Kurt D. Fredrickson

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Education

The University of Texas, Austin, TX
Ph.D. in Physics, Condensed Matter Theory **08/15/2015**
Advisor: Prof. Alex Demkov
Thesis: First-Principles Studies of Perovskite Thin Films and Heterostructures

University of California, Davis, CA
B.S. in Physics **06/15/2009**
Advisor: Prof. Warren Pickett

Professional Career

Postdoctoral Scholar **08/24/2015-Present**
Department of Chemical Engineering
Stanford University
Advisor: Prof. Jens Nørskov

Postdoctoral Scholar **08/24/2015-Present**
SUNCAT Center for Interface Science and Catalysis
SLAC National Accelerator Laboratory
Advisor: Dr. Aleksandra Vojvodic

Postdoctoral Scholar **07/15/2016-Present**
Department of Chemical and Biomolecular Engineering
University of Pennsylvania
Advisor: Prof. Aleksandra Vojvodic

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 $BaTiO_3$ and gave an invited talk

- Collaborated with Paul Scherrer Institute on angle-resolved photoemission spectroscopy of $BaTiO_3/SrTiO_3$/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, elastic coefficients, phonons with long-range corrections, optical mode splitting, nonlinear optics effects, doping effects, vacancy effects
- Surface properties: work functions, electron affinities, surface energies, atomic reconstruction, adatom adsorption and two-dimensional states for various metals and oxides of varying terminations
- Interface properties: wetting conditions, band offsets, Schottky barriers, passivation layers, interfacial atoms and vacancies, 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
- Theoretical atomic layer deposition modeling of oxide growth using a multistep precursor processes, adatom adsorption
- Molecular analysis, including electronic structure and vibrational modes, and physi- and chemisorption
- Electrocatalysis modeling (Hydrogen evolution reaction) and related (Pourbaix diagrams, free energy calculations, electrochemical potential calculations)
- High-performance computing, with experience at the Texas Advanced Computing Center (TACC), Stanford University Sherlock cluster, SUNCAT SLAC Cluster, and National Energy Research Scientific Computing Center (NERSC)

Awards

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

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

Recipient, Ovshinsky Travel Award, American Physical Society, 2015

Publications and Book Chapters

"Two-Dimensional Molybdenum Carbide (MXene) as an Efficient Electrocatalyst for Hydrogen Evolution", Z.W. Seh*, **K.D. Fredrickson***, B. Anasori, J. Kibsgaard, A.L. Strickler, M.R. Lukatskaya, Y. Gogosti, T.F. Jaramillo and A. Vojvodic, ACS Energy Lett. **1**, 589 (2016). Link
*Co-first authors

"Oxidation Protection of the Adsorbed Si(001) Surface due to Adsorbed Sr", **K.D. Fredrickson**, H. Seo and A.A. Demkov, J. Appl. Phys. **120**, 065301 (2016). Link

"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, J. Chem. Phys. **145**, 064701 (2016). Link

"Recent studies of oxide-semiconductor heterostructures using aberration-corrected scanning transmission electron microscopy", D.J. Smith, H.W. Wu, S. Lu, T. Aoki, P. Ponath, **K.D. Fredrickson**, M.D. McDaniel, E. Lin, A.B. Posadas, A.A. Demkov, J. Ekerdt and M.R. McCartney, J. Mater. Res. (2016). Link

"Two-dimensional electron gas at oxide interfaces", A.A. Demkov, K.J. Kormondy and **K.D**. **Fredrickson**, in *Oxide Materials at the Two-Dimensional Limit,* edited by F.P. Netzer and A. Fortunelli (Springer, New York, 2016). Link

"Theoretical study of negative optical mode splitting in $LaAlO_3$", **K.D. Fredrickson,** C. Lin, S. Zollner and A.A. Demkov, Phys. Rev. B **93**, 134301 (2016). Link

"Spin-polarized, orbital-selected hole gas at the EuO/Pt interface", **K.D. Fredrickson** and A.A. Demkov, J. Appl. Phys. **119**, 095309 (2016). Link

"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). Link

"Switchable Conductivity at the Ferroelectric Interface: Nonpolar Oxides", **K.D. Fredrickson** and A.A. Demkov, Phys. Rev. B **91**, 115126 (2015). Link

"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). **Link**

"Atomic and Electronic Structure of the Ferroelectric $BaTiO_3$/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). **Link**

"Surface Electronic Structure for Various Surface Preparations of Nb-doped $SrTiO_3$ (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). **Link**

"Wetting at the $BaTiO_3$/Pt Interface", **K.D. Fredrickson**, A.B. Posadas, A.A. Demkov, C. Dubourdieu and J. Bruley, J. Appl. Phys. **113**, 184102 (2013). **Link**

"Induced Metallization and Rumpling in H-Adsorbed Thin $BaTiO_3$ Films", **K.D. Fredrickson** and A.A. Demkov, submitted to Phys. Rev. B

"Layered functionalized MXenes and the effect of intercalated water", **K. D. Fredrickson**, B. Anasori, Z.W. Seh, Y. Gogotsi and A. Vovjodic, submitted to J. Phys. Chem. C.

"Adsorbate-mediated phase transitions in 2D transitional metal carbide MXenes", **K.D. Fredrickson** and A. Jovjodic, in preparation.

"Enormous nonlinear electro-optical response in thin strained $BaTiO_3$ 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

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Contributed Talks and Posters

2016

"Two-Dimensional Carbides/Nitrides (MXenes) for HER", Theoretic Atomic-Scale Physics Summer School, Copenhagen, Denmark (Poster)

"Two-Dimensional Carbides/Nitrides (MXenes) for HER", Center for Individual Nanoparticle Functionality Summer School, Gilleleje, Denmark (Poster)

"Effect of functionalization on the electronic and atomic properties of layered MXenes", American Physical Society March Meeting, Baltimore, MD (Oral)

2015

"Theoretical modeling and experimental observations of the atomic layer deposition of SrO using a cyclopentadienyl Sr precursor", Materials Research Society Fall Meeting, Boston, MA (Oral)

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

"Two-dimensional electron gas at the interface of two nonpolar oxides: $BaTiO_3$ and $SrTiO_3$", European Materials Research Society Spring Meeting, Lille, France (Oral)

"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 (Oral)

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

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

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

2014

"Atomic and electronic structure of the ferroelectric $BaTiO_3$(001)/Ge interface", AVS International Symposium, Baltimore, MD (Oral)

"Atomic and electronic structure of the $BaTiO_3$/Ge interface", International Conference of the Physics of Semiconductors, Austin, TX (Poster)

"Negative capacitance in epitaxial oxide heterostructures", NSF Grant Opportunities for Academic Liaison with Industry (GOALI) Presentation, Austin, TX (Poster)

"Integration of ferroelectric $BaTiO_3$ on Ge(001)", Materials Research Society Spring Meeting, San Francisco, CA (Oral)

"Theoretical study of the HyperSr precursor and atomic layer deposition of $SrTiO_3$", Materials Research Society Spring Meeting, San Francisco, CA (Poster)

"Atomic and electronic structure of the $BaTiO_3$/Ge(001) interface", American Physical Society March Meeting, Denver, CO (Oral)

2013

"Theory of wetting at Ge/$BaTiO_3$ interfaces", Materials Research Society Spring Meeting, San Francisco, CA (Oral)

"Theoretical and experimental study of growth of Pt film on $BaTiO_3$", American Physical Society March Meeting, Baltimore, MD (Oral)

2012

"Theoretical study of growth of switchable ferroelectric $BaTiO_3$", Oxide Fest, Austin, TX (Oral)

"Theoretical study of ferroelectric switching in Pt/$BaTiO_3$ slabs", American Physical Society March Meeting, Boston, MA (Oral)

"Interface clamping and ferroelectric switching of $BaTiO_3$ films", Conference on Physics and Chemistry of Surfaces and Interfaces, Santa Fe, NM (Poster)

2011

"Theoretical study of $BaTiO_3$/Ge interfaces", American Physical Society March Meeting, Dallas, TX (Poster)

Proposals

NERSC Proposal: Computational Search for highly efficient 2D & 3D nano-catalysts for water splitting (A. Vojvodic *et al.*, in preparation)

Research Projects

<u>MXene screening study</u>

- Two-dimensional transition metal carbides and nitrides, also known as MXenes, represent an attractive class of materials for a multitude of electrochemical applications. I investigated the structural and electronic effects of water intercalation, multiple functional groups and applied potential on layered bulk Ti_2C and Mo_2C MXenes using density functional theory. The out-of plane lattice parameter, c, was found to vary significantly with the functional group, and is greatly increased upon intercalation of water.
- I screened 20 possible M_2X MXenes (M = {Sc, Ti, Zr, Hf, Nb, V, Ta, Cr, Mo and W}, X = {C and N}), along with different adsorbates {H, OH, O and H_2O}. The type of adsorbate determines whether the system is insulating or metallic. We change the coverage of all the MXenes from O covered at positive applied potentials to H covered at negative applied potentials; in Ti_2C, Zr_2C, and Hf_2C, this results in a metal-insulator phase transition. These novel transitions are mediated by the species of adsorbates, which can be controlled via a change in applied potential, temperature, and pH. This paves the way for new phase transitions that are mediated by the type of adsorbate.
- I also computationally screened 20 2D MXenes, and predicted Mo_2CT_x to be an active catalyst candidate for hydrogen electrocatalysis. We synthesized both Mo_2CT_x and Ti_2CT_x MXenes and, in agreement with our theoretical predictions, Mo_2CT_x was found to exhibit far higher HER activity than Ti_2CT_x. Theory suggests that the basal planes of Mo_2CT_x are catalytically active towards the HER, unlike in the case of widely-studied MoS_2, in which only the edge sites of the 2H-phase are active. (3 papers total)

<u>Interface studies</u>

- I explored the magnetic behavior of a EuO/Pt heterostructure. The calculations suggest that the heterostructure could be used as a spin filter. We discover that the interfacial and second layer of EuO, both have a reduced magnetic moment, while the remainder of the oxide maintains bulk magnetization. These first two layers support a localized mid-gap electronic state (2D hole gas) that protects the remainder of EuO from losing charge into the large work function Pt, which in turn results in the magnetic moment reduction.
- I also investigated the interface between a ferroelectric $BaTiO_3$ film and a nonpolar insulating $SrTiO_3$ substrate. I find that thin $BaTiO_3$ (under 5 nm) can stabilize a nonpolarized state, and an

additional metastable polarized state. While the nonpolarized state is insulating, for the polarized heterostructure, we discover the existence of two-dimensional charge carrier gases. 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.

- In a related study, I demonstrated that switching of $BaTiO_3$ polarization results in a large electric potential change in a $BaTiO_3/SrTiO_3$/Ge heterostructure. I showed that the $BaTiO_3/SrTiO_3$/Ge heterostructure has two stable polarization states; an unpolarized case, and one where $BaTiO_3$ 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 $BaTiO_3$, 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 $SrTiO_3$. The non-volatile, switchable nature of the single-domain out-of-plane ferroelectric polarization of BaTiO3 is confirmed using piezoelectric force microscopy.
- 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 $BaTiO_3$/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 $BaTiO_3$/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 SrO_2 dipole.
- Using density functional theory, I calculated the wetting conditions for Pt on the (001) surface of ferroelectric $BaTiO_3$ (BTO). 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. (7 papers total)

<u>Surface studies</u>

- First principles calculations are used to model the adsorption and hydration of strontium bis(cyclopentadienyl) [$Sr(Cp)_2$] on TiO_2-terminated strontium titanate, $SrTiO_3$ (STO) for the deposition of strontium oxide, SrO, by atomic layer deposition (ALD). The surface does not need to be hydrogenated for precursor adsorption, contrary to previous suggestions. The calculations are compared with experimental observations for a related Sr cyclopendienyl precursor, strontium bis(triisopropylcyclopentadienyl) [$Sr(^{i}Pr_3Cp)_2$], adsorbed onto TiO_2-terminated STO.
- We investigate theoretically the oxidation stability of the Si(001) (2×1) reconstructed surface passivated by ½ monolayer of Sr. Using density functional theory, we find that with Sr present the surface is protected against oxidation. The presence of Sr delays the oxidation of the surface dimer, and even when the dimer is oxidized, O does not react with the back-bond, preventing the

unwanted vertical growth of SiO_2. We also show that ¼ monolayer of Sr protects the Si surface in a different way. In the presence of ¼ monolayer of Sr, O atoms are attracted to the Sr-Si dimer complexes, thus preventing the formation of SiO_2.

- Theoretical modeling using density functional theory suggests that a mid-gap state seen in the samples is not related to the SrO- and TiO_2-terminated surfaces, but rather, is due to a partial hydrogenation of the $SrTiO_3$ 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 TiO_2 surface is electronically similar to the adsorption of H on the surface. (3 papers total)

Collaborators

- Prof. Warren Pickett, University of California, Davis (Density functional theory)
- Prof. Alex Demkov, University of Texas at Austin (Density functional theory/molecular beam epitaxy)
- Prof. David Smith, Arizona State University (Microscopy)
- Prof. Stefan Zollner, New Mexico State University (Ellipsometry)
- Prof. John Ekerdt, University of Texas at Austin (Atomic layer deposition)
- Prof. Keji Lai, University of Texas at Austin (Microwave impendence microscopy)
- Dr. Jean Fompeyrine, IBM Zurich (Electro-optical measurements)
- Prof. Jens Nørskov, Stanford University (Density functional theory)
- Prof. Aleksandra Vojvodic, SLAC National Accelerator Laboratory & University of Pennsylvania (Density functional theory)
- Prof. Thomas Jaramillo, Stanford University (Electrocatalysis measurements)
- Dr. Zhi Wei Seh, Stanford University & A*STAR (Electrocatalysis measurements)
- Prof. Yury Gogotsi, Drexel University (MXene synthesis)

Teaching Experience

- Teaching Assistant—Electricity & Magnetism Laboratory (University of Texas at Austin, Supervised by Prof. Roy Schwitters) 2009-2011: 4 semesters. Taught physics electricity and magnetism lab class for premed students. Graded lab reports, met with students during office hours and additional hours upon request, helped design laboratory finals, graded lab finals
- Physics Coach—All levels (University of Texas at Austin) 2009-2011: 4 semesters. Paid position by University that included helping students with homework. A student of any physics class could come by without appointment for help with their class. Helped students of every year, of every level of physics (physics majors, engineering majors, bioscience majors).
- Private tutor—2009-2012: 6 semesters
  Tutored several students, ranging from high school to college, with physics homework.
