psi_i(r)$$

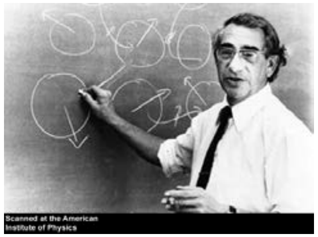


$$V_{KS}(r)=V_{ext}(r)+\int\frac{n(r')}{|r-r'|}dr'+V_{XC}(r)$$



$$F_i=-\frac{\partial E}{\partial R_i}\longrightarrow F_i=m_i\ddot{x}_i$$

$$H=-t\sum_{<i,j>,\sigma}c^{\dagger}_{i,\sigma}c_{j,\sigma}+U\sum_{i=1}^{N}n_{i\uparrow}n_{i\downarrow}$$



Scanned at the American Institute of Physics

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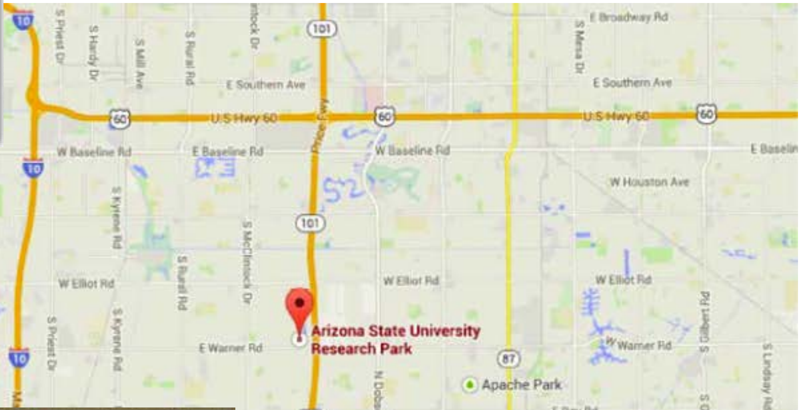
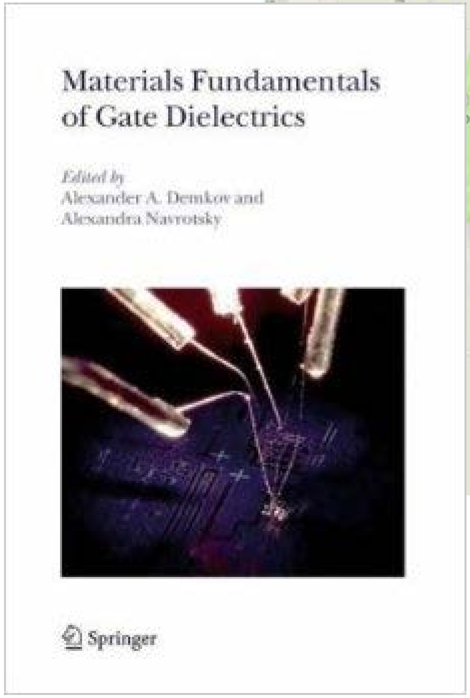
Motorola
Physical Sciences Research Lab
Tempe, Arizona

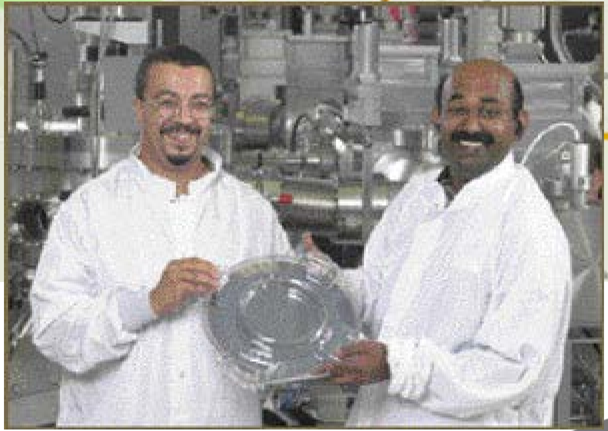


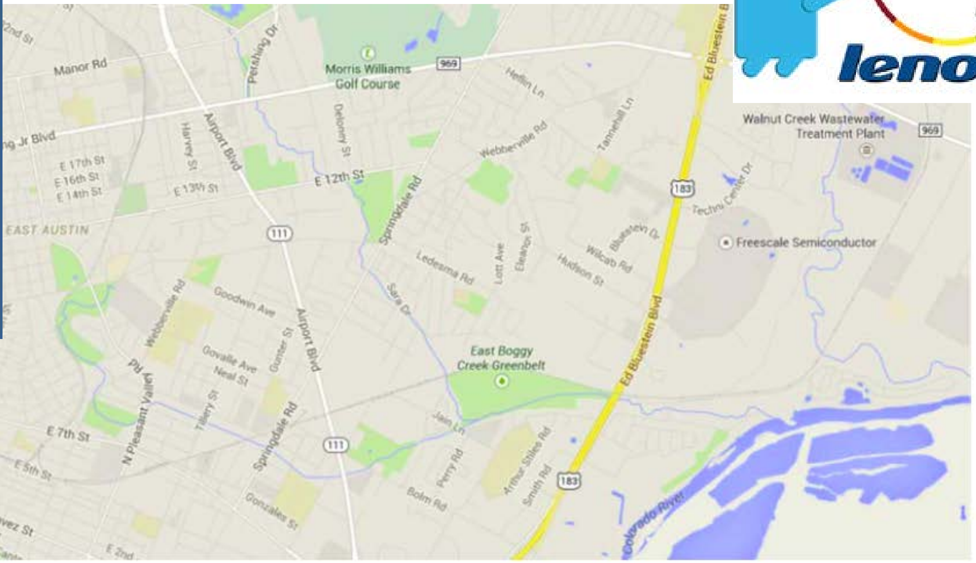


Materials Fundamentals of Gate Dielectrics

Edited by
Alexander A. Demkov and
Alexandra Navrotsky

Springer





Motorola Advanced Products Research and Development Laboratory, Austin, TX

7,365,410 Semiconductor structure having a metallic buffer layer and method for forming
7,235,847 Semiconductor device having a gate with a thin conductive layer
7,141,857 Semiconductor structures and methods of fabricating semiconductor structures …
7,091,568 Electronic device including dielectric layer, and a process for forming the electronic device
6,791,125 Semiconductor device structures which utilize metal sulfides
6,693,033 Method of removing an amorphous oxide from a monocrystalline surface
6,479,173 Semiconductor structure having a crystalline alkaline earth metal silicon nitride/oxide …

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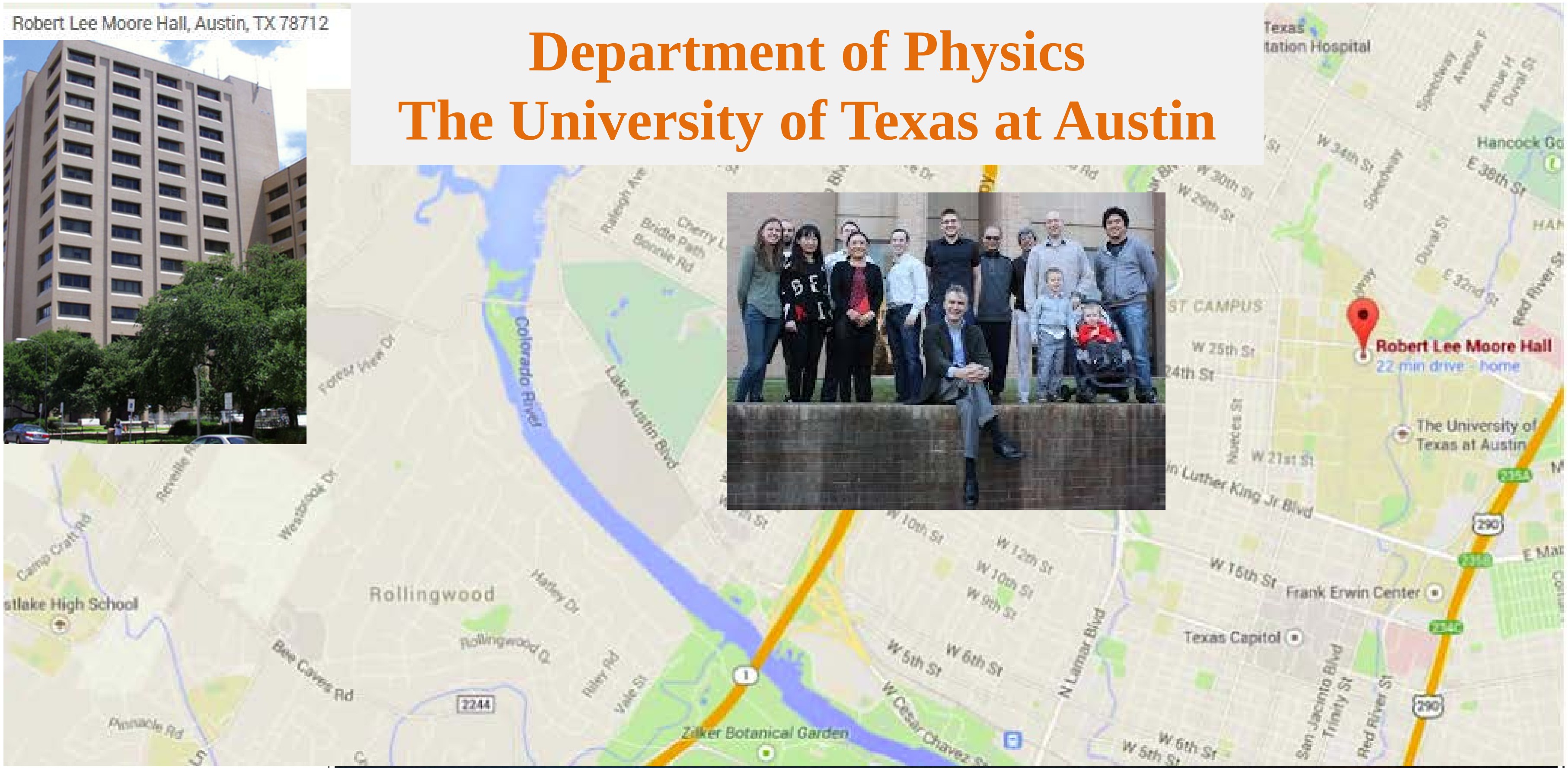
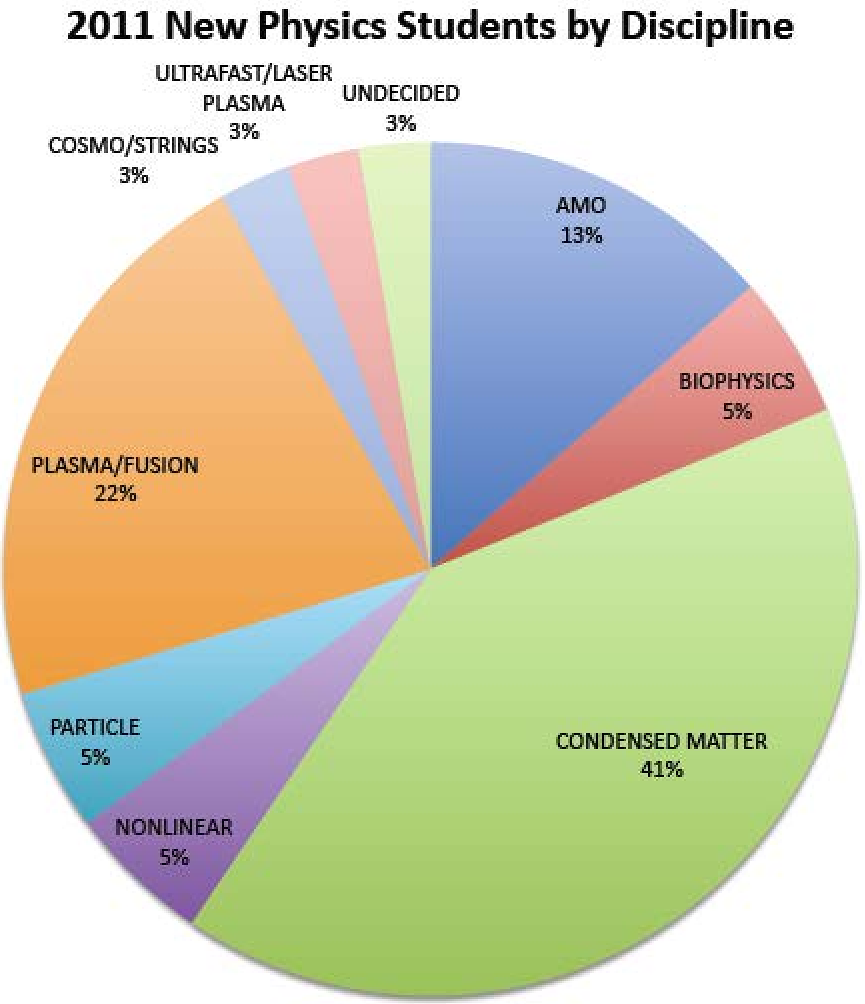
Department of Physics
The University of Texas at Austin



Ming

UT Physics Department at a glance



Atomic, Molecular, and Optical Physics
Biophysics/Biological Physics
Condensed Matter Physics
Center for Particles and Fields
Center for Nonlinear Dynamics
Center for Relativity
Institute for Fusion Studies
Center for Complex Quantum Systems
Weinberg Theory Group
Center for High Energy Density Science

60 faculty members
270 undergraduate majors
227 graduate students

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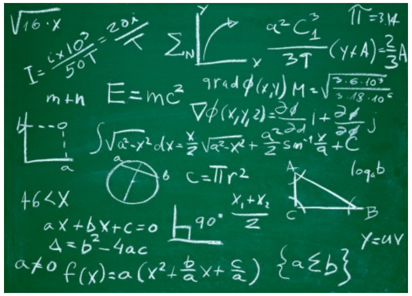
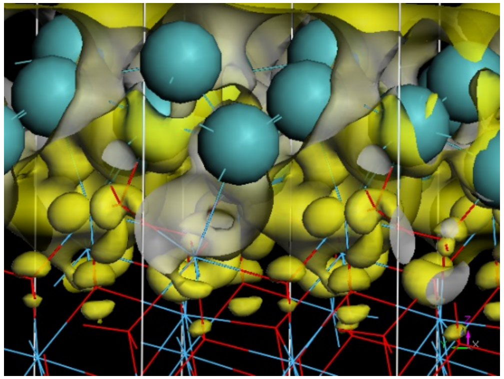
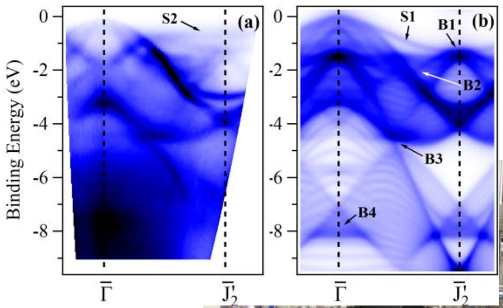
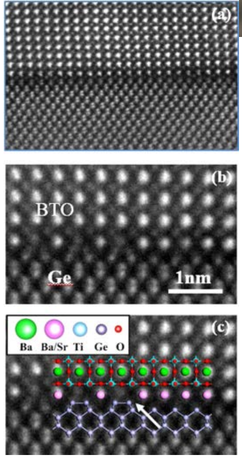
Theory, algorithms and computation



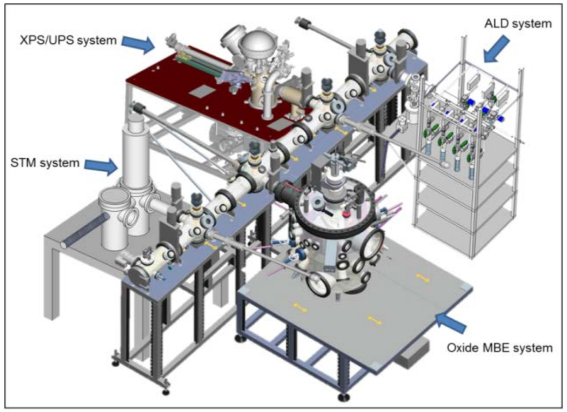


Materials characterization





Materials Growth



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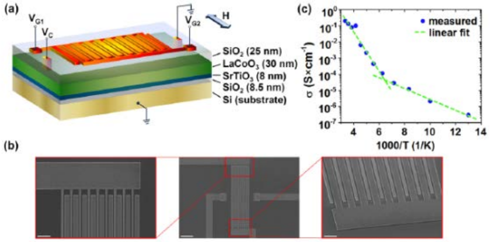

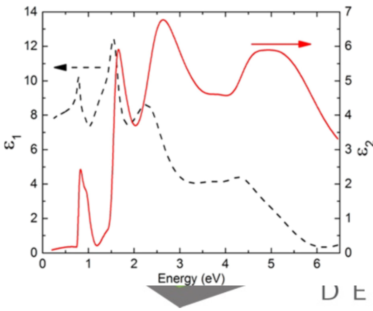

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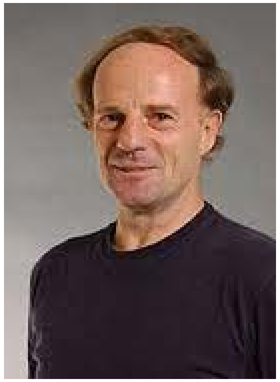
Electrical and Magnetic measurements

Outline of the rest of the talk

- Acknowledgments
- Functional transition metal oxides
- Challenges of oxide/semicon. integration
- STO on Si
- Ferroelectric insulator on Si
- Ferroelectric insulator on Ge
- Conclusions

Students and collaborators



Prof. D. Smith

Prof. M. McCarthy

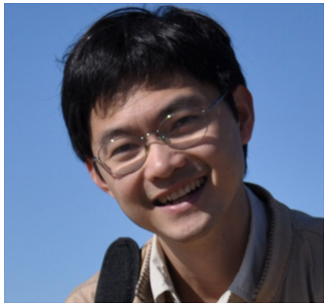
P. Ponath

K. Fredrickson

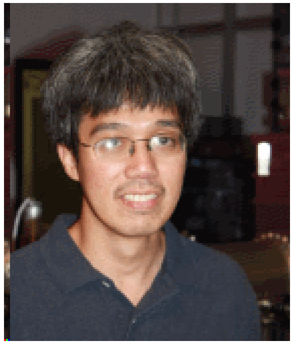
H. Seo

ARIZONA STATE UNIVERSITY

Dr. S. Kalinin



Prof. K. Lai



Dr. A. Posadas

M. Choi

Dr. R. Hatch

TACC

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Oxides

Quartz SiO_2

Hematite Fe_2O_3

Ilmenite $FeTiO_3$

Cassiterite SnO_2

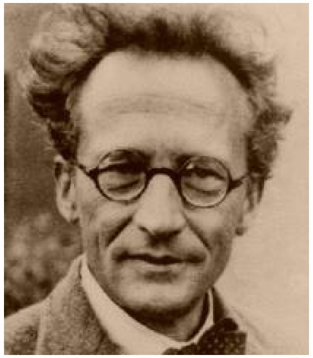
Uraninite UO_2

Perovskite $CaTiO_3$

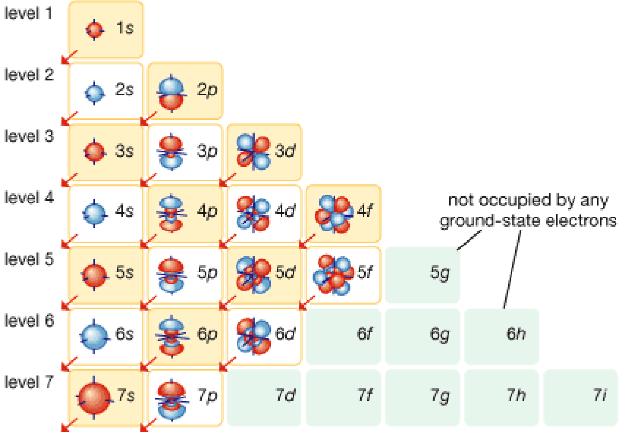
Spinel $MgAl_2O_4$

Transition metals

A transition metal is one which forms one or more stable ions which have ***incompletely filled d orbitals***.



Erwin Schrödinger



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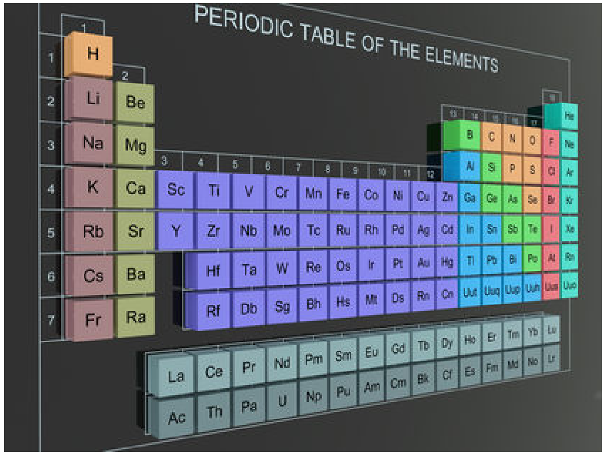
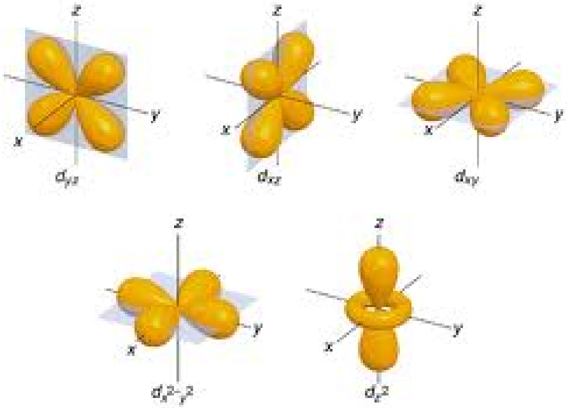


$[Ar] = 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

$[Ti] = [Ar]3d^2 4s^2$

$[V] = [Ar]3d^3 4s^2$



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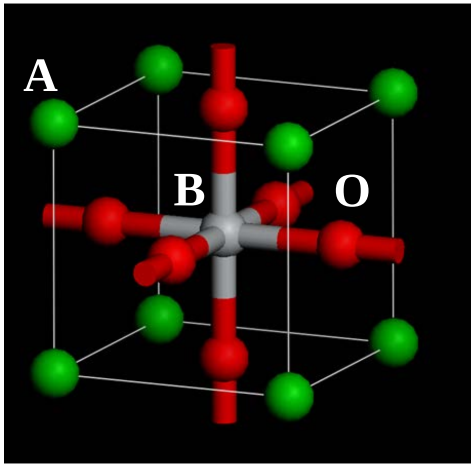
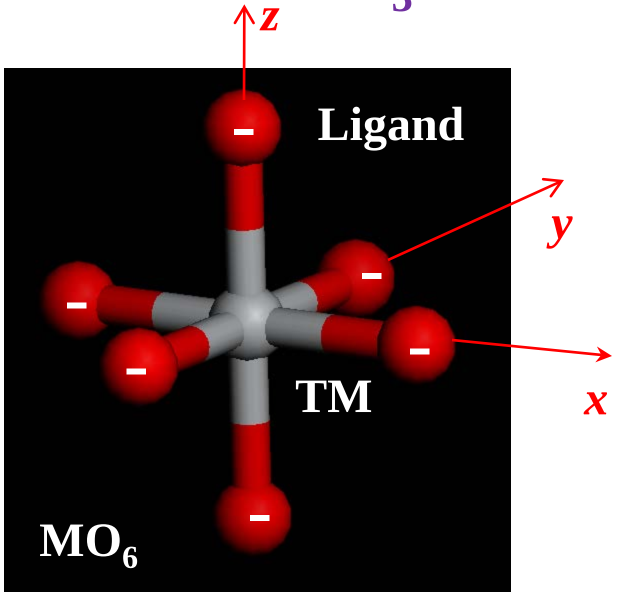
Perovskite oxides ABO$_3$

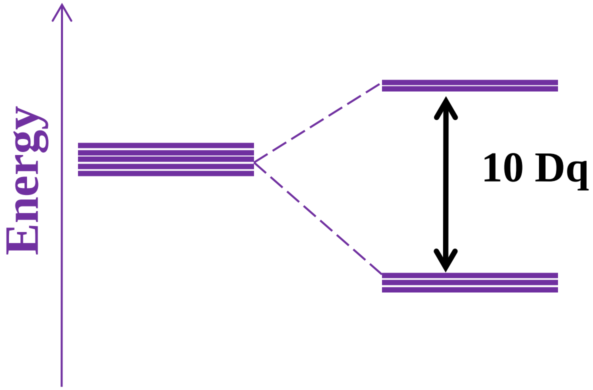


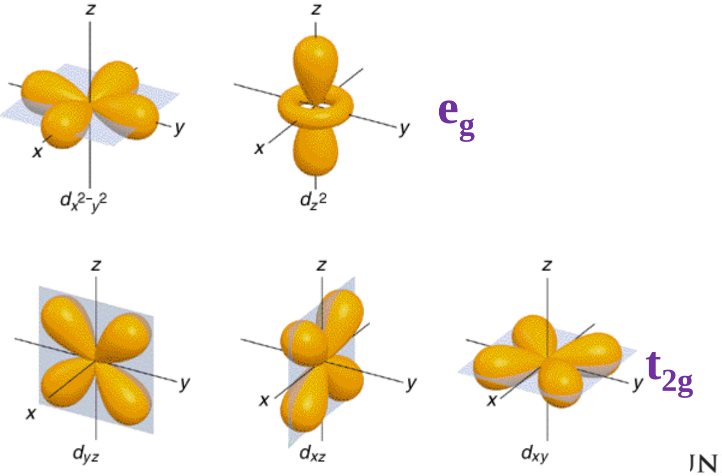


Count Lev Alekseevich Perovski
1792-1856

CaTiO$_3$, BaTiO$_3$, SrHfO$_3$,…

Octahedral symmetry (O$_h$):

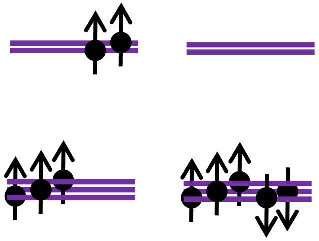




Ligand field theory

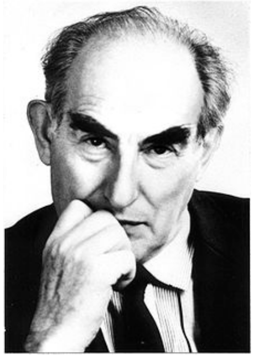
High spin   Low spin

Fe^{3+} (d^5)



$E^S-E^T=2J$

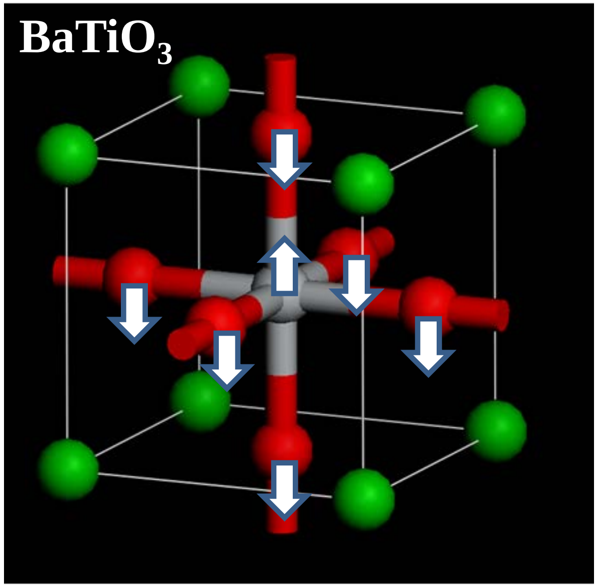
Ferroelectricity

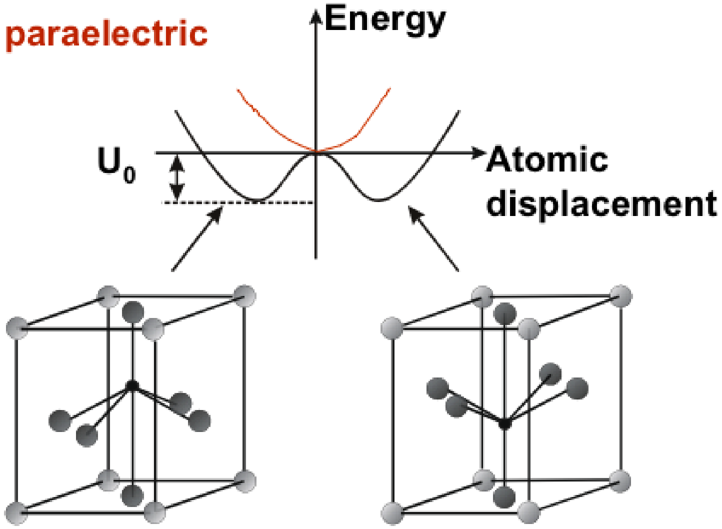


V.L. Ginzburg
1916-2009

L.D. Landau
1908-1968

B.M. Vul
1903-1985





$$\Delta E = \frac{1}{2}\alpha_0 \left(T - T_0\right) P_x^2 + \frac{1}{4}\alpha_{11} P_x^4 + \frac{1}{6}\alpha_{111} P_x^6$$

Integrating ferroelectric on Si (001)

Negative capacitance for steep sub threshold slope -S. Salahuddin and S. Datta

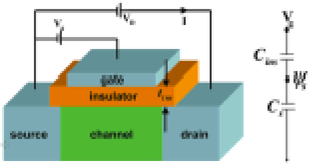
NANO LETTERS
2008
Vol. 8, No. 2
405−410

Use of Negative Capacitance to Provide Voltage Amplification for Low Power Nanoscale Devices

Sayeef Salahuddin* and Supriyo Datta†

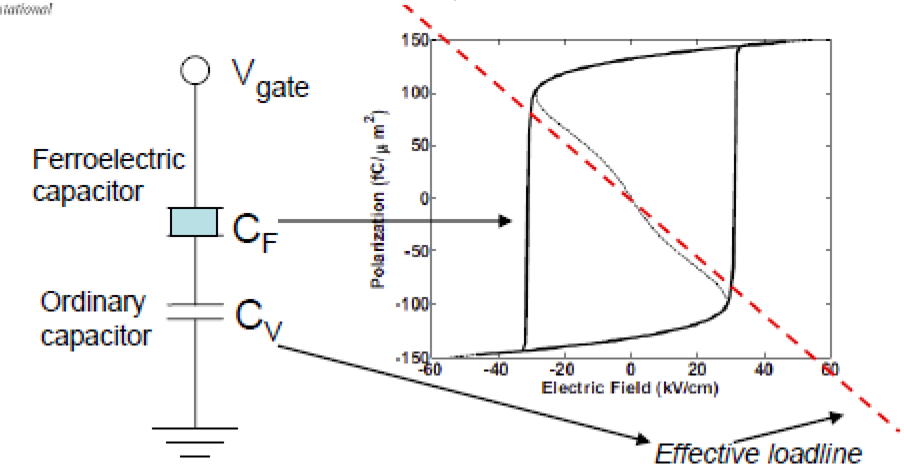
School of Electrical and Computer Engineering and NSF Center for Computational Nanotechnology (NCN), Purdue University, West Lafayette, Indiana 47907

Received July 21, 2007; Revised Manuscript Received October 3, 2007



Concept:

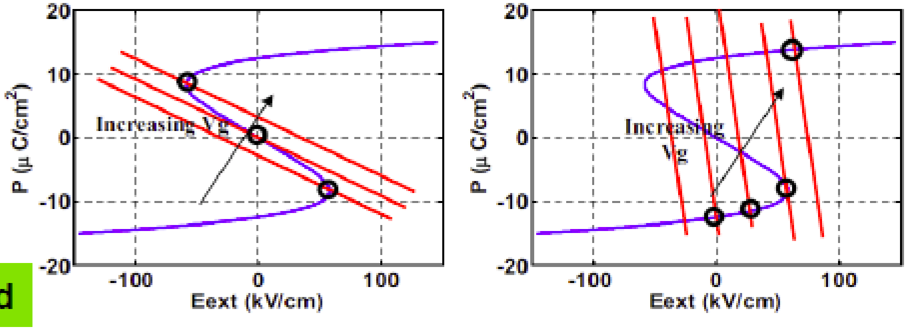
The hysteretic parts of a ferroelectric's QV curves represent negative capacitance. If carefully balanced with positive capacitance in series, the two can cancel, giving very high effective capacitance, so that a small change in gate bias could control a large change in channel charge in an FET.



$$S \equiv \frac{\partial V_g}{\partial(\log_{10} I)} = \underbrace{\frac{\partial V_g}{\partial \psi_s}}_{=m} \underbrace{\frac{\partial \psi_s}{\partial(\log_{10} I)}}_{60\ \mathrm{mV/dec}}$$

$$\frac{\partial V_g}{\partial \psi_s} = 1 + \frac{C_s}{C_{ins}}$$

> 1 unless C_{ins} is negative



S lower than 60 mV/dec could be obtained

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nature COMMUNICATIONS

ARTICLE

Received 3 Sep 2012 | Accepted 5 Mar 2013 | Published 9 Apr 2013

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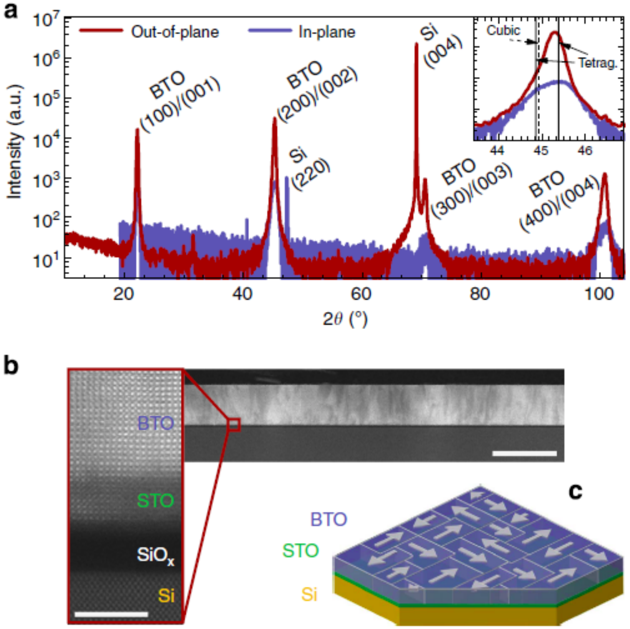
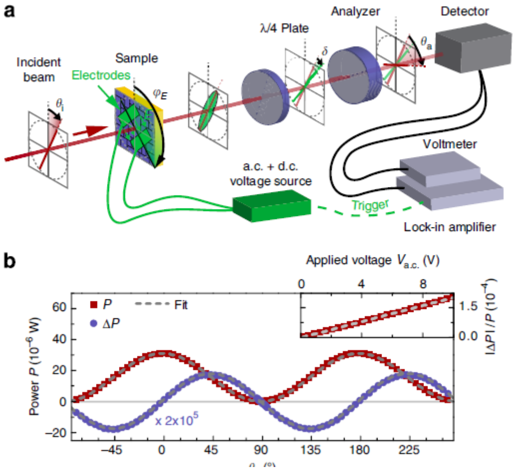
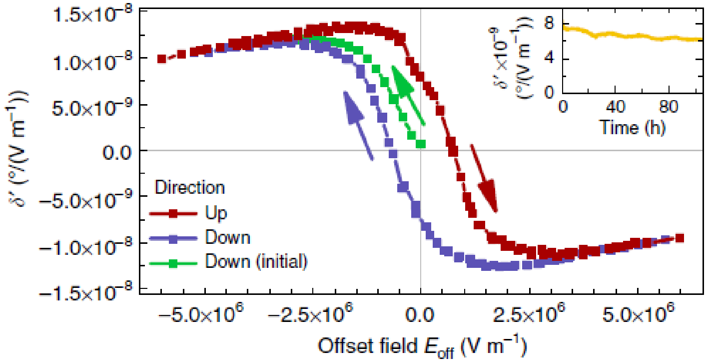
A strong electro-optically active lead-free ferroelectric integrated on silicon

Stefan Abel[1], Thilo Stöferle[1], Chiara Marchiori[1], Christophe Rossel[1], Marta D. Rossell[2], Rolf Erni[2], Daniele Caimi[1], Marilyne Sousa[1], Alexei Chelnokov[3], Bert J. Offrein[1] & Jean Fompeyrine[1]







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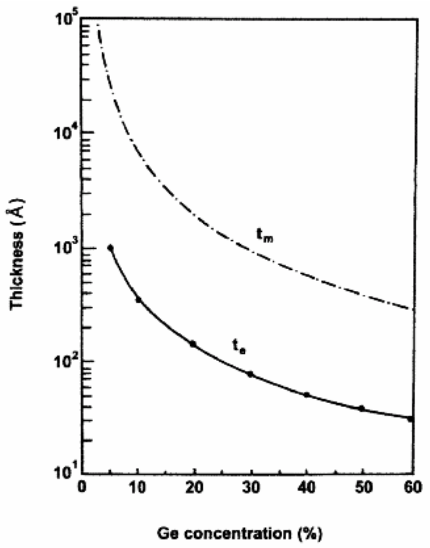
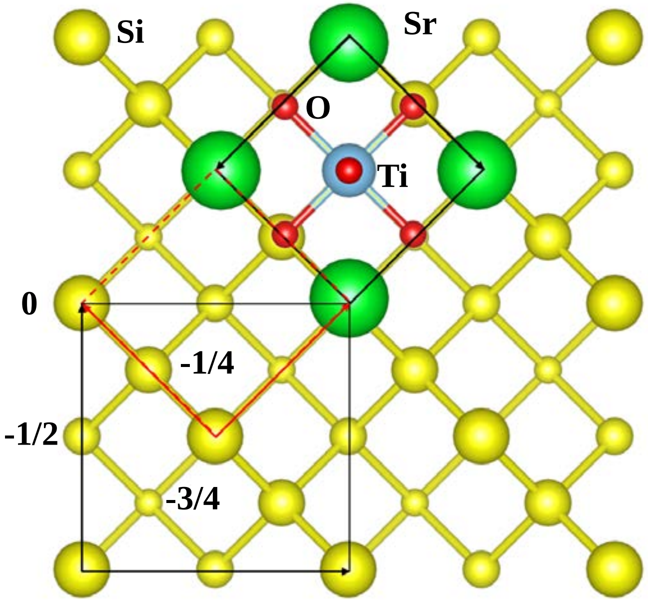
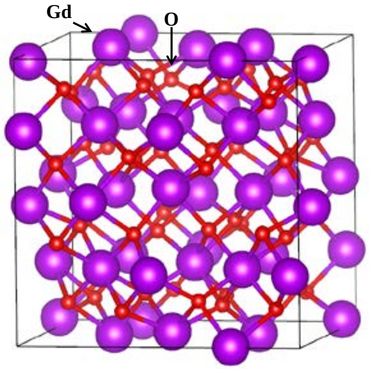
Critical issues of oxide/semiconductor epitaxy*:

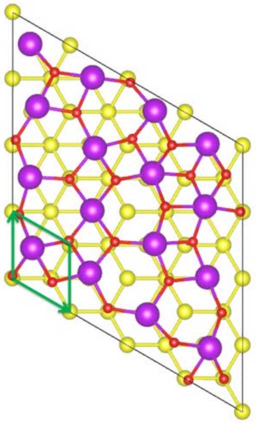


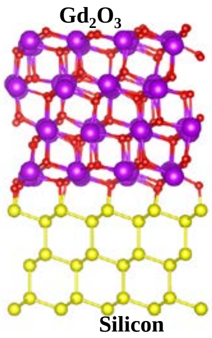
Strain



Thermal mismatch







***A. A. Demkov and A. B. Posadas**
"Integration of Functional Oxides with Semiconductors"
Springer, New York (2014).

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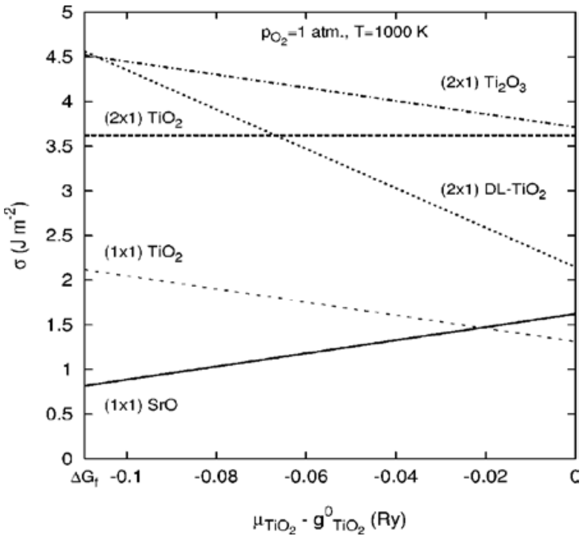
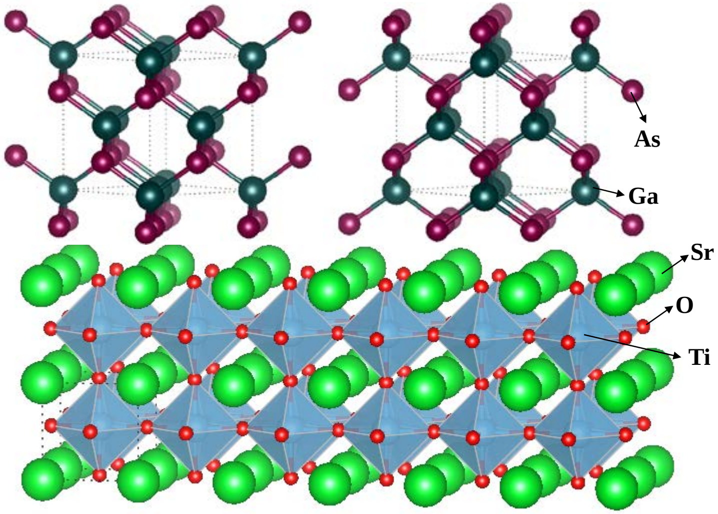
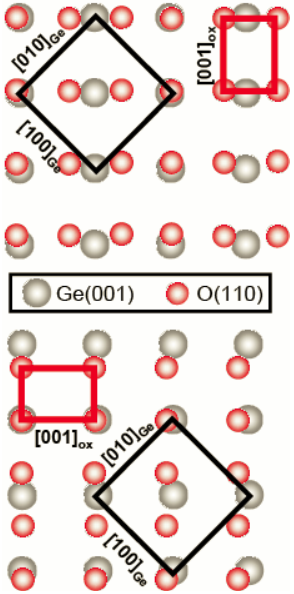
Wetting



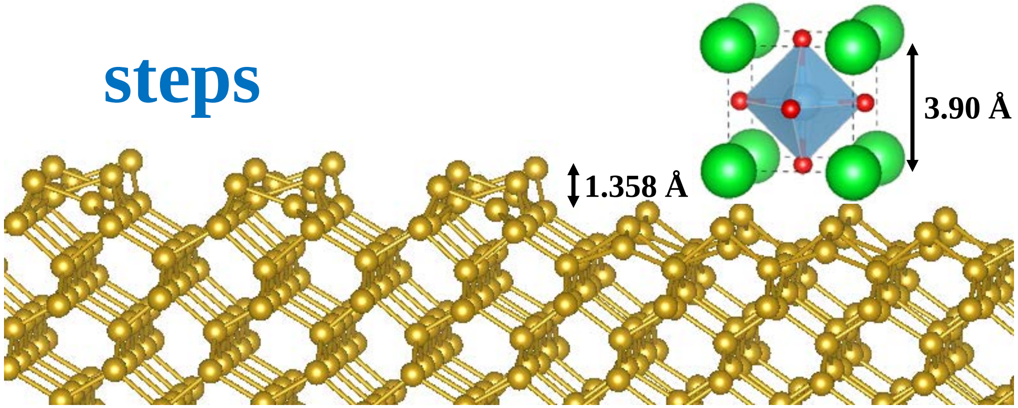
$$\gamma_{sub} > \gamma_{film} + \gamma_{interface}$$

Symmetry





steps



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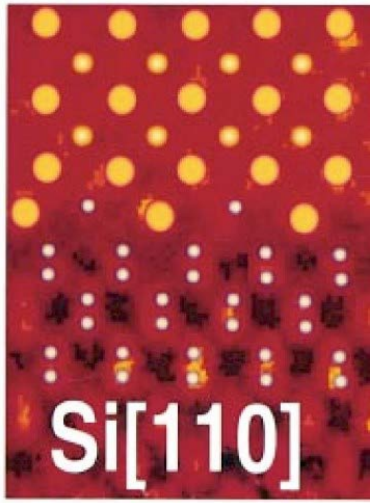
Epitaxial oxide on semiconductors

R. McKee, F. Walker, M. Chisholm, *PRL* 81 3014 (1998)
R. McKee, F. Walker, M. Chisholm, *Science 293, 468 (2001)*

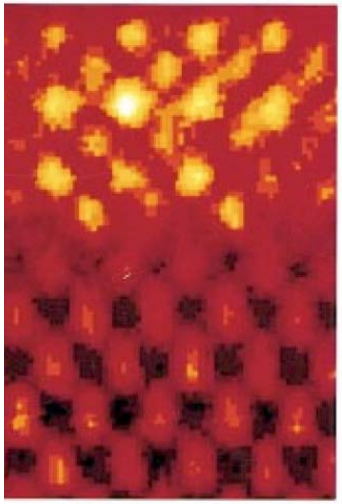
Rodney McKee and Fred Walker achieved high quality monolithic Integration of perovskites on Si and Ge

$SrTiO_3$ on Si

Model



Experiment



$BaTiO_3$ on Ge

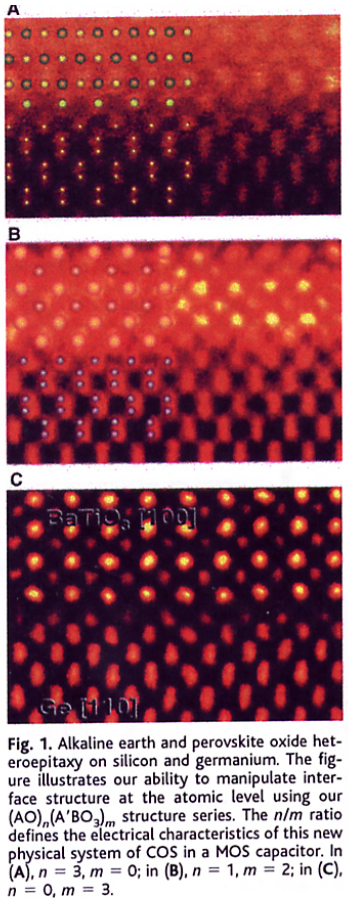
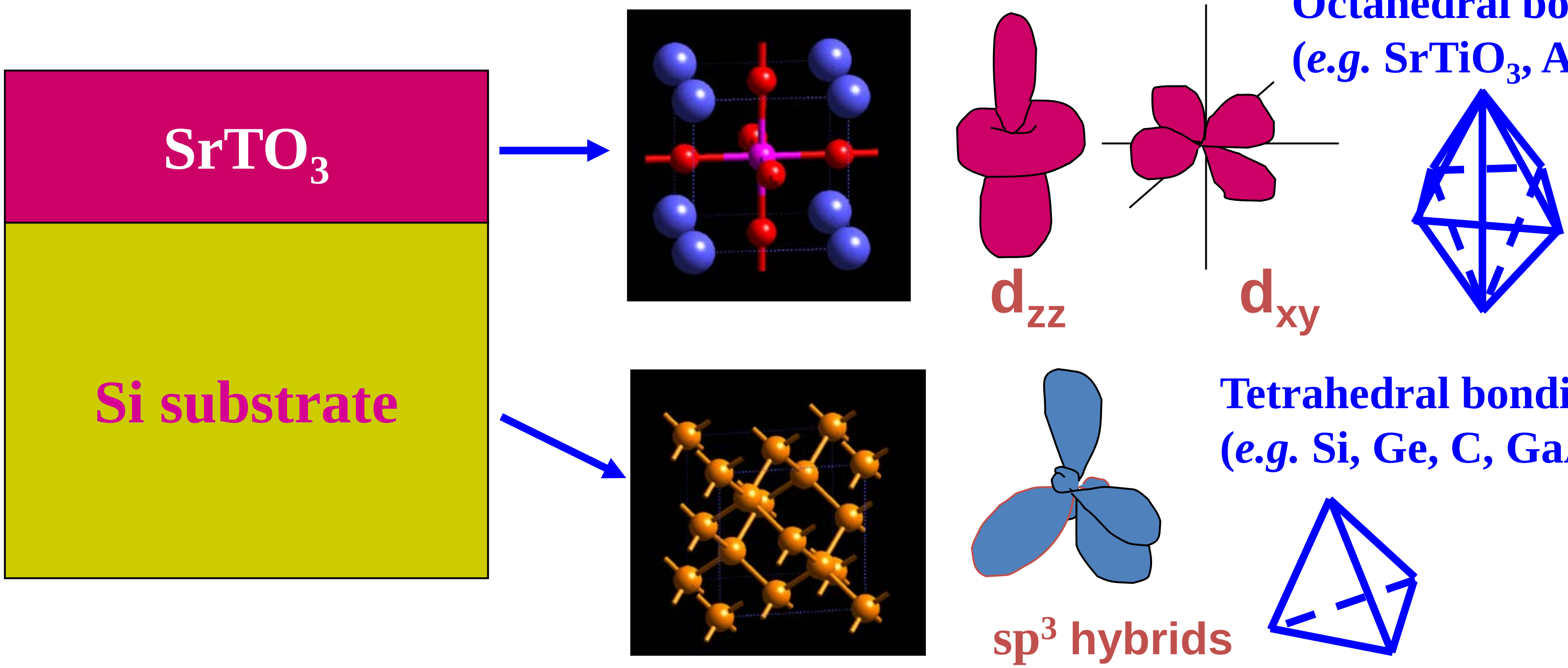


Fig. 1. Alkaline earth and perovskite oxide heteroepitaxy on silicon and germanium. The figure illustrates our ability to manipulate interface structure at the atomic level using our $(AO)_n(A'BO_3)_m$ structure series. The n/m ratio defines the electrical characteristics of this new physical system of COS in a MOS capacitor. In (**A**), $n = 3$, $m = 0$; in (**B**), $n = 1$, $m = 2$; in (**C**), $n = 0$, $m = 3$.

Question: how do you bond materials with not just different lattice constants but different types of bonding (*i.e.* ionic *vs.* covalent)?

If the energy of the interface is too high, you will get 3D growth



Octahedral bonding
(*e.g.* $SrTiO_3$, Al_2O_3)

Tetrahedral bonding
(*e.g.* Si, Ge, C, GaAs)

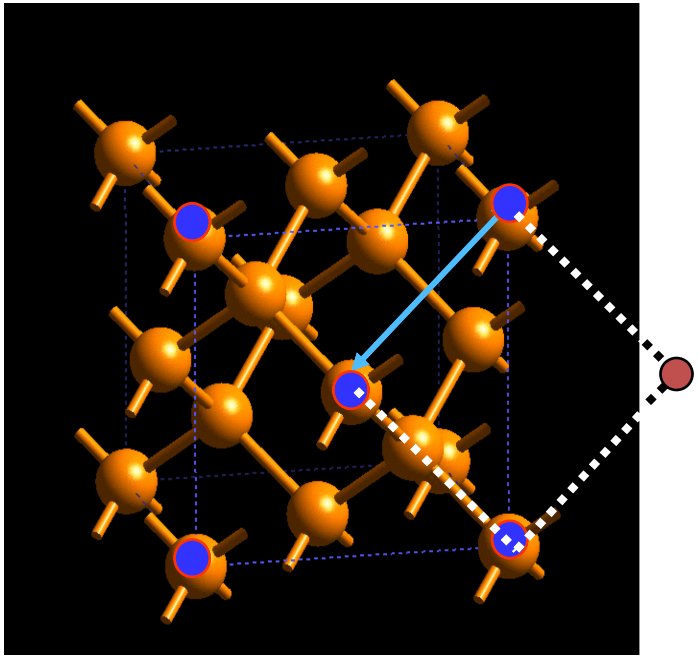
With Si-SiO_2 we have got lucky, they are both covalent sp^3 networks!

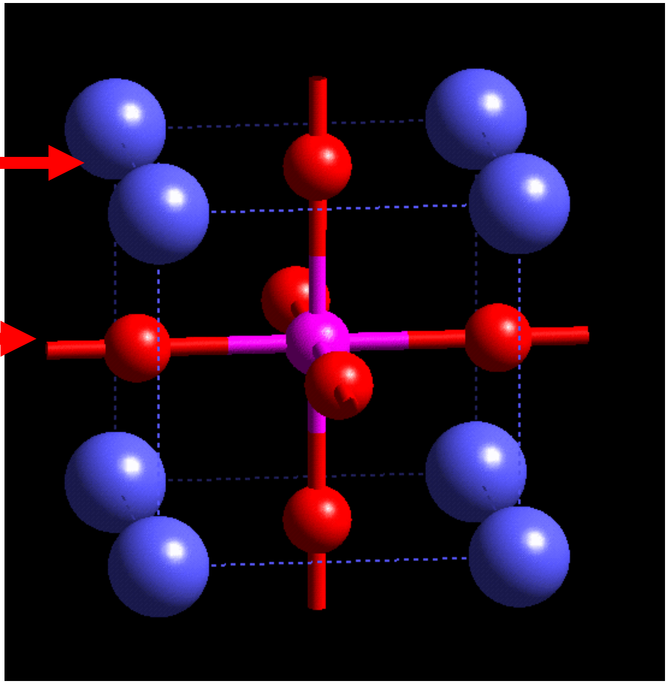
Geometry problem can be fixed:

Silicon

45 ° "rotation"

ABO_3





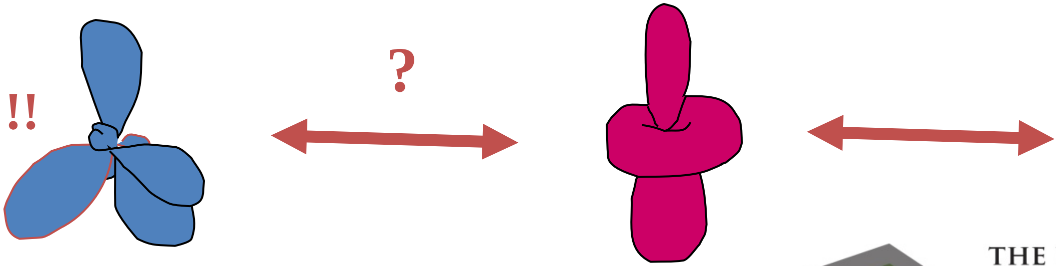
A-layer

B-layer

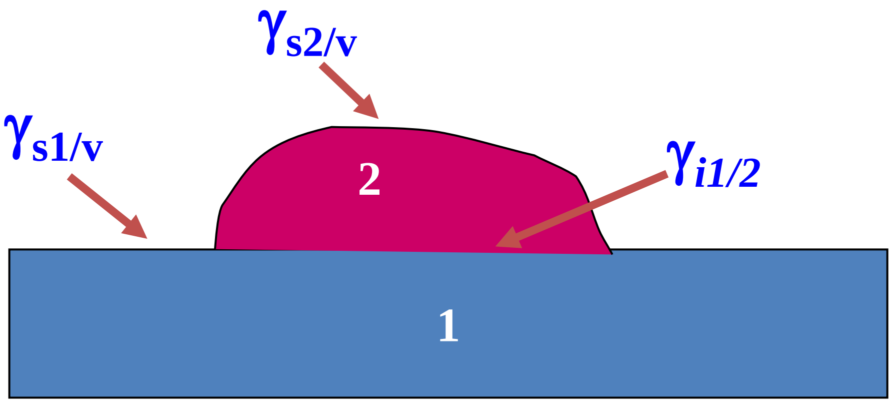
$a_{Si}/(2)^{0.5}$=3.84 Å

a_{STO}=3.905 Å

Chemistry!!!

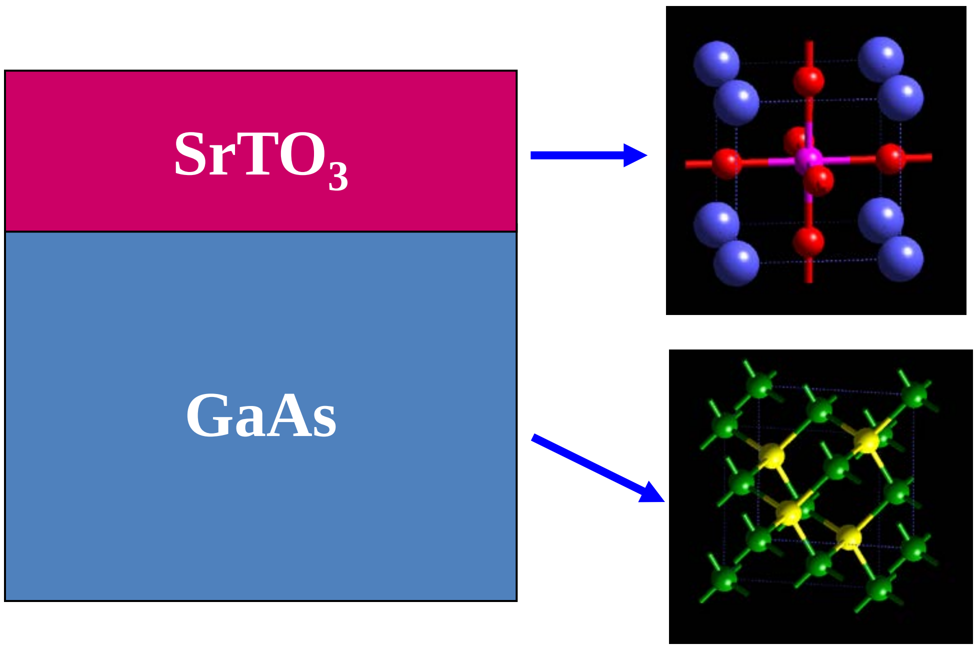


Zintl template

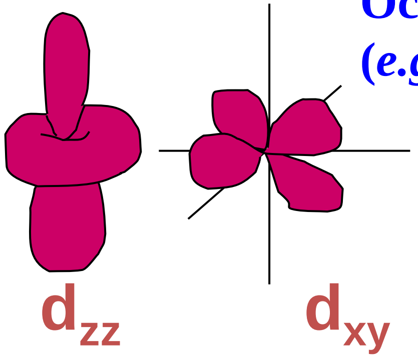


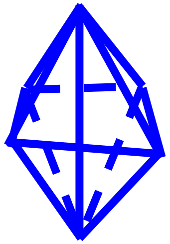
2D growth condition:

$$\gamma_{s1/v} > \gamma_{s2/v}+\gamma_{i1/2}$$

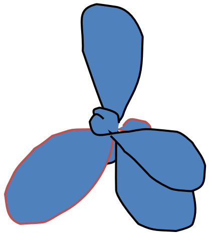


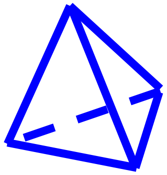
Octahedral bonding (*e.g.* $SrTiO_3$, Al_2O_3)





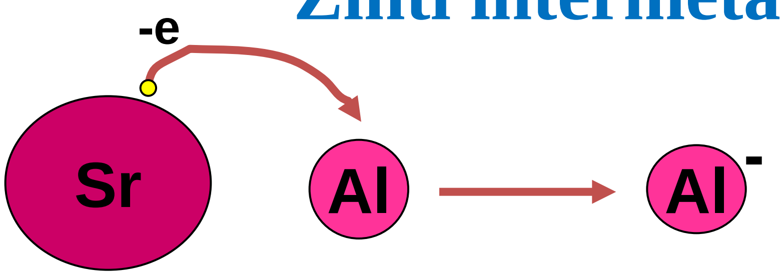
Tetrahedral bonding (*e.g.* Si, Ge, C, GaAs)

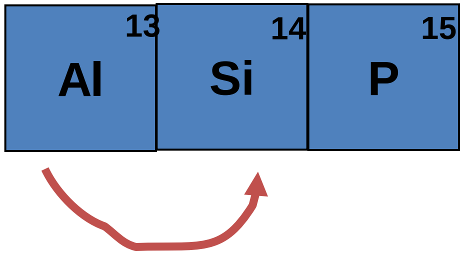




- **Stable interlayer reduces the interface energy**
- **Mixed bonding serves as a bridge**

Zintl intermetallics: SrAl$_2$



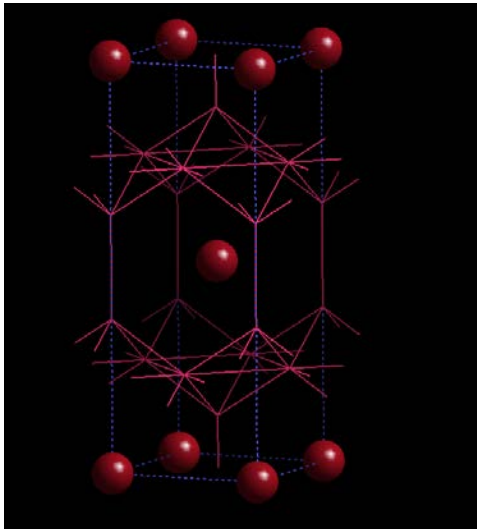


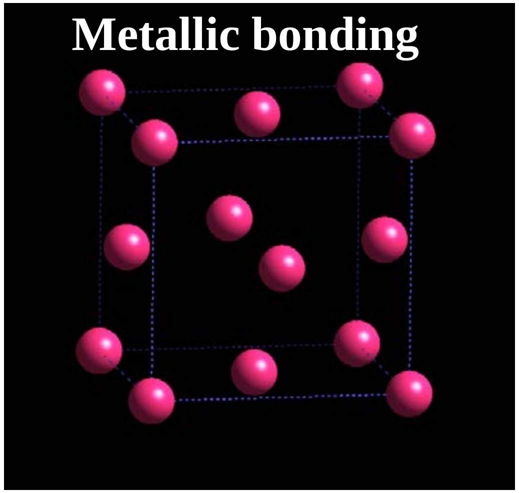
Zintl Alchemy:

Charge transfer makes electro-negative metal behave as if it were in the next column of the Periodic Table: Al → Si

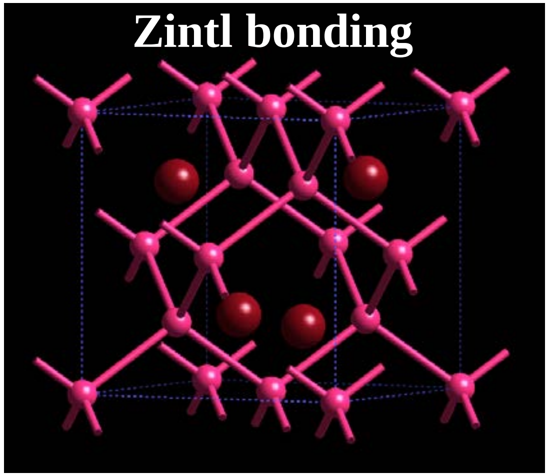
Edward Zintl (1898-1941)

tI10 SrAl$_4$ structure

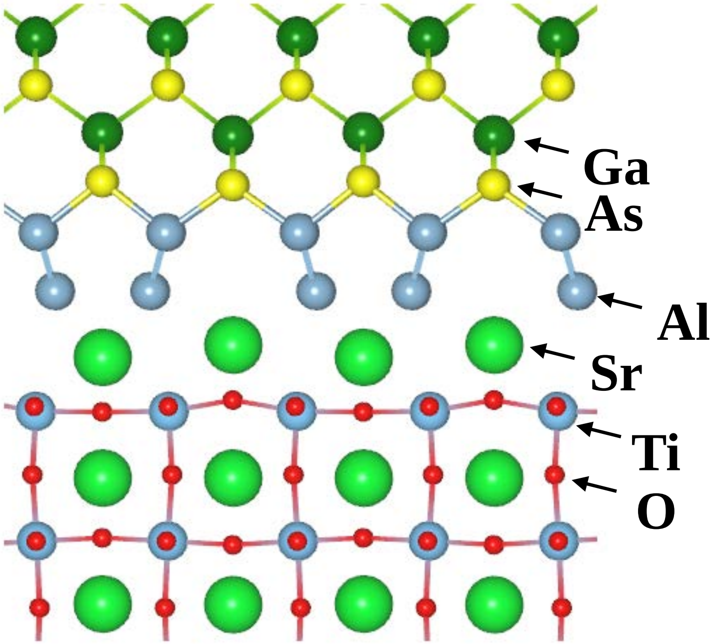


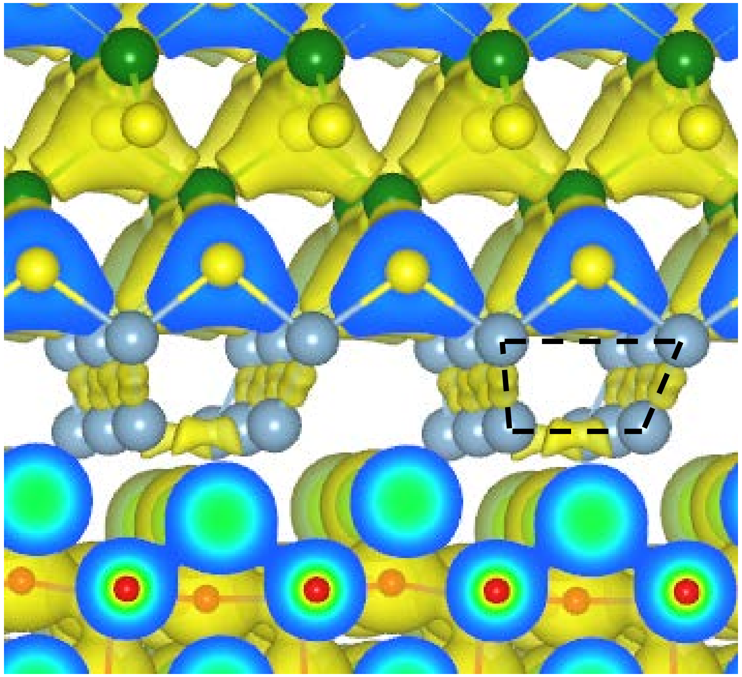


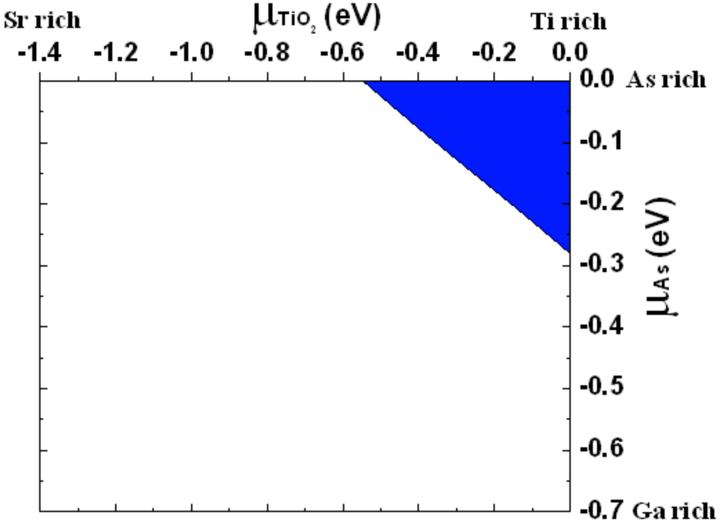
fcc Al metal

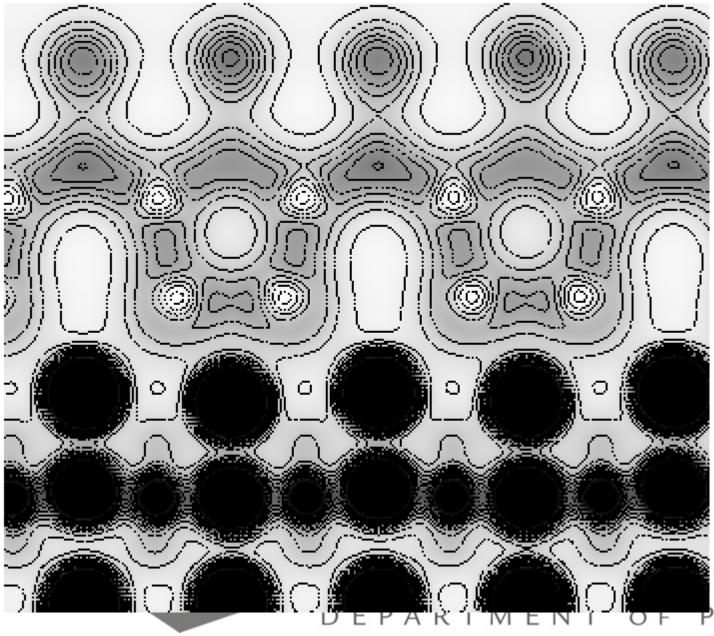


SrAl$_2$ structure





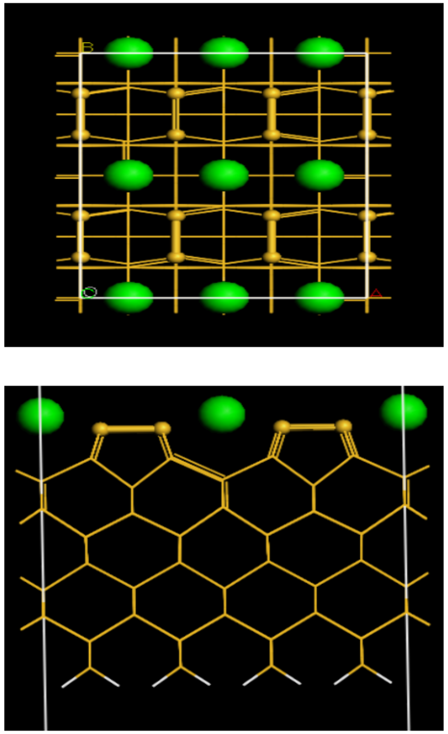




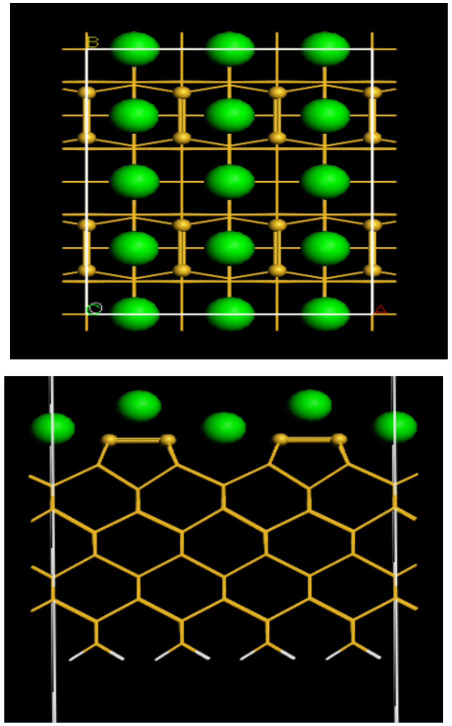
Demkov et al. Appl. Phys. Lett. 100, 071602 (2012).

Electropositive metal template: ½ ML Sr results in 2D growth

Sr on Si(001):



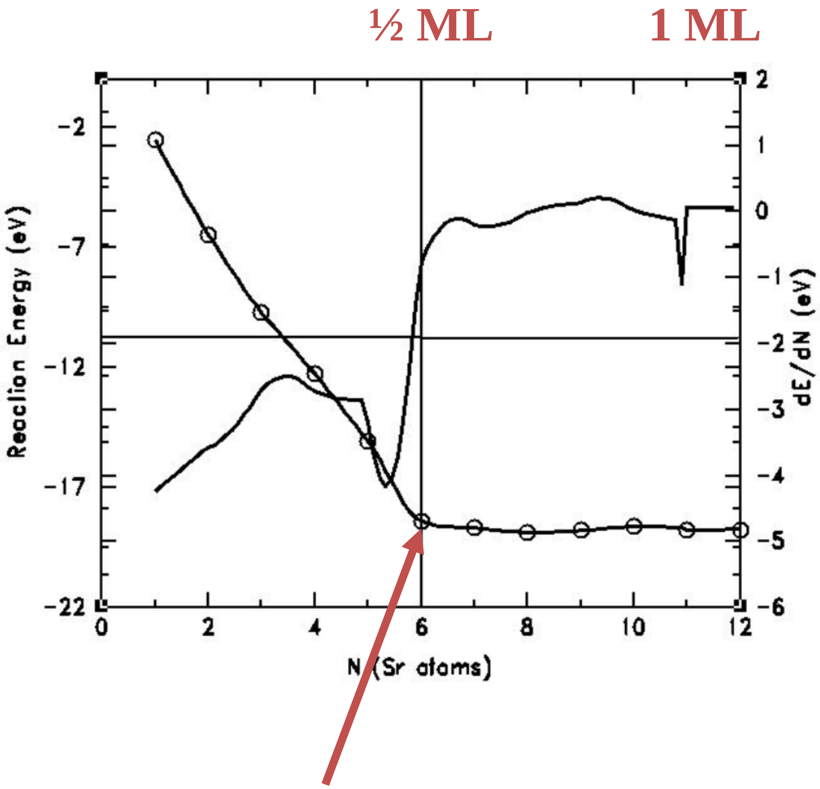
½ ML 2x1



1 ML 2x1

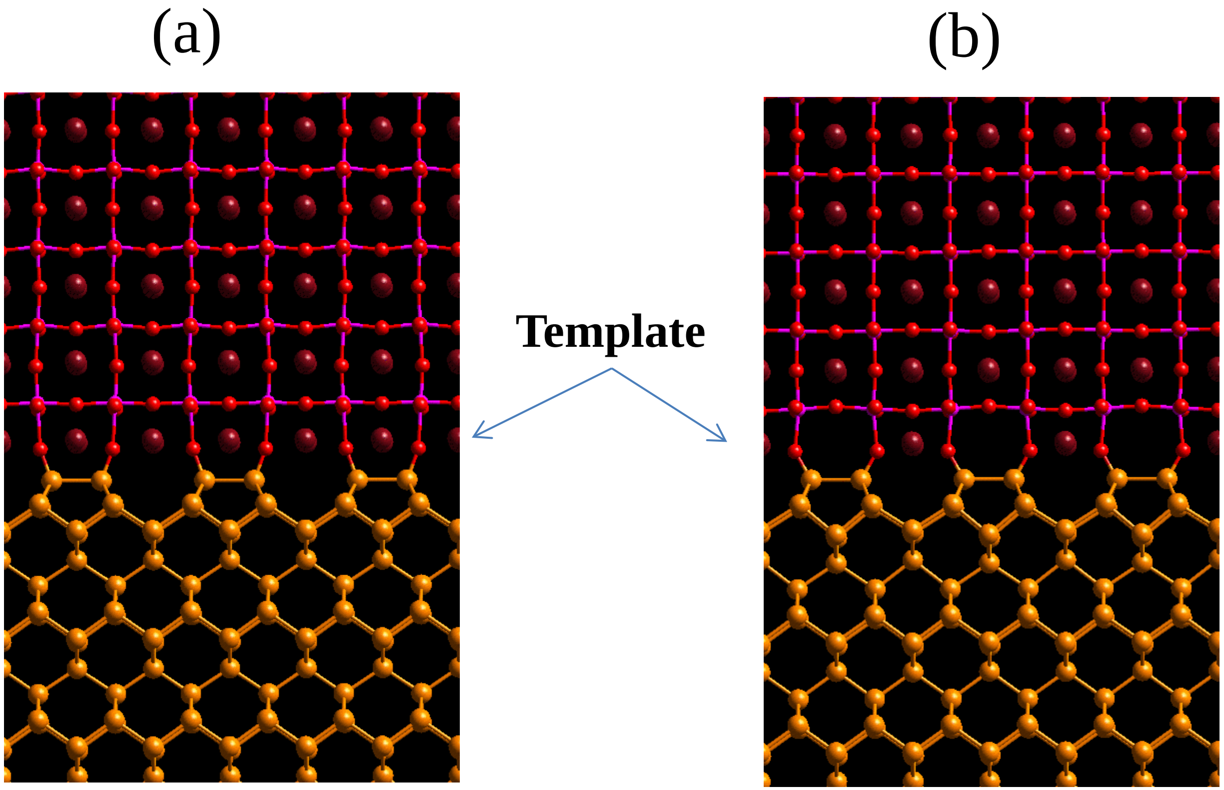
McKee, et al., *PRL* 81 3014 (1998)
Droopad, *et al.*, J. of Crystal Growth, 251, 638 (2003).
Demkov, *et al.*, J. of Appl . Phys., 103, 103710 (2008).
Demkov, *et al.*, Appl. Phys. Lett. 100, 071602 (2012).
A. Slepko,, *et al.*, Phys. Rev. B 85, 195462 (2012).

$$E_r=E_{Sr@Si}-NE_{Sr}-E_{Si}$$
$$\mu=dE_r/dN$$



$SrSi_2$ (Zintl) stoichiometry

$SrTiO_3$/Si interface structure

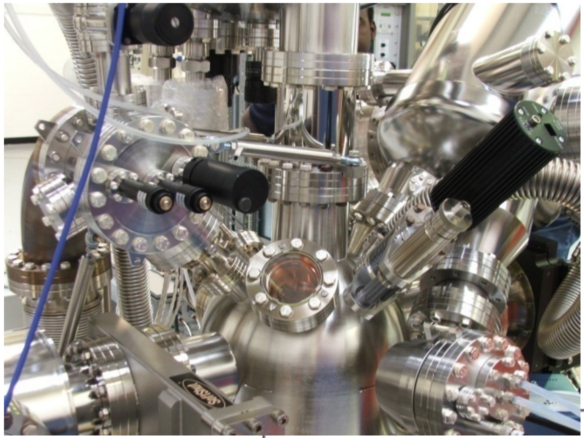


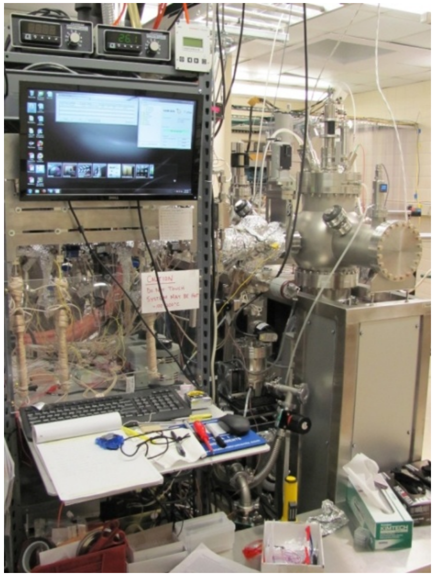
Edward Zintl
1898-1941

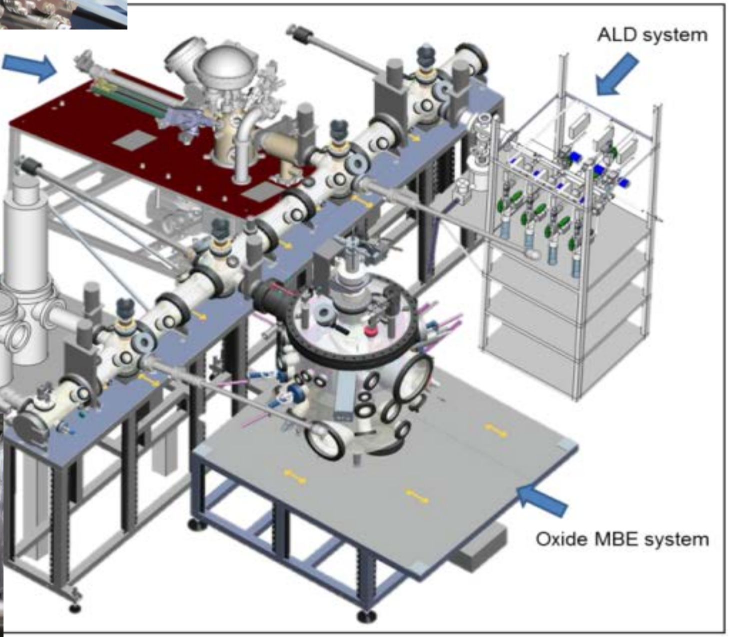
Both structures have 2x1 symmetry. Structure (a) has a full ML of Sr at the interface (1ML), structure (b) has a half ML of Sr at the interface (1/2 ML)

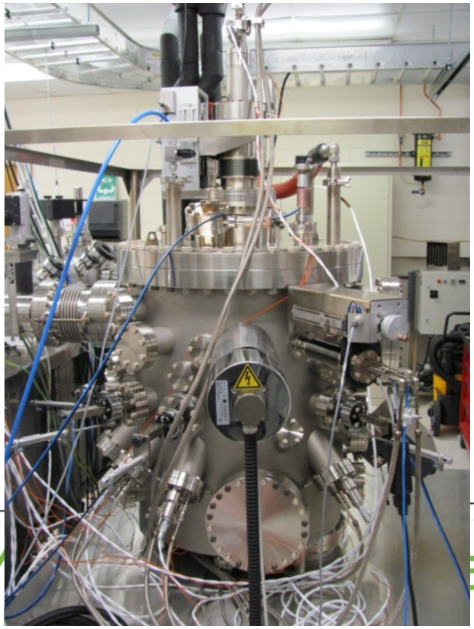
X. Zhang, A.A. Demkov, H. Li, X. Hu, Y. Wei, and J. Kulik, Phys. Rev. B 68, 125323 (2003).

Growth and in-situ characterization

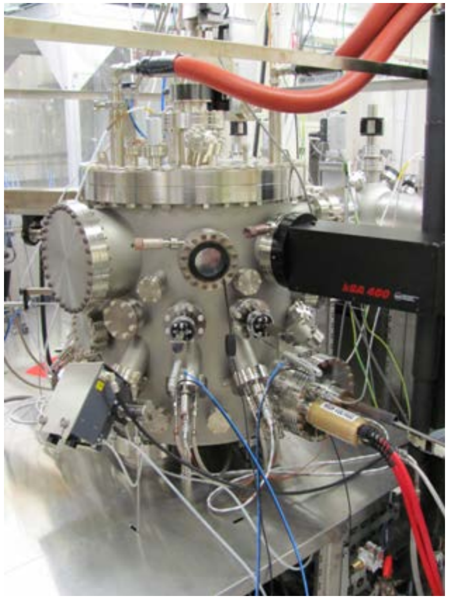








$SrTiO_3$ deposition on Si



- Sr-assisted SiO_2 desorption
- ½ monolayer Sr on Si

  (Zintl template layer)

Edward Zintl
1898-1941

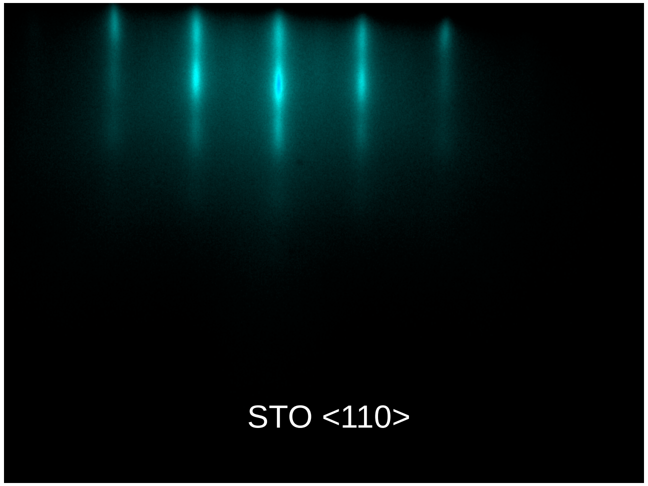
- Initial amorphous $SrTiO_3$ seed layer at 200°C (4 unit cells)

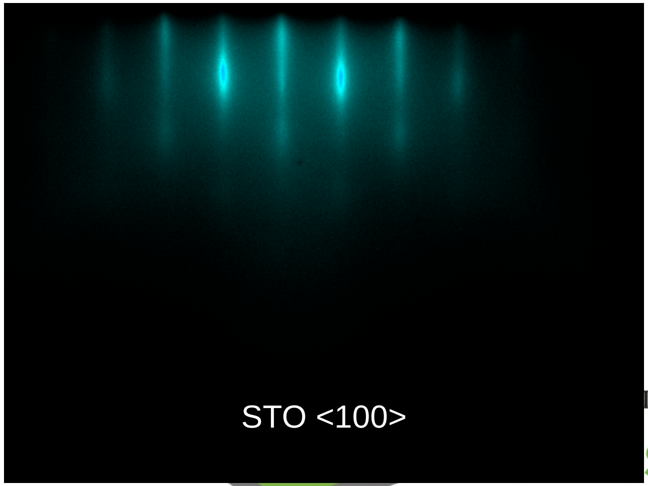
  Crystallize at 550°C
- Main $SrTiO_3$ deposition

  $4x10^{-7}$ torr O_2 at 550°C

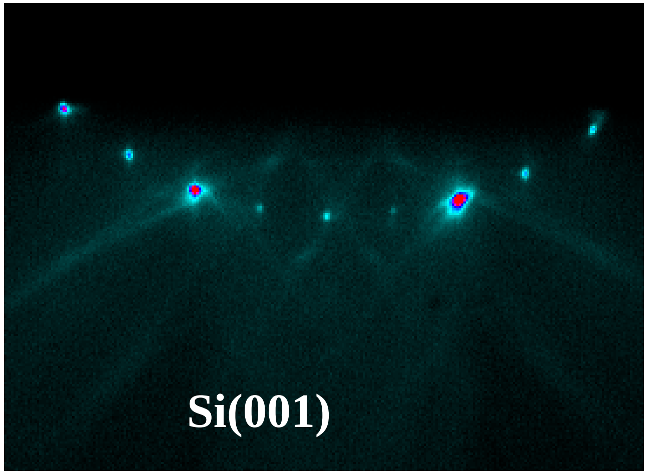
  Co-evaporation of Sr and Ti at 1 monolayer per minute

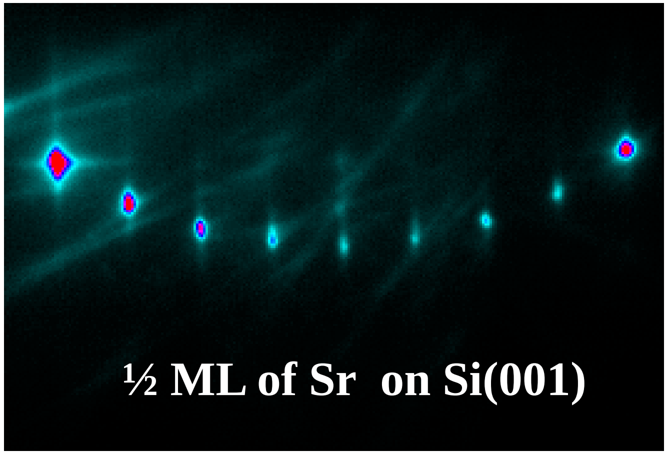
  20 unit cells (fully relaxed)


STO <110>

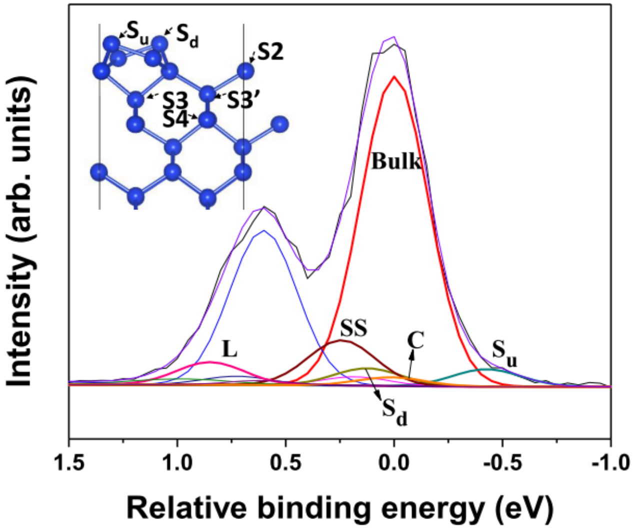

STO <100>

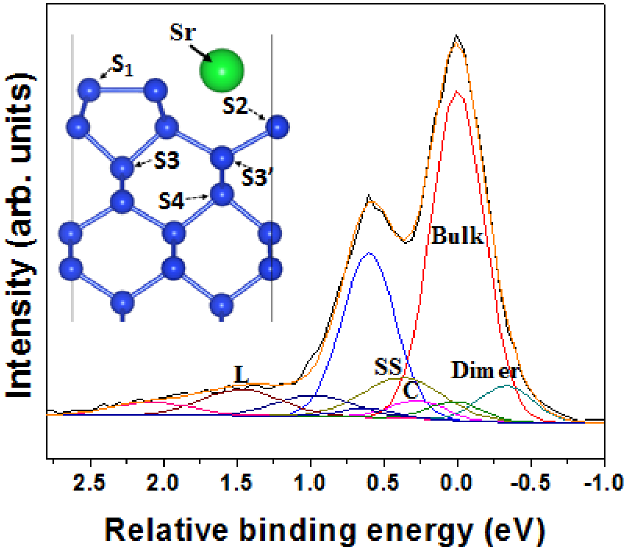
RHEED





XPS





M. Choi, et al., Appl. Phys. Lett. **102**, 031604 (2013).

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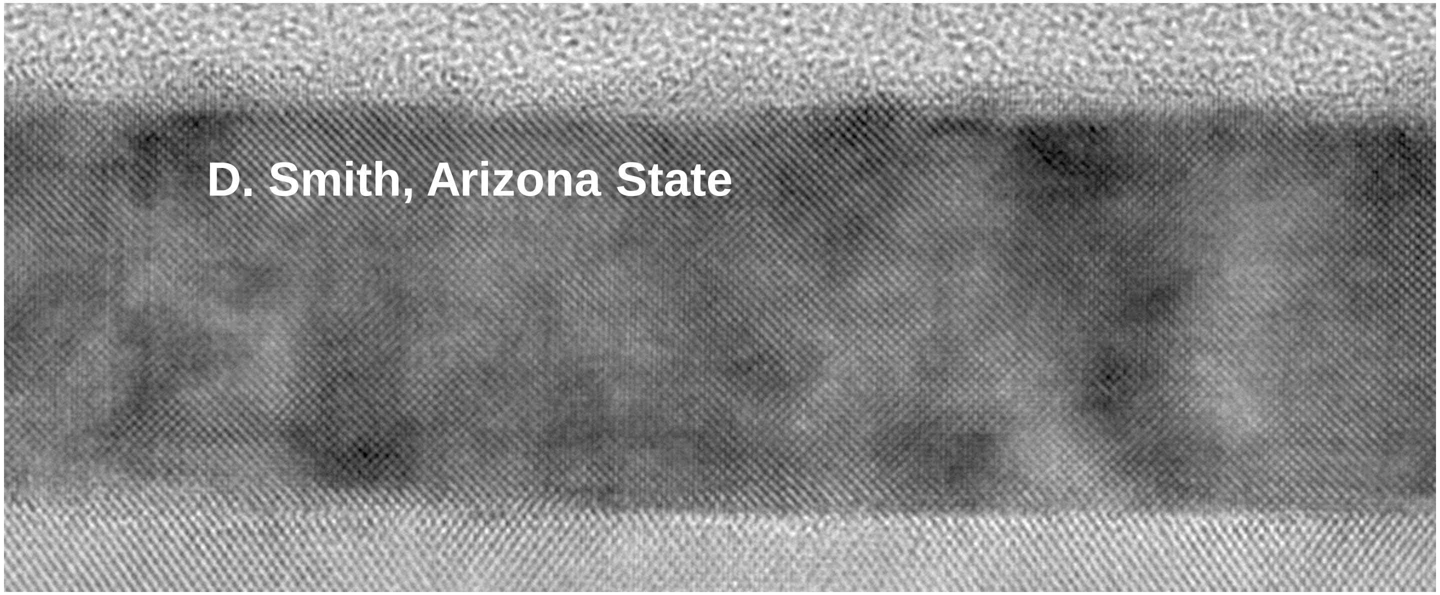
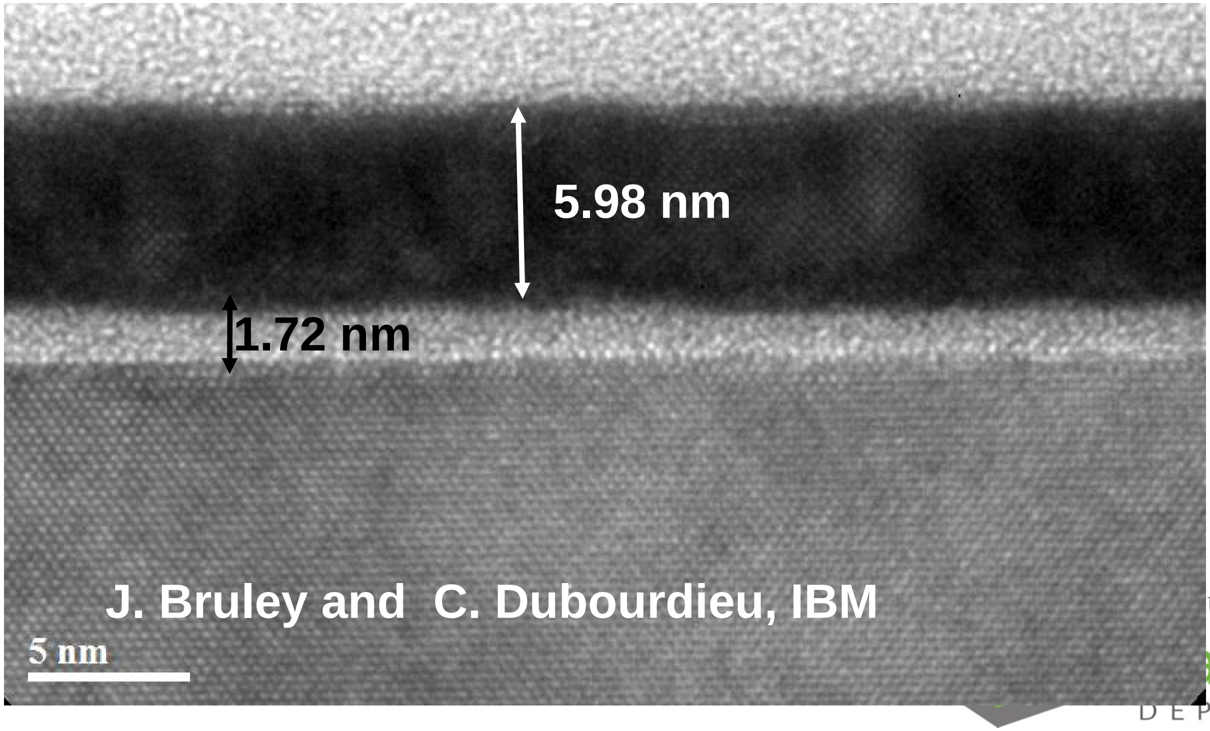


D. Smith, Arizona State



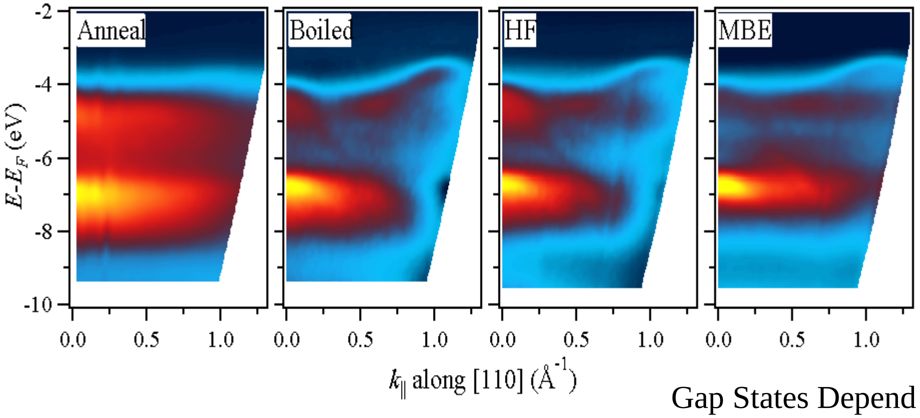
J. Bruley and C. Dubourdieu, IBM

Surface quality by ARPES

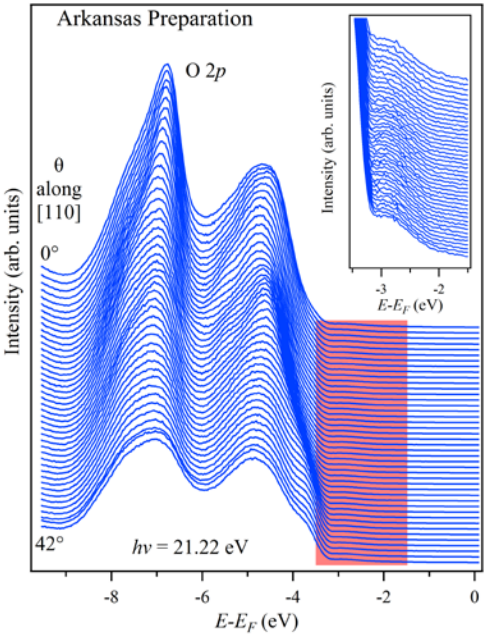
$SrTiO_3$ Surface Preparations

Rough Surface

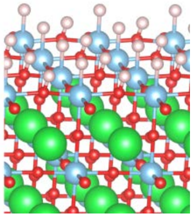
Smooth Surface



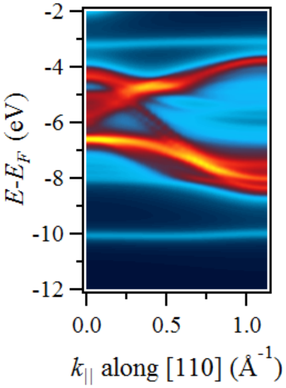
Adsorbates?



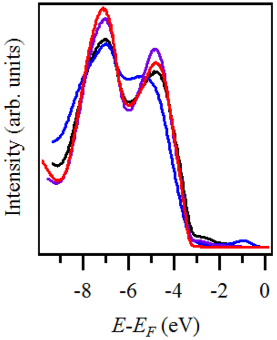
H on Ti and O

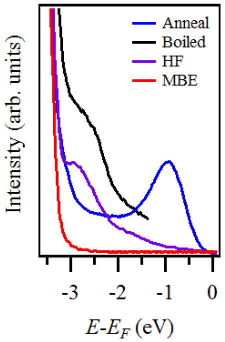


DFT



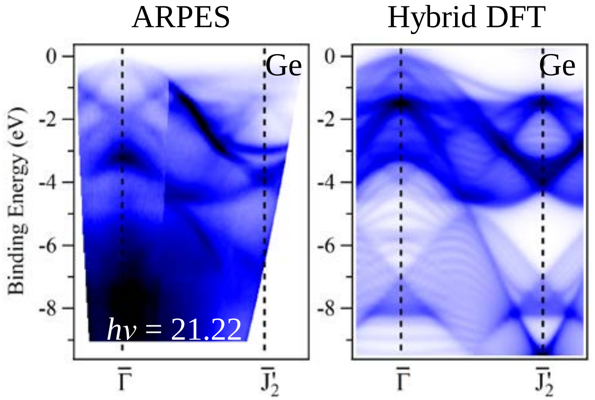
Gap States Depend on Preparation



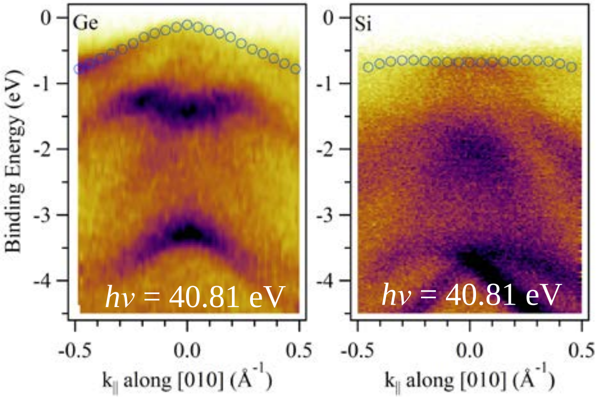


Semiconductor Surfaces

Does Theory Work?



Surface States In Gap!



R. C. Hatch, et al., J. Appl. Phys. **114**, 103710 (2013).
H. Seo, et al., Phys. Rev. B **89**, 115318 (2014)

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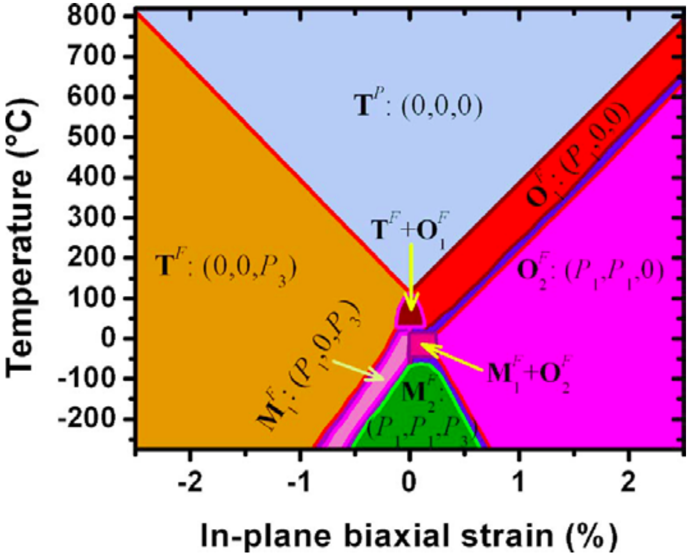
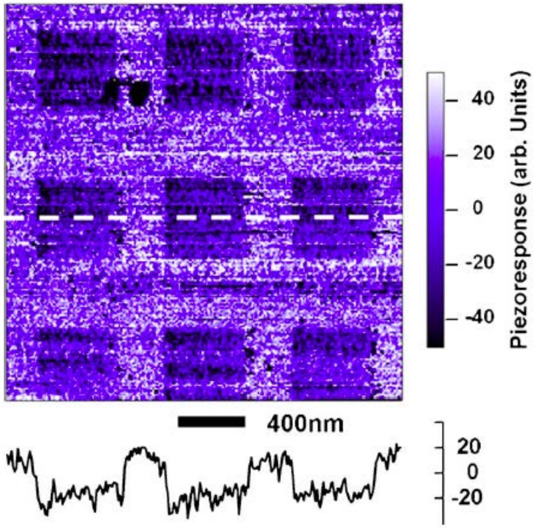
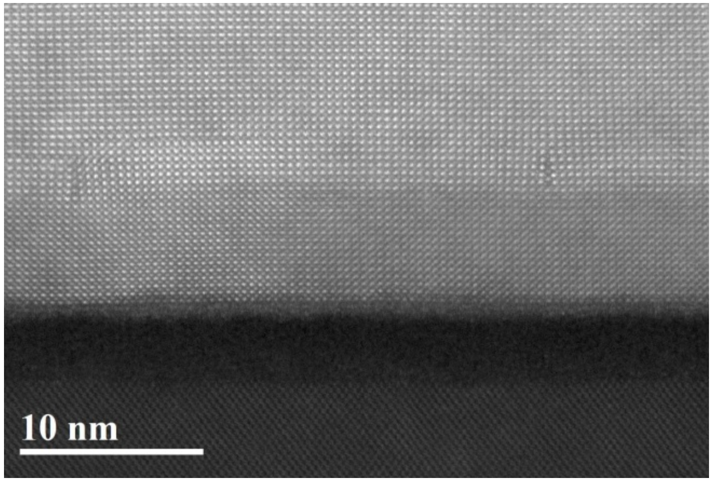
Strain stabilized out-of-plane ferroelectricity

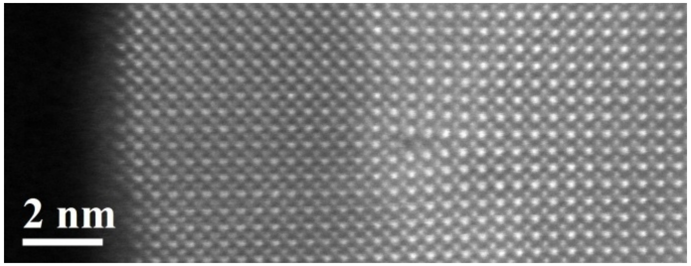


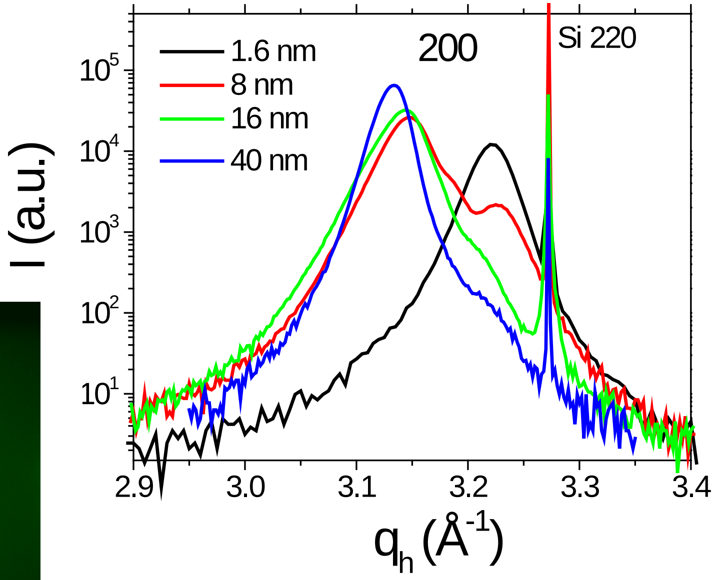


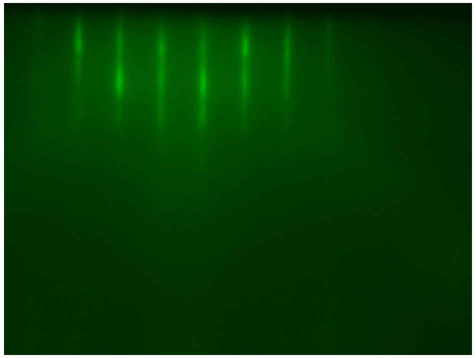
V. Vaithyanathan, J. Lettieri, W. Tian, A. Sharan, A. Vasudevarao, and Y. L. Li, A. Kochhar, H. Ma, and J. Levy, P. Zschack, J. C. Woicik, L. Q. Chen, V. Gopalan, and D. G. Schlom, J. Appl. Phys. 100, 024108 (2006).

Ferroelectric $BaTiO_3$ on Si (001)

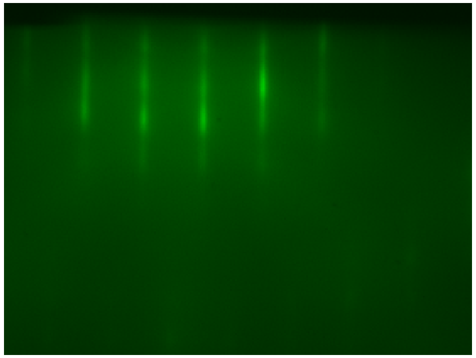








$BaTiO_3$ <100>



$BaTiO_3$ <110>

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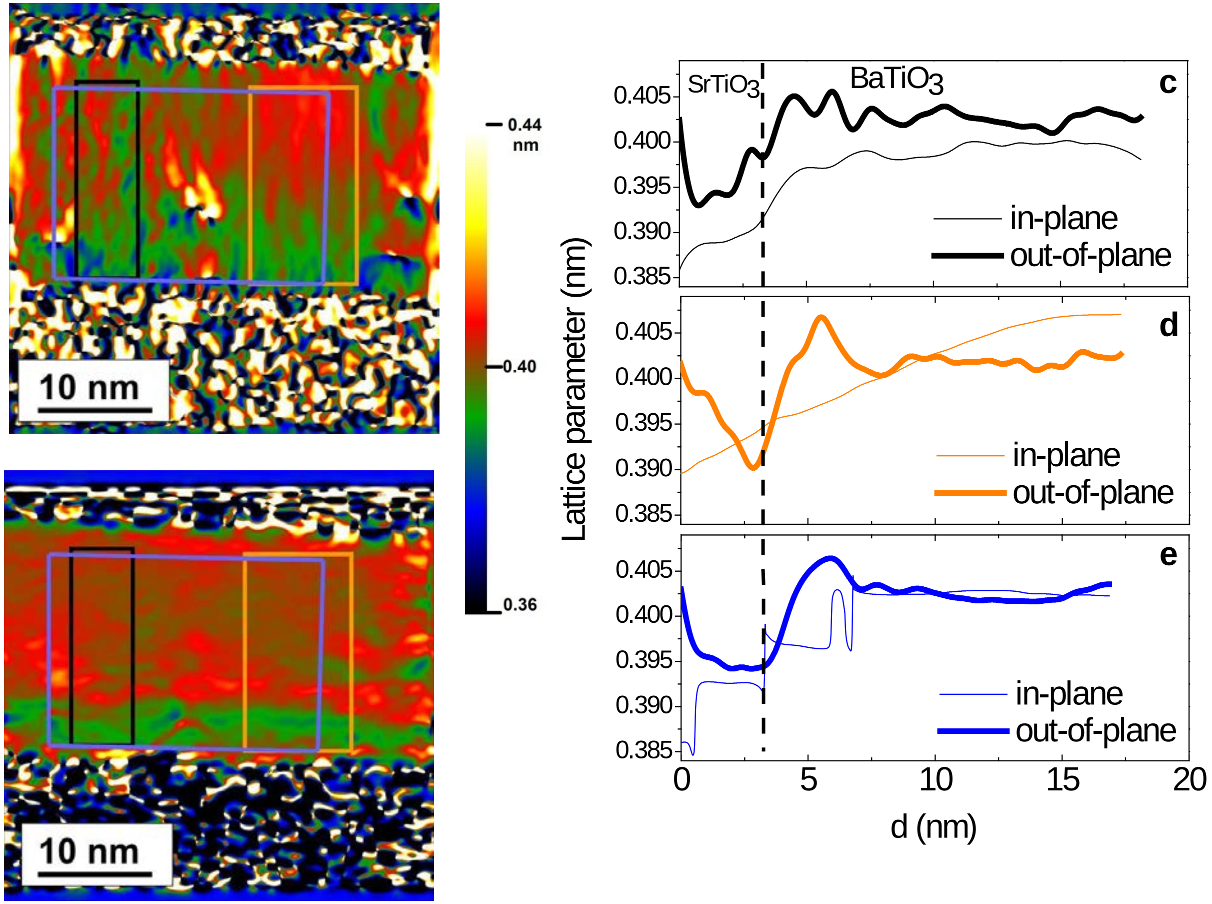
a

16 nm $BaTiO_3$ strain analysis



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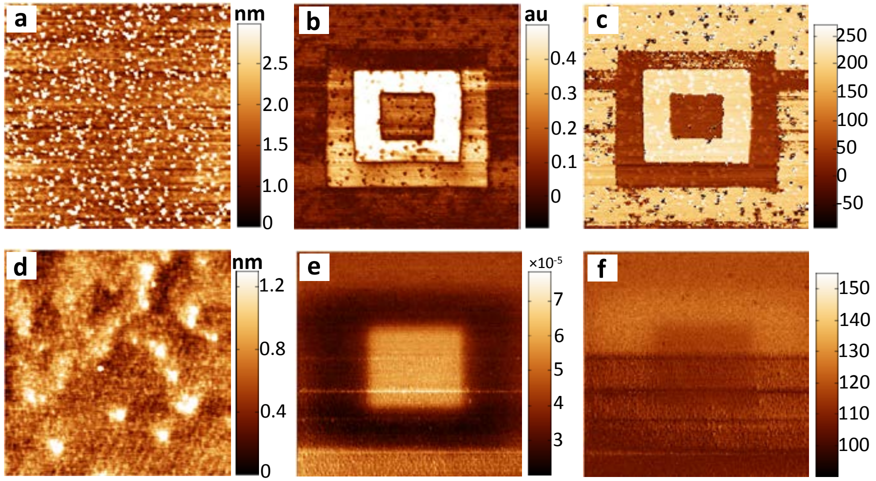
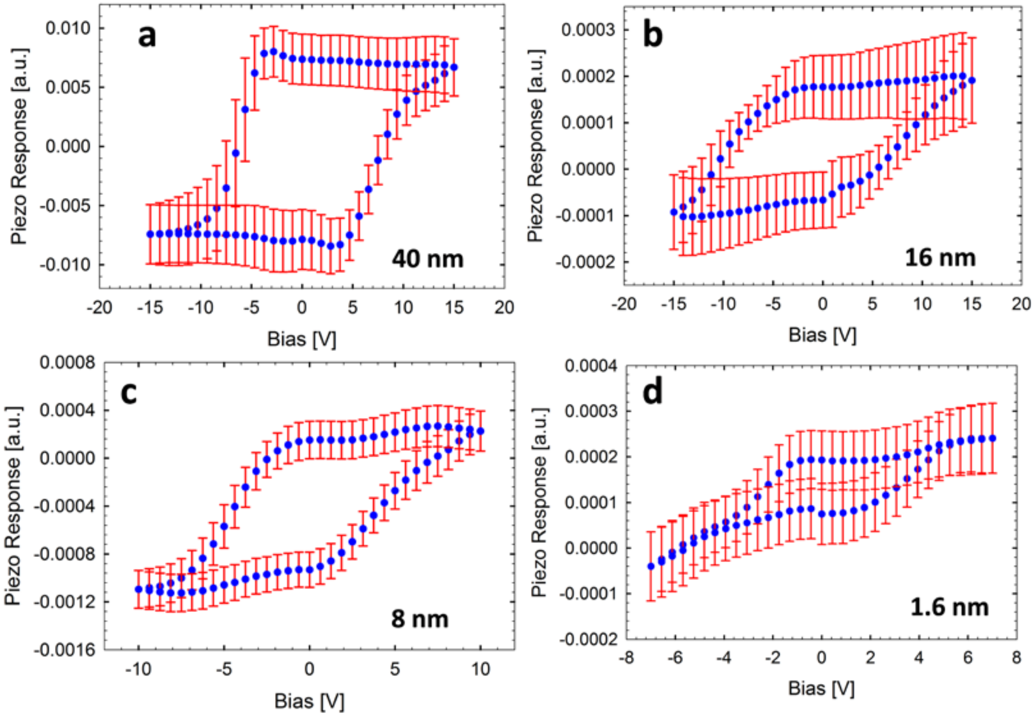


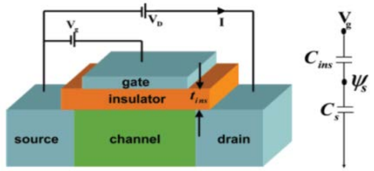
16 nm BTO

1.6 nm BTO

AFM **amplitude** **phase**



Summary: BaTiO$_3$ on Si (001)



Use of Negative Capacitance to Provide Voltage Amplification for Low Power Nanoscale Devices

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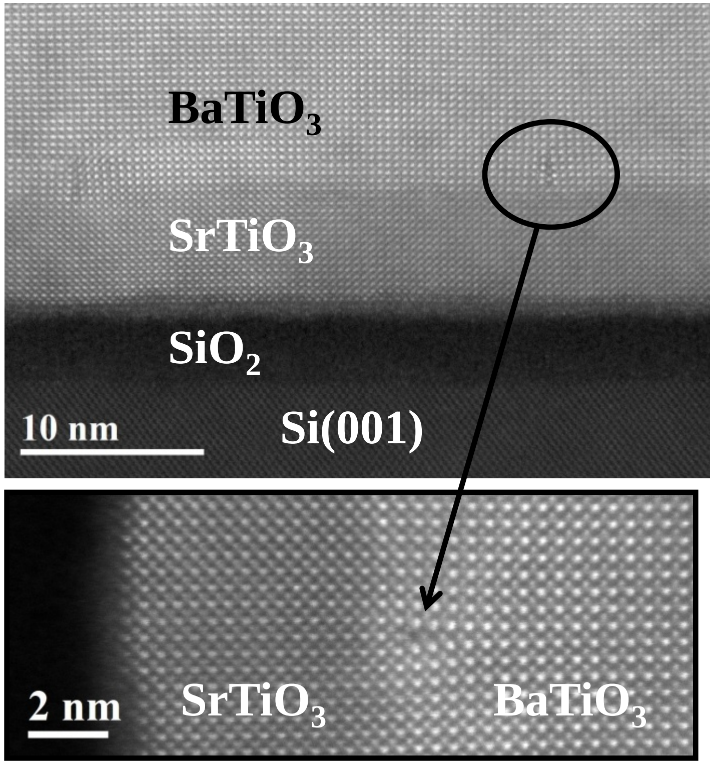
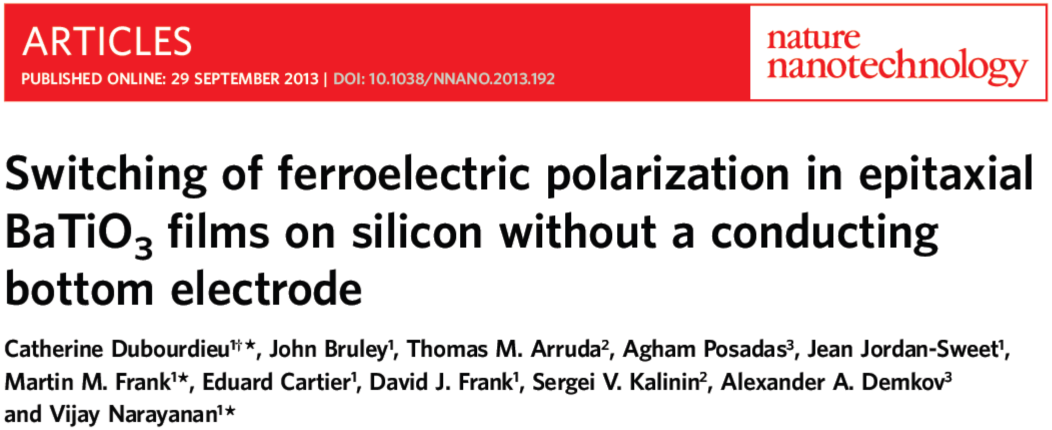


Integration of a ferroelectric layer into the CMOS gate stack enables the use of a new phenomenon "negative capacitance" in a traditional field effect transistor to reduce the power consumption. TEM allows optimizing the growth process to achieve a true ferroelectric state indicated by hysteretic loops.



ARTICLES

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nature nanotechnology

Switching of ferroelectric polarization in epitaxial BaTiO$_3$ films on silicon without a conducting bottom electrode

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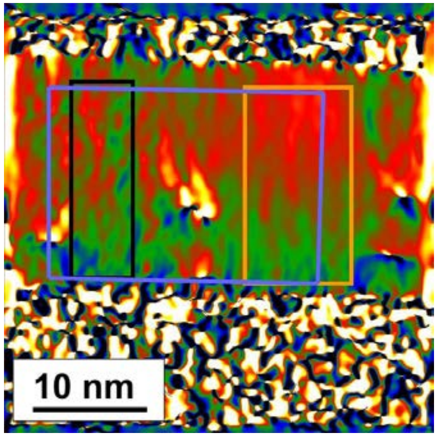
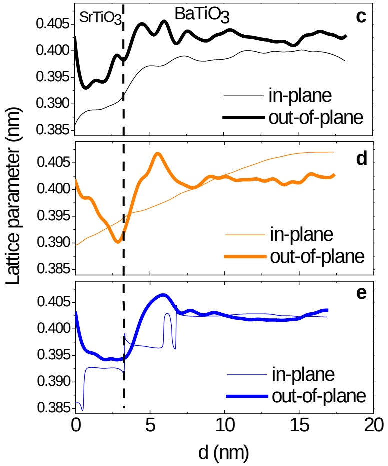
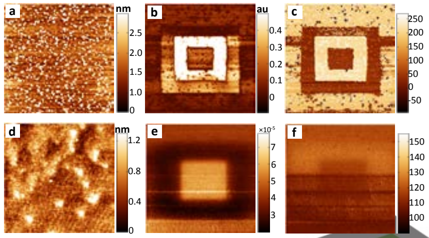
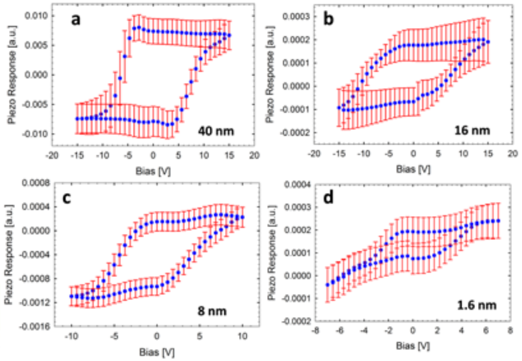


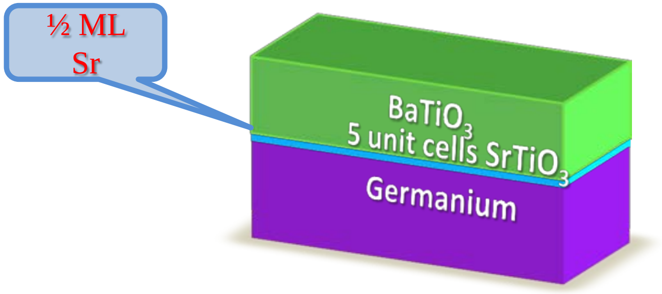


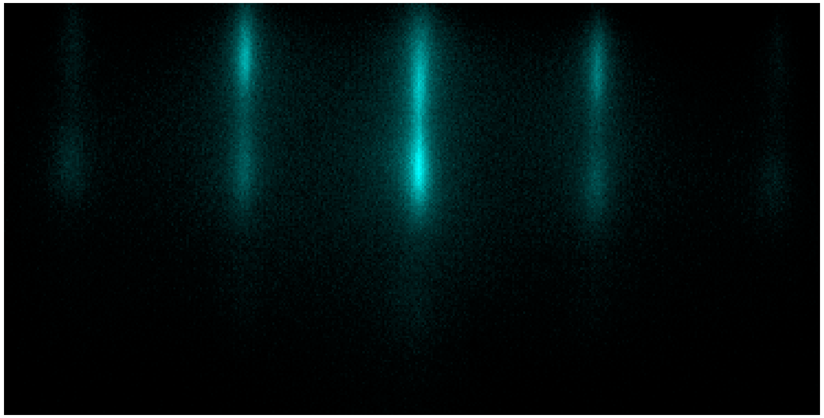




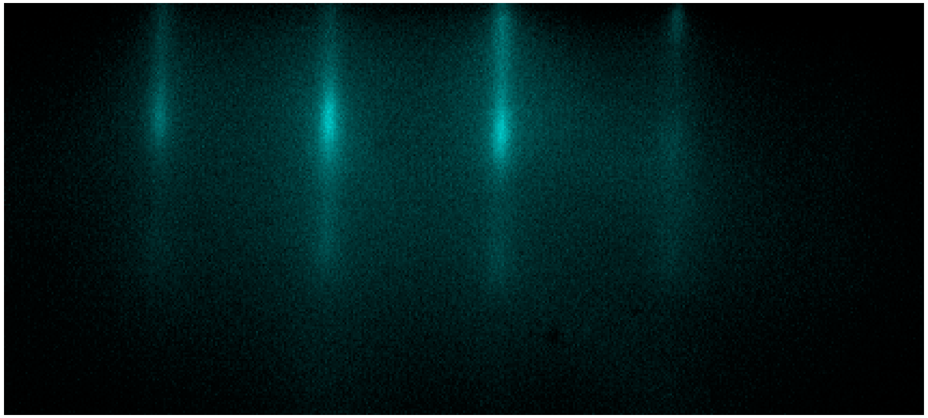
Ferroelectric on Ge: BTO/STO/Ge (001)

- ½ ML Sr on Ge (550°C)
- Shuttered growth of 5 unit cells of STO at 200°C => Anneal to 700°C for crystallization
- Shuttered deposition of BTO at 700°C





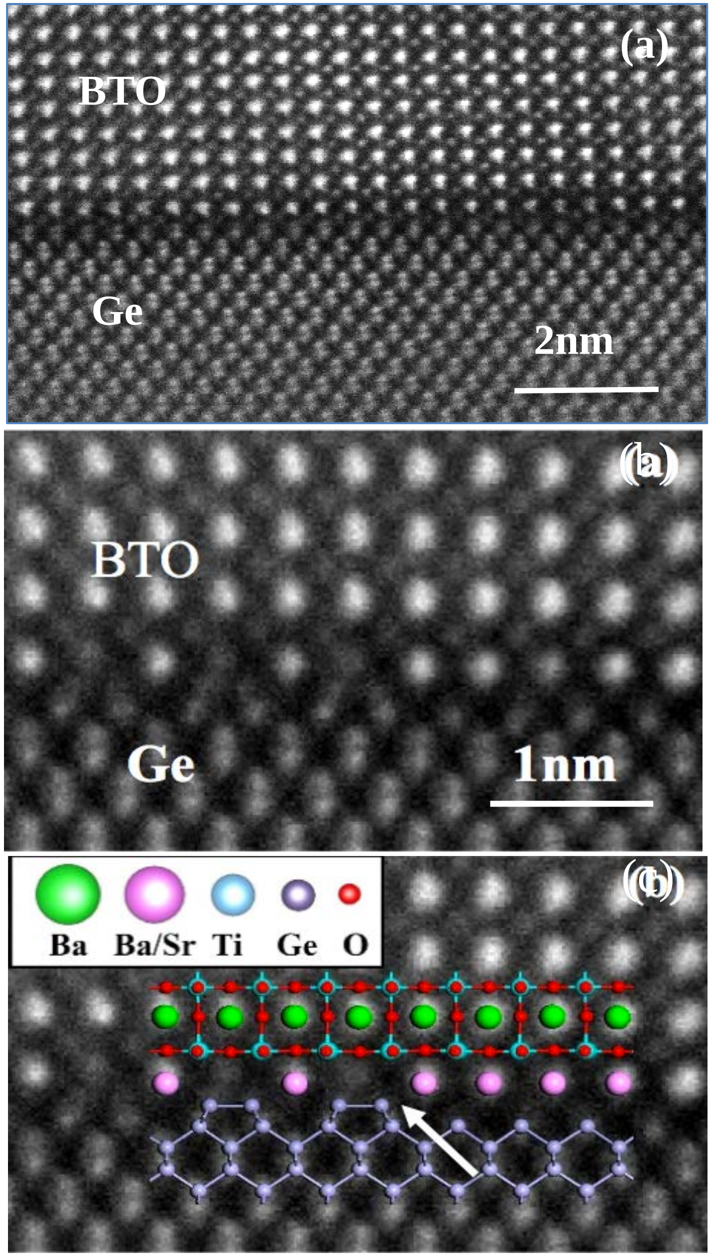
RHEED: 2-nm thick epitaxially grown STO film on Ge taken along the <110> direction of STO

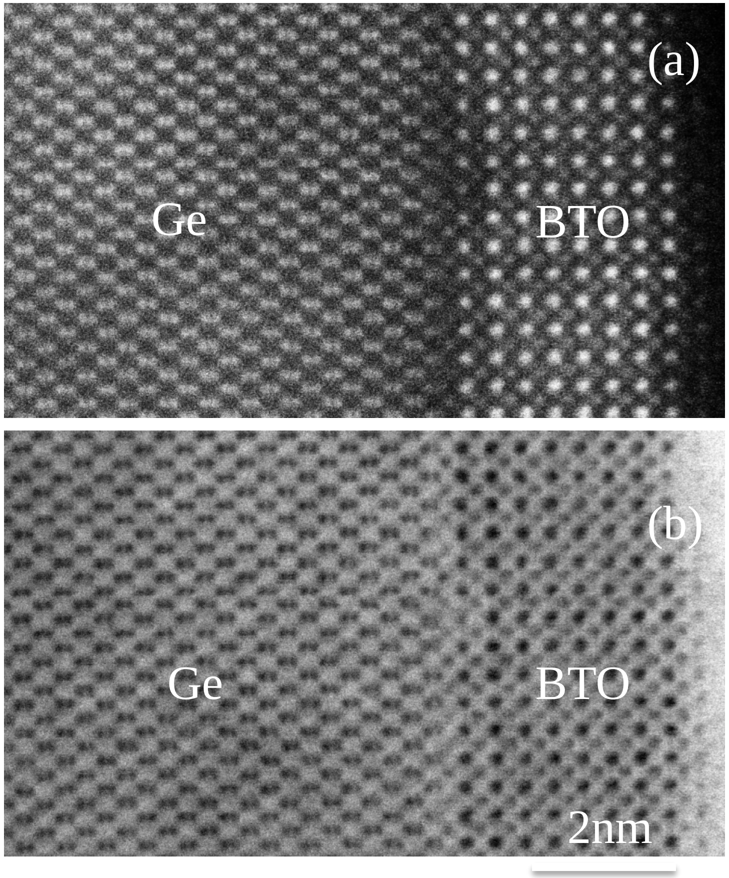


RHEED: 16-nm thick epitaxially grown BTO film on STO

Aberration-corrected STEM: BTO/Ge(001) interface

K. D. Fredrickson, et al., Appl. Phys. Lett. **104**, 242908 (2014).





BTO/Ge(001) heterostructure grown by MBE. Left: a) HAADF image showing abrupt BTO/Ge interface; b) Enlargement showing 2x and 1x periodicities of Ge(001) surface; c) Structural model. Right: *Sample imaged at 120keV*: a) HAADF image; b) BF image.

Summary

- High quality BTO with in-plane polarization may be grown directly on Si (001).
- High quality BTO with in-plane polarization may be grown directly on Ge (001).
- Using a thin STO buffer layer stabilizes out-of-plane polarized BTO on Ge.