

Kurt D. Fredrickson

Department of Chemical Engineering, Stanford University

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Education

The University of Texas, Austin, TX

Ph.D. in Physics, Condensed Matter Theory

08/15/2015

Advisor: Dr. Alex Demkov

University of California, Davis, CA

B.S. in Physics

06/15/2009

Advisor: Dr. Warren Pickett

Professional Career

Postdoctoral Scholar

SUNCAT, Department of Chemical Engineering, Stanford University

08/24/2015-Present

Postdoctoral Scholar

SUNCAT, SLAC National Accelerator Laboratory

08/24/2015-Present

Internships

International Research Experiences for Students (IRES)

05/2015

- Attended European Materials Research Society Spring Meeting in Lille, France, and gave two talks and presented a poster
- Collaborated with IBM Zürich on effect of strain and substrate on the nonlinear optical properties of BaTiO₃ and gave an invited talk
- Collaborated with Paul Scherrer Institute on angle-resolved photoemission spectroscopy of BaTiO₃/SrTiO₃/Ge heterostructures
- Collaborated with ETH Zürich on the applicability of Aurivillius phases for nonlinear optic devices and gave an invited talk

Research Experience:

Density functional theory calculations for:

- Bulk properties, such as band structure, density of states, local density of states, and elastic coefficients
- Work functions, electron affinities, and surface energies for various metals and oxides of varying terminations
- Analysis of surfaces, including atomic reconstruction and two-dimensional states
- Heterostructure analysis, including calculating wetting conditions, band offsets, and Schottky barriers for oxide/metal, oxide/oxide, and oxide/semiconductor interfaces
- Analysis of ferroelectric materials, including effects of capping on polarization and band offsets, polarization changes due to strain and interfacial effects, and potential shifts in substrates in response to switching
- Analysis of ferromagnetic materials, effects of magnetization due to metallic capping layers
- Phonon dispersions in oxides, including effects of long-range correction and negative optical mode splitting
- Theoretical atomic layer deposition modeling of oxide growth using a multistep precursor processes
- Analysis of adatom adsorption on oxide and semiconductor surfaces, including effects on further atomic adsorption
- Molecular analysis, including electronic structure and vibrational modes

Awards and Memberships

Member, Student Physical Society, 2007

Dean's Honor List, University of California, Davis College of Letters and Sciences, 2008

Member, Sigma Pi Sigma, 2009

Member, American Physical Society, 2010

Member, Materials Research Society, 2011

Recipient, Professional Development Award, University of Texas at Austin Graduate School, 2014

Member, AVS, 2014

Recipient, Ovshinsky Travel Award, American Physical Society, 2015

Member, European Materials Research Society, 2015

Publications:

“Integrated Films of Transition Metal Oxides for Information Technology”, A.A. Demkov, P. Ponath, **K.D. Fredrickson**, A.B. Posadas, M.D. McDaniel, T.Q. Ngo and J.G. Ekerdt, *Microelectron. Eng.* **147**, 285 (2015). [DOI](#)

“Switchable Conductivity at the Ferroelectric Interface: Nonpolar Oxides”, **K.D. Fredrickson** and A.A. Demkov, *Phys. Rev. B* **91**, 115126 (2015). [DOI](#)

“Carrier Density Modulation in a Ge Heterostructure by Ferroelectric Switching”, P. Ponath, **K.D. Fredrickson**, A.B. Posadas, Y. Ren, X. Wu, R.K. Vasudevan, M.B. Okatan, S. Jesse, T. Aoki, M.R. McCartney, D.J. Smith, S.V. Kalinin, K. Lai and A.A. Demkov, *Nat. Commun.* **6**, 6067 (2015). [DOI](#)

“Atomic and Electronic Structure of the Ferroelectric BaTiO₃/Ge Interface”, **K.D. Fredrickson**, P. Ponath, A.B. Posadas, M.R. McCartney, T. Aoki, D.J. Smith and A.A. Demkov, *Appl. Phys. Lett.* **104**, 242908 (2014). [DOI](#)

“Surface Electronic Structure for Various Surface Preparations of Nb-doped SrTiO₃ (001)”, R.C. Hatch, **K.D. Fredrickson**, M. Choi, C. Lin, H. Seo, A.B. Posadas and A.A. Demkov, *J. Appl. Phys.* **114**, 103710 (2013). [DOI](#)

“Wetting at the BaTiO₃/Pt Interface”, **K.D. Fredrickson**, A.B. Posadas, A.A. Demkov, C. Dubourdieu and J. Bruley, *J. Appl. Phys.* **113**, 184102 (2013). [DOI](#)

Papers in preparation:

“Theoretical Study of Negative Optical Mode Splitting in LaAlO₃”, **K.D. Fredrickson**, C. Lin, S. Zollner and A.A. Demkov, submitted to *Phys. Rev. B*.

“Spin-polarized, orbital-selected hole gas at the EuO/Pt interface”, **K.D. Fredrickson** and A.A. Demkov, submitted to *J. Appl. Phys.*

“Theoretical Modeling and Experimental Observations of the Atomic Layer Deposition of SrO Using a Cyclopentadienyl Sr Precursor”, **K.D. Fredrickson**, M.D. McDaniel, J.G. Ekerdt and A.A. Demkov, in preparation.

“Oxidation Protection of the Adsorbed Si(001) Surface due to Adsorbed Sr”, **K.D. Fredrickson**, H. Seo and A.A. Demkov, in preparation.

“Induced Metallization and Rumpling in H-Adsorbed Thin BaTiO₃ Films”, **K.D. Fredrickson** and A.A. Demkov, in preparation.

“Enormous nonlinear electro-optical response in thin strained BaTiO₃ films”, **K.D. Fredrickson** and A.A. Demkov, in preparation.

Invited Talks:

2015

“Two-dimensional gases at oxide interfaces”, ETH, Zürich, Switzerland

“First-principles modeling of atomic layer deposition in oxides”, IBM Research Laboratory, Zürich, Switzerland

Contributed Talks and Posters:

2015

“Oxidation protection of the Si(001) surface due to adsorbed Sr”, SUNCAT Summer Institute, Stanford, CA

“Two-dimensional electron gas at the interface of two nonpolar oxides: BaTiO₃ and SrTiO₃”, European Materials Research Society Spring Meeting, Lille, France

“Theoretical modeling and experimental observations of the atomic layer deposition of SrO using a cyclopentadienyl Sr precursor”, European Materials Research Society Spring Meeting, Lille, France

“Oxidation protection of the Si(001) surface due to adsorbed Sr”, European Materials Research Society Spring Meeting, Lille, France

“Oxidation protection of the Si(001) surface due to adsorbed Sr”, Materials Research Society Spring Meeting, San Francisco, CA

“Switchable two-dimensional electron gas at the interface of a ferroelectric and nonpolar insulator”, American Physical Society March Meeting, San Antonio, TX

2014

“Atomic and electronic structure of the ferroelectric BaTiO₃(001)/Ge interface”, AVS International Symposium, Baltimore, MD

“Atomic and electronic structure of the BaTiO₃/Ge interface”, International Conference of the Physics of Semiconductors, Austin, TX

“Negative capacitance in epitaxial oxide heterostructures”, NSF GOALI Presentation, Austin, TX

“Integration of ferroelectric BaTiO₃ on Ge(001)”, Materials Research Society Spring Meeting, San Francisco, CA

“Theoretical study of the HyperSr precursor and atomic layer deposition of SrTiO₃”, Materials Research Society Spring Meeting, San Francisco, CA

“Atomic and electronic structure of the BaTiO₃/Ge(001) interface”, American Physical Society March Meeting, Denver, CO

2013

“Theory of wetting at Ge/BaTiO₃ interfaces”, Materials Research Society Spring Meeting, San Francisco, CA

“Theoretical and experimental study of growth of Pt film on BaTiO₃”, American Physical Society March Meeting, Baltimore, MD

2012

“Theoretical study of growth of switchable ferroelectric BaTiO₃”, Oxide Fest, Austin, TX

“Theoretical study of ferroelectric switching in Pt/BaTiO₃ slabs”, American Physical Society March Meeting, Boston, MA

“Interface clamping and ferroelectric switching of BaTiO₃ films”, Conference on Physics and Chemistry of Surfaces and Interfaces, Santa Fe, NM

2011

“Theoretical study of BaTiO₃/Ge interfaces”, American Physical Society March Meeting, Dallas, TX

Research Projects:

Carrier density modulation in a Ge heterostructure by ferroelectric switching (P. Ponath *et al.*, Nat. Commun. **6**, 6067 (2015)).

The development of non-volatile logic through direct coupling of spontaneous ferroelectric polarization with semiconductor charge carriers is nontrivial, with many issues, including epitaxial ferroelectric growth, demonstration of ferroelectric switching and measurable semiconductor modulation. Here we report a true ferroelectric field effect—carrier density modulation in an underlying Ge(001) substrate by switching of the ferroelectric polarization in epitaxial c-axis-oriented BaTiO₃ grown by molecular beam epitaxy. Using density functional theory, I demonstrated that switching of BaTiO₃ polarization results in a large electric potential change in Ge. I showed that the BaTiO₃/SrTiO₃/Ge heterostructure has two stable polarization states; an unpolarized case, and one where BaTiO₃ is polarized away from the surface, and toward Ge. There is a notable change in the electrostatic potential due to the field cause by the polarization of BaTiO₃, and the change in potential extends throughout the entire heterostructure, most crucially in Ge, showing that the field-effect is not diminished by the presence of SrTiO₃. Also, I have shown that the doping of Ge with B also does not destroy the change in potential in the center of Ge.

Atomic and electronic structure of the ferroelectric BaTiO₃/Ge (001) interface (K.D. Fredrickson *et al.*, Appl. Phys. Lett. **104**, 242908 (2014)).

BaTiO₃ is an oxide that is ferroelectric at room temperature, which provides strong motivation for integration with Ge, in part, due to the potential for realizing a ferroelectric field-effect transistor. To date, very little is known about the atomic and electronic structure of the BaTiO₃/Ge interface. Such knowledge is crucial for controlling the properties of devices based on this materials system. In this study, we demonstrate the epitaxial growth of BaTiO₃ on Ge(001) by molecular beam epitaxy using a thin Zintl template buffer layer. A combination of density functional theory, atomic-resolution electron

microscopy and in situ photoemission spectroscopy is used to investigate the electronic properties and atomic structure of the BaTiO₃/Ge interface. The measured valence band offset of 2.7 eV matches well with the theoretical value of 2.5 eV based on the model structure for an in-plane-polarized interface. The agreement between the calculated and measured band offsets, which are highly sensitive to the detailed atomic arrangement, indicates that the most likely BaTiO₃/Ge(001) interface structure has been identified. To calculate the band alignment, I showed that atomic placement at the interface is extremely important, as the band offsets change hugely depending on the direction and strength of the atomic SrO₂ dipole. I changed this dipole by hand to see the effects on the band offset, showing that the dipole helped push back evanescent states from Ge in order to obtain the experimental alignment.

Surface electronic structure for various surface preparations of Nb-doped SrTiO₃ (001) (R.C. Hatch *et al.*, J. Appl. Phys. **114**, 103710 (2013)).

Since many of the unique properties of oxide heterostructures require atomically abrupt interfaces, the preparation of atomically flat, defect-free substrates is of utmost importance. The surfaces of SrTiO₃(001) crystals, as provided by the manufacturer, do not typically have a unique surface termination as a result of mechanical polishing. While water-leaching methods result in flat, TiO₂-terminated SrTiO₃, a thorough study comparing the effectiveness of acid-based etching and water-leaching is not yet available. High-resolution angle-resolved photoemission spectroscopy was used to study the surface electronic structure of Nb-doped SrTiO₃ single crystals prepared using a variety of surface preparations. Theoretical modeling using density functional theory suggests that a mid-gap state seen in the samples is not related to the SrO- and TiO₂-terminated surfaces, but rather, is due to a partial hydrogenation of the SrTiO₃ surface that occurs during etching. I examined the effect of F substitution and its effect on H adsorption, and saw that the incorporation of F at the TiO₂ surface is electronically similar to the adsorption of H on the surface. I used band structure calculations to analyze the localization of the H and F states, and their location in energy, either midgap, within the valence band, or below the valence band. I also showed that the sharp midgap state is related to the H-Ti bond, which can exist with the present of F substituting for O at the surface, or an already present O-H group.

Wetting at the BaTiO₃/Pt interface (K.D. Fredrickson *et al.*, J. Appl. Phys. **113**, 184102 (2013)).

While in the case of contacts and capping layers where a smooth continuous film, preferably epitaxial, is needed, in the case of catalysis, the use of nano-crystalline islands on the oxide support is beneficial to obtaining larger surface to volume ratios. Metal-oxide interfaces have also been the subject of many fundamental studies concerning their structure and electronic properties. The growth of epitaxial interfaces is determined by a variety of factors; however, for growth near equilibrium, the lattice mismatch and the relative surface and interface energies dictate what the global nature of the interface would be. Using density functional theory, I calculated the wetting conditions for Pt on the (001) surface of ferroelectric BaTiO₃ (BTO). I estimated the surface energy of (100), (110), and (111) Pt to be 2.42, 2.49, and 2.00 J/m², respectively. I found the BTO surface energy to vary between 0.26 and 2.28 J/m² depending on termination, polarization, and chemical environment. The interface energy between TiO₂-terminated out-of-plane polarized BTO and (100) Pt is found to be between 1.64 and 2.62 J/m². Using Young's equation, I saw that (100) Pt cannot wet BTO for this interface. A similar result is found for an interface with (110) Pt. Cross-sectional transmission electron microscopy of Pt films grown on BTO by molecular beam epitaxy with a low flux at high deposition temperature shows Volmer-Weber islands,

consistent with first principles calculations. I also calculate the effect of polarization, Pt thickness, O vacancies in BTO, and Pt orientation on the Schottky barrier for these heterostructures. I used the reference potential method, in comparison with the plane-by-plane density of states, to calculate the Schottky barrier between BTO and Pt.

Switchable conductivity at the ferroelectric interface: nonpolar oxides (K.D. Fredrickson *et al.*, Phys. Rev. B **91**, 115126 (2015))

The astounding discovery of a conducting layer at the interface of two large band gap, insulating oxides, LaAlO_3 and SrTiO_3 , has led to an obvious question: how can the interface of two insulators be conductive? The answer is widely believed to be a phenomenon known as the polar catastrophe. There is evidence that ferroelectrics may allow for the creation of surface charge; there is experimental and theoretical evidence of the formation of a two-dimensional conducting layer on the surface of clean ferroelectrics, which is attributed to the uncompensated surface charge due to the ferroelectric nature of the material. We investigate theoretically the interface between a ferroelectric BaTiO_3 film and a non-polar insulating SrTiO_3 substrate. We find that thin BaTiO_3 , under 5 nm, can stabilize a non-polarized state, and an additional metastable polarization state. While the non-polarized state is insulating, for the polarized heterostructure, upon examining the local DOS, I discovered the existence of two-dimensional charge carrier gases; a two-dimensional electron gas forms at the $\text{SrTiO}_3/\text{BaTiO}_3$ interface, and a two-dimensional hole gas forms at the BaTiO_3 surface. In this case, the heterostructure undergoes an electronic reconstruction in order to prevent the polar catastrophe. The two-dimensional gases, formed as a result, screen the polarization, leading to a substantially reduced potential drop across the ferroelectric film. I also use the reference potential method to calculate the change in electrostatic potential between the SrTiO_3 depending on the polarization of the structure. We emphasize that the two-dimensional electron and hole gases are created by the polarization of the sample, and are not due to polar nature of the material or doping. I also use electrostatic arguments to calculate the dielectric constant of the BaTiO_3 layer.

Theoretical study of negative optical mode splitting in LaAlO_3 (Submitted to PRB)

Longitudinal optical/transverse optical splitting arises from long-range Coulomb forces and is known as Lyddane-Sachs-Teller splitting. These long-wavelength phonons include an additional coupling to macroscopic electric fields that affects the frequency of the longitudinal optical modes while leaving the transverse optical modes unaffected. There is, though, interesting experimental work showing that in LaAlO_3 the splitting may be negative. We analyze the general circumstances that can lead to the negative Lyddane-Sachs-Teller splitting. As a specific example, we consider the optical phonon frequencies of perovskite LaAlO_3 computed within density functional theory, and compare them to prior experimental reports. The experimental results and theoretical calculation convincingly show that one of the optical mode splittings is indeed negative. The specific optical mode in experiment experiencing the negative splitting is consistent with our analysis. To calculate the phonon spectrum of the material, I helped develop a code in MATLAB to calculate the effects of long-range correction on different directions in k -space, and show that the value of the splittings are k -direction dependent. I used perturbation theory to show that, while the splitting of individual optical modes is always greater than or equal to 0, the coupling of the modes allows a perturbation to cause the entire splitting to be negative. I also used group theory to assign modes as either IR- or Raman-active, or silent. I also showed how that the existence of long-

range splitting determines when the phonon mode is longitudinal optical or transverse optical, even in crystals of low symmetry where the assignment of longitudinal optical or transverse optical is ambiguous.

Theoretical modeling and experimental observations of the atomic layer deposition of SrO using a cyclopentadienyl Sr precursor (In preparation)

We use first principles calculations to model the surface adsorption and hydration of strontium bis(cyclopentadienyl) $[\text{Sr}(\text{Cp})_2]$ for the deposition of strontium oxide, SrO, by atomic layer deposition. TiO_2 -terminated strontium titanate, SrTiO_3 , is taken to be the bulk substrate for deposition. I calculated the lowest-energy adsorption of the $\text{Sr}(\text{Cp})_2$ precursor on the TiO_2 -terminated surface, modeling three different molecule approaches and six different adsorption sites. The $\text{Sr}(\text{Cp})_2$ precursor is shown to adsorb on the TiO_2 -terminated surface, with the Sr atom assuming essentially the bulk position in SrTiO_3 . I performed a vibrational analysis of the free $\text{Sr}(\text{Cp})_2$ using density functional perturbation theory to show the low-frequency mode of rotation should be activated at typical growth temperatures, make the adsorption of the $\text{Sr}(\text{Cp})_2$ molecule easier. The C-Sr bonds are weaker than in the free molecule, with a Ti atom at the surface bonding to one of the C atoms in the cyclopentadienyl rings. I found that the surface does not need to be hydrogenated for precursor adsorption, contrary to prior predictions. To determine the detachment of the Cp ligands, I placed H atoms on different parts of the Cp ring to find the lowest-energy arrangement. I also showed that the addition of H to the Cp groups caused spontaneous detachment of the Cp group from the adsorbed molecule. I also showed the step-by-step addition of H leads to complete dissociation of the $\text{Sr}(\text{Cp})_2$ into adsorbed Sr and separate C_5H_6 . The calculations are compared with experimental observations for a Sr cyclopentadienyl precursor, $\text{Sr}(\text{Pr}_3\text{Cp})_2$ adsorbed onto the TiO_2 -terminated STO. High-resolution x-ray photoelectron spectroscopy shows adsorption of the Sr precursor on the TiO_2 -terminated STO after a single precursor dose. This study suggests that $\text{Sr}(\text{Cp})_2$ precursors may be used for ALD growth on non-hydroxylated surfaces.

Oxidation protection of the Si(001) surface due to adsorbed Sr (In preparation)

In the presence of SiO_2 at the interface of an high- k dielectric and Si, the dielectric performance of the gate oxide is significantly reduced; therefore, one of the largest challenge of high- k oxides integration with Si is to prevent the unwanted formation of SiO_2 . Previous studies have achieved the growth of high- k SrTiO_3 on Si(001) by employing a sub-monolayer Sr passivation layer. The method of the protection of the Si passivation is not completely understood; previous theoretical studies showed that the Sr electronically blocks the adsorption of O in the Si backbond, but the addition of extra O above the first has not been shown. I used density functional theory to model the adsorption of O on a bare Si(001)(2×1) reconstructed surface and on the same surface passivated by $\frac{1}{2}$ monolayer of Sr. I found that the first two O for the bare surface are adsorbed at a bridging site in the Si dimer and then in its associated backbond, in agreement with prior theoretical results. With Sr passivating the surface, however, we see that a surface with two Si dimers is protected up to five adsorbed O. Most crucially, there is no backbond adsorption with Sr present, and therefore the oxidation does not proceed deeper into Si and SiO_2 does not form. This is in good agreement with experimental results that the Sr passivation layer prevents the formation of SiO_2 . I use nudged elastic band calculations to determine the energy barriers of Sr on the Si surface, both with and without the presence of adsorbed O, and show that the O prefers to adsorb on a dimer near an adsorbed Sr, even though there are dimers without Sr present.

Magnetization depletion of EuO/Pt heterostructures (In preparation)

EuO is a narrow gap semiconductor that shows very interesting magnetic behavior. It crystallizes in a rock salt structure, and below 69 K it undergoes a ferromagnetic transition. Mixing of the Eu *f*-states and O-*p* states contribute to the ferromagnetic ordering. Due to its' large magnetic moment, the bands are spin-split, leading to differences in transport for the spin-up and spin-down electrons; prior research has shown that the interface of EuO with many materials results in novel and interesting properties, including the enhancement of EuO's magnetic moment due to oxygen vacancies, and a decrease in magnetic moment due to band-bending at the EuO/Pt interface. Using density functional theory, I analyzed the magnetic behavior of an EuO/Pt heterojunction. We discover that the interfacial and second layer of EuO have a reduced magnetic moment, while the remainder of the layers are the same as bulk. The explanation for the drop in magnetic moment is due to the formation of EuPt_2 , with charge from the nearby EuO layers relocating to the interface. I also discovered a sharply localized state at the second layer of EuO from the interface, which arises due to the disruption of second-nearest-neighbor hopping between Eu *d* and *f* states.

Teaching Experience

Teaching Assistant—To Professor Roy Schwitters for Electricity & Magnetism Laboratory 2009-2011

Taught physics lab class, graded lab reports, met with students on request, collaborated on and gave lab finals
