PRINCETON PLASMA PHYSICS LABORATORY

Diamond growth by plasma

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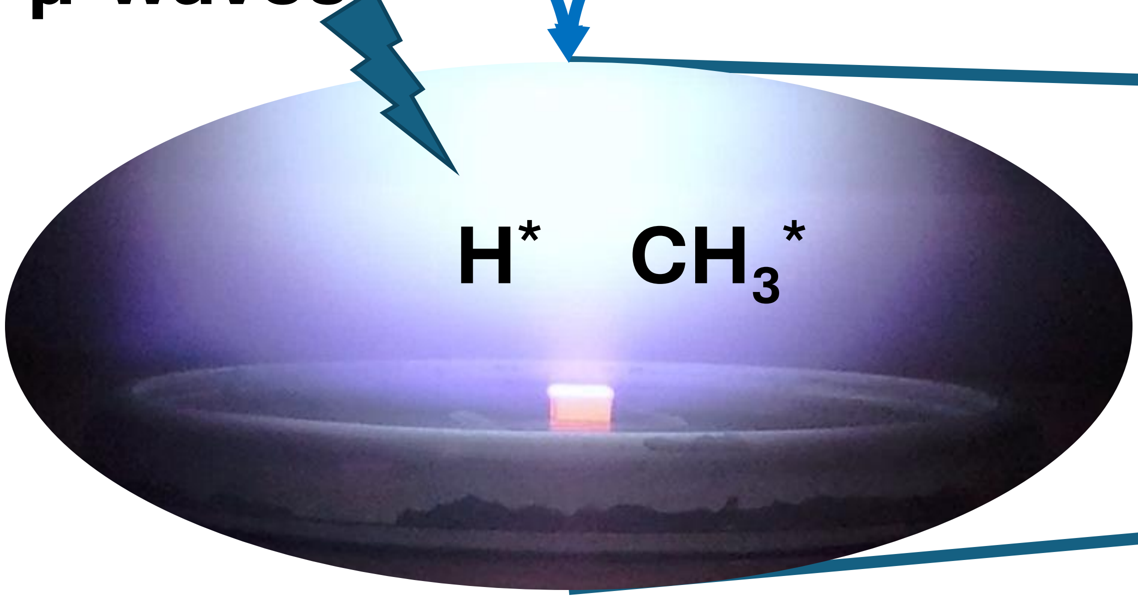
Princeton Plasma Physics Laboratory (PPPL)

Presented to
PPPL School on Plasmas for Microelectronics and Quantum Information Science
July 28 - August 1, 2025

Don’t do this at home!



Tequila
arXiv:0806.1485v1

And a microwave oven

Radical chemistry + Kinetics
→ Cheating thermodynamics

iBIONICS

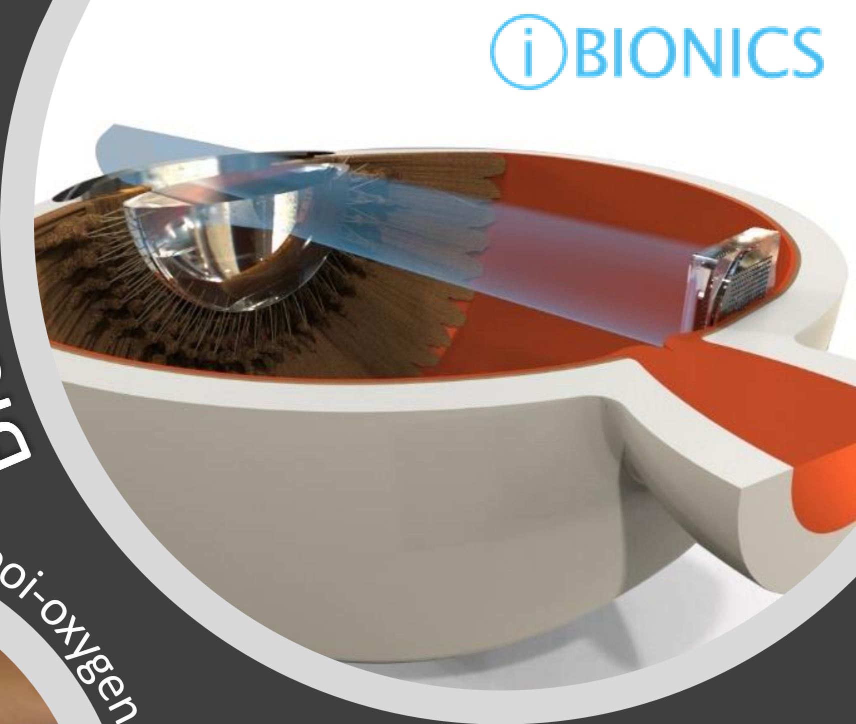
Diamond
Extreme Properties

- Hardest material
- Highest thermal conductivity
- Very transparent
- Chemically inert

Acoustics

bowers-wilkins.com

Bionics



Electro-chemistry

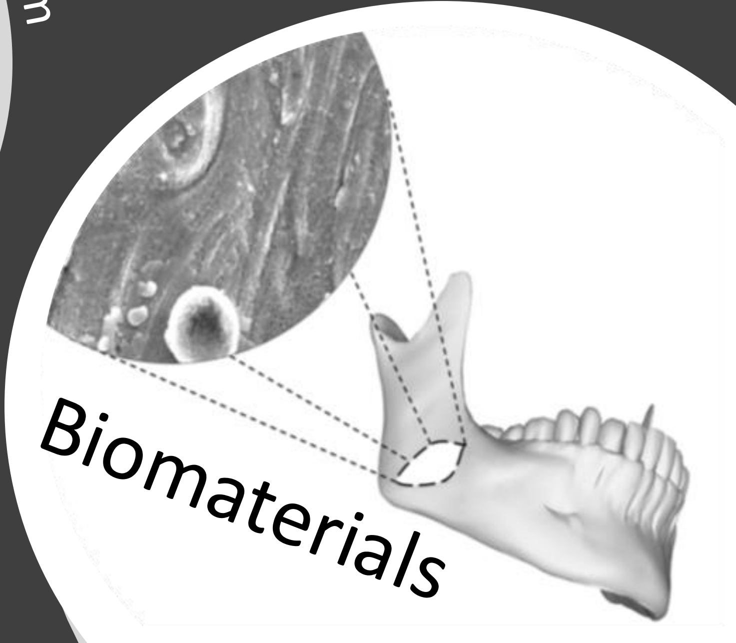
eoi-oxygen.com

+ Water treatment

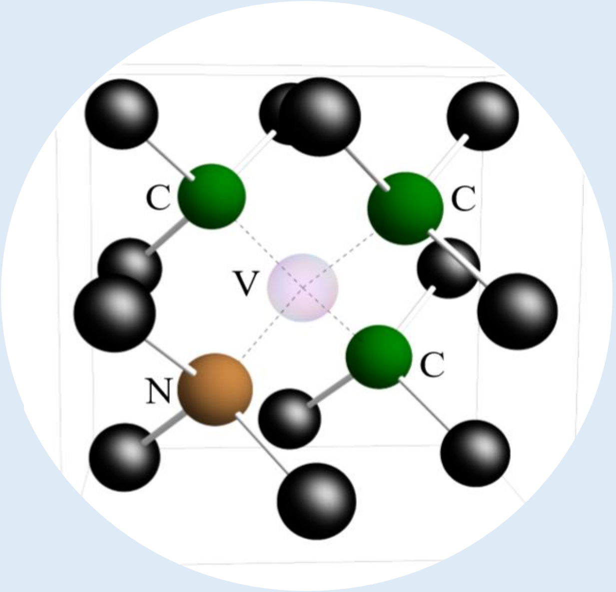
High Power Windows

E6.com

accutome.com



Biomaterials

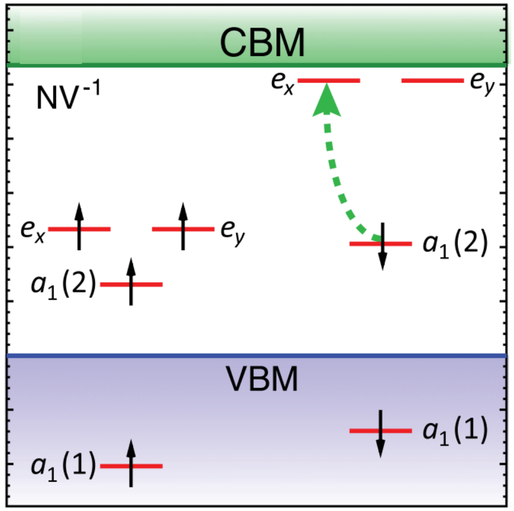


+ e⁻

NV defect in diamond

Diamond Material:

- → Wide band-gap
- → Low spin-orbit coupling
- → Abundant spin-free isotopes
- → High Debye temperature



$$\hat{H}_{gs} = D_{gs}\left[\hat{S}_z^2 - S(S+1)/3\right] + A_{gs}^{\parallel}\hat{S}_z\hat{I}_z + A_{gs}^{\perp}\left[\hat{S}_x\hat{I}_x + \hat{S}_y\hat{I}_y\right] + P_{gs}\left[\hat{I}_z^2 - I(I+1)/3\right]$$

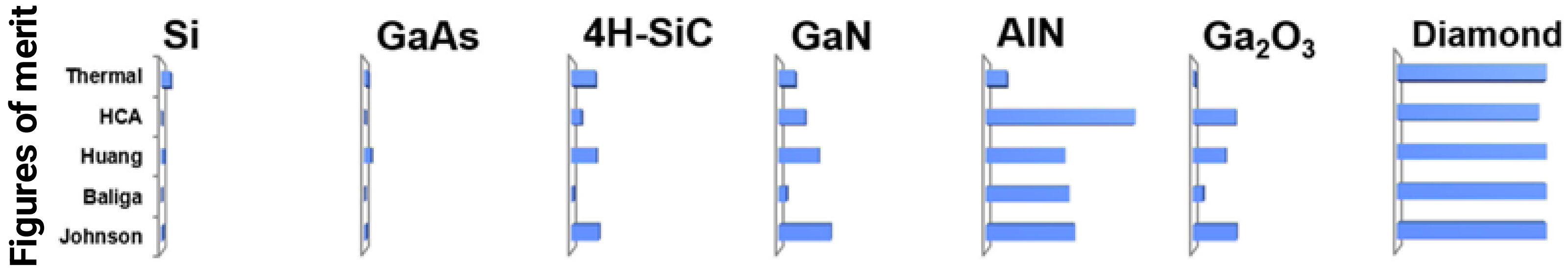
T2 > 1ms at room-temperature

- Long quantum coherence times → quantum operation
- Room-temperature operation → real-world application
- Optical initialization & readout → non-invasive nano-scale

Doherty, et al., Physics Reports 2013, 528 (1), 1-45

Diamond Extreme Electronics: Fundamental Opportunities

Parameter	Diamond	c-BN	β-Ga_2O_3	AlN	GaN	SiC	GaAs	Si
$\sigma_{thermal}$ (W/m•K)	2,290 - 3,450	940 - 2,145	11 - 27	319	≤ 253	370	55	145
e^- mobility (cm²/V•s)	4,500	825	180	426	2,260	900	8,500	1,450
hole mobility (cm²/V•s)	3,800	500	--	--	24	120	400	480
$E_{breakdown}$ (MV/cm)	~13.0	~17.5	~10.3	~15.4	~4.9	~3.0	~0.4	~0.3
v_{sat} (10^7 cm/s)	2.3 (e^-) 1.4 (h^+)	--	1.1	1.3	1.4	2.0	1.0	1.0
Rel. permittivity	5.7	7.1	10.0	9.8	10.4	9.7	12.9	11.8
Maturity								



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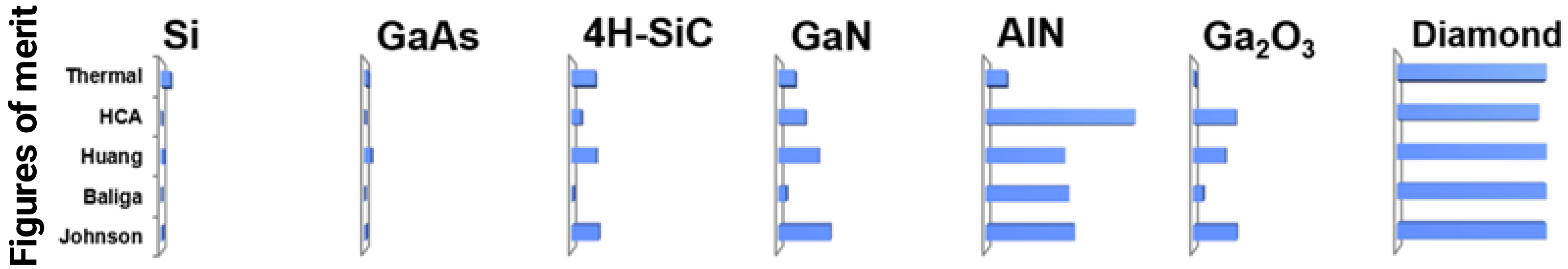
v_{sat} (10^7 cm/s)	2.3 (e^-) 1.4 (h^+)
Rel. permittivity	5.7
Maturity	

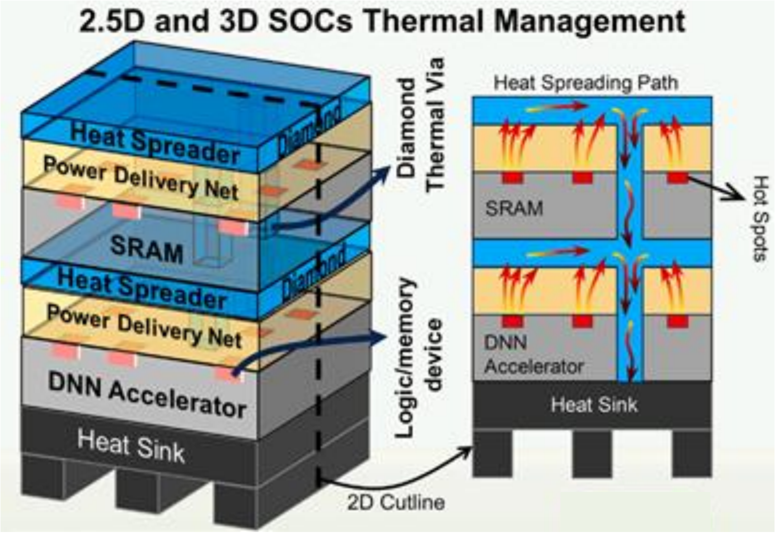
Challenges:

> No high mobility devices (e.g. HEMT)
> Underdeveloped doping
> Unexplored nano-electronics
> Untapped cold cathode properties
> Anomalous charge transport



M. Geis et al. Phys. Stat. Sol. A 2018, 215, 1800681

Diamond Extreme Electronics: Application Areas



High power electronics

Smart Grid
Electrification
Defense / Aerospace

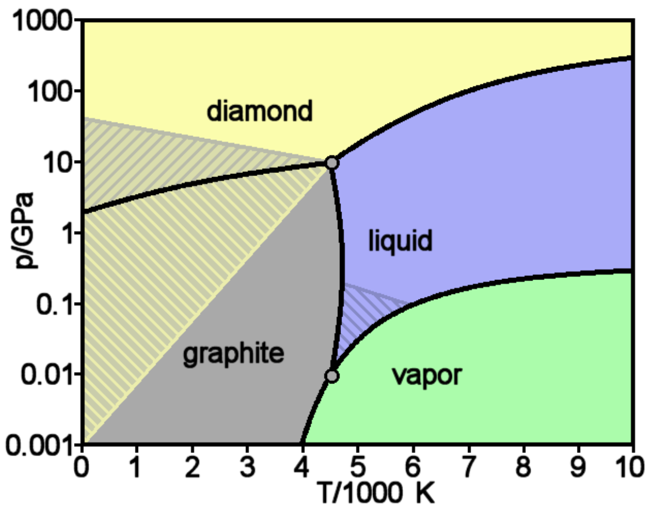
Thermal management

High Performance Compute / AI
High Power Switching

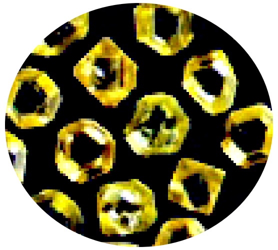
Particle detectors

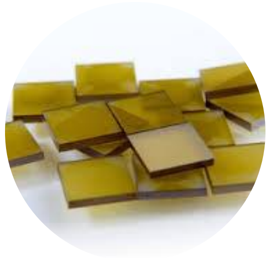
High Energy Physics
Nuclear Technologies

debeersgroup.com



wikimedia.com





e6.com

Why is diamond annoying?

- Diamond *doesn't* want to exist at STP
- It is happy at High Pressure / High Temperature
- This is a problem for growth, but also for processing and device fabrication

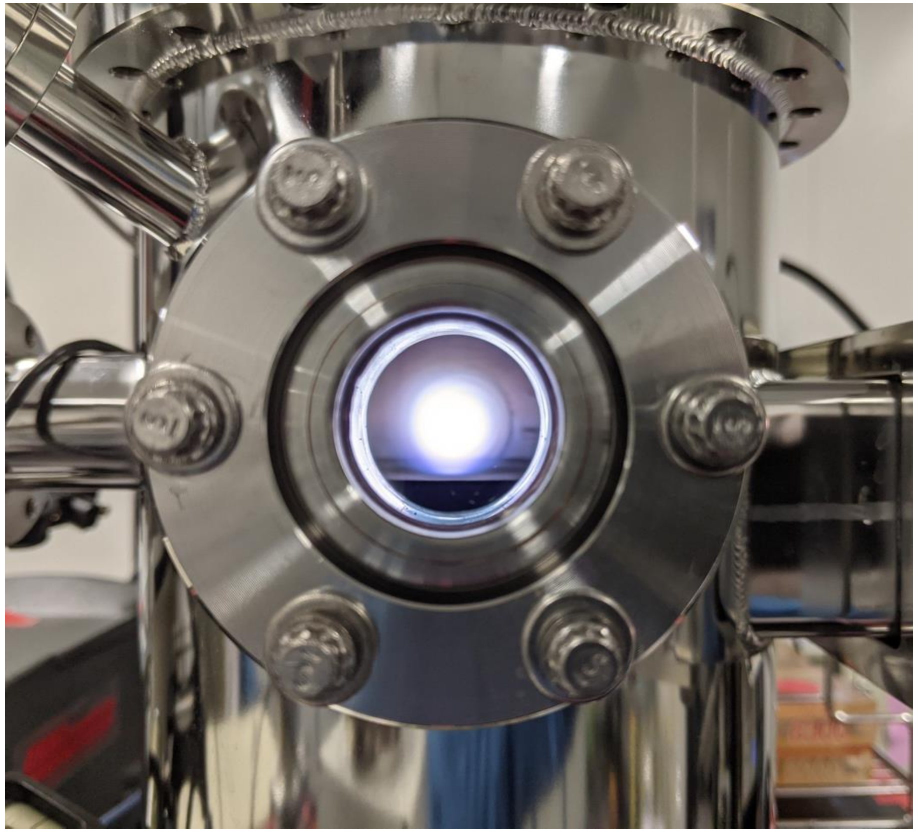
Diamond growth reactors in practice

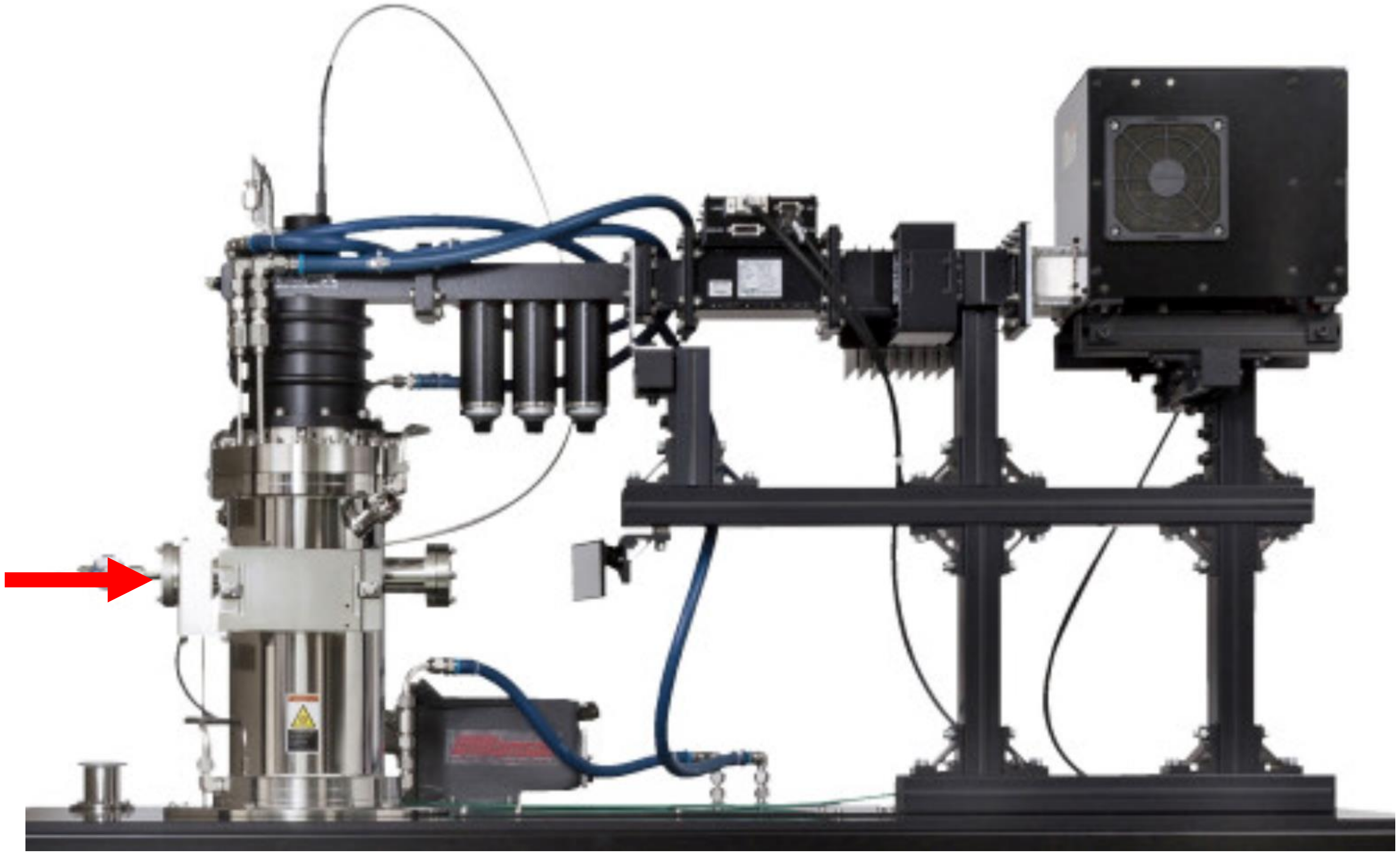
THE UNIVERSITY OF MELBOURNE

MCN
Melbourne Centre for Nanofabrication

PPPL
PRINCETON PLASMA PHYSICS LABORATORY

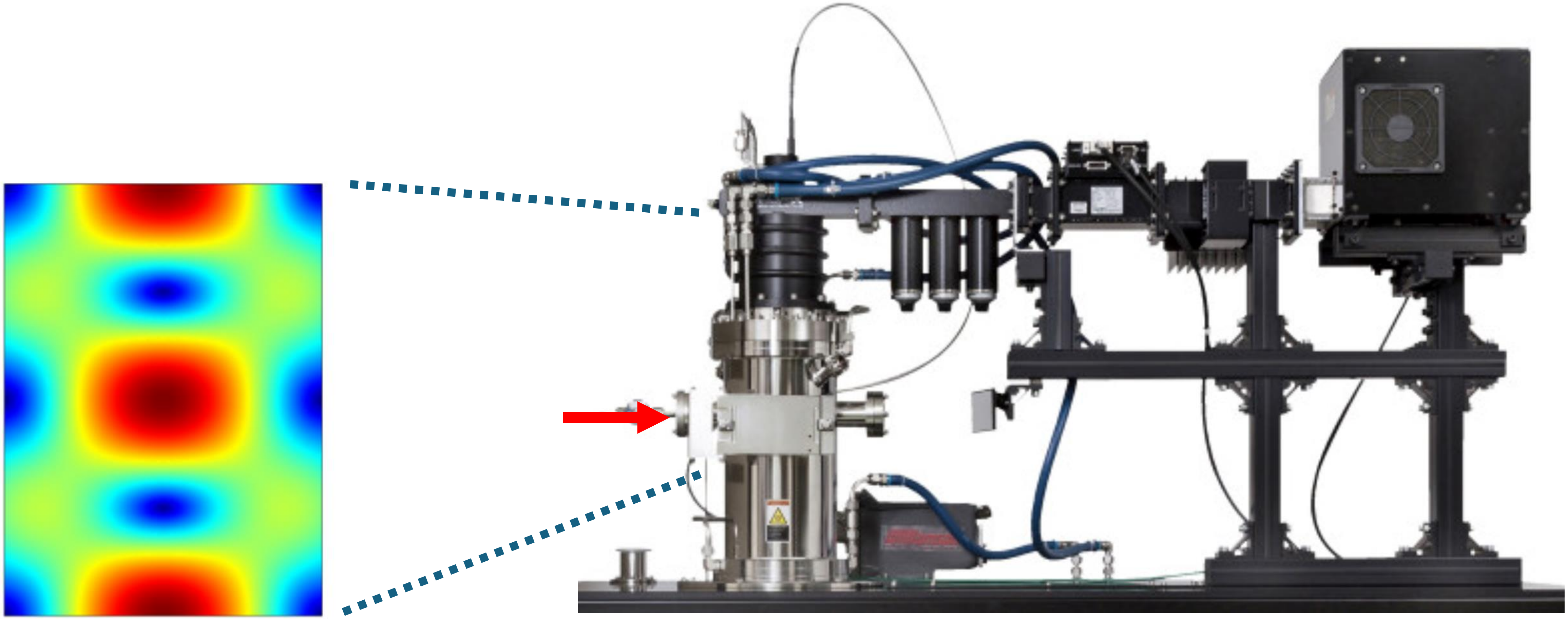
Diamond growth MW plasma reactor





sekidiamond.com

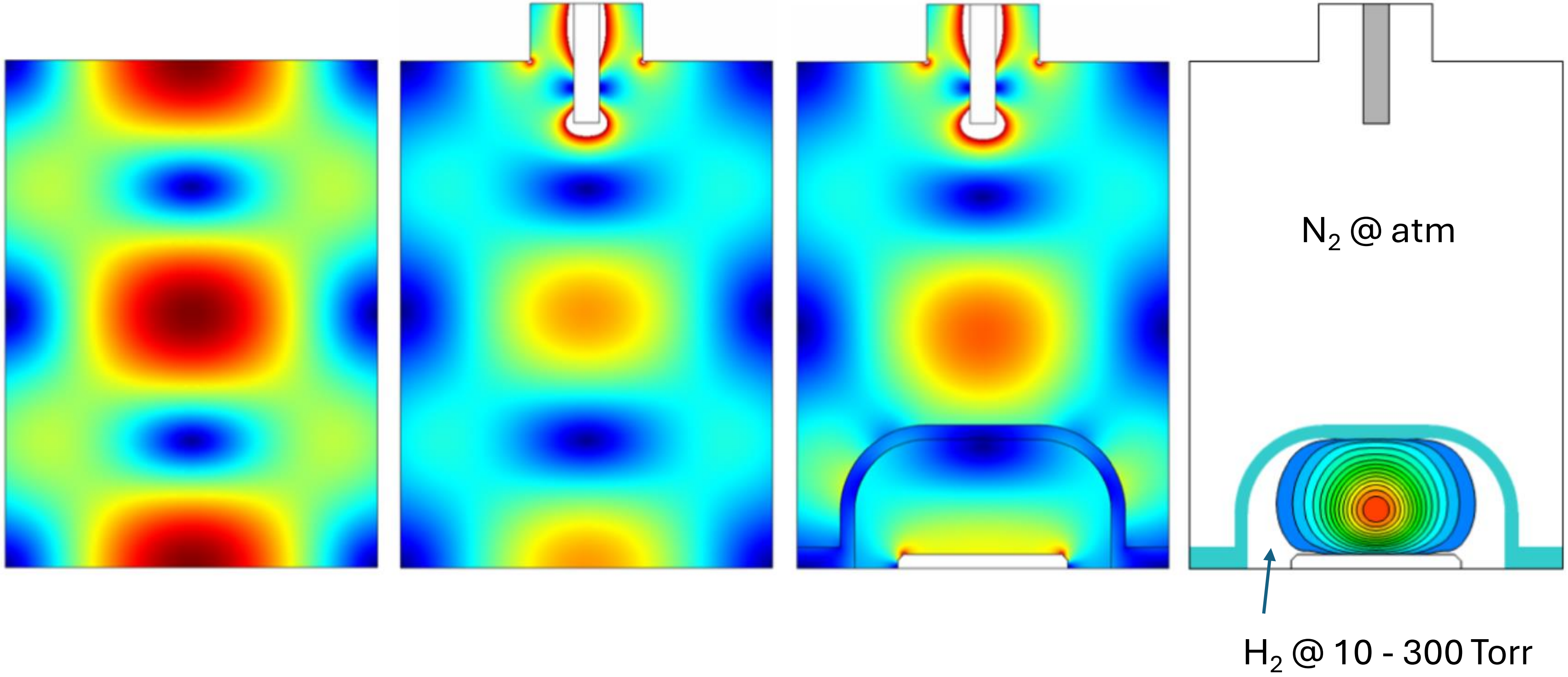
Diamond growth MW plasma reactor



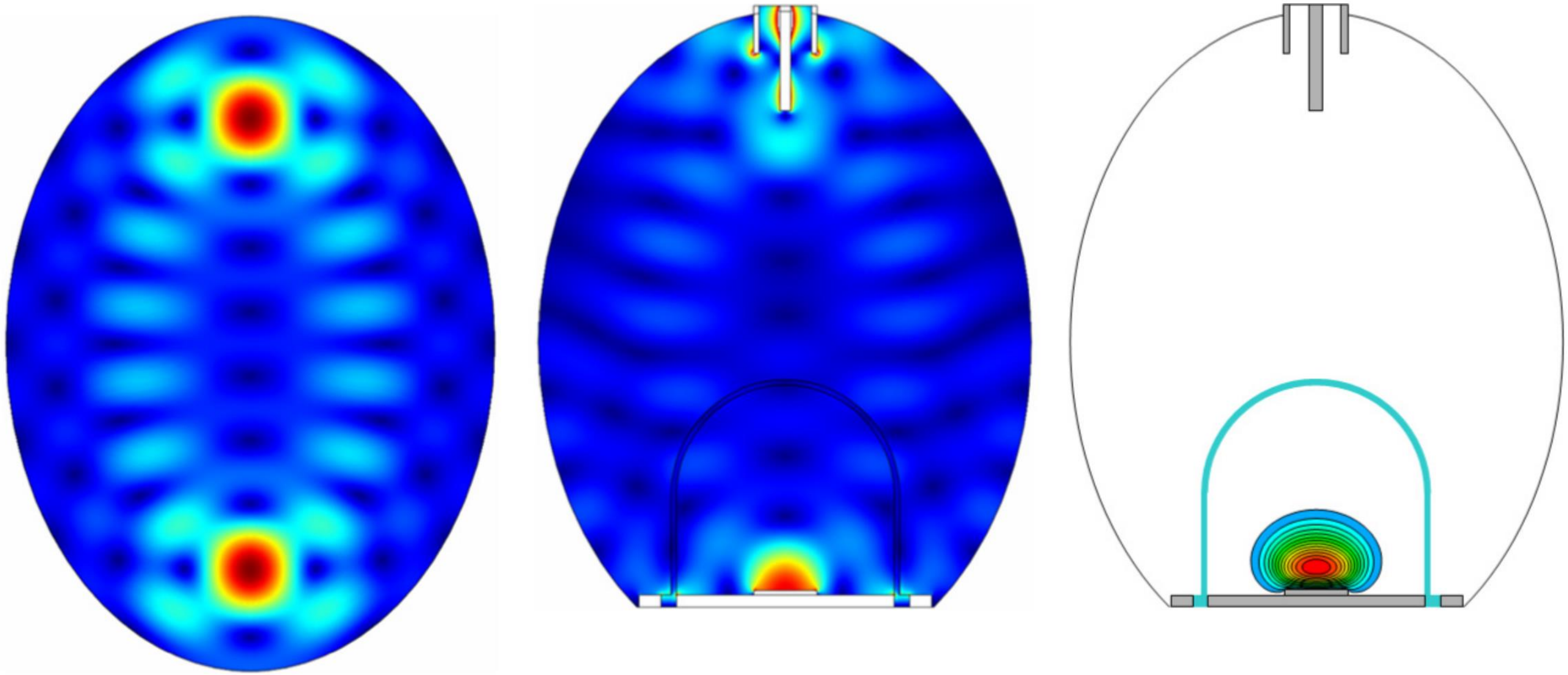
sekidiamond.com

doi.org/10.1088/0953-8984/21/36/364202

Diamond growth MW plasma reactor

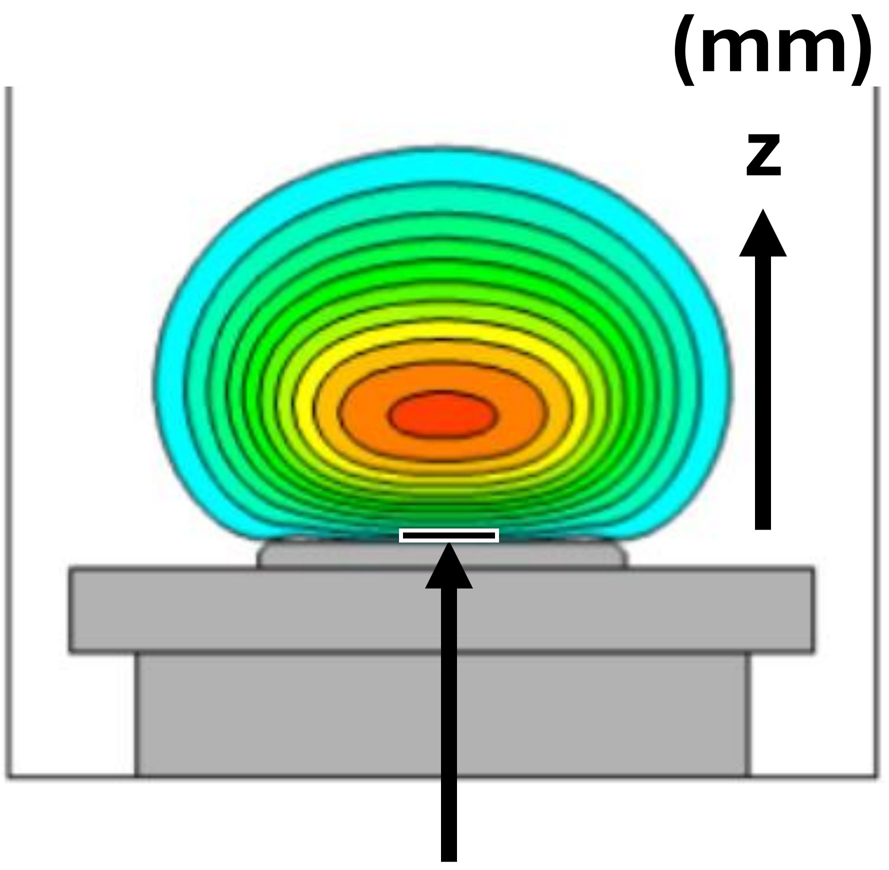


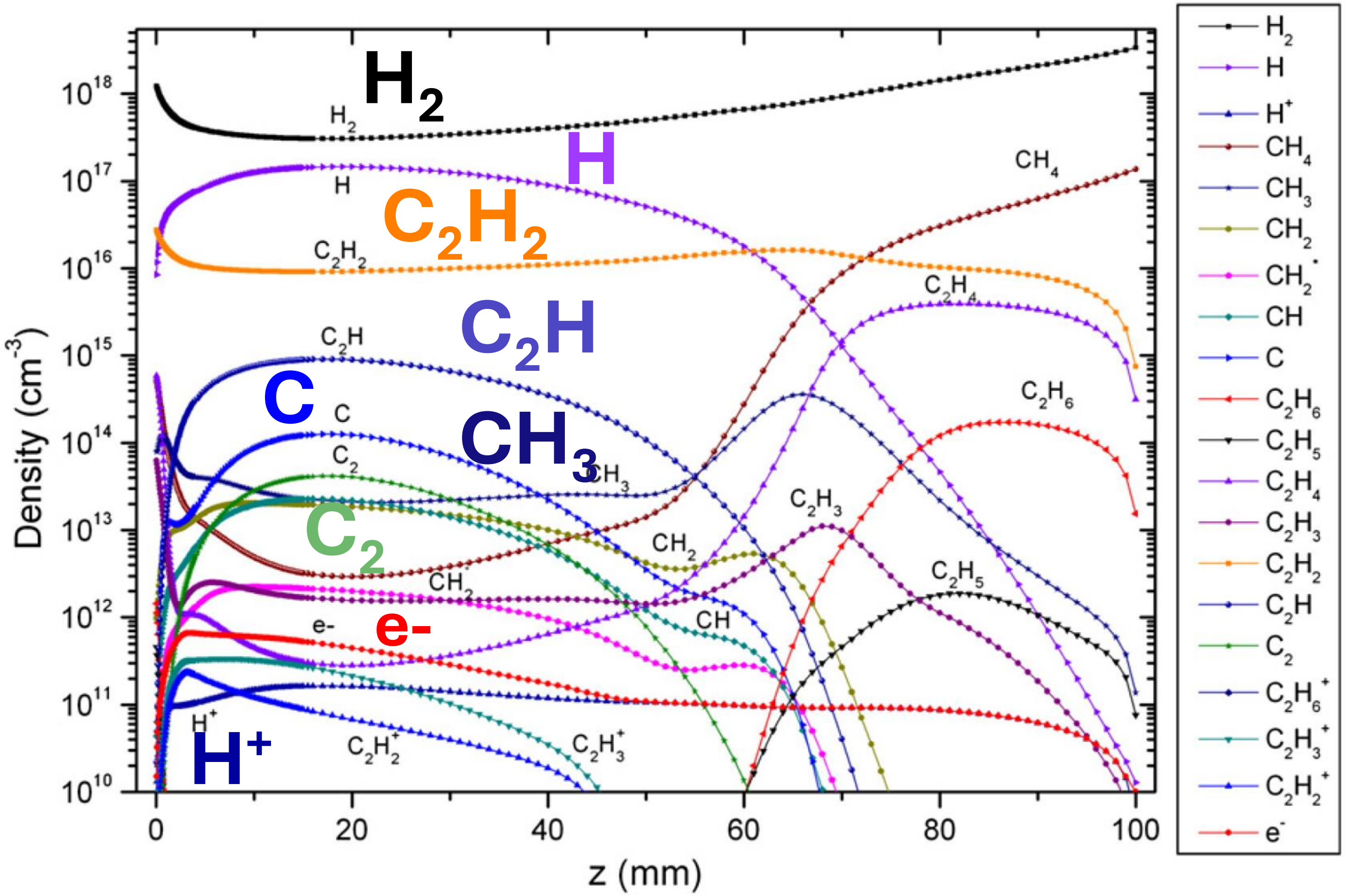
Diamond growth plasma MW reactor



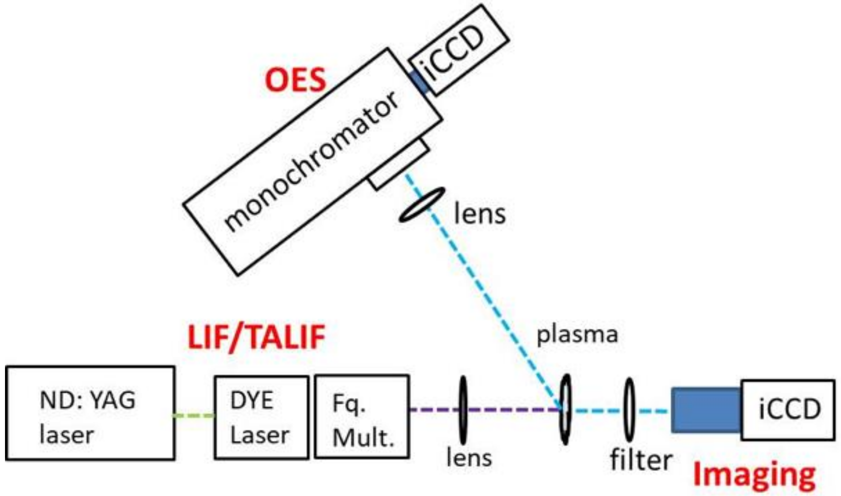
doi.org/10.1088/0953-8984/21/36/364202

Diamond growth plasma chemistry



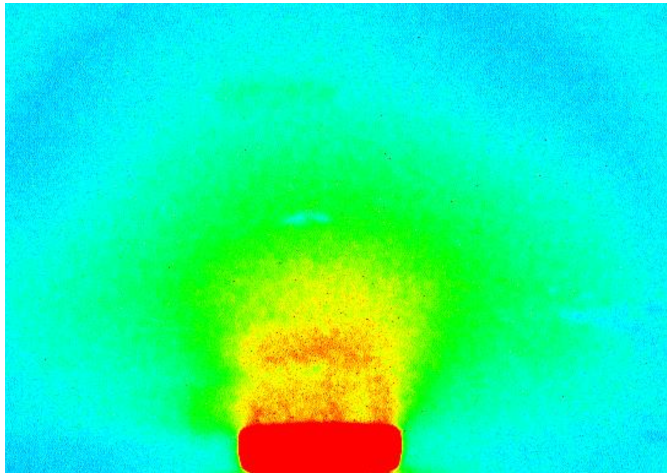


Diagnostics of Diamond Growth Plasmas: Example



Two-Photon Absorption Laser-Induced Fluorescence (TALIF)

H_α distribution



Plasma diagnostics

→ Actinometric OES
→ LIF (TALIF)
→ CRDS

Frontiers

→ Doping chemistry
→ Model validation

PCRF

Shota Abe

Diamond surface stabilized by hydrogen

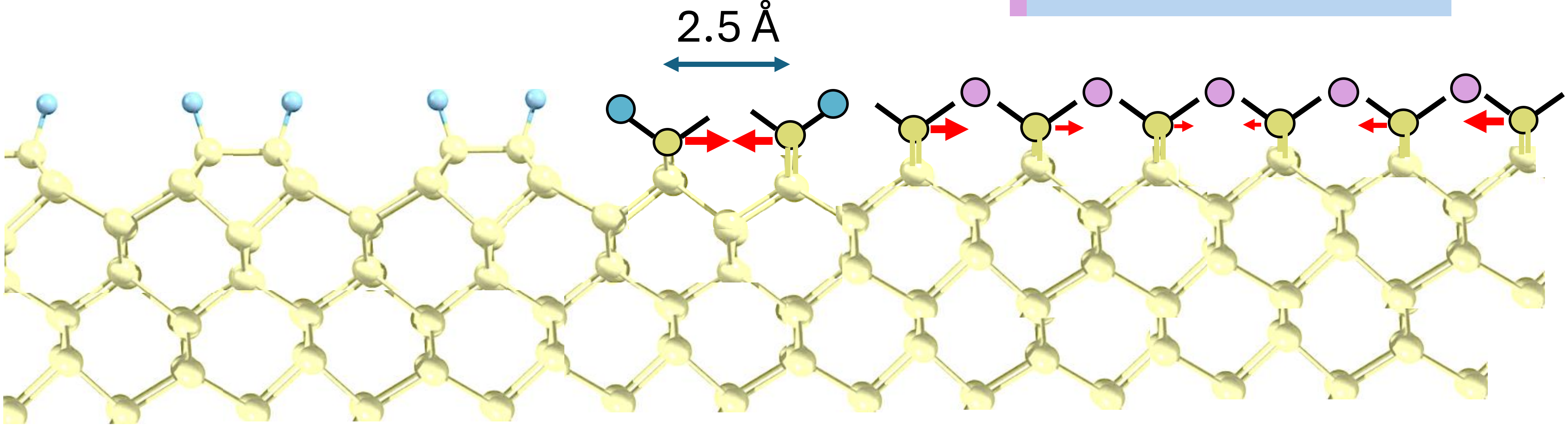
| Dense diamond surface limits options

Steric hindrance and dense surface sites

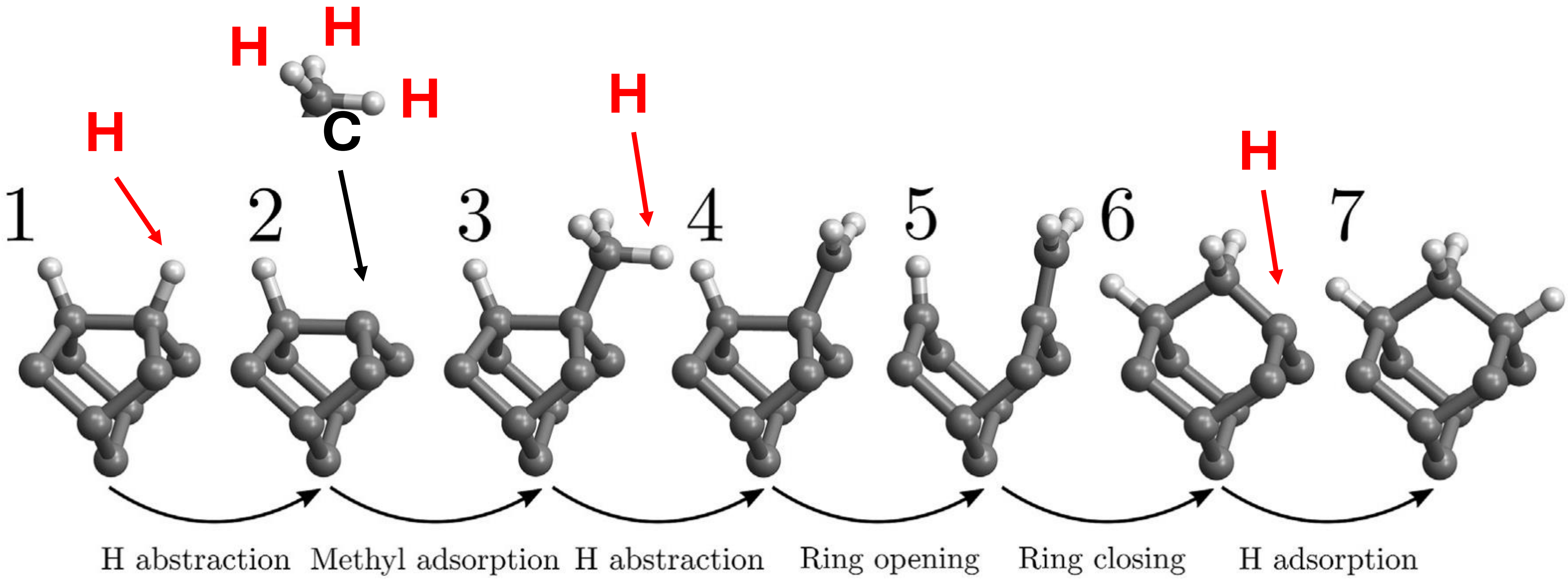
Limits reaction geometry / pathways

Limits termination chemistries

Long range order is difficult to accommodate



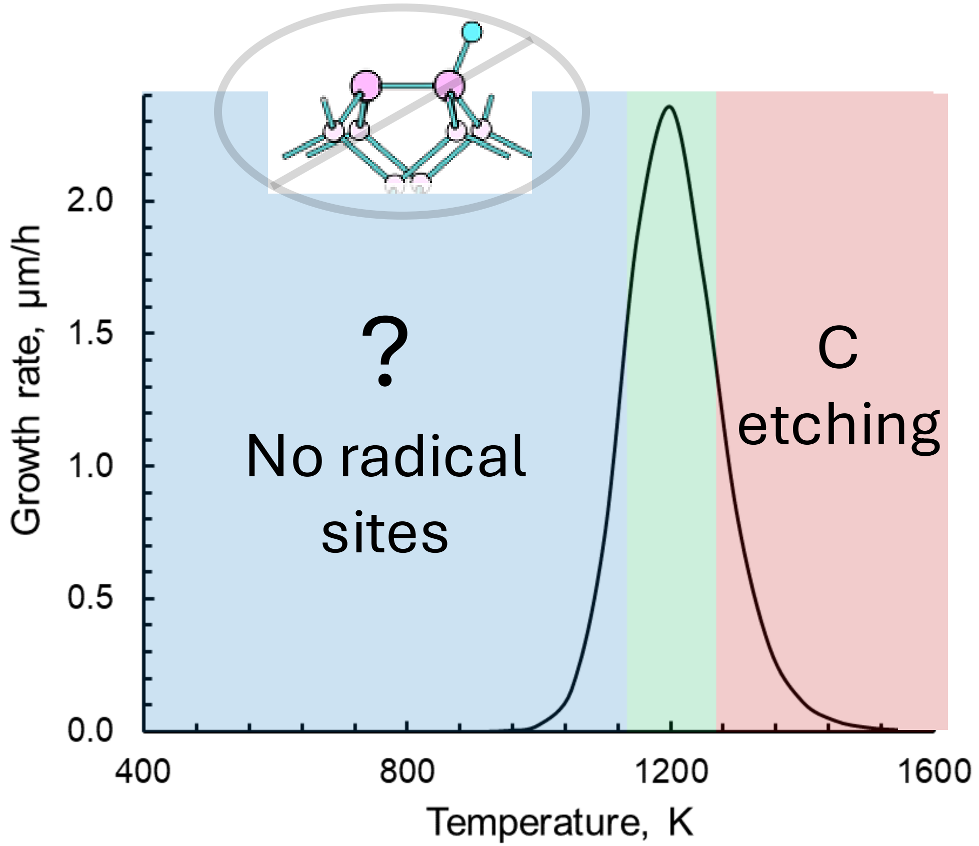
Basic diamond growth model



[100] diamond surface growth model

L.M. Oberg, et al. Carbon 178 (2021) 606-615 (see within for primary references)

Growth parameter windows limit co-doping options



(100) diamond growth model

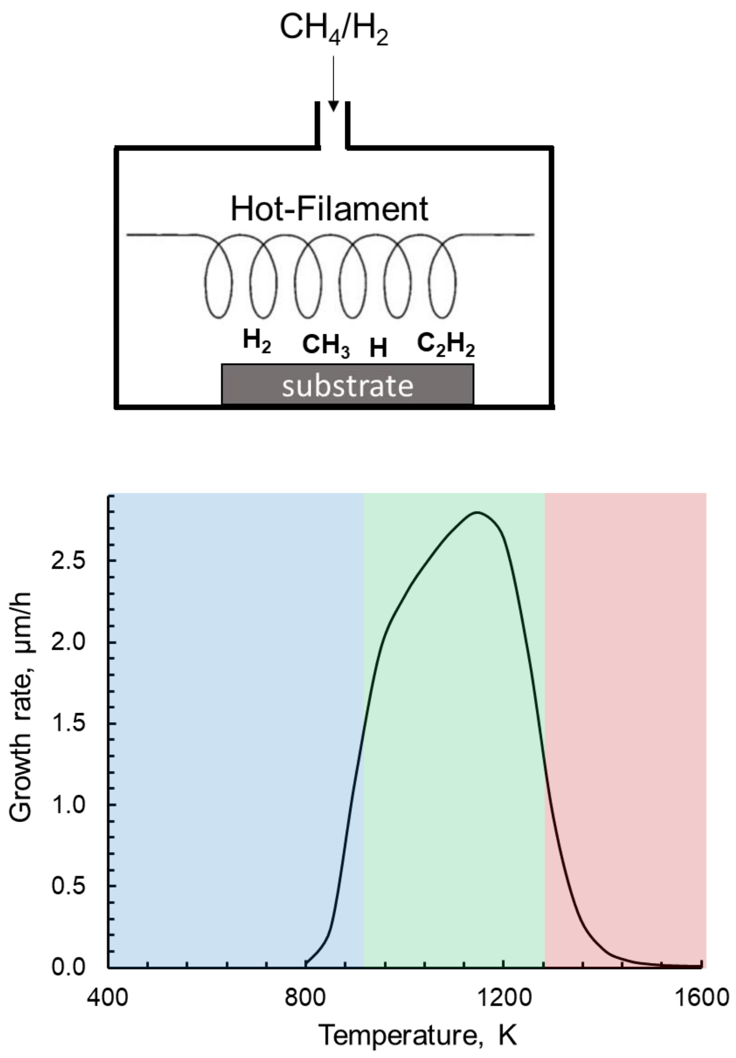
Harris and Goodwin (1993)

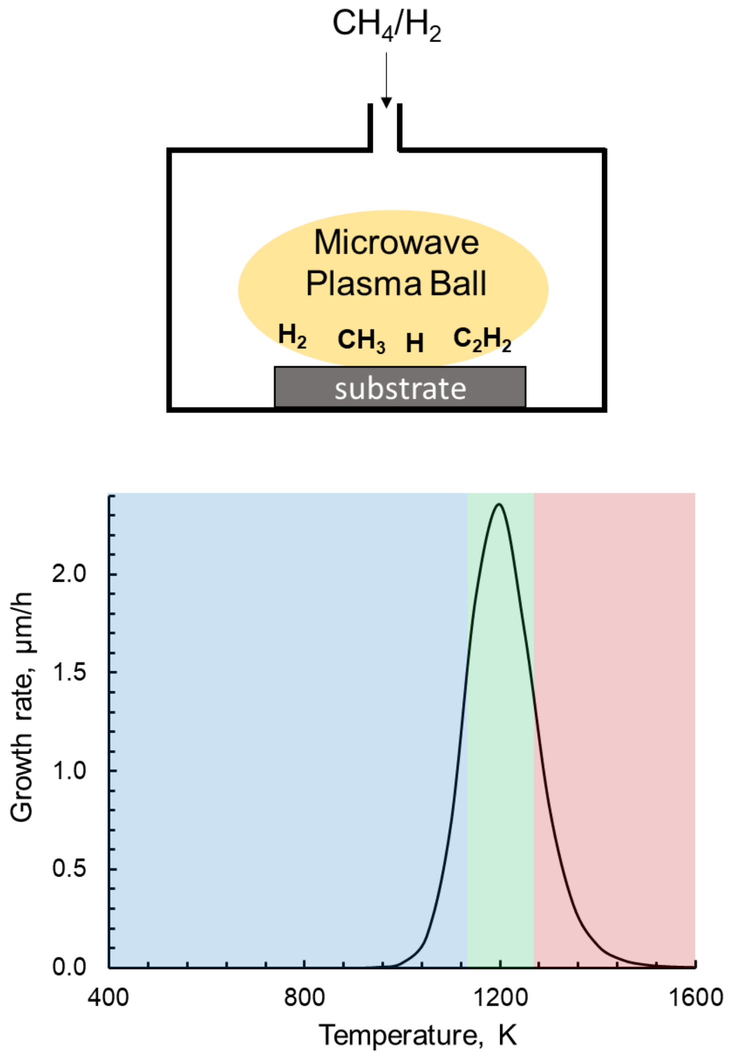
- **Atomic hydrogen (H)**
- **Methyl radicals (CH_3)**

Narrow growth window ~1200 K

- **< 1000 K insufficient surface radical site generation (step 1)**
- **Increased dopant incorporation < 1000 K**

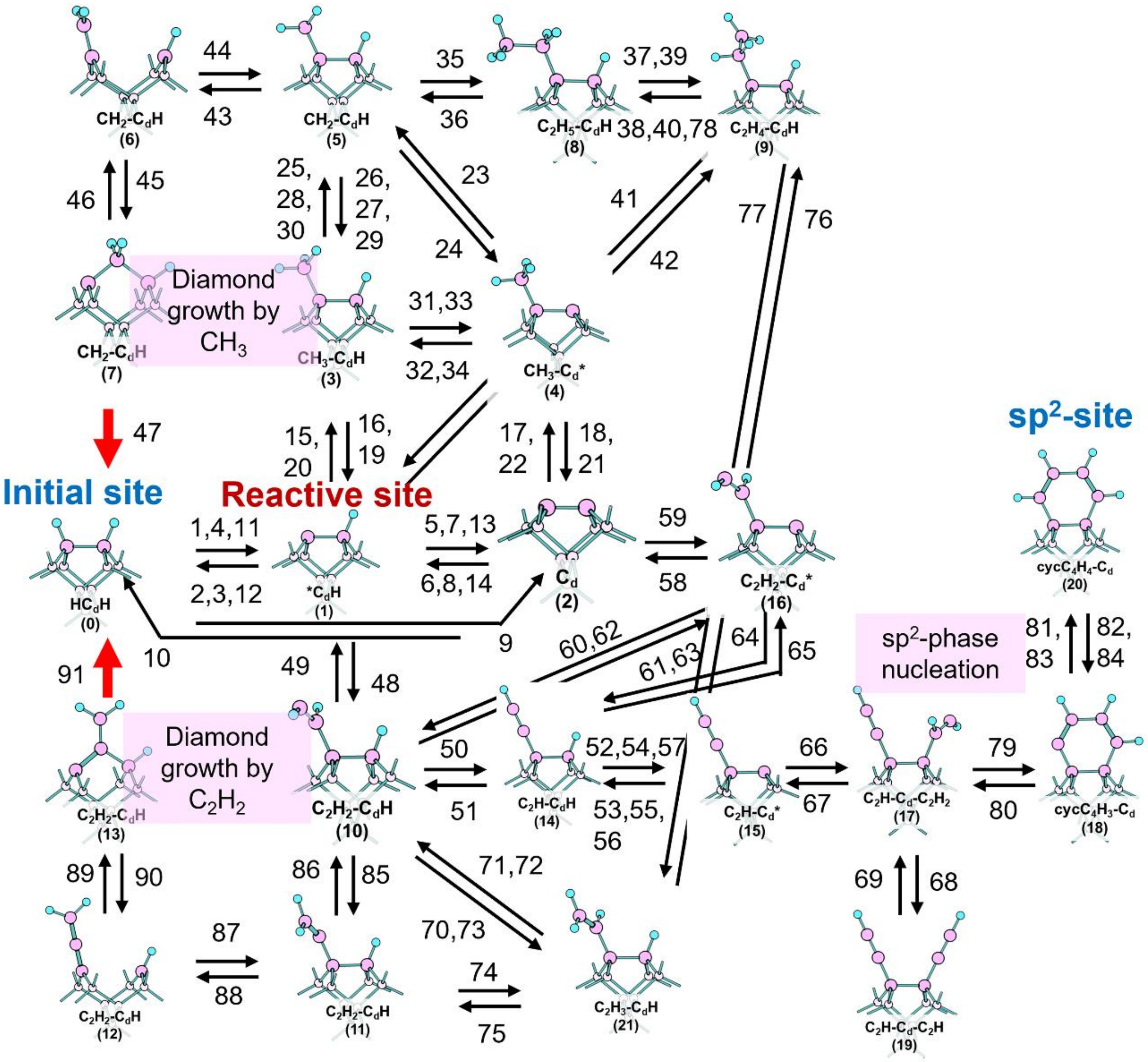
Unexplained difference in growth windows : missing science





- **Plasma sources both create CH_3 and H**

→ Need new explanation for low-temperature limit of growth window



Adding chemistry to growth model: C_2H_2 nucleates sp^2

https://doi.org/10.1016/j.diamond.2024.111577

→ 91 rates for reactions in 27 possible surface configurations

Modeling: plasma surface interaction

Chemical kinetics

Quantum chemistry

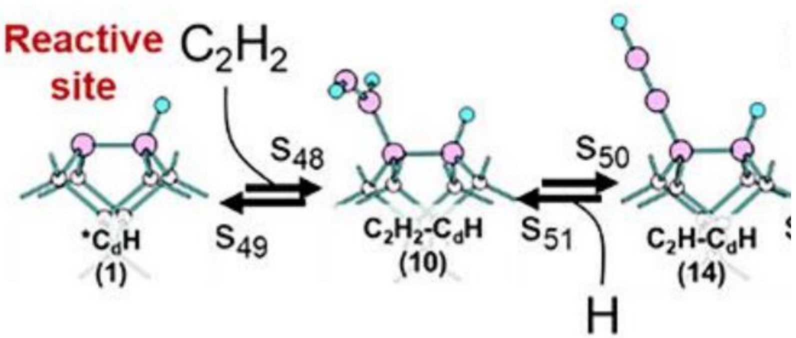
$$\frac{k_B T}{h} \frac{Z_{vib}^{TS}}{Z_{vib}^{surf} Z_{tot}^{gas}}$$

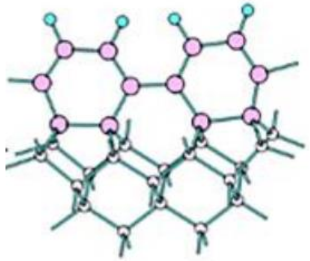
Activation Energy

Plasma modeling

$$ReactionRate = A * \exp\left(-\frac{E_a}{kT}\right) * [X] * [surface]$$

? ?

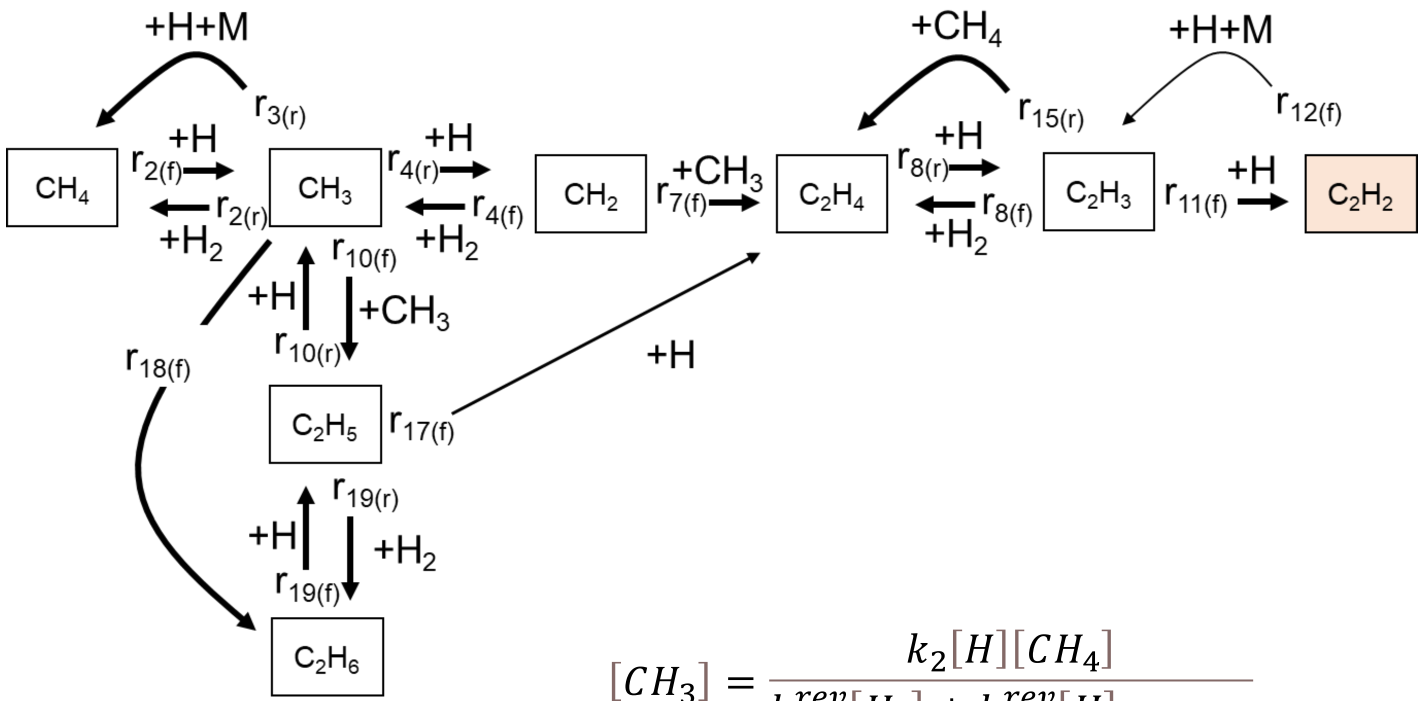




?

→ **Model predicts likely outcomes**

Gas-phase chemistry model: C_2H_2 fluxes depend on plasma source



$$[CH_3] = \frac{k_2[H][CH_4]}{k_2^{rev}[H_2] + k_3^{rev}[H] - v_{CH_3}}$$

$$[C_2H_2] = \frac{\left(k_{11}[H] + k_{12}^{rev}\right)/v_{C_2H_2} \times k_7 k_8 \left(k_5^{rev} + k_6\, k_4^{rev}/k_4\right)[CH_3]^2[H]^2}{\left\{\left(k_8[H] - v_{C_2H_4}\right)\left(k_{11}[H] + k_{12}^{rev} + v_{C_2H_3}\right) - k_8^{rev}[H_2]v_{C_2H_4}\right\}\left\{\left(k_5 + k_6^{rev}\right)[H_2] + v_{CH2}\right\}}$$

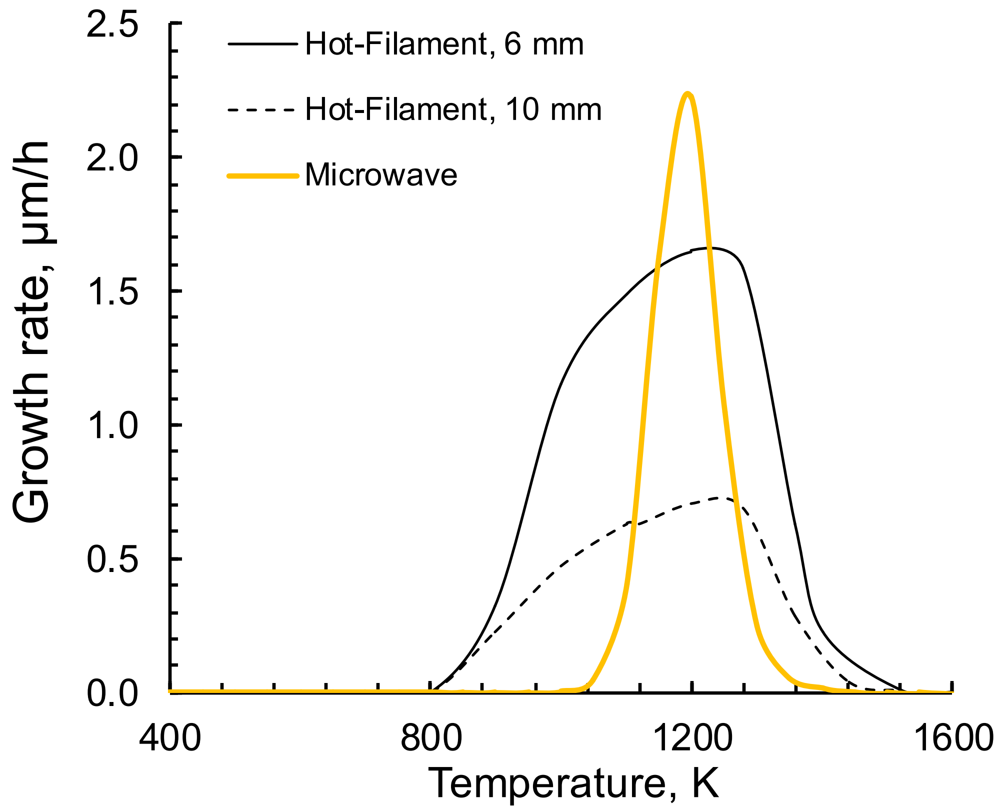
Plasma chemistry model:

- **Hot-filament systems generate lower relative C_2H_2 fluxes**

→ Combine plasma-chemical and quantum-chemical (surface) models to predict growth window

https://doi.org/10.1016/j.diamond.2024.111577

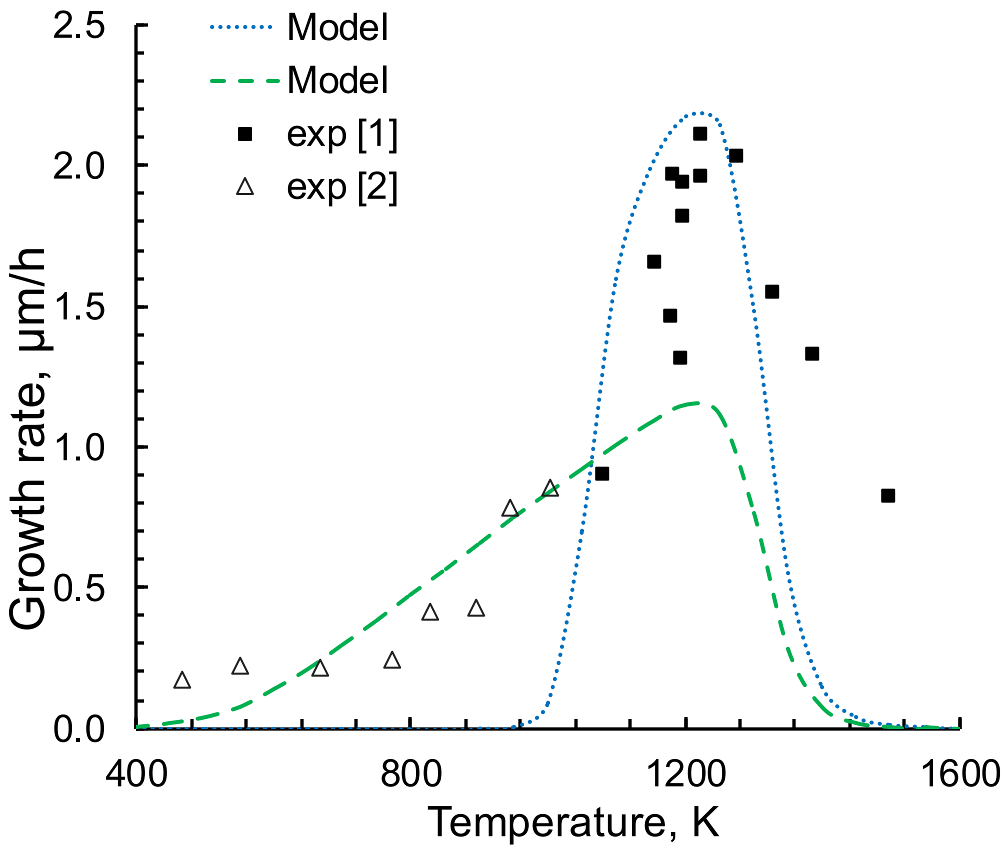
Model confirmation: C_2H_2 flux limits growth rate at low temperatures



- **C_2H_2 flux is the primary limiting factor in low temperature growth rates**

https://doi.org/10.1016/j.diamond.2024.111577

Model confirmation: C_2H_2 flux limits growth rate at low temperatures



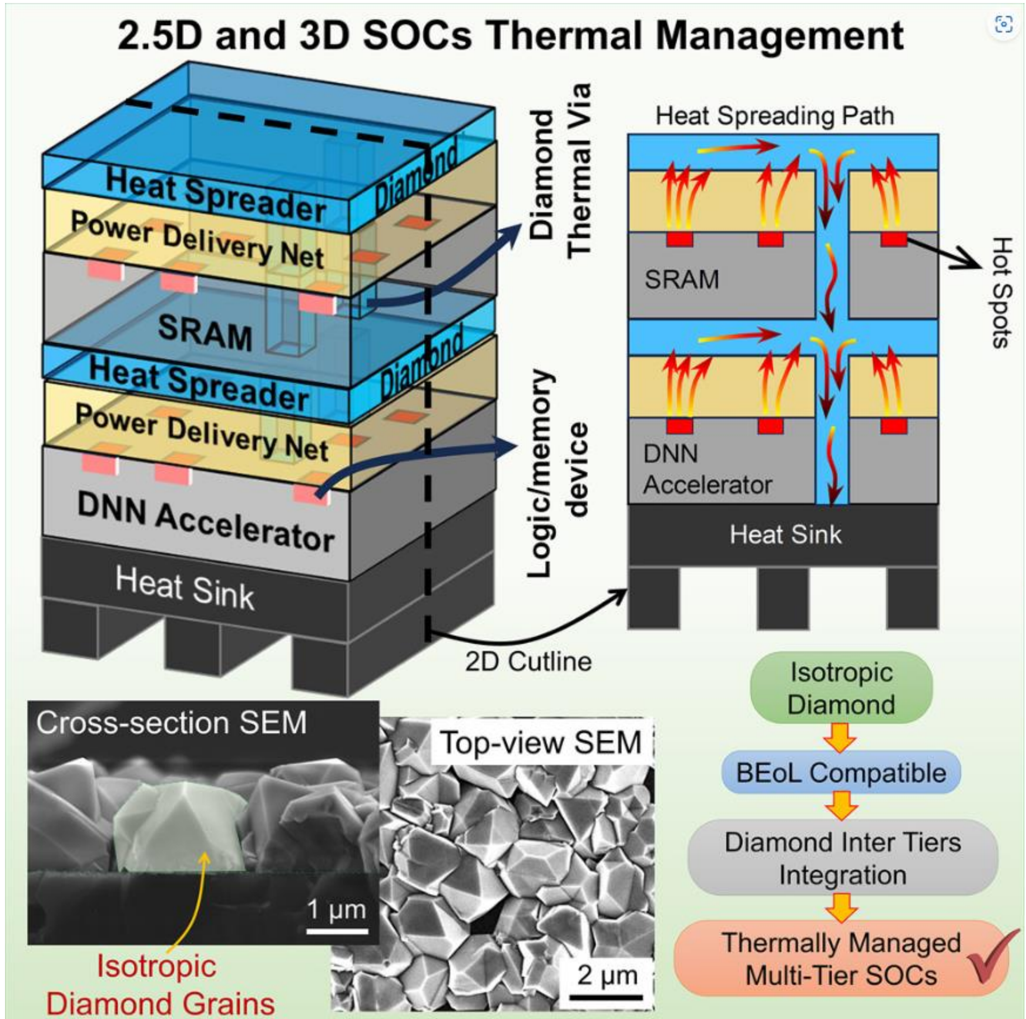
- **C_2H_2 flux is the primary limiting factor in low temperature growth rates**
- **Removing C_2H_2 from model enables much lower growth temps**

→ Model consistent with experimental data

[1] Kondoh et al. Appl. Phys. Lett. 59, 22 (1991)
[2] Yamaguchi et al. Appl. Phys. Lett. 64, 1306 (1994).

https://doi.org/10.1016/j.diamond.2024.111577

Future developments: wider growth windows, full plasma models

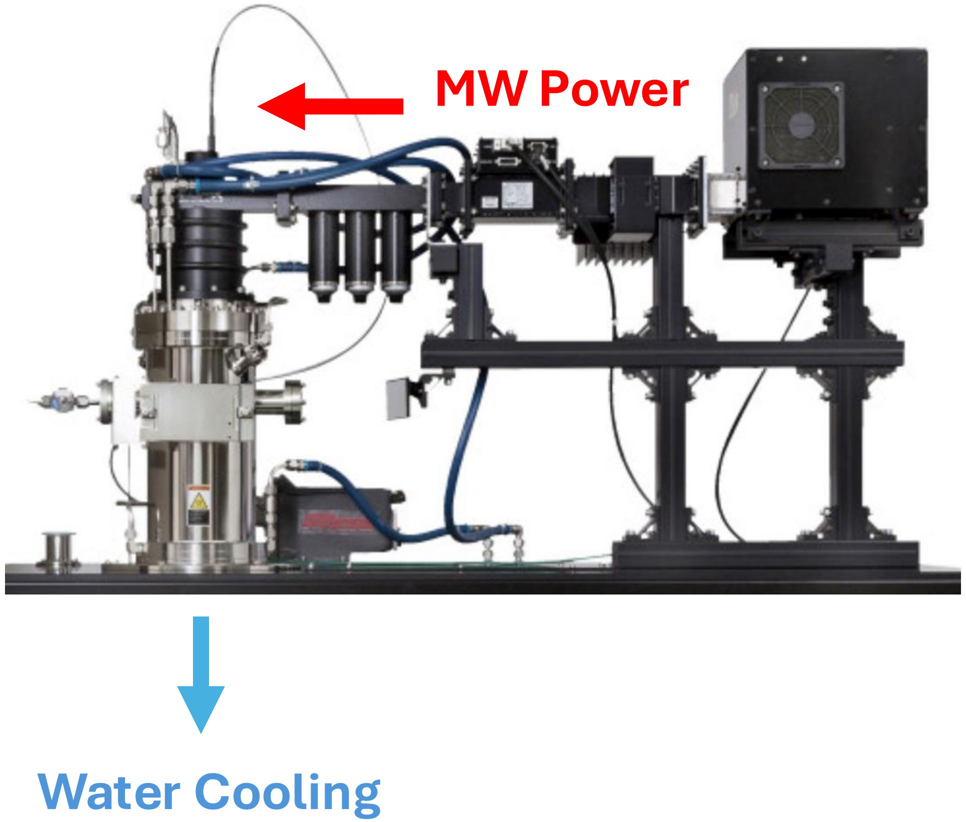


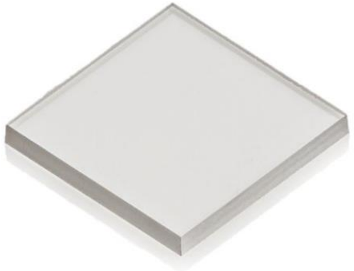
- **Low temperature growths may enable new designs for silicon electronics (SOCs)**
- **O_2 addition increases growth window but limits doping → explainable with our model**

Model-directed epitaxy development:
→ Lower temperature deposition for microelectronics
→ Improved co-doping for quantum devices

https://doi.org/10.1016/j.xcrp.2023.101686 - also see Stanford publications on O-affected growth

Diamond cost limitations



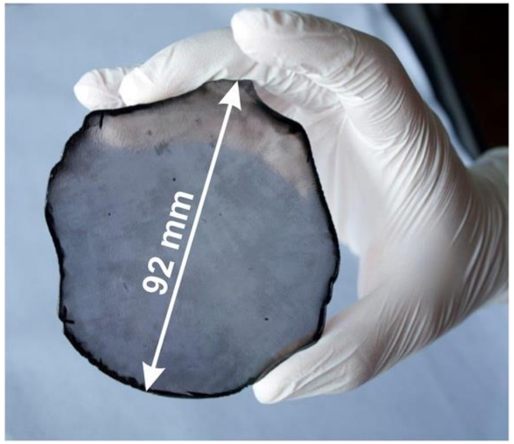


$\$1,000\ cm^{-3}$

$\$1,000\ cm^{-3}$

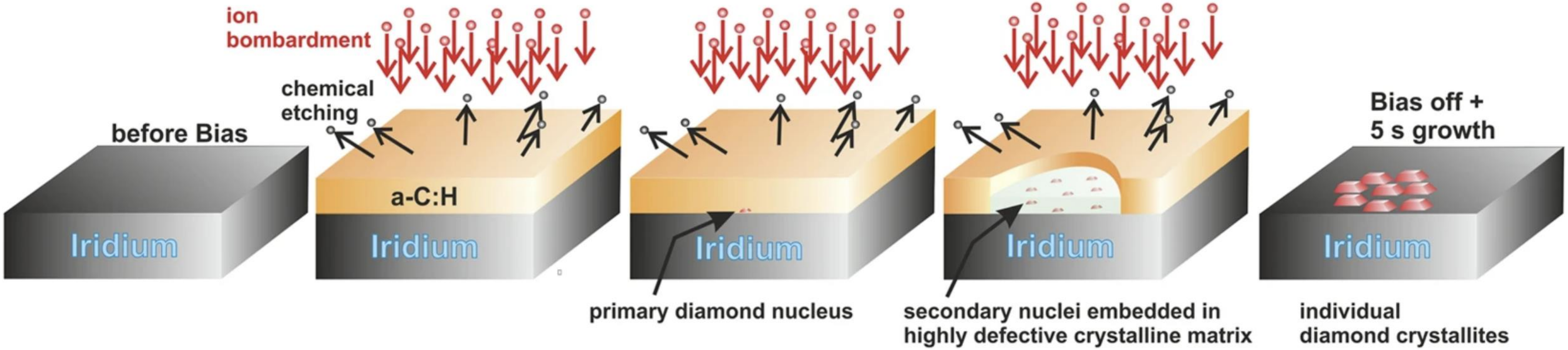
$\$1\ cm^{-3}$

Towards wafer-scale (single-crystal) diamond



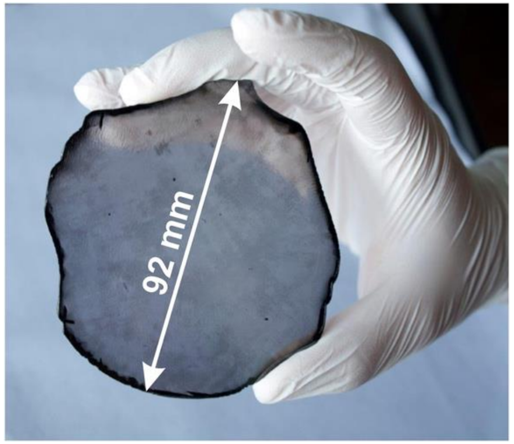
Key Science

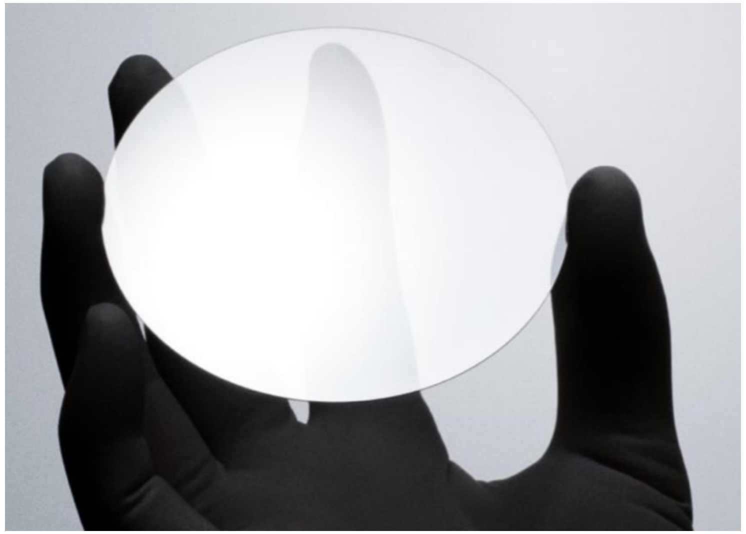
→ Diamond nucleation is 'unnatural'
→ Iridium / diamond lattice mismatch ~7%
→ Dislocations produced and need mitigation



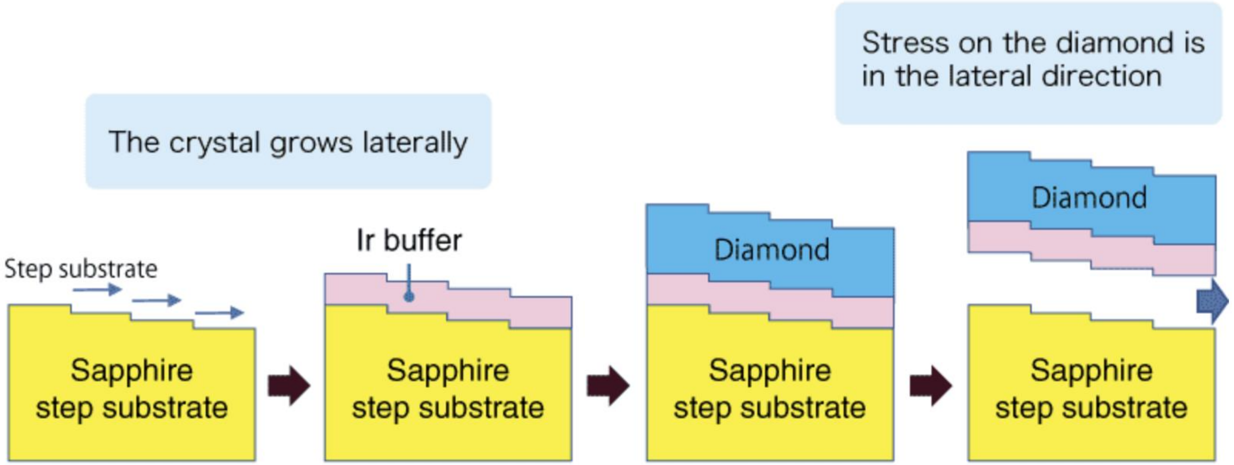
doi.org/10.1038/srep44462 (2017)

Towards wafer-scale (single-crystal) diamond





www.df.com



orbray.com

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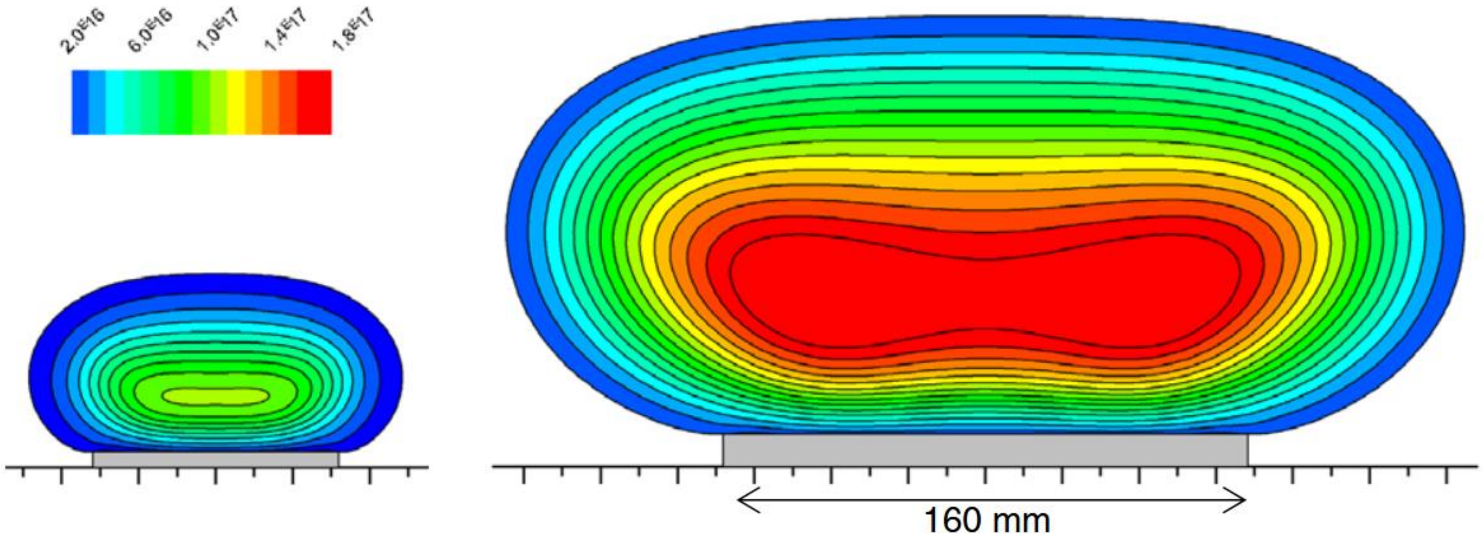
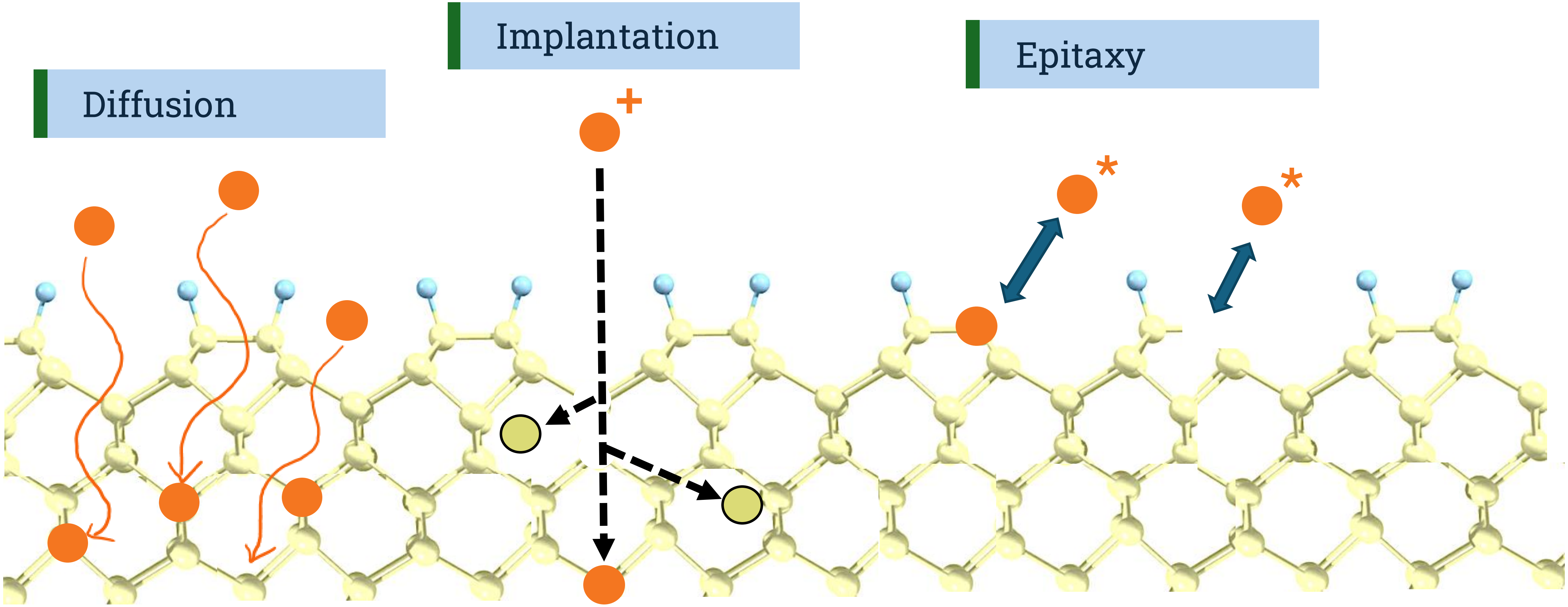


2.45 GHz → 3” 915 MHz → 6” ? → 12”

doi.org/10.1088/0953-8984/21/36/364202

Plasma enabled doping

Doping without plasma is hard in diamond



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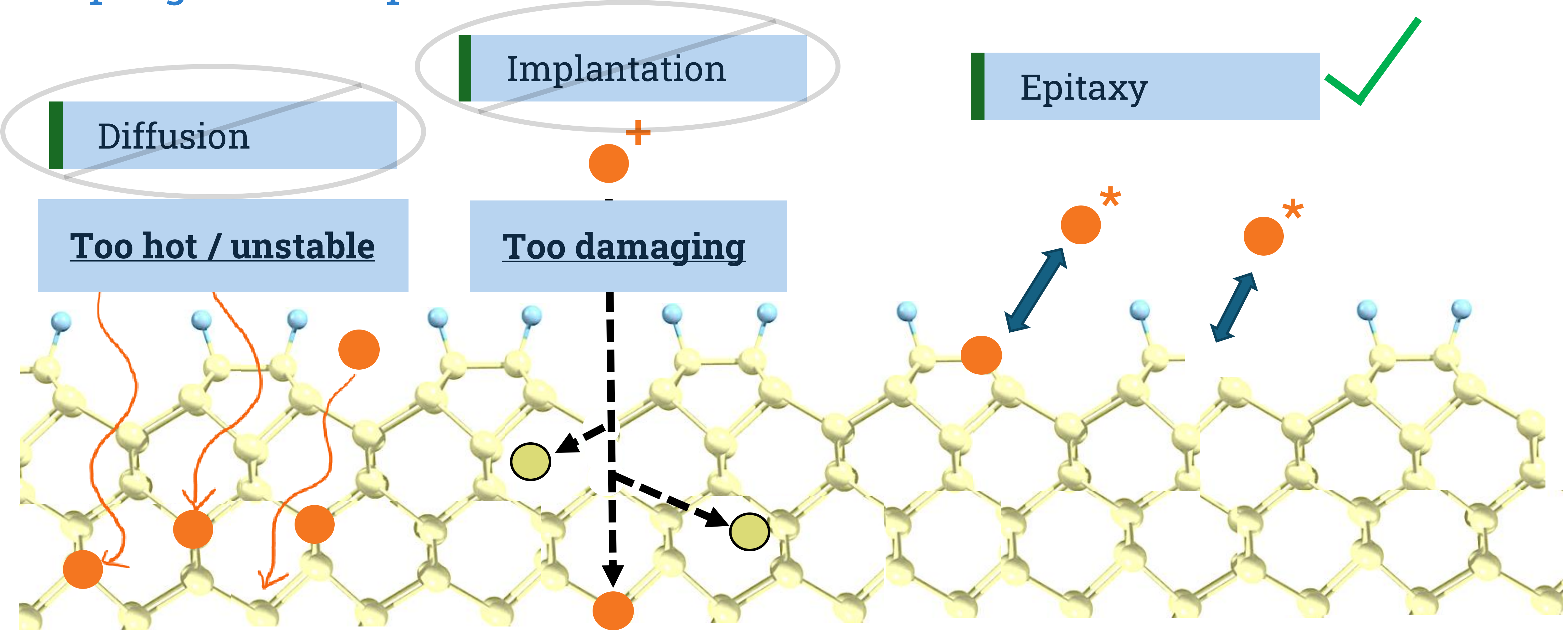
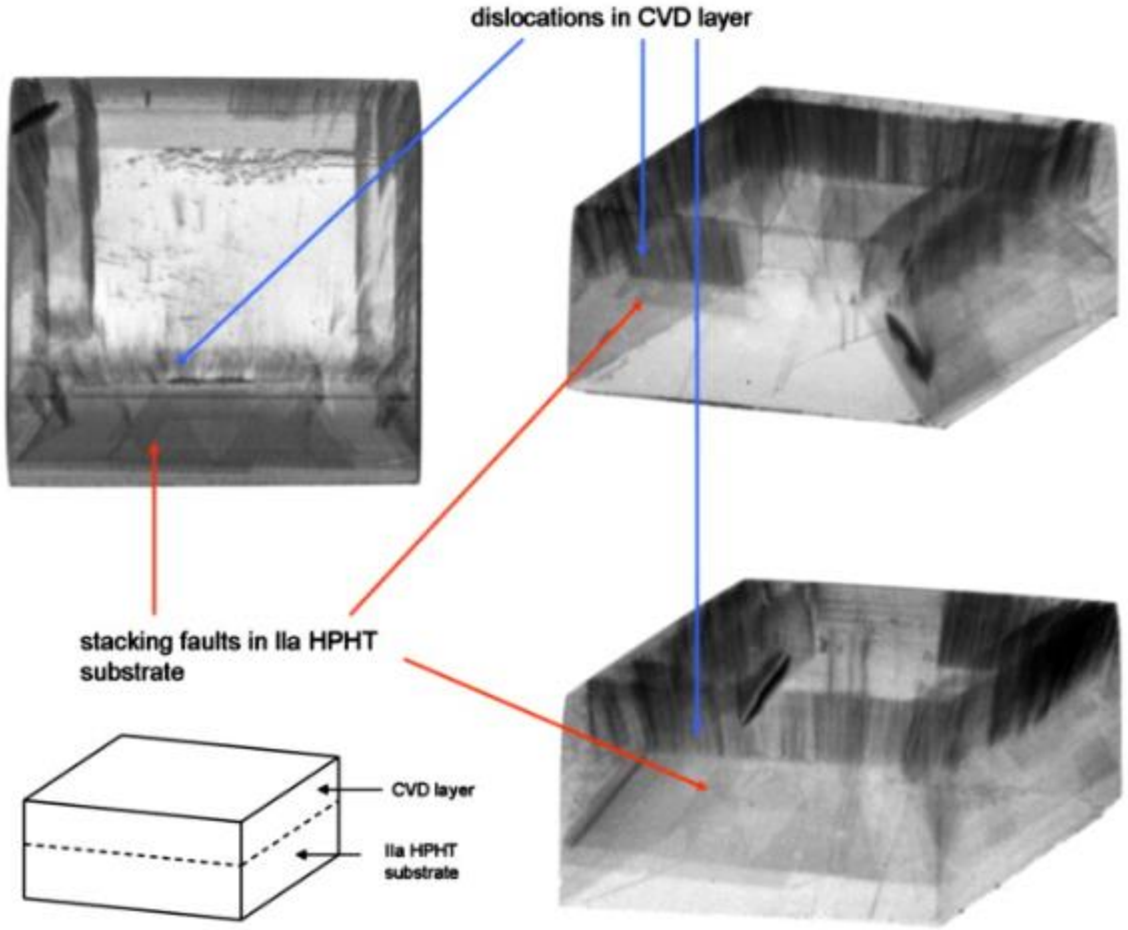
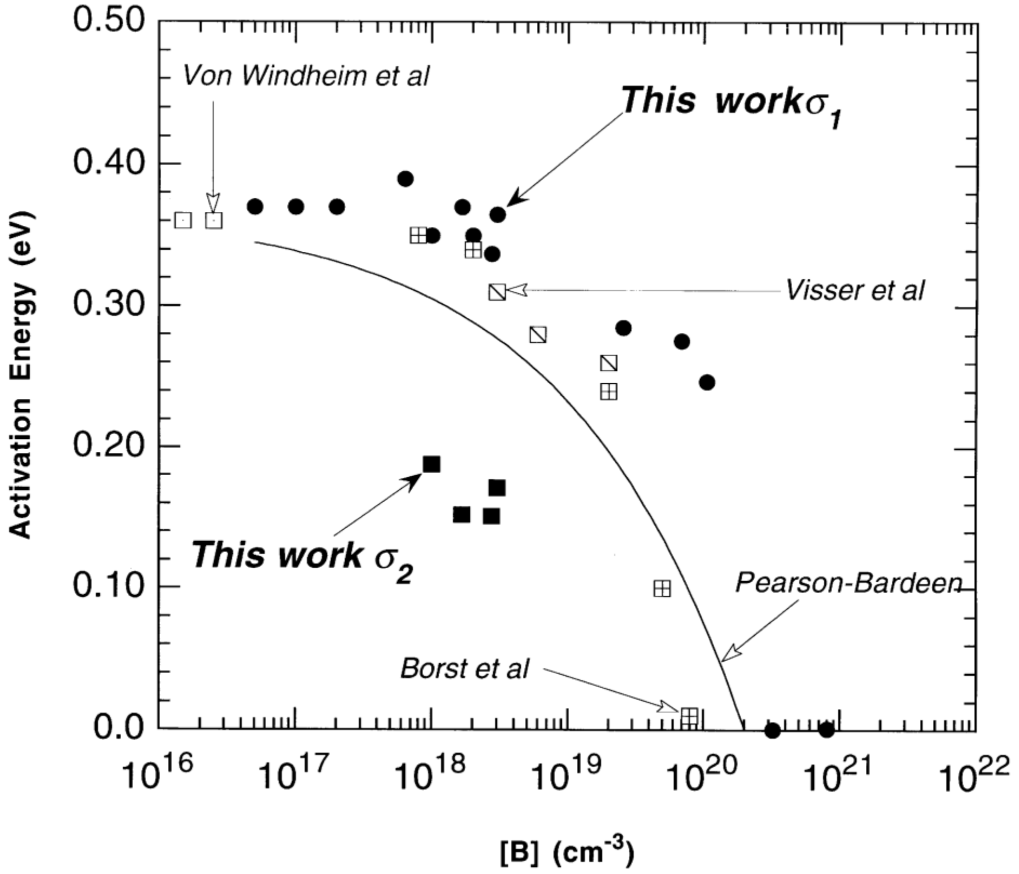


Doping related issues in diamond

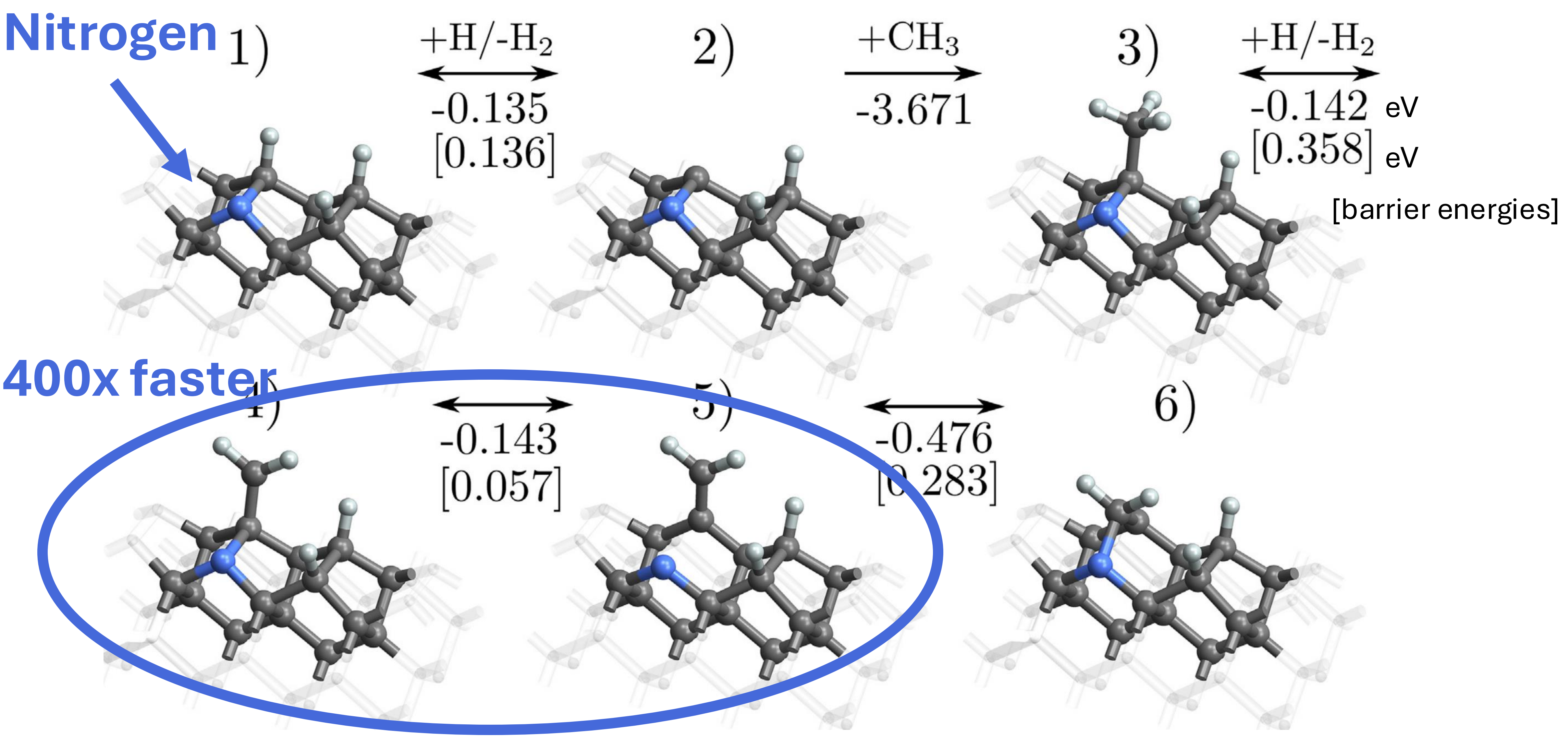
Doping can cause growth defects



High concentrations often needed



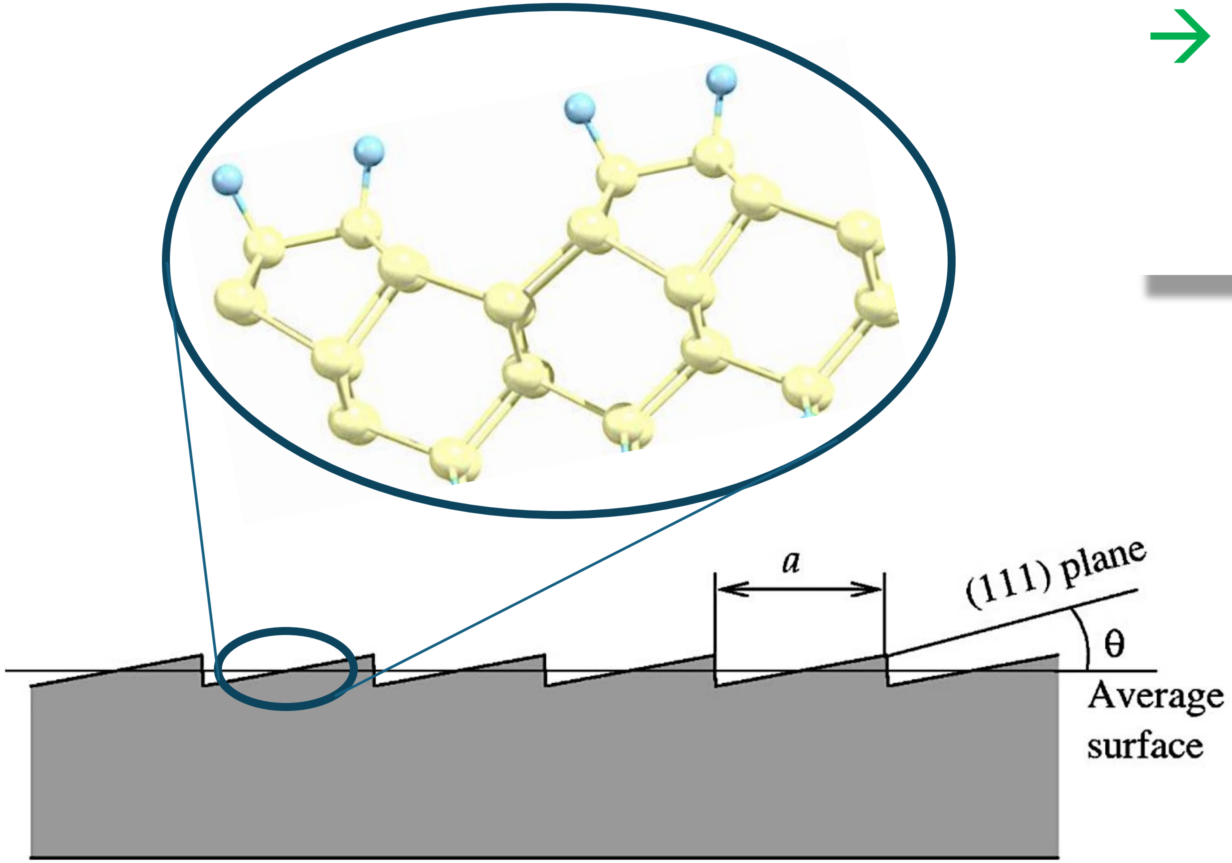
Doping affected growth in diamond

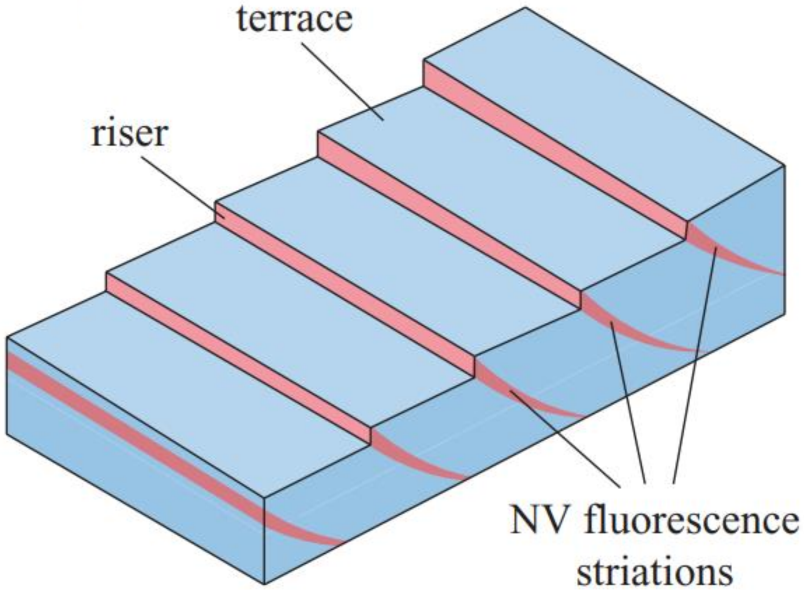


L.M. Oberg, et al. Carbon 178 (2021) 606-615

Doping affected growth in diamond

→ **Misorientation (miscut) angle affects step edge density, doping and morphology**





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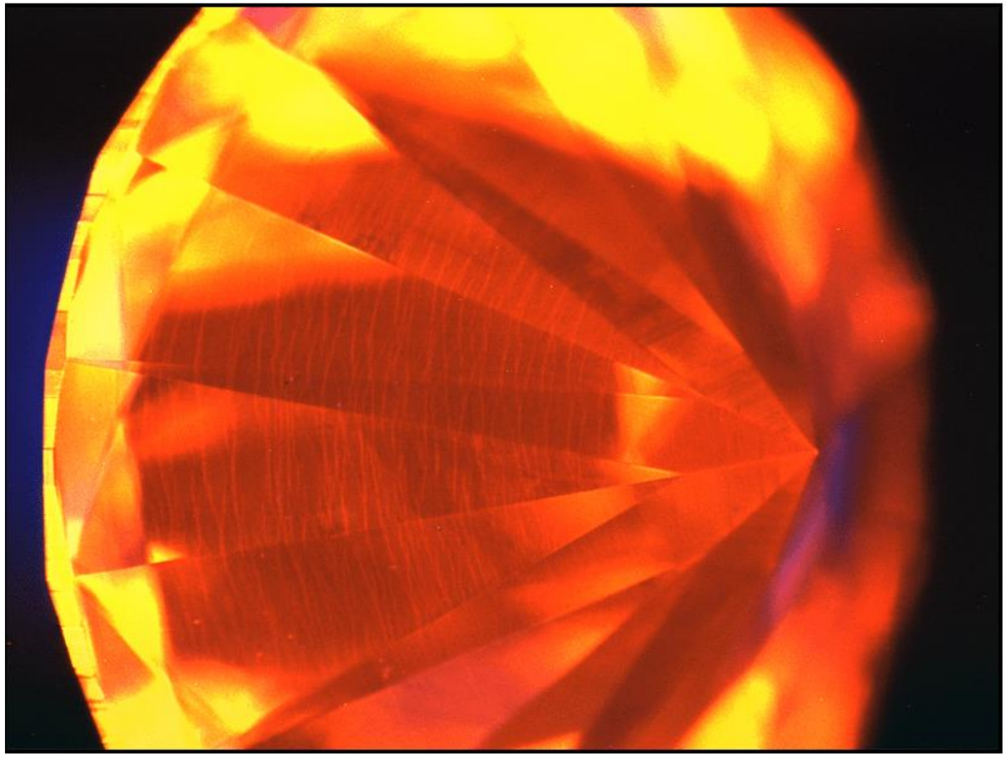

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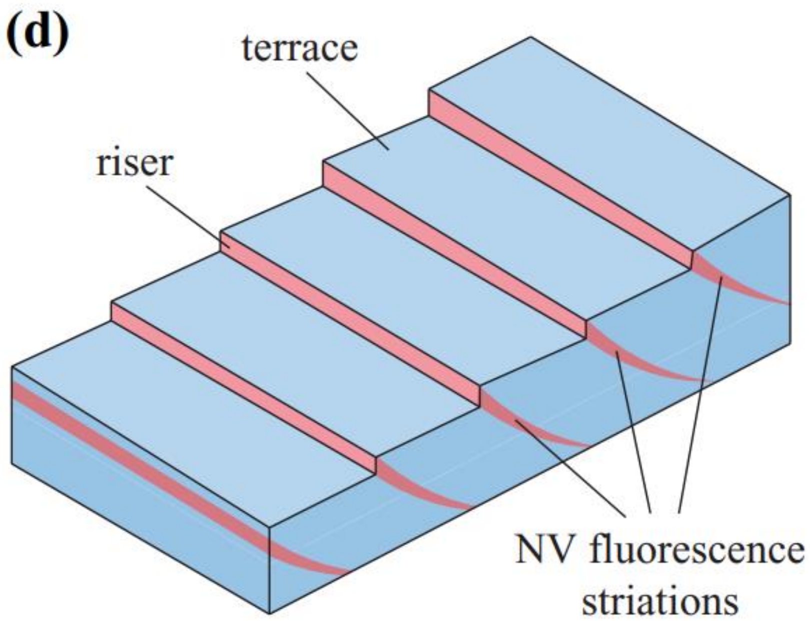
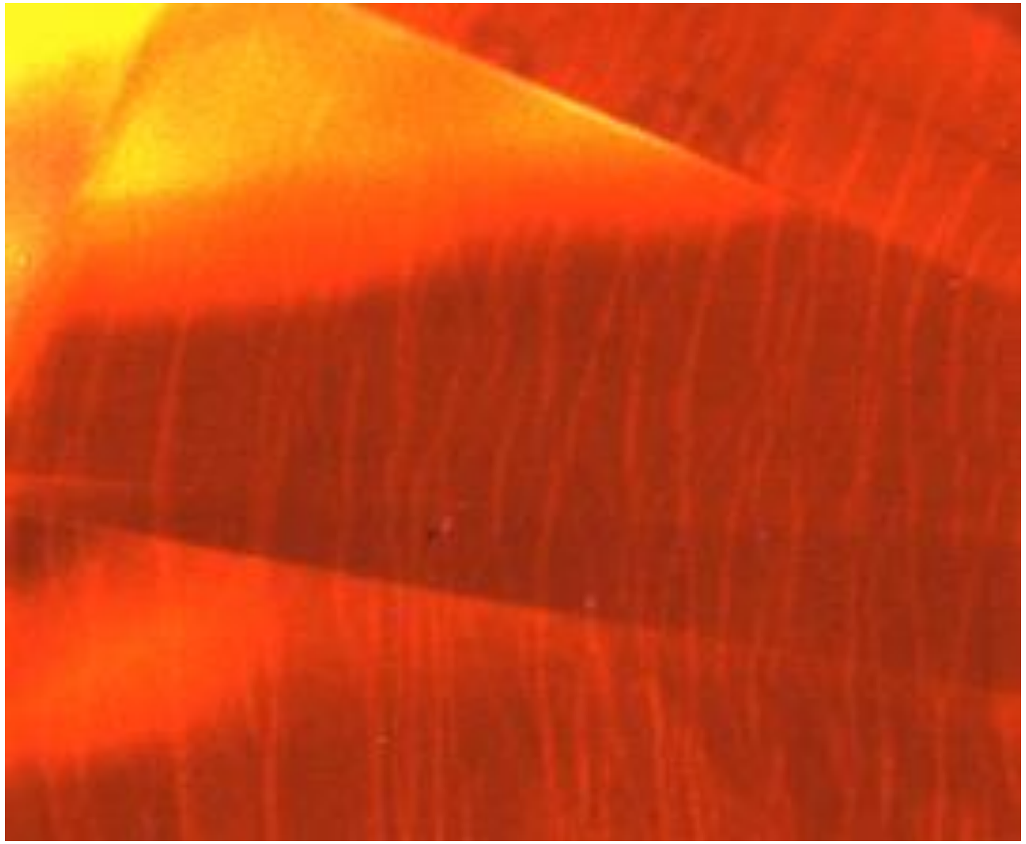


L.M. Pham, et al., Phys. Rev. B **86** (2012) 121202(R)

Doping affected growth in diamond



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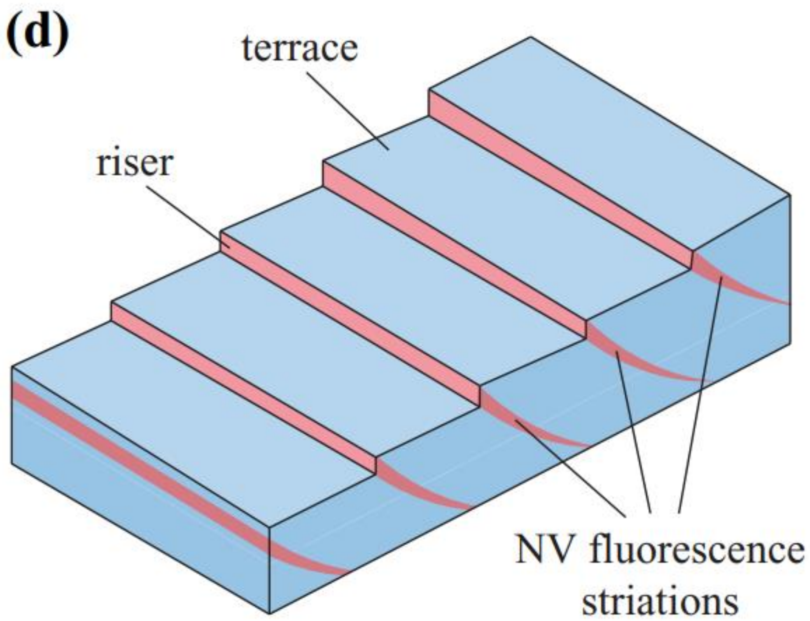
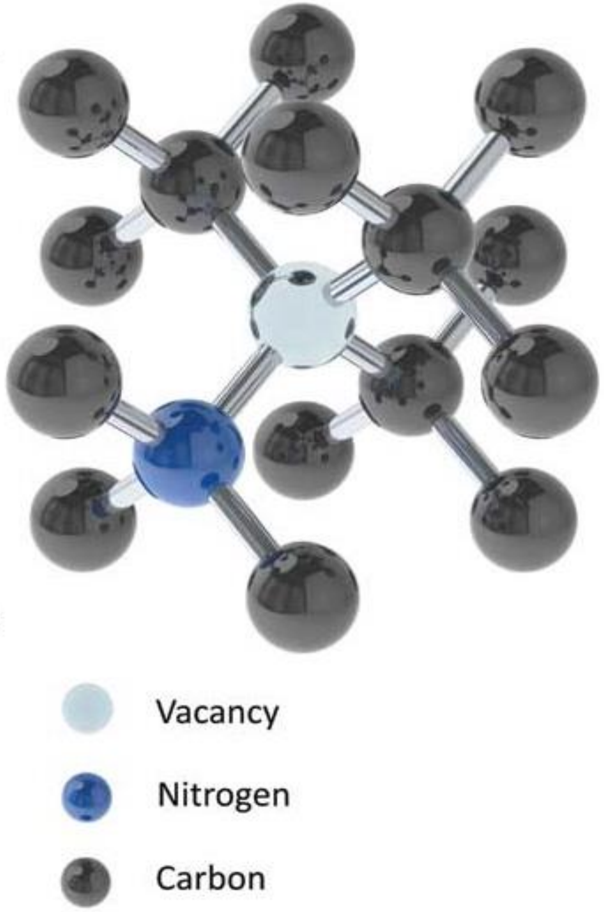
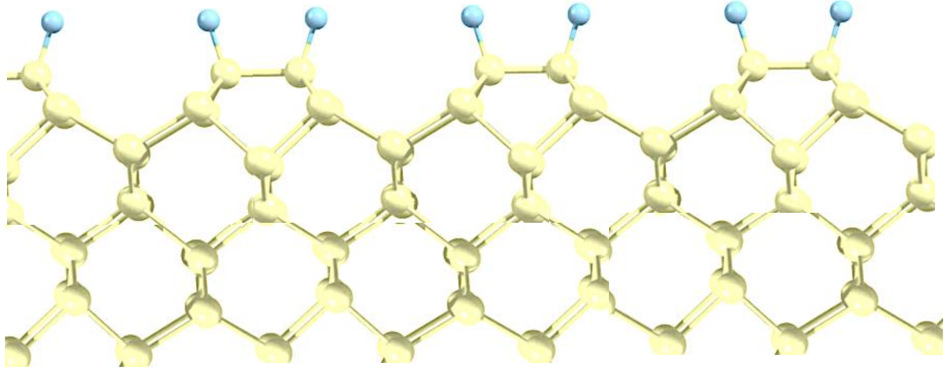
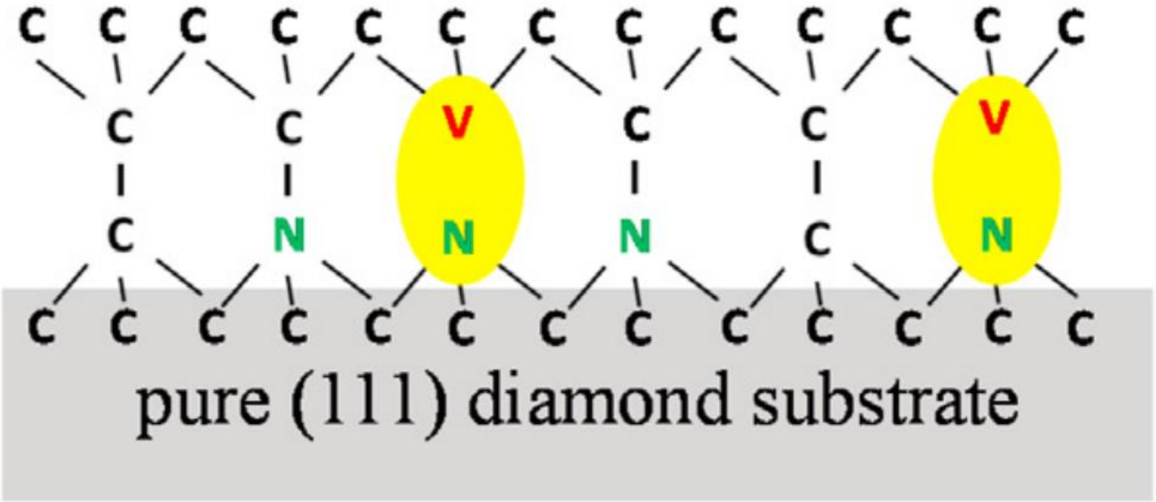


L.M. Pham, et al., Phys. Rev. B **86** (2012) 121202(R)

Aligned NV centres by growth on [111] substrates

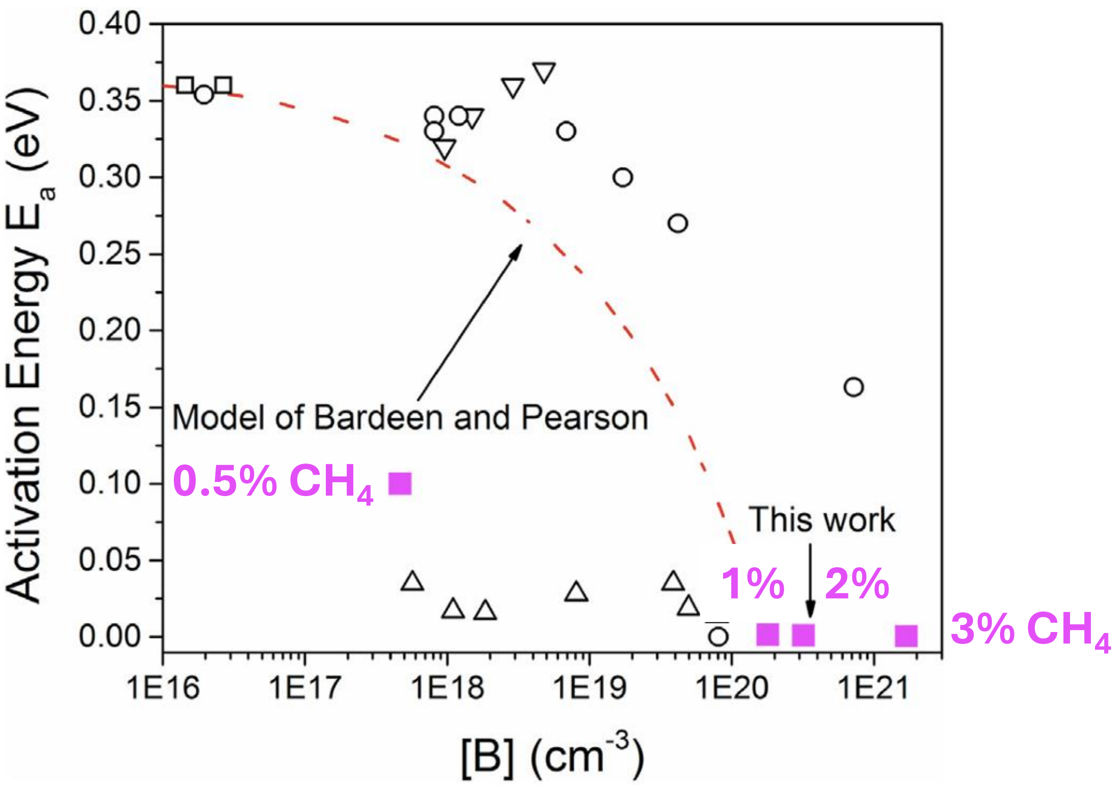


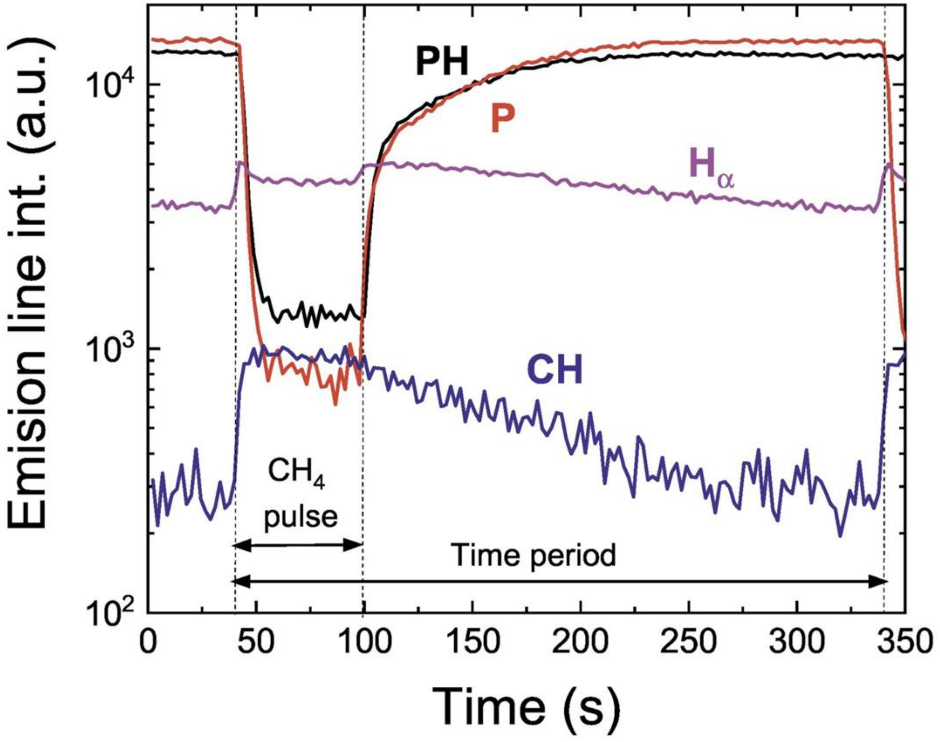




https://doi.org/10.1016/j.carbon.2021.04.057

Doping / growth interference

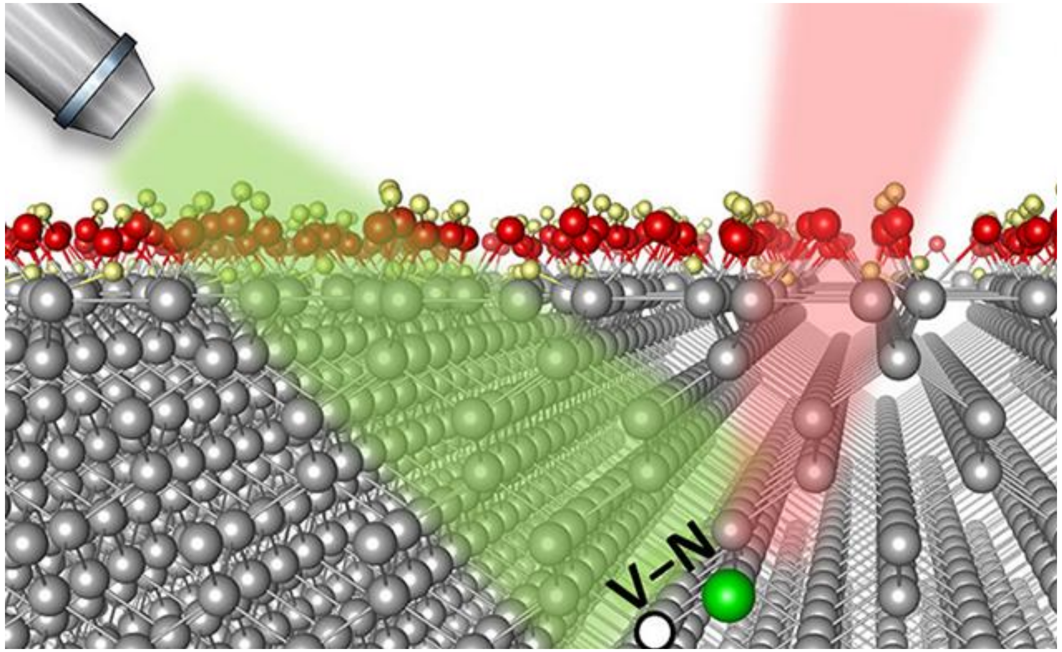


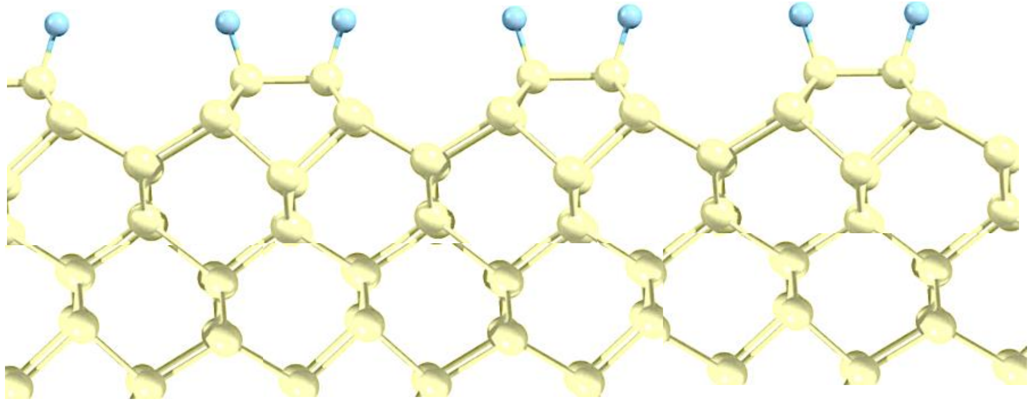


Increase CH4 → Increase [B]

Increase CH4 → Decrease [P]

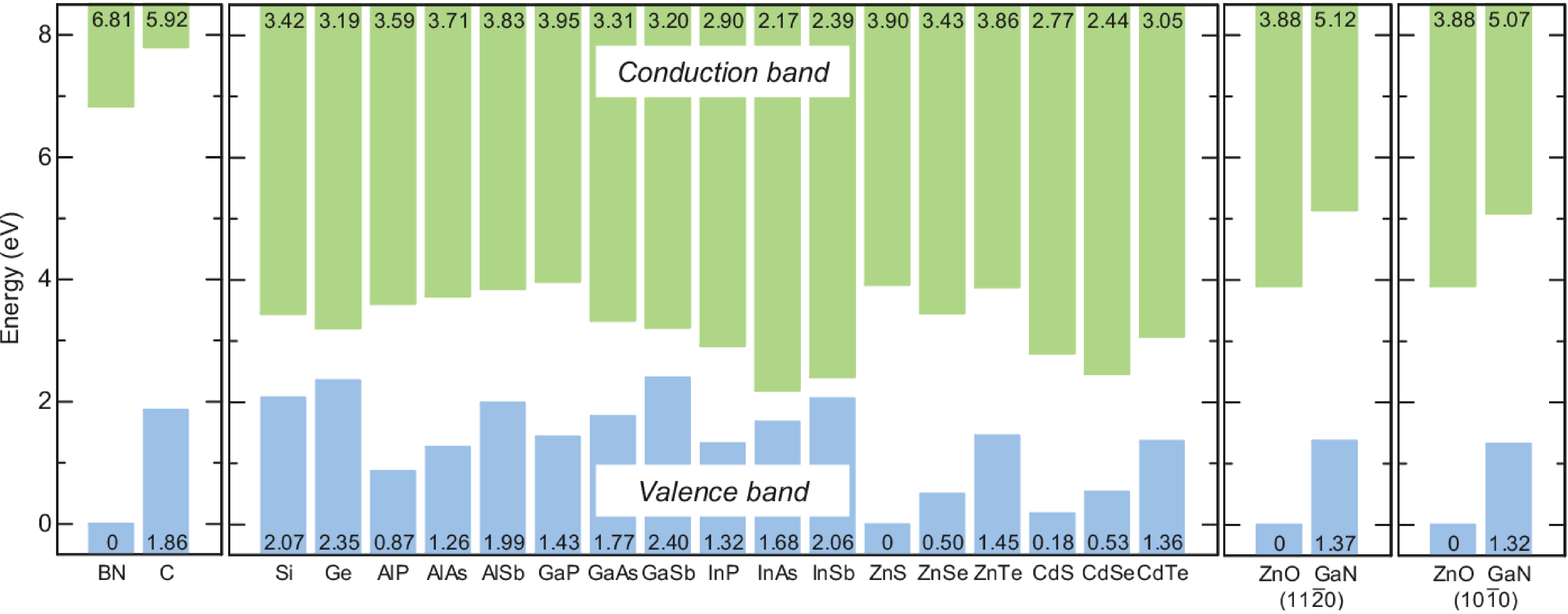
Surface termination peculiarities with diamond





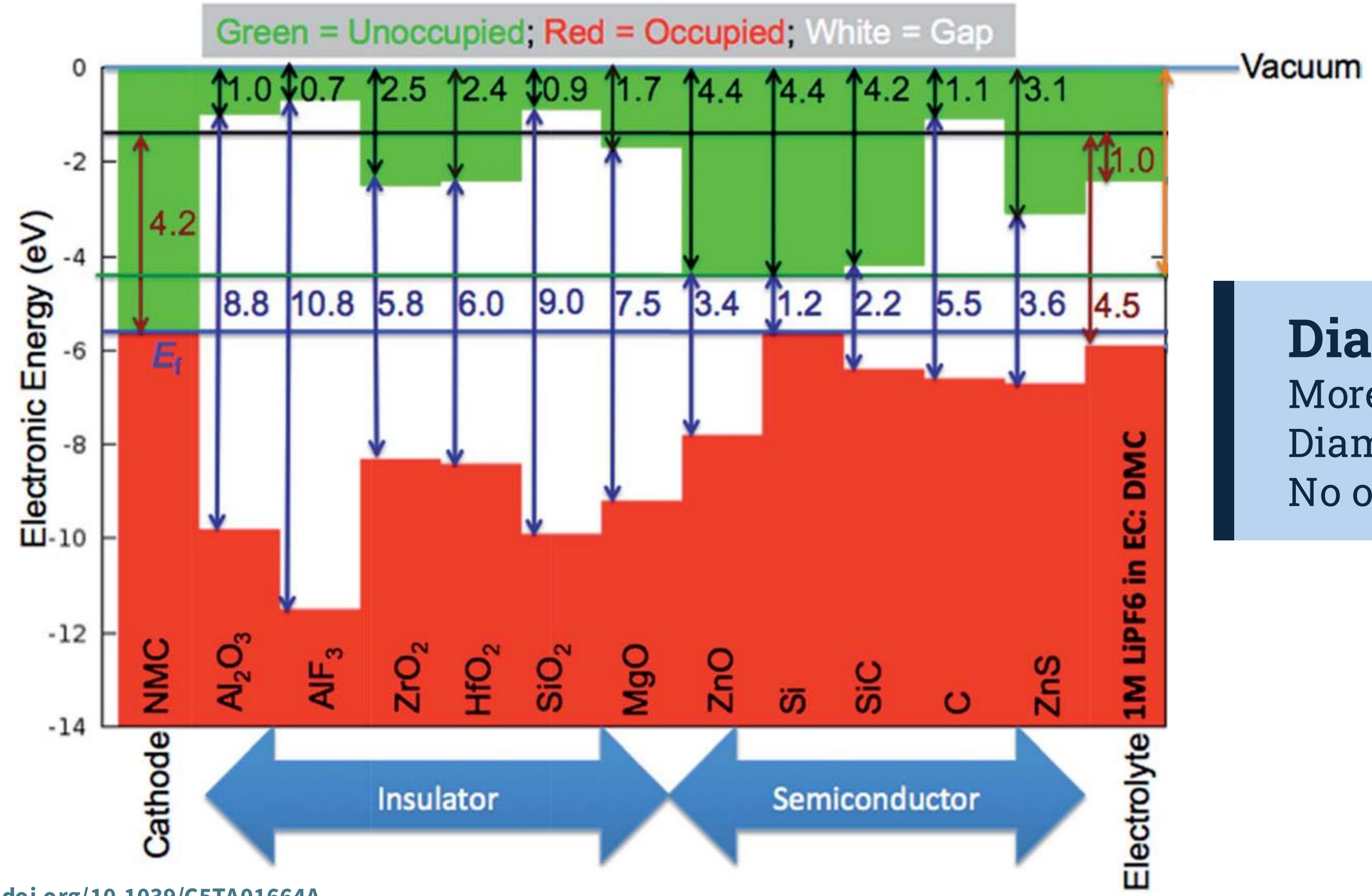
→ Why not use H-termination?

Surface termination peculiarities with diamond



(DFT study) - DOI:10.1103/PHYSREVB.90.155405

Surface termination peculiarities with diamond

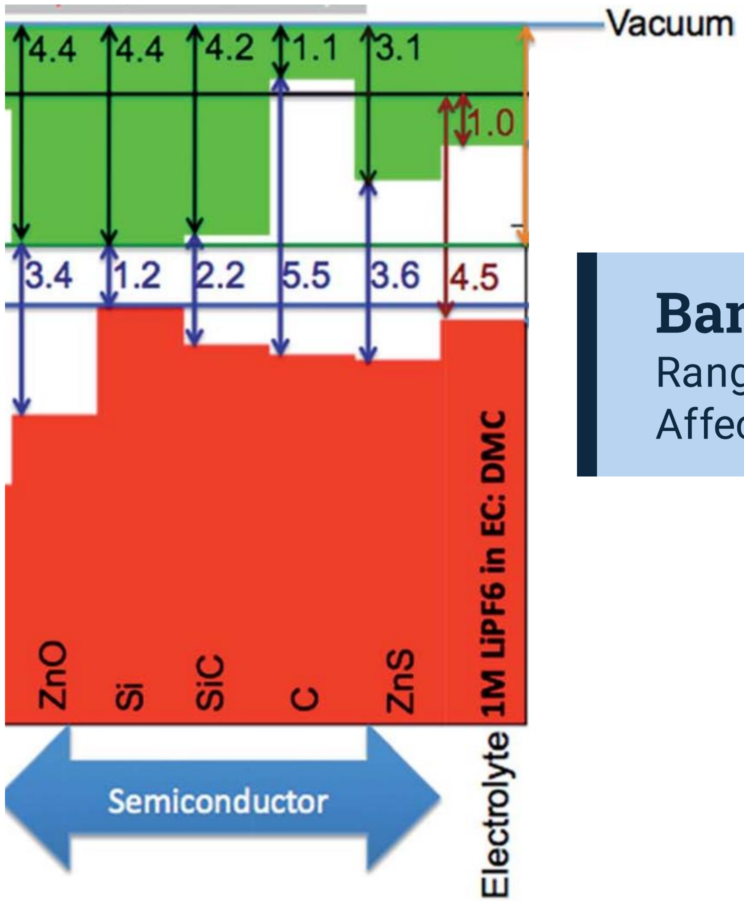


Diamond CBM is very high

More consistent with classic insulators
Diamond can be doped
No oxide or surface polarization doping

DOI https://doi.org/10.1039/C5TA01664A

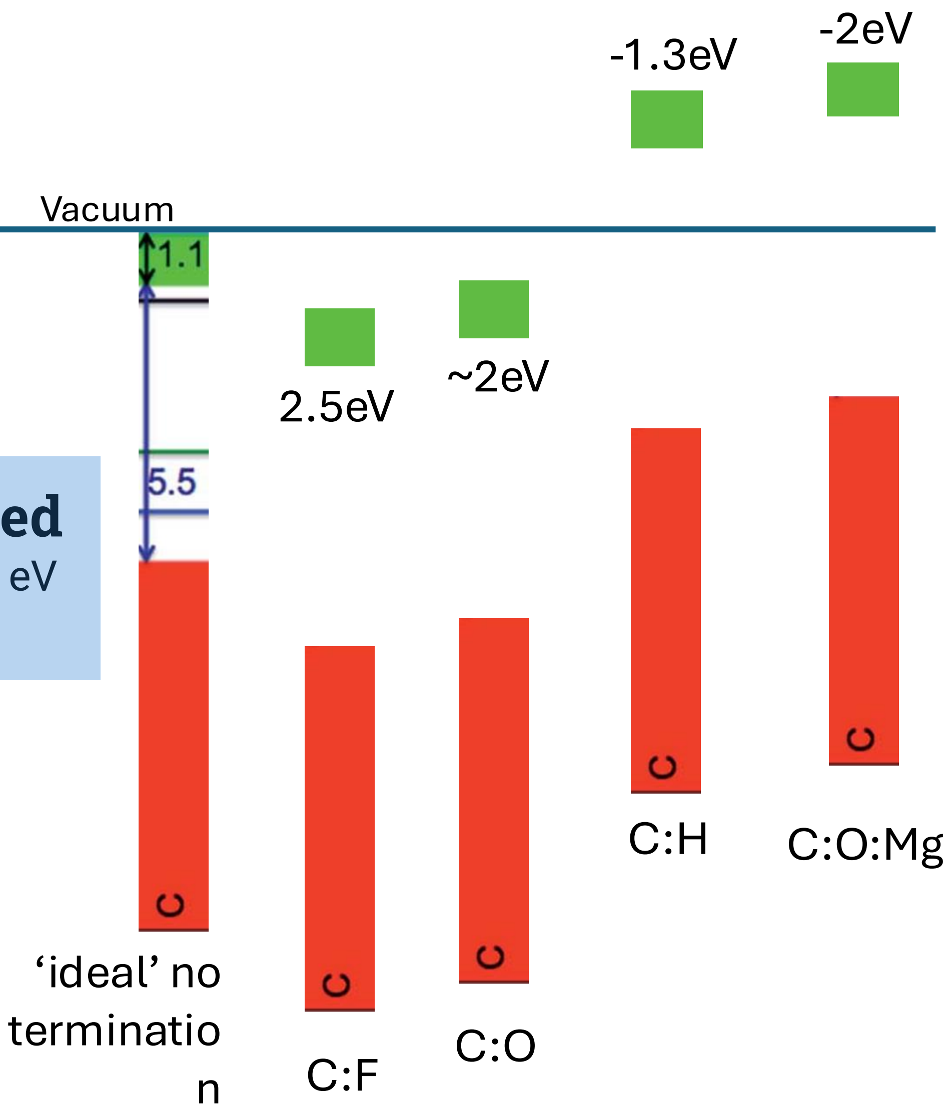
Surface termination affects band alignment



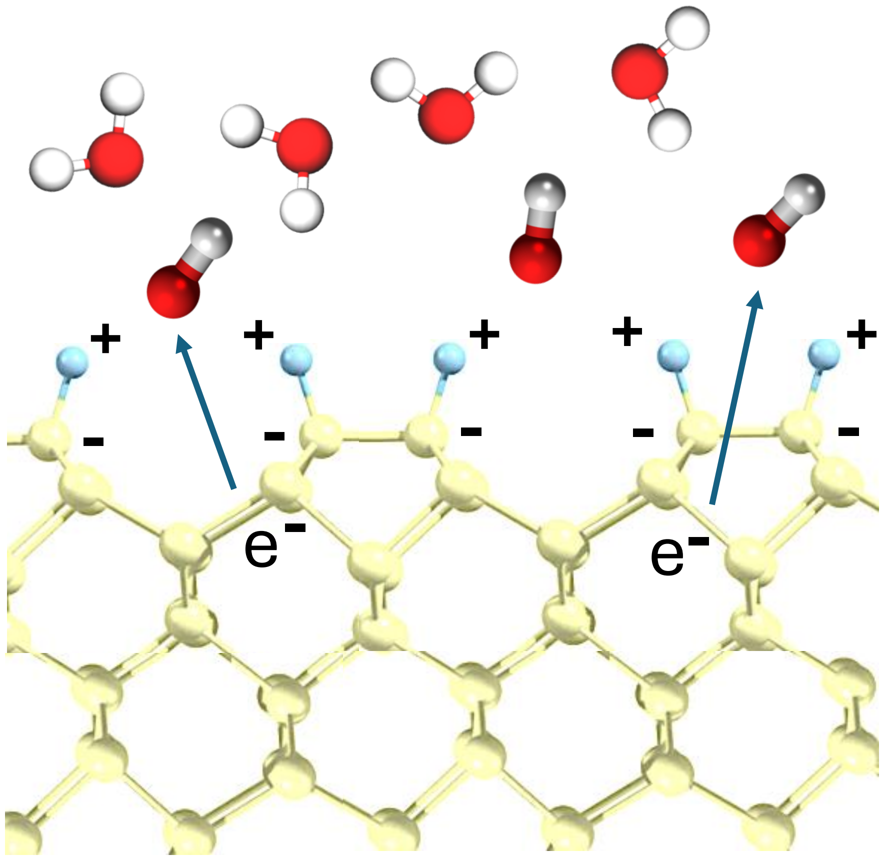
Band can be raised or lowered

Range of electron affinity ~ -2 eV → 2.5 eV

Affected by surface termination dipoles

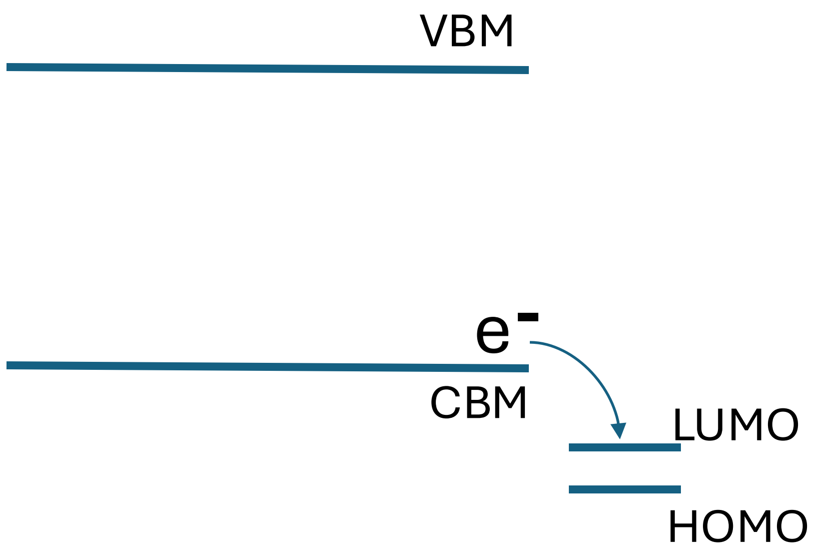


H-termination induced surface conductivity

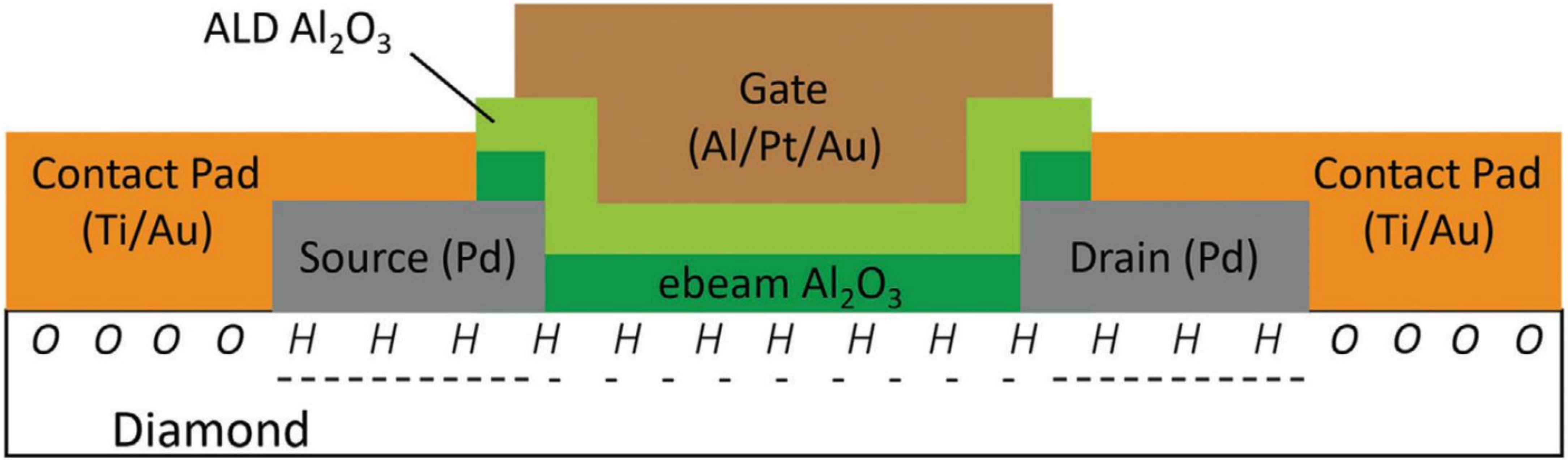


C-H dipole induces electron transfer

External acceptor species become ionized
Leaves behind holes at the diamond surface
Behaves as a 2D-hole-gas (2DHG)

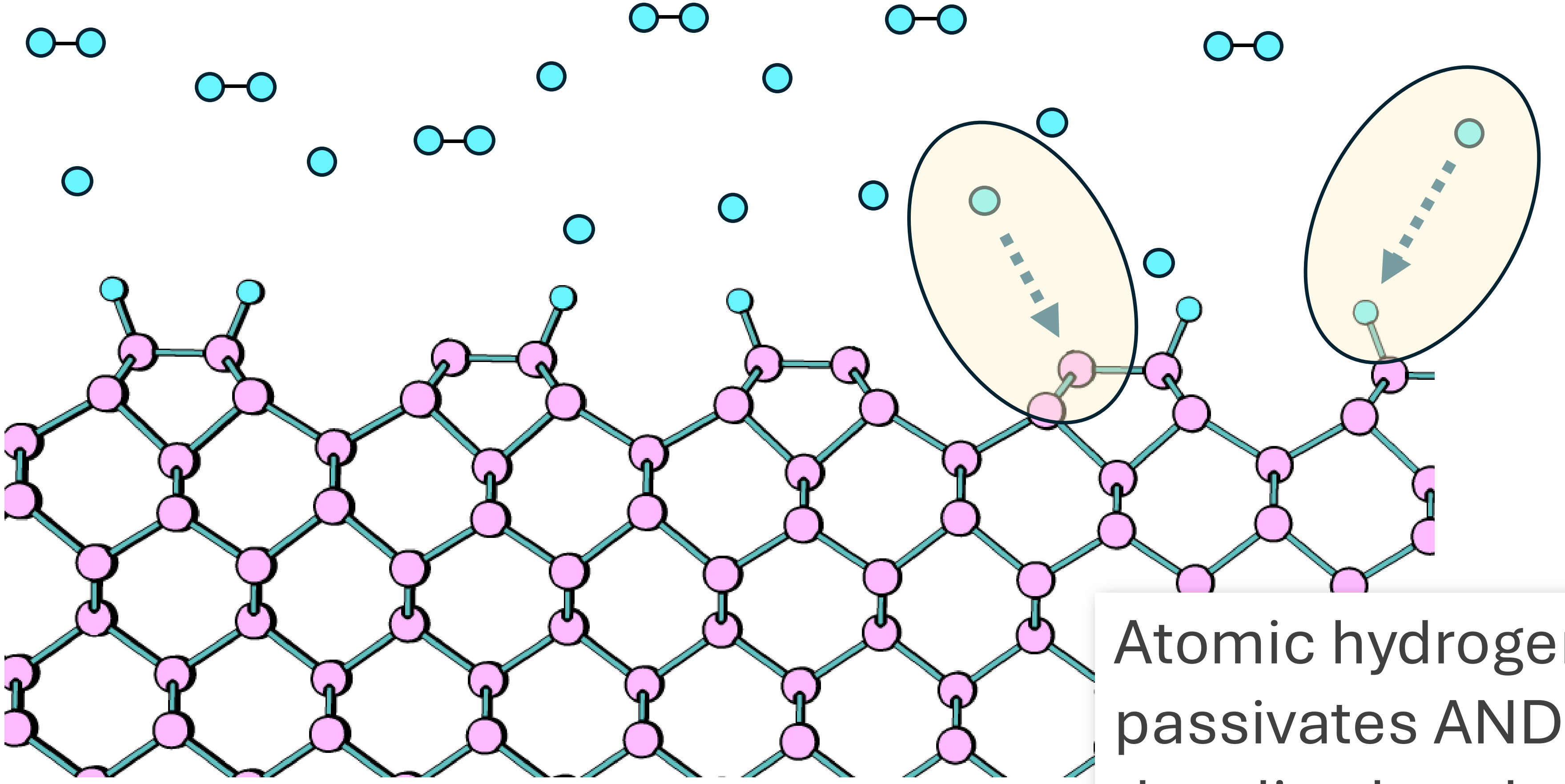


Accumulation mode FET trials



D. Moran group Glasgow U.

Hydrogen termination without diffusion/etching



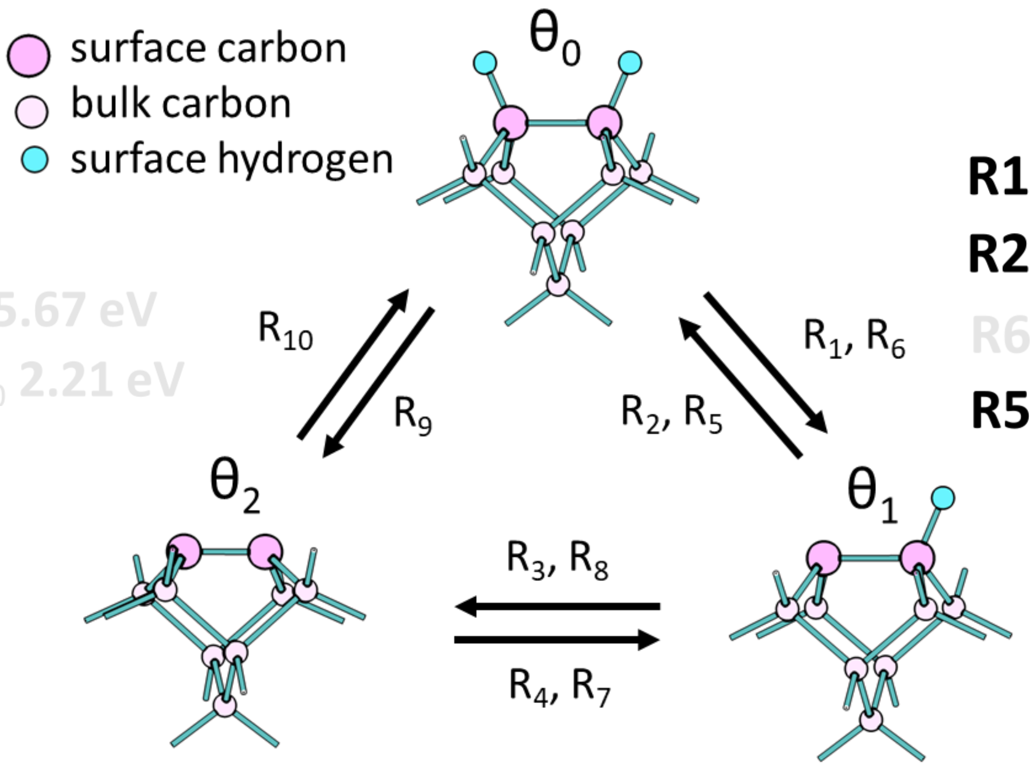
Atomic hydrogen both passivates AND creates dangling bonds

Barsukov, PPPL

→ Can we hydrogen terminate without atomic hydrogen?

Modeling H-termination with H˙ and H2

Y. Barsukov & I. Kaganovich
Princeton Plasma Physics Laboratory



R1: $H^* + \theta_0 \rightarrow H_2 + \theta_1$ **0.33 eV**

R2: $H_2 + \theta_1 \rightarrow H^* + \theta_0$ **0.30 eV**

R6: $\theta_0 \rightarrow H^* + \theta_1$ **4.40 eV**

R5: $H^* + \theta_1 \rightarrow \theta_0$ **0 eV**

R9: $\theta_0 \rightarrow H_2 + \theta_0$ **5.67 eV**

R10: $H_2 + \theta_2 \rightarrow \theta_0$ **2.21 eV**

R3: $H^* + \theta_1 \rightarrow H_2 + \theta_2$ **0.16 eV**

R4: $H_2 + \theta_2 \rightarrow H^* + \theta_1$ **1.11 eV**

R7: $H^* + \theta_2 \rightarrow \theta_1$ **0.03 eV**

R8: $\theta_1 \rightarrow H^* + \theta_2$ **3.46 eV**

D. McCloskey *et al*, https://doi.org/10.1002/admi.202400242

Modeling H-termination with H˙ and H2

Y. Barsukov & I. Kaganovich

Model with fluxes and populations

R1: $H^* + \theta_0 \rightarrow H_2 + \theta_1$ **0.33 eV**

R2: $H_2 + \theta_1 \rightarrow H^* + \theta_0$ **0.30 eV**

R6: $\theta_0 \rightarrow H^* + \theta_1$ **4.40 eV**

R5: $H^* + \theta_1 \rightarrow \theta_0$ **0 eV**

R9: $\theta_0 \rightarrow H_2 + \theta_0$ **5.67 eV**

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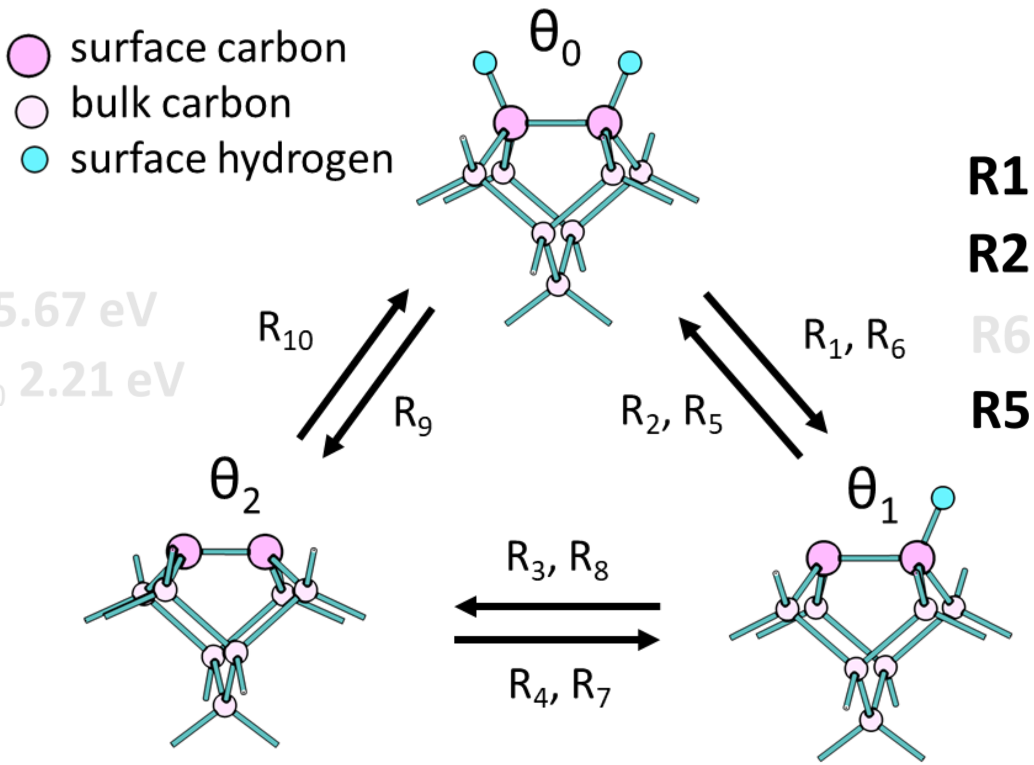

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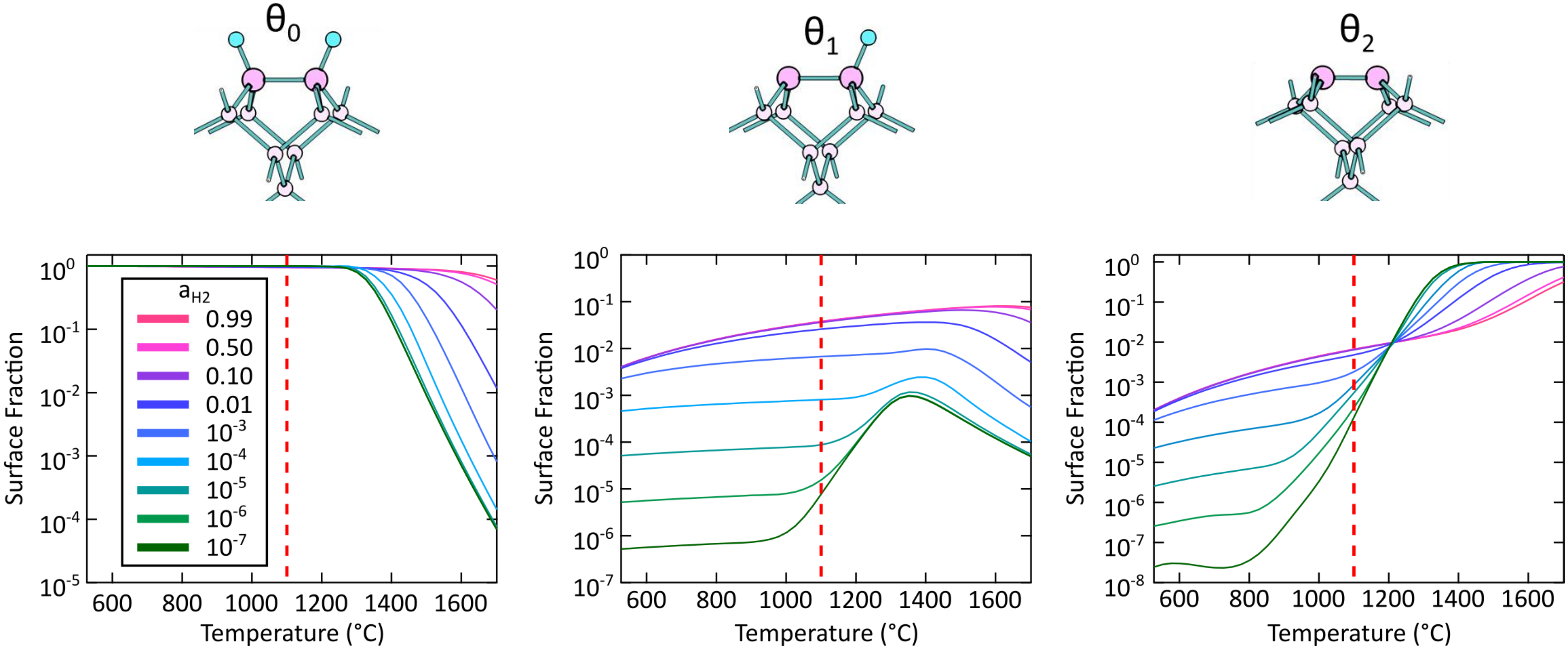
R8: $\theta_1 \rightarrow H^* + \theta_2$ **3.46 eV**

H2 reactions important

Include thermal desorption of H

D. McCloskey *et al*, https://doi.org/10.1002/admi.202400242

Modeling H-termination with $H^{\bullet}$ and H_2



D. McCloskey *et al*, https://doi.org/10.1002/admi.202400242

→ H_2 can be used to H-terminate diamond

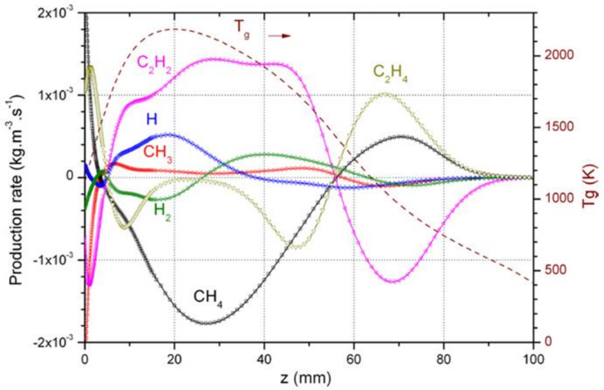
Conclusions

- Diamond growth by plasma is maturing for both QIS and Microelectronics applications
- Much plasma & plasma-surface/epitaxy science to be done in controlling dopants, cost, area
- Surface chemistry requires a focus on low-ion-damage processes

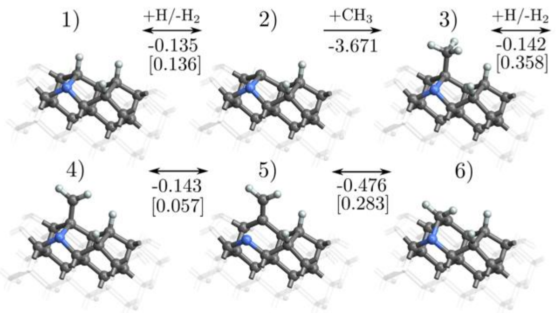
Integrated Plasma Science for Quantum Diamond

| Modeling

Igor Kaganovich

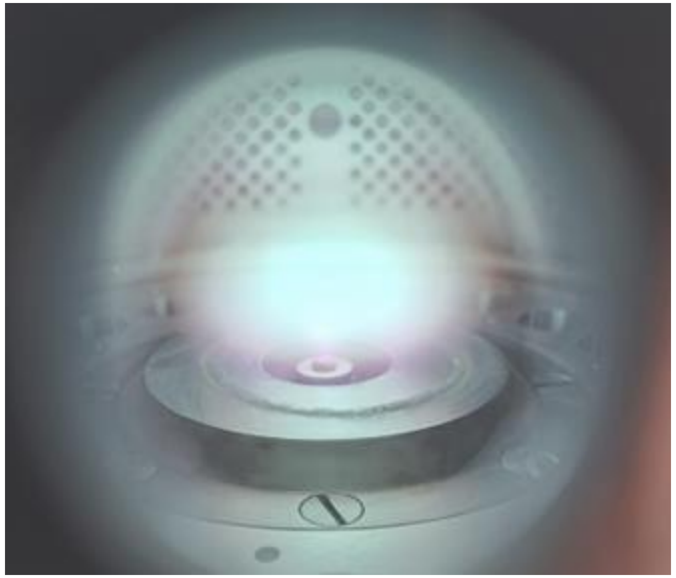


K. Hassouni, et al., J.Phys.D:Appl.Phys. 43(2010)153001



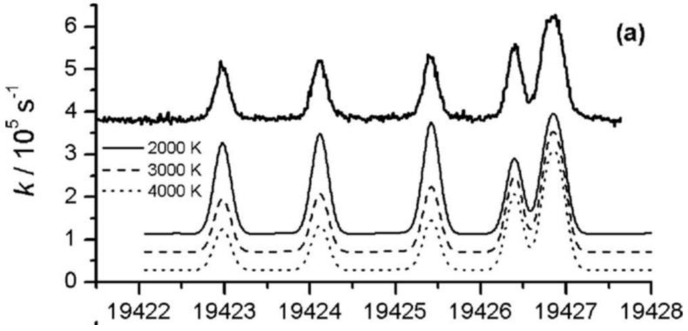
Oberg, Stacey, et al, 2021

| Growth

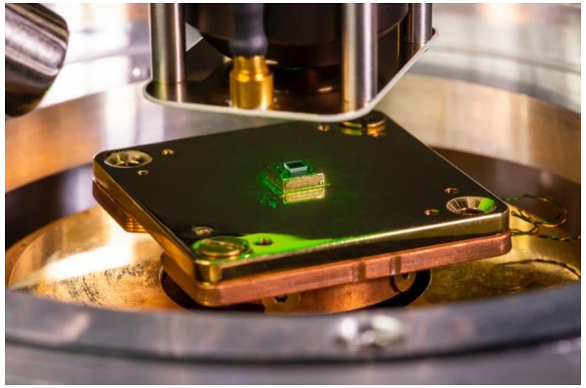


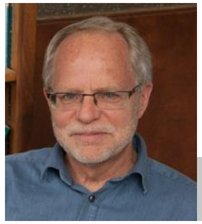
| Diagnostics

Yevgeny Raitses



J. Ma, et al., J.Appl.Phys.104,103305 2008





David Graves

Nathalie de Leon