Physics as a Journey

and

Integration of Ferroelectric Oxides on Semiconductors

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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
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 in 1934.
My advisor: Otto Sankey

John Page

Kevin Schmidt

Mike O'Keefe
Electronic Structure Theory

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

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

\[
H_e \chi(r) = E_e \chi(r)
\]

\[
[T_n + E_e(R)] \phi(R) = E \phi(R)
\]

\[
E_{KS}[n] = \left\langle \hat{\psi} | H | \hat{\psi} \right\rangle = E_{K.E}[n] + E_{\text{Ryv}}[n] + E_{\text{electron}}[n] + E_{\text{ion-ion}} + E_{\text{XC}}[n]
\]

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

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

\[
F_i = -\frac{\partial E}{\partial R_i} \quad \rightarrow \quad F_i = m_i \ddot{x}_i
\]

\[
H = -t \sum_{\left\langle i, j, \sigma \right\rangle} c_{i, \sigma}^\dagger c_{j, \sigma} + U \sum_{i=1}^{N} n_{i\uparrow} n_{i\downarrow}
\]
Motorola
Physical Sciences Research Lab
Tempe, Arizona
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 ...

THE UNIVERSITY OF TEXAS AT AUSTIN
Materials Physics Lab
department of physics
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
Theory, algorithms and computation

Materials characterization

Materials Growth

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
Prof. K. Lai
Dr. A. Posadas
M. Choi
Dr. R. Hatch
Dr. S. Kalinin
Oxides

Quartz $\text{SiO}_2$

Hematite $\text{Fe}_2\text{O}_3$

Ilmenite $\text{FeTiO}_3$

Cassiterite $\text{SnO}_2$

Perovskite $\text{CaTiO}_3$

Uraninite $\text{UO}_2$

Spinel $\text{MgAl}_2\text{O}_4$
A transition metal is one which forms one or more stable ions which have *incompletely filled d orbitals*.

\[
\begin{align*}
\text{[Ar]} &= 1s^2 \ 2s^2 \ 2p^6 \ 3s^2 \ 3p^6 \\
\text{[Ti]} &= \text{[Ar]}3d^24s^2 \\
\text{[V]} &= \text{[Ar]}3d^34s^2
\end{align*}
\]
Perovskite oxides ABO$_3$

CaTiO$_3$, BaTiO$_3$, SrHfO$_3$,...

Octahedral symmetry ($O_h$):

High spin  Low spin  Fe$^{3+}$ (d$^5$)

Ligand field theory

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

paraelectric

\[ \Delta E = \frac{1}{2} \alpha_0 (T - T_0) P_x^2 + \frac{1}{4} \alpha_{11} P_x^4 + \frac{1}{6} \alpha_{111} P_x^6 \]
Integrating ferroelectric on Si (001)

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

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.

\[ S = \frac{\partial V_g}{\partial (\log_{10} I)} = \frac{\partial V_g}{\partial \psi_s} \frac{\partial \psi_s}{\partial (\log_{10} I)} \]

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

60 mV/dec

> 1 unless \( C_{ins} \) is negative

\( S \) lower than 60 mV/dec could be obtained
A strong electro-optically active lead-free ferroelectric integrated on silicon

Stefan Abel¹, Thilo Stöferle¹, Chiara Marchiori¹, Christophe Rossel¹, Marta D. Rossel², Rolf Erni², Daniele Caimi³, Marilyne Sousa⁴, Alexei Chelnokov³, Bert J. Offrein¹ & Jean Fompeyrine¹
Critical issues of oxide/semiconductor epitaxy*:

Strain

Thermal mismatch

* A. A. Demkov and A. B. Posadas
Wetting

\[ \gamma_{sub} > \gamma_{film} + \gamma_{interface} \]

Symmetry

steps

[Graph and images related to wetting and material properties]
Epitaxial oxide on semiconductors


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

**BaTiO_3 on Ge**

**SrTiO_3 on Si**

Model

Experiment

Fig. 1. Alkaline earth and perovskite oxide heteropitaxy on silicon and germanium. The figure illustrates our ability to manipulate interface structure at the atomic level using our \((\text{AO})_{n} \text{(ABO}_3\text{)}_{m}\) 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

With Si-SiO₂ we have got lucky, they are both covalent sp³ networks!
Geometry problem can be fixed:

Silicon

45 ° “rotation”

A-layer

B-layer

$\sqrt{2} \cdot \frac{a_{Si}}{2} = 3.84 \text{ Å}$

$a_{STO} = 3.905 \text{ Å}$

Chemistry!!!

Zintl template
GaAs
SrTO₃
Tetrahedral bonding (e.g. Si, Ge, C, GaAs)

Octahedral bonding (e.g. SrTiO₃, Al₂O₃)

sp³ hybrids

2D growth condition:
\[ \gamma_{s1/v} > \gamma_{s2/v} + \gamma_{i1/2} \]

- Stable interlayer reduces the interface energy
- Mixed bonding serves as a bridge
Zintl intermetallics: SrAl$_2$

**Zintl Alchemy:**
Charge transfer makes electronegative metal behave as if it were in the next column of the Periodic Table: Al $\rightarrow$ Si

Edward Zintl (1898-1941)

tI10 SrAl$_4$ structure

Metallic bonding

Zintl bonding

fcc Al metal

SrAl$_2$ structure
Electropositive metal template: $\frac{1}{2}$ ML Sr results in 2D growth

Sr on Si(001):

$E_r = E_{Sr@Si} - N E_{Sr} - E_{Si}$

$\mu = \frac{dE_r}{dN}$

$\frac{1}{2}$ ML 2x1

$1$ ML 2x1

$1$ ML 2x1


SrSi$_2$ (Zintl) stoichiometry
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).

Growth and in-situ characterization
SrTiO$_3$ deposition on Si

- Sr-assisted SiO$_2$ desorption
- $\frac{1}{2}$ monolayer Sr on Si
  (Zintl template layer)

- 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)
½ ML of Sr on Si(001)

Surface quality by ARPES

SrTiO₃ Surface Preparations

- Rough Surface
- Smooth Surface

Adsorbates?

Gap States Depend on Preparation

Semiconductor Surfaces

Does Theory Work?

Surface States In Gap!

H on Ti and O

DFT

Arkansas Preparation

O 2p

H on Ti and O Adsorbates?

Gap States Depend on Preparation

Strain stabilized out-of-plane ferroelectricity

Ferroelectric BaTiO$_3$ on Si (001)
16 nm BaTiO$_3$ strain analysis
AFM

amplitude

phase

16 nm BTO

1.6 nm BTO

AFM amplitude phase

16 nm BTO

1.6 nm BTO
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.
Ferroelectric on Ge: BTO/STO/Ge (001)

- $\frac{1}{2}$ 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

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.