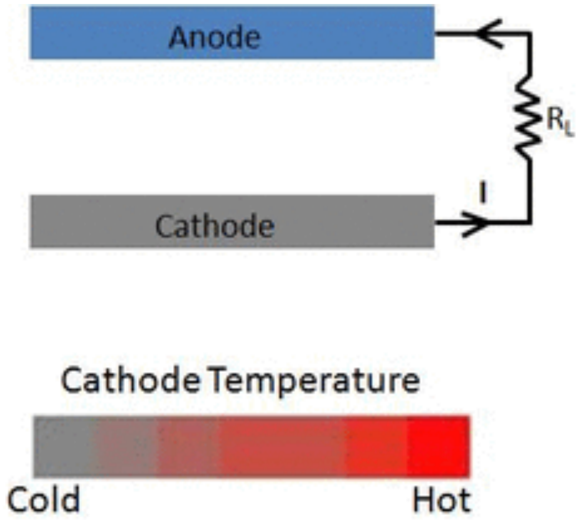
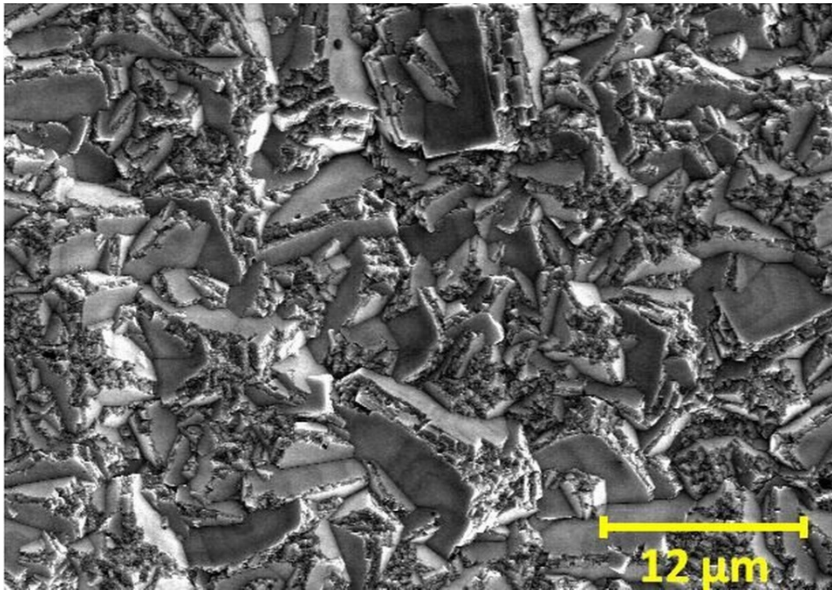
Diamond-based TEC Devices: Promise and Challenges





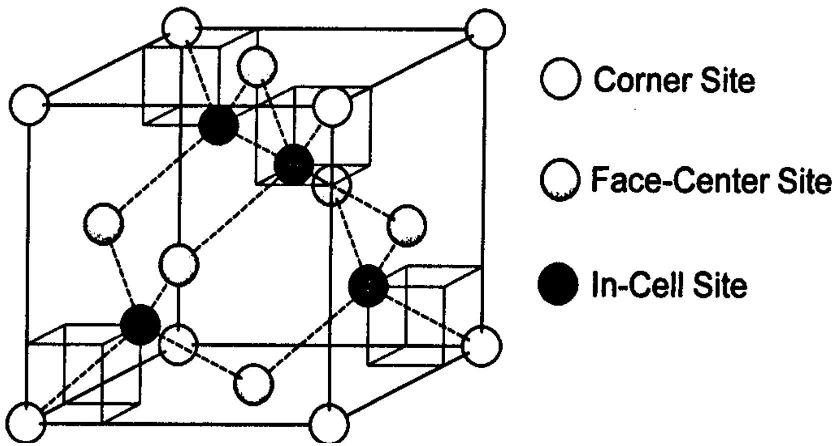
William (Hank) Paxton, Ph.D.

- President, Cofounder, Chief Engineer IOP Technologies;
- Assistant Research Professor, Dept. Electrical Engineering, Vanderbilt University

Introduction

- **Ph.D. from Vanderbilt University in 2013**
  - Research focused on diamond-based TEC devices
- **Formed a company called IOP Technologies**
  - Based in Nashville, TN
  - Focus on developing diamond-based TEC devices for commercialization
- **Continuing research on diamond-based TEC devices at Vanderbilt University and IOP Technologies**

Diamond as an Electronic Material



Diamond lattice structure from S. J. Pearton, "Wide Bandgap Semiconductors - Growth, Processing and Applications"

- Carbon is a unique element that can form several different allotropes
- Diamond is one such allotrope consisting of two intersecting FCC lattices
- Diamond can be doped to alter its electrical properties but suffers from an a-symmetrical doping problem[1]

- Diamond has numerous advantages over silicon as an electronic material
- With a large bandgap, diamond can operate as both and effective electrical insulator and an efficient electrical conductor[2]
- Diamond's radiation tolerance also allows it to operate in harsh conditions[2]

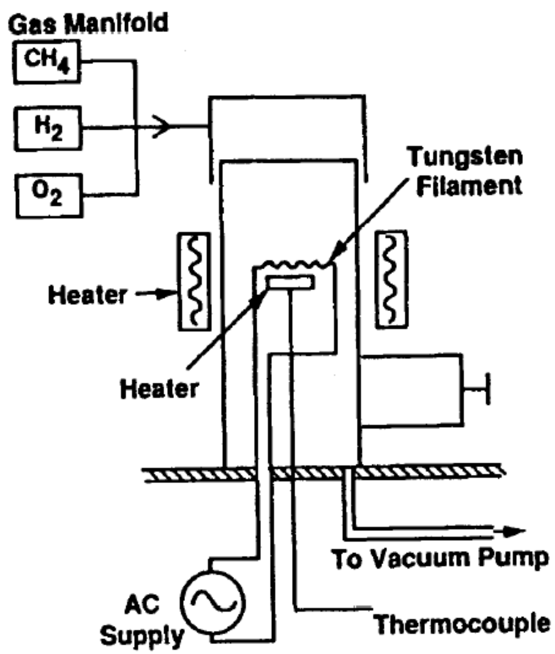
Property	Diamond	Silicon
Lattice Constant (Å)	3.567	5.430
Density (g·cm^{-3})	3.515	2.328
Atomic Mass (g·mol^{-1})	12.011	28.0855
Hardness (kg·mm^{-2})	~10^4	10^3
Young's Modulus (GPa)	10.5 x 10^3	1.13 x 10^3
Sound Velocity (m/s)	18000	7500
Poisson's Ratio	0.07*	0.223
Bandgap (eV)	5.45	1.1
Resistivity (ý cm)	>10^{15}	10^3
Electron Mobility (cm^2·V^{-1}·s^{-1})	2200	1500
Hole Mobility (cm^2·V^{-1}·s^{-1})	1600	480
Dielectric Constant	5.7	11.8
Thermal Conductivity (W·cm^{-1}·K^{-1})	20.0	1.47
Molar Heat Capacity, $c_{p, 298\,K}$ (J·mol^{-1}·K^{-1})	6.19	19.85
Debye Temperature, Θ_D (K)	1860 ±10	650

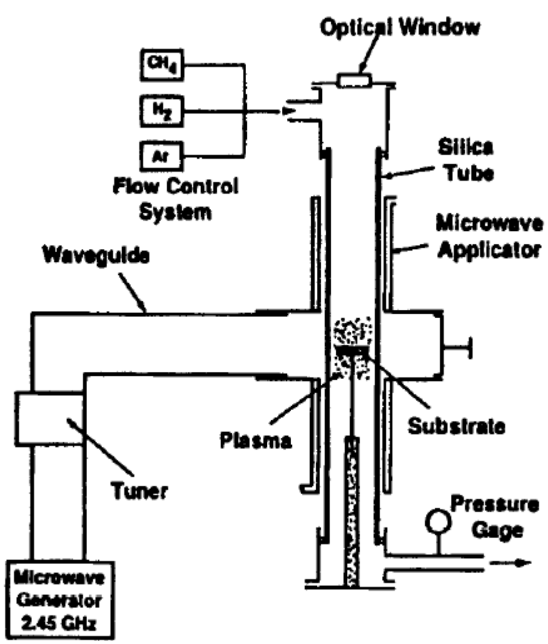
Diamond properties from S. J. Pearton, "Wide Bandgap Semiconductors - Growth, Processing and Applications"

[1]M. A. Pinault et. al, "The n-type doping of diamond: Present status and pending questions," *Physica B: Condensed Matter,* vol. 401-402, pp. 51-56, 2007.
[2]Diamond lattice structure from S. J. Pearton, "Wide Bandgap Semiconductors - Growth, Processing and Applications"

Fabrication of Diamond

- More difficult to fabricate than many common semiconductors (Silicon)
- Chemical Vapor Deposition (CVD) is the most common fabrication technique
  - Predominant methods are HFCVD and MPCVD
- Gas species used are typically hydrogen and a carbon containing gas (i.e. methane)
- Other gases can be fed into the deposition process to alter the electronic properties





H. Liu and D. S. Dandy, "Diamond Chemical Vapor Deposition," William Andrew Publishing/Noyes, 1995.

Doping of Diamond

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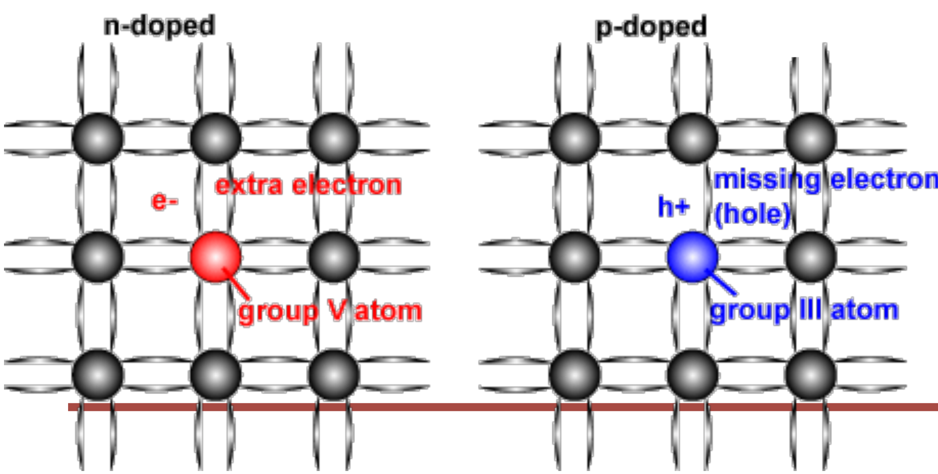
Diamond suffers from an asymmetric doping problem

P-type doping (relatively easy)

1. Boron in the form of TMB is fed into the deposition process
2. Acceptor level lies favorably at 0.37eV above the valence band
   a) Allows for thermal activation at relatively low temperatures
3. Hole motilities exceeding $1000cm^2V^{-1}s^{-1}$ and resistivities less than $10^{-2}\Omega cm$ have been reported



N-type doping (much more difficult)

1. Phosphorus

a) Much larger in size than carbon and has a high equilibrium formation energy

b) Acceptor level at 0.6eV below conduction band

c) Concentrations up to $5*10^{19}cm^{-3}$ have been achieved with electrical activity in the (111) direction

2. Sulfur

a) Donor level is positioned favorable at only ~0.37eV below the conduction band

b) Useful concentration levels (exceeding $10^{15}cm^{-3}$) have yet to be achieved

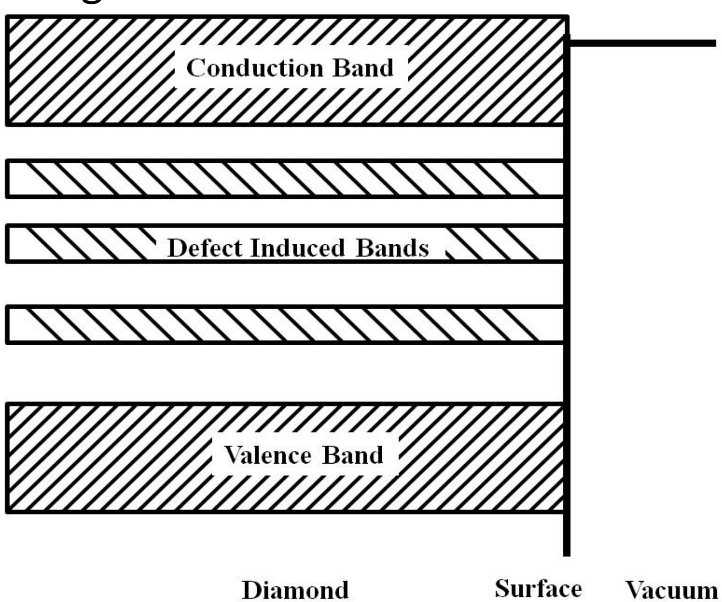
3. Nitrogen

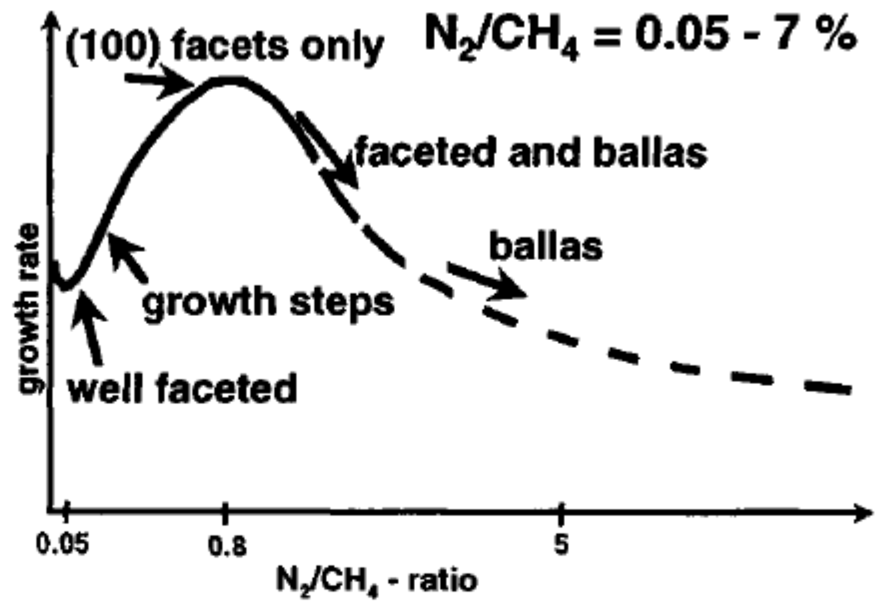
a) Easily enters the diamond lattice as a substitutional dopant with a -3.4eV formation energy

b) Deep donor level at 1.7 eV below the conduction band

Nitrogen in Diamond

- The deep donor level of 1.7 eV below the conduction band requires extremely high temperatures to activate the nitrogen dopants[1]
- Proposed that nitrogen promotes defect induced energy bands allowing conduction band carrier "hopping"[2]
- Recent observations indicate highly doped phosphorus might have this same effect
- Nitrogen can affect the growth of diamond by promoting (100) oriented crystal growth[3]



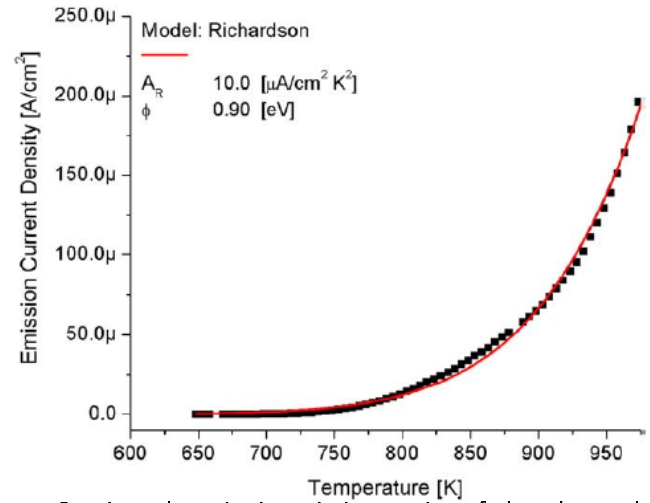


[1]S. Bhattacharyya, "Mechanism of high n -type conduction in nitrogen-doped nanocrystalline diamond," *Physical Review B*, vol. 70, p. 125412, 2004
[2]Y. Show, *et al.*, "Effects of defects introduced by nitrogen doping on electron emission from diamond films," *Mat. Chem. and Phys.*, V72, pp. 201-203, 2001.
[3]R. Haubner and B. Lux, "Effect of B, N and P on low-temperature diamond growth," in *Properties, Growth and Applications of Diamond*, M. Nazare and A. J. Neves, Eds., 2000.

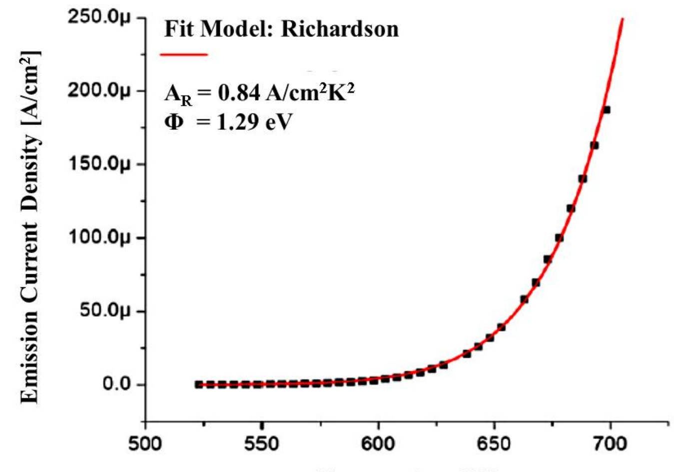
6

Diamond as a Thermionic Emitter

- Diamond shown to be a promising cathode material for thermionic applications including TEC
- Previous studies on phosphorus doped diamond reported work functions less than 1 eV (but with extremely low Richardson constants)[1]
- Nitrogen-incorporated diamond films have also proven favorable with work functions as low as 1.29 eV[2]
- Studies show that a sample must have both a low work function AND a high Richardson constant to be of significant value



Previous thermionic emission testing of phosphorus doped diamond films[1]



Previous thermionic emission testing of nitrogen-incorporated diamond films[2]

[1] F. A. M. Koeck, *et al.*, "Thermionic electron emission from low work-function phosphorus doped diamond films," *Diamond and Related Materials,* vol. 18, pp. 789-791, 2009.

[2] F. A. M. Koeck and R. J. Nemanich, "Low temperature onset for thermionic emitters based on nitrogen incorporated UNCD films," *Diamond and Related Materials,* vol. 18, pp. 232-234, 2009.

Hydrogen in Diamond

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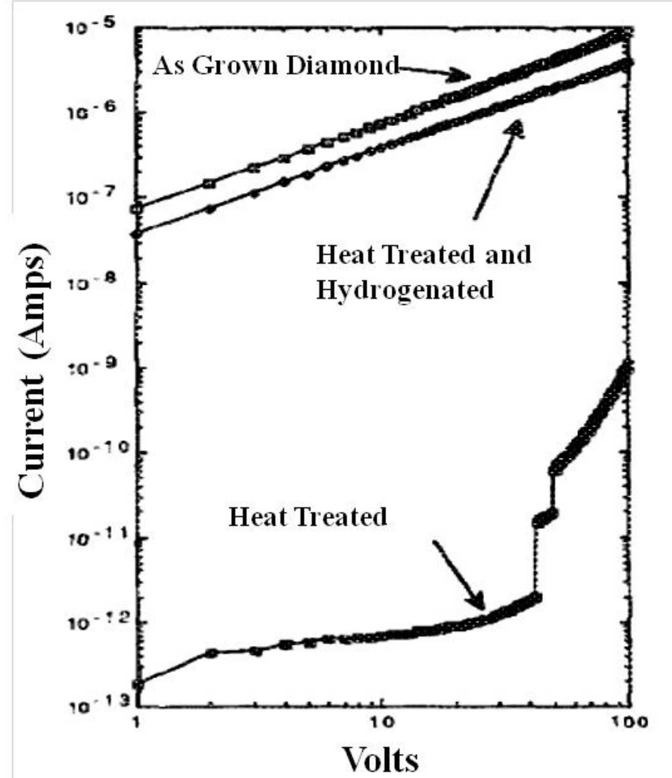
Hydrogen shown to enhance many of diamond's electrical properties

1. Electron Transport

- Landstrass and Ravi were the first to observe that hydrogen influences the resistivity of diamond films[1]
- They found that the resistivity would greatly increased following an 800°C anneal
- Upon exposing the samples to a hydrogen plasma, the resistivity was seen to decrease back to it's initial state

2. Electron Affinity

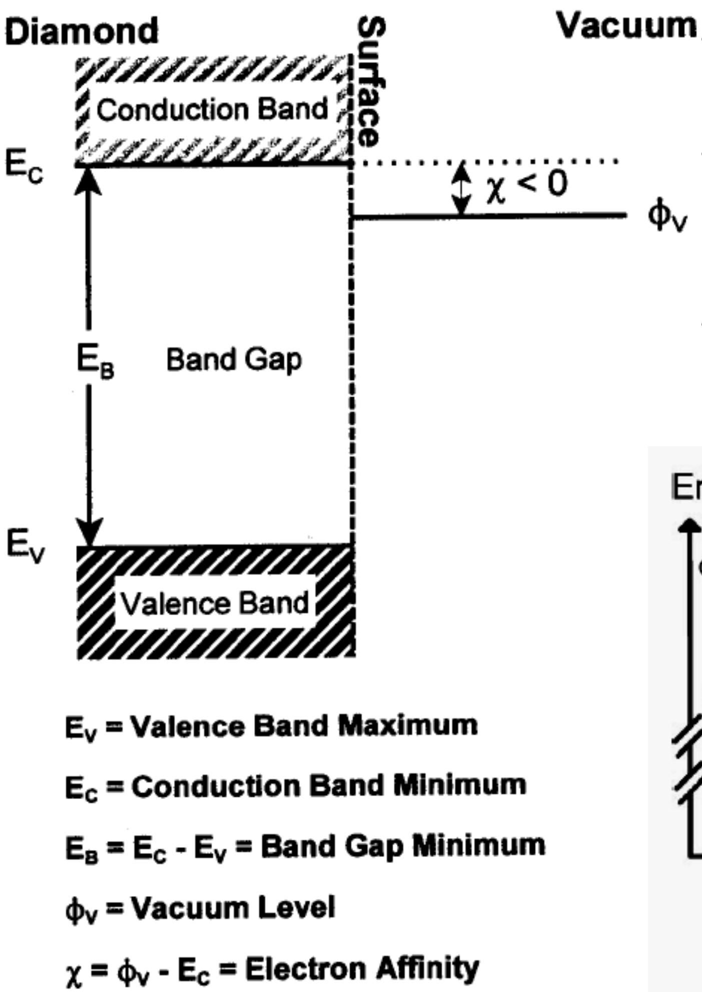
- Using photoemission spectroscopy, Himpsel et al. first observed that (111) diamond exhibits a negative electron affinity[2]
- Cui et al. first noted that hydrogen was responsible for the detected negative electron affinity in diamond via photo-electron microscopy[3]



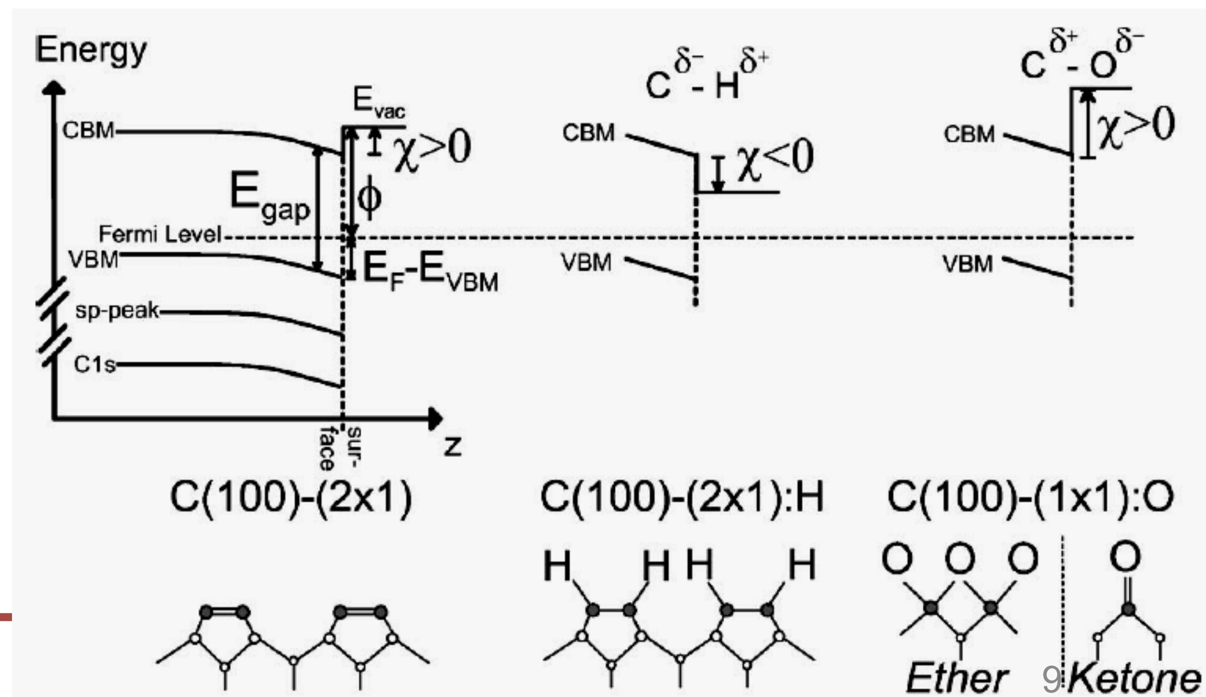
[1] M. I. Landstrass and K. V. Ravi, "Resistivity of chemical vapor deposited diamond films," *Applied Physics Letters,* vol. 55, pp. 975-977, 1989.
[2] F. J. Himpsel*, et al.*, "Quantum photoyield of diamond(111)—A stable negative-affinity emitter," *Physical Review B,* vol. 20, pp. 624-627, 1979.
[3] J. B. Cui*, et al.*, "Hydrogen termination and electron emission from CVD diamond surfaces: a combined secondary electron emission, photoelectron emission microscopy, photoelectron yield, and field emission study," *Diamond and Related Materials,* vol. 9, pp. 1143-1147, 2000.

Negative Electron Affinity of Diamond

- Hydrogen is believed to introduce a surface dipole layer similar to Cs in previous metallic TEC implementations
- Hydrogen has a lower electronegativity than carbon, resulting in a C-H bond that is polarized with a positive charge on the H atom
- This charge provides a potential step that pulls the vacuum level below the conduction band minimum



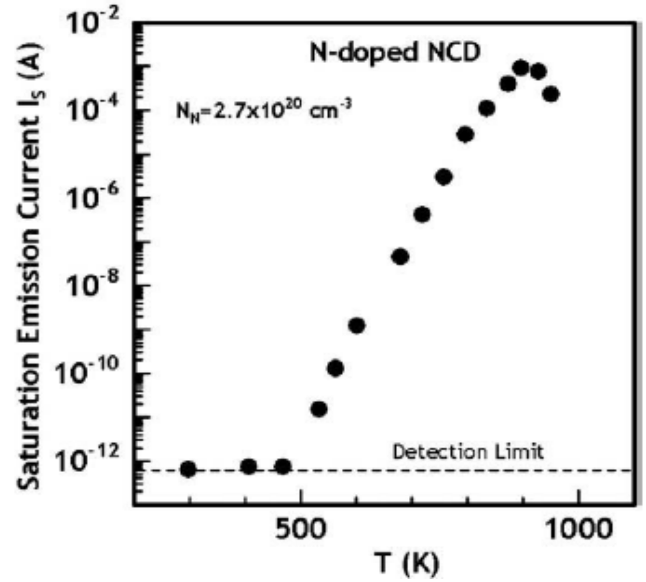
Electron affinity band diagram of diamond from S. J. Pearton, "Wide Bandgap Semiconductors - Growth, Processing and Applications"



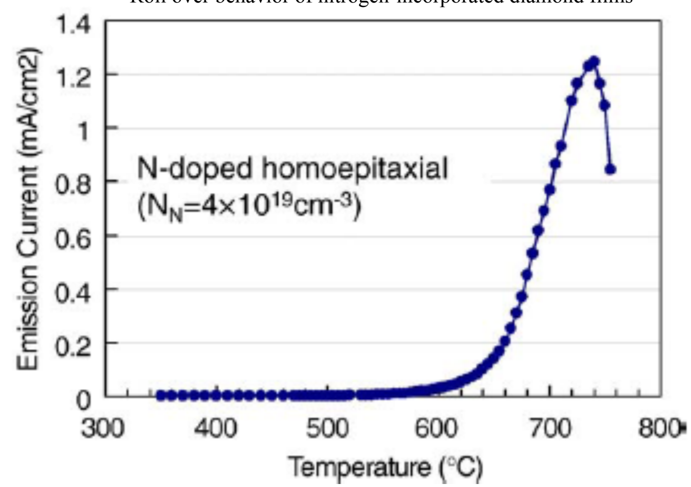
F. Maier, *et al.*, *"Electron affinity of plasma-hydrogenated and chemically oxidized diamond (100) surfaces," Physical Review B, vol. 64, p. 165411, 2001*

Influence of hydrogen on the thermionic emission of diamond films

- Has been shown that hydrogen is responsible for many of diamond's superior electrical properties
- Numerous studies show "roll over" in thermionic emission current when heated to temperatures of ~750°C[1,2]
    - Attributed to hydrogen desorbing from the diamond surface
- Little prior work has studied this desorption process
- More detailed studies are required to better understand this process so that a practical diamond based thermionic energy converter can be realized



Roll over behavior of nitrogen-incorporated diamond films[1]



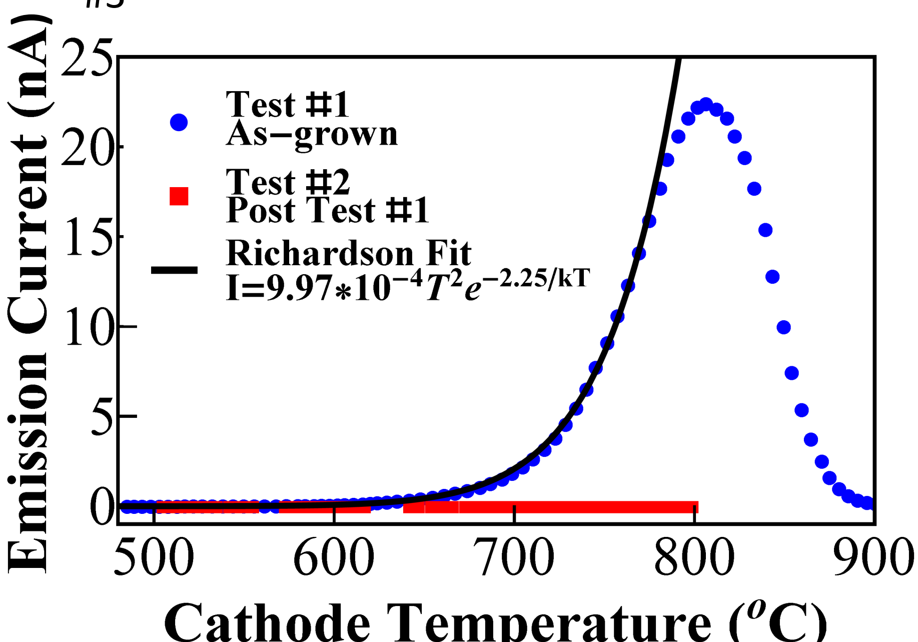
Roll over behavior of nitrogen-incorporated diamond films[2]

[1]M. Suzuki, T. Ono, N. Sakuma, T. Sakai. "Low-temperature thermionic emission from nitrogen-doped nanocrystalline diamond films on n-type Si grown by MPCVD" 2009

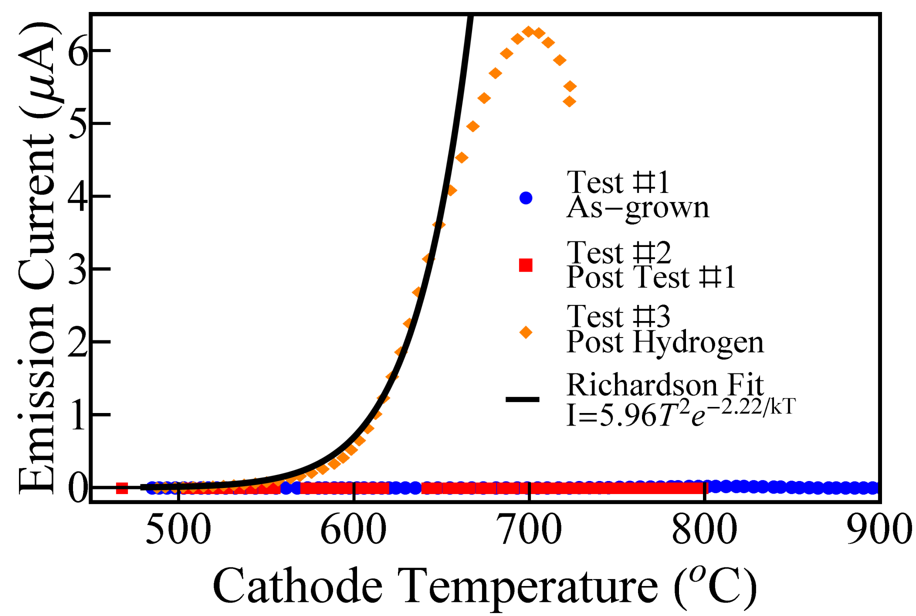
[2]M. Kataoka, C. Zhu, F. Koeck, R. Nemanich, "Thermionic Electron Emission from nitrogen-doped homoepitaxial diamond" 2009

Deeper Look into Hydrogen Influence on Thermionic Emission

- The emission current for Test #1 and Test #3, were observed to follow the Richardson equation before the "roll off" temperature
- The sample after exposure to hydrogen plasma achieved much higher emission current values than the as-grown sample but experienced the "roll off" at a lower temperature
- The fit of the Richardson equation to Test #1 and Test #3 demonstrated that there was little change in the sample's work function, but the Richardson constant was ***4 orders of magnitude*** higher for Test #3



Thermionic emission current vs. cathode temperature for the as-grown sample



Comparison of thermionic emission current vs. cathode temperature for the as-grown sample and the hydrogenated sample

Analyses of hydrogen's effect on thermionic emission

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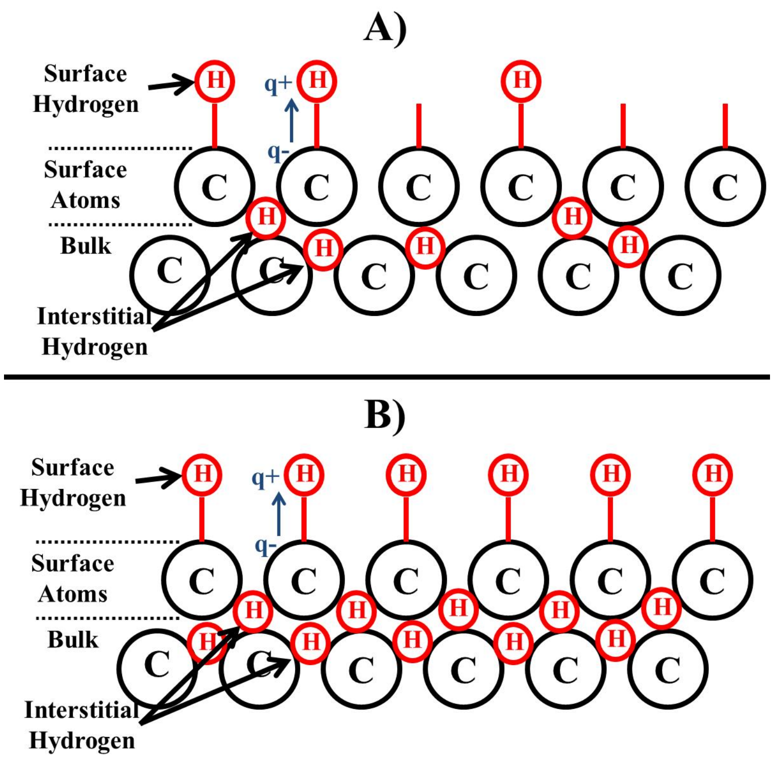
Two possible explanations for improvement in electron emission due to hydrogen plasma exposure

1. **Cui *et al* found that hydrogen termination on the diamond surface reduces the electron affinity[1]**
   - The small change in Φ indicates emission primarily arose from sites with hydrogen bonds
   - Hydrogenation then must increase the hydrogen surface concentration thus providing more emission sites
2. **Studies have also shown that hydrogen can reduce the bulk resistivity**
   - Hydrogenation passivates both grain boundaries as well as deep traps present in the bulk[2]
   - Subsequent decreases in resistivity equate to enhanced electron transport to the diamond surface



Visual depiction of the as-grown diamond sample A) compared with a hydrogenated sample B)

[1]J. B. Cui, J. Ristein, M. Stammler, K. Janischowsky, G. Kleber, and L. Ley, "Hydrogen termination and electron emission from CVD diamond surfaces: a combined secondary electron emission, photoelectron emission microscopy, photoelectron yield, and field emission study," *Diamond and Related Materials,* vol. 9, pp. 1143-1147, 2000.
[2]S. Albin and L. Watkins, "Current-voltage characteristics of thin film and bulk diamond treated in hydrogen plasma," *Electron Device Letters, IEEE,* vol. 11, pp. 159-161, 1990.

Isothermal Desorption of Hydrogen from Diamond

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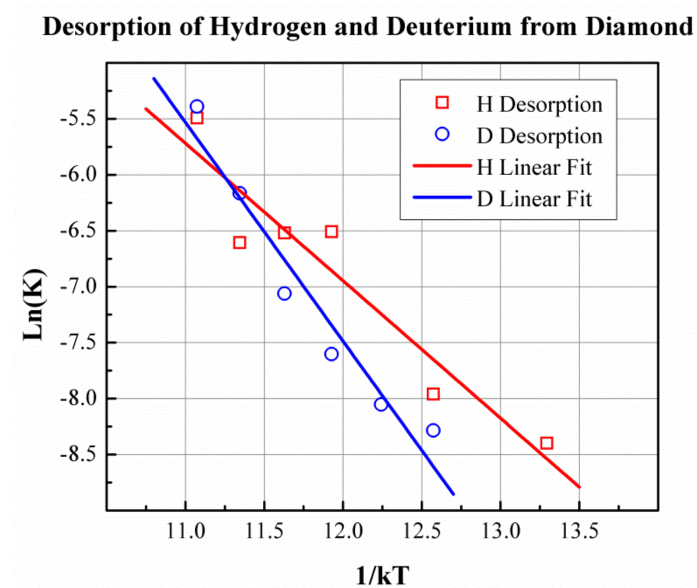
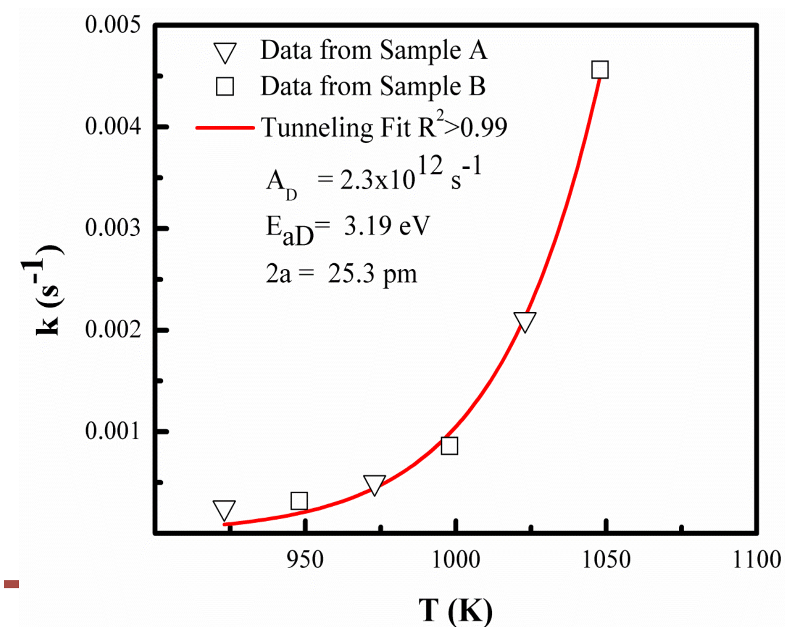
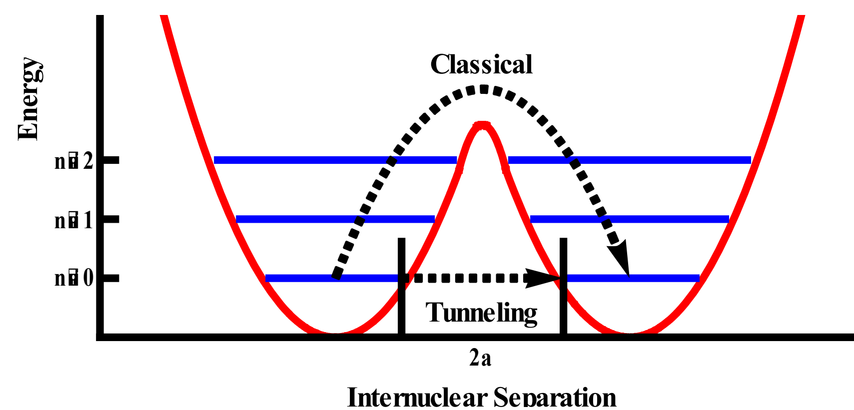
- The desorption of hydrogen (deuterium) was examined from diamond by monitoring the isothermal thermionic emission current
- Isothermal current decreased for both hydrogen and deuterium at a rate that increased with temperature
- Arrhenius plot did not exhibit a linear trend as to be expected, suggesting tunneling



Arrhenius plot of the desorption data



Fit of the k values at each temperature taking into account tunneling



Generic parabolic potential diagram comparing the classical to the tunneling desorption mechanism.

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Diamond-based TEC in Gaseous Environments

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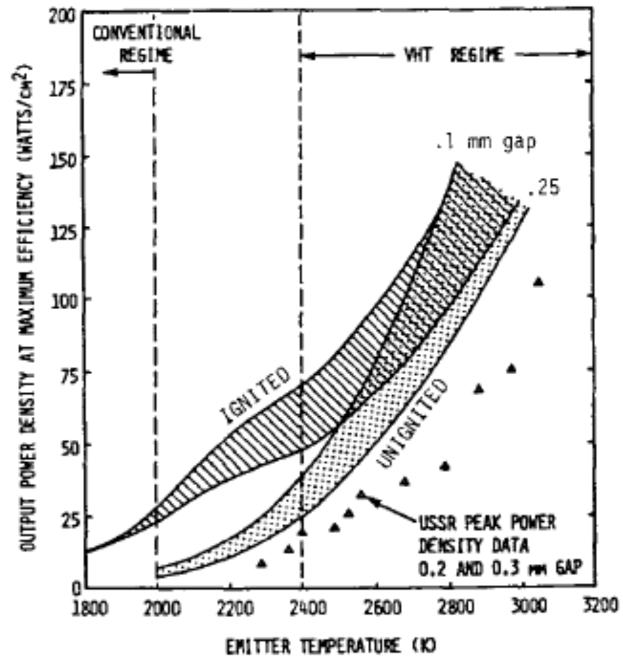
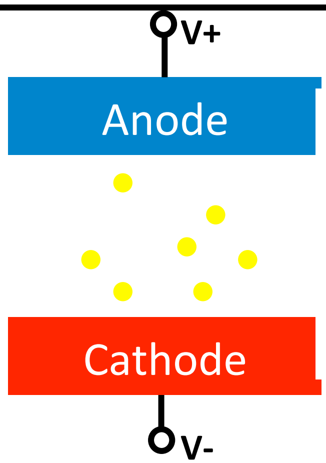
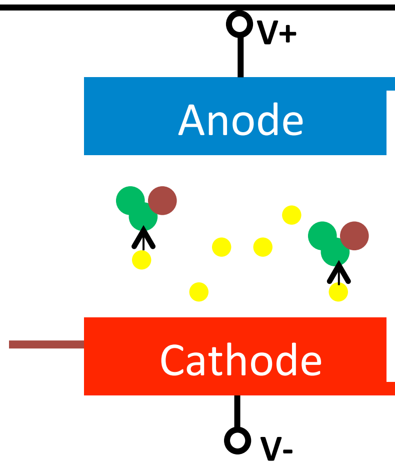
- Previous thermionic energy converters used cathodes with high work functions (e.g., tungsten)
- Cesium was used to improve the performance of these cathodes
    1. Lowered the work function of the cathode surface
    2. Mitigated space charge effects arising between the cathode and anode
- Hydrogen-containing gaseous species could accomplish this same effect



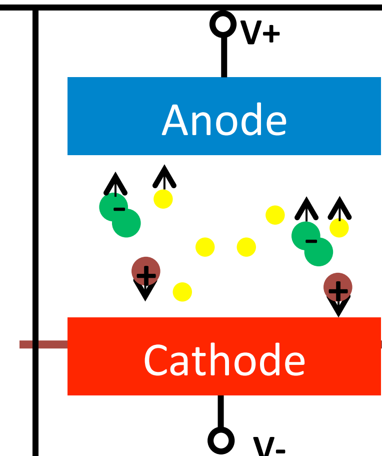
N. S. Rasor, "Thermionic energy conversion plasmas," *Plasma Science, IEEE Transactions on*, vol. 19, pp. 1191-1208, 1991.



Electrons in the vacuum gap create space charge



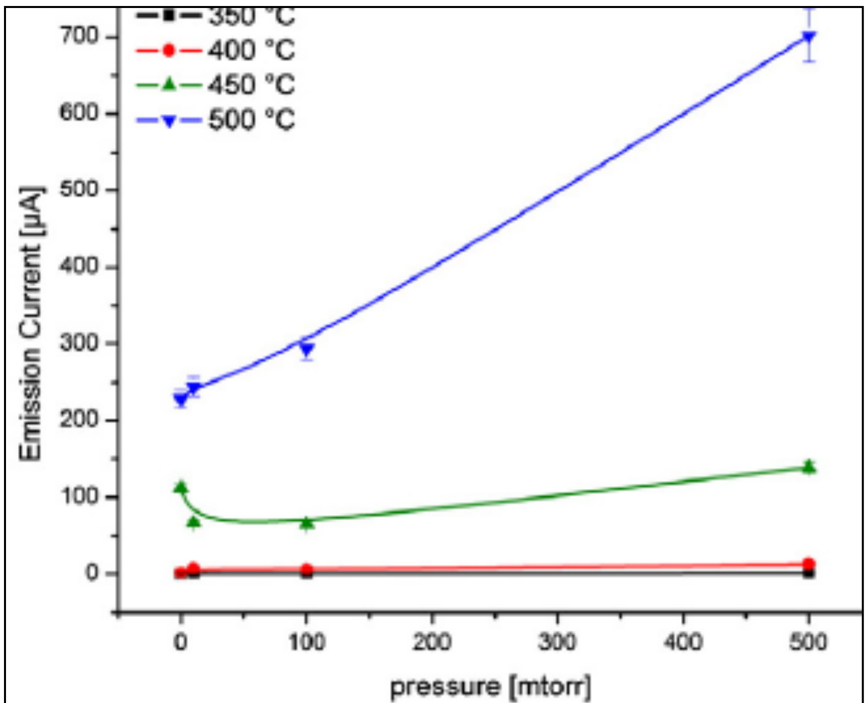
This can be mitigated by feeding gaseous species into the gap



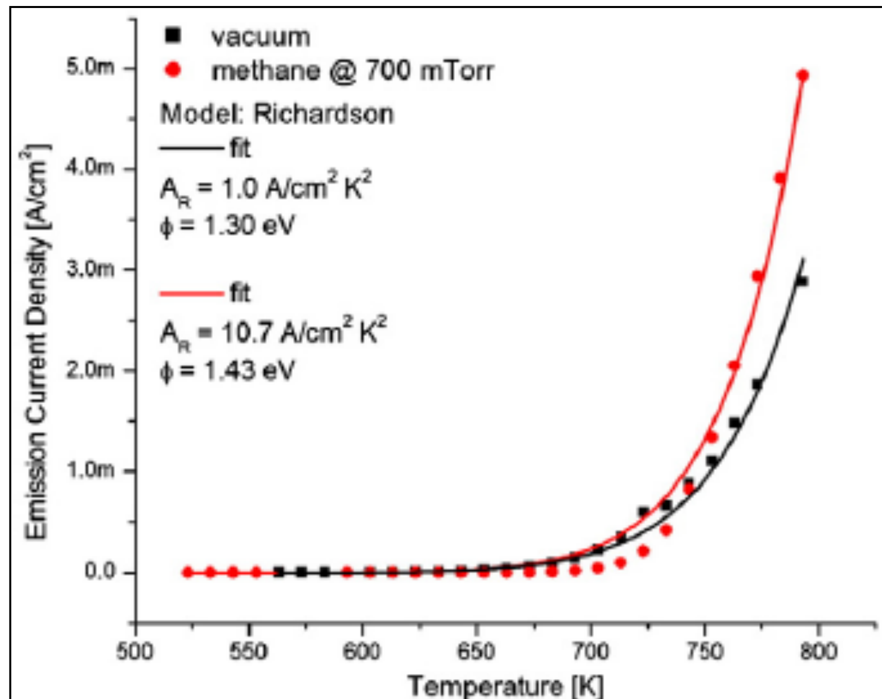
- **Electrons cause gas to ionize.**
- **Positive ions go to cathode**
- **Negative ions and electrons go to cathode**

Methane to Enhance TEC Performance

- Methane can improve the performance of a diamond thermionic energy converter
- With a slightly positive EA of 0.083eV, methane can produce stable negative ion states that significantly affect the thermionic emission from diamond



Thermionic emission data from phosphorus doped diamond films as a function of methane pressure



Thermionic electron emission from nitrogen doped diamond in vacuum and under methane ambience and the corresponding fit to the Richardson equation.

[1]F. A. M. Koeck et al, "Enhanced thermionic energy conversion and thermionic emission from doped diamond films through methane exposure," *Diam. Relat.Mater*, vol. 20, pp. 1229-1233, 2011.

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Difficulties in Utilizing Methane

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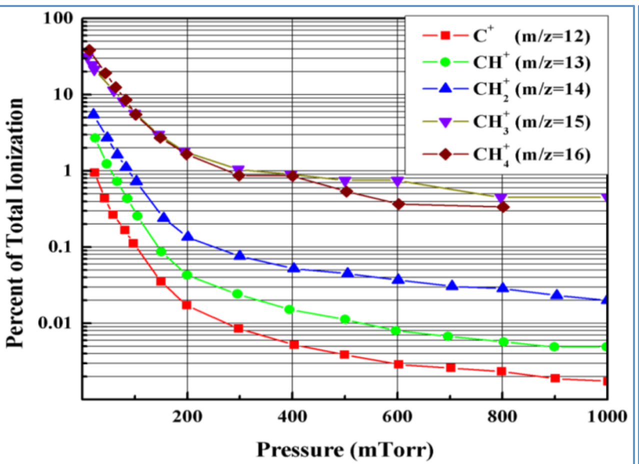
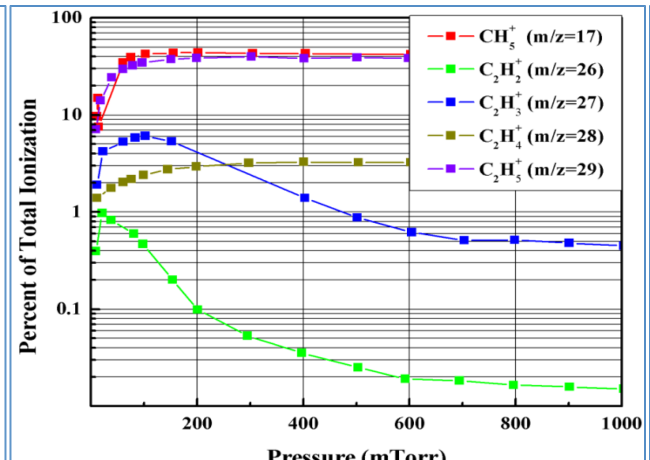
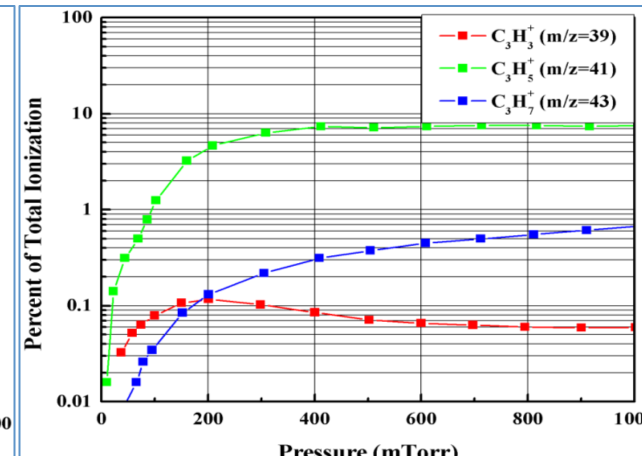
- **CH_4 would appear to be an ideal gas to enhance thermionic emission**
  i. Low, positive electron affinity of 0.083eV[1]
  ii. Forms a TNI that undergoes dissociative electron attachment[1]
  iii. Used in the deposition of diamond
- These effects are likely not sustainable due to the complex carbon radicals formed[3]
- The lower pressures tested in the present research study do not form complex carbon molecules, but the effect is very small compared to molecular hydrogen[3]



Plot of the percent of total ionization of the primary methane dissociation products as a function of pressure



Plot of the percent of total ionization of the secondary methane dissociation products as a function of pressure



Plot of the percent of total ionization of the tertiary methane dissociation products as a function of pressure

[1]M. Born, S. Ingemann, and N. M. M. Nibbering, "Formation and chemistry of radical anions in the gas phase," *Mass Spect. Revs.,* vol. 16, pp. 181-200, 1997.
[2]F. A. M. Koeck, *et al*, "Enhanced thermionic energy conversion and thermionic emission from doped diamond films through methane exposure," *Diam. Relat. Mater.* vol. 20
[3]G. Drabner, *et al*, "The composition of the CH4 plasma," *International Journal of Mass Spectrometry and Ion Processes,* vol. 97, pp. 1-33, 1990.

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Electron Interactions with Molecules

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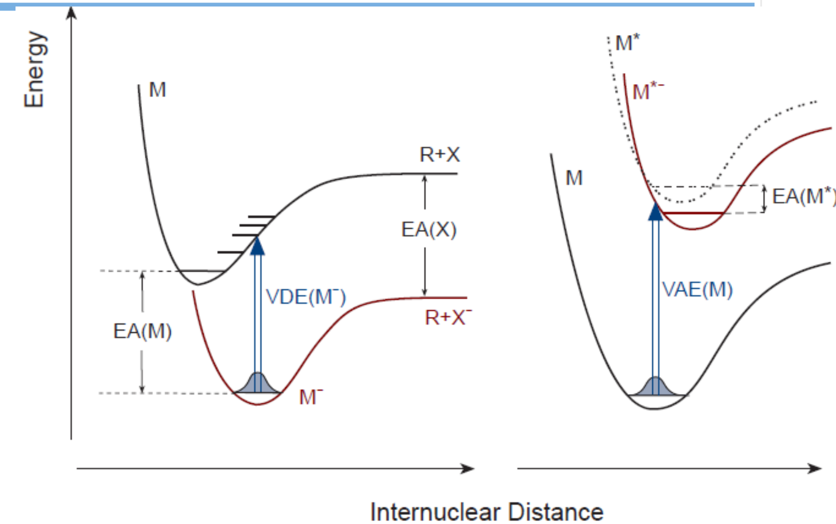

- Improved performance of TEC devices in gaseous environments will likely require molecules that interact with electron to form Transient Negative Ions (TNIs)[1]
- The ability of a molecule to form a TNI is determined by its electron affinity[1]
- The formation of a TNI can result in two possible outcomes:[1]

1. Autodetachment– Emission of an extra electron → $e^{-}(\varepsilon_1) + M \rightarrow M + e(\varepsilon_2 \approx \varepsilon_1)$
   a) Elastic resonant scattering
   b) Inelastic resonant scattering $e^{-}(\varepsilon_1) + M \rightarrow M^{*} + e(\varepsilon_2 < \varepsilon_1)$
2. Dissociative electron attachment– Decomposition into stable charged and neutral fragments → $e^{-} + M \rightarrow M^{*} \rightarrow R + X$

   Likely case for ammonia[2]

   Hypothesize a two step process that ionizes resulting hydrogen to create positive H at cathode to reduce space charge

$$e^{-} + NH_3 \rightarrow NH_3^{-} \rightarrow NH_2 + H^{-}$$
$$\rightarrow NH_2^{-} + H$$
$$\rightarrow NH + H + H^{-}$$
$$\rightarrow NH^{-} + H + H$$

1. E. V. Anslyn and D. A. Dougherty, *Modern Physical Organic Chemistry*: University Science Books, 2006
2. N. B. Ram and E. Krishnakumar, The Journal of Chemical Physics **136** (16), - (2012).

Photon-Enhanced TEC from Diamond

- **Has already been explained perfectly. I look forward to reading more interesting results.**

The end

- **Questions?**

Electron Emission Studies at Vanderbilt

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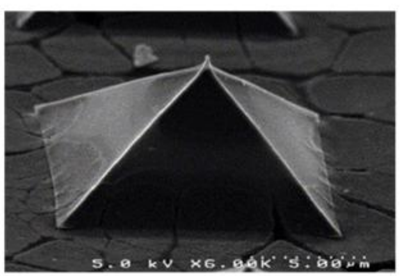
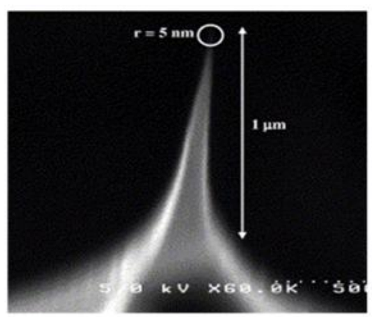
- Current studies in the Vanderbilt University Diamond Lab are examining the electron emission of diamond structures through Fowler-Nordheim Tunneling
- By fabricating structures with sharp tips the total effective field required for electrons to tunnel to the vacuum level is decreased
- Current applications explored for these devices are high frequency vacuum diodes and triodes with transistor-like behavior



A)



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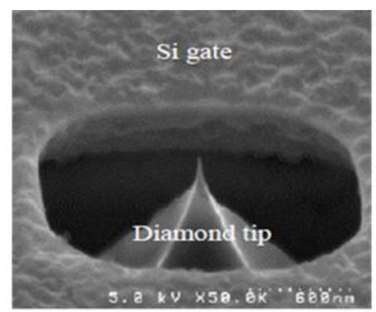
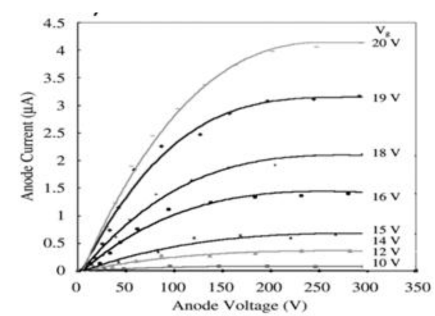


C)



D)

A) Micropatterned pyramid for use as an electron emitter.

. **B)** Sharp tips at the top of the field emitter to promote Fowler-Nordeheim Tunneling at low Electric Fields.

C) Micropatterned pyramidal electron emitter fabricated with a silicon gate electrode used to extract electrons. .

D) Transistor like behavior of pyramidal electron emitters with a gate electrode.