Advances in N-doped Diamond Thin Films grown by Microwave Plasma CVD

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Diamond Growth

Naturally occurring diamonds are formed 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

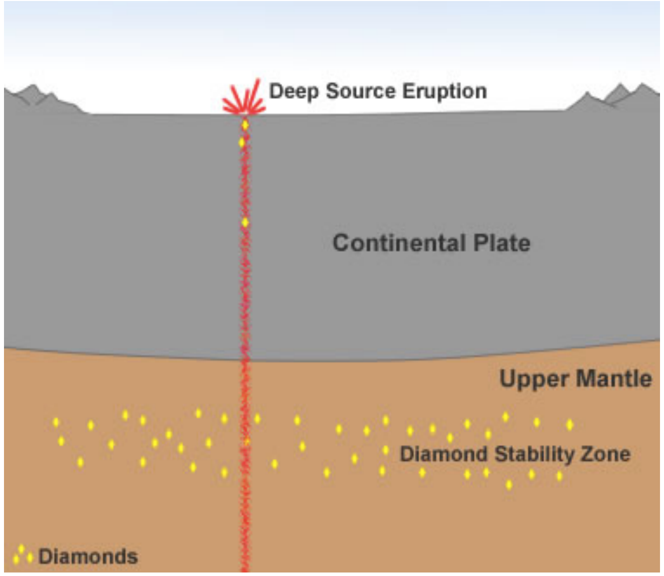
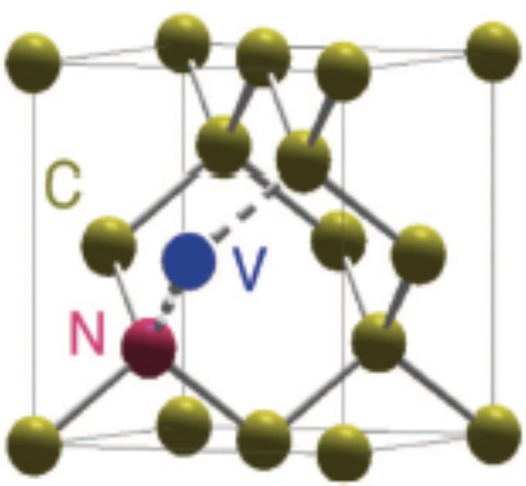


Figure credit: geology.com

Applications of Diamond Films

- Beyond the gemstone market, diamond films have a number of applications (hard coatings, transparent windows, etc.)
- Diamond is also a wide bandgap semiconductor and can also be doped
- a particularly interesting dopant is nitrogen (N)

The Diamond NV Centre



The NV Centre in Diamond- a special type of defect:
A substitutional nitrogen (N) *adjacent* to a vacancy (V)
Can be made in various ways:

- e-beam or Ion implantation followed by annealing at 800 C
- Nitrogen Ion implantation (introduces N and creates vacancies)
- Direct deposition of N-doped diamond films via CVD

Two NV Centre Charge States:

- NV0, with a zero-phonon line at 575 nm
- &
- Negatively charged NV−, with a zero-phonon line at 637 nm

NV Centre in Diamond Schematic
[Figure Credit: D. Zheng, Ph.D. Thesis (Ecole Normale Cachan, 2010) Fig 2.3]

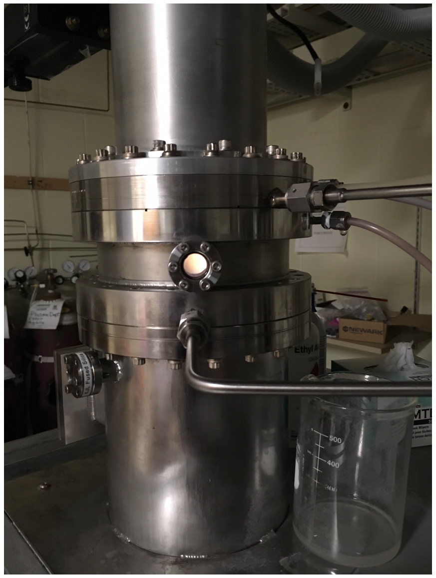
Magnetometry using the NV^- Centre

The NV- centre acts like a localized "artificial atom" with narrow atomic-like energy states and a magnetic fine structure

→Sub-nanotesla precision measurement of magnetic fields using NV centres is possible. This has many interesting sensor applications

- Geomagnetism: currently SQUIDS are the best sensors, but they require bulky cryogenic systems
- Electric Power Systems, Biomagnetism (pT required)
- Diamond NV centres are also possible Quantum Information Qbits

Microwave Plasma-Enhanced CVD for diamond film growth



Microwave plasma Regime

Frequency 2.45 GHz

Power: 500 - 800 Watt
Pressure: 23 - 100 Torr

Feed gas ratio ~ 99% H_2/1% CH_4 (excess hydrogen)

Film growth rate:

~ 0.1 – 1 μm/hour

I. Synthesis of NV Centres in polycrystalline diamonds at low pressure

- Polycrystalline diamond (PCD) films were deposited on a 3 mm x 3 mm x 0.5 mm
- P-type boron doped silicon substrate of
- resistivity 5Ωcm (Silicon Material Inc.) in a 2.45 GHz MPCVD reactor (Plasmionique Inc.).

- The silicon substrate has a ⟨100⟩ orientation.
- Prior to growth, the silicon substrates were nucleated by treating the surface with a mixture of diamond powder and ethyl-alcohol in an ultrasonic bath for 30 min.

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Diamond deposition was carried out at 800 W microwave power. Film growth in large excess of H_2 and 30 Torr (4 kPa) process pressure

Group	Sample	H_2–CH_4–N_2 flow (sccm)	Growth time + Doping time (hrs)	
1	S1	100–1–0	14 + 0	11 ± 0.1 μm
	S5	100–1–1.5	13 + 1	
	S9	100–1–10	13 + 1	
2	S2	200–1–0	14 + 0	
	S6	200–1–2	12 + 2	
	S10	200–1–20	12 + 2	
3	S3	300–0.75–0	14 + 0	
	S7	300–0.75–3	13 + 3	
	S11	300–0.75–30	11 + 3	
4	S4	400–0.5–0	14 + 0	2.5 ± 0.07 μm
	S8	400–0.5–4	10 + 4	
	S12	400–0.5–40	10 + 4	

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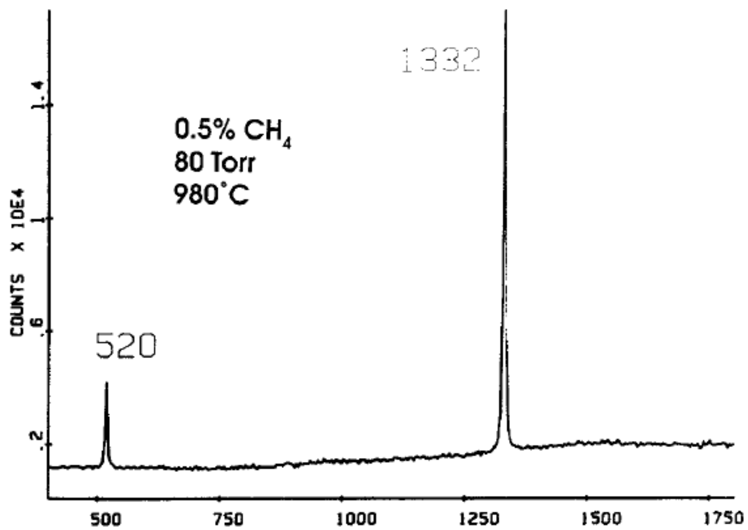
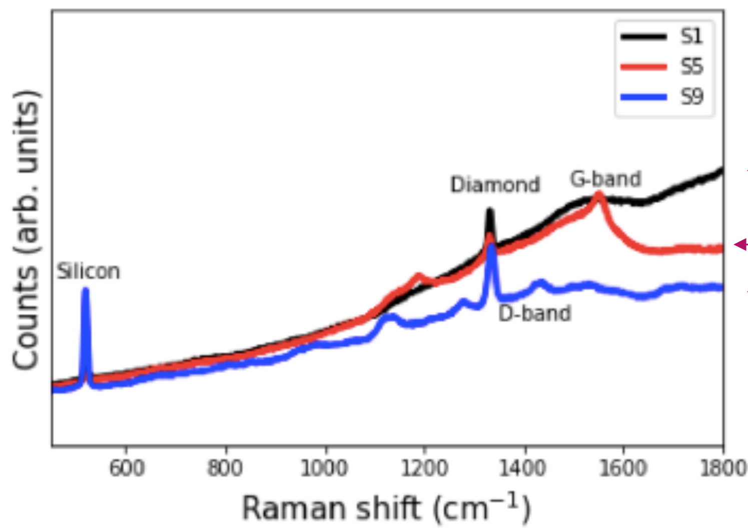
Signature of Diamond: Raman line at 1332 cm^{-1}



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

Raman Spectra of Films in Group 1 (100 sccm H_2/1.5 sccm CH_4)



N_2 flow =0 sccm

N_2 flow =1.5 sccm

N_2 flow = 10 sccm

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Raman Peak

Group	Sample	FWHM (D) (cm^{-1})	Center of Diamond peak (cm^{-1})	Color
1	S1	8.232	1331.2	Grey
	S5	7.695	1331.7	Lustrous grey
	S9	7.792	1332.0	Lustrous grey
2	S2	10.989	1331.3	Grey
	S6	11.268	1331.9	Lustrous grey
	S10	8.875	1331.9	Lustrous grey
3	S3	8.201	1332.0	Grey
	S7	13.320	1331.2	Grey
	S11	14.662	1332.5	Black
4	S4	8.586	1331.5	Grey
	S8	8.752	1331.4	Dark grey
	S12	15.463	1333.8	Black

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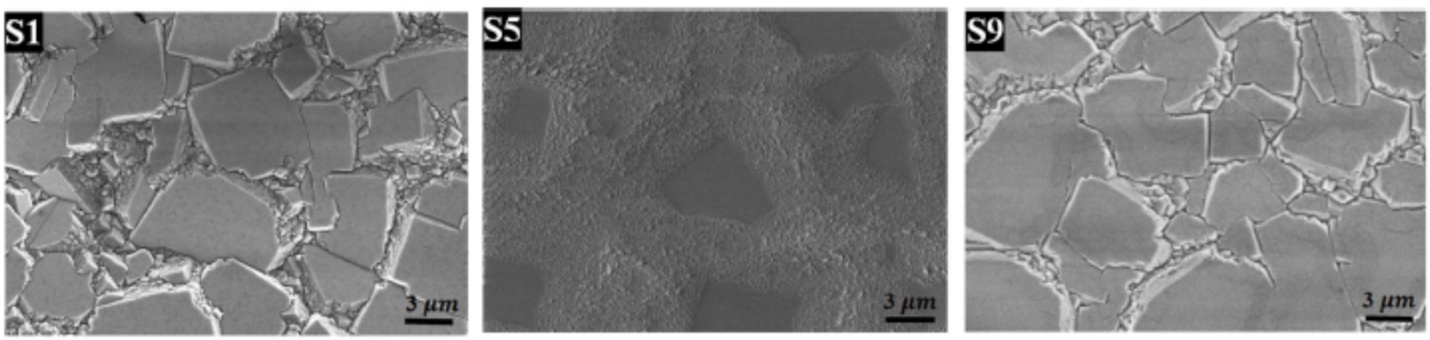
Surface Morphology Group 1 Samples



Lowest H_2 flow case: 100 sccm

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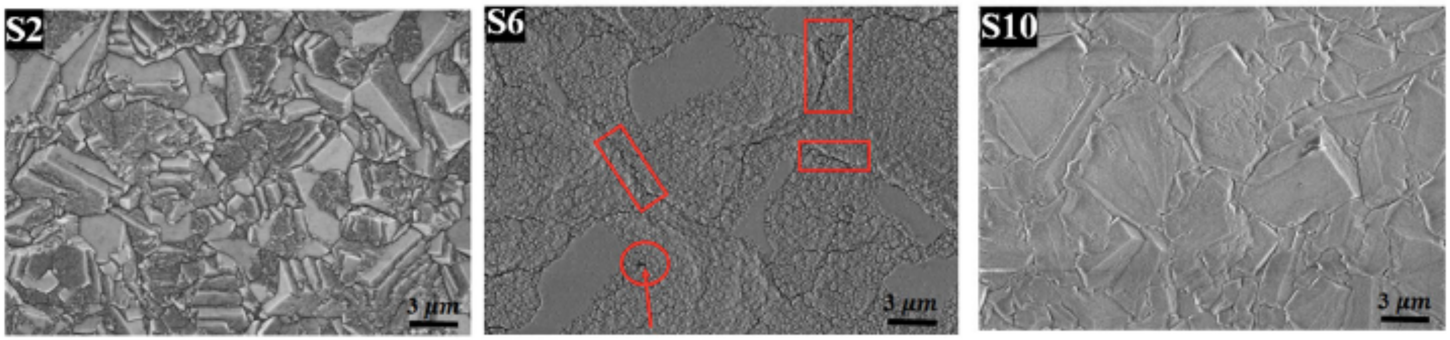
Surface Morphology Group 2 Samples



Note presence of cracks

Higher H_2 flow case: 200 sccm

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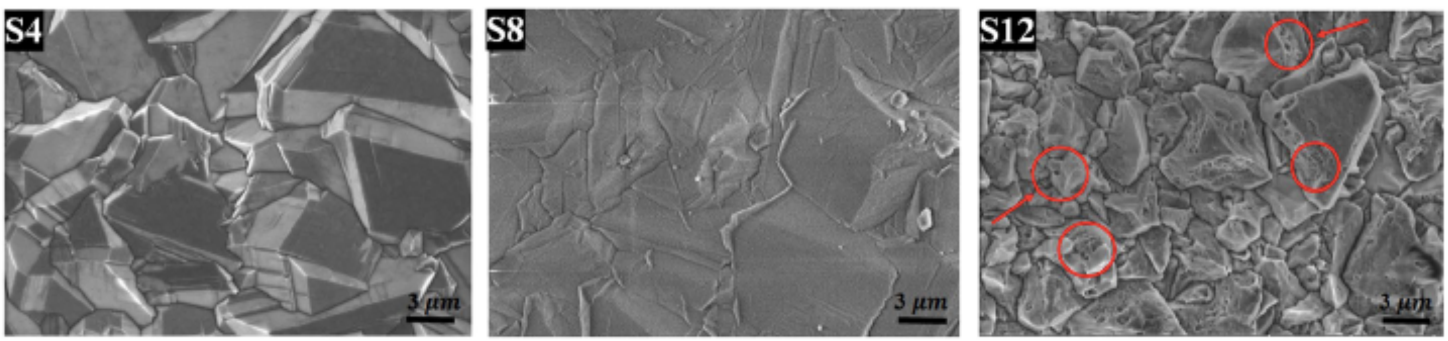
Surface Morphology Group 4 Samples



Highest H_2 flow case: 400 sccm

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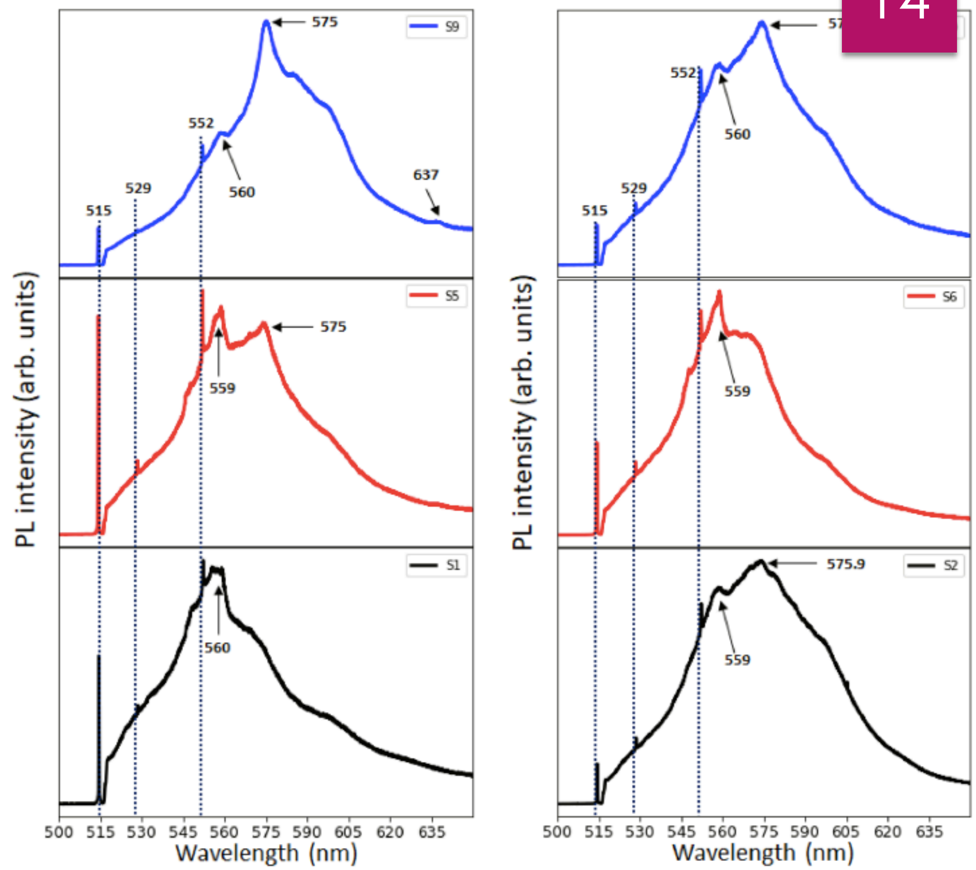
Photoluminescence Spectra

- 515 nm line: Ar ion laser
- 575 nm: NV0
- 637 nm: NV^-



Group 1 Group 2

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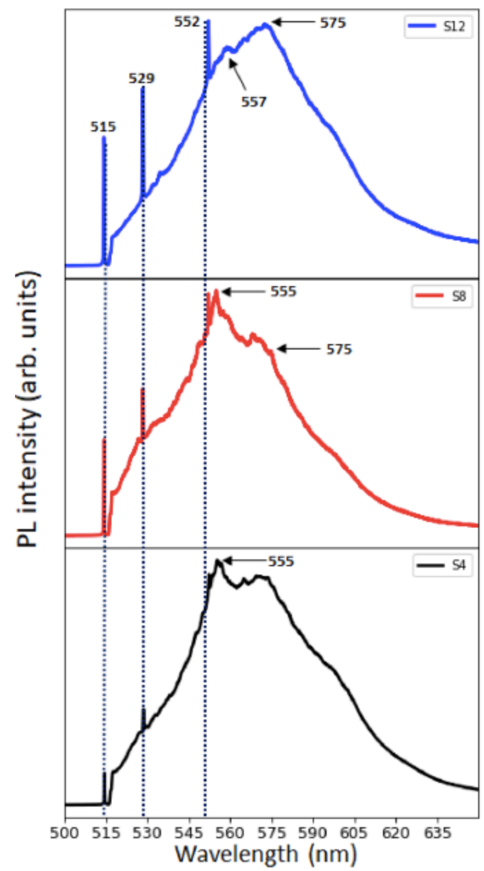
Photoluminescence Spectra

- 515 nm line: Ar ion laser
- 575 nm: NV0
- 637 nm: NV$^-$



Group 4

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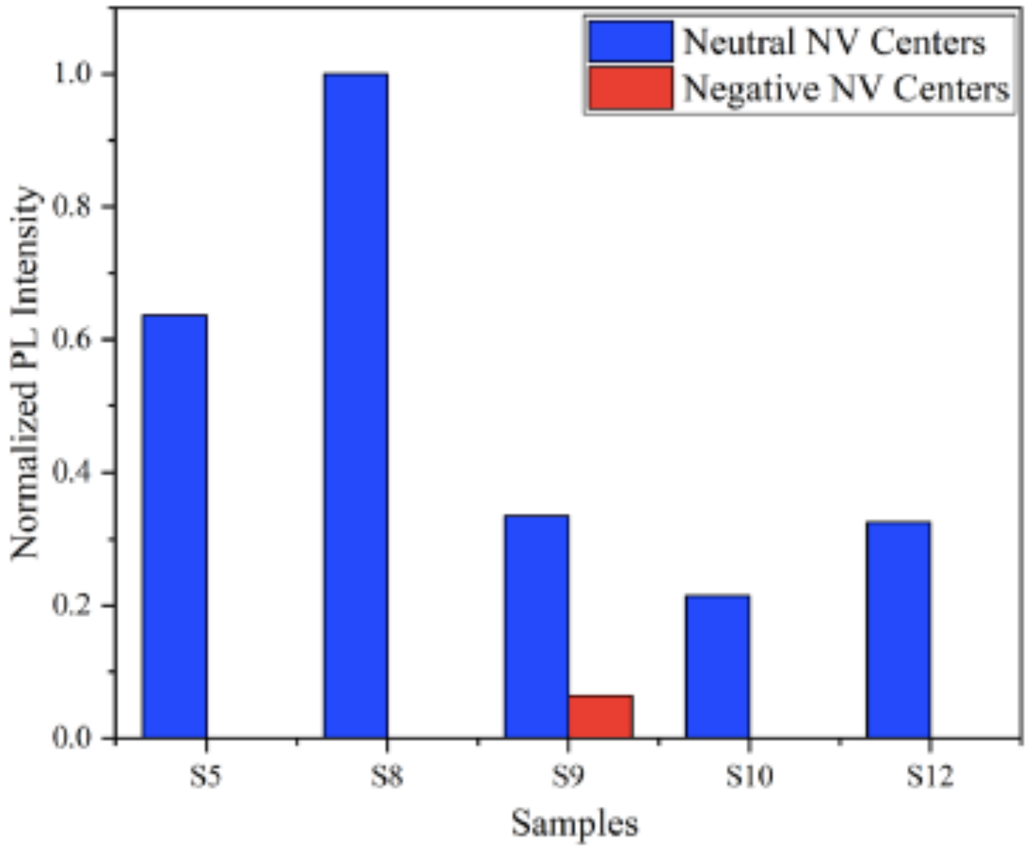
Only sample S9 exhibited a (small) NV^- 637 nm PL peak
S9 growth conditions: 100 -1-10 H_2-CH_4-N_2 flow (sccm)



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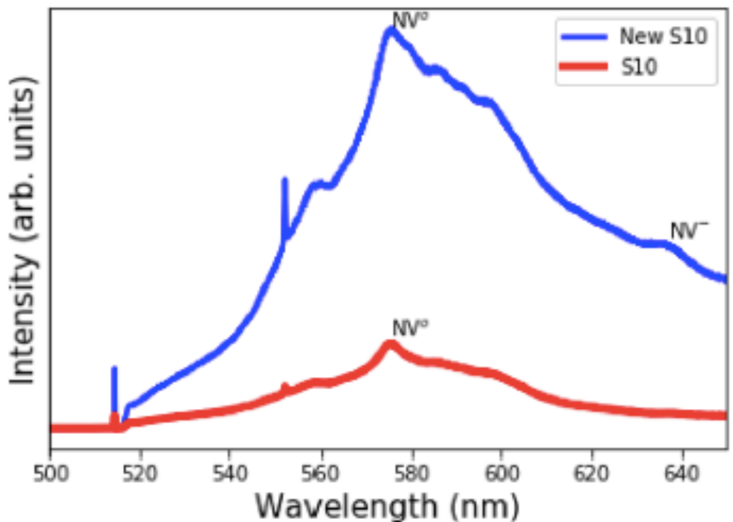
Getting an NV- Centre: operate at higher pressure

Sample "New S10": Higher process pressure 50 Torr (6.7 kPa) process pressure & microwave power (900 W) with same flow rates as sample S10 (200 sccm H_2, 1 sccm of CH_4, and 20 sccm of N_2).



637 nm NV- Photoluminescence peak

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II. Step-wise surface nitrogen doping in MPECVD grown polycrystalline diamonds

Focused on the 100 sccm H2 / 1 sccm CH_4 flow regime & vary N_2 flow

Samples	H_2/CH_4 flow (sccm)	N_2 flow (sccm)	Growth time (h)	Doping time (h)
P1	100/ 1	0	18	0
P2	100/ 1	2	17	1
P3	100/ 1	4	17	1
P4	100/ 1	6	17	1
P5	100/ 1	8	17	1
P6	100/ 1	10	17	1

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- 1. At low surface nitrogen flow rates ([N/C] < 0.0020), the diamond
- growth mechanism is slow enhancing secondary nucleation
- process that favours the growth of nanocrystalline grains. The nanocrystalline
- grains formed have large grain boundary density
- containing a large quantity of disordered sp2/a-C content in the
- grain boundaries.

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- 2. At medium surface nitrogen flow rates (0.0020 < [N/C]
- < 0.0022), grain size increases which introduces some degree of
- orderliness to the sp2 content in the grains and at the grain boundaries.
- The quantity of sp2/a-C phases present at this stage still prevents
- the formation of NV^- centres.

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- 3. At high surface nitrogen flow rates([N/C] > 0.0025), the
- quantity of nano-grain sized diamond reduces except at the grain
- boundaries.The degree of disordered sp2/a-C content decreases with
- increasing grain size thereby enabling the formation of NV− centres
- on the grains. Also, the grain boundary line density is greatly reduced

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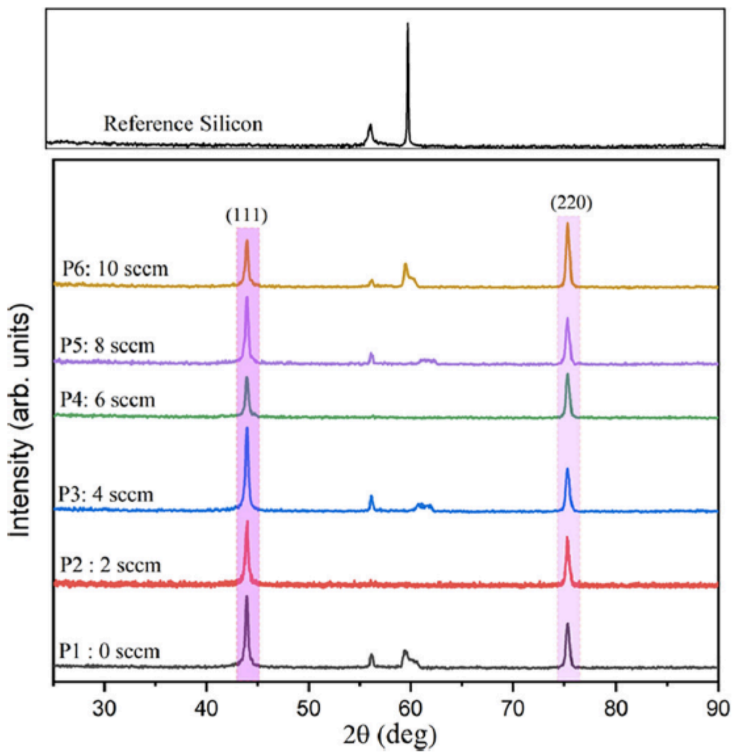
Grazing Incidence X-Ray Diffraction



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Shifting the preferred diamond grain orientation by varying N2 flow

Table 4
Preferential orientation of the deposited films under varying surface nitrogen concentration.

Samples	Experiment A [$I_{(111)}$/ $I_{(220)}$]	Experiment B [$I_{(111)}$/ $I_{(220)}$]	Preferred Orientation
P1	1.583	0.532	Random
P2	1.313	0.584	Random
P3	1.912	1.242	⟨1 1 1⟩
P4	0.922	0.844	⟨1 1 1⟩
P5	1.444	0.935	Random
P6	0.738	0.724	⟨2 2 0⟩

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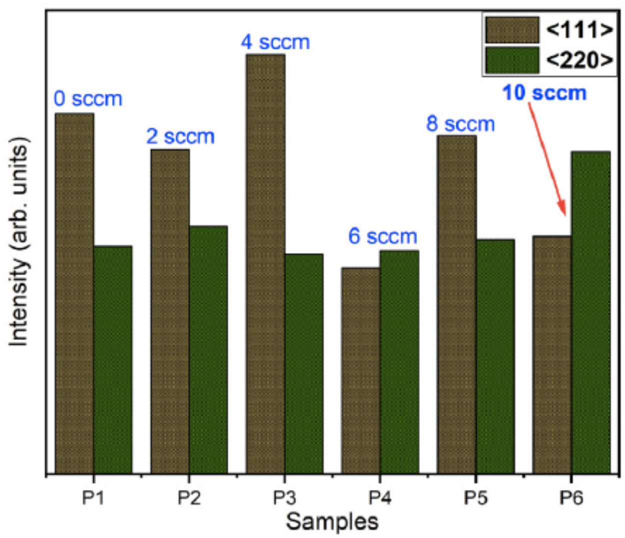
“Experiment A”



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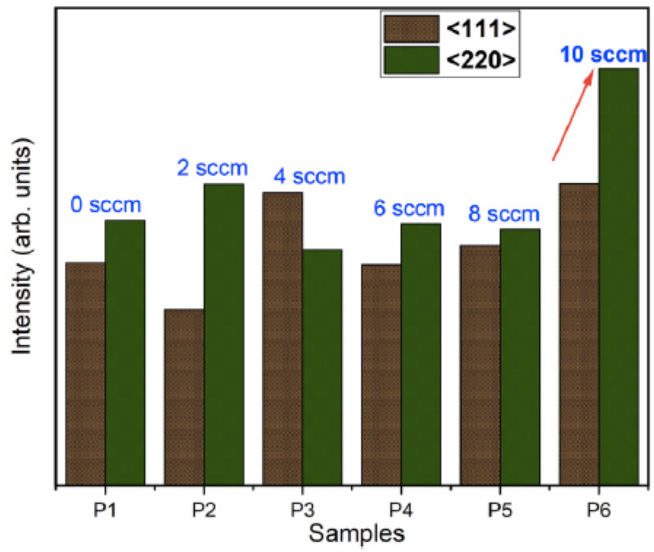
"Experiment B"



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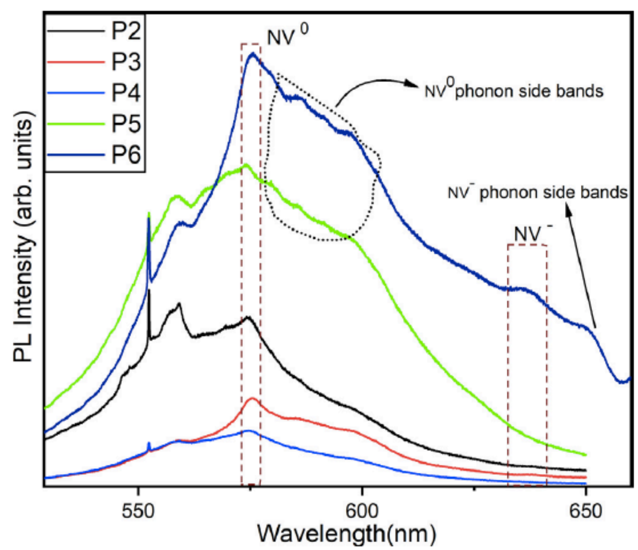
Only highest N_2 flow sample shows evidence of NV- centres



Room temperature PL emission spectra of nitrogen doped films showing
the presence of NV0 centres in sample P2–P6 and their phonon side bands. Only
sample P6 indicates the presence of NV− centres.

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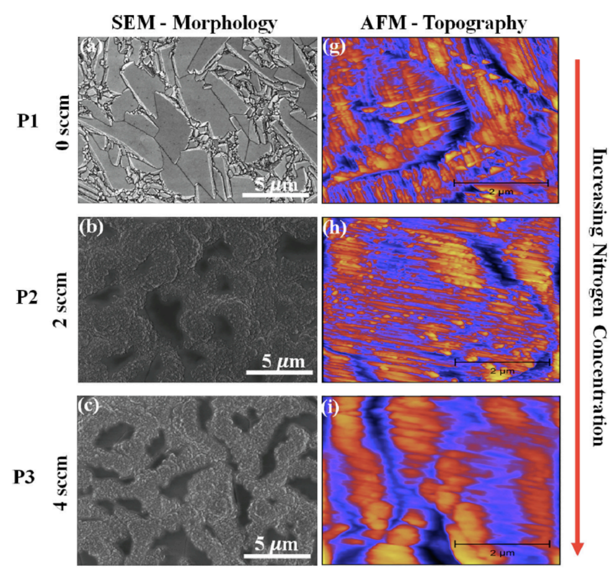
Surface Roughness: SEM & AFM Study



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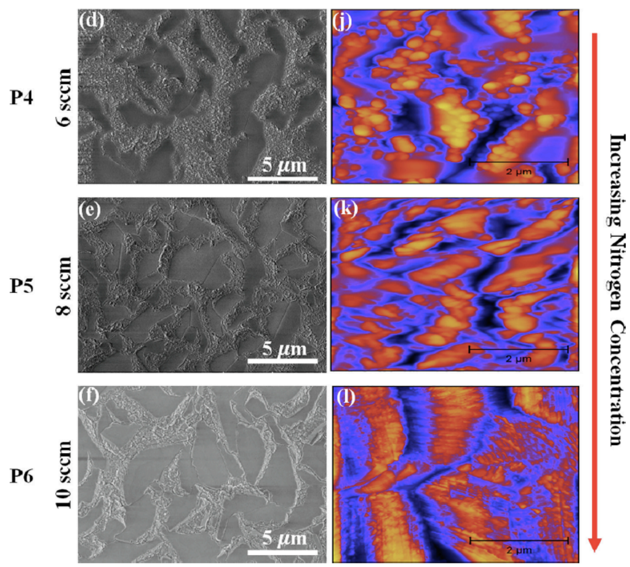
Surface Roughness: SEM & AFM Study



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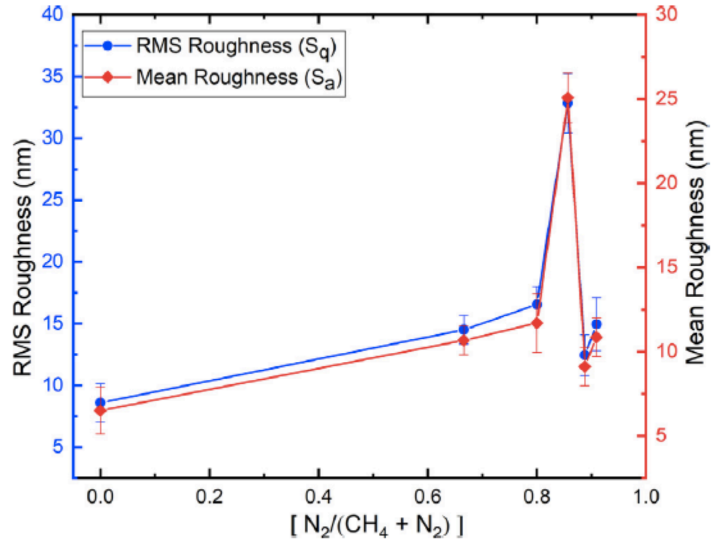
Surface Properties: drop in surface Roughness at Higher N2 flows



$$S_a = \frac{1}{A} \iint_A |P(x, y)| \, dx \, dy$$

$$S_q = \sqrt{\frac{1}{A} \iint_A P^2(x, y) \, dx \, dy}$$

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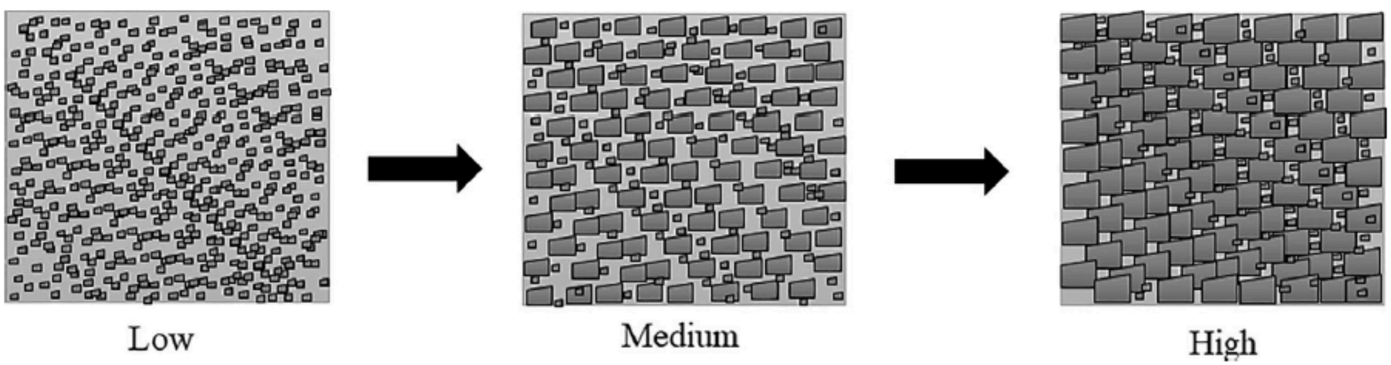
Schematic Growth Model



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Conclusions

- Growth of N-doped diamond films investigated under different growth conditions
- In general NV0 centres can be observed in the as-grown films
- Film morphological properties relevant to sensor applications
- NV- centres more difficult to achieve.
- Next step: determine plasma parameters of film growth conditions

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