Using First-Principles Simulations to Discover Materials with Ultra-low Work Functions for Energy Conversion Applications

Global Climate and Energy Project Annual Report
April 14, 2014

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

This project’s goal is to discover new nanostructured materials with ultra-low work functions for achieving high-efficiency thermionic energy conversion. Since starting in October 2011, we have made progress on all three thrusts: (1) density functional theory (DFT) calculations of the work functions and emission currents from multi-layer surfaces, (2) fabrication of multilayer surfaces with low work functions, and (3) measurements of surface properties of multi-layer surfaces.

Over the past year, we have continued DFT calculations to predict the work function of alkali-earth oxides containing barium, calcium, and strontium with lithium or scandium doping, which are useful for lowering the work function of thermionic emitters. A systematic study of both work function and the energy of formation is currently being published [1], which provides a guideline for developing stable and efficient thermionic emitters. Our work on a new DFT-based method for calculating thermionic emission currents using a non-equilibrium Green’s function (NEGF) was completed [2]. This paper was selected by the editors of J. Chem. Phys. as one of the most innovative and influential papers of 2013. Since the new model can provides quantitative predictions of thermionic emission for adsorbate-coated surfaces, it is a breakthrough in the computational design of improved emitters. Low work function is a necessary, but not sufficient, condition for achieving high emission currents.

The experimental thrusts have ramped up substantially over the past year. We have improved the fabrication process for the graphene-hafnia laminate, by reducing leakage currents in the alumina and defects in the graphene layer. This structure is promising since graphene’s workfunction can be shifted lower by applying an electrostatic field by biased the substrate. This effect, known as electrostatic doping, has been demonstrated in vacuum measurements at SSRL. We are microfabricating emitters for testing the DFT predictions for emission from tungsten thin films coated with mixed-oxide coatings. Finally, we have begun construction of a vacuum chamber in which these micro-emitters can be optically heated, with the thermionic current collected by a graphene-hafnia laminate spaced from it by about 10 μm.
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. 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.

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 $T_{\text{anode}}/(700 \text{ K})$, 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

![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. 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. 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.](image-url)
main challenges for thermionic converters in the past, explaining both their high cost and limited applicability.

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 ($\sim 500^\circ$ 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.

**DFT Simulations of Alkali-Earth Oxides with Scandium or Lithium Doping**

We are examining tungsten surfaces coated with alkali-earth oxides that contain either scandium or lithium as film dopants. The alloyed surfaces are set up with *Quantum Espresso*, a DFT-based simulator. As many commercial dispenser cathodes operate with an emissive mixture of barium, calcium, and strontium oxides, we are surveying the full range of mixing ratios for their work functions and their formation energies, which we use as a metric of thermodynamic stability (Figs. 2 and 3). By visualizing the optimal regions with both low work function and high stability, we can motivate further experimentation with the coating compositional mixtures located in those regions.

*Figure 2: The work function distribution (a) and relative formation energy (b) of adsorbed Ba+Ca+Sr oxide with scandium on W(100).*
We find that the lowest work function for the scandium-doped mixed alkali-earth oxide films is 1.16 eV occurring at 20% calcium content (Fig. 2a). This value is below the work function of any of the pure phases, showing that alloying can lead to new materials with desirable properties outside the range of the pure phases. We find that the thermodynamically most stable alloy film consists of a ~30%:5%:65% ratio of Ca:Sr:Ba, corresponding to the lowest formation energy in Fig. 2b. Small calcium contents have been observed experimentally to improve the stability of dispenser cathodes. Since both optimum work function and stability are achieved with non-zero, but small calcium content, these properties can be optimized simultaneously for scandium-doped films.

Computational screening of lithium-doped mixed alkali-earth films reveals low work functions without sacrificing stability (Fig. 3). Here as well, the optimum stability is found for approximately 20% calcium with high barium content (~30%:5%:65% Ca:Sr:Ba mixing). In contrast to scandium-doping, lithium-doping does not decrease the stability relative to the undoped films. Lithium-doping only increases the formation energy by about 0.05 eV, while the work function is lowered by as much as 0.4 eV. The minimum work function found is 1.22 eV, comparable to the optimum in the case of scandium-doped films. The optimum is reached for ~15% calcium content in this case. The minimal work function is not found for the most stable alloy, however, the system provides a good compromise between low work function and stability. Therefore, lithium could be preferred as a film dopant over scandium when long lifetime is favored over maximized emission current density.

Figure 3: The work function distribution (a) and relative formation energy (b) of adsorbed Ba+Ca+Sr oxide with lithium on W(100).

In summary, the work function and stability of a wide range of alloyed alkali earth oxide films on W(100) have been calculated using density functional theory. Low work functions are achieved by doping the films with scandium or lithium and alloys containing small amounts of calcium. In particular, lithium-doped systems with small calcium content also show favorable thermodynamic stability and promising application in micro-thermionic converters.
Electrostatic Doping of Graphene for Ultra-low Work Functions

Traditional methods of work-function lowering rely on these alkali-earth oxide coatings, which date to the first half of the 20th century. However, these coatings typically enable work functions only as low as 1.5 eV. However, for applications such as thermionic emission converters (TEC), whose output efficiency is highly dependent on its anode’s (collector’s) work function, a work function of over 1 eV is not low enough for efficient operation. Extensions of the analysis shown in Fig. 1 indicates that with an anode work function of 0.5 eV, a TEC can reach an efficiency of over 50% under 1000x concentrated solar radiation. The recent discovery and development of 2D materials open a wholly unexplored avenue for achieving ultra-low work functions. We are exploring a new approach to work function reduction that exploits material’s unique properties – the electrostatic doping of graphene.

The laminate structure for electrostatic doping is shown schematically in Fig. 4a, in which graphene is electrically isolated from a bulk silicon substrate via a thin insulating layer. By biasing graphene relative to the substrate, compensating charges build up at the surface. This excess electron population shifts the Fermi level relative to the equilibrium value, directly reducing the work function at the surface. This doping-driven work function reduction is in direct contrast to typical three-dimensional semiconductor materials, where doping has minimal influence on work function due to surface Fermi-level pinning. Furthermore, electrostatic doping can be directly combined with conventional coatings, like Cs or Ba, which dramatically lowers the vacuum level (Fig. 4b).

Our graphene is grown on copper foil through chemical vapor deposition (CVD), which is a well-established technique. It is then transferred onto a doped silicon substrate coated with a 20 nm-thick layer of hafnium dioxide (HfO₂), which is formed by atomic layer deposition (ALD). The quality of graphene after transferring is characterized by optical microscopy and Raman spectroscopy (Fig. 5a). The transfer process has been optimized to remove trapped water between the graphene and hafnia before the removal of the PMMA carrier layer (coated on graphene for the transfer process). High quality hafnia is achieved, through annealing in forming gas for 30 minutes at 400°C. We learned that the leakage between the graphene and substrate is due to the edges of the graphene. When the four corners of the graphene are clipped, the leakage current decreases significantly (Fig. 5b.)
Figure 5. (a) optical microscope image showing over 95% continuity of CVD graphene transferred onto a 300 nm-thick silicon oxide film on silicon. The inset figure is a typical single point Raman spectrum. (b) I-V curve for 20 nm-thick hafnia film after graphene is transferred, with edges of no treatment (green), and edges clipped (blue). They are compared to the I-V curve for a platinum metal contact without graphene (red).

Recent photo-emission experiments have shown a work-function decrease of at least 0.4 eV (Fig. 6a) before oxide breakdown, based on a complementary error function fit for each low-energy cutoff (Fig. 5b). With improved insulator quality, we expect a shift of at least 0.5 eV. The reduction of work function due to electrostatic doping fits very well to the second quadratic polynomial (Fig. 5c), as predicted by a first-order calculation based on graphene’s linear dispersion relationship, $E = \nu \hbar |\mathbf{k}|$, where $\nu$ is the Fermi velocity [3].

Figure 6. Work function reduction of graphene by electrostatic doping, without surface activation by cesium or barium. (a) Low energy photo-emission cutoff data obtained from Stanford Synchrotron Radiation Lightsource (SSRL), beam line 8-1. Beam energy is 120eV, with 1mm² in size. (b). an example of work function reading by fitting the cutoff of $V_{\text{bias}}=0$V to complementary error function $I = a \cdot \text{erfc}(\frac{\phi_{WF} - b}{\sqrt{2} \sigma}) + I_{\text{min}}$, where $\phi_{WF}$ is the work function and $\sigma$ is the half-width of the rising side of the peak. (c). work function vs. different bias voltages, compared to the curve-fit: $V_{\text{bias}} = a(\phi_{WF} - b)^2 + c$, where $a = 44.37$, $b = 4.41$, $c = -0.05$. 
To further reduce graphene’s work function, we can activate the surface by depositing a sub-monolayer of cesium or barium in a vacuum, as these alkali materials are very reactive with oxygen. During deposition, the graphene was illuminated with a blue laser to monitor its quantum efficiency (QE). We stopped the cesium deposition when the QE reached its maximum and found that the work function decreased to about 1.5 eV. However, due to contamination in the chamber, the work function shift decayed rapidly (Figs. 7 and 7b). The change due to decay in activation by cesium is mixed with the shift due to electrostatic doping. As a result, we are not yet able to extract the work function reduction by electrostatic doping in the presence of alkali metal deposition.

**Figure 7.** Work function decay after sub-monolayer cesium deposition. (a) Low energy cutoff shifts from left to right over time. (b) extracted work function from (a) as a function of time.

In the near future, we will install an additional vacuum pump to this chamber at SSRL beam line 8-1 to lower the chamber pressure. After a more thorough bake-out of the chamber, we will repeat the activation of graphene with cesium. From previous experience, these improvements should give us a stable enough surface to allow electrostatic doping measurements before significant decays occurs. We expect to see lower than 1.5 eV work function after activation, and lower than 1 eV work function, when combined with electrostatic doping.

**Testbed for Thermionic Electrodes**

The efficiency of thermionic energy converters is a strong function of the inter-electrode separation due to space-charge limitations. Our group has shown that the optimum inter-electrode gaps are in the 2–10 μm range to minimize space charge limitations while simultaneously avoiding significant near-field thermal exchange. [4] Micro-thermionic emitters have been demonstrated recently by our group, with gaps to the substrate in this range fabricated using MEMS technology. The suspended structure is fabricated from poly-SiC, with an oxide-coated tungsten emissive surface [5,6].

This breakthrough is the foundation for a testbed for the characterization of thermionic emitters and collectors. We have designed an improved poly-SiC suspended micro-emitter process, which is designed for testing the emissive performance of oxide-coated tungsten surfaces, as well as the
performance of low work function collectors (Fig. 8). The micro-emitter is heated optically through an aperture in the silicon substrate.

Figure 8. Micro-fabricated emitter structure. (a) Top view of a single suspended poly-SiC micro-emitter. The suspended plate is either 200 x 200 μm² or 500 x 500 μm² in area and is suspended 10 μm above the surface of the silicon substrate, (b) cross section along A-A’ in (a), (c) cross section along B-B’ in (a). The tungsten film and low work function oxide coating are deposited on the suspended plate.

In order to use one or an array of micro-emitters to test the work functions of the graphene collectors, the latter must be separated from their upper surface (in Fig. 8) by a gap 2–10 μm. Our group has previously developed a solution for this problem: the use of alumina micro-spheres to separate the electrodes while maintaining thermal isolation [7]. In the initial experiments, a conventional dispenser cathode was separated from a tungsten anode using randomly dispersing micro-spheres. A more controlled spatial distribution of tightly controlled sphere diameters is needed for the technique to be sufficiently reproducible to define the separation of the anode and the fragile suspended micro-cathodes shown in Fig. 8. The poly-SiC is patterned to form holes to confine the micro-spheres at locations around the perimeter of the cathode chip, as shown in Figs. 9a and 9b in plan view and cross section. The alumina micro-sphere’s diameter determines the gap size, which can be selected to be in the optimal range. The micro-spheres are not in contact with the optimally heated, suspended micro-emitters. A rendering with a perspective view and cross section of the test assembly is shown in Fig. 9c.

During thermionic converter operation, either a high vacuum or a special low-pressure gas environment is required to prevent degradation of the heated micro-emitter. The latter is typically used for the ignited mode, in which a plasma is generated to compensate space charge, at the cost of decrease of output voltage [8]. Since the separation is below the gap where space-charge begins to form, we will mount the test fixture mounted in a vacuum chamber.
Figure 9. (a) Layout of one cathode dye. The darker green bars surrounding the cathodes are the lip ring region. Holes for alumina beads, separated by 1 mm from each other, are created within regions marked by dashed rectangles. (b) Zoom-in of the lip ring region with alumina beads. (c) Solidworks™ sketch to show the two glass holders, onto which cathode and anode chips are mounted. These two holders are held in slight compression by three 0-80 screws and nuts (not shown), to ensure that the alumina micro-spheres define the cathode-anode separation.

The high vacuum chamber and optical system is shown in Fig. 10. The 405 nm laser is mounted outside viewport and is collimated and focused to a beam width of less than 75 μm; a CCD camera and white LED allow the in situ monitoring of the laser beam position on the cathode substrate (Fig. 10a, 10b). A five-axis vacuum compatible translation stage allows the sample to be moved precisely, so that the laser can illuminate each micro-emitter on the die (Fig. 10c).

Figure 10. (a) Optical system to focus a 405 nm laser to less than 75 um in diameter at the aperture in the silicon wafer, as well as real-time monitoring of its position the sample. (b) Test chamber overview. Additional ports are provided for potential future expansions. (c) Chamber inside view: five-axis translation stage is mounted on a breadboard, which is attached to the laser flange. A pyrometer is used to measure the temperature of the micro-emitter via a separate port.
Summary and Research Plan

The computational modeling effort has yielded a detailed map of work functions and energies of formation for complex alkali earth oxide coatings. The micro-emitter fabrication run is approximately half finished, with an expected completion date in June 2014. The model predictions will be used for compositional screening to develop stable alkali earth oxide coatings for the micro-emitter with relatively low work functions ($\leq 1.5$ eV). The coating will be formed by successive depositions of simple oxides using atomic-layer deposition, followed by thermal annealing. We estimate that the coating process development will be completed this summer.

Micro-emitters with stable oxide coating are essential for characterizing the performance of the low-work function, electrostatically doped graphene anodes. In contrast to commercial dispenser cathodes, our micro-emitters will not outgas contaminants across the electrode gap. In order to assemble the emitter (cathode) and collector (anode) chips so that the electrode surfaces are separated by only a few microns, we have invested several months in the design of a precision test fixture. The suspended micro-emitter will be heated by a blue laser focused through an aperture in the silicon substrate, which will allow the anode’s performance to be tested under the high current densities found in operating thermionic energy converters. The test fixture will be operated in a vacuum system with optical and electrical ports.

The test fixture, vacuum, and optical system design have been thoroughly reviewed and the components will be ordered this month. Building the vacuum system and the optical system will require several months. Full de-bugging of the system should be complete by October. Testing of the micro-emitters with low-work function coatings together with the electrostatically doped graphene anodes will require another four months, through the end of February 2015. The delays in developing a high-quality graphene transfer process with low-leakage and high breakdown field ALD insulating films have delayed the experimental thrusts of the project.

Publications