

Photon Enhanced Thermionic Emission for Solar Energy Harvesting Progress Report to the Global Climate and Energy Project

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Investigators

Nicholas Melosh,
Department of Materials Science and Engineering, Stanford University
Stanford Institute for Materials and Energy Science (SIMES)

Zhi-Xun Shen
Department of Physics and Applied Physics, Stanford University
SLAC National Accelerator Laboratory
Stanford Institute for Materials and Energy Science (SIMES)

Graduate Student Researchers

Jared Schwede and Dan Riley, Department of Physics, Stanford University.
Sam Rosenthal, Department of Materials Science, Stanford University

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 the high temperatures typical for thermal solar devices. PETE devices are intended to operate by converting a fraction of incident concentrated solar illumination directly into electricity, then transferring its waste heat to a thermal cycle such as a Stirling engine or thermoelectric convertor. Theoretical efficiencies of combined PETE/solar thermal cycles can reach above 50% due to the unique combination of PV and thermal cycles. The key challenge to this technology is developing high efficiency photocathodes that are stable at elevated temperatures. In the past months, theoretical work has established efficiency limits for a range of materials parameters, and determined several key materials properties and geometries to optimize PETE efficiency. We have constructed a new surface preparation and characterization chamber designed specially for PETE that can provide detailed control and measurement of material performance, including simultaneous heating, illumination, Cs-coating and electron emission current. Measurements of Cs-coated GaN have provided direct confirmation that the fundamental physics of PETE behaves as predicted, and can partially convert thermal energy into higher output voltages. Materials with bandgaps better matched to the solar spectrum are now under investigation, and are anticipated to considerably improve overall device efficiency.

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 1). 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.

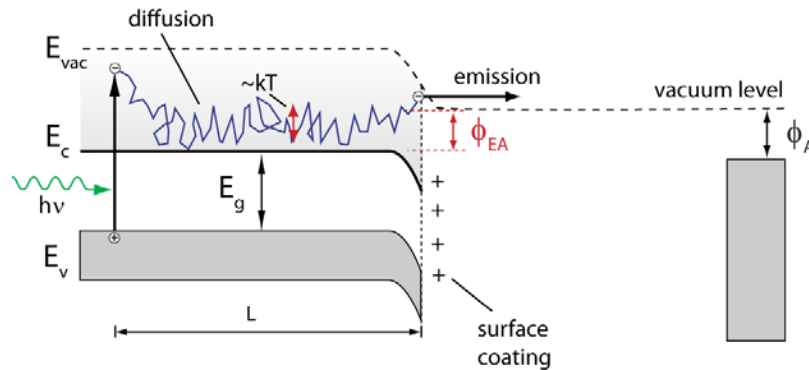


Figure 1: Schematic of the PETE process. Thermal energy assists photoelectron emission, harvesting both photon and thermal energy in the process

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 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%.

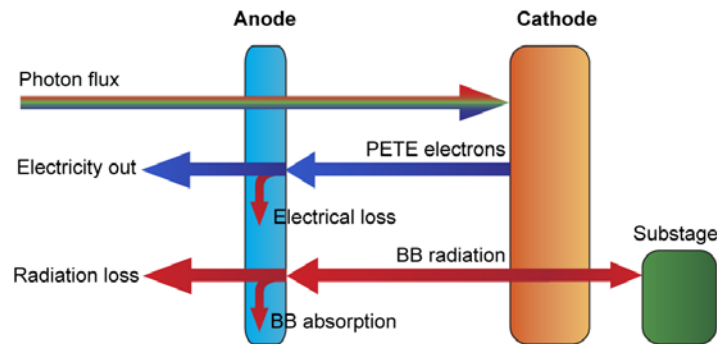


Figure 2: Energy flow for a tandem PETE/solar thermal cycle. Waste heat from the PETE device is used to power a conventional thermal engine, boosting the overall efficiency.

Background

Thermionic emission has been explored previously as a possible method of solar energy harvesting. In this scheme, concentrated solar radiation heats a refractory metal cathode to excite electrons above the vacuum level. Because thermionic current density depends exponentially on cathode temperature and work function, temperatures exceeding 1600°C are often necessary to generate usable current densities. While possible efficiencies of 20-30% or more are predicted, measured efficiencies are typically less than 10%. [6-7] In contrast, photoexcited electrons in the PETE cathode must only overcome the electron affinity which can be much smaller than a material's work function. By relaxing this requirement a wide range of materials and operating temperatures become feasible.

While progress towards a practical thermionic device has been limited, research into thermionic emitter materials may hold promise for PETE. F.A.M. Koeck, et al. recently reported that phosphorous doped diamond has an exceptionally low work function of 0.9 eV and is stable to at least 765°C.[8] PETE efficiency depends strongly on the work function of the anode, thus this advancement make PETE more realizable. Using phosphorous doped diamond as an anode material, efficiencies of over 40% may be possible, providing significant encouragement for the prospect of creating high-efficiency devices.

Progress

We have achieved several essential steps by laying theoretical groundwork and demonstrating the basic physical principles of PETE over the last year. Theoretical analysis has been developed for a range of realistic semiconductor properties. Calculations in Figure 3 show the results for a material with the electrical and recombination properties of Si, with the exception of the bandgap, which is allowed to vary arbitrarily. The maximum PETE efficiencies reveal that the optimal bandgap is in the range of 1.2-1.6 eV, and that higher solar concentrations improve efficiency, as expected. In this model, we solely treat the emission of electrons which have thermalized within the conduction band, conservatively 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 1000°C with an anode workfunction of 0.9 (the best reported) can produce up to 45% conversion efficiency for PETE alone at 3000x concentration. When combined with a thermal cycle to harvest the waste heat, this maximum increases to over 60%. From this theoretical analysis, the most critical factors for PETE are the bandgap, bulk recombination rate, and surface recombination velocity.

Further calculations show that the power output is dependent on temperature and electron affinity. Figure 3B shows that at low temperatures the electrons do not acquire much additional thermal energy, thus low electron affinities and low operating voltages are necessary. The reverse is true at high temperatures, predicting significant operating voltages are possible.

Calculated current-voltage plots in 3C show very different behavior compared to photovoltaic devices due to the fundamentally different mechanism.

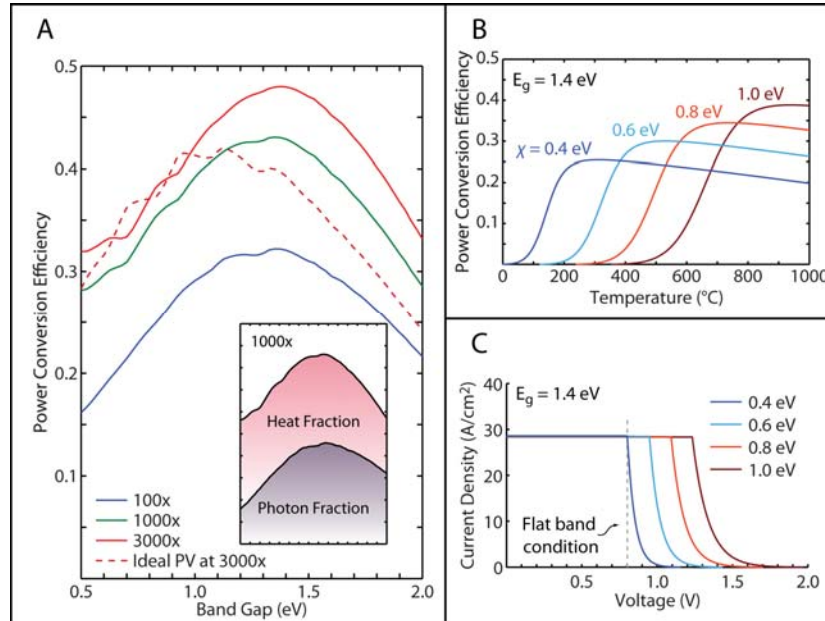


Figure 3: (A) Theoretical PETE efficiency as a function of bandgap. The inset shows that the energy out comes from both photon- and thermal sources. (B) Fractional power efficiency as a function of temperature shows the competition between temperature and electron affinity. (C) The calculated current as a function of operating voltage has a plateau for voltages less than difference of the band gap (here taken to be 1.4 eV), and the electron affinity. Above this voltage the current falls off exponentially in a manner quite different than standard photovoltaic devices.

Establishing the fundamental mechanisms behind PETE is well underway. The critical questions are whether the emitted electrons can obtain extra energy by being at a high substrate temperature, whether they are fully thermalized or are ‘hot’ electrons, and whether this process becomes more efficient as the temperature increases. If these are true, then PETE can indeed harvest both thermal and photon energies simultaneously. Figure 4 shows experimental results supporting these claims for a cesiated GaN sample, chosen for its known temperature stability. Figure 4A shows that as temperature increases the quantum yield at a number of different wavelengths also increases. The effect is more dramatic for lower energy photons, as they have little chance of inducing direct photoemission and almost all the emission current is due to the PETE process. For high energy photons there is a direct photoemission component which decreases with temperature, as previously observed. The PETE effect thus enhances electron emission at elevated temperatures.

The second key information comes from measuring the energy distribution of the electrons emitted. For the PETE process we would expect these electrons to come from a fully thermalized electron population. One rigorous way to test this is to examine emission from two different wavelengths of light, 330 nm (3.7eV) and 375 nm(3.3eV) in this case. If the electrons fully thermalized after absorbing a photon, their emitted energy should not depend on the wavelength

of light used to excite them. This is indeed the case, as shown in Fig 4B. This establishes that the electrons collected are not from ‘hot’ directly photoemission processes. The final and perhaps most exciting observation was that the electrons could gain a significant amount of usable energy from the high substrate temperature. The average emitted electron energy was at 3.8eV, fully 0.5 eV higher than the 3.3 eV, 375nm light used to excite them. The remainder of the energy came from the thermal energy in the substrate, which could come from waste heat and recombination losses in an operating solar convertor. Thus the PETE electrons have higher energies than possible with these photons by themselves, which could be used to increase the operating voltage of the actual device. While a 0.5V voltage boost for GaN is a modest ~12% increase, an additional 0.5V for a Si solar cell is a significant ~50% improvement. Further work is required to demonstrate similar performance on materials with band gaps closer to the ideal 1.2-1.6 eV range, however these results are quite encouraging.

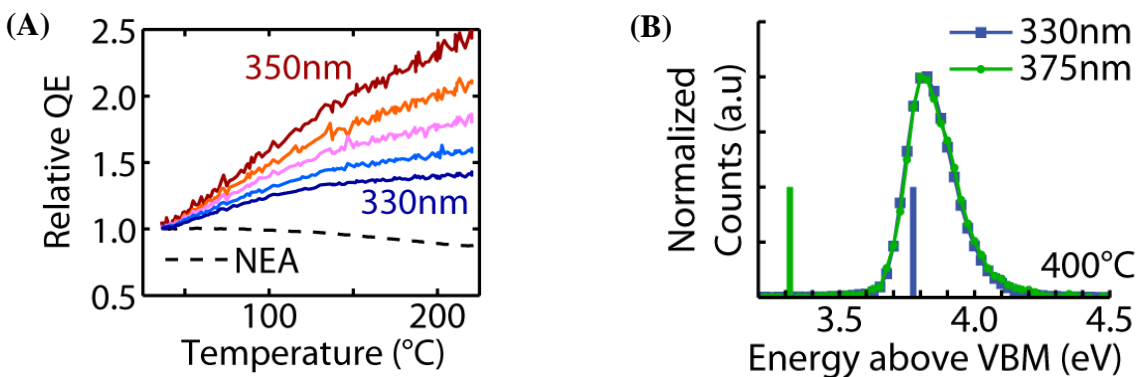


Figure 4. Experimental measurements of electrons emitted through the PETE process. (A) The relative electron emission quantum yield increases with temperature, unlike standard photoemitters. The amount of enhancement depends on the incident wavelength. (B) The energies above the valence band of the emitted electrons for a GaN sample at 400 C for two different wavelengths of light. Note that the energy spectra are virtually identical, even though the 375 nm light was a full 0.5 eV below the average emission energy. This shows the emitted electrons can obtain thermal additional energy from the cathode.

Future Plans

Several parameters that will be vital to this project’s success have been identified through recent work. These efforts will focus on 1) experimentally demonstrating increase in photoyield with temperature for a material with suitable band gap, and 2) finding highly thermally stable cathode materials and surface treatments. The ultimate goal will be to combine a high temperature, visible spectrum photocathode with low work function anode to create a highly efficient solar harvesting device.

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, R.T. Howe, Z.-X. Shen, and N.A. Melosh, “Photon Enhanced Thermionic Emission (PETE) for Solar Concentrator Systems,” under review.

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2. G. Conibeer *et al.*, *Solar Energy Materials and Solar Cells* In Press, Corrected Proof, (2008).
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Contacts

Nicholas Melosh: nmelosh@stanford.edu

Z.-X. Shen: zxshen@stanford.edu

Jared Schwede: schwede@stanford.edu

Daniel Riley: danriley@stanford.edu

Sam Rosenthal: srosenthal@stanford.edu