Photon Enhanced Thermionic Emission for Solar Energy Harvesting

Final Report to the Global Climate and Energy Project

April 20, 2012

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Abstract

Photon Enhanced Thermionic Emission (PETE) is a newly proposed form of solar energy harvesting which relies upon a combination of quantum and thermal processes to generate electricity. Unlike standard solar cells which rapidly lose efficiency at elevated temperatures, PETE is designed to operate at temperatures commensurate with thermal solar devices. In concentrated solar power designs the PETE module will receive the direct incident light, convert a fraction to electricity and transfer its waste heat to a solar thermal cycle. Theoretical efficiencies of combined PETE/solar thermal cycles reach above 50% and may provide a route to affordable renewable energy on the utility scale. The key challenges to this technology are developing higher-efficiency cathodes that are stable at elevated temperatures, requiring both theoretical and experimental analysis of new materials. Over the last year we have demonstrated experimental results which match extremely well to the predicted physics for the PETE process, validating our initial concept. These experiments allow us to follow the behavior of a photoexcited electron, and prove that the electrons emitted from the PETE process come from a thermalized population, and also demonstrate a thermally-boosted output voltage of up to 0.5 eV. These proof-of-concept devices based on GaN provide the first example of a combined thermionic and photo-excited device. The device performance highlights two key challenges for improving the PETE device efficiency: carrier recombination and high-temperature material stability. In addition, we are constructing a new surface preparation and characterization chamber designed specially for PETE that can provide detailed measurements of material performance under anticipated operating conditions.

Introduction

Solar harvesting technology usually takes one of two forms; the 'quantum' approach using the large per-photon energy as in photovoltaic (PV) cells, or the 'thermal' approach using solar radiation as the heat source for a classical heat engine. Quantum processes boast high theoretical efficiencies but suffer in practice from a limited spectral energy collection window, whereas thermal processes have inherently lower efficiency limits but take advantage of energy throughout the entire solar spectrum. Simple combinations of the two fail because PV cells rapidly lose efficiency at elevated temperatures, while heat engines rapidly lose efficiency at low temperatures. As a result, these two approaches remain disjointed.

Photon Enhanced Thermionic Emission (PETE) is a method of solar harvesting that uses the quantum nature of solar photons along with thermal energy to generate electricity at temperatures compatible with solar thermal engines. The method relies on a semiconductor cathode separated by vacuum gap from an anode (Figure 1a). Incident photons excite electrons into the cathode's conduction band. If these carriers reach the surface before recombination, they can emit into vacuum and be collected by the anode, generating a voltage. Physical separation of the anode and cathode allows a large temperature differential, reducing the thermally generated reverse current which limits PV cells at high temperatures.[1] Thus, unlike other proposed "hot-electron" devices, [2-5] the PETE process is still efficient for fully thermalized electrons, providing a more realistic path to hot electron harvesting.
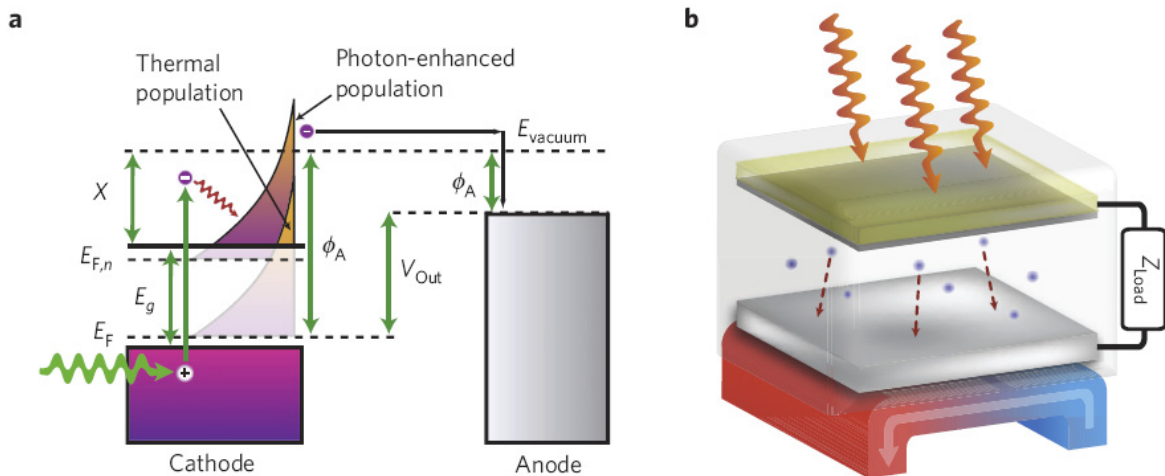
Figure 1: The PETE process. **a**, Energy diagram of the PETE process. Photoexcitation increases the conduction band population, leading to larger thermionic currents and allowing the device to harvest both photon and heat energy. **b**, One possible implementation of a parallel plate PETE converter. Photons impinge on a nanostructured cathode and excite electrons, which then emit into vacuum and are collected by an anode. Unused heat from the PETE cycle is used to drive a thermal engine.

The possibility for efficient operation at elevated temperatures makes PETE an ideal candidate for high concentration solar applications, including use as a "topping cycle" for a solar thermal generator, wherein the PETE device would harvest a fraction of incident
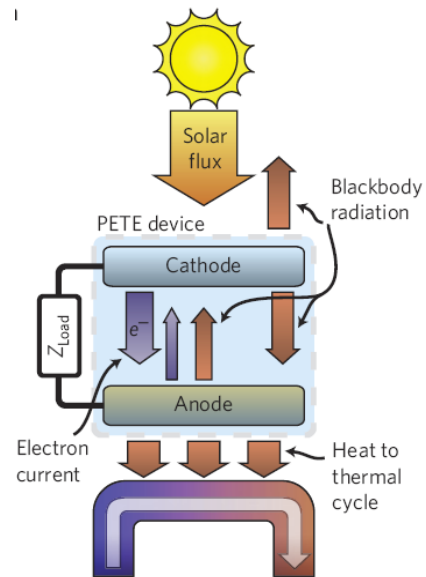
solar energy and deliver the rest as heat to a backing solar thermal engine (Figure 1b, 2). Even a PETE module with modest 20% efficiency in tandem with a 30% efficient Stirling solar thermal engine could boast a remarkable total system efficiency of 44%.

Background

In a photovoltaic cell, solar photons with energies above the semiconductor's band gap excite electrons into the conduction band, which diffuse to electrodes and generate current. In high-performance solar cells, charge separation and collection are very efficient. However, the quantum approach of PV cells places intrinsic limitations on single-junction conversion efficiency. Photon energy in excess of the band gap is lost as heat, known as thermalization loss, and sub-bandgap photons are not absorbed at all, known as absorption loss. In silicon solar cells, thermalization and absorption losses account for approximately 50% of the incident solar energy – the majority of the total energy loss. In principle, these losses could be reclaimed by using this waste heat from the PV cell to power a secondary thermal cycle. Combinations of PV and thermal engines are predicted to have efficiencies >60%, yet fail in practice because PV cells rapidly lose efficiency at elevated temperatures, while heat engines rapidly lose efficiency at low temperatures.

Figure 2: Energy flow for a tandem PETE/solar thermal cycle. Waste heat from the PETE device is used to power a conventional thermal engine, boosting the overall efficiency.

Thermionic energy converters (TEC) are less well-known heat engines which directly convert heat into electricity. A simple thermionic converter consists of a hot cathode and cooler anode separated by a vacuum gap. In the TEC cathode, a fraction of the electrons have sufficient thermal energy to overcome the material's work function and escape into vacuum, generating current between the two electrodes. The thermionic current density is dictated by the cathode work function and temperature according to the Richardson-Dushman (RD) equation: $J = A_C^* T_C^2 e^{-\phi_C/kT_C}$ where ϕ_C is the cathode work function, T_C the temperature, and A_C^* is the material-specific Richardson constant. Thermionic converters were first proposed and fabricated in the 1950s, with experimental conversion efficiencies eventually reaching 10-15%. Both NASA and the Soviet space program funded the development of TECs for deep space missions and other applications requiring high-power autonomous generators, but the technology was never commercialized. Thermionic conversion's main challenges relate to the very high temperatures and substantial current densities required for efficient operation.

Photon Enhanced Thermionic Emission (PETE) combines photovoltaic and thermionic effects into a single physical process to take advantage of both the high per-quanta energy of photons, and the available thermal energy due to thermalization and absorption losses. A PETE device has the same vacuum gap parallel plate architecture as

a TEC, except with a p-type semiconductor as the cathode (Fig. 1). PETE occurs in a simple three-step process: First, electrons in the PETE cathode are excited by solar radiation into the conduction band. Secondly, they rapidly thermalize within the conduction band to the equilibrium thermal distribution according to the material's temperature and diffuse throughout the cathode. Finally, electrons that encounter the surface with energies greater than the electron affinity can emit directly into vacuum and are collected at the anode, generating current (Fig. 1a). Each emitted electron thus harvests photon energy to overcome the material bandgap, and also thermal energy to overcome the material's electron affinity. The total voltage produced can therefore be higher than for a photovoltaic of the same bandgap due to this 'thermal boost,' thus more completely utilizing the solar spectrum.
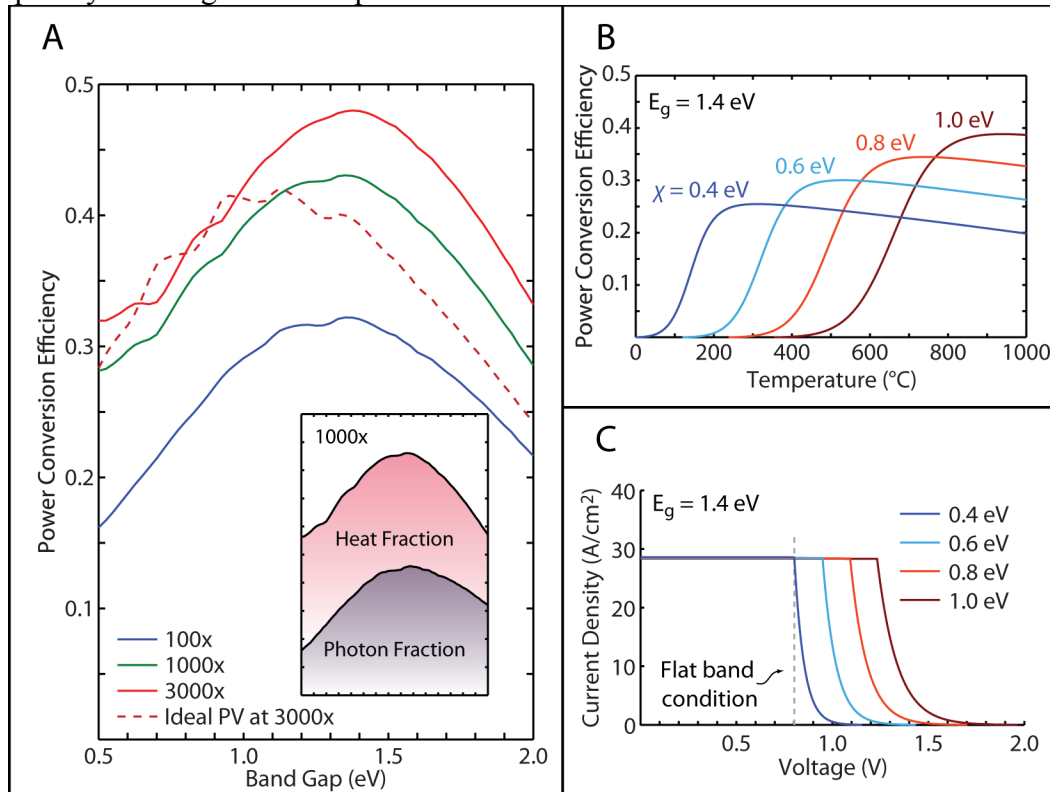
Figure 3: Theoretical PETE efficiency. **a**, PETE efficiency for the AM1.5 direct+circumsolar spectrum as a function of band gap. Cathode temperature and electron affinity are chosen to maximize overall efficiency. Anode temperature is 227°C to minimize reverse current. In the inset, the power output at 1000x is shown to be due to roughly equal contributions from thermal (χ) and photon (E_g) energy. **b**, Power conversion efficiency increases with χ due to larger voltage but requires higher temperatures. Power output decreases almost linearly with temperature after current saturation in the PETE regime due to the increasing cathode Fermi level. Concentration is 1000x. **c**, J-V curves for PETE devices with the same electron affinities in (b), showing the flat band condition for χ=0.4eV The temperatures are those at which the efficiencies in (b) are maximized.

Results

Both calculations of the theoretical conversion efficiencies and the first demonstration devices have been achieved within the past twelve months. Theoretical analysis has been developed for the PETE process, which considers electron emission from thermally

excited carriers within the conduction band. The maximum PETE efficiency calculated for different concentrations of the AM 1.5 solar spectrum is shown in Figure 3a as a function of material band gap. In this model, we focus on the emission probabilities of electrons which have thermalized within the conduction band, discounting the contributions of hot electrons. Even using existing anode materials and operation at moderate temperatures, PETE efficiency can be higher than the Shockley-Queisser limit for Si (~34%). Operation at 1000ºC with an anode workfunction of 0.9 (the best reported) can produce up to 50% conversion efficiency for PETE alone. When combined with a thermal cycle to harvest the waste heat, this increases to 55%.[6] The influence of electron affinity on electron emission yield (Fig 3b) and output voltage (Fig 3c) shows that the temperature and electron affinity need to be tuned in order to maximize performance.

As a proof-of-principle of the PETE mechanism, we measured the temperature dependent electron emission of cesiated GaN, a UV photocathode on which cesium forms a coating with unusually high thermal-stability.[15] Samples were loaded into an ultra-high vacuum chamber (low 10^{-10} Torr base pressure) with sample heating, monochromatic illumination, and electron energy analysis capabilities. The GaN was carefully dosed with Cs vapor to lower the electron affinity to roughly 0.3-0.4eV, as determined by the low energy cutoff of emitted electrons. In Fig. 3a, the emitted electron energy distributions with 3.75eV (330nm) illumination are shown as a function of temperature. The distributions have the characteristic shape of thermally emitted electrons, as the distribution widths broaden with temperature. The slight non-monotonic temperature dependence of the peak position is due to an analyzer work function change of ~25meV over the course of measurement, but this shift does not affect the broadening results.

Fig. 3b provides further confirmation that at high temperatures the electrons thermalized before emission and provides a powerful example of the potential of PETE for power conversion. The sample was illuminated with either 3.75eV photons (330nm, energy approximately equal to the work function) or 3.3eV photons (375nm, energy barely exceeding the bandgap at 400ºC). The two distributions are virtually identical, indicating the electron energy distribution immediately following photoexcitation was unimportant, as would be expected from PETE. Interestingly, since the average emitted electron energy was approximately 3.8 eV, each electron excited with 3.3eV light acquired ~0.5eV in thermal energy prior to emission. In an energy converter this thermal boost could be harvested by using a proportionately higher operating voltage. For small bandgap semiconductors, such as Si (1.1eV) or GaAs (1.4eV), a similar thermal boost would represent a considerable increase over the bandgap energy. The energy distribution without illumination was considerably smaller and has been subtracted from these curves, demonstrating the emission is not purely thermionic.

While electron thermalization most clearly identifies the PETE process, the electron yield increased with temperature as well. The temperature dependent emission current from a GaN sample with a small positive electron affinity was measured in a separate vacuum chamber (Fig. 3c). As the sample temperature varied from approximately 50 to 225ºC, the emission current from 350nm illumination more than doubled. The increase in yield for higher energy photons was less dramatic, likely reflecting a contribution from

direct photoemission which decreases with temperature due to increased scattering. More detail on the quantum yield measurements can be found in the Supplemental Information. For comparison, the same sample was further dosed with cesium to reach a state of negative electron affinity (NEA), with the result shown as a black dashed line in Fig. 3c. The stability of the NEA coating restricted the maximum temperature for these experiments to ~200ºC. Because electrons do not need to overcome an additional barrier at the surface when the electron affinity is highly negative, the dominant temperature effect at 350nm is a reduction in diffusion length. As a result, this trace shows a weak decrease in yield with temperature, clearly differentiating photoemission vs PETE processes.

Establishing instrumentation to create and measure PETE devices is well underway. Because most material work functions are too high for visible light to emit electrons, a low work function coating must be deposited onto a cathode's surface. A surface preparation and characterization chamber has been constructed in which photoyield can be measured during the surface preparation process and at high temperatures. This chamber is being integrated with existing analysis tools such as low energy electron diffraction and angle resolved photoemission spectroscopy to gather detailed information about a cathode's surface geometry and underlying electronic structure. With this foundation in place, progress is being made towards determining a cathode material and geometry that could be used in a realistic PETE device.

Through integration with existing solar thermal infrastructure, a modular PETE module could boost utility scale power generation efficiency while minimizing additional expense. This would substantially lower the cost of utility scale power generation, potentially lowering the cost below that of non-renewable resources. This research could thus have an obvious and dramatic impact on global greenhouse gas emissions. The progress, both theoretical and experimental, is encouraging for this new approach to solar energy harvesting.

Publications
1. J.W. Schwede, N.A. Melosh, and Z.-X. Shen,"Thermally Enhanced Photoemission for Solar Energy Harvesting," patent pending.
2. 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, "Photon Enhanced Thermionic Emission for Solar Concentrator Systems," Nature Materials, 9, 762-767, 2010.

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