Solid-state Photon Enhanced Thermionic Emission for Solar Energy Conversion

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Abstract

Global climate imperatives require a worldwide shift away from greenhouse gas-emitting activities such as fossil fuel combustion. Concentrated solar thermal installations are particularly appealing as they can store a fraction of their power in the form of heat to provide baseload power, yet current conversion efficiencies prevent them from reaching competitive market prices. One extremely promising avenue to make these CSP technologies cost competitive adding a topping cycle to increase the total efficiency without increasing the land footprint required. Solar thermal topping cycles operate by receiving the incident solar radiation, converting a portion of it to electricity, and then delivering the excess heat to the CSP system. These two systems in tandem could reach much higher efficiencies than possible with one unit alone. However, increasing the efficiency of these add-on devices, such as thermoelectrics, at the operating temperatures required for steam or molten salt conversion processes is still a significant challenge.

Our group recently described a new physical mechanism for direct conversion of solar energy to electricity called Photon-Enhanced Thermionic Emission (PETE), based on research conducted under a prior GCEP program. PETE operates at elevated temperatures (600 to 900 ºC) under high solar concentration (100s to 1000s of suns) appropriate for CSP. The process operates by thermionically emitting photoexcited electrons from a light absorbing p-type semiconductor cathode into vacuum, where they are collected by a lower temperature, low work function anode. Due to the combination of photovoltaic and thermal energy collection processes, PETE has the potential to achieve power conversion efficiencies above 47%, higher than the fundamental limits for single-junction PV. Furthermore, PETE devices integrated with solar thermal converters could achieve efficiencies over 55%.

One of the most challenging aspects to the PETE process is that it requires direct emission of electrons into vacuum. Here, we explore whether this direct emission is necessary, or if it is possible to use a wide-bandgap semiconductor to create a solid-state PETE device (SS-PETE) instead. This device configuration has several advantages. First, the device consists of a monolithic body, and does not require a good quality vacuum between separated plates. Secondly, the operating voltage can be engineered based on the semiconductor band alignment rather than the material workfunctions. Finally, the device form factor would allow simple integration with several different CSP designs. We have evaluated the potential efficiency of these devices and demonstrated some initial device fabrication steps. Theoretically these devices could be quite efficient, yet do require a substantial temperature gradient. We investigate a simple test- collector based on this design.

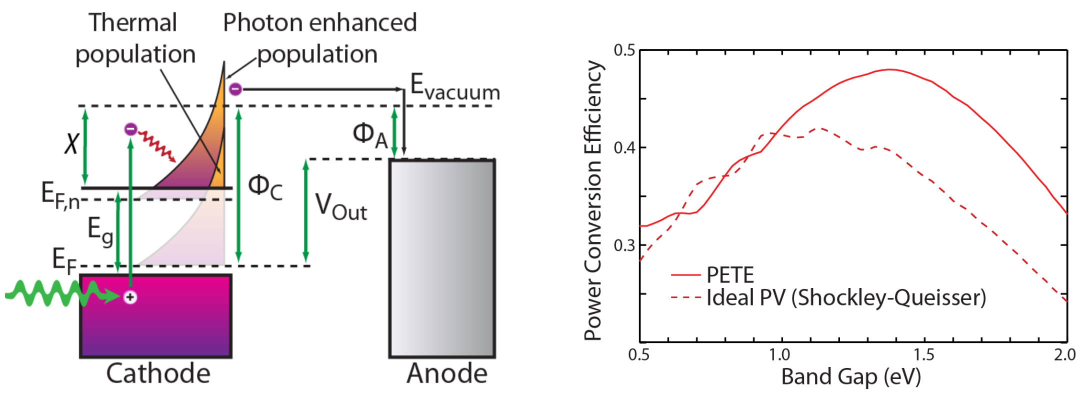

Figure 1: The PETE process. **a**, Energy diagram of the PETE process. Photoexcitation increases the conduction band population, leading to larger thermionic currents and allowing the device to harvest both photon and heat energy. **b**, Maximum theoretical PETE and PV efficiency as a function of bandgap for illumination by 3000 suns intensity AM1.5 direct + circumsolar spectrum. PETE anode work function is fixed at 0.9 eV.

Introduction

Photon Enhanced Thermionic Emission (PETE)[1] 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.[2] Unlike many hot-electron devices, [3-6] the PETE process operates using equilibrated electrons that have fully thermalized with the lattice temperature.

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). 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%.

While this technology holds great promise for concentrated solar energy conversion, many challenges arise from the vacuum gap-based architecture of the proposed PETE device. Here we propose a new architecture exploiting the unique PETE device physics in an all-solid state system, in which the vacuum gap is replaced with another semiconductor layer, a substantial step away from previously described PETE devices. The basic architecture of the device consists of a top layer of photon-absorbing semiconductor which acts as the cathode, connected to the metal anode by sparsely spaced semiconductor nanowires (Figure 2). Photoexcited electrons are generated in the absorber cathode and emit into the conduction band of the nanowires before collection at the anode.

Background

Photon Enhanced Thermionic Emission (PETE) combines photovoltaic and

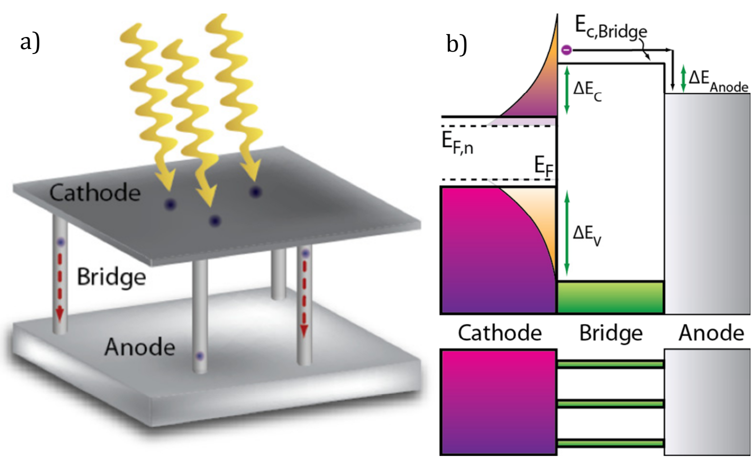

Figure 2: a) Solid-state PETE device schematic, showing photon absorption and carrier excitation in the cathode, carrier transport through the bridging nanowires, and collection at the anode. b) Energy diagram showing the relevant band offsets for the solid-state PETE process. Valence band offset must be larger than conduction band to prevent hole emission.

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. 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 (Fig. 1a). 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. 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.

One key benefit of solid-state PETE (SSP) is that it eliminates the vacuum gap, and offers extremely high potential efficiencies through optimization of the anode energy barrier. The device operating voltage is equal to the difference between the cathode and anode Fermi levels. Thus, a lower anode energy barrier (for vacuum-based PETE, the anode work function) can lead to increased output power. The lowest reported work function is 0.9 eV [7] with more typical low-work function materials in the 1.0-1.7 eV range, representing a significant loss in overall efficiency for vacuum-based PETE. In the SSP device, the semiconductor compositions can be tuned to adjust their energy band levels, allowing arbitrary control over the energy barriers at each interface and obviating the need for an ultra-low work function anode. SSP devices could thus achieve standalone efficiencies above 60% from 1000 suns illumination using an anode with an energy barrier of 0.5 eV. This offset is quite reasonable, and for the expected nanowire materials could be achieved with metals such as Ti, Ta, or Mn, all of which are stable far above the temperatures required for PETE.

Research

SSP is an exciting avenue to a high efficiency conversion device. However, the solid state architecture poses several hurdles. A small anode energy barrier provides greater output voltage, but can also lead to substantial reverse current if the anode temperature is too high, just as in PV cells operating at high temperature. A hot cathode is needed to achieve electron emission, so efficient PETE operation requires a large temperature difference between the electrodes. Removing the vacuum gap places the device electrodes in direct thermal contact, greatly increasing the difficulty of maintaining an acceptable temperature difference between them.

We will eliminate this challenge using a nanostructured device architecture, with a sparse array of semiconductor nanowires bridging the gap between the electrodes. The sparse nanowire array reduces the total area available for phonon conduction, but charge carrier transport is maintained since PETE operates with a defined number of photoexcited carriers, rather than requiring high total charge conductance like a thermoelectric. In addition, small diameter nanowires result in phonon scattering off of

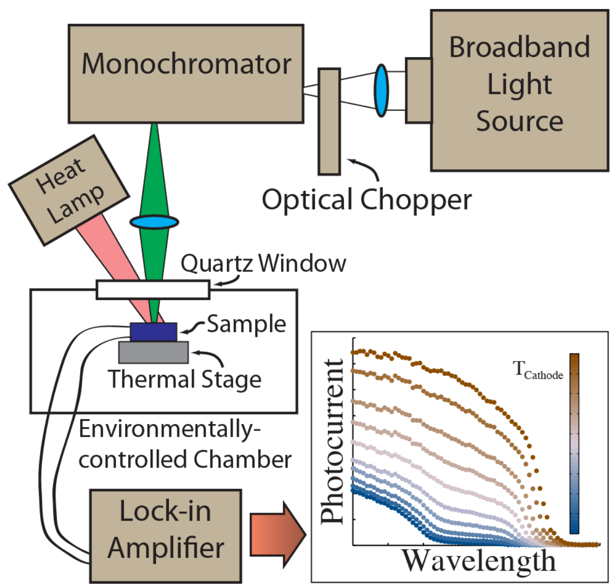

Figure3. SSP Experimental Schematic. Sample is kept in controlled environment to prevent oxidation and minimize convection between electrodes. The lower (anode) temperature is measured by a Pt resistor inside the hot/cold stage. The upper temperature is determined from the optical band edge of the absorber, using the Varshni relation. Excitation light is chopped, allowing lock-in amplifier to isolate signal from background.

nanowire walls, greatly reducing thermal conductivity below the bulk values, while electron mobility is only minimally affected due to the much shorter electron mean free path.

Initial measurements have focused on planar thin film junctions to eliminate additional complications introduced by nanostructuring. External quantum efficiency (EQE) measurements were performed on a test device consisting of a p-type GaAs absorber topped by a thin $Al_{0.15}Ga_{0.85}As$ layer. The device was illuminated through a semi-transparent Ni top contact, and the wavelength-dependent photocurrent was measured over a range of temperatures. A schematic of the temperature-controlled electrical/optical test stage is shown in Figure 3. Using optical heating on the top surface, in a manner similar to the way a real SS-PETE device will be heated by sunlight, this stage allows independent temperature control at each electrode separately to create well-defined temperature gradients, as well as characterizing the heat conduction across the

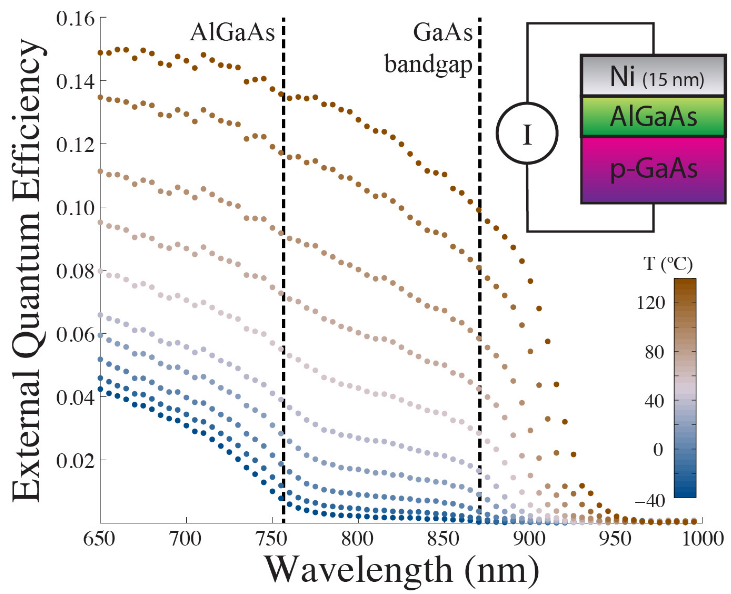

Figure 4. Measured temperature dependence of external quantum efficiency in a thin-film test device. Inset: test device structure, consisting of $Al_{0.15}Ga_{0.85}As$ (120 nm p-type, 40 nm n-type) and Ni (15 nm) deposited by MBE on a p-type GaAs substrate.

device. Current density-voltage (J-V) characteristics are measured under white light illumination and spectrally-resolved external quantum efficiency (EQE) using monochromated light. Varied light intensities from 0.1 to 1000 suns are provided by an optical lamp over a range of anode and cathode temperatures to identify appropriate device operating temperatures. EQE can be used as a diagnostic, highlighting wavelength ranges in which absorption or carrier collection are sub-optimal. J-V characteristics provide insight to the device physics, and allow determination of the power conversion efficiency.

To investigate whether the SSP concept is viable for efficient power conversion, we have performed preliminary EQE measurements on a test device consisting of a p-type GaAs absorber topped by a thin $Al_{0.15}Ga_{0.85}As$ layer. The device was illuminated through a semi-transparent Ni top contact, and the wavelength-dependent photocurrent was measured over a range of temperatures (Figure 4). A uniform temperature was maintained throughout this thin film device, as significant temperature gradients cannot be achieved without nanostructuring. Strong temperature positive dependence is observed in the photon energy range between the bandgaps of GaAs and $Al_{0.15}Ga_{0.85}As$, the range in which photocurrent could only arise from the internal PETE effect, when photoexcited carriers are generated only in the GaAs, then thermionically emit into the $Al_{0.15}Ga_{0.85}As$ before collection at the Ni. This is in direct contrast to a p-n junction solar cell, where efficiency uniformly decreases with increasing temperature. Despite the unoptimized nature of the device, parasitic absorption from the top contact, and the low temperatures used for measurement, we still obtain external quantum efficiencies of almost 14%, an order of magnitude greater than the best vacuum-based PETE devices. This result is highly promising, and motivated us to propose an exploratory project to create a full-fledged SSP device.

The SSP project could have a large impact on greenhouse gas emissions. It offers potential power conversion efficiencies far greater than the fundamental limits on single junction PV, and even possibly exceeding vacuum-based PETE devices. In addition, high-efficiency SSP devices are potentially much closer to realization than vacuum-based PETE, as the solid-state architecture avoids several of the largest challenges facing PETE. If successful, solid-state PETE, coupled with existing solar thermal technologies, will radically boost concentrated solar installation efficiencies, thereby significantly reducing the solar energy prices to be competitive with coal-burning plants.

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