Using First-principles Simulations to Discover Materials with Ultra-low Work Functions for Energy Conversion Applications Progress report 2012

Investigators

Roger T. Howe, Professor, Electrical Engineering
Jens K. Nørskov, Professor, Chemical Engineering/SLAC
Piero A. Pianetta, Professor, Electrical Engineering/SLAC

Igor Bargatin (research associate, Electrical Engineering), Frank Abild-Pedersen (staff scientist, SLAC), Johannes Voss (postdoctoral scholar, Chemical Engineering), Aleksandra Vojvodic (postdoctoral scholar, Chemical Engineering)

Sharon Chou (PhD student, Electrical Engineering), Hongyuan Yuan (PhD student, Physics)

Abstract

Our objective is to discover new nanostructured materials with ultra-low work functions for achieving high-efficiency thermionic energy conversion. Since the start of the project in October 2011, we have initiated work on all thee thrusts: (1) DFT calculations of the work functions of multi-layer surfaces, (2) fabrication of multilayer surfaces with low work functions, and (3) measurements of surface properties of multi-layer surfaces.

The DFT calculations we have performed thus far offered new insights into the atomistic processes that control the work functions of various surfaces. In particular, we have studied and visualized the formation of dipoles on the surfaces of materials with low-work-function coatings, such as cesium and cesium oxide. The density of surface dipoles created by adsorbates is directly proportional to the changes in the work function induced by the coating. We have also calculated the charge distributions and the corresponding changes in the work function for a variety of cesiated transition metals and observed general trends in the behavior of such binary systems (one substrate + one coating).

We have also launched experiments described to the second and third thrust of the project. In particular, we are currently fabricating multilayer structures by depositing thin ALD-deposited alumina films on silicon and measuring their work function with and without cesiation. We are also preparing measurements of the work function of heavily p-doped graphene, which our DFT simulations predict to have a work function of ~1 eV. In addition, we are performing upgrades to the vacuum chamber at SSRL that would increase flexibility in handling and characterizing samples using XPS. Measurements in the upgraded chamber will test these theoretical predictions and quantify the stability of the cesiated graphene samples under relatively high and low vacuum conditions.

Introduction

The work function is the interfacial parameter of the surface of a material that determines how easily electrons can escape into a vacuum or gas environment, with lower work functions generally facilitating electron emission. Sub-nanometer coatings have long been

known to modify the work function. For example, coatings of cesium and oxygen are routinely used to make the low-work-function photocathodes used in photomultipliers and night-vision devices. However, the theory of work-function reductions by such coatings is still poorly understood; the most effective coatings were discovered largely by trial and error. By employing theoretical DFT methods and nanofabrication techniques, this interdisciplinary project will undertake a systematic approach to gain such understanding and apply it to discover new nanostructured multilayer materials with ultra-low work functions. As a result, many promising material-coating combinations will be efficiently investigated for the first time. Successful completion of this project will result in new stable surfaces with record-low work functions and prototypes of efficient thermionic energy converters that utilize such surfaces. The research team has the combined expertise in the critical areas of DFT calculations, surface characterization, and nano/micro-fabrication.

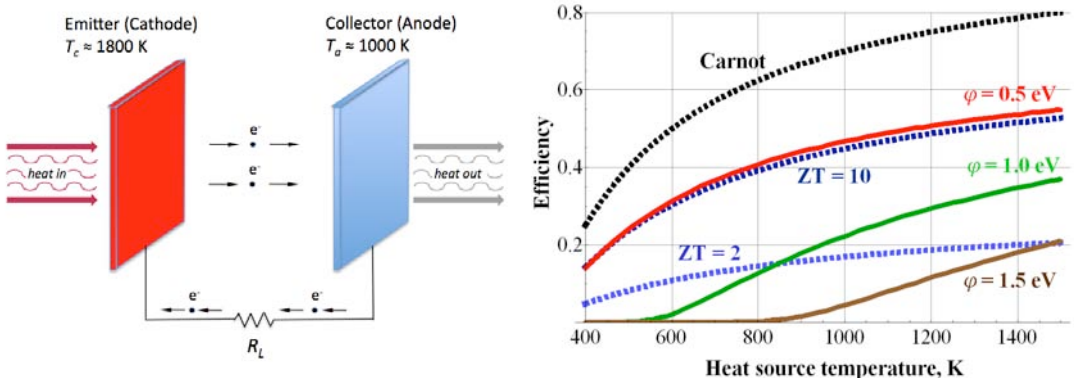


Figure 1: *Left: Schematic of a traditional thermionic energy converter. The incoming heat makes the emitter (cathode) hot enough to evaporate electrons off its surface (thermionic effect). The electrons then traverse the vacuum gap, are absorbed by the collector (anode), and drive the electric current through the external load [DTRA2001]. Right: Calculated efficiency limit for a thermionic energy converter as a function of the cathode temperature for three values of the collector (anode) work function: 1.5, 1.0, and 0.5 eV (based on [Hatsopoulos1973]). For comparison, the dashed curves show the Carnot efficiency limit and the efficiency limits for a thermoelectric converter with a figure of merit of ZT=2, which roughly corresponds to the best existing thermoelectric materials, and ZT = 10, which is much better than the current state of the art. The heat sink is assumed to be at room temperature (300 K) in all cases.*

We are interested in the discovery of new materials with low work functions because such materials could dramatically improve the efficiency of thermionic energy converters (TECs)—a type of heat engine that directly convert heat into electricity (Fig. 1). The efficiency limit of thermionic energy converters depends very strongly on the work function of the collector (anode), as shown in Fig. 1. For a given anode temperature, the optimal work function of the anode is approximately T_{anode}/(700 K), expressed in eV [Hatsopoulos1973]. For example, for anodes rejecting heat near room temperature, the optimal anode work function would be approximately 0.5 eV. Materials with such low work functions have not been discovered yet and therefore, thermionic converters typically use the anodes with the lowest work functions available. In practice, most thermionic converters have used cesiated

tungsten anodes with work functions on the order of 1.5 eV, which means that traditional thermionic converters could have competitive efficiencies only at heat source temperatures above 1500 K (Fig. 1). The lack of materials with lower work functions and the associated high operating temperatures were the main challenges for thermionic converters in the past, explaining both their high cost and limited applicability.

Note that there is no known fundamental limit on how low a work function of a specially engineered surface can be. Experimentation over the last few decades has produced steady albeit small improvements in lowest-work-function surfaces and their stability. The lowest work functions reported in the literature are currently on the order of 1 eV, but most of these surfaces require an ultra-high-vacuum (UHV) environment and are therefore not suitable for high-temperature energy conversion applications. By combining theoretical simulation, experimental characterization, and device demonstration in this proposal, we plan to dramatically speed-up the search for new stable materials with work functions on the order of 1 eV and less. Discovery of new materials that have work functions in the 0.5 – 1.0 eV range and are stable at elevated temperatures in low-vacuum environments will dramatically increase the efficiency of all thermionic energy converters, making them competitive with both thermoelectric converters and mechanical heat engines (Fig. 1). It would also open up new applications for thermionic converters, such as heat harvesting at moderately high temperatures (~ 500° C) in residential combined heat and power systems (micro-CHP). Because thermionic converters have no mechanical moving parts, they produce low noise and need very low maintenance, providing inherent advantages over the mechanical heat engines currently used for CHP systems.

Background

Density Functional Theory (DFT) is a well-established method for first principles calculations that has been remarkably successful when modeling various properties of solid-state systems [Marzari2006, Hafner2006]. Our primary goal is to harness the predictive power of DFT to guide the discovery of new surfaces with the lowest possible work functions.

The best candidate material combinations from the DFT calculations will be tested experimentally by measuring work functions using both thermionic emission and photoemission. Benchmarking against experiment will test the theoretical predictions and provide guidance to further experiments. In this manner, the experimental and theoretical efforts will interact, hence allowing us to screen and test a larger number of promising material combinations than was possible before.

We will study surfaces involving new nano-scale materials, such as graphene, as well as various substrates with nano-scale coatings consisting of, for example, alkali metals or oxides. These coatings can be created using physical vapor deposition and advanced nanofabrication techniques, such as atomic layer deposition (ALD). Layered coatings allow for many more combinations of materials and may therefore lead to lower work functions. For example, it was discovered that oxygen-cesium covered silicon has much lower work function silicon covered with pure cesium [Levine1973]. However, the quantum-level

fundamental understanding of this effect is still lacking. The proposed DFT calculations of such multi-component coatings can both address the existing gaps in our fundamental understanding of such materials and lead to the discovery of new stable surfaces with record-low work functions.

First-principles calculations solve the quantum mechanical Schrödinger equation; DFT is the most widely used computational method because of its accuracy and reliability at a reasonable computational cost. The use of such quantum-mechanical computations for studying materials has today reached a sufficient level of accuracy where it can not only explain experiments, but also predict properties of yet unmeasured systems. This success is owing to significant advances in available computational power and efficient simulation software development. As a result, it is now possible to screen dozens of material candidates without the need for synthesizing and then characterizing them.

The work function is the minimum energy needed to remove an electron from the bulk of a material through a surface to a point outside the material, and is defined as: $\Phi = V_{vac} - E_f$, where E_f, is the Fermi level and V_{vac} is the vacuum level, *i.e.,* the potential energy of electrons immediately outside the material. This quantity can be determined by calculating the charge density distribution obtained from the DFT calculation. In our simulations, the work function will be calculated using the periodic slab/supercell approximation (Fig. 2). We will test when adequate convergence is achieved as a function of atomic layers, number of *k*-points, and the energy cut-off. We will choose different sizes of unit cells to mimic appropriate coverage ratios for cesium or other coatings. The calculations will be performed using both the DACAPO code and the newly developed GPAW code [Enkovaara2010].

Among elemental materials, alkali metals are known to have the lowest work functions. However, in practical applications, a number of alloys and compounds, such as thoriated tungsten and lanthanum hexaboride, are used because they offer relatively low work functions (~2.5 eV) in combination with much better chemical and thermal stability. It has also been known since the pioneering works of Taylor and Langmuir in 1930s [Langmuir1933] that it is possible to create surfaces with work functions lower than those of any elemental materials by using coatings with thicknesses on the order of a monolayer. For example, a tungsten surface with a sub-monolayer coating of cesium (W/Cs system) has a minimum work function of 1.5 eV—significantly lower than the work function of either cesium (~2.0 eV) or tungsten (~4.5 eV). For the W/Cs system, the lowest work function is observed in experiments when the cesium layer has an average thickness on the order of three quarters of a monolayer—a condition described as a coverage ratio of 0.75. This observation is in accordance with our preliminary DFT results as shown in the right panel of Figure 2.

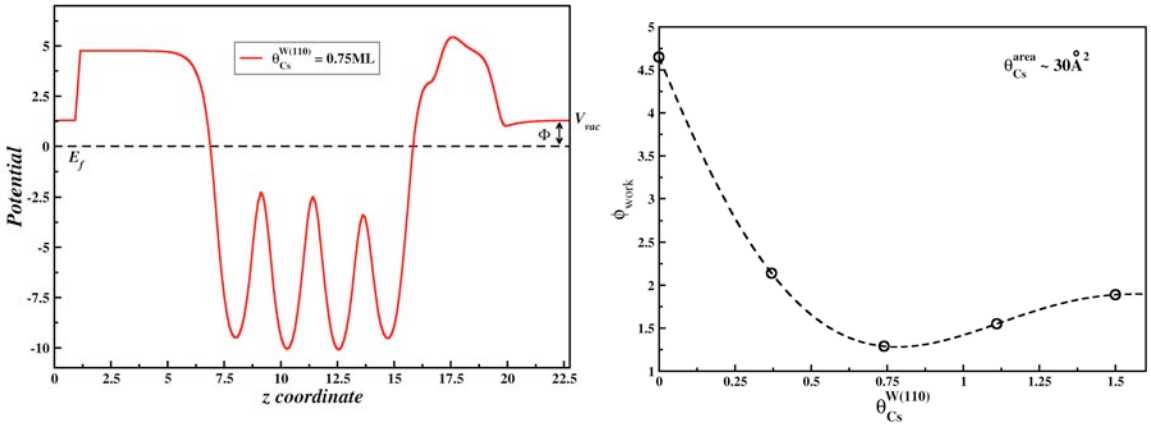


Figure 2: *Left: the electrostatic potential of cesium covered tungsten (110) at a coverage of ~0.75 monolayer (ML). The step in the potential at z ≈ 1 is due to the dipole correction, which is done for computational convenience and does not represent a real change in the potential. The "hump" in the potential near z ≈ 18 is the additional barrier caused by the adsorbed cesium atom. The width and height of this barrier determine the Richardson-Dushman constant of the surface. Right: calculated work function of cesiated tungsten plotted against the coverage of cesium (Nørskov group, 2011).*

The charge transfer at the interface between the surface and the coating plays a crucial role in determining the emissive properties of the surface. It influences not only the work function by shifting the vacuum potential level relative to the Fermi energy of the metal, but also the Richardson-Dushman constant of the surface, by affecting the width and the height of the barrier due by the adsorbate atoms. For optimal electron emission, both a low work function and a low barrier (high Richardson-Dushman constant) are required.

DFT can model surfaces of arbitrary complexity, subject only to the available computational power. So far, the work functions of many solid surfaces have been successfully calculated using DFT, including pure metal surfaces [Fall1999, Fall2001, Singh-Miller2009] as well as metal surfaces with some organic [Natan2006, Rusu2006] and inorganic coatings (overlayers) [Giordano2005, Lina2008, Magkoe2001, Neugebauer1992, Prada2008, Steckel2008, Todorova2004,Vlahos2010]. These prior studies have explained some of the experimental observations and demonstrated that the work function of a surface can be affected by a coating in a variety of ways. This proposal aims to use DFT to both explain and discover new combinations of substrates and coatings that would achieve work functions below 1 eV.

Results

As a first step towards finding new low-work function systems, DFT calculations have been employed to study the cesium-coverage dependence of the work function of various transition metal surfaces. The DFT results confirm the trend of large reduction from the bare transition metal work function to cesiated surfaces at low coverage for high bare work functions (Figure 3); the calculated slope of work function *vs*. coverage at zero coverage indeed shows an almost linear scaling with the bare work function. The DFT calculations,

also capture the deviating behavior of cesiated platinum, which shows a negative slope of lower absolute magnitude than an interpolation of the generally linear trend at the high work function of bare platinum would predict.

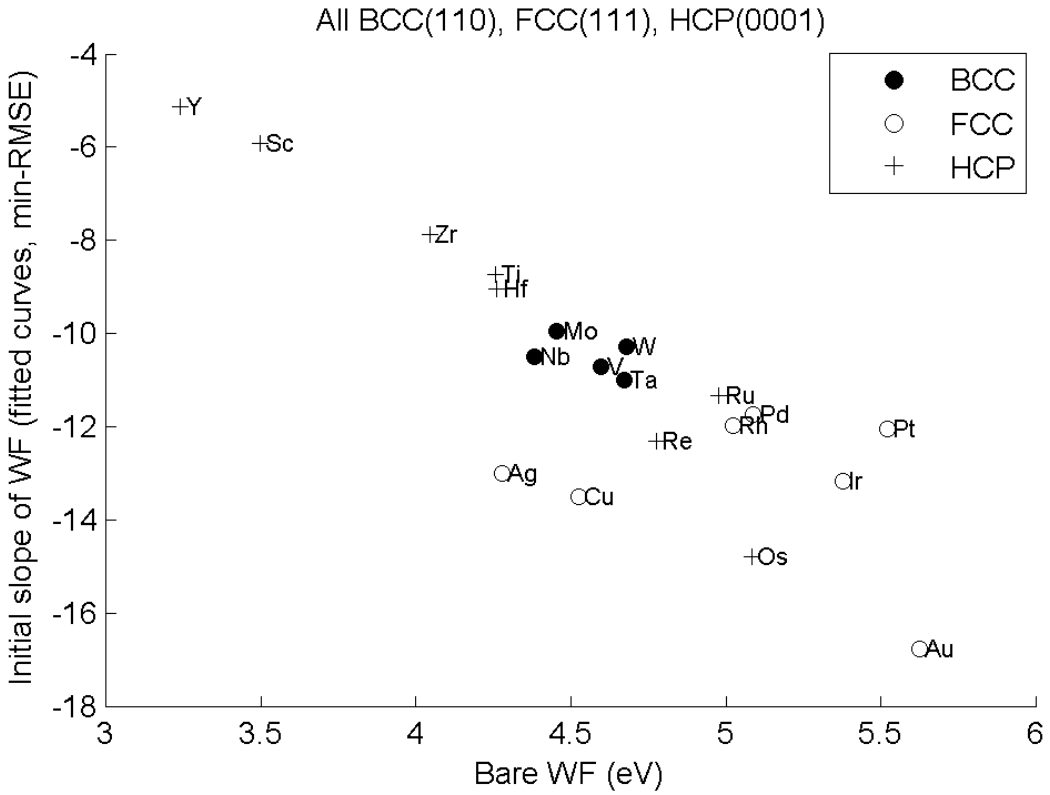


***Figure 3**: Initial slope of work function vs. cesium coverage as a function of the bare transition metal work function.*

The slope at low coverage is governed by the magnitude of the surface dipoles induced by charge transfer from cesium to the surface (Figure 4, left panel), explaining the strong work function reduction for cesiated, highly electronegative transition metals. With increasing coverage, the slope of work function decreases due to depolarization at the cesium sites caused by the electric field-mediated interaction between the dipoles. As a result, the work function initially decreases with increasing coverage as the number of dipoles per unit area increases. Eventually, however, the depolarization effects become too strong; the work function reaches a minimum and then starts to increase again.

However, this old model [Hatsopoulos1973] is incomplete. At optimal cesium coverage (minimum work function), there is non-negligible orbital overlap between neighboring cesium sites (Figure 4, right panel). The work function is very sensitive to the cesium-cesium spacings in our supercell calculations near optimal coverage, indicating that the optimal coverage and hence minimum work function is governed by a crossover from classical, electrostatic-dipole behavior to covalent cesium-cesium bonding dominated behavior. At

even higher coverages, *i.e.* with vanishing area of exposed transition metal atoms, the work function finally saturates to a value around 2eV for all transition metal substrates, which is close to the theoretically predicted and experimentally observed work function of bulk cesium.

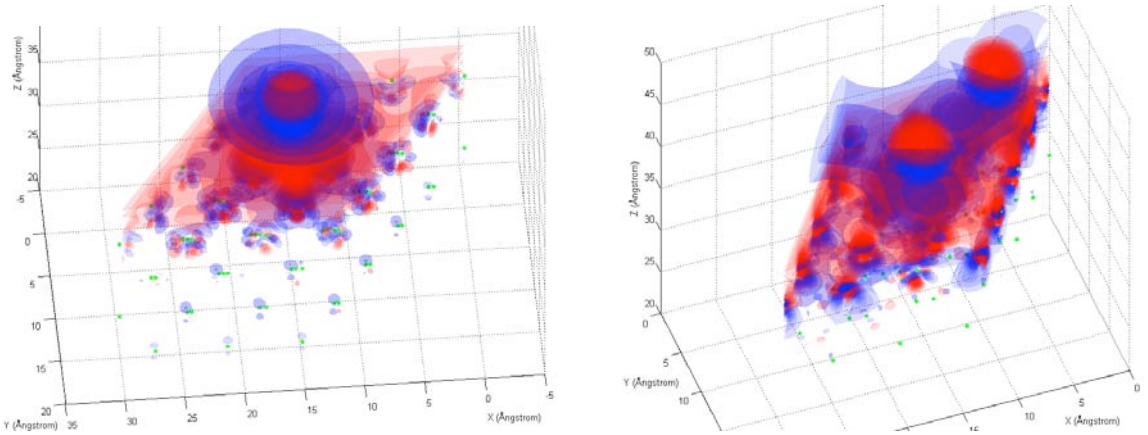


***Figure 4**: Charge density difference plots of cesiated tungsten 110 surfaces at 38% (Left) and 75% coverage (Right) with respect to separately calculated charge densities of the clean surface and cesium atoms. These difference plots serve as a visualization of the induced dipoles (blue color denotes electron rich regions, red color electron poor regions) and of the overlap of cesium orbitals (Right).*

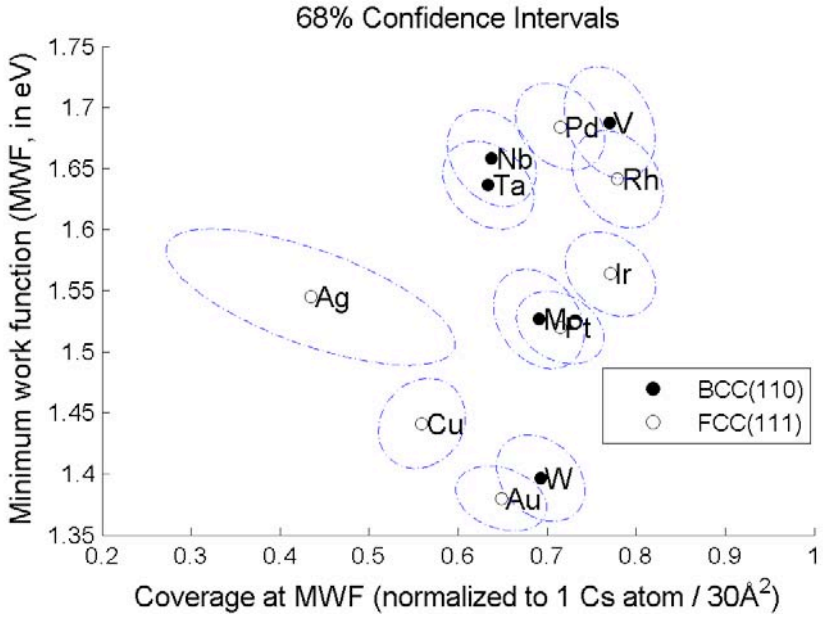
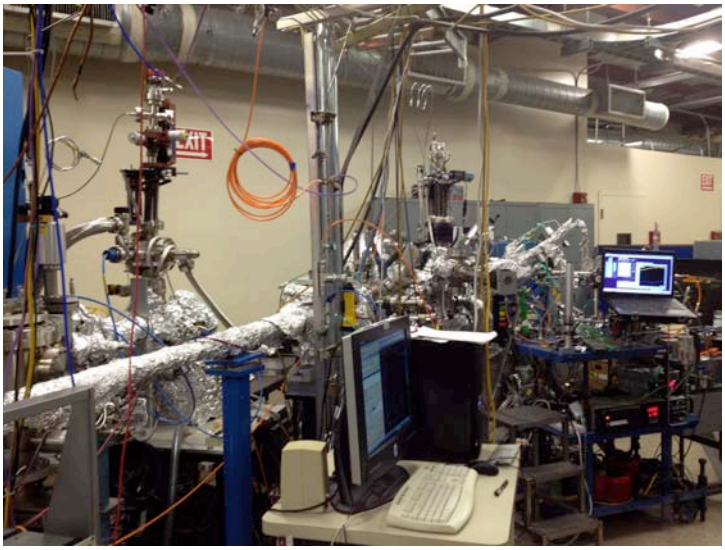


***Figure 5**: Minimum work function and optimal coverage calculated for closed packed body-centered and face-centered transition metal surfaces. The ellipses show confidence integrals while the tilting illustrates to the correlation of optimal coverage and minimal work function as fitting parameters.*

An important design rule for new low-work function materials follows from this crossover in behavior: Since the high-coverage regime dominated by adsorbate overlap is generally only weakly affected by a non-polar substrate, the cesium-substrate dipoles must be strong enough so that a low work function is reached before the crossover to the high-coverage regime occurs. (This constraint can be lifted by considering compound substrates with layered, polar structure in the future.) The calculated work function minimum for the transition metals (Figure 5) generally is lower for those systems where the magnitude of the initial slope is large, *i.e.*, for the transition metals with high electronegativity and high bare work function.



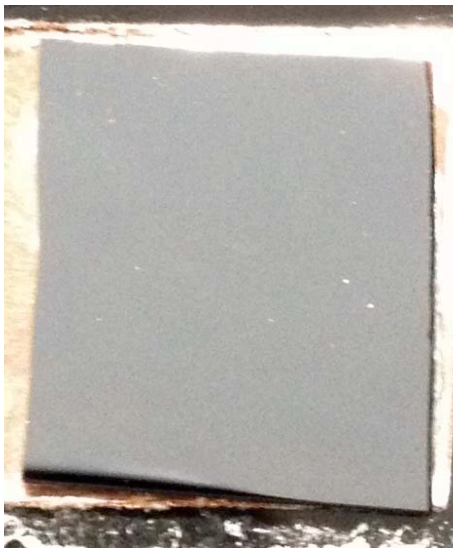


***Figure 6**: (Left) A photograph of the XPS experimental setup at SSRL that is used for surface characterization measurements. The setup has been recently upgraded for measurements of graphene samples. (Right) A piece of a silicon wafer coated with 10-nm-thick layer of alumina using ALD tool at SNF. The white dots show the marks left by the probe station tip during electrical characterization.*

On the experimental front, we have started fabrication of multi-layer structures using an Atomic Layer Deposition (ALD) tool at Stanford Nanofabrication Facility (SNF). In particular, we have prepared 10-nm-thick layers of alumina on doped silicon wafers. Initial electrical characterization measurements showed that the film is continuous and does not break down dielectrically up to ~10 V (breakdown field ~ 1 V/nm), which indicates good film quality. At elevated temperature typical of thermionic converters (>1000 °C), such a thin film of alumina is likely to become a conductor and therefore be useful as a thermionic electrode. In the future, we plan to work with even thinner films of alumina, creating nanoscale two-layer coating consisting of alumina and cesium. Alumina ALD films as thin as 1 nm have been shown to be continuous [Grigoras2008].

We are planning to characterize the work function of this system with and without cesium in the X-Ray Photoemission Spectroscopy (XPS) setup at Stanford Synchrotron Radiation Light Source (SSRL). The setup has been recently upgraded (additional electrical

feedthrough installed) to allow a wider range of electrical measurements. By measuring the low energy cutoff (LEC) of the electron energy distribution, we should be able to determine the work function of arbitrary multi-layer structures. By measuring the high energy cutoff (LEC) of the electron energy distribution as well as the positions of core levels, we should be able to determine the electron affinities, bandgap, and other properties of the semiconducting /insulating coatings.

Using this system, we should also be able to measure the work function of doped graphene samples. Our earlier calculations have indicated that p-doped graphene should exhibit very low work functions (<1.0 eV) when optimally cesiated. The newly upgraded experimental setup will be particularly suitable for such measurements.

Progress

- Visualized the formation of dipoles on the surfaces of materials with low-work-function coatings, such as cesium and cesium oxide.
- Validated the predictions of the used DFT package by observing general trends in the behavior of binary systems consisting of transition metal substrates and cesium coating.
- Fabricated initial experimental samples and upgraded measurement setup

Future plans

In the near future, we plan to extend the theoretical simulations to other surfaces of transition metals in order to better simulate the behavior of polycrystalline substrates. We are also in the process of developing a model predicting the work function of cesiated transition metals as a function of cesium coverage. Further in the future, we will screen various tertiary systems (substrate + coating #1 + coating#2) that have not yet been realized in experiments on order to find ones with the lowest predicted work functions. On the experimental side, we will soon perform measurements of cesiated alumina and graphene surfaces. Further out, we will fabricate and characterize new tertiary systems identified by the theoretical effort.

Publications and Patents

none (project started in Oct 2011)

References

[DTRA2001] National Research Council, "Thermionics: Quo Vadis" (National Academy Press) (2001)

[Enkovaara 2010] J. Enkovaara, C. Rostgaard, J. J. Mortensen et al., J. Phys.: Condens. Matter 22, 253202 (2010)]

[Fall1999] C.J. Fall, N. Binggeli, A. Baldereschi, J. Phys.: Condens. Matter 11 2689–2696 (1999)

[Fall2001]C. J. Fall, N. Binggeli, A. Baldereschi, Phys. Rev. B 65, 045401 (2001)

[Giordano2005] L. Giordano, F. Cinquini, G. Pacchioni, Phys. Rev. B 73, 045414 (2005)

[Grigoras2008] K. Grigoras, S. Franssila, V.-M. Airaksinen, Thin Solid Films 516, 5551–5556 (2008)

[Hatsopoulos1973] G. N. Hatsopoulos and E. P. Gyftopoulos, “Thermionic Energy Conversion”, vol. 1 (Cambridge, MA.: MIT Press, 1973).

[Hafner2006] J. Hafner, C. Wolverton, G. Ceder, MRS Bull. 31, 659 (2006).

[Langmuir1933] J.B. Taylor, I. Langmuir, Phys. Rev. 44, 423–458 (1933)

[Levine1973] J.D. Levine, Surface science 34, 90 (1973)

[Lina2008] M.-C. Lina, R.-F. Jao, W.-C. Lin, J. Vac. Sci. Technol. B 26, 821 (2008)

[Magkoe2001] T.T. Magkoe, G.G. Vladimirov, J. Phys.: Condens. Matter 13, L655 (2001)

[Marzari2006] N. Marzari, MRS Bull. 31, 681 (2006).

[Natan2006]A. Natan, L. Kronik, Y. Shapira, Appl. Surf. Sc.252 7608 (2006)
[Neugebauer1992] J. Neugebauer, M. Scheffler, Phys. Rev. B 46, 16067 (1992)
[Prada2008] S. Prada, U. Martinez, G. Pacchioni, Phys. Rev. B 78, 235423 (2008)
[Rusu2006] P.C. Rusu, G. Brocks, Phys. Rev. B 74, 073414 (2006)
[Singh-Miller2009] N.E. Singh-Miller, N. Marzari, Phys. Rev. B 80, 235407 (2009)
[Steckel2008] Janice A. Steckel, Phys. Rev. B 77, 115412 (2008)
[Todorova2004] M. Todorova, K. Reuter, M. Scheffler, J. Phys. Chem. B 108, 14477 (2004)
[Vlahos2010] V. Vlahos, J.H. Booske, D. Morgan, Phys. Rev. B 81, 054207 (2010)

Contact

Roger T. Howe: rthowe@stanford.edu
Jens K. Nørskov: norskov@stanford.edu
Piero A. Pianetta: pianetta@stanford.edu
Igor Bargatin: bargatin@stanford.edu
Johannes Voss: vossj@stanford.edu
Frank Abild-Pedersen: abild@slac.stanford.edu
Aleksandra Vojvodic: alevoj@slac.stanford.edu
Sharon Chou: cnorahs@stanford.edu
Hongyuan Yuan: hyyuan36@stanford.edu