

Aspects of Negative Ions in Microwave PECVD Plasmas for Diamond Thin Film Deposition

MICHAEL P. BRADLEY

PROFESSOR, PHYSICS & ENGINEERING PHYSICS & DEAN, COLLEGE OF ENGINEERING

UNIVERSITY OF SASKATCHEWAN



UNIVERSITY OF
SASKATCHEWAN

Diamonds!



Koh-i-noor
(Persian: light of the mountain)

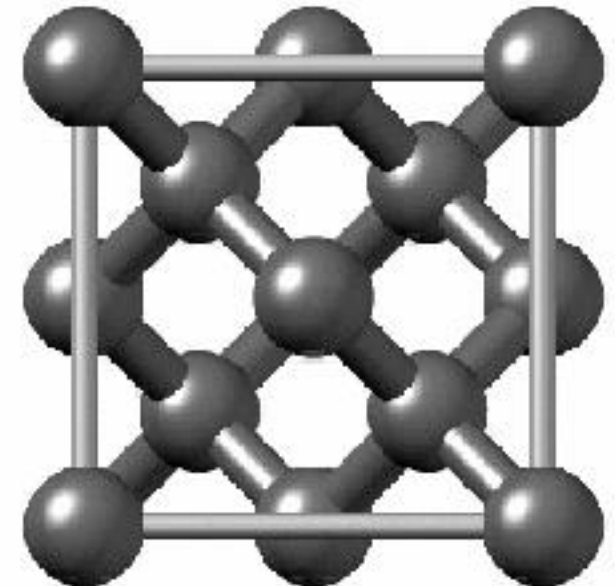
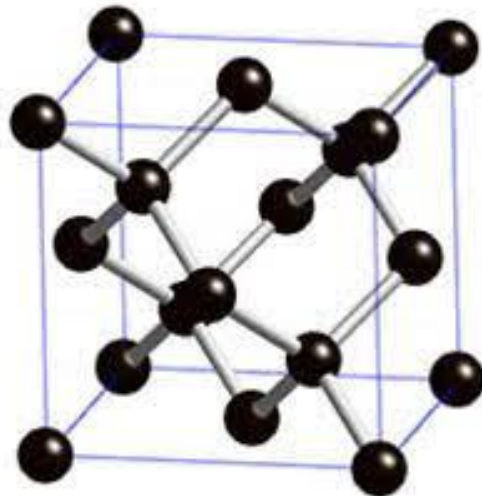


Gemstone diamonds

Diamonds have fascinated humanity since ancient times. In addition to their great natural beauty as gemstones, diamonds were the hardest known natural material.

Diamond to the physicist

- ▶ Diamond to the physicist is a little more prosaic: it is carbon bonded in a tetrahedral configuration
- ▶ The group-IV crystalline semiconductors silicon and germanium have this same lattice structure
- ▶ → usually just called the diamond lattice



Defects in Diamonds

Impurities (Dopants)
give rise to coloured
Diamonds, e.g.

- ▶ Boron → Blue
- ▶ Nitrogen → Yellow



<https://www.capetowndiamondmuseum.org/blog/2019/05/5666/>

Diamond Growth

Naturally occurring diamonds are formed in the mantle of the Earth, under conditions of high temperature and pressure

In the laboratory, diamond films can be grown using microwave plasma chemical vapour deposition (MPCVD) using a feedstock of methane gas with excess H_2

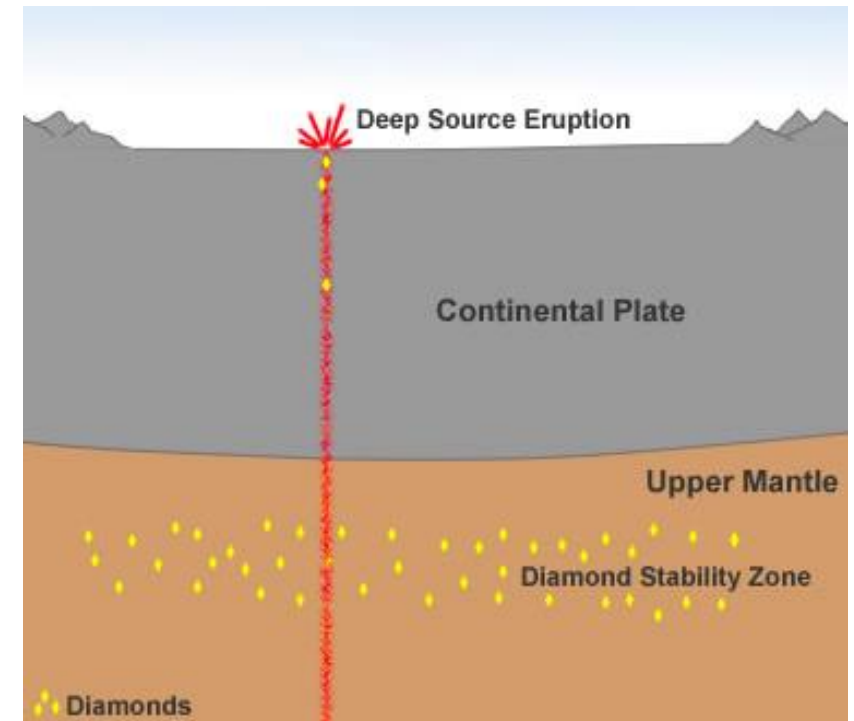


Figure credit: geology.com

Plasmas & Connection to Catalysis

In the laboratory, diamond films can be grown using microwave plasma chemical vapour deposition (MPCVD) using a feedstock of methane gas with excess H_2

Analogy to catalysis- energetic plasma electrons enable reactions



Plasma Parameters

- ▶ There are two basic plasma parameters:

Plasma density: n_0

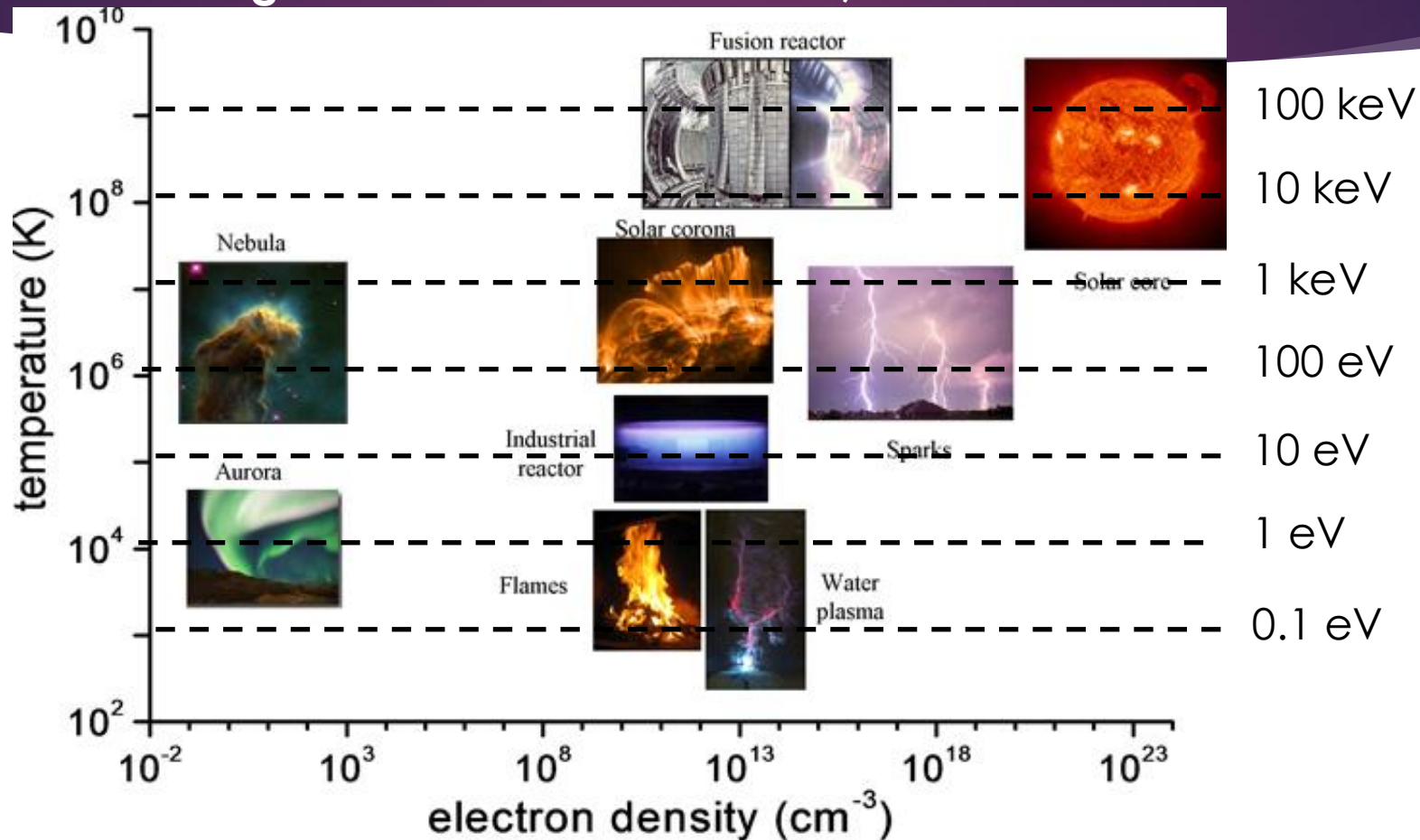
&

Plasma Temperature: T

- ▶ These parameters determine the plasma behaviour-
they cover an **extremely wide** dynamic range

Plasma Density & Temperature: a Very Wide Dynamic Range

Logarithmic scale. 1 eV $\leftrightarrow$ 11,608 K



Plasma
Temperature
Scale:

1 eV $\rightarrow$ 11000 K

Cold Plasmas- Not in Equilibrium

- ▶ A plasma in equilibrium would have a common temperature T for all species (e.g. electrons and ions)

$$T_i \approx T_e = T_{plasma}$$

In practice, many laboratory cold plasmas for materials processing are non-equilibrium plasmas, with

$$T_e \gg T_i$$

Cold Plasmas- Connection to Catalysis

$$T_{\text{gas}} \sim 350 \text{ K}$$

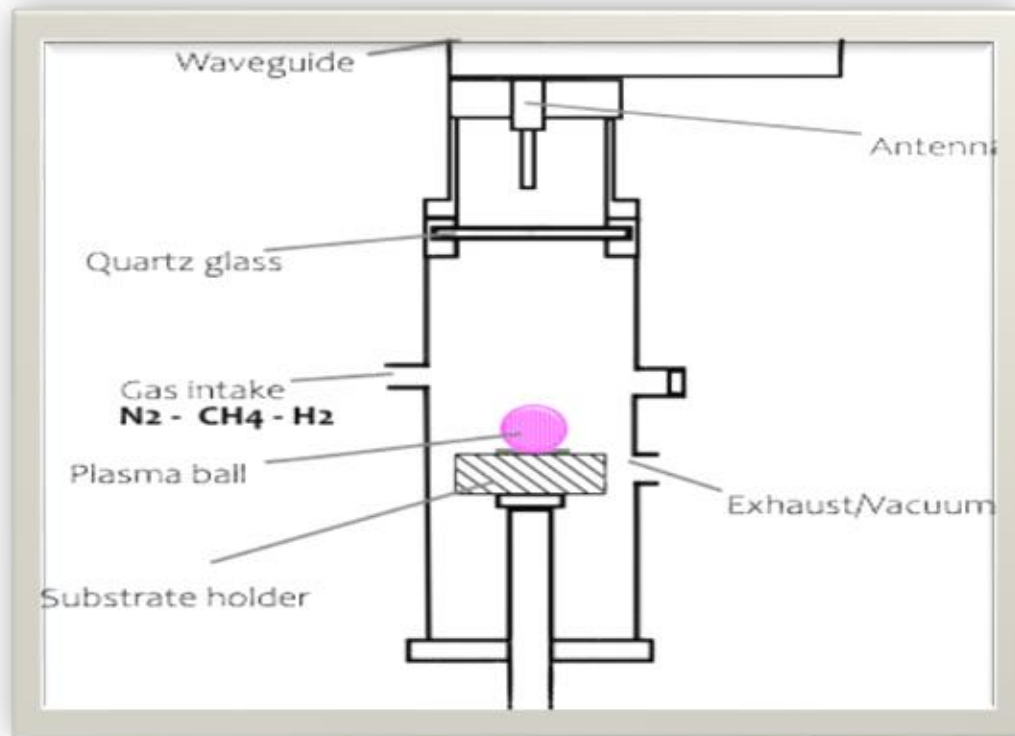
$$T_i \sim 600 \text{ K}$$

$$k_B T_e / e \sim 2\text{-}5 \text{ eV} \rightarrow T_e \sim 20000 - 50000 \text{ K (!)}$$

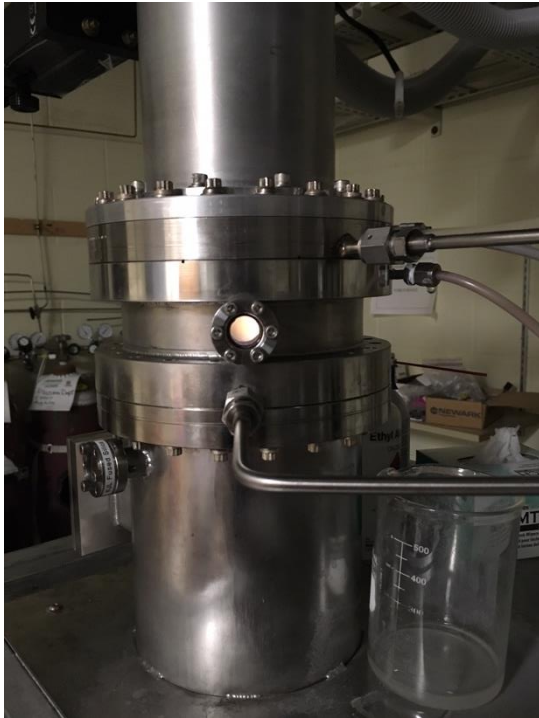
Analogy to catalysis- energetic plasma electrons enable reactions



MPECVD System Schematic



Microwave Plasma-Enhanced CVD for diamond film growth



Microwave Plasma Chamber

Frequency 2.45 GHz

Power: 500 - 800 Watt

Pressure: 23 - 100 Torr

Substrate Temperatures >500 C

**Feed gas ratio ~ 99% H₂/1% CH₄
(excess hydrogen)**

Film growth rate:

~ 0.1 – 1 μm /hour

Applications

- ▶ **Hard Coatings**
- ▶ **Semiconductor Chip Applications**
 - ▶ Thermal conductivity of diamond $\sim 2400 \text{ W/m.K}$ (!)
 - ▶ $\sim 6\text{x}$ copper
- ▶ **N-doped Diamond Films: Diamond NV- Centres**

Growth of in-situ N-doped diamond films

Grown on p-doped (111) silicon

MPECVD Conditions:

30 Torr

800 Watt

Feed gas flow rates:

CH₄ 1 sccm

H₂ 100 sccm

During doping:

N₂ 10 sccm



Sample Name	Time without doping(Hours)	N ₂ doping time(Hours)
J1	13	1
J2	13	1
K1	12	2
K2	12	2
L1	11	3
L2	11	3
M1	10	4
M2	10	4
N1	11	3
N2	11	3
O1	9	5
O2	9	5

Growth of in-situ N-doped diamond films

Grown on p-doped (111) silicon

MPECVD Conditions:

30 Torr

800 Watt

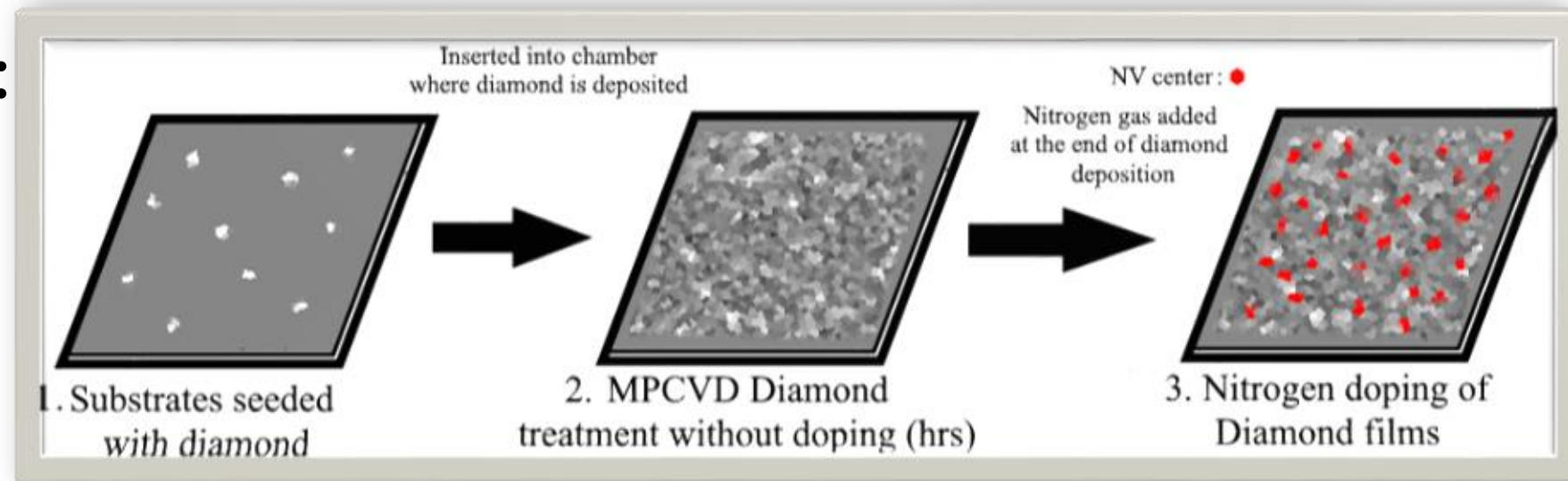
Feed gas flow rates:

CH_4 1 sccm

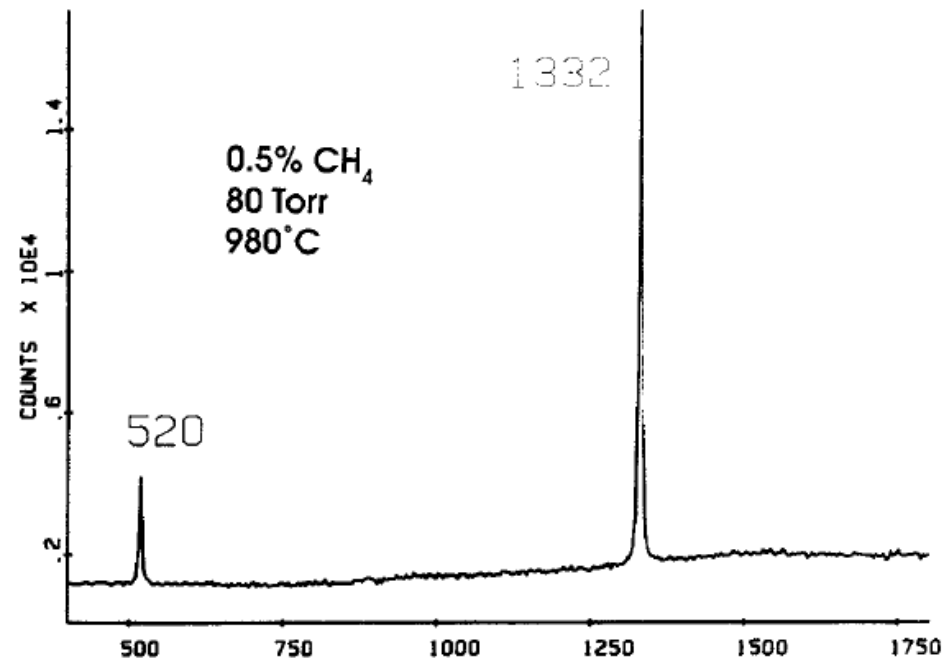
H_2 100 sccm

During doping:

N_2 10 sccm



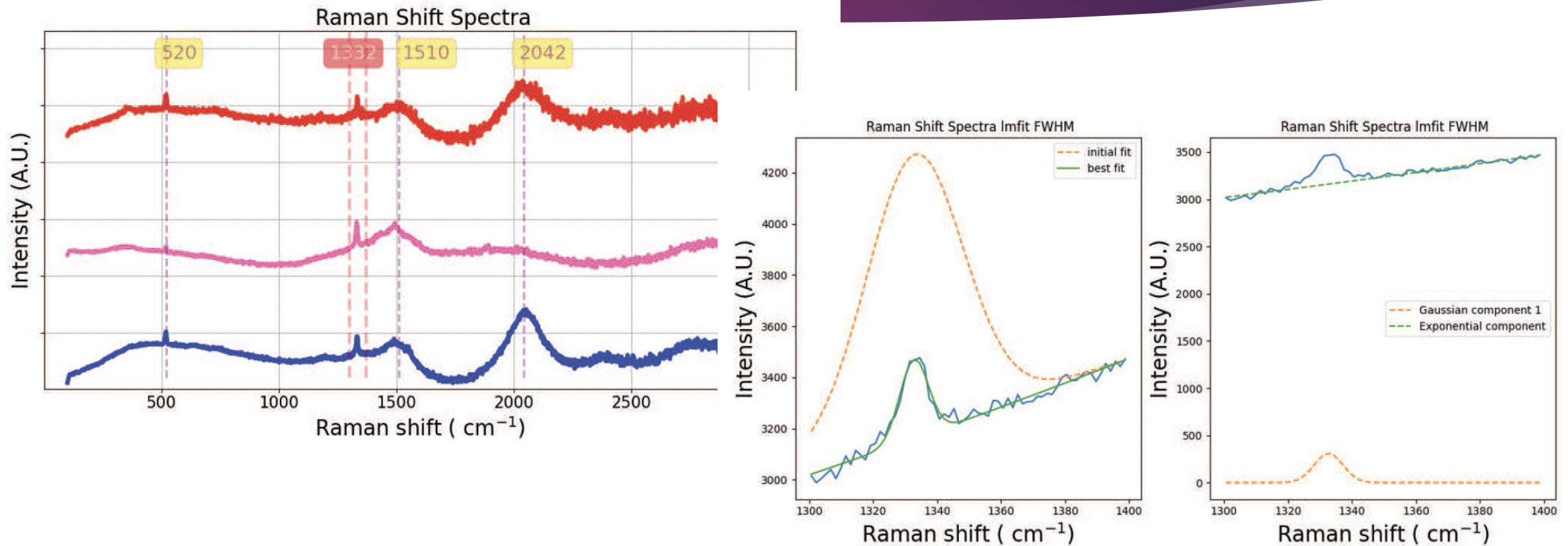
Signatures of Diamond: Raman line at 1332 cm^{-1}



D.S. Knight and W.B. White, J. Mater. Res., Vol. 4, No. 2, Mar/Apr 1989

Signatures of Diamond: Raman line at 1332 cm^{-1}

16



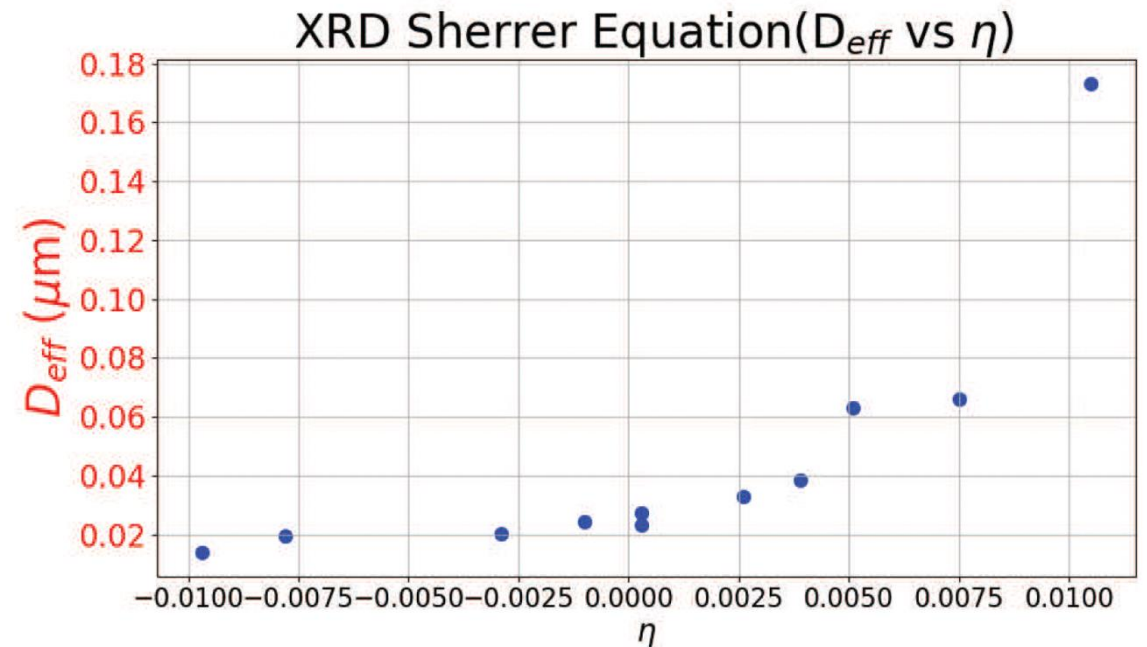
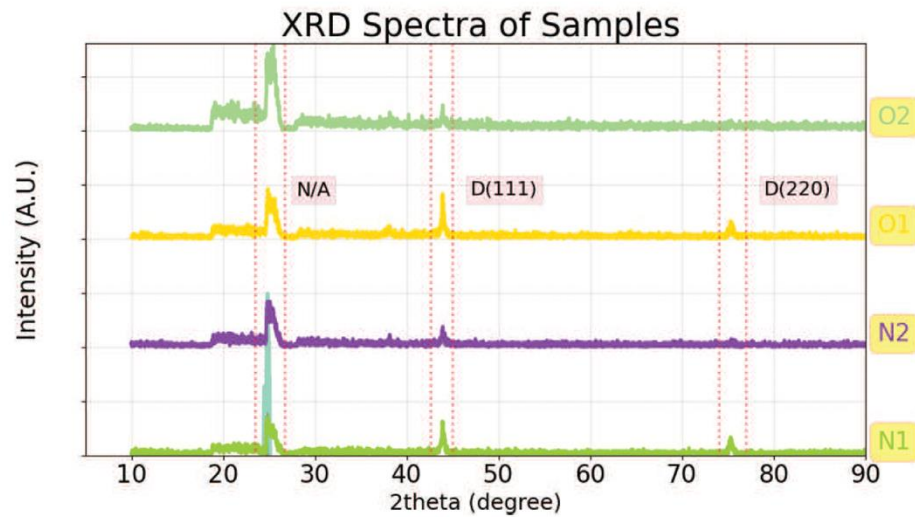
IEEE TRANSACTIONS ON PLASMA SCIENCE, VOL. 53, NO. 10, OCTOBER 2025

Signatures of Diamond: Raman line at 1332 cm^{-1}

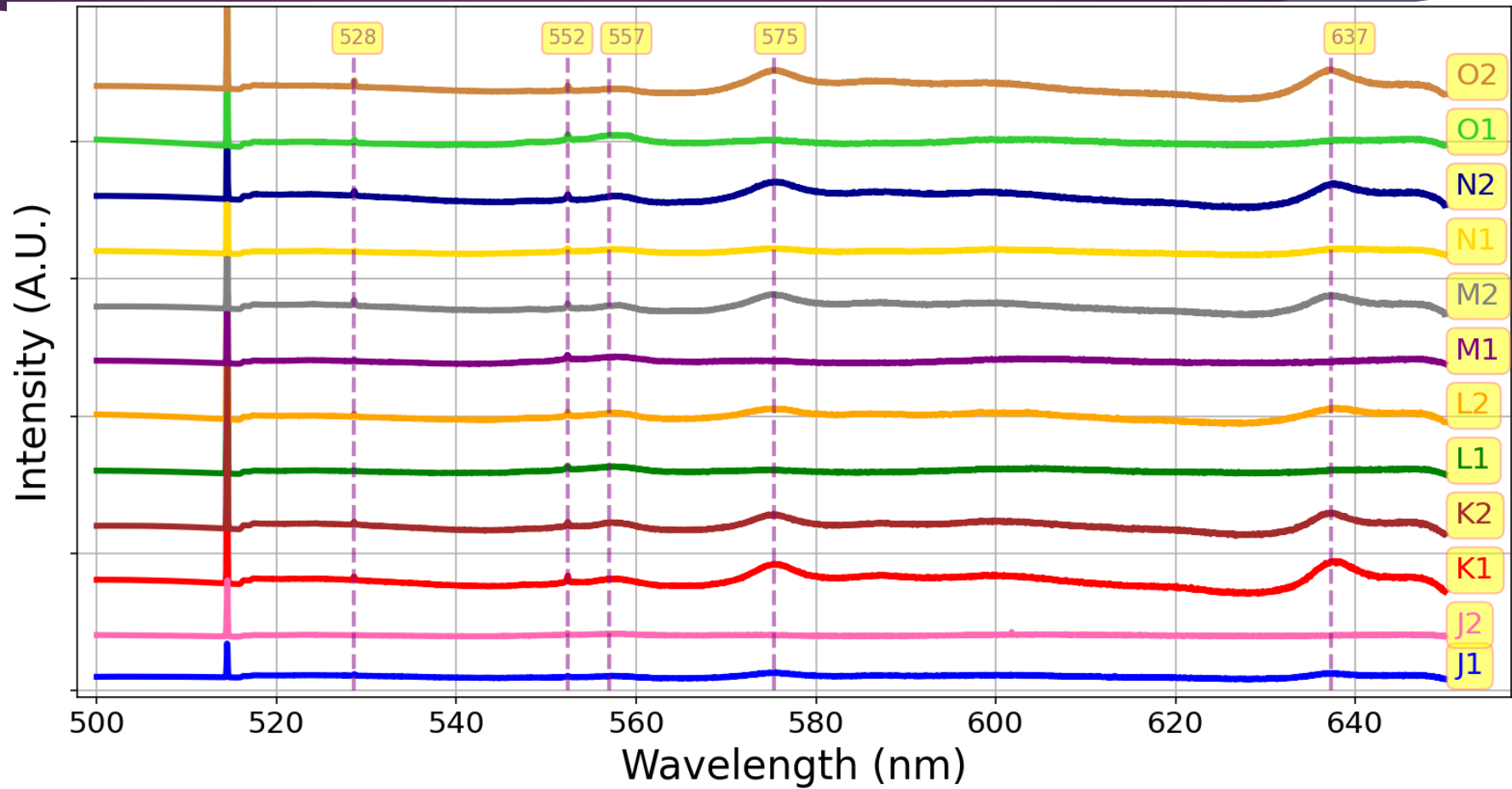
Sample Name	FWHM(cm^{-1})	Center of Diamond Peak(cm^{-1})
J1	7.9	1332.7
J2	8.4910	1331.5542
K1	7.2478	1333.8289
K2	6.9308	1333.5591
L1	8.1483	1332.5262
L2	8.0594	1332.5918
M1	8.4072	1332.7276
M2	6.7966	1333.0020
N1	9.0607	1333.2091
N2	7.7347	1333.7214
O1	8.3247	1333.2240
O2	7.8048	1333.9806

XRD

$$\underbrace{\beta}_{\text{Total Peak Width}} = \underbrace{\frac{k\lambda}{D_{\text{eff}} \cos\theta}}_{\beta \text{ Size}} + \underbrace{\eta \tan\theta}_{\beta \text{ Strain}}$$



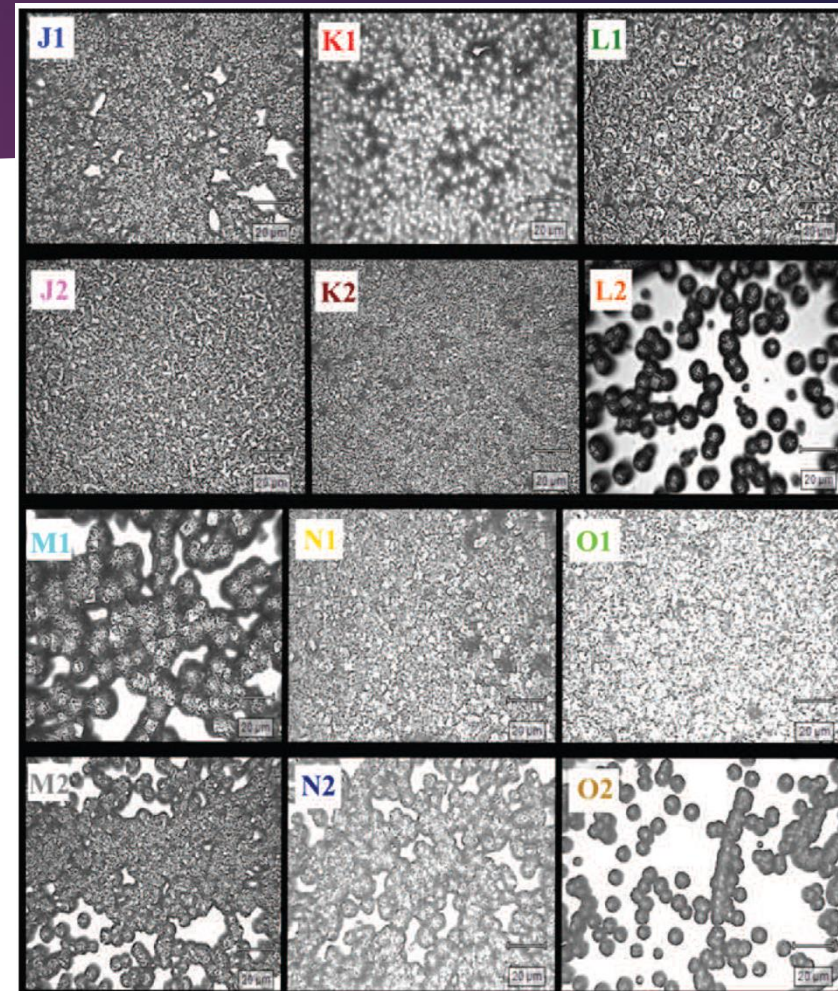
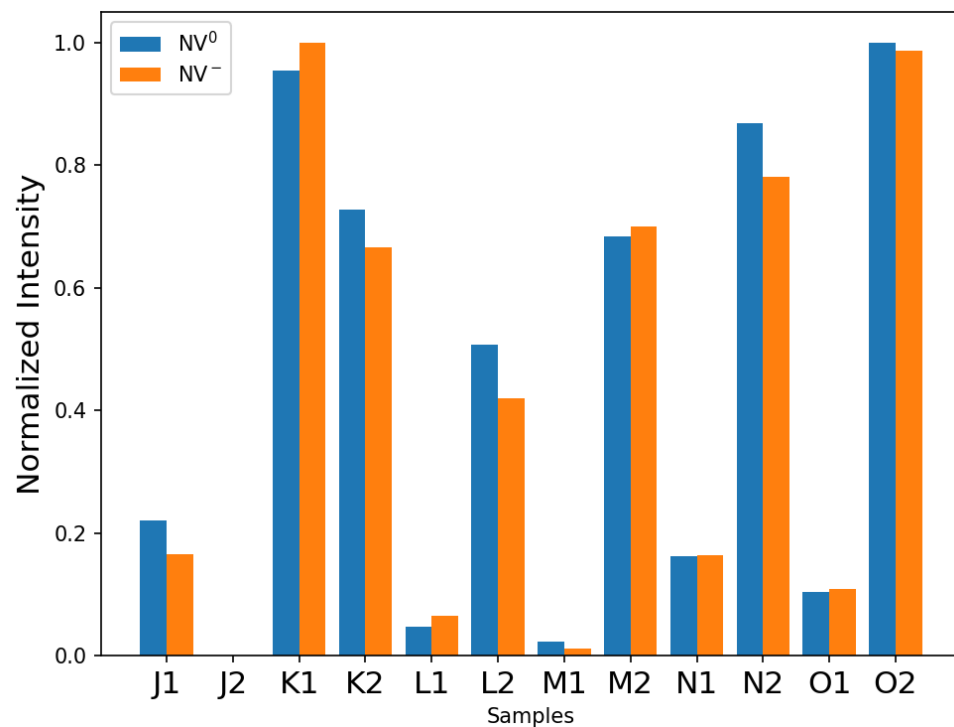
Photoluminescence Results



NV- Photoluminescence (PL)

Sample Name	FWHM(nm)	Center of NV ⁻ (nm)	Notes
J1	5.6805	637.17	Peak
J2	15.35	641.29	No Peak
K1	5.32	637.54	Peak
K2	5.056	637.15	Peak
L1	4.65	638.012	Peak
L2	6.77	637.43	Peak
M1	28.28	638.16	No Peak
M2	6.026	637.26	Peak
N1	6.57	638.043	No Peak
N2	5.89	637.53	Peak
O1	5.85	637.8	Peak
O2	6.197	637.1	Peak

PL Intensity and Film Structure



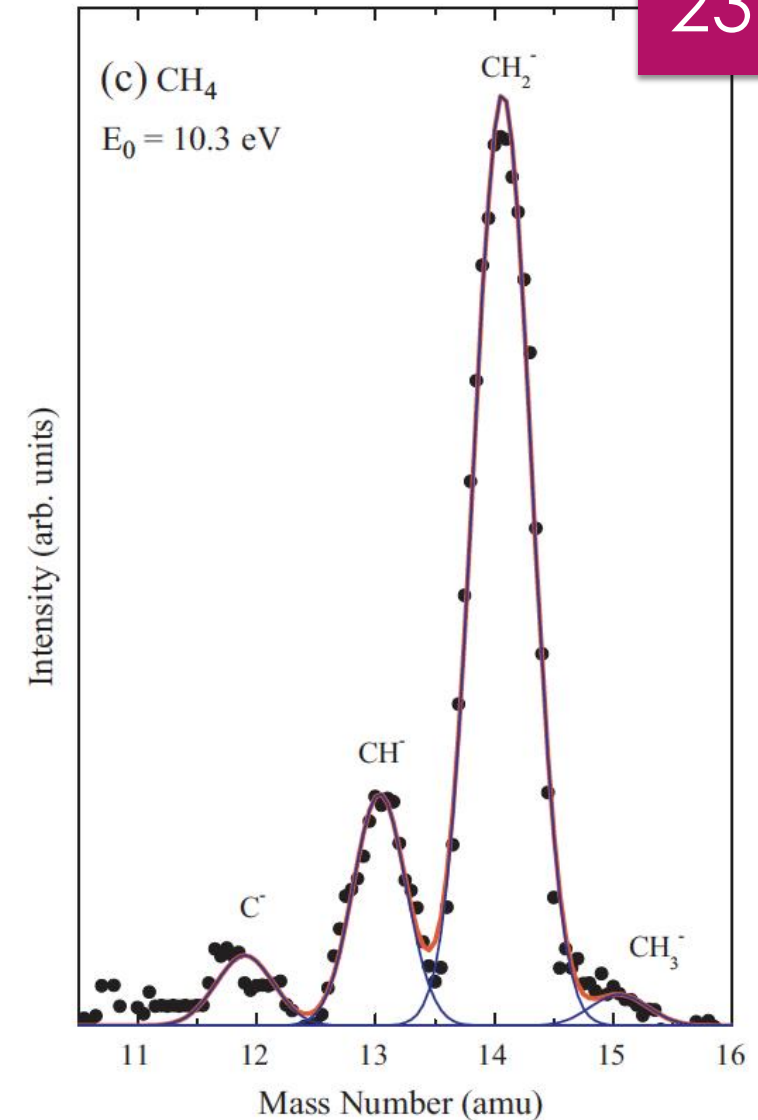
Less tightly packed films → higher PL intensity

Negative Ions in Processing Plasmas

- ▶ Negative ions can form in materials processing plasmas:
- ▶ Kono et al. measured negative ions in SF_6 , NF_3 , CF_4 , and C_4F_8 gases diluted with Ar
- ▶ Used a laser photodetachment method combined with millimeter-wave resonance
- ▶ At a molecular-gas mixing ratio as low as 5–10% and $n_e \sim 10^{11}$ the negative ion density was comparable to or higher than the electron density.
- ▶ Kono et al., Thin Solid Films **407** (2002) 198–203.

Negative Ions in Processing Plasmas: Methane Feedstock

- ▶ Hoshino et al. → Negative ion formation in CH_4 for electron energies from 6-11 eV
- ▶ Resonant dissociative electron attachment ~ 10.3 eV
- ▶ M. Hoshino et al. / International Journal of Mass Spectrometry 306 (2011) 51–56



Langmuir Probes for Negative Ion Measurements

- ▶ Expecting that negative ions may be present in our hydrogen-methane diamond deposition plasmas, how to measure their density ?
- ▶ Langmuir probe analysis ?
- ▶ Ordinary Langmuir probe analysis: measures n_+ , n_e , and T_e
- ▶ Negative ion Langmuir probe analysis attempts to measure an additional parameter n_- : the negative ion density [1],[2]
- ▶ Goal: measure the electronegativity parameter $\alpha_0 = \frac{n_-}{n_e}$
- ▶ [1] C. Poggi, et. al. “Measure of negative ion density in a large negative ion source using Langmuir probes”. 8th Symposium on Negative Ion Beams and Sources, JINST, 2022.
- ▶ [2] J. Bredin, P. Chabert and A. Aanesland, “Langmuir probe analysis in electronegative plasmas”, Phys. of Plasmas 21 (2014) 123502.

Langmuir Probe Equations [1], [2]

For $V < V_p$:

$$I_e(V) = \frac{1}{4} eA \frac{n_+}{1+\alpha} v_e \exp\left(\frac{e(V-V_p)}{T_e}\right)$$

$$I_+(V) = eA_{eff} n_+ u_B^+$$

$$I_-(V) = eA \frac{n_+}{1+\alpha} u_B^- \exp\left(\frac{e(V-V_p)}{T_-}\right)$$

where:

$$v_e = \sqrt{\frac{8k_B T_e}{\pi m_e}}$$

$$u_B^+ = \sqrt{\frac{k_B T_e}{m_+}} \sqrt{\frac{1+\alpha}{1+\gamma\alpha}}$$

$$u_B^- = \sqrt{\frac{k_B T_+}{m_-}}$$

[1] C. Poggi, et. al. "Measure of negative ion density in a large negative ion source using Langmuir probes". 8th Symposium on Negative Ion Beams and Sources, JINST, 2022.

[2] J. Bredin, P. Chabert and A. Aanesland, "Langmuir probe analysis in electronegative plasmas", Phys. of Plasmas 21(1) (2014) 123502.

Langmuir Probe Equations

For $V > V_p$:

$$I_e(V) = \frac{1}{4} eA \frac{n_+}{1+\alpha} v_e \left\{ 2 \sqrt{\frac{e(V-V_p)}{\pi T_e}} + \exp\left(\frac{e(V-V_p)}{T_e}\right) \left[1 - \operatorname{erf}\left(\sqrt{\frac{e(V-V_p)}{T_e}}\right) \right] \right\}$$

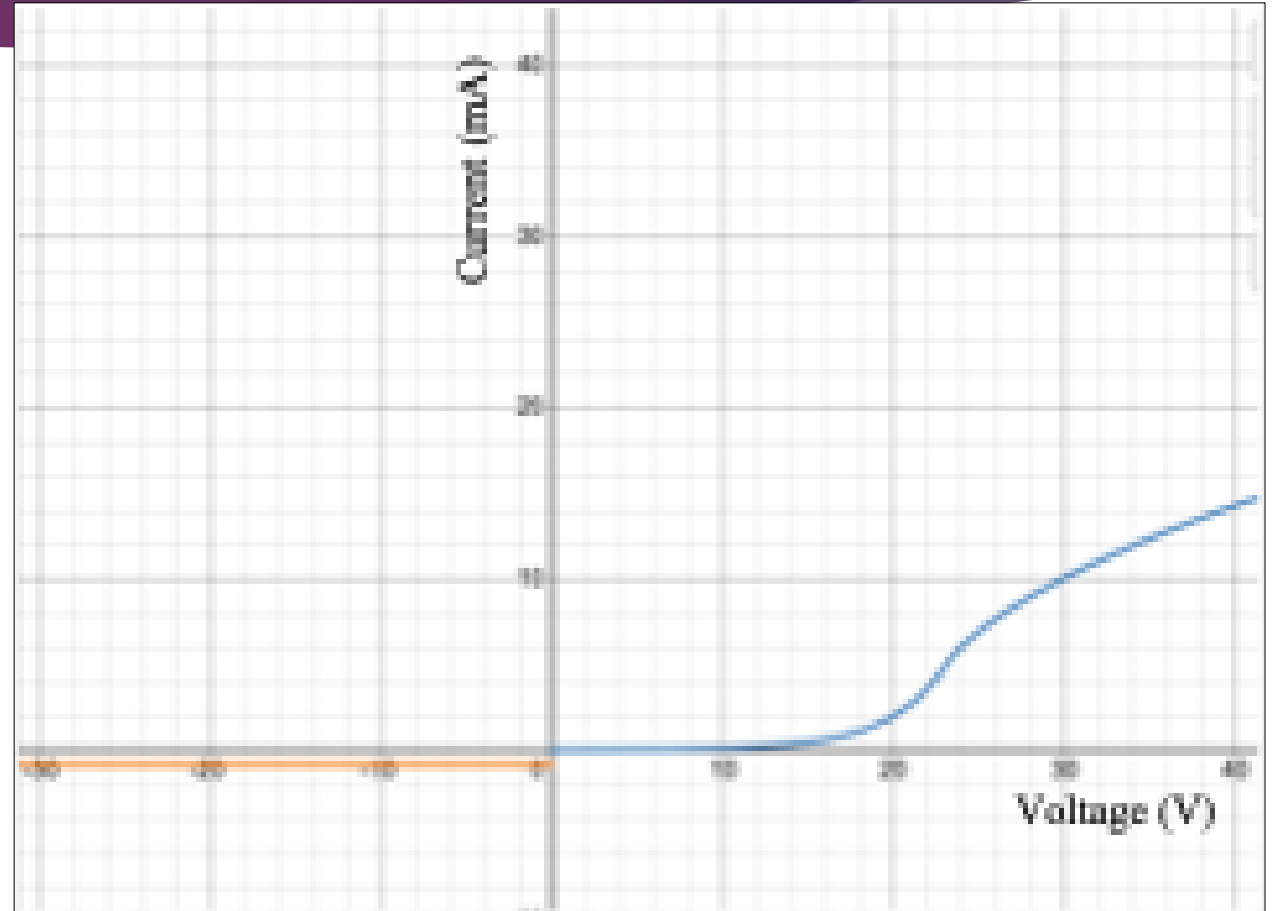
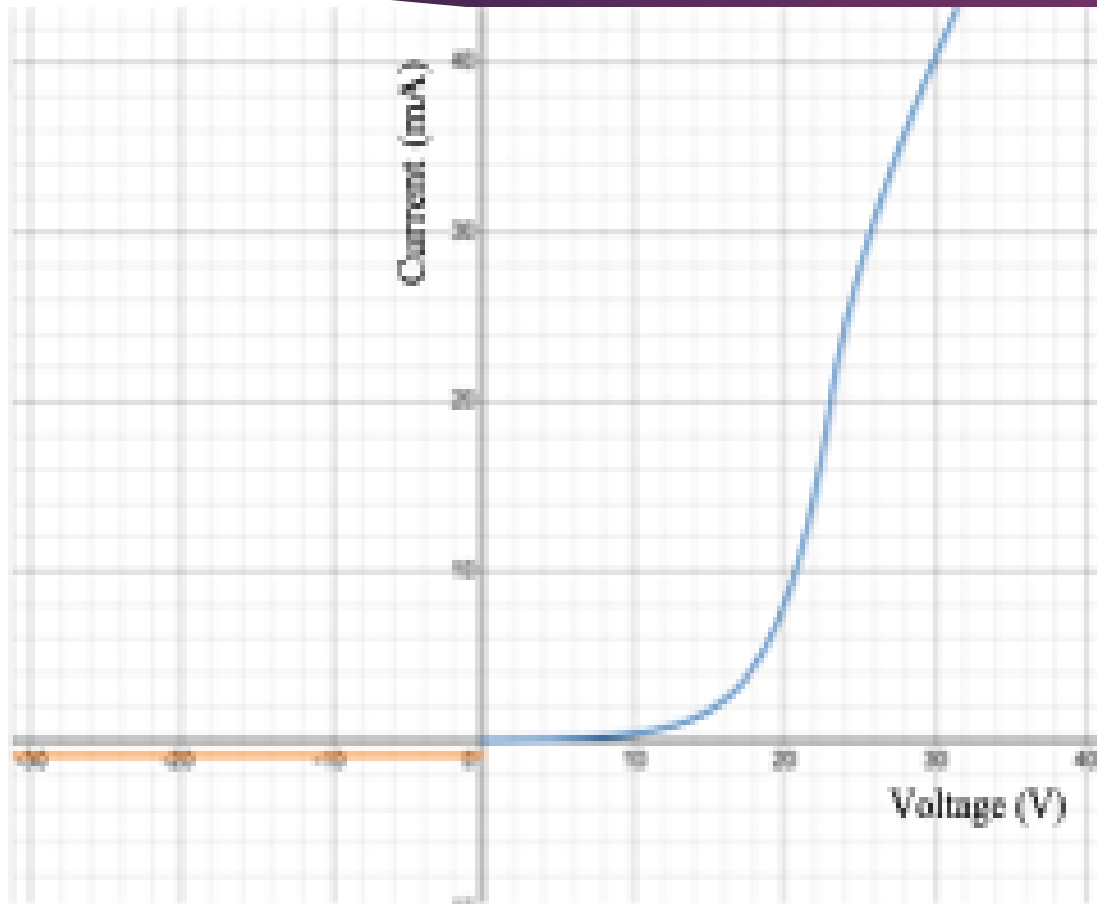
$$I_+(V) = eA_{eff} n_+ u_B^+ \exp\left(\frac{e(V-V_p)}{T_+}\right)$$

$$I_-(V) = eA n_+ u_B^- \frac{\alpha}{1+\alpha}$$

[1] C. Poggi, et. al. “Measure of negative ion density in a large negative ion source using Langmuir probes”. 8th Symposium on Negative Ion Beams and Sources, JINST, 2022.

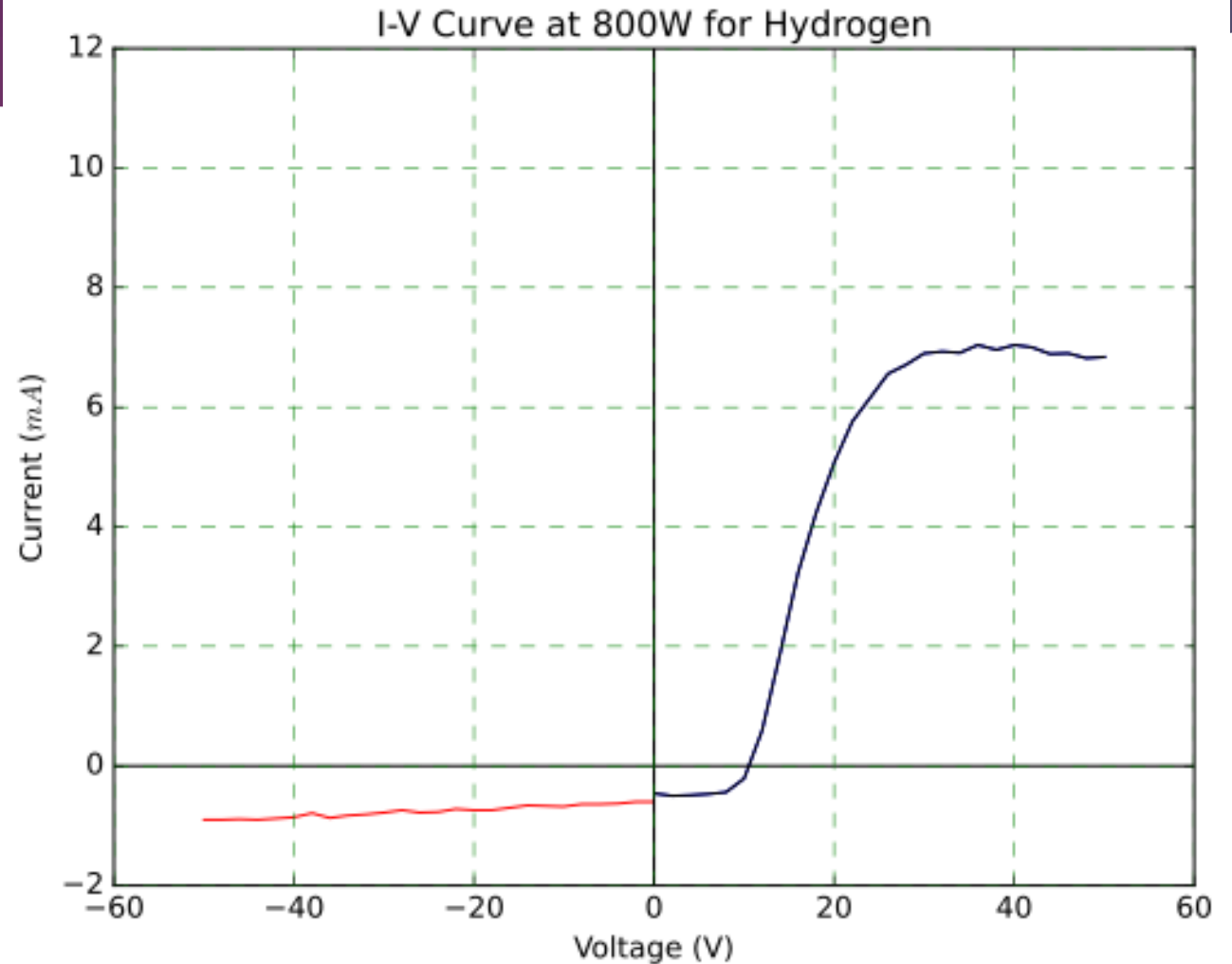
[2] J. Bredin, P. Chabert and A. Aanesland, “Langmuir probe analysis in electronegative plasmas”, Phys. of Plasmas 21(1) (2014) 123502.

Langmuir Probe Theoretical Curves ($\alpha=0$ and $\alpha=3$)



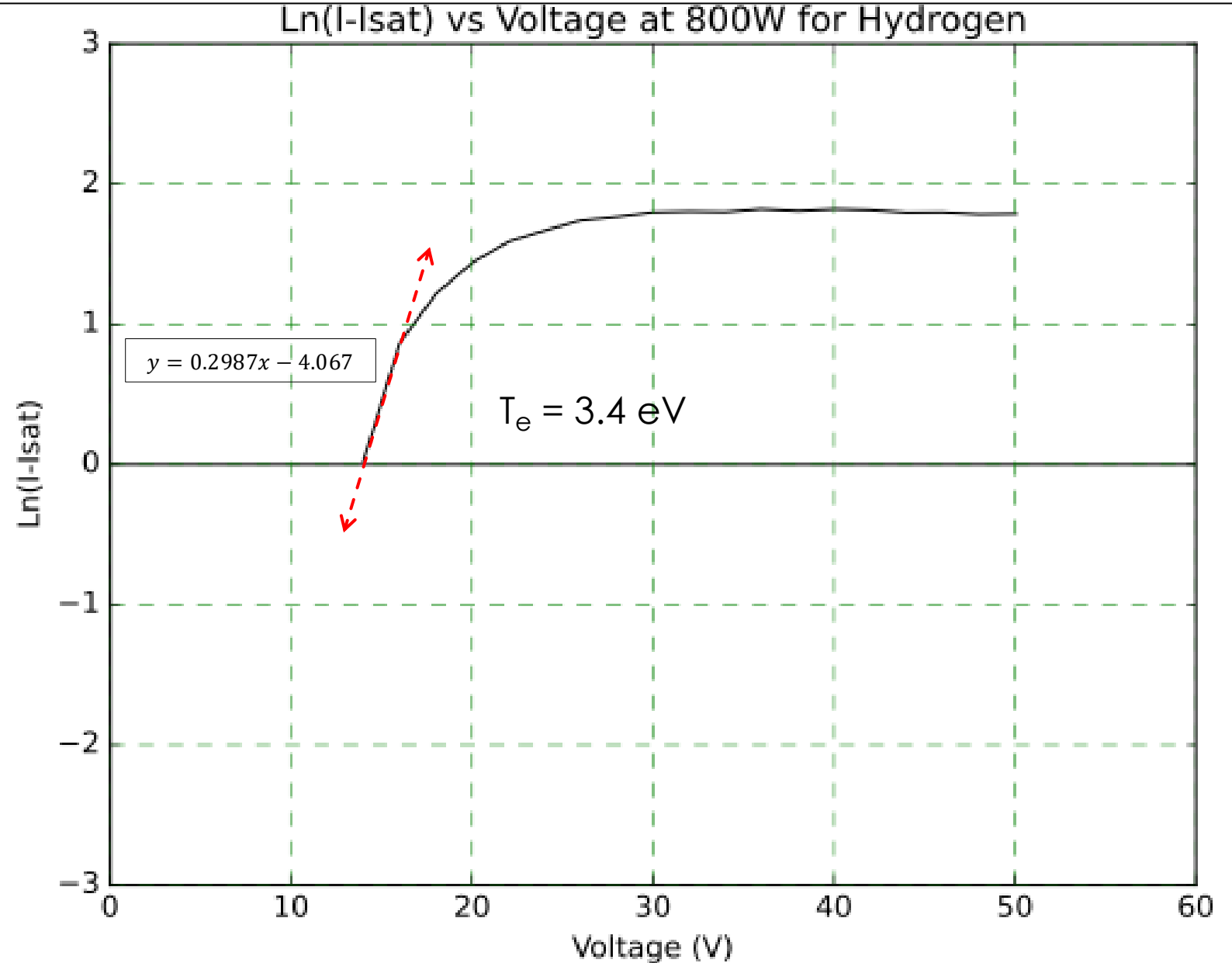
Representative Data

- ▶ 800 W microwave discharge
- ▶ Pure hydrogen (100 sccm)
- ▶ P=30 Torr
- ▶ Cylindrical Langmuir Probe
- ▶ $A_{\text{probe}} = 25.3 \times 10^{-6} \text{ m}^2$



T_e

$\ln(I - I_{sat})$ vs Voltage for Hydrogen at 800 W

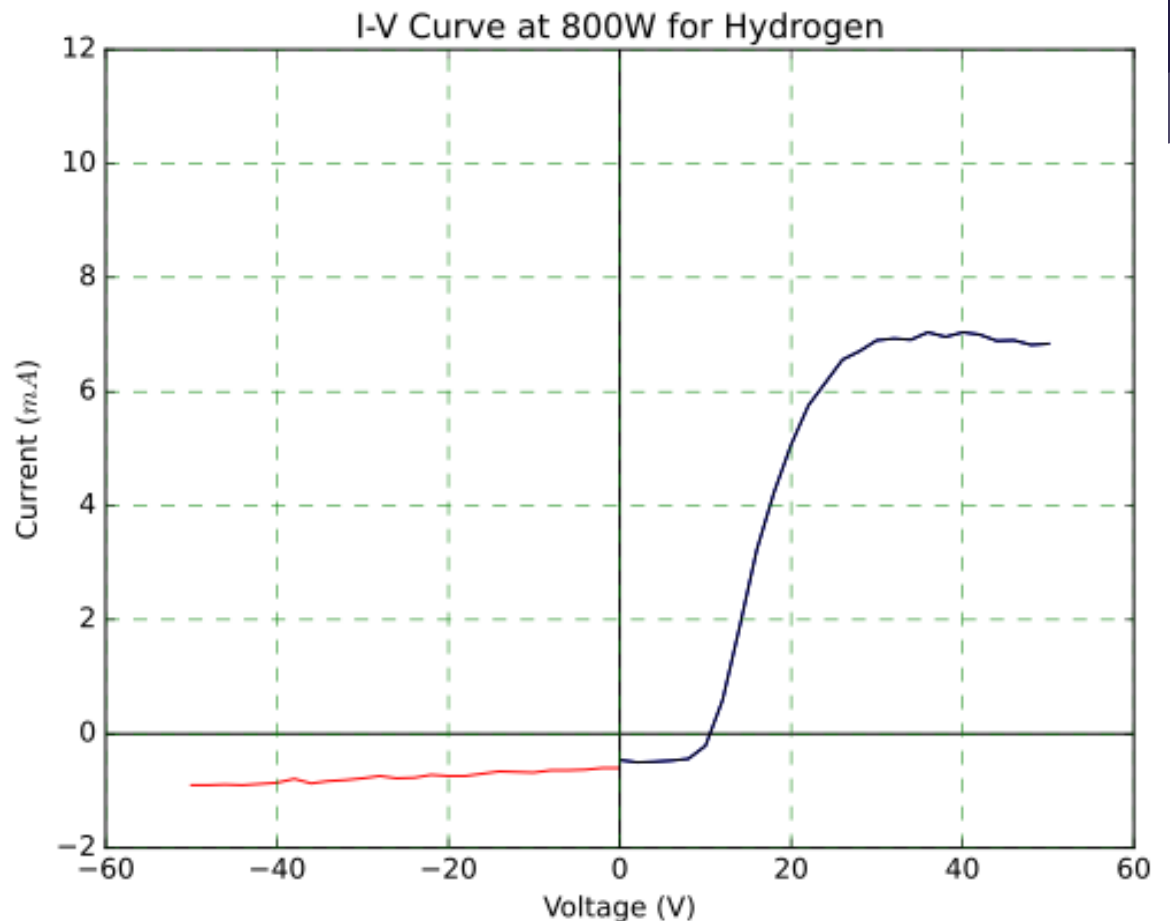


Analysis

- ▶ Using BRL analysis [1],[2]
- ▶ $I_+ = \frac{1}{4} e A n_+ v_+ \gamma$
- ▶ with $T_e = 3.4$ eV and $\gamma = 1.9$
- ▶ gives $n_+ = 2.2 \times 10^{16} \text{ m}^{-3}$
- ▶ If $\alpha = 0 \rightarrow n_+ = n_e = 2.2 \times 10^{16} \text{ m}^{-3}$
- ▶ $\rightarrow$ electron saturation current
- ▶ is then predicted to be 21 mA
- ▶ But....observed electron sat'n ~ 6-7 mA

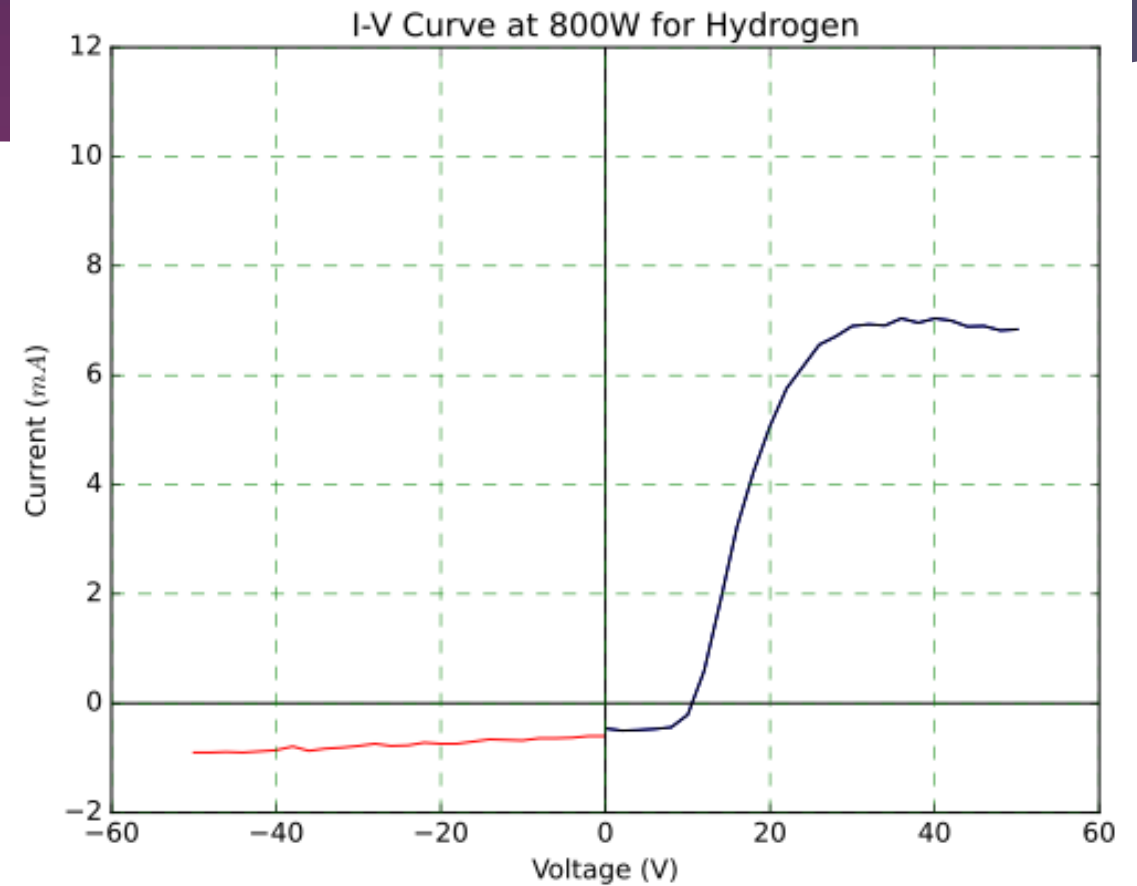
[1] M Tuszewski and J A Tobin 1996 *Plasma Sources Sci. Technol.* **5** 640

[2] Laframboise J G 1966 University of Toronto Institute for Aerospace Studies Report 100



Analysis II

- ▶ Using electron sat'n current = 7 ma
 - ▶ Predicts $n_e = 5.5 \times 10^{15} \text{ m}^{-3}$
 - ▶ And hence $\alpha \sim 3$
- Non-trivial negative ion density ?



Conclusions

- ▶ Diamond films can be grown effectively on silicon substrates using MPECVD
- ▶ This has many applications: hard coatings, thermal interface layer for advanced chip cooling, and NV- centre work
- ▶ $\text{H}_2:\text{CH}_4$ plasmas are used for diamond film growth
- ▶ Both hydrogen and methane plasma can contain negative ions
- ▶ Therefore study of negative ion densities in MPECVD Chambers is relevant
- ▶ Preliminary results suggest $a \sim 3$ for common processing conditions

Acknowledgements

Portia Switzer (see poster)
William Davis MSc thesis & current PhD work
Hammed Ejalonibu PhD thesis
SSSC for materials characterization

The diamond growth work was financially supported by the NSERC
Discovery Grants program as well as a Canadian Space Agency (CSA)
FAST grant for development of a compact spaceborne MRI



NIBS 2026- Nelson, BC 21 Sept. 2026



UNIVERSITY OF
SASKATCHEWAN



NSERC
CRSNG

Funders: NSERC, DND, CSA



National
Defence

Défense
nationale



- ▶ NSERC Discovery Grants Program
- ▶ NSERC/DND Defence Supplement
- ▶ Canada-UK Joint-Quantum Technologies grant program (w/ M Squared Lasers (Glasgow), and Prof. Mark Fromhold of the University of Nottingham)
- ▶ CSA FAST Grant with Prof. G. Sarty