Low work function diamond film thermionic and photon enhanced electron sources for direct energy conversion

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Revolutionary Research . . . Relevant Results

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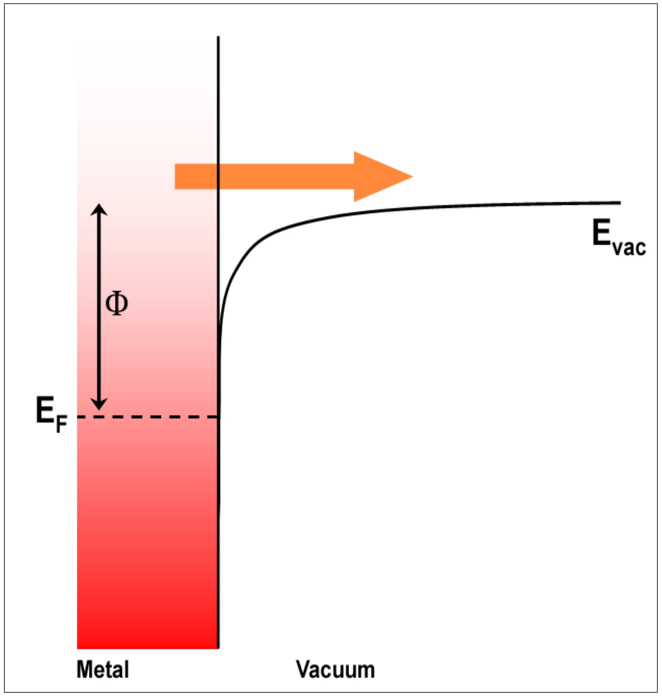
Outline

- **Introduction**
  - Vacuum thermionic **electron emission** and **energy conversion**
  - **Surface ionization** for enhanced **energy conversion**

- **Efficient Thermionic Electron Emitters**
  - **Nitrogen doped diamond/UNCD**
  - **Device engineering – Substrate/Diamond Interface**
- **Enhancing Thermionic Electron Emission**
  - **Surface Ionization** from doped diamond films
  - Application: **Thermionic energy conversion**

- **Conclusions**

Describing Thermionic Electron Emission



Material	Richardson A [A/cm² K²]	Work Function [eV]
W	74	4.5
Mo	55	4.1
Re	200	5.1
Graphite	48	4.8

Thermionic Emission

Richardson – Dushman Equation

$$j(T) = A_R T^2 \exp\left[-\frac{\phi}{k_B T}\right]$$

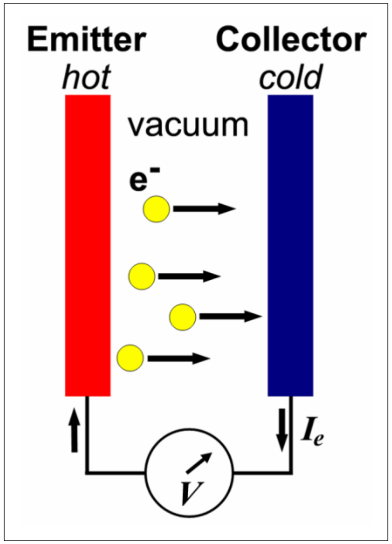
$$A_R = \frac{emk_B^{\,2}}{2\pi^2\hbar^3} = 120\,Acm^{-2}K^{-2}$$ *Theoretical value*

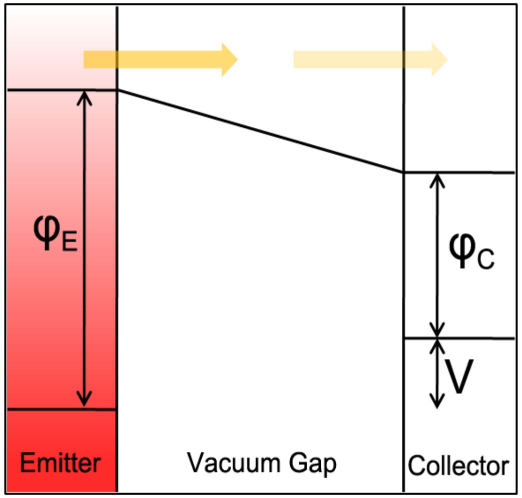
Fitting parameters

A_R Richardson constant

ϕ work function

For a thermionic emitter a **low work function φ AND significant Richardson constant A_R** are preferred.





φ_E emitter work function
φ_C collector work function
V *potential due to the temperature difference*

Vacuum thermionic energy conversion

Transforming Heat into Electricity

Hot Side: Thermionic Electron Emitter

Cold Site: Collector

Separated by a **vacuum gap**

Thermal electrons cross this vacuum gap

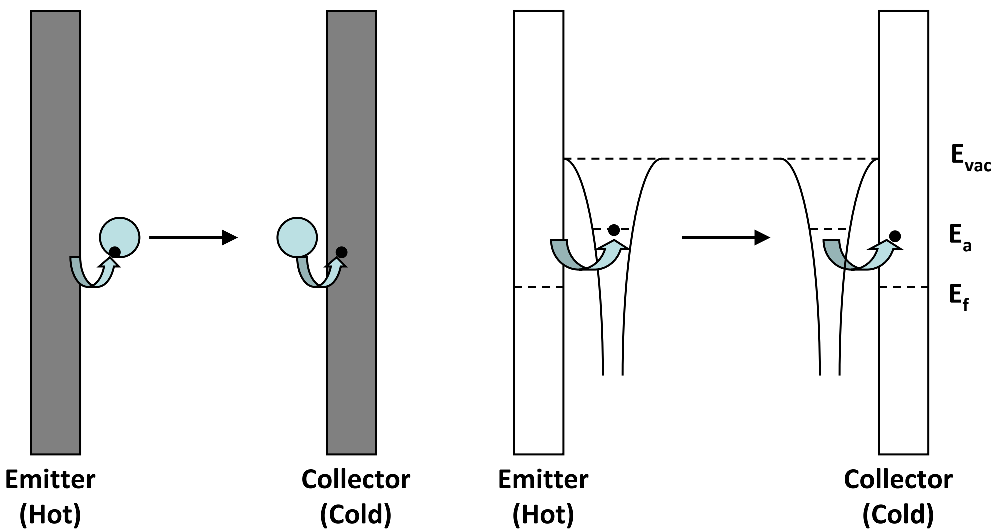
Electrostatic Potential difference is established
Thermovoltage ***V***

Closing the electrical circuit results in
Current I_e

Electrical power is generated

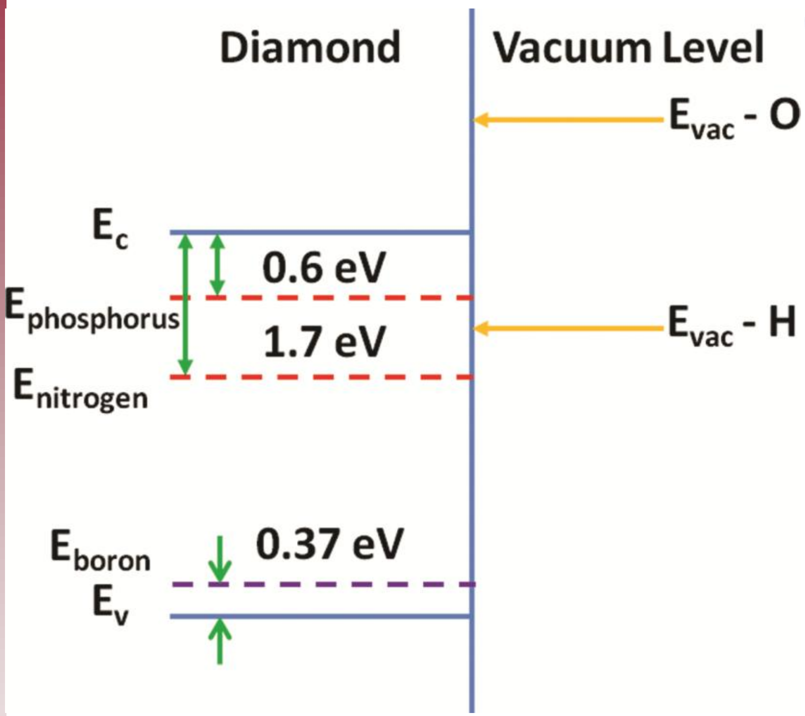
Objective:
To increase charge transfer from the emitter utilizing a negative ion source thus increasing power output.

Surface Ionization for Molecular Charge Transport



The Fermi energy (E_f) of the emitter and collector surfaces, the lowest unoccupied molecular level is indicated as E_a, and the vacuum level (E_{vac}) is indicated.

- **Molecule** approaches the surface: its **vacuum level** will **align** with surface vacuum level.
- **Ionization** will occur through **quantum mechanical tunneling**.
- Molecule traverses the gap at the **thermal velocity** of the gas
- **Electron transfer** to the cold collector is again achieved through tunneling.
- Identifying molecular species with **appropriate electron affinity**.

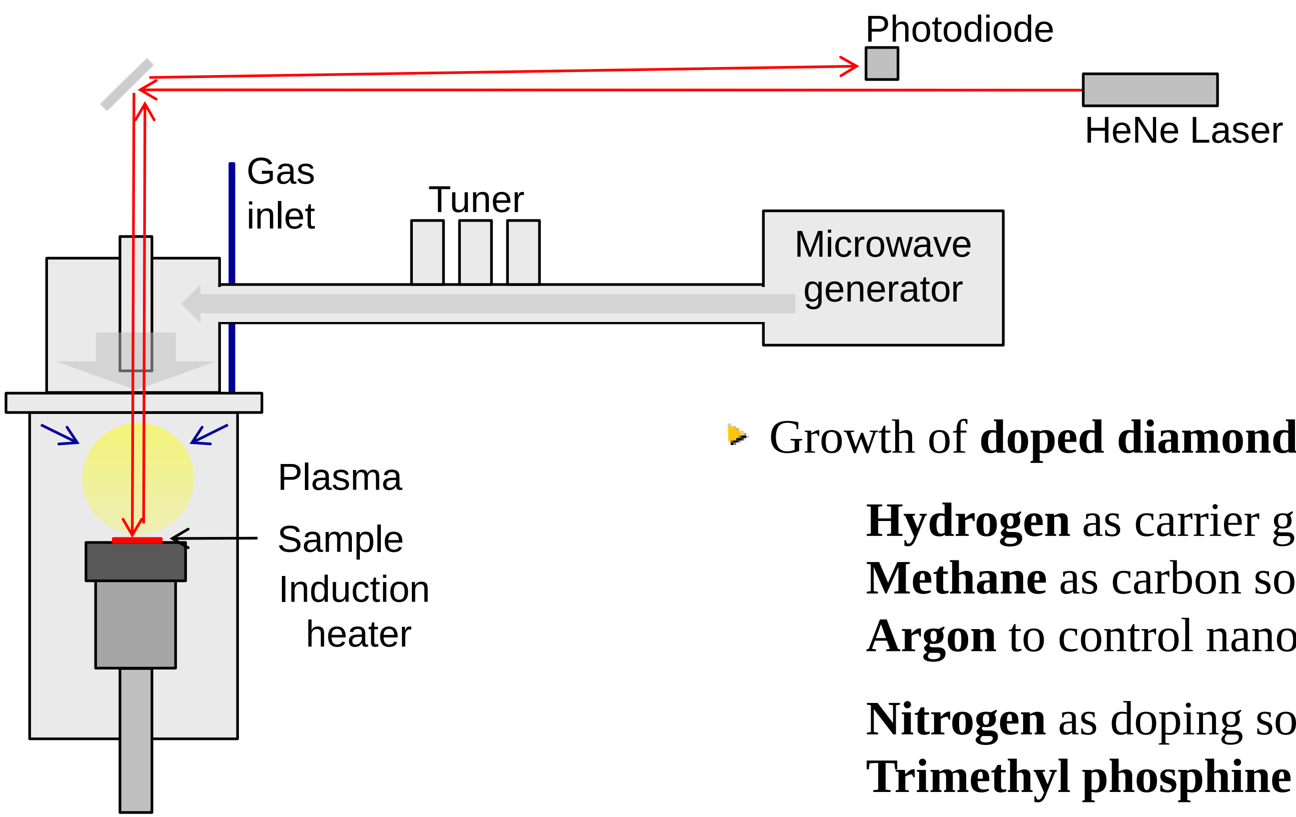


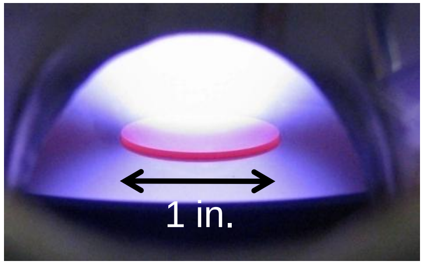
- **Negative electron affinity** (NEA) of diamond films – hydrogen passivation
- The electron affinity: the energy required to remove an electron from CBM to vacuum
- Vacuum level **~ 1 eV below CBM** for hydrogen terminated diamond
- Doping
  - **Nitrogen:**
    1.7 eV below CBM
  - **Phosphorus:**
    0.6 eV below CBM

NEA and *n*-type doping lead to lowering of the emission barrier (effective work function)

F.J. Himpsel, et. al., *Phys. Rev. B* 20 (1979): 624.
J. van der Weide, et. al., *Phys. Rev. B* 60 (1994): 5803.
B.B. Pate, *Surf. Sci.* 165 (1986): 83.

Plasma Assisted Chemical Vapor Deposition (PCVD)





- Growth of **doped diamond films**

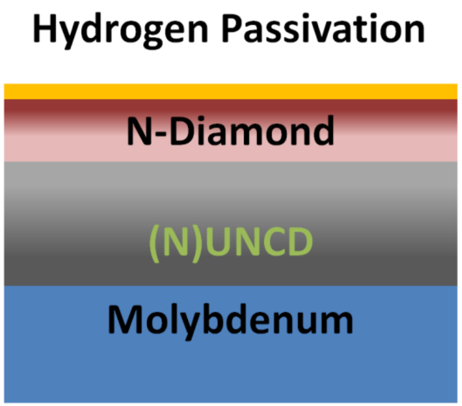
  Hydrogen as carrier gas
  Methane as carbon source
  Argon to control nanostructure

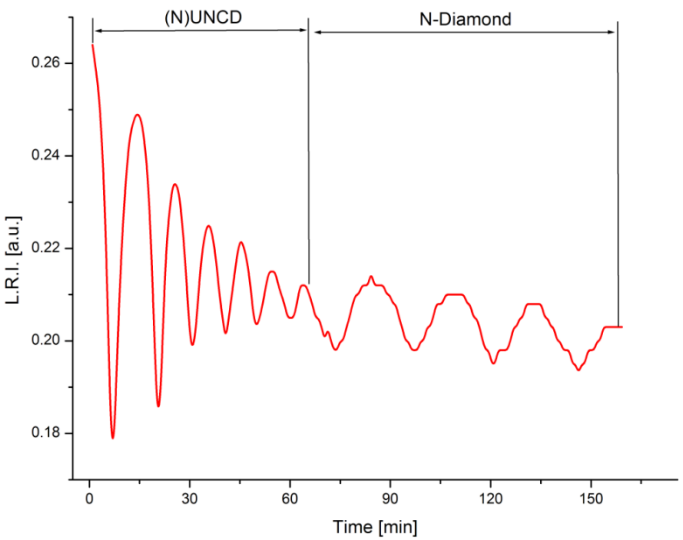
  Nitrogen as doping source
  Trimethyl phosphine (TMP) as doping source

- Control of chamber **pressure**, sample **temperature** and **microwave power** for deposition.

- **Laser reflectance interferometry** for in situ thickness measurement.

Growth of *n*-Type Doped Diamond Films





- Microwave plasma enhanced chemical vapor deposition (**MPCVD**) for diamond growth

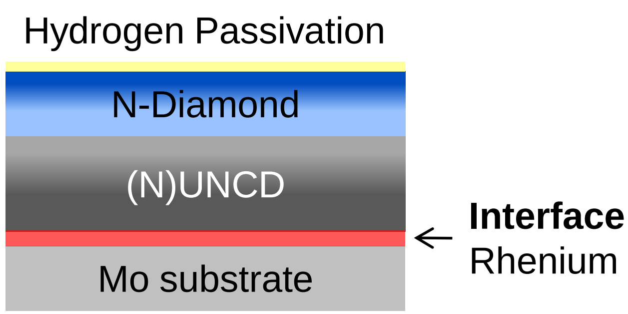
- Structure:
  Molybdenum or silicon
  Nitrogen incorporated ultra-nanocrystalline diamond ((N)UNCD) (for N-doping only)
  Nitrogen / phosphorus doped diamond

- **NEA surface** is obtained by exposing the film to a hydrogen plasma

Efficient Thermionic Electron Emitters

Device Engineering

Thermionic emission characterization



- **N-doped Diamond**
  - Molybdenum substrate + Interface Layer
  - UNCD(N) + N-doped diamond
  - Hydrogen passivation

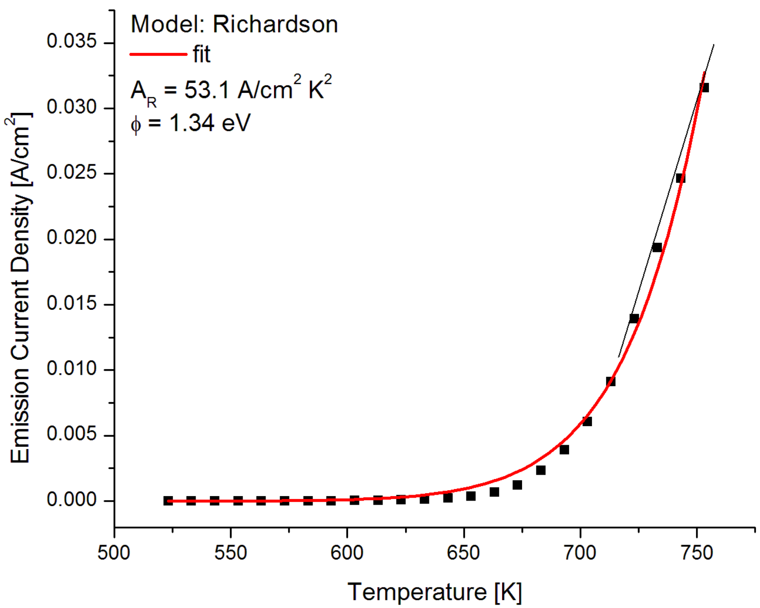
High density of grain boundaries (nitrogen incorporated sp^2 bonded carbon), defect states → **low resistivity**

- Control of the **substrate - (N)UNCD interface** by insertion of an interstitial metal layer.

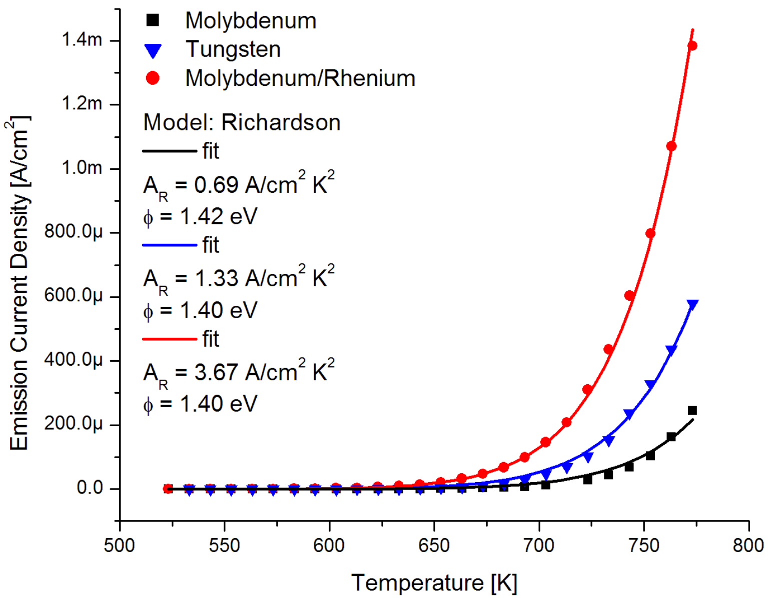
Element	A_R [A/cm² K²]	Carbide	ΔG [kJ mol⁻¹]	Resistivity [μΩ cm]
Mo	**55**	**Mo_2C**	**-59**	**130**
Re	**200**	**-**	**-**	**56**

Resistivity at 500 °C

- Significant improvement of emission current by utilizing **non-carbide forming, high Richardson** material, Rhenium → **43.85 mA/cm² at 530 °C.**
- **Significant Richardson constant A_R = 53 A/cm²K².**



Thermionic emission characterization

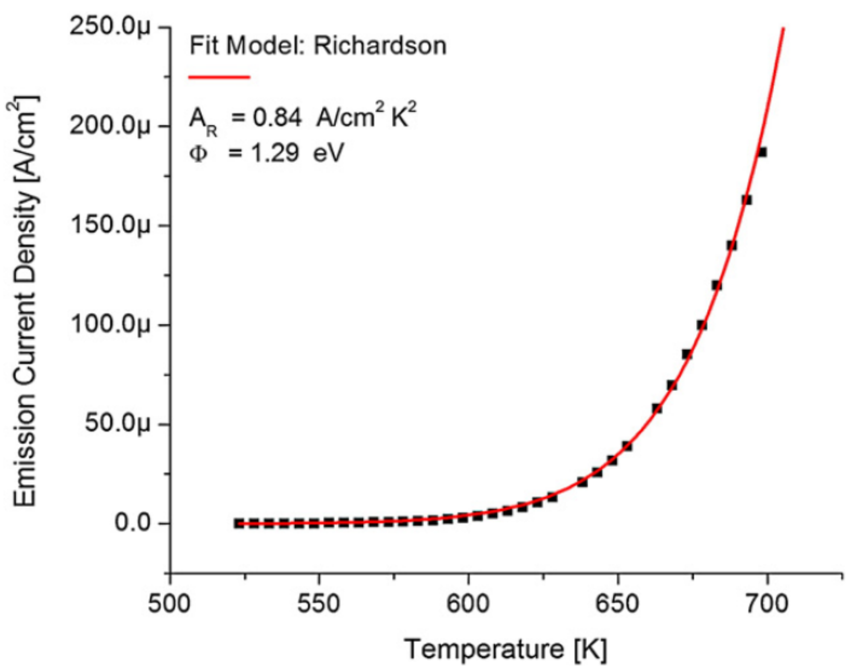


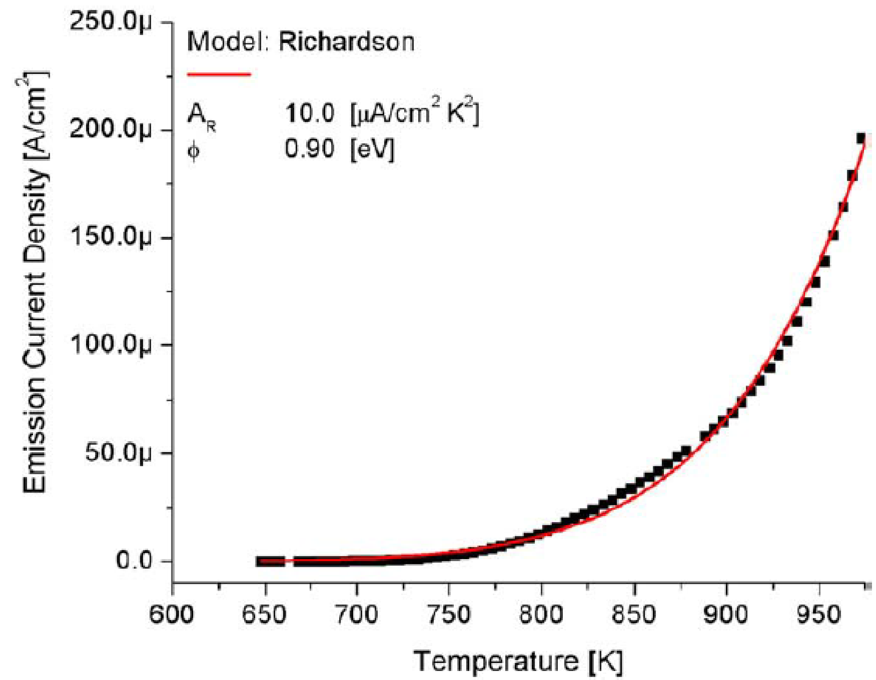
	Substrate		Emitter	
Material	**φ [eV]**	**A_R [A/cm² K²]**	**A_R [A/cm² K²]**	**φ [eV]**
Mo	4.1	55	0.69	1.42
W	4.5	74	1.33	1.40
Re	5.1	200	3.67	1.40

- **N-doped Diamond Emitter**
  - Substrate: Molybdenum (Mo)
    - Tungsten (W)
    - Molybdenum/Rhenium (Mo/Re)
  - UNCD(N)
  - N-doped diamond
  - Hydrogen passivation
- Significant range for the **value of Richardson's constant** for various metals.
- **Correlation** of **substrate material** parameters to **emission parameters** of the diamond emitter.*
- Significant improvement of emission current due to **increased Richardson's constant**.

*Substrate - diamond interface considerations for enhanced thermionic electron emission from nitrogen doped diamond films.
J. Appl. Phys. **112**, 113707 (2012)

Diamond Based Thermionic Emitter





- Thermionic emission observed at < 500˚C from *n*-type NEA diamond, due to a **low effective work function**
- Effective work functions: **1.3 eV** with **nitrogen** doping and **0.9 eV** with **phosphorus** doping
- Diamond films and coatings are now promising candidates for TEC applications

F.A.M. Koeck, et. al., *Diam. Relat. Mater.* 18 (2009): 232-234.
F.A.M. Koeck, et. al., *Diam. Relat. Mater.* 18 (2009): 789-791.

Enhancing Thermionic Electron Emission

Surface Ionization

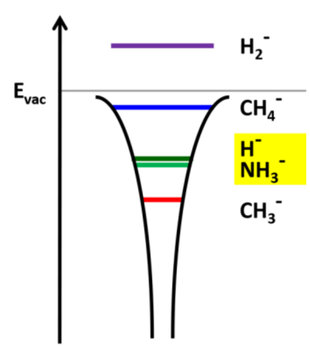
- **Surface Ionization**
  The negative ion fraction, β⁻, is given by the Saha - Langmuir equation

$$\beta^- = \frac{n^-}{n^- + n^0} \propto \frac{1}{1+\exp\left(-\frac{E_a - \varphi}{k_B T}\right)}$$

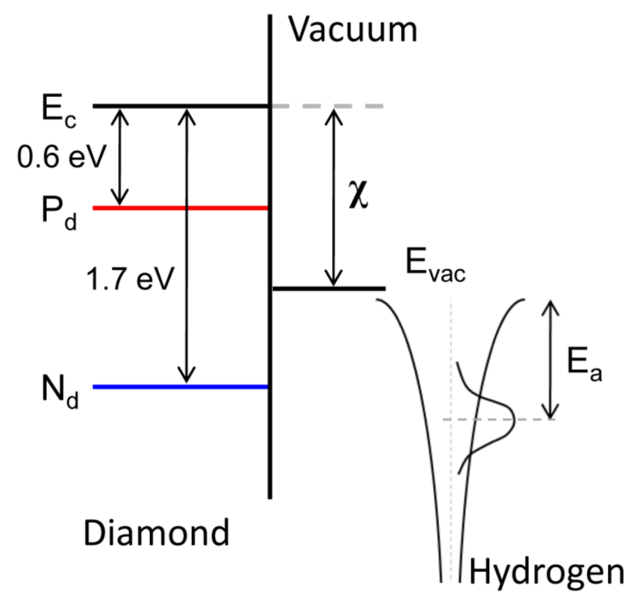
n^- is ionized particle flux, n^0 is the neutral particle flux, E_a is the electron affinity of the particle, φ, the surface work function, T, the surface temperature.

- **Gaseous Species for Surface Ionization**
  Formation of **atomic H** at a **hot filament.**

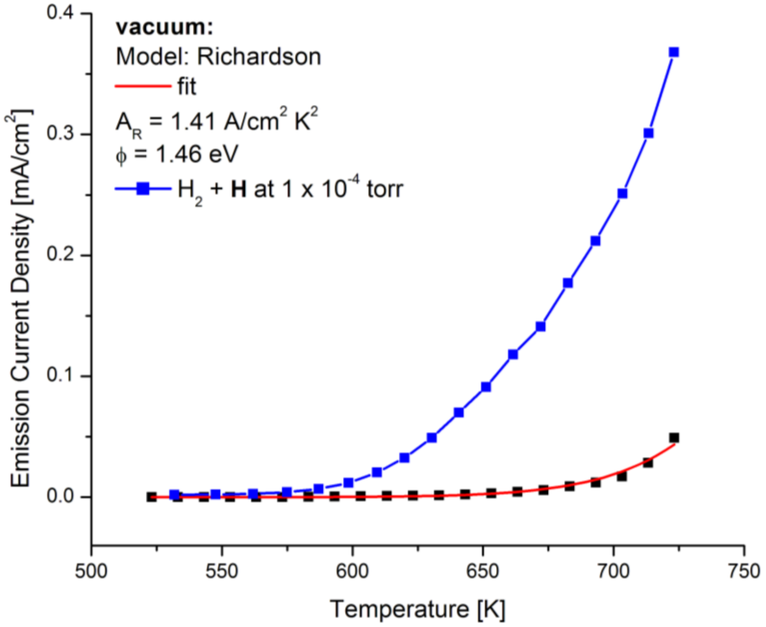
Species	E_a [eV]	Notes
H_2	-0.76	H_2^- $\tau \sim 10^{-15}$ s
H	0.75	$e^- + H_2 \rightleftharpoons H + H^-$
NH_3	0.76	
CH_3	1.08	
CH_4	0.08	



- **Negative electron affinity** (NEA) of diamond films through **Hydrogen** Passivation
- **Vacuum level ~ 1 eV below CBM**
- **Impurities**
  Nitrogen: 1.7 eV below CBM
  Phosphorus: 0.6 eV below CBM

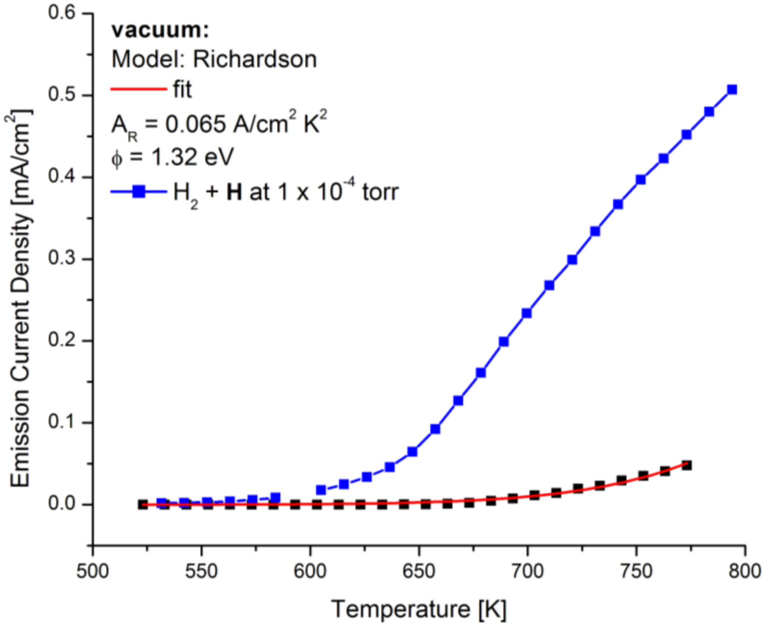


(N)UNCD/N-doped Diamond



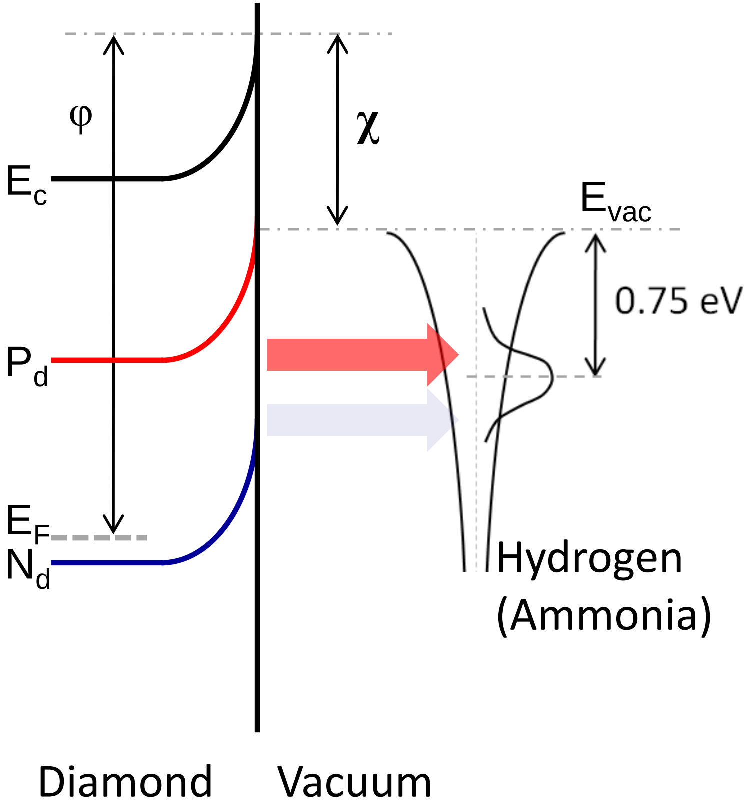
- **High density of grain boundaries** (nitrogen incorporated sp^2 bonded carbon)
- Emitter with a **work function of 1.46 eV** effects **significant emission enhancement**.

P-doped Diamond

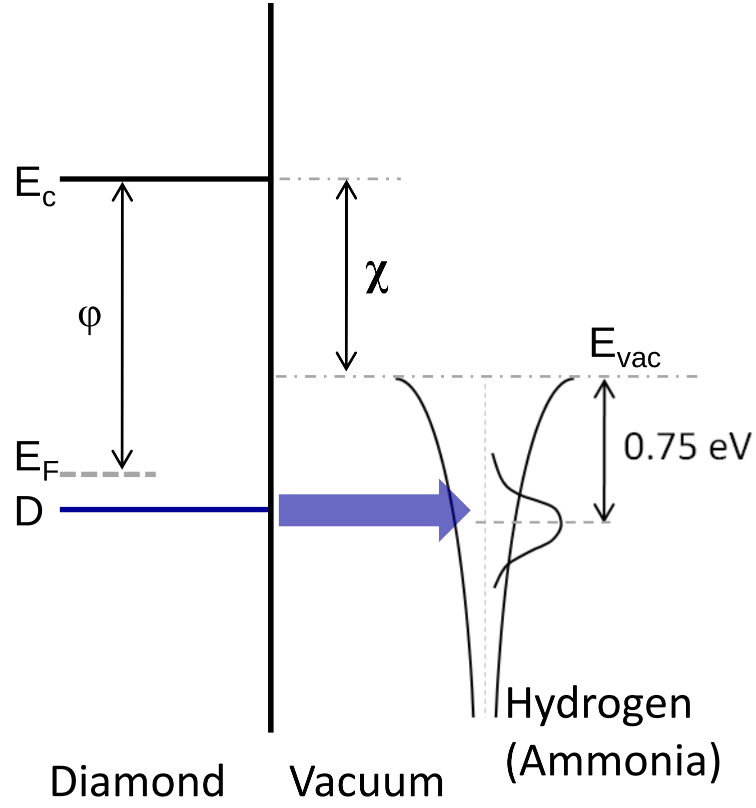


- **High sp^3 bonded carbon concentration.**
- Emitter with a **work function of 1.32 eV** effects **significant emission enhancement**.

Band Bending Model

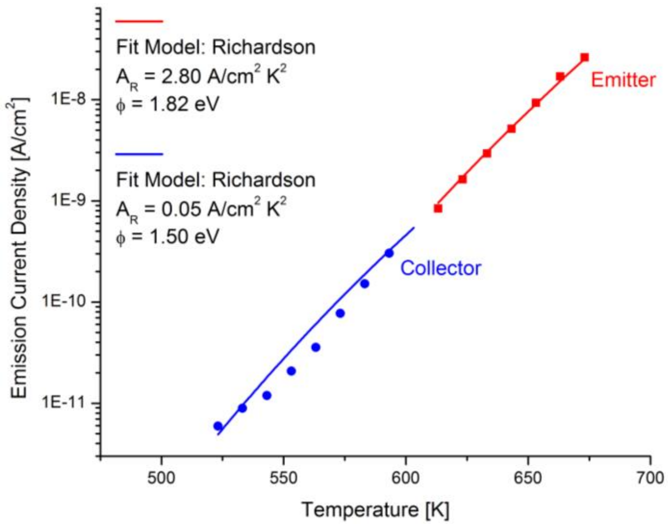


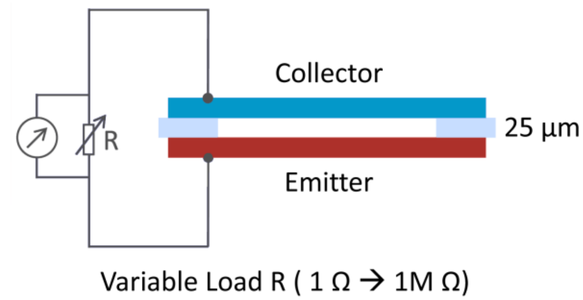
Defect Model

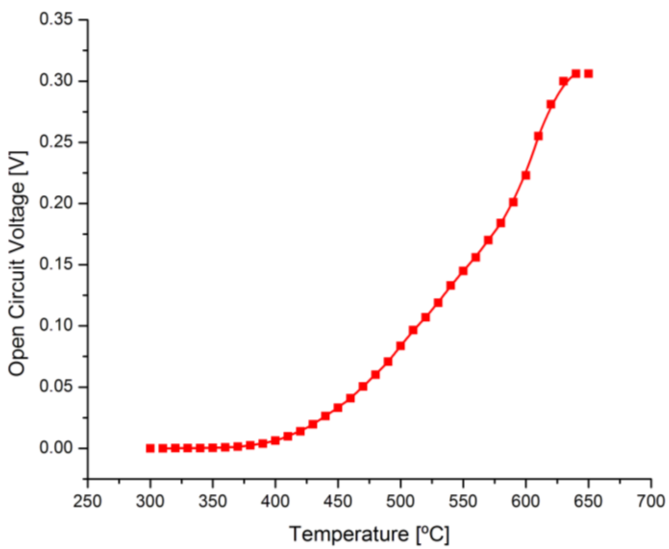


- **Efficient charge transfer for levels (shallow donors) that align with the molecular affinity level.**
- **Alignment for efficient charge transfer for flat band conditions and NEA of 1 eV.**

Vacuum Thermionic Energy Conversion



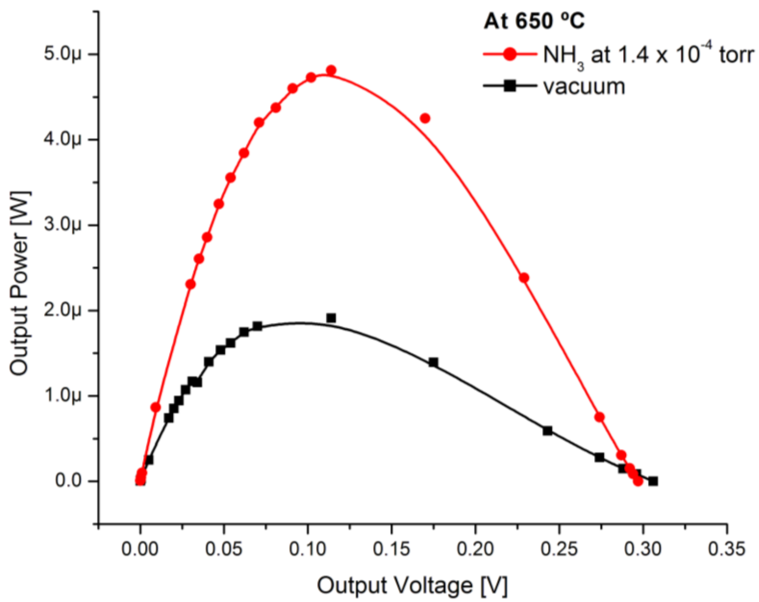


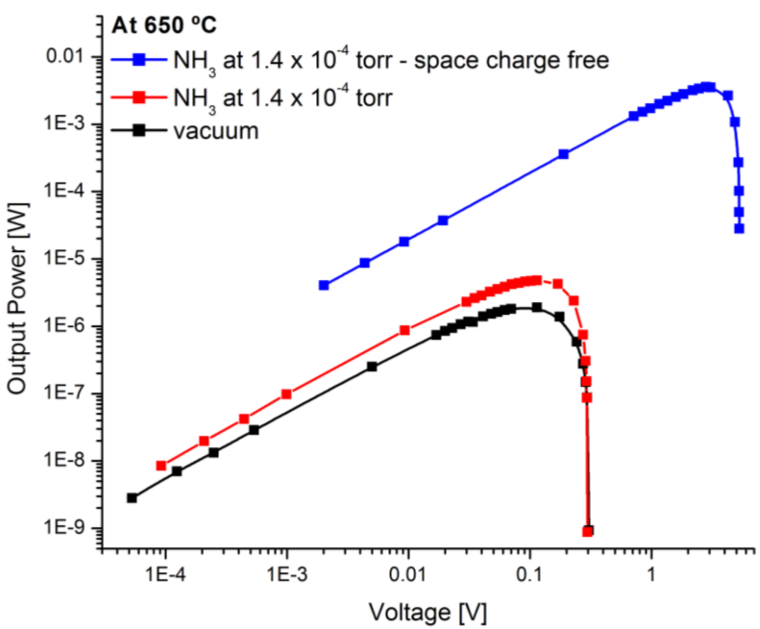


- **(N)UNCD based Diamond Electrodes**

$$\varphi_{emitter} = 1.82 \text{ eV}, \quad \varphi_{collector} = 1.50 \text{ eV} \quad \Rightarrow \quad \Delta\varphi = 0.32 \text{ eV}$$

- Electrode spacing **25 µm**.
- Significant **open circuit voltage of 0.3 V.**



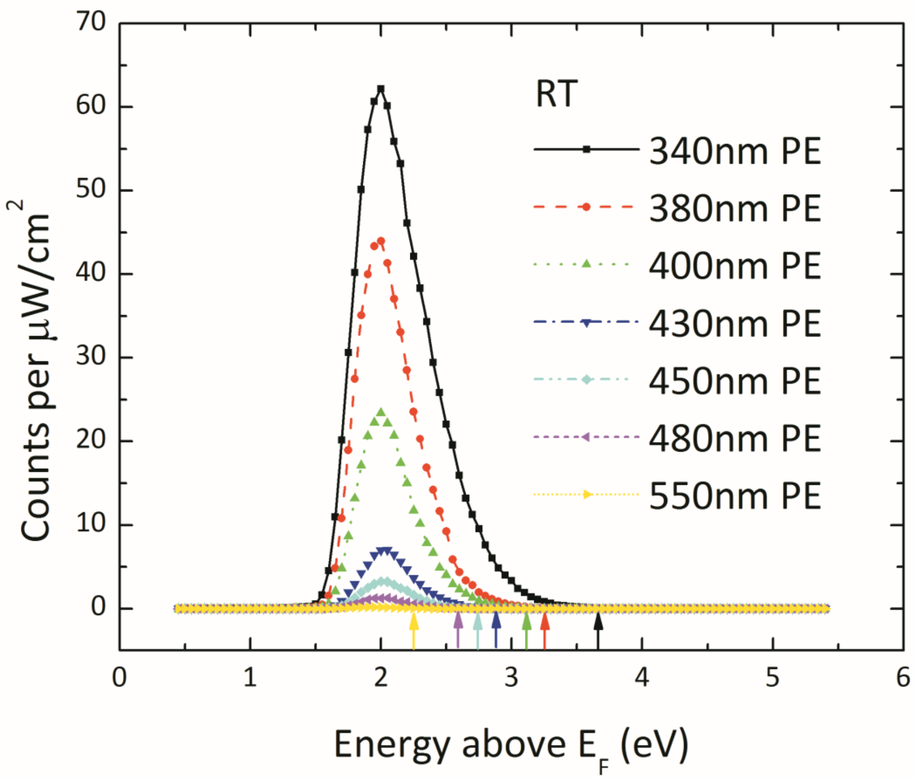


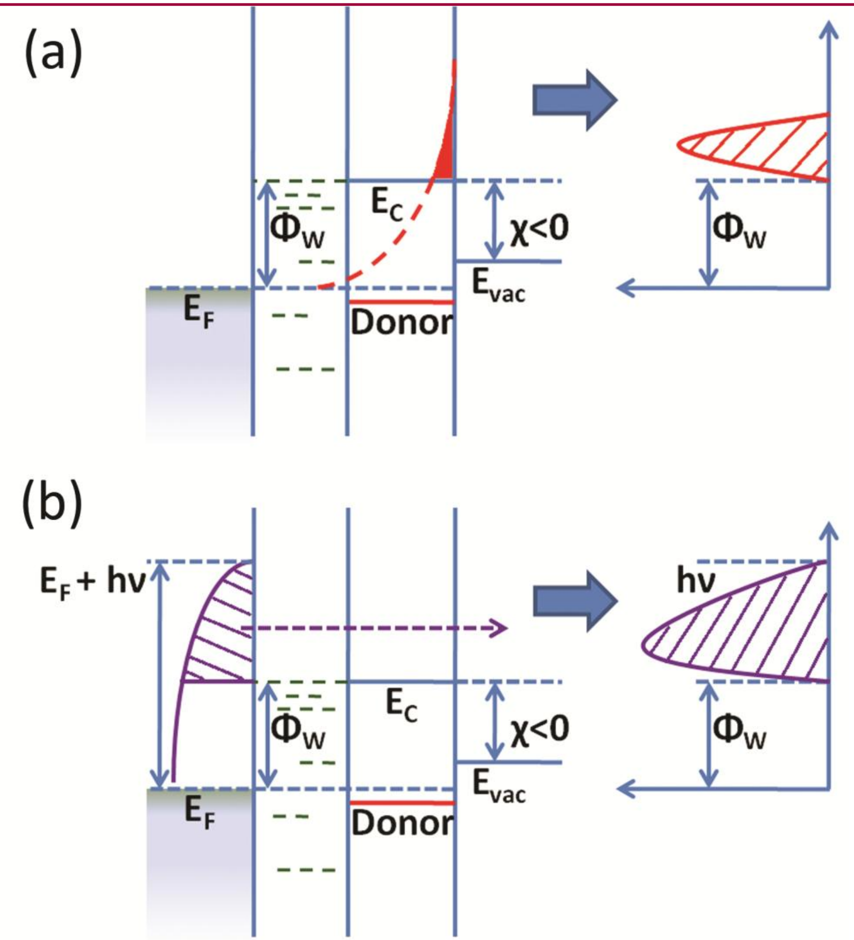
Energy Conversion Enhancement

- Significant **power output increase with application of ammonia** due to surface ionization effects.
- **Ionization at the emitter** and **de-ionization at the collector**.
- **Self sustained** power output enhancement.
- **Space charge effects** will limit the power output.
- Application of **small bias of 5V** to alleviate space charge limited operation.
- **Power output is increased** by several orders of magnitude.
- **Device resistivity** may contribute to reduced power output.

Photo-Induced Emission from Diamond/Metal Structures

Photo-Induced Emission from N-doped Diamond on Metal Substrates

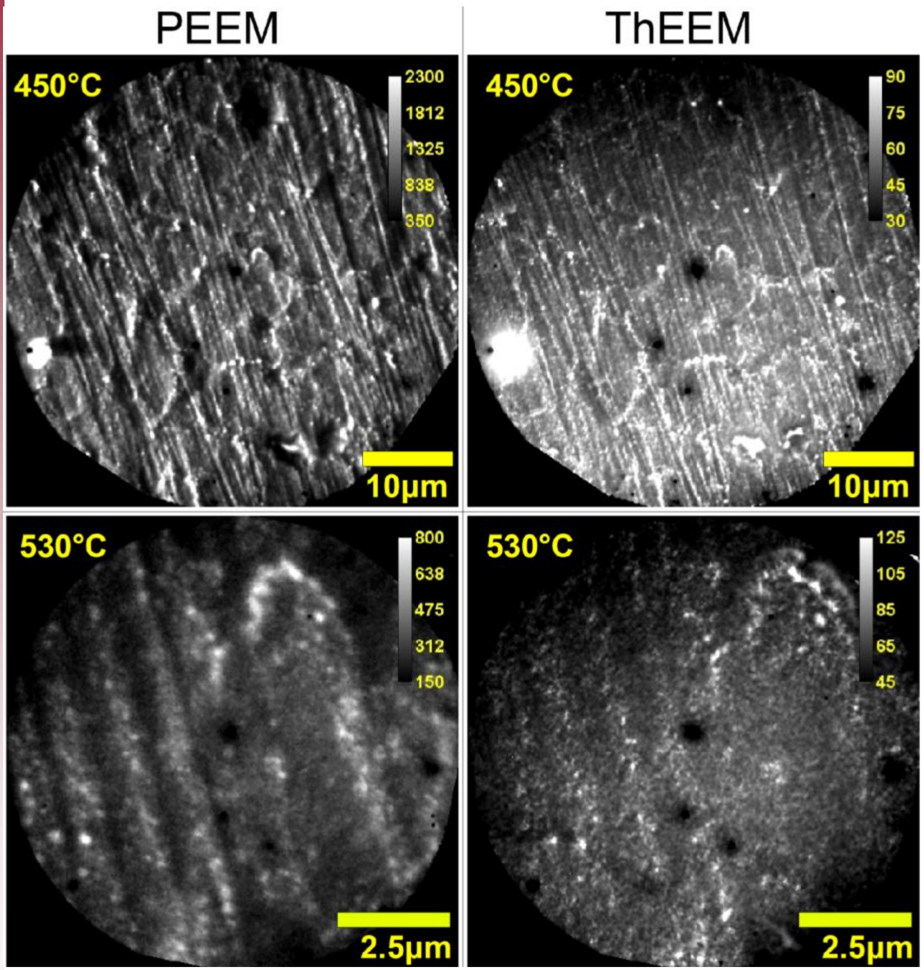


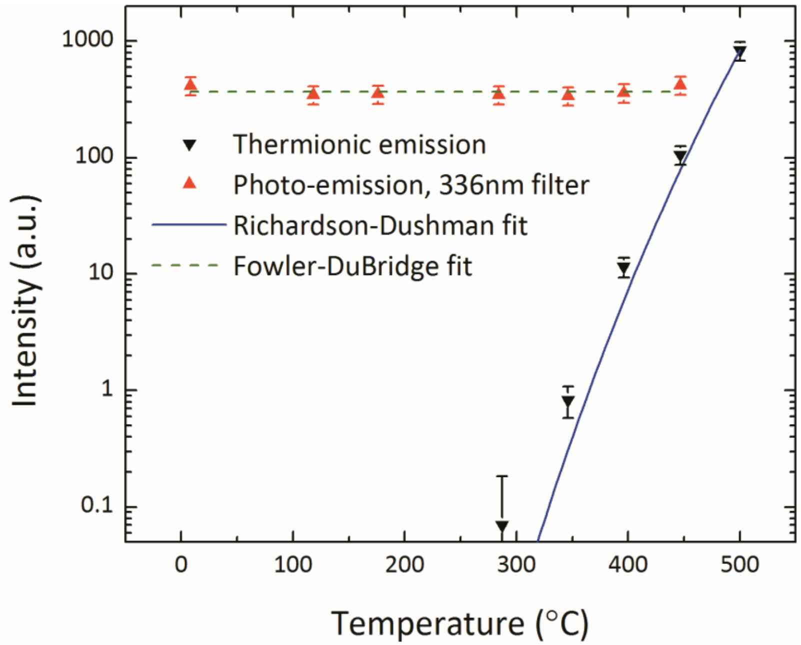


- **Visible light photo-induced emission** has been established from the diamond film. Photons transmit through the film and generated photo-electrons **at or near the interface**

T. Sun, et. al., *Appl. Phys. Lett.* 99 (2011): 202101.

Spatial Correlation of Photo- and Thermionic Emission



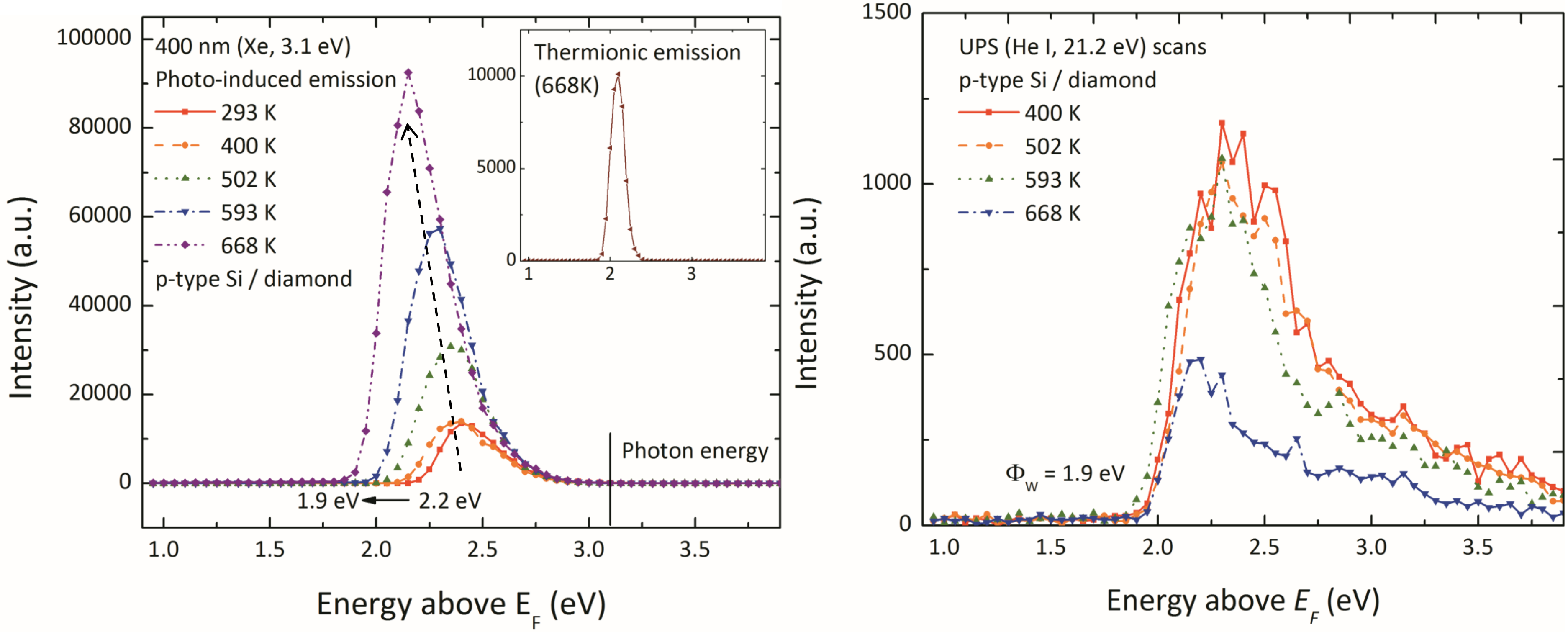


- Both photo- and thermionic emission images share significant similarities
- The **surface morphology** has a significant influence on the spatial distribution
- Photo-induced emission is **relatively constant** while thermionic emission is **temperature dependent**

N. Neugebohrn, et. al., *Diam. Relat. Mater.* 40 (2013): 12-16.

Photo-Induced Emission from Diamond/Si Heterostructure

NEA Diamond / Si Structure for Photon-Enhanced Emission



- At elevated temperatures, **significantly increased emission intensity** has been measured experimentally
- **The PETE mechanism** could contribute to the enhanced emission

T. Sun, et. al., *Appl. Phys. Lett.* 99 (2011): 202101.
T. Sun, et. al., *under review by Phys. Rev. Lett.*

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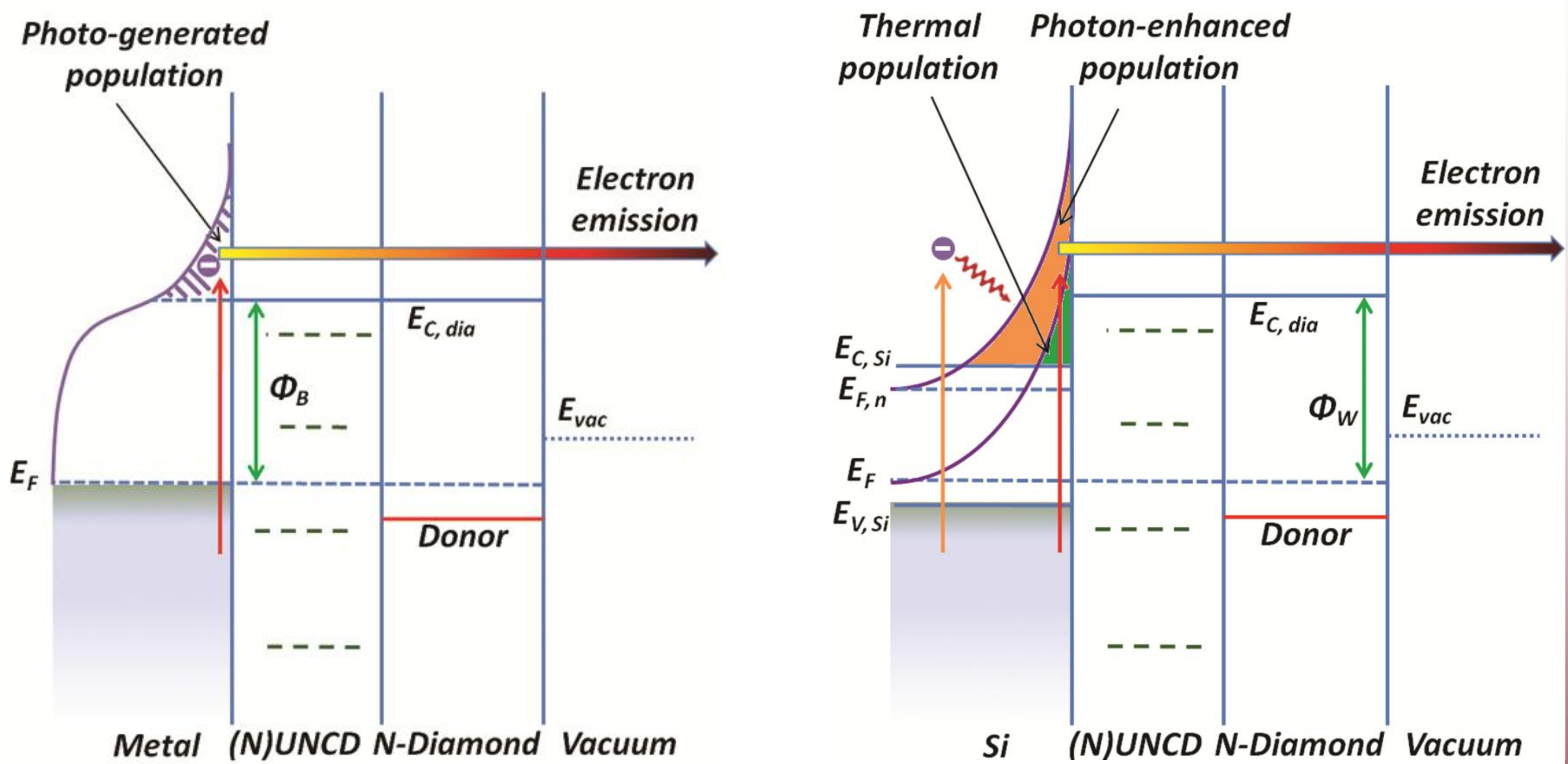
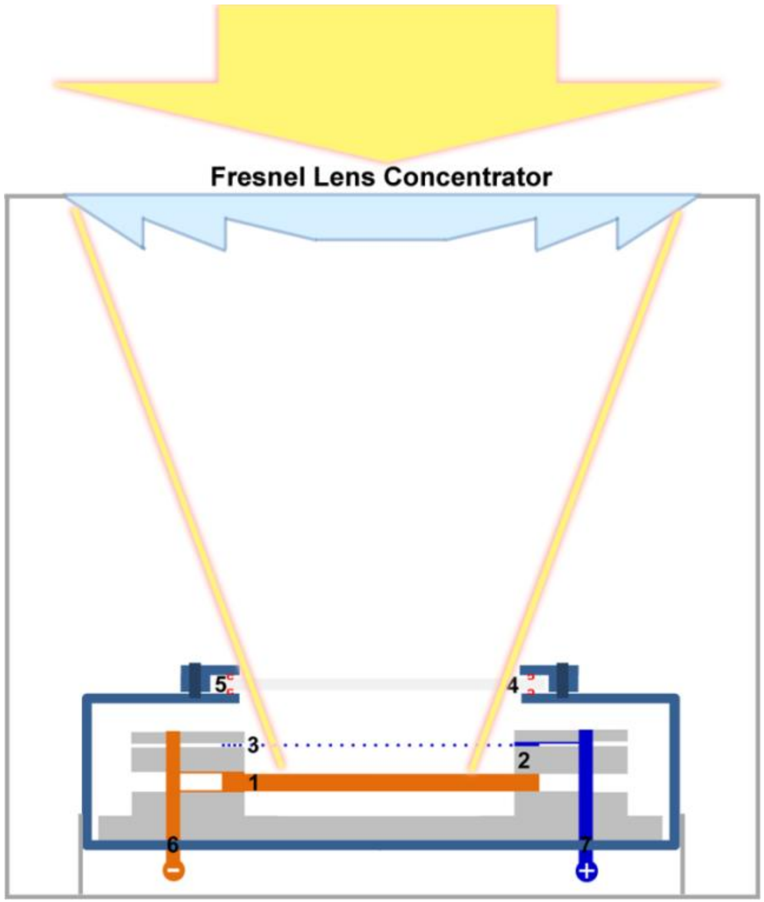
NEA Diamond / Si Structure for Photon-Enhanced Emission



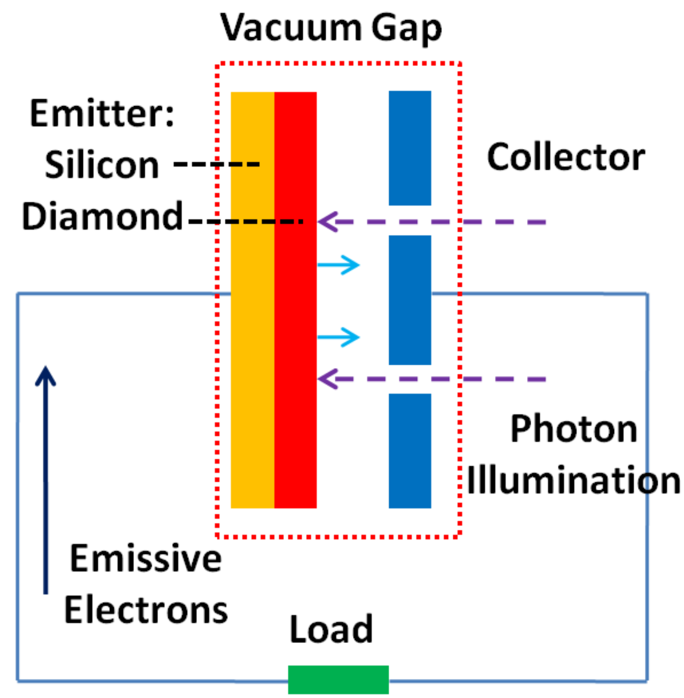
- For a metal substrate, photo-electrons are directly generated
- For a *p*-type semiconductor substrate, the PETE mechanism may lead to **enhanced electron emission at elevated temperatures**

Potential Diamond-Based PETE Device Configurations

Diamond Based PETE Converter (Regular)

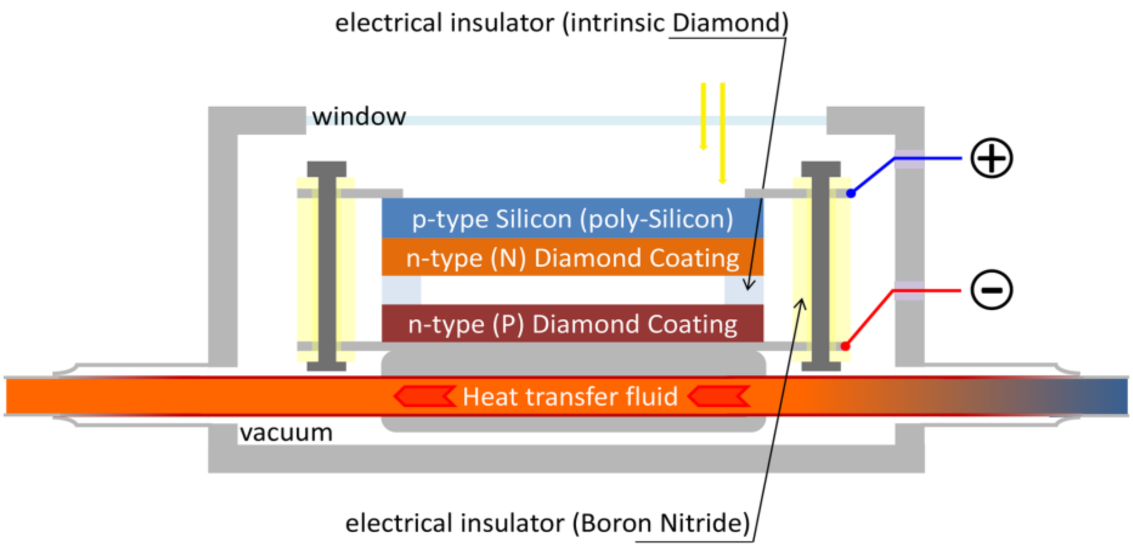


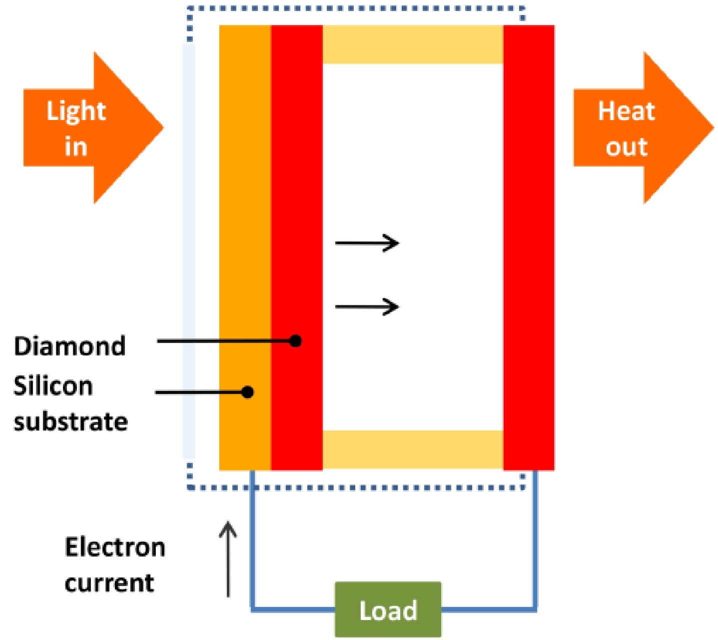
- *Schematic of a vacuum-encapsulated converter device with the diamond coated emitter (1) and collector grid (3)*



- The collector operates at a lower temperature than the emitter
- Substantial engineering is required

Diamond Based PETE Converter (Isothermal)

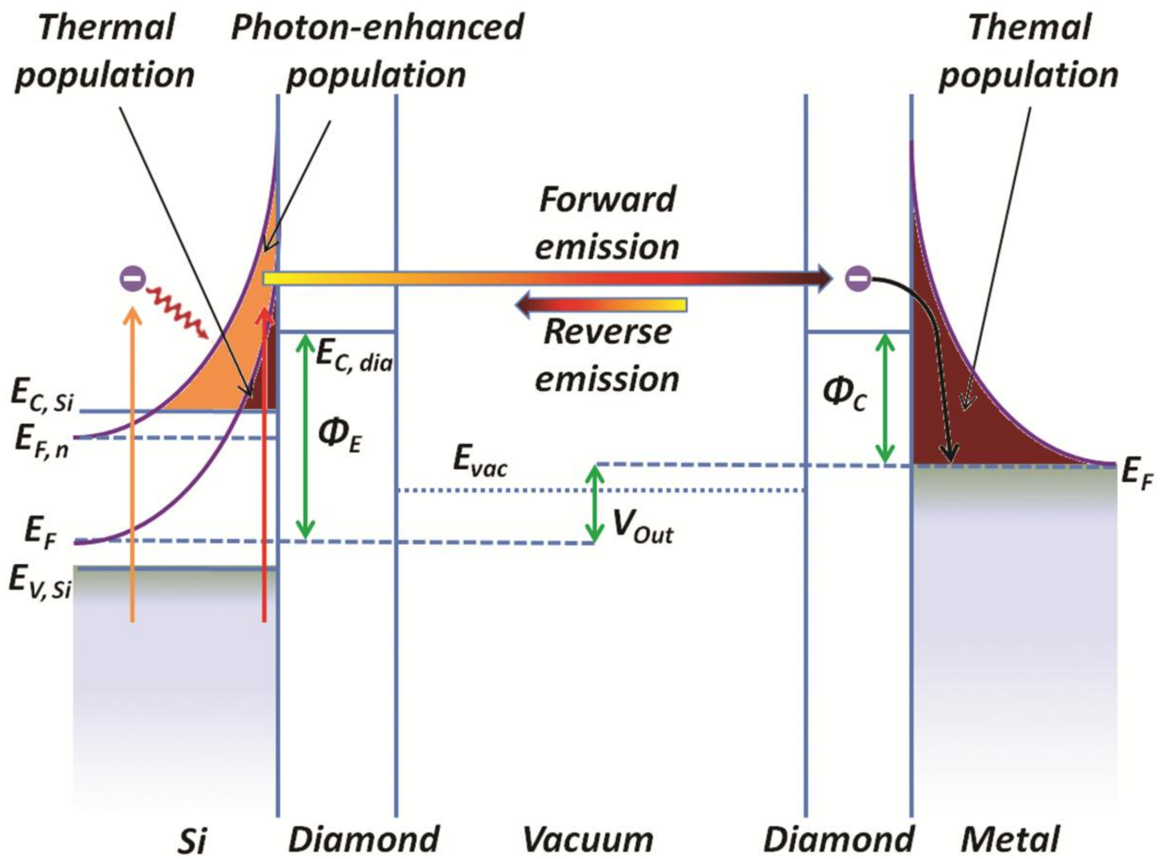




- A multi-layer structure for an **isothermal-PETE solar energy converter**
- The emitter and collector are maintained **at the same temperature**
- **Space-charge limitation can also be mitigated**

G. Segev et al. Sol. Energ. Mat. Sol. C. 113 (2013): 114-123.
J.R. Smith. J. Appl. Phys. 114 (2013): 164514.

Principles of the Isothermal PETE Topping Device

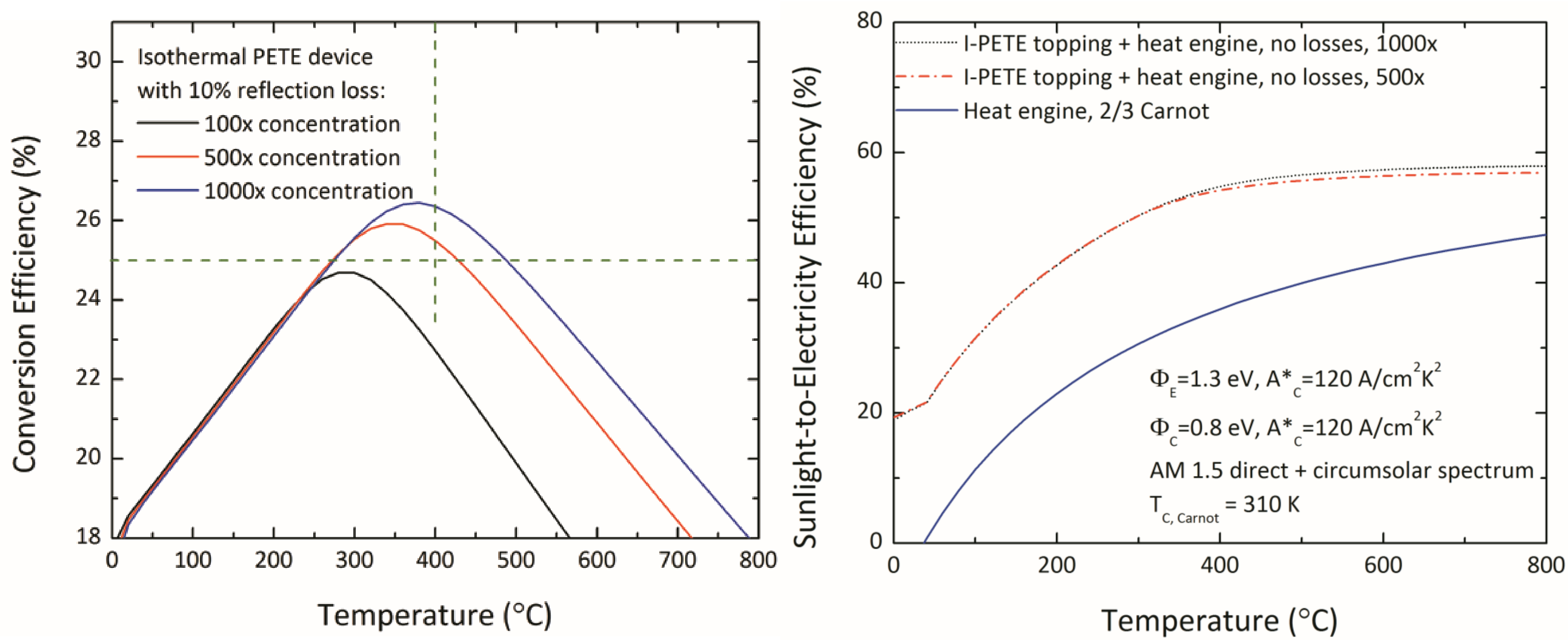


Photon-enhanced thermionic emission in the isothermal device:

$$e\left(\Gamma_P - R\right) = J_{forward} - J_{rev}$$

Equilibrium of photo-generation and recombination

Modeling Results



- An **optimized operation regime** exists in the parameter space
- Higher efficiency may be achieved from **a tandem cycle**
- Ideal Richardson constant can be difficult to obtain

Revolutionary Research . . . Relevant Results

Conclusions

- **Efficient thermionic electron emitters**

  are comprised of **individual layers** and utilize **nitrogen incorporated UNCD** and a **non – carbide (rhenium) forming** substrate/diamond **interface**.

- **Doped diamond films for surface ionization**

  nitrogen, **phosphorus** and nitrogen incorporated **UNCD** present various energetic levels for surface ionization.

- **Surface ionization of atomic hydrogen and ammonia**

  Similar electron affinity level for **atomic hydrogen (0.75 eV)** and **ammonia (0.76 eV)**.

  Saha-Langmuir relation can describe surface ionization effects.

  Efficient charge transfer observation **for phosphorus doped diamond** and **nitrogen incorporated UNCD films**.

- **Thermionic energy conversion**

  in an **ammonia ambient** effects a **large increase in the power output** of the device indicative of **efficient ionic charge transfer across the gap**.

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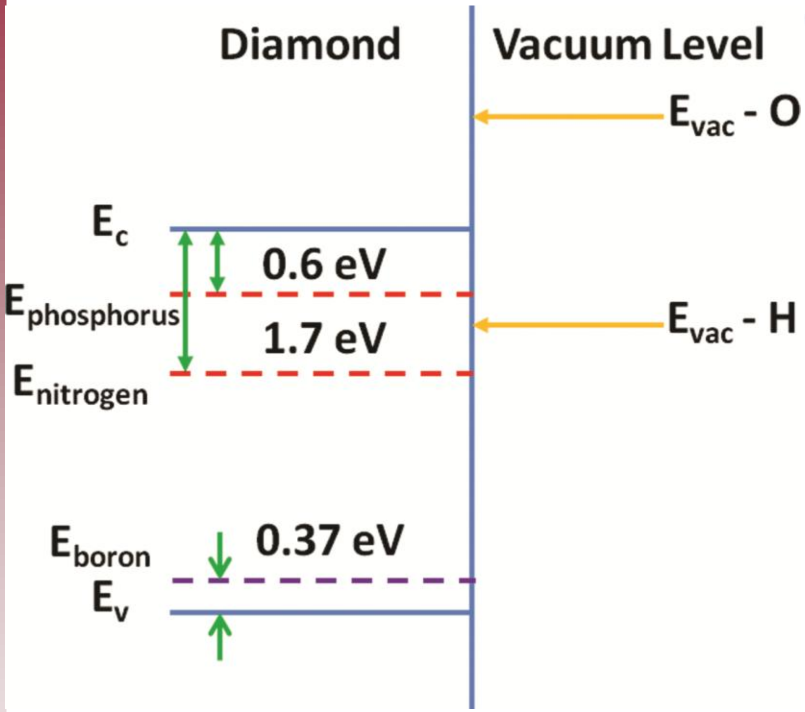
Summary & Plans

- **Summary:**
  - Low work function diamond films prepared by MPCVD hold great potential in PETE-related applications
  - Significant increase of photo-induced electron emission at elevated temperatures from a diamond/Si heterostructure has been observed experimentally
  - The observed temperature dependence appears to be consisted with the PETE phenomena
  - Modeling shows an energy conversion efficiency > 25% at optimized conditions

- **Future work:**
  - Incorporating transport loss into the electron emission process
  - Fabricating and testing of demonstration conversion devices



- **Negative electron affinity** (NEA)
- **Diamond (N, P doping)**
  cubic BN (Si doping)
  AlGaN (Si doping)
- **Controlling Band Bending**
- **NEA and *n*-type doping lead to lowering of the emission barrier (effective work function)**

Current Status Reviews