When 2D material and MEMS meet - new generation thermionic energy conversion

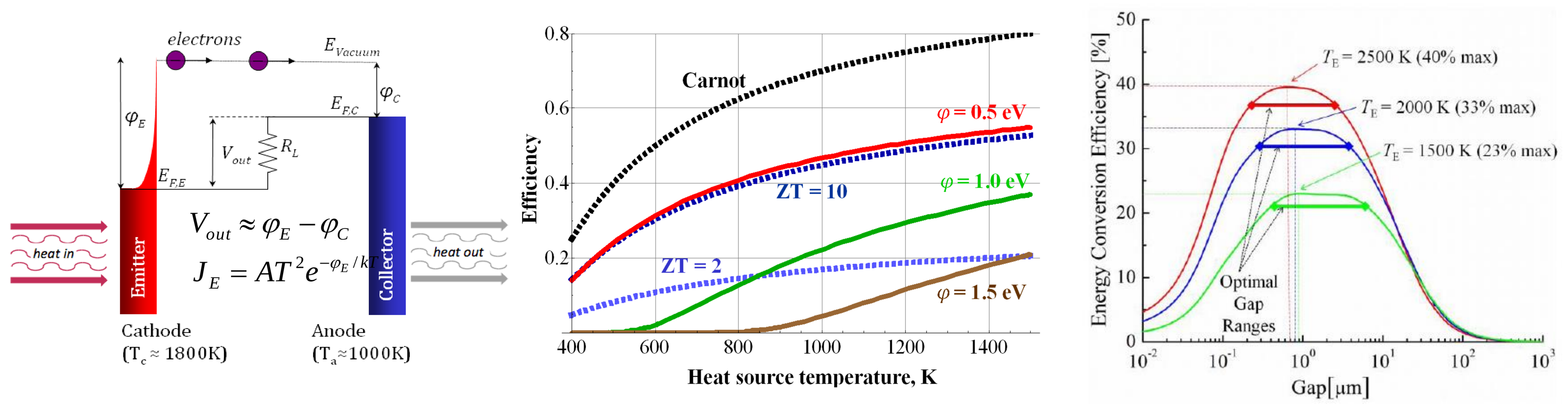
Hongyuan Yuan*[1], Nandita Bhaskhar[2], Igor Bargatin[5], J Provine[5], Nicolas A. Melsoh[3], Piero A. Pianetta[2,4], Roger T. Howe[2]

Motivation

We are interested in the discovery of new materials with low work functions because the efficiency of both traditional thermionic energy converters (TECs) and photon-enhanced thermionic emission (PETE) converters depends critically on the work function of the anode (ϕ_c in figure). For anodes rejecting heat near room temperature, the optimal anode work function is approximately T_{anode}/(700 K) = 0.5 eV [Hatsopoulos1973].

Materials with such low work functions have not been discovered yet. Therefore, thermionic converters typically use the anodes with the lowest work functions available, such as cesiated tungsten anodes with work functions ≈ 1.5 eV. This means that traditional thermionic converters could have appreciable efficiencies only at heat source temperatures above 1500 °C.

A new mechanism - photon-enhanced thermionic emission (PETE) - can be particularly useful for solar energy applications as it can use both the high per-photon energy of solar photons and the heat resulting from sub-bandgap photons and other losses. Similar to conventional TECs, the efficiency of PETE converters is strongly dependent on the work function of the anode. For anode work function of ~0.5 eV, the efficiency of PETE converters can exceed 60% [Schwede2010].



Left: schematic illustration of traditional thermionic emission converter during operation. The output voltage is the difference of work function between cathode(or emitter) and anode(or collector). Output current is described by Richardson-Dushman equation. During optimal operation, we assume no back current comes out from anode, which maintains at room temperature.
Middle: Calculated efficiency limit for a thermionic energy converter as a function of the cathode temperature for three values of the collector (anode) work function [Hatsopoulos1973]. The dashed curves show the Carnot efficiency limit, limits for a converter with a figure of merit ZT = 2 (roughly corresponds to the best existing thermoelectric materials), and ZT = 10 (much better than the current state of the art). The heat sink is assumed to be at room temperature (300 K) in all cases.
Right: Maximum energy conversion efficiency versus gaps for emitter temperatures of 1500 K, 2000 K and 2500 K, collector temperature of 900 K, and collector work-function of 1.5 eV

Electrostatic doping graphene to change work function

From Linear Dispersion Relationship:

$$E = \hbar v|k|$$

Based on 2D electron free gas, assuming E_F lies at the Dirac cone when V_{bias}=0, we have:

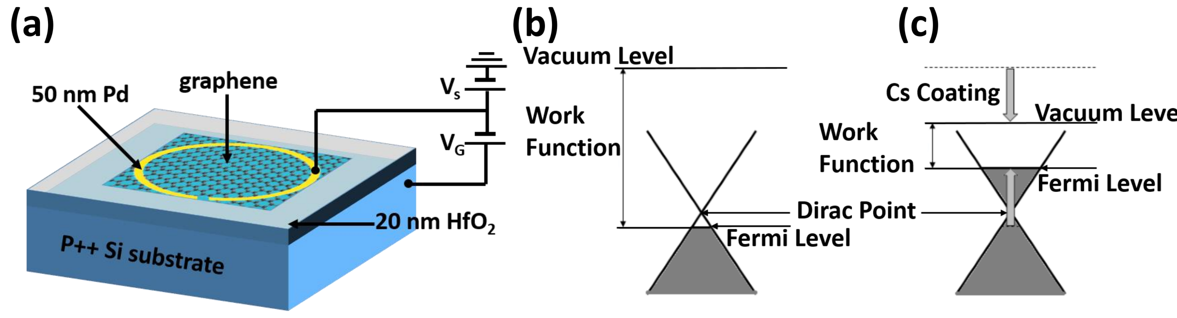
$$E - E_{f0} = \sqrt{n_0 \pi \hbar^2 v^2}$$

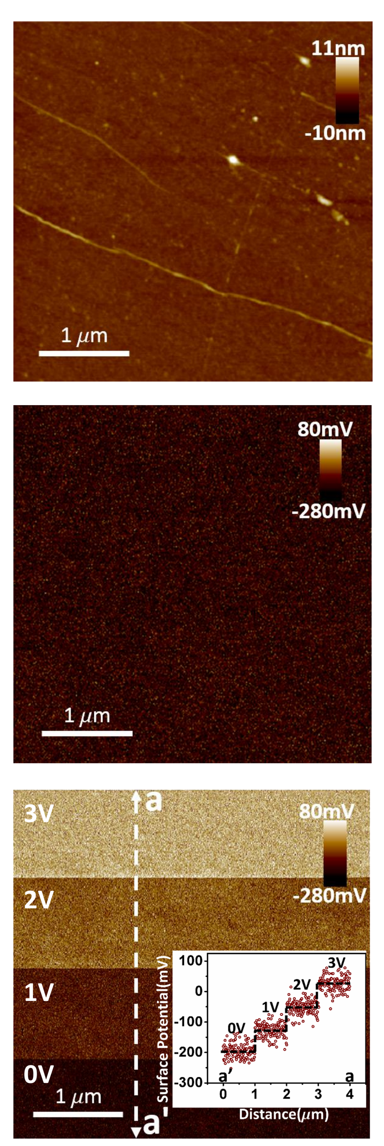
Where n_0 is the density of electrons by electrostatic doping.

Based on ideal planar capacitor: $n_0 = \varepsilon \frac{V_{bias}}{de}$

We then have:

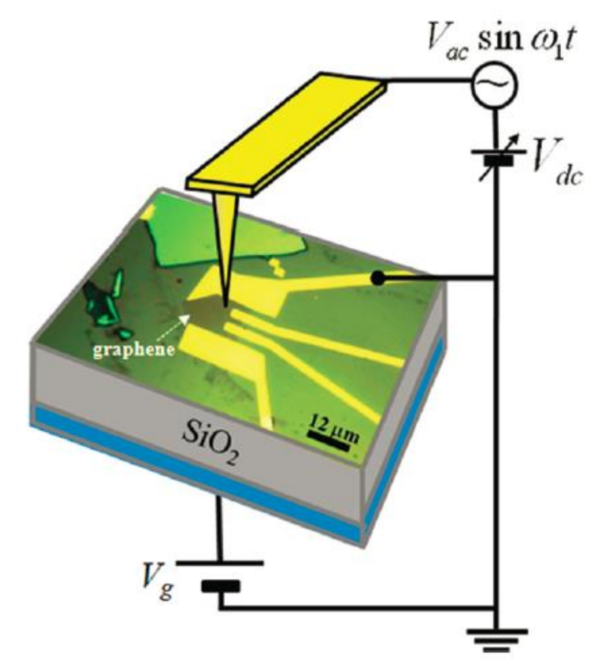
$$E - E_{f0} = \hbar v \sqrt{\frac{\pi \varepsilon V_{bias}}{de}}$$





Challenges:
1. High dielectric constant, high breakdown voltage, low leakage current thin oxide.
2. Near 100% of graphene transferring
3. Process Compatibility

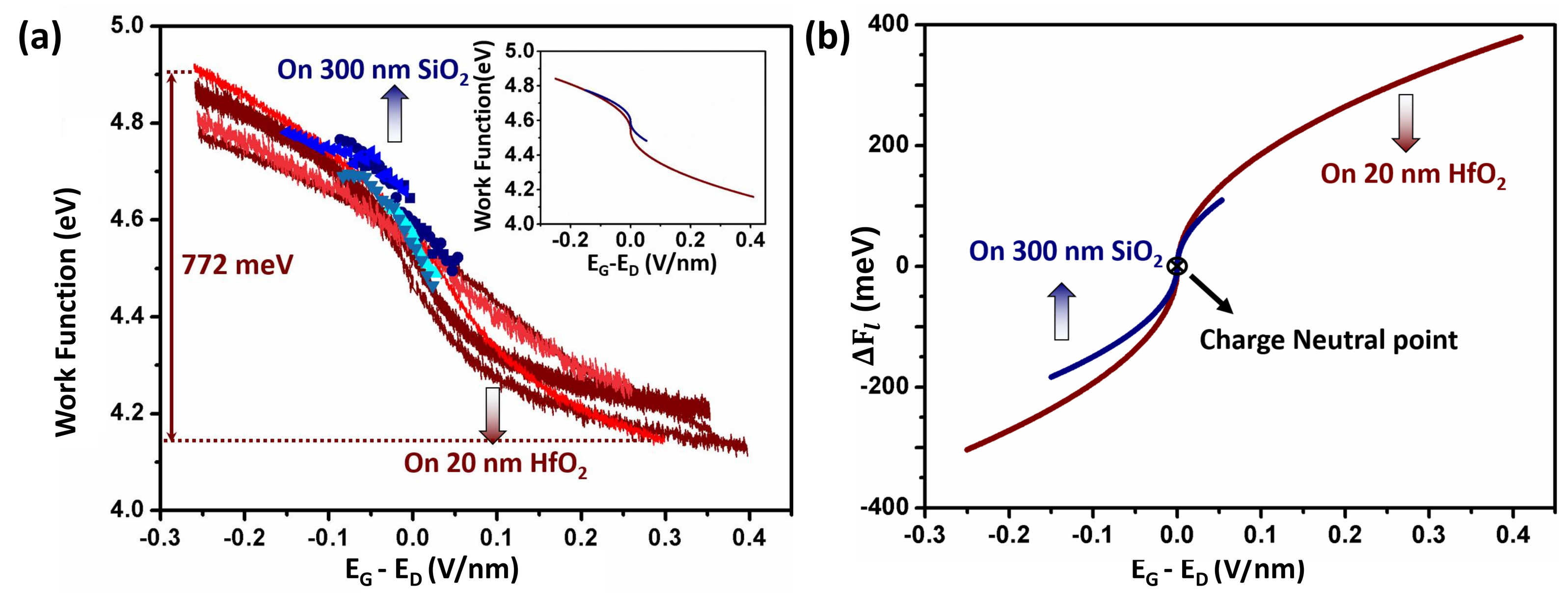
Scanning Kelvin Probe



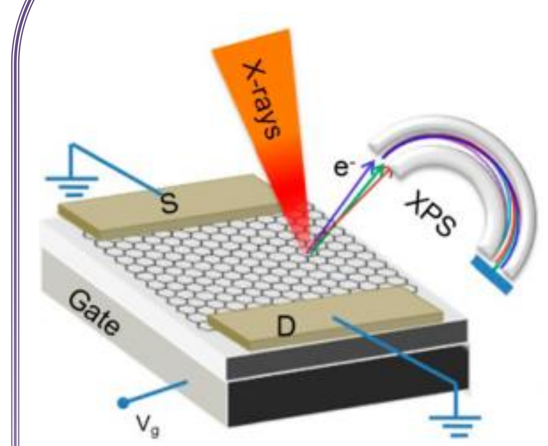
Scanning Kelvin Probe uses the tip's work function as a reference to measure sample's work function by measuring the contact voltage drop.

Top left: schematic diagram for measuring graphene's work function using Kelvin Force Microscopy
Top middle: Switching the back gate voltage form -4V to 8V, measure the local work function change at one single position for each sample 1 to 5
Top right: KFM scan at a clean graphene area with back gate voltage change. Each contrast change corresponds to 1V back gate change
Bottom left: KFM results at a contaminated graphene region. The contamination is likely to be PMMA. At contaminated region, the work function change is reluctant to back gate voltage change.

The biggest work function change due to electrostatic doping achieved is 0.82eV, which TRIPLES the state of the art performance so far! (Yu2009)



Photoemission Spectroscopy



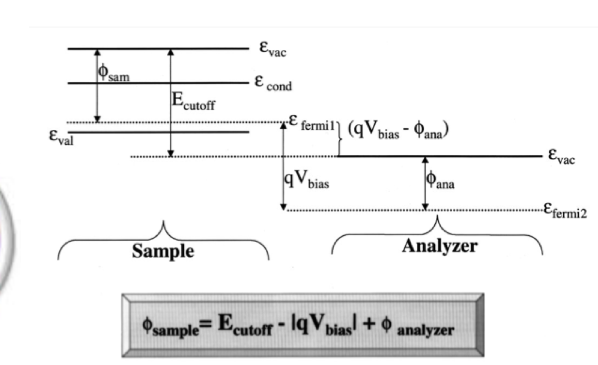
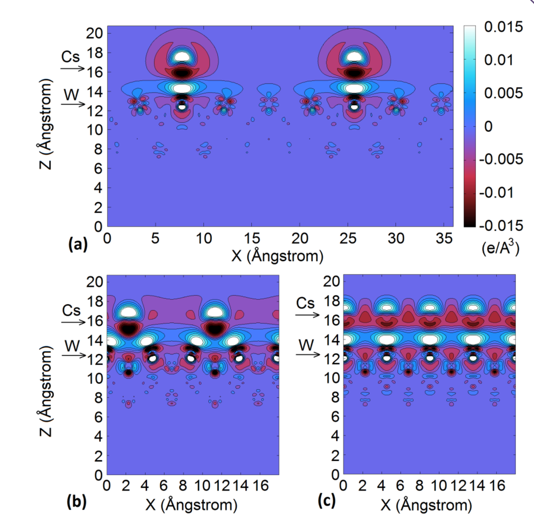
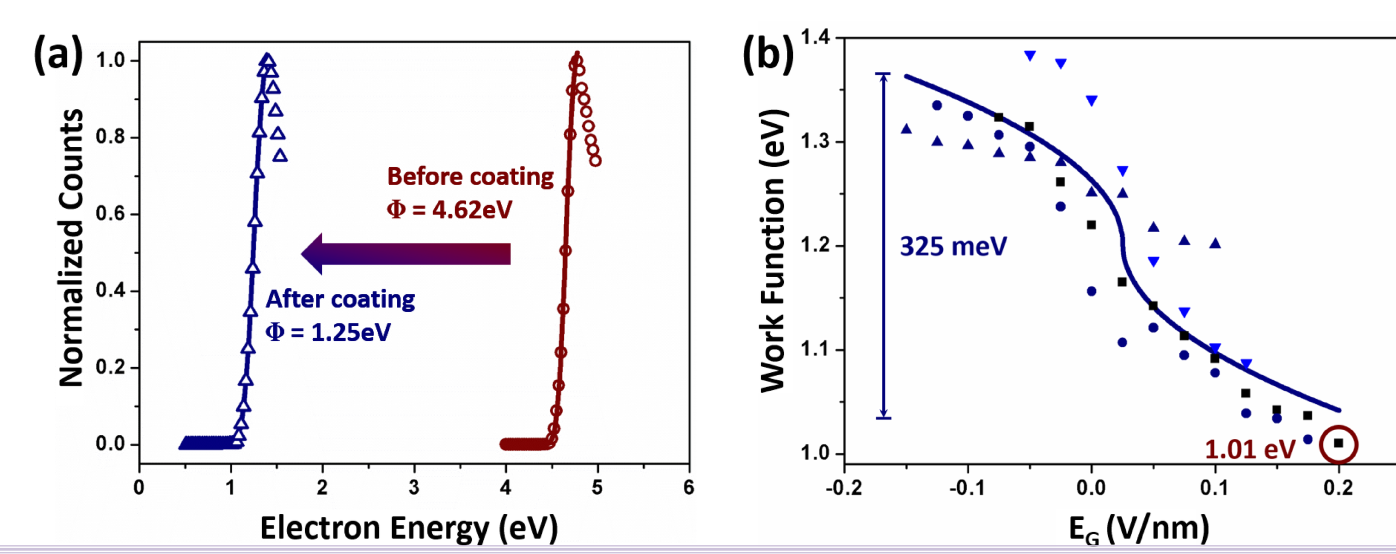


FIG. 1. Schematic view of the energy bands of the sample and the analyzer collection electrode through a bias voltage V_{bias} during a work function measurement. The value of E_{cutoff} is used to calculate the work function of the sample.

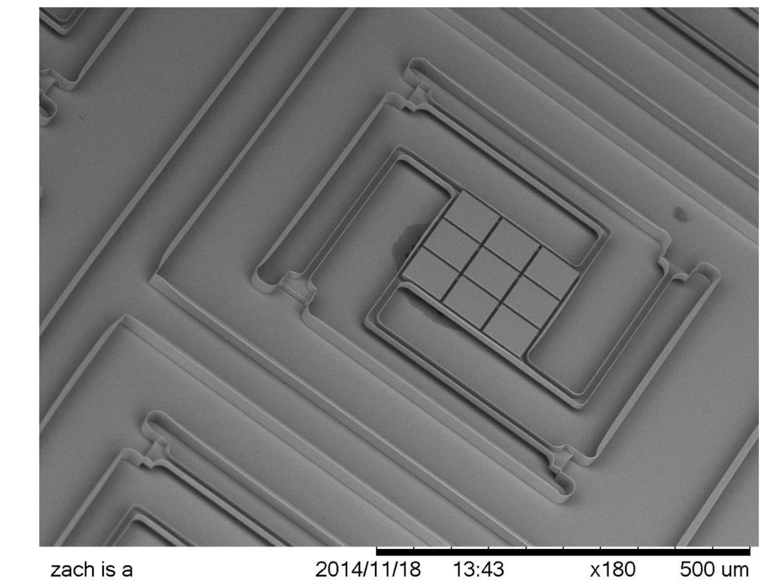


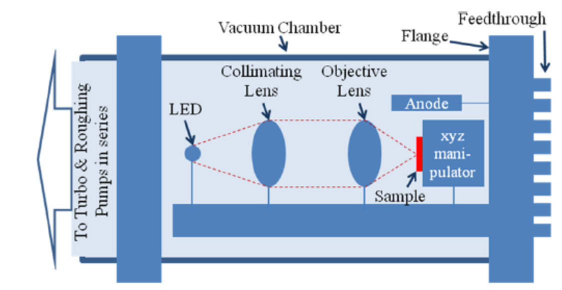
- Another way for measuring work function is through photoemission. By looking at its low energy cut-off, we can directly measure sample's work function precisely.
- Less than one monolayer of Cesium oxygen would usually lead to very low work function, which has been discovered on many materials. In this work, for the first time, we demonstrate that this combination, in combination with electrostatic doping, would give the lowest work function reported so far on graphene: 1.01 eV!
- Without any coating (shown as red on the left), photoemission measurement shows about 4.62 eV work function
- After less than one mono-layer of Cs/O being deposited, work function is reduced down to 1.25 eV.
- Electrostatic doping remained after Cs/O coating, on the range of around 325 meV.

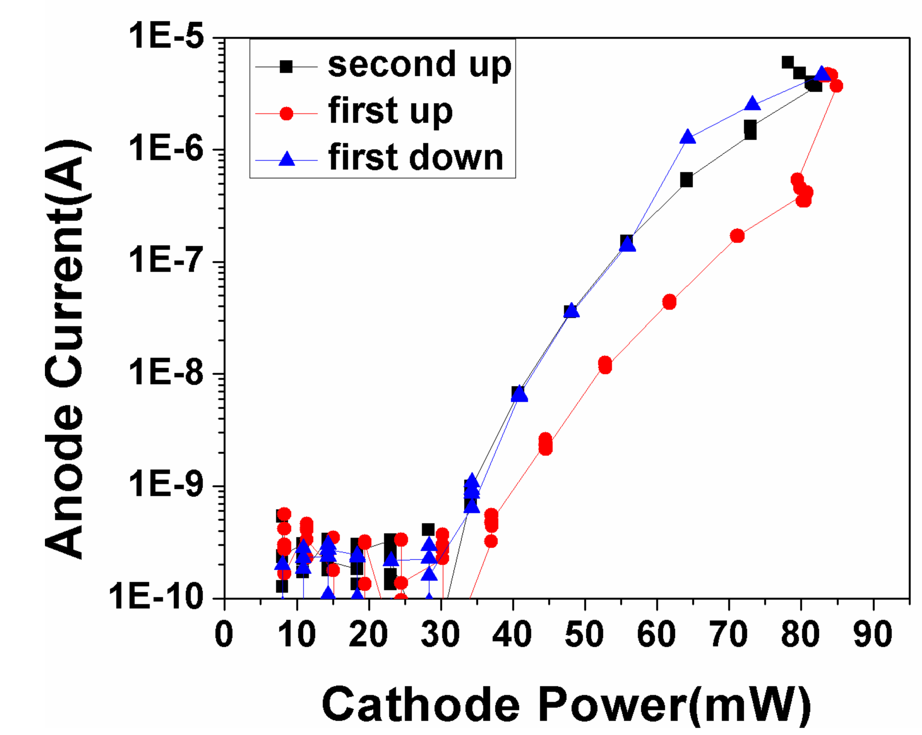


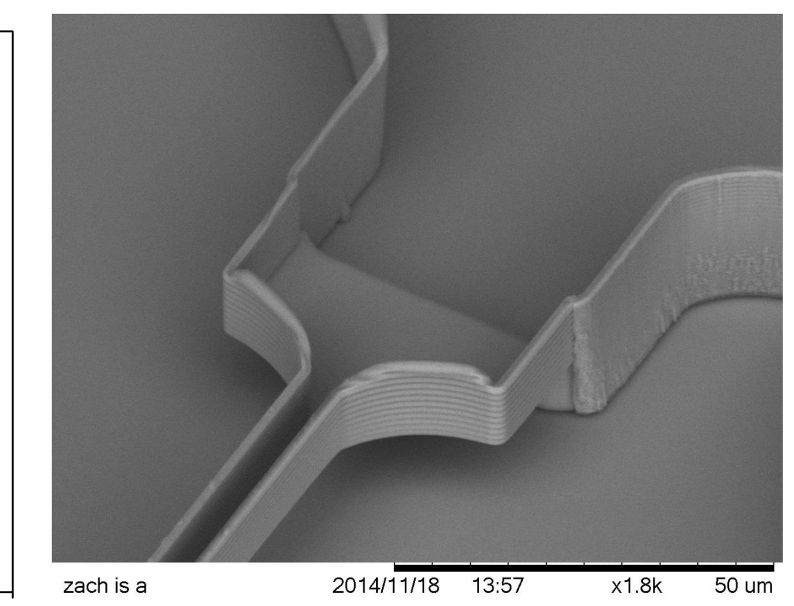
Microfabricated Cathodes

- Good Thermal Management
- Strong Mechanical Strength
- High Temperature Tolerance
- Optical and Resistive Heating Capability
- Ultra-High Vacuum Compatibility

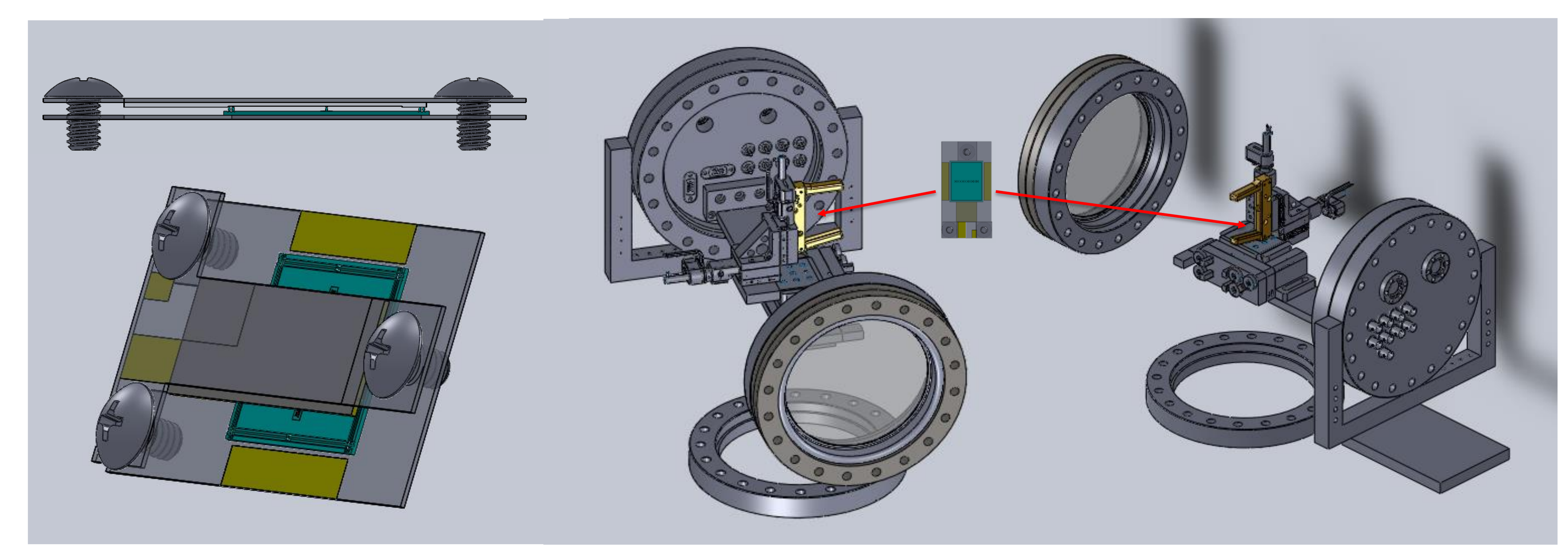








Testing Prototype Design



Authors' affiliations and acknowledgement

*hyyuan36@Stanford.edu
[1]Department of Physics, Stanford
[2]Department of Electrical Engineering, Stanford
[3]Department of Material Science & Engineering, Stanford
[4]Stanford Synchrotron Radiation Lightsource (SSRL)
[5]Department of Mechanical Engineering, U Penn

GCEP Global Climate & Energy Project STANFORD UNIVERSITY
SLAC
STANFORD ELECTRICAL ENGINEERING

References

[BV2007] Black and Veatch corporation, "20 percent wind energy penetration in the United States", Final Report Project Number 144864
[Hatsopoulos1973] G. N. Hatsopoulos and E. P. Gyftopoulos, "Thermionic Energy Conversion", vols. 1 (Cambridge, MA.: MIT Press, 1973)
[HK1964] Hohenberg P, Kohn W. Inhomogeneous electron gas. Physical Review 136 (3B): B864–B871. (1964)
[Schwede2010] J.W. Schwede, I. Bargatin, D.C. Riley, B.E. Hardin, S.J. Rosenthal, Y. Sun, F. Schmitt, P. Pianetta, R.T. Howe, Z.-X. Shen, N.A. Melosh, Nature Mat., 9 762 (2010)
[Yu2009] Y-J Yu, Y Zhao, S Ryu, L Brus, K Kim, P Kim. Nano Letter 9(10): pp 3430-3434, 2009
[Copuroglu2014] M Copuroglu, P Aydogan, E Polat, C Kocabas, S Suzer. Nano Letter 14(5): pp 2837-2842, 2014