Photon Enhanced Thermionic Emission (PETE)

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Nanomaterials Behavior at Interfaces

- Fabricating, interrogating, and controlling nanoscale materials at interfaces
- Applications for biology, electronics and optics
A lot of high-temperature energy is available from the sun... how can we best extract it?

**Thermal Collectors**
- collects almost all energy
- “low grade” energy
- thermal systems well known
- efficiencies of 20-30%

**Photovoltaics**
- collects fraction of incident energy
- “high grade” photon energy
- distributed power
- efficiencies of 24% (single Si-junction), 43% multijunction
A simplistic comparison

**Thermal Collectors**

- 5800°C
  - $\Delta T = 5200°C$; un-used

- 600°C
  - $\Delta T = 500°C$, $\eta_{\text{max}} = 83.3%$; $\eta_{\text{real}} \sim 25%$

- 100°C
  - full use of low grade heat

**Photovoltaics**

- 5800°C

- 100°C
  - absorption losses
  - thermalization losses
  - recombination losses

- partial use of high grade heat (high per-quanta energy)
Premise: A high-temperature photovoltaic combined with a thermal engine is the most effective way to maximize output efficiency.
Combined HT-PV/Thermo Cycle

Combined cycles can take two modest performance devices to form a very high efficiency device.

PV Stage

"Quantum process"

5800º C

600º C

η ~ 25%

100º C

η ~ 25%

75º C

η ~ 25%

100%*(25%) = 25%

75%*(25%) = 19%

total: 44%
The key is to develop a PV cell that can operate at high temperatures

- Doesn’t need to beat a performance bar—every % is in addition to thermal stage
- A 20% efficient HT-PV would increase current thermal performance by 60%
- Current ~12¢/kWh LCOE would decrease to ~7¢/kWh
- Only a small device area required
- Compatible with current designs of dish collectors

Can we make a High-Temperature Photovoltaic? Not yet.
Ideal combined PV+HE efficiencies are ~62% at 500K (Luque, 1999), yet actual devices are nowhere close. Why?

*PV does not operate well at high temperatures!*

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**Ideal Diode equation:**

\[
J = J_{SC} - J_0 \left( e^{\frac{eV}{kT}} - 1 \right)
\]

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Energy

\(h^+\)

\(p\)-type

\(h\nu\)

\(n\)-type

\(e^-\)

Dark current

\(V_{bi}\)

Carrier generation

Dark current

Usable photo-voltage (qV)
We need a device that can use large per quanta photon energy (like PV), and combine it with the high temperature operation and thermal harvesting.

What processes can operate at high temperatures?
Thermionic Emission

Boiling electrons from the surface:

- Operates at very high temperatures; generally >1200ºC
- Very long lifetime
- Space charge issues
- Low output voltages

\[ J = AT^2 e^{-\phi_C/kT} \]
\[ P = J (\phi_C - \phi_A) \]
Solar to Thermionic Testing

**FIGURES.** Primary Mirror and Vacuum Chamber During On-Sun Testing.
A new idea to combine Photon absorption with thermionic emission?
Photo-enhanced Thermionic Emission (PETE)

- Photo-excite carriers into conduction band
- Thermionically emit these excited carriers
- Overcome electron affinity barrier (not full work-function)
- Collected at low work-function anode

Nature Materials, in press
Photon Enhanced Thermionic Emission (PETE)

Thermionic Current:

\[ J = A T^2 e^{-\phi_C/kT} \]

PETE Current:

\[ J = A T^2 e^{-\phi_C/kT} e^{\Delta E_f/kT} \]

If \( E_g = 1.4 \) eV, then at 300 C:

\[ J_{\text{pete}}/J_{\text{therm}} = e^{\Delta E_f/kT} = 1.4 \times 10^9 \]
PETE vs PV

- PETE harvests both thermal and photon energy
  - sub-band gap, thermalization, and recombination “losses” collected
- Optimal PETE performance by balancing photon absorption and heat generation
- High temperatures beneficial- doesn’t degrade performance

Seems good... but how do the actual numbers compare?
**PETE calculations:**

- Each photon $h\nu > E_g$ is absorbed and excites one electron
- Sub-bandgap photons are absorbed as heat
- BB radiation losses and transfer included
- Radiative and Auger recombination losses (Si params) included
- ‘dark current’ from anode treated as thermionic emission
- Variables: solar concentration, $T_C$, $T_A$, $\chi$, $E_g$, $\phi_A$,
To adjust: $E_g$, $\chi$, $T_C$

- $\varphi_A = 0.9 \text{ eV}$
  - [Koeck, Nemanich, Lazea, & Haenen 2009]
- $T_A \leq 300^\circ \text{C}$
- Other parameters similar to Si
  - $1 \times 10^{19}$ Boron doped
Maximizing PETE performance

Maximize $E_{F,n}$:
- High solar concentration
- Low recombination rates; electrons emit before relaxing

Maximize $V$:
- Highest $\chi$ possible while still getting good electron yield at given $T$
- Minimize anode work function

Maximize electron emission probability!
• [Cs]GaN thermally stable
  – Resistant to poisoning
  – $E_g = 3.3$ eV
  – 0.1 $\mu$m Mg doped
  – $5 \times 10^{18}$ cm$^{-3}$

Experimental Apparatus:

- Xe or Hg(Xe) lamp
- Monochromator
- Filter Wheel
- Photodetector
- Anode
- Evaporator
- Cs
- Sample
- Optical Fiber
- O2 leak valve
- UHV Chamber
- Heater
Experimental Apparatus

- removable sample mount
- optical access
- heater

Not visible:
- anode
- Cs deposition source
Temperature Dependent Yield

Direct Photoemission

Temperature Dependent Yield vs. PETE:

From Spicer and Herrera-Gomez (1993)
T-Dependent Emission Energy

- PETE electrons should show thermal distribution
- Distribution should broaden with temperature
- Measure emitted electron energy

Thermal distribution

\[ E_{\text{vacuum}} \]
\[ \chi \]
\[ E_g \]
\[ E_F \]
\[ \Phi_C \]

Cathode

Energy Distribution Width

Normalized Counts (a.u.)

Energy above Valence Band Maximum (eV)

increasing \( T \)

FWHM (eV)

Temperature (°C)

Values:
- 170 eV
- 180 eV
- 190 eV
- 200 eV
- 210 eV
- 220 eV
- 230 eV
- 240 eV
- 250 eV
- 260 eV
- 270 eV
- 280 eV
- 290 eV
- 300 eV
- 310 eV
- 320 eV
- 330 eV
- 340 eV
- 350 eV
- 360 eV
- 370 eV
- 380 eV
- 390 eV
- 400 eV
Photon-independent Emission Energy

- Photon energy should not matter above band gap
- Very different from photoemission
- Green = just above gap
- Blue = well above gap, not above $E_{\text{vac}}$

Energy distribution for different excitation energy

- Identical energy distributions
- 0.5 eV thermal voltage boost significant
- $400^\circ\text{C} = 0.056$ eV
Yield dependence on temperature
- decreases for direct photoemission
  - *increases for above gap, but sub-ionization energies*

Emitted electron energy increases with temperature
- >0.1-0.2 eV higher than photon energy

Electron energy follows thermal distribution

330nm and 375nm illumination produce same electron energy distributions at elevated temperature
- electrons harvested up to 0.5 eV additional energy from thermal reservoir
Why is it not more efficient?

- GaN is a sub-optimal material:
  - High dislocation and surface defect density
  - Short recombination times scales don’t allow electrons to thermally emit
  - Large bandgap (3.3 eV)
  - Cs coating may form trap states
Adding PETE onto Existing Equipment

- Several companies already operate Stirling-based CSP
- Record: 32% efficiency; annual efficiency ~23% to grid
- Add PETE front stage, thermally connect anode, cathode or both
- Use nanostructured PETE cathode to absorb light and emit electrons
31.5% Thermal to electricity conversion [Mills, Morrison & Le Lieve 2004]
285°C Anode temperature [Mills, Le Lievre, & Morrison 2004]
LCOE Estimates

Based on NREL LCOE cost analysis of SunCatcher parabolic Dish array with additional PETE cost and efficiencies.

https://www.nrel.gov/analysis/sam/
http://www.energy.ca.gov/sitingcases/solartwo/documents/applicant/afc/volume_02+03/MASTER_Appendix%20B.pdf

Cost Estimates:

- Original SunCatcher LCOE = 12¢/kWh
- 25% PETE module cost $25,000 for a 50kW plant
- $0.50/kW, +25% efficiency
- LCOE = 7¢/kWh
- $Coal ~ $PETE/Stirling < $Gas < $Nuclear
- Near coal parity possible without subsidies.
Challenges for PETE

**What materials?**

- High-temperature stable (~500-800°C)
- $E_g \approx 1.1-1.8$
- low surface recombination
- Non-reactive with coating materials

Candidates: Si, InGaP, GaAs, ternary III-V compounds, II-VI’s?

**What coatings?**

- Need stable, non-reactive work function lowering coatings
- $\chi$ unknown for coatings on semiconductors at elevated temps
- Reactivity and phase transformations can be problematic

**Device Architecture?**

- Microfabricated cells, parallel plates
- Light coupling, Plasmonics?
A New Class of Materials: Diamondoids

- \(sp^3\) carbon nanomaterial
- Molecular fragments of the diamond lattice
- Crystalline solids at RT
- Newest form of nano-carbon
- Higher diamondoids discovered in quantity in oil by Chevron, 2003
Isolated Higher Diamondoid Structures
Diamond Nanocrystals

Diamonds range in size from gemstones to small molecules

~ mm

10’s μm

> 2 nm

1-2 nm

<1 nm

Diamond (Cartier)

Microscopic Diamond (CVD, Sunkara)

Ultrananocrystalline (detonation diamond)

Higher Diamondoids

Lower Diamondoids (adamantane, diamantane)
Fascinating (electronic) Diamond Properties...

- Very high resistivity and dielectric breakdown
- $E_g \approx 5.5$ eV
- Very high electron and hole mobilities (4800 and 3800 cm$^2$V$^{-1}$s$^{-1}$)
- Excellent electron field emitter, especially for nano-crystalline diamond films
- $H$-terminated diamond is negative electron affinity

Making Diamondoid Monolayers

Apical modified

1-adamantane thiol

4-diamantane thiol

2-triamantane thiol

6-tetramantane thiol

Side modified

3-triamantane thiol

2-tetramantane thiol

Au

Synthesized by P. Schreiner, A. Fokin, Univ. Giessen
High Quality Monolayers

STM images of Diamondoid Thiols on Au

Jason Randel and Hari Manoharan
Diamondoids are also NEA materials

- Monolayers of 6-tetramantane thiol
- 55 eV photons
- 68% of total electron emission in NEA peak
- Dwarfs previous NEA peaks
- Excellent electron emitters

Yang, Fabbri et al., Science, 2007, p.1460
Work Function Lowering: Field Emission

*Field emission* is the process of electrons tunneling from the material surface into vacuum.

• Surprisingly, diamond is an excellent field emitter
• The more nanocrystalline, the better field emitter

Field Emission Display:
**Electronic Field Emission**

**Fowler-Nordheim Equation**

\[
J_{FN} = \frac{c_1 (\beta E)^2}{\phi} \exp \left( -\frac{c_2 \phi^{3/2}}{\beta E} \right)
\]

- \( E \) = electric field
- \( \phi \) = barrier height
- \( \beta \) = field enhancement factor

Diamondoids as a Model System

Diamondoids are a perfect candidates for elucidating some of that is happening:

- Completely H-terminated, no patchiness
- No graphitic impurities
- Can be deposited onto a well-characterized surface to separate changes to $\beta$ and $\phi$
- Facile electron injection from substrate
- Monolayer too thin to allow significant electron acceleration

Measure field emission from Au coated Ge nanowires before and after addition of diamondoids.
- Use Ge NW for some geometric enhancement
- Ge Nanowires ~50-150 nm in diameter
- Ge NW ~5-20 um long
- Expect field enhancements of ~10 um/100 nm = 100 times
- Coat with Au or Ag to create diamondoid SAMs
The average diameter of the Ge nanowires is around 140 – 180 nm. The average length of single Ge nanowire is around 10 – 15 μm.
Emission from Au coated Ge wires

- Coat Ge wires with 10/40 nm Ti/Au to allow diamondoid attachment
- Au by itself allows field emission at ~750 V
- Emission is stable and highly repeatable
- Measure at different mylar thickness - extract 38 um distance at 50 um thick spacer
Diamondoid-modified Field Emission

Key Points:

- Large emission enhancement without changing $\beta$
- Enhancement must be related to work function change
- Workfunction $\sim 2.7$ times lower with 6-tetramantane monolayer

- SAM of 6-Tetramantane thiol
- $\sim 1.3$ V/µm turn-on field
- Exact same sample, just with diamondoids
- Lowered work function by 3.0 eV!

Ge et al., in preparation
Other diamondoids behave similarly

- Both side-attached and end-attached tetramantane show increased emission
- Alkane thiols show much smaller benefit
- Electron rich terminal groups make emission worse
Comparison to other diamond materials

- 1.3 V/μm
  *Equivalent to best reported devices*

- No graphitic material necessary

- Lower currents due to Au-S stability

![Graph showing comparison of different diamond materials](image)

Au/diamondoid device

Mechanism: FN Analysis

Derive WF lowering effect

\[ J_{FN} = \frac{c_1 (\beta E)^2}{\phi} \exp \left( -\frac{c_2 \phi^{3/2}}{\beta E} \right) \]

Slope = \[ \frac{-c_2 d\phi^{3/2}}{\beta} \]

same before and after diamondoids

\[ \phi_{Au+diamondoids} = \left( \frac{b_{diamondoids}}{b_{Au}} \right)^{2/3} \phi_{Au} \]

6-tetramantane FN Plot:

- Au \( b = -13400 \)
- Au+ 6-tetramantane = -2960
- \( \phi_{Au} \approx 4.85 \text{ eV from PES} \)
- \( \phi_{6-tetra} = 1.88 \text{ eV} \)

A change of -3 V!
# Gold Work-function Lowering

<table>
<thead>
<tr>
<th>Compound</th>
<th>Work function</th>
<th>Reduction</th>
<th>Reduction from UPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bare gold</td>
<td>4.85 eV</td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>6-Tetramantane thiol</td>
<td>1.88 eV</td>
<td>2.99 eV</td>
<td>1.1 eV</td>
</tr>
<tr>
<td>2-Tetramantane thiol</td>
<td>1.88</td>
<td>2.99</td>
<td></td>
</tr>
<tr>
<td>7-Pentamantane thiol</td>
<td>2.08</td>
<td>2.79</td>
<td></td>
</tr>
<tr>
<td>Dodecanethiol</td>
<td>3 +/- 0.39 eV</td>
<td>1.85 +/- 0.39 eV</td>
<td>1.2 eV</td>
</tr>
<tr>
<td>16-Mercapto hexadecanoic acid</td>
<td>4.86 +/-0.62</td>
<td>-0.01 +/- 0.62</td>
<td>-0.2 eV</td>
</tr>
</tbody>
</table>
3 V is a **huge** amount for a molecule to alter the surface potential. This is equivalent to a + and – charge held 0.48 nm apart.

$$V = \frac{q}{4\pi\varepsilon_0 d}$$  \hspace{1cm} \text{Coulomb’s Law}

$$d = \frac{1.6 \times 10^{-19}}{4\pi\varepsilon_0 (3V)} = 0.48 \text{nm}$$

Furthermore, UPS measurements show that the bulk of the Au surface is only bent by ~1.0-1.2 eV. So what could make field emission so effective?
Due to dipoles in Diamondoid?

6-[121]-tetramantane thiol

\[ \begin{align*}
6-[121]-tetramantane
\end{align*} \]

- Total: \(~2.3\) eV reduction
- Observations \(~3.3\) eV
- Cannot be explained by dipole arguments

\( E_{\text{vac}} \)

\( \phi \)

\( \phi_{\text{eff}} \)

\( E_{\text{vac, surface}} \)

\( E_V \)

\( E_F \)

\(~1\) nm

\(~1\) Å

\(~0.7\) eV, C-H dipole

\(~1.6\) eV, Au-S dipole

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Summary

- **PETE approach combines thermal and quantum processes**
- **Theoretically can exceed single solar cell efficiency**
- **Dual cycles can increase efficiency even more**
- **Diamondoids are fascinating additions to the Carbon nanomaterial family**
- **Diamondoids have excellent work-function lowering properties**
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