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Development of Diamond-Based Materials Systems for High-Power RF Electronics: Third-Year Report

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Leonard De La Cruz, Derwin Washington, Stephen B Kelley,
and Brittany Kaufmann**

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This report details the third-year research effort that is part of the cooperative agreement between Rice University and the DEVCOM Army Research Laboratory (ARL). The project aims to develop diamond and diamond-based heterostructures for the next generation of ultrawide bandgap electronic devices, with performances far exceeding existing diamond devices and other wide bandgap materials-based devices. The Rice team focuses on the growth of high-quality single crystal diamond substrates and heterostructures of diamond and boron nitride (BN), and ARL is building high-performance electronic devices based on diamond, specifically using transfer doping of hydrogenated diamond surfaces. Rice has established a world-class facility to grow single crystal diamonds and heterostructures. First- and second-year work have included growth and transfer of BN on commercially available diamond substrates; doping using ion implantation; deposition of BN structures on the diamond; development of unique metrology tools to characterize diamond surfaces, heterostructures, and devices; surface modification using hydrogenation and oxygenation; and theoretical models to understand growth, adhesion energy, and surface characteristics of diamond and diamond/BN heterostructures. During the third year, polycrystalline and single crystalline diamond wafer growth are attempted in-house, and optimized growth protocols for varied thicknesses of epilayers and growth rates at desired substrates. When it comes to BN growth, exploration of the phase diagram for different phases of BN (hexagonal, cubic, turbo-static, wurtzite) is being attempted. Metrology is improving for the resolution in microscopy and spectroscopy aspects of the grown single crystal structures and epitaxially grown heterostructures. Surface functionalization approaches are being performed to improve the functionalities of diamond surfaces and are being understood by theoretical and computational modeling. In addition, low-energy ion implantation experiments are being performed to n-dope diamond wafers. The synergy between the two institutions establishes a close working relationship, leading to the synthesis of controlled diamond materials and their use in high-power devices.									
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Contents

List of Figures	vi
List of Tables	xi
Acknowledgments	xii
1. Introduction	1
2. Events	2
3. Materials of Interest and Growth Approaches	3
3.1 Single Crystal Diamond Growth and Optimization	3
3.2 Development of Characterization Techniques	3
3.3 Plasma Etching of Single Crystal Diamond Substrate	4
3.4 Optimization of Diamond Epilayer Growth: Substrate Holder Engineering	6
3.5 Gas Concentrations	10
3.5.1 Addition of Oxygen	10
3.5.2 Methane Concentration	10
3.6 Ion Implantation and Lift-off Process	11
3.7 Growth of Cubic Boron Nitride/Diamond by Pulsed Laser Deposition	13
3.8 Pulsed Laser Deposition Thin Film Growth Facility at Rice University	15
3.9 Single Crystal Diamond Substrate Characterizations	17
3.10 Room Temperature Growth and In-situ Annealing	18
3.11 High-Temperature Growth and In-situ Annealing	19
3.12 Comparison in Room Temperature vs. High-Temperature Growth and Annealing	20
3.13 Pressure-Dependent BN Growth on SCD at High Temperature	20
3.14 Frequency-Dependent BN Growth on SCD at High Temperature	21
3.15 Doping-Dependent BN Growth on SCD at High Temperature	22

3.16	Pressure-Dependent Mg-Doped BN Thin Film Growth on SCD	23
3.17	Temperature-Dependent Mg-Doped BN Growth on Functionalized SCD	24
3.18	Energy-Dependent Growth of Intrinsic BN	25
3.19	BN Growth on N-Functionalized Hydrogenated SCD Substrates	26
3.20	BN Growth on Implanted SCD Surface	27
3.21	c-BN/SCD Growth Summary and Future Plans	28
4.	State-of-the-Art Metrology Approaches: Microscopy and Spectroscopy of BN-Diamond Heterostructures	29
4.1	BN Grown at Room Temperatures	30
4.2	BN Structures Deposited on Single Crystalline Diamond	31
4.3	BN Structures Deposited on Al ₂ O ₃	32
4.4	BN Structures Deposited on GaN	33
4.5	BN Structures Deposited on SiC	35
4.6	Cubic Boron Nitride Microcrystals	36
4.7	h-BN and c-BN Composite Structures as Annealed	37
4.8	h-BN and c-BN Composite Structures after Plasma Sintering	38
4.9	B-Implanted SCD	39
4.10	Electrical Conductivity Evolution of SCD vs. Hydrogenation Conditions	41
4.11	Cathodoluminescence Studies on Pristine, Doped, and Functionalized Diamond Surfaces	41
5.	Diamond Doping and Surface Modification	43
5.1	Low-Energy Ion Implantation: An Approach to Develop RT n-type Diamond Wafers	43
5.2	Reactive Ion Etching Toward Clean and Roughness-Free Diamond Surfaces	47
5.3	Heteroatom Functionalization of Diamond Surfaces for Improved Transfer Doping	50
5.4	Fluorination of Diamond Surfaces and the Study of Fluorine Color Centers	57

6. Theoretical Studies Performed with Classical and Quantum Theory Levels	62
6.1 Amination of Diamond Surfaces	62
6.2 Stability of Oxygenated Groups in Diamond Surfaces	62
7. Collaborations between Rice University and ARL	63
8. Conclusions	64
9. List of Publications	67
10. References	69
List of Symbols, Abbreviations, and Acronyms	74
Distribution List	77

List of Figures

Fig. 1	Single crystal diamond epitaxial growth.....	3
Fig. 2	SEM images of diamond surface after (a,b) H ₂ plasma etching and (c,d) O ₂ plasma etching.....	4
Fig. 3	(a,b) SEM images of ESCD1 after H ₂ plasma etching. (c) AFM measurement of etch pits. (d,e) SEM images of ESCD2 after H ₂ plasma etching. (f) AFM measurement of the surface showing atomical smoothness. (g) AFM measurement of an as-received diamond surface.	5
Fig. 4	AFM measurement of ESCD4 surface revealing its evolution with H ₂ plasma etching	6
Fig. 5	(a–c) Plasma plume over the substrate holders with different heights. (d) Etch rate comparison with different substrate holders.	7
Fig. 6	Raman spectra of diamond epilayer grown using different holders with (a–c) 5-mm height, (d–f) 4-mm height, and (g–i) 3-mm height	8
Fig. 7	(a,b) Optical images of ESCD4 after epilayer growth. (c) Raman spectra and (d) XRD rocking curve measurement of ESCD4. (e) Raman spectra and (d) XRD rocking curve measurement of a pristine electronic-grade single crystal diamond from Element Six.	9
Fig. 8	Comparison of diamond growth using substrate holders with 10- and 20-mm diameters	9
Fig. 9	Comparison of diamond growth with different O ₂ concentrations	10
Fig. 10	Comparison of diamond growth with different CH ₄ concentrations from 1% to 0.5%.	11
Fig. 11	Comparison of diamond growth with different CH ₄ concentrations from 1% to 4%	11
Fig. 12	Ion implantation and lift-off process.....	12
Fig. 13	(a) Optical images of polycrystalline diamond and single crystal diamond before and after ion implantation. (b) Raman spectra of diamond substrates after ion implantation. (c) Optical image and (d) SEM image of a piece of polycrystalline diamond with a lift-off area. (f) Raman spectra collected on the epilayer and the substrate.....	13
Fig. 14	(a) Wide and ultrawide-bandgap semiconductors with Baliga figure of merit (BFOM). (b) Schematic of the field-effect transistor with c-BN and diamond. (c) Growth of various phases of BN while growing the c-BN phases.	14
Fig. 15	(a) Schematic of a PLD process in which pulsed laser ablates the target surface and generates plasma impinging onto the substrate and deposits as a film. (b) PLD facility installed at Rice University. (c)	

	Typical image of BN films with multiple targets mounted in the PLD chamber.....	16
Fig. 16	(a,b) X-ray photoelectron spectroscopy, (c) X-ray diffraction, (d) omega rocking curve, (e) azimuthal angle dependence omega scan to measure the miscut angle, and (f) Raman spectra of the normal-grade single crystal (001) diamond substrates.....	18
Fig. 17	(a) Raman spectra, (b) grazing-angle X-ray diffraction, (c) surface topography, (d) X-ray photoelectron spectroscopy, and (e) refractive index of the BN films grown at room temperature with subsequent high-temperature annealing	19
Fig. 18	(a) Grazing-angle X-ray diffraction, (b) Raman spectra, and (c) refractive index of the BN films grown at high temperature with subsequent annealing at the same growth temperature.....	20
Fig. 19	Comparison of (a) grazing-angle X-ray diffraction and (b) Raman spectra of the BN films grown at high and low temperature with subsequent high-temperature annealing.....	20
Fig. 20	(a) X-ray photoelectron spectroscopy and (b) grazing-angle X-ray diffraction of the pressure-dependent BN thin films growth.....	21
Fig. 21	Comparison of (a) grazing-angle X-ray diffraction and (b) Raman spectra of the repetition rate–dependent BN films grown at high temperature	22
Fig. 22	(a) X-ray photoelectron spectroscopy, (b) grazing-angle X-ray diffraction, (c) Raman spectra, and (d,e) FTIR of the BN thin films grown by using the Mg- and Si-doped BN as a target.....	23
Fig. 23	(a,b) Grazing-angle X-ray diffraction and (c) Raman spectra of Mg-doped BN thin film growth at different pressures	23
Fig. 24	(a) X-ray photoelectron spectroscopy, (b) grazing-angle X-ray diffraction, (c) Raman spectra, and (d) FTIR of Mg-doped BN thin films grown on N-functionalized (001) SCD substrates at different growth temperatures.....	25
Fig. 25	(a,b) Grazing-angle X-ray diffraction, (b) Raman spectra, and (c,d) FTIR spectra of pure and Mg-doped BN thin films grown at different laser energies.....	26
Fig. 26	(a,b) X-ray photoelectron spectroscopy, (c) Raman spectra, and (d) FTIR of BN thin film grown on N-functionalized hydrogenated SCD surface at different temperatures.....	27
Fig. 27	(a) Grazing angle X-ray diffraction, (b,c) Raman spectra, and (d) FTIR of BN thin films grown on implanted SCD substrate at different growth temperatures.....	28
Fig. 28	Summary of c-BN/diamond thin film heterostructures: (a–e) XPS, Raman spectra, grazing incident angle XRD, atomic force surface topography, and FTIR spectra showing the growth of (111) c-BN thin films on (001) diamond substrates.....	29

Fig. 29	(top) Schematic showing the BN deposition onto a TEM grid at room temperature; specifications of the grid are provided in the inset. (bottom) The morphology, crystallinity, and diffraction patterns of BN flakes (left)/sheets (right) deposited with 50 and 100 laser shots, respectively.	31
Fig. 30	(top) Schematic showing the interface of diamond and BN layer. (bottom) Low-magnification STEM image of cross section prepared via FIB and the high-magnification images of the interface, amorphous BN layer, and diamond substrate.	32
Fig. 31	(top) Cross-sectional lamella of BN deposited on Al ₂ O ₃ substrate. (bottom) Moderate magnified image of the area of interest and atomic resolution images of the interface region and EELS spectra collected from different BN-containing regions as shown in the color mapped image.	33
Fig. 32	(top) Schematic of BN deposited on GaN substrate. (bottom) Low-magnification STEM image of the cross-sectional lamella, GaN-BN interface, and atomic resolution images of GAN and BN nanocrystals, respectively.	34
Fig. 33	The lattice constants of GaN lattice and BN nanocrystal are computed from the fast Fourier transform (FFT) pattern based on the intensity variation from the center to outward regions.	35
Fig. 34	The distribution of BN (C-rich and C-poor regions) and the GaN regions were mapped based on the EELS spectra and machine learning approach.	35
Fig. 35	(top) Low-magnification bright field image of the BN deposited on SiC lamella and atomic resolution images of the SiC and BN layers, corresponding to the FFT and dark-field image. (bottom) EELS spectra and mapping of the BN region.	36
Fig. 36	(top) Low-magnification and atomic resolution images of the cBN crystal and corresponding diffraction pattern. The DFT-modelled cBN structure with zone axis [100] is also provided in the inset. (bottom) EDS spectra and EDS mapping of B and N elements. The region from the EDS spectra where mapping of B and N is performed is appended in the inset.	37
Fig. 37	(top) Schematic showing the pellet made of cBN and hBN microcrystalline powders. (bottom) Low-magnification and atomic resolution images of the cBN-hBN composite after the annealing treatment and corresponding diffraction pattern showing the presence of both cubic and hexagonal phases.	38
Fig. 38	(Left to right) STEM image of spark plasma-sintered BN crystal. EDS spectrum and EDS mapping correspond to B, O, N, and C. (bottom) Atomic resolution images of the sample showing the pure hexagonal crystal nature of the sintered sample.	39
Fig. 39	(top) Low-mag and high-resolution STEM images of the cross-sectional lamella of treated B implanted sample. (bottom) Intensity	

	variation across the different regions of the lamella, EELS spectra from three different regions, and line scans of EELS spectra across the sp ² and sp ³ region of the implanted diamond wafer.	40
Fig. 40	Mapping of B and C density across the sp ² -sp ³ interface: (left) boron map and (right) C map. The implanted B density is found to be higher in the sp ² region than the sp ³ region.	40
Fig. 41	(left) Schematic showing the hydrogenated diamond surface and the optical microscopy image (50x) of the sample surface. (right) AFM height image showing the modification of the diamond surface on H termination treatment and the IV curves showing the change in sheet resistance (high to low).	41
Fig. 42	(top) Schematic showing the diamond wafer sample under study where half of the geometric surface area is H terminated and half is oxygen terminated. (Bottom) Gray scale and false color cathodoluminescent images of the sample clearly differentiating the H- and O-terminated surfaces.	42
Fig. 43	Schematic showing the proposed low-energy implantation process where the ions can be placed to the very surface region without damaging the parent lattice	44
Fig. 44	SRIM modelling output for Li, Na, B, N, P, and As. The implantation energy is computed based on the required depth of implantation, which is within the first 10 nm for the diamond wafer.....	45
Fig. 45	The Raman and PL spectra of B-implanted diamond sample with and without substrate temperature	45
Fig. 46	The Raman spectra of pristine and low-energy implanted samples with Li, N, F, Na, P, and As.....	46
Fig. 47	The photoluminescence spectra of pristine and low-energy implanted samples with Li, N, F, Na, P, and As.....	46
Fig. 48	ToF SIMS results showing the concentration of implanted species with respect to the depth from the surface and the homogeneity of the implanted species on the diamond surface (inset) for Li, Na, N, and F	47
Fig. 49	AFM measurements for both (a) the pristine PCD sample and (b) an ICP-RIE treated PCD sample with CF ₄ +O ₂ (50:50 sccm) at 5 mTorr, 200-W bias, and 400-W coil for 10 min	49
Fig. 50	XPS spectra for various fluorinated diamond substrates treated via ICP-RIE.....	49
Fig. 51	SEM measurements for (a) pristine PCD sample, (b) PCD sample etched with Ar+Cl ₂ (10:40 sccm) at 200-W bias, 400-W coil, 5 mTorr for 10 min, and (c) PCD sample etched with Ar+Cl ₂ (25:40 sccm) at 200-W bias, 400-W coil, 5 mTorr for 10 min.....	50
Fig. 52	The PCD film was grown and passivated with H plasma (HPCD) inside the MPCVD system. The UV-irradiation process in NH ₃	

	medium was utilized to aminate the HPCD surface (N-HPCD). The sulphuration of HPCD (S-HPCD) was conducted with the same process in dissolved S powder. S-HPCD was subjected to amination to acquire a co-functionalized surface (N-S-HPCD).	52
Fig. 53	Attenuated total reflectance–FTIR (a) spectra revealed the surface composition of functionalized diamond surfaces. The ionized mapping of nitrogen groups (b) and depth profile analysis (c) were accomplished by ToF-SIMS on the N-S-HPCD-2 surface. The elemental ratios (d) of N, S, and H on functionalized samples were also examined by ToF-SIMS. To be noted, the larger-ranking sequence indicates the higher atomic coverage on the diamond surface (e.g., N-S-HPCD-2 has a higher N-S ratio than that of N-S-HPCD-1).	53
Fig. 54	The deconvolution of XPS S 2p spectra of S-HPCD-2 (a), and N-S-HPCD-2 (b); XPS N 1s spectra of N-HPCD (c), and N-S-HPCD-2 (d). The featured peaks from each spectrum were highlighted with distinct colors. All spectra under the same core analyses were plotted in the same scales.	55
Fig. 55	Schematic view (a) of fabricated device; values stand for the thickness of layers. The I-V characteristics of functionalized diamond surfaces: (a) HPCD (black), N-HPCD (cyan), S-HPCD-1 (violet), and N-S-HPCD-1 (blue); (b) S-HPCD-1 (violet), and S-HPCD-2 (olive); (c) N-S-HPCD-1 (blue), N-S-HPCD-2 (red). The forward and backward voltage sweeps were from +10 V to –10 V with 200-mV step.	56
Fig. 56	Schematic depicting the experiment design (top) and illustration of the reaction setup (bottom)	58
Fig. 57	(a) XPS data confirming the functionalization of diamond with fluorine group and (b) contact-angle data corroborating the higher coverage of fluorine on the surface as a function of temperature and the resulting increased hydrophobicity arising from the higher contact angle.	59
Fig. 58	AFM measurements done to validate the decrease in surface roughness while depicting nano-hill-like symmetrical features arising from the surface etching	59
Fig. 59	Raman spectroscopy corroborated the increased fluorination and posited the possibility of increased density of vacancy centers from the increased surface etching compared to the pristine surface.	60
Fig. 60	PL spectra of a pristine PCD sample showing broad spectral emission	61
Fig. 61	PL spectra of fluorinated diamond under 6 h, and room temperature conditions on Location 1 (left) and Location 2 (right) under similar conditions.	61
Fig. 62	(a) Pristine bare (110), (111), and (311) diamond surfaces in top and perspective views. (b) Defective (110) and (111) diamond surfaces. In (113) surface, the yellow and orange atoms represent the ones with one	

and two dangling bonds, respectively. For the other cases, the yellow atoms represent the most exposed carbon atoms. 63

List of Tables

Table 1	Property comparison of bulk c-BN and diamond	14
Table 2	The ionization energy of various elements in the diamond lattice and the maximum achievable doping levels in the diamond lattice	44
Table 3	Low-energy implantation parameters	45
Table 4	Samples exchanging between Rice and ARL	64

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1. Introduction

With the increasing demand for silicon electronics in terms of power and energy considerations, wide bandgap semiconductors have become a viable option, enabling new device architectures and the use of new semiconductor materials.¹ Among these, silicon carbide (SiC) and gallium nitride (GaN)-based devices have been explored widely.^{2–4} However, it has been realized recently that diamond, an ultrawide bandgap (UWBG) (> 5 eV) material, has significant advantages compared to GaN or SiC if implemented in high-power devices.⁵ Owing to the ultra-high bandgap and extremely high thermal conductivity, diamond has been touted as the next-generation material for high-voltage, high-power, high-temperature, and high-frequency devices.⁶ The band structure in diamond allows it to act as easy electron emitters to vacuum levels, at higher voltages, which can be captured in a dielectric layer placed on top of the diamond, and in the process also generating high hole conduction in the diamond layer.⁷ Hence diamond, with the right kind of interface dielectric layer and doping, can become exciting building blocks for transistors and metal–oxide–semiconductor field-effect transistors (FETs), the drivers of the semiconductor industry. The high thermal conductivity⁸ of diamond also allows excellent intrinsic thermal management, so far a bottleneck with silicon and other semiconductor device technologies.

The advantages aside, there are significant challenges ahead in realizing diamond-based device technologies. These are mainly related to the growth of high-quality diamond films, selection and adoption of the right interface dielectric layer, controlled doping to enable device polarity, and contact issues with metal lines. In recent years various attempts have been made to address these issues and improve the performance of diamond devices. Recent advances in chemical vapor deposition (CVD)⁹ of diamond have resulted in the ability to grow good-quality single- and poly-crystalline films over areas ranging from a few millimeters to several centimeters.¹⁰ For the dielectric layer over diamond, several metal-oxide films have been explored (e.g., alumina, molybdenum trioxide) with varying degrees of success based on the interface structure, epitaxy, and charges present. For the doping part, various approaches have enabled p-type and n-type structures to be produced with dopants such as boron and phosphorus.¹¹ However, uniform and controlled doping has been extremely challenging, leading to techniques that alter diamond surface terminations (hydrogen or oxygen). These surface modifications, termed as transfer doping, alter the bandgap and electronic structure of diamond and enable higher charge carrier densities and mobilities, although the interface layer selection has to match the nature of transfer doping used.

Specific objectives of the project are as follows:

- Establishing a CVD facility for the growth of large-area, high-quality diamond films, vapor phase doping methods, and electronic and thermal characterization tools for the grown diamond films and diamond-based heterostructures.
- Developing and optimizing various approaches that would enable the synthesis of heteroepitaxial diamond/boron nitride (BN) heterostructures, including diamond/BN (hexagonal and cubic), diamond/h-BCN (boron carbo-nitride), and other multilayer structures, including the gate dielectric.
- Developing methods that would enable various types of doping of the diamond films to engineer its bandgap and electronic structure and understanding the interface electronic properties of doped diamond films and BN layers.
- Engineering low resistance contacts between diamond/BN/dielectric films and selection of metals and alloys and integration and testing these in FET diamond devices.
- Developing close collaborations to develop device architectures for the diamond-BN heterostructures grown at Rice University, and fabricating and testing these devices both at Rice and the US Army Combat Capabilities Development Command Army Research Laboratory (ARL). The goal will be to achieve far better device performance compared to existing diamond ultrawide bandgap devices, based on well-defined device metrics.
- Explore, in subsequent years, novel applications, outside of semiconductor device applications, for the diamond-BN heterostructures such as quantum sensing, single-photon emission, thermal management, and optoelectronics.

2. Events

- Biweekly meetings, online
- GOMACTech 2022, 2022 March 21–24, Miami
- Sarah E Jones' visit (Safety and Occupational Health Office, ARL), 2022 July 21, Rice University
- Meeting with Dr Han Wang (Taiwan Semiconductor Manufacturing Company/ University of Southern California), 2022 July 22, online

- Dr Bradford Pate's visit (Naval Research Laboratory), 2022 November 2–4, Rice University

3. Materials of Interest and Growth Approaches

3.1 Single Crystal Diamond Growth and Optimization

In year 3, with the installation of the Seki microwave plasma chemical vapor deposition (MPCVD) system, we started to concentrate on single crystal diamond (SCD) epitaxial growth, shown in Figure 1. After receiving commercial SCD substrates from external vendors, such as Element Six, we performed acid cleaning, which is essential to removing graphite and metal contaminations on the surface. Reactive ion etching (RIE) helps remove the defective layer induced by the polishing process and makes the surface smooth. After loading the substrate to the reactor, hydrogen plasma etches the surface to remove contamination. With the introduction of methane, the diamond epilayer growth begins. The growth rate and epilayer quality are closely affected by microwave power, chamber pressure, substrate temperature, plasma density, and so on. After the growth, the diamond epilayer will be carefully characterized by a series of techniques. The qualified samples will be used for further applications, such as transistor fabrication and BN growth.

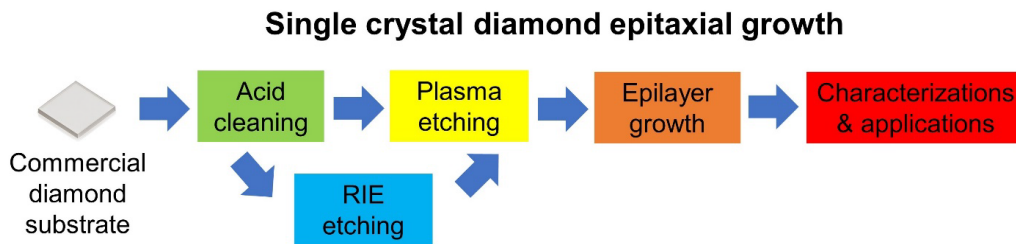


Fig. 1 Single crystal diamond epitaxial growth

3.2 Development of Characterization Techniques

The in-situ characterization techniques include temperature measurement through a dual-wavelength pyrometer and a disappearing filament optical pyrometer, plasma density analysis by taking photos from the viewport with a H α line filter, and the plasma diagnostic through an optical emission spectrometer (OES). OES is a simple, non-perturbing, in situ method that probes electronically excited atoms and molecules, species concentrations, atomic relative densities, gas temperature, and the electron temperature of plasma discharge.

The post-growth characterization techniques include Raman spectroscopy, scanning electron microscopy (SEM), cathodoluminescence (CL), photoluminescence (PL), Birefringence, X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), atomic force microscopy (AFM), etc. The thickness of the epilayer is calculated by weight gain, measured by a microbalance.

3.3 Plasma Etching of Single Crystal Diamond Substrate

Plasma etching by H_2 or H_2/O_2 is an important and inevitable step before the epilayer growth. It removes surface contamination and potentially makes the surface smoother, and can reveal the defects and dislocations in the diamond substrates. We first performed plasma etching on regular-grade SCD from Element Six. The conditions are 3000 W, 160 Torr, temperature approximately 630 °C, H_2 500 sccm or H_2 490 sccm, O_2 10 sccm (2% O_2/H_2). The etch rate of H_2 plasma turns out to be 1 $\mu m/h$ while H_2/O_2 plasma etches faster and reaches 6 $\mu m/h$. Figure 2 shows the SEM images of diamond surface after etching. Different types of etch pits can be observed. The flat-bottom ones correspond to the dislocations or microfractures introduced during surface polishing. The point-bottom ones correspond to intrinsic dislocations included originally inside the bulk substrates.¹² It reveals that the general-grade SCD contains a lot of intrinsic dislocations.

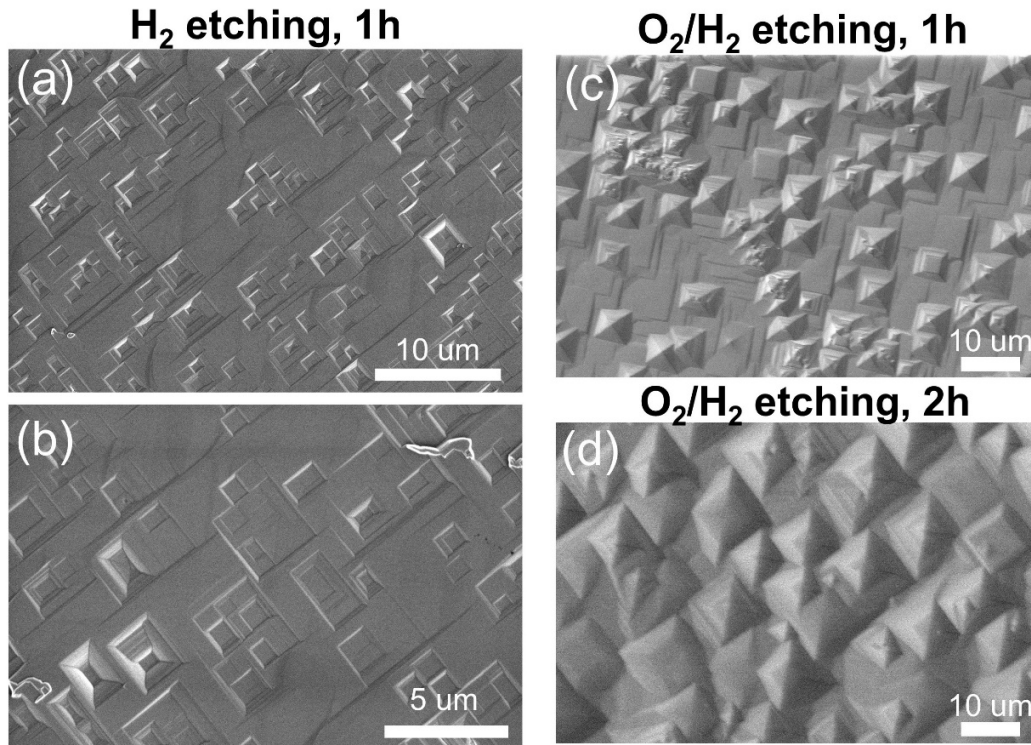


Fig. 2 SEM images of diamond surface after (a,b) H_2 plasma etching and (c,d) O_2 plasma etching

Next, H₂ plasma was carried out on electronic-grade SCD from Element Six. The first electronic-grade SCD sample, notated by ESCD1, was etched by H₂ plasma for 1 h with 2000 W, 150 Torr at temperature approximately 780 °C. Figure 3a displays the SEM image of the entire surface showing its overall smoothness. Figures 3b,c show a few etch pits with similar shape and orientation. Another electronic-grade SCD sample, notated by ESCD2, was etched by H₂ plasma for 1 h with 1600 W, 160 Torr at temperature approximately 825 °C. The SEM images in Figs. 3d,e demonstrate the surface remains high smoothness without obvious etch pits, which is confirmed by the AFM measurement in Fig. 3f. The surface roughness is calculated to be 0.1 nm, lower than the original diamond substrate surface roughness 0.4 nm (Fig. 3g). Additionally, it can be observed that the polishing marks on the original diamond substrate have been completely removed. These results show that the electronic-grade diamond substrates contain a very low density of dislocations, and the H₂ plasma etching is capable of making the surface smoother.

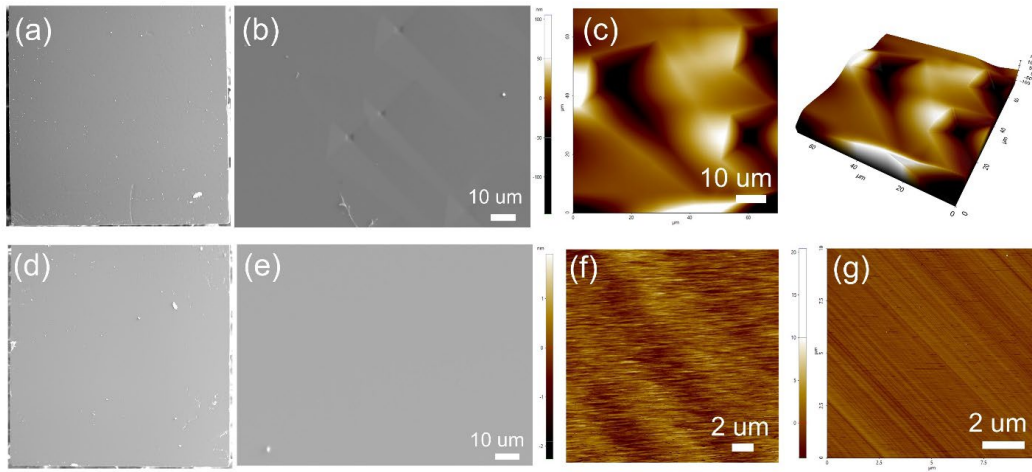


Fig. 3 (a,b) SEM images of ESCD1 after H₂ plasma etching. (c) AFM measurement of etch pits. (d,e) SEM images of ESCD2 after H₂ plasma etching. (f) AFM measurement of the surface showing atomic smoothness. (g) AFM measurement of an as-received diamond surface.

To understand the influence of H₂ plasma etching duration on diamond substrate, we conducted a series of H₂ plasma etching on an electronic-grade diamond (ESCD4) while maintaining microwave power 1600 W, chamber pressure 160 Torr, and duration approximately 5 min. The AFM images of the diamond surface after each etching are displayed in Figs. 4a–j, respectively. Irregular-shaped etch pits were obtained, and the polishing marks still exist after the first etch. After the second etch, the polishing marks disappeared, while round-shaped etch pits can be observed. As the etching continues, the substrate temperature increased to approximately 1000 °C or higher. The diamond surface became highly porous after the third etch. Square-shaped etch pits and straight lines can be observed after the

fourth and fifth etch, respectively. It turned out that the diamond surface could not reach the same low surface roughness as ESCD2, which could be attributed to a small amount of water vapor coming from the hydrogen generator. Even though we tried to keep each etch for approximately 5 min, etching still takes place during the microwave power and chamber pressure ramping up and down process. More experiments need to be done to understand the diamond surface evolution with H₂ plasma etching.

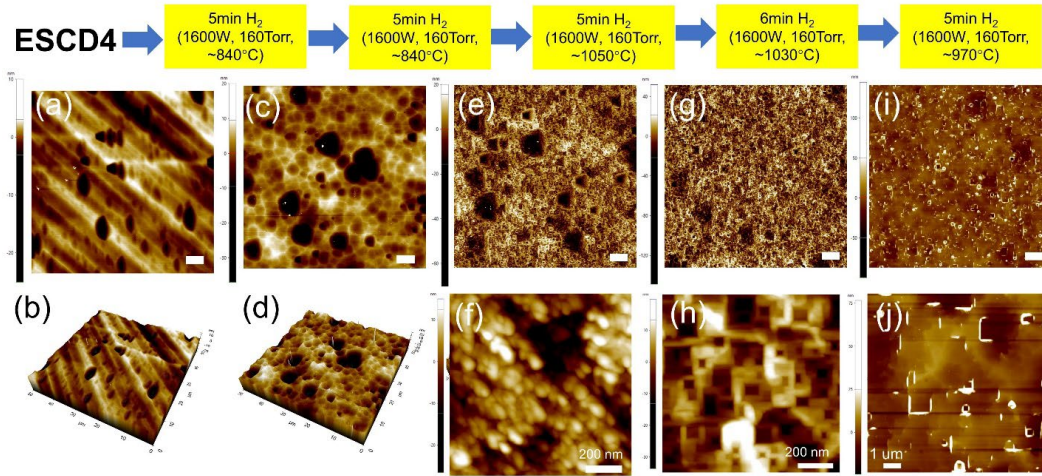


Fig. 4 AFM measurement of ESCD4 surface revealing its evolution with H₂ plasma etching

3.4 Optimization of Diamond Epilayer Growth: Substrate Holder Engineering

The substrate holder configurations play a critical role in diamond epilayer growth because they can affect thermal loss and plasma distribution, thus impacting the substrate temperature and plasma power density. Many efforts are reported in the literature that study the influence of the substrate holder design on diamond growth. It is also very important for us to customize the substrate holder based on our reactor and research goals.

We designed three substrate holders with the same diameter, 10 mm, but different heights: 2 mm, 5 mm, and 10 mm. The same electronic-grade SCD sample was placed on these substrate holders and heated to similar temperatures in the H₂ plasma. The microwave power, chamber pressure, and diamond substrate temperature for these holders are 160 W, 160 Torr, 944 °C (2 mm); 1050 W, 110 Torr, 953 °C (5 mm); and 800 W, 80 Torr, 965 °C (10 mm), respectively. The photos in Figs. 5a–c demonstrate that the plasma plume has different volumes and shapes. The H₂ plasma was kept for 1 h, and the etch rate was compared in Fig. 5d. It can be observed that even though the diamond temperature is similar, the etch

rate increases from 125 nm/h (10 mm) to 314 nm/h (5 mm), and 1.6 $\mu\text{m/h}$ (2 mm). These results demonstrate that a suitable substrate holder is of great importance to diamond growth and etch. If the substrate holder height is too large (10 mm), the microwave power and chamber pressure cannot be set high enough to ensure the growth quality. If the substrate holder height is too low (2 mm), to keep the growth temperature high enough, the microwave power and chamber pressure have to be very high, which greatly enhances the etching rate.

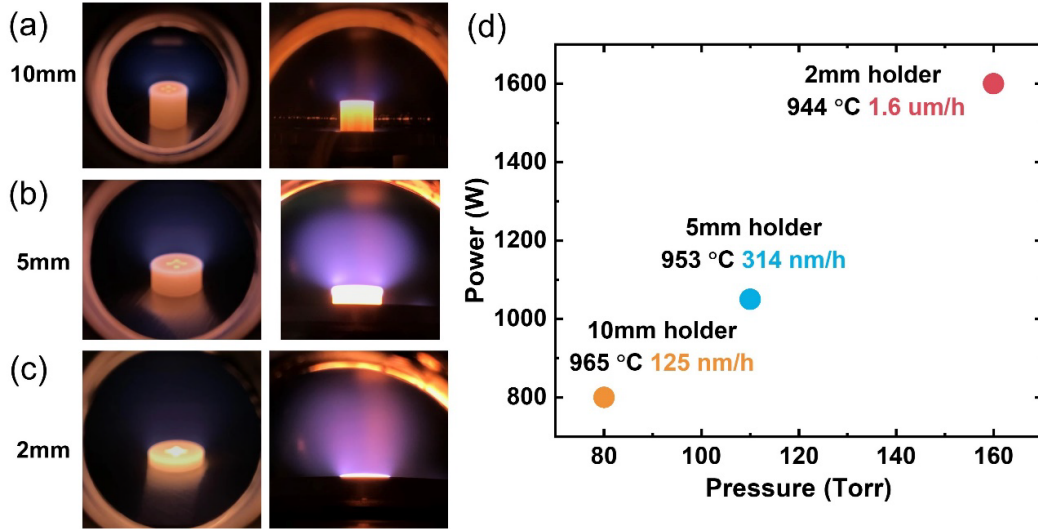


Fig. 5 (a–c) Plasma plume over the substrate holders with different heights. (d) Etch rate comparison with different substrate holders.

We further adjusted the height of the substrate holder closely around 5 mm to optimize the growth quality. For each substrate holder height (5 mm, 4 mm, and 3 mm), at least three 1-h growths were carried out on different diamond substrates. Raman spectra on the epilayer collected post-growth are shown in Fig. 6 together with growth conditions. The CH_4/H_2 ratio was kept at 1% for all the growths. It can be observed that for the 5-mm holder, two growths resulted in some amount of sp^2 carbon (Figs. 6a,b). The only growth that did not exhibit sp^2 carbon turned out to be more etch than the growth (Fig. 6c). In terms of the 3-mm holder, Fig. 6g demonstrates an sp^3/sp^2 ratio of 140. No sp^2 carbon was observed for the rest of the growths (Figs. 6h,i), but the growth rate was relatively higher among all the growth, which might not be favorable if a very thin epilayer is required. As for the 4-mm holder, all the growths resulted in negligible sp^2 carbon and the growth rate was very stable. More importantly, the full width at half maximum (FWHM) of the diamond Raman peak is relatively smaller compared to the growths using other holders. Therefore, it can be concluded that the 4-mm holder should be the most suitable substrate holder to achieve high-quality growth with a stable growth rate.

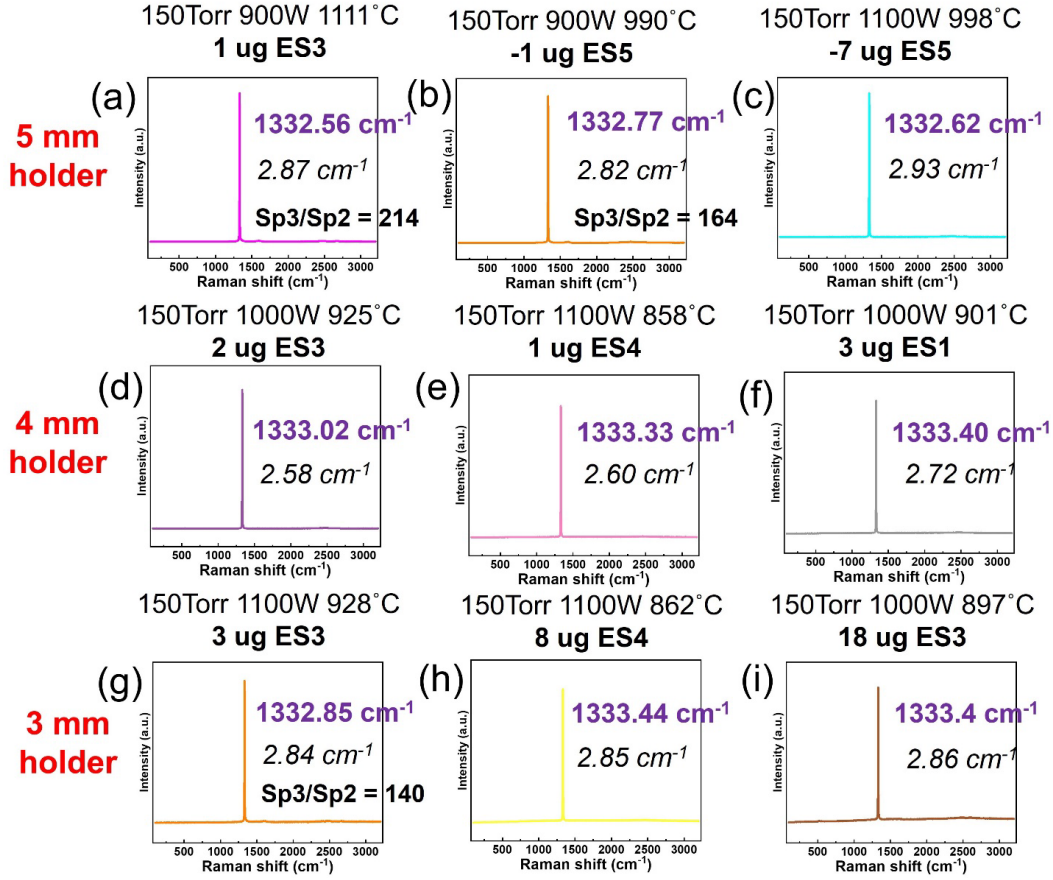


Fig. 6 Raman spectra of diamond epilayer grown using different holders with (a–c) 5-mm height, (d–f) 4-mm height, and (g–i) 3-mm height

We then performed a 5-h growth with 1100 W, 150 Torr, and 1% CH₄/H₂. The average temperature was 857 °C. After the growth, the weight gain was measured to be 106 µg, corresponding to an approximately 6.6-µm-thick epilayer. The growth rate is calculated to be 1.3 µm/h. The optical images in Figs. 7a,b demonstrate that the diamond surface is relatively flat with a few hillocks. The Raman spectra in Fig. 7c shows a sharp diamond peak at 1333.18 cm⁻¹ with an FWHM of 2.09 cm⁻¹. The XRD rocking curve measurement shows the (400) peak has an FWHM of 0.00795 degree. Compared to the as-received electronic-grade SCD from Element Six (Figs. 7e,f), the epilayer exhibits a sharper Raman peak and comparable (400) XRD peak, indicating high quality and high purity growth.

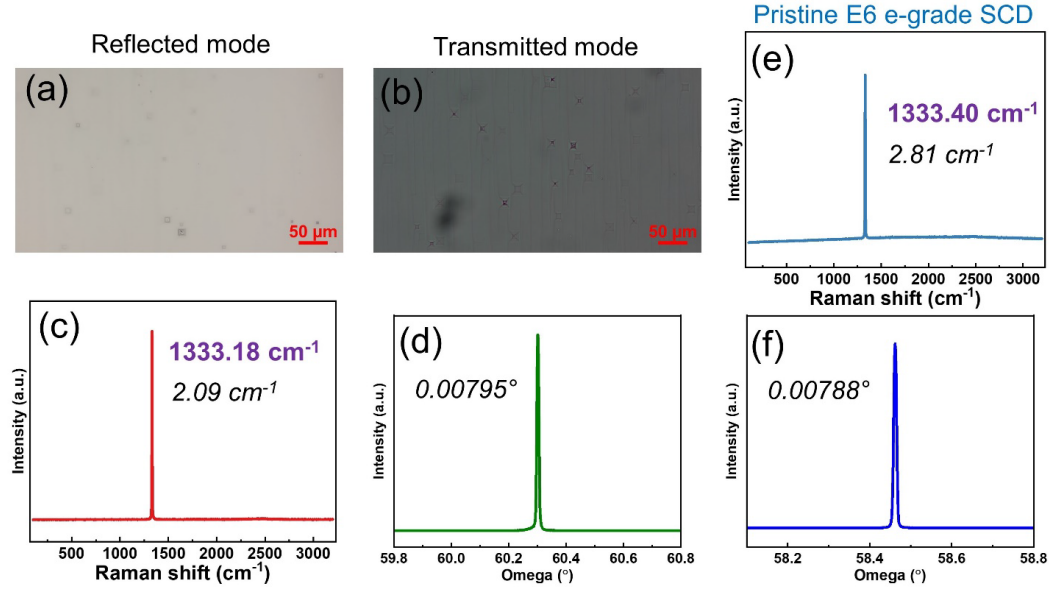


Fig. 7 (a,b) Optical images of ESCD4 after epilayer growth. (c) Raman spectra and (d) XRD rocking curve measurement of ESCD4. (e) Raman spectra and (f) XRD rocking curve measurement of a pristine electronic-grade single crystal diamond from Element Six.

We also changed the diameter of the substrate holder from 10 to 20 mm. A larger diameter might help make the plasma more uniform over the diamond substrate. This modification provides the opportunity to grow multiple diamond at the same time. Figure 8 shows the results of growths performed using two types of substrate holders. The larger-diameter holder allows higher microwave power and chamber pressure without increasing the substrate temperature. We were able to use up to 1900 W and 180 Torr with the 20-mm-diameter holder. The epilayer growth rate at such conditions is comparably reasonable and stable.

Substrate holder	10mm dia. holder		20mm dia. holder	
Growth conditions	150Torr 1200W 879°C	160Torr 1700W 817°C	180Torr 1800W 828°C	180Torr 1900W 881°C
Growth rate	1.3 um/h	1.0 um/h	1.3 um/h	1.5 um/h
Diamond Raman peak position and FWHM	1333.65 cm ⁻¹ 2.87 cm ⁻¹	1334.04 cm ⁻¹ 2.91 cm ⁻¹	1334.05 cm ⁻¹ 2.89 cm ⁻¹	1333.51 cm ⁻¹ 3.01 cm ⁻¹

Fig. 8 Comparison of diamond growth using substrate holders with 10- and 20-mm diameters

3.5 Gas Concentrations

3.5.1 Addition of Oxygen

It was reported that adding O₂ during the diamond growth can help suppress the polycrystalline diamond (PCD) growth on the substrate holder as well as improve the diamond quality by reducing the impurity concentrations. Therefore, we performed growths with different O₂ content, 0.1% and 0.2%, to study the effect of adding O₂ during the growth. Figure 9 shows the plasma photo, growth conditions, calculated growth rate, and Raman peak information of four 1-h growths conducted on the same electronic-grade SCD substrate. It can be found that with the addition of O₂, the growth rate was significantly reduced. The higher the O₂ concentration, the lower the growth rate. However, it seems that adding O₂ during the growth did not improve the quality of diamond epilayer since the FWHM of diamond Raman peak does not reduce.

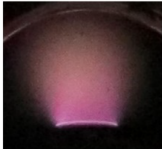
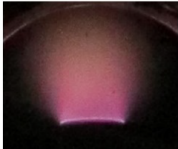
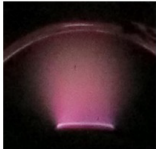
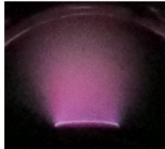
Plasma photo				
Growth conditions	150Torr 1100W-1000W 1%CH ₄ 871°C	150Torr 1000W 1%CH ₄ 860°C	150Torr 1000W-950W 1%CH ₄ , 0.1% O ₂ 877°C	150Torr 1000W 1%CH ₄ , 0.2% O ₂ 921°C
Growth rate	0.94 $\mu\text{m/h}$	1.07 $\mu\text{m/h}$	0.55 $\mu\text{m/h}$	0.26 $\mu\text{m/h}$
Diamond Raman peak position and FWHM	1333.11 cm^{-1} 2.79 cm^{-1}	1333.68 cm^{-1} 2.78 cm^{-1}	1333.72 cm^{-1} 2.91 cm^{-1}	1333.51 cm^{-1} 2.91 cm^{-1}

Fig. 9 Comparison of diamond growth with different O₂ concentrations

3.5.2 Methane Concentration

CH₄/H₂ concentration is expected to be a key factor affecting the growth rate. In this section, we performed growths by varying CH₄/H₂ concentration while the growth duration is fixed for 1 h. Microwave power, chamber pressure, and growth temperature are kept similar among all the growths. The results in Figure 10 show that the growth rate keeps reducing with decreased CH₄/H₂ concentration. A good linear relationship between growth rate and CH₄/H₂ concentration can be resolved in Fig. 10. Although CH₄/H₂ concentration varied for the growths, the FWHM of diamond Raman peak looks similar.

CH ₄ /H ₂ concentrations	1%	0.8%	0.6%		0.5%
Growth conditions	150Torr 1000W 875°C	150Torr 1000W 889°C	150Torr 1100W 845°C	150Torr 950W 881°C	150Torr 900W 871°C
Growth rate	1.07 um/h	0.82 um/h	0.38 um/h	0.47 um/h	0.23 um/h
Diamond Raman peak position and FWHM	1333.57 cm ⁻¹ 2.88 cm ⁻¹	1333.97 cm ⁻¹ 2.86 cm ⁻¹	1333.76 cm ⁻¹ 2.97 cm ⁻¹	1333.99 cm ⁻¹ 2.75 cm ⁻¹	1333.96 cm ⁻¹ 2.78 cm ⁻¹

Fig. 10 Comparison of diamond growth with different CH₄ concentrations from 1% to 0.5%.

Next, we increased the CH₄/H₂ concentration from 1% to 4%. The results in Fig. 11 demonstrate that the growth rate does increase with higher CH₄/H₂ concentration. In order to use higher microwave power but keep the growth temperature similar, the last growth was performed using a 2-mm holder, which turns out to have the highest growth rate. Meanwhile, the photos show that the color of plasma becomes brighter with higher CH₄/H₂ concentration or higher chamber pressure, showing an increased plasma temperature.

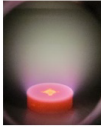
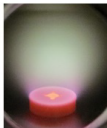
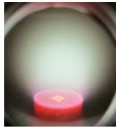
CH ₄ /H ₂ concentrations	1%	2%	4%		4% (2mm holder)
Growth conditions	150Torr 1200W 879°C	150Torr 1200W 867°C	150Torr 1200W 892°C	180Torr 1250W 886°C	180Torr 1400W 888°C
Growth rate	1.3 um/h	2.5 um/h	6.9 um/h	9.6 um/h	12.9 um/h
Diamond Raman peak position and FWHM	1333.65 cm ⁻¹ 2.87 cm ⁻¹	1333.99 cm ⁻¹ 2.79 cm ⁻¹	1334.03 cm ⁻¹ 2.82 cm ⁻¹	1333.71 cm ⁻¹ 2.86 cm ⁻¹	1333.91 cm ⁻¹ 2.73 cm ⁻¹
Plasma photo					

Fig. 11 Comparison of diamond growth with different CH₄ concentrations from 1% to 4%

3.6 Ion Implantation and Lift-off Process

Having diamond substrates with similar properties is very important for researchers to systematically optimize the epilayer growth conditions. However, the bulk and surface properties of commercially available diamond substrates usually vary from batch to batch depending on growth and polishing conditions. Moreover, the price of high-quality and high-purity diamond substrates is very high and lead time is becoming longer due to high demand. Therefore, we aim to come up with solutions to reuse the diamond substrates while keeping the surface properties the same.

The most promising process for these purposes is the lift-off process through ion implantation, which was developed in the 1990s¹³ and illustrated in Fig. 12. First, carbon ion implantation with high-energy 3 MeV is performed on diamond

substrate, which induced a damaged layer sitting at 1.6 μm below the surface, leaving low damage near the surface. After ion implantation, the diamond substrate is loaded into the reactor for epilayer growth. The growth temperature is high enough to convert the damaged layer into the graphite layer. After the growth, the graphite layer is removed by etching, making the CVD-grown epilayer separate from the original diamond substrate. The separated surface is found to be smooth and identical to the original diamond surface, which can be reused for more growth without the need for polishing. Three major steps may need optimization: ion implantation, diamond epilayer growth, and etching process. The diamond epilayer growth optimization has already been stated in the previous sections. We will need to focus on the etching process. The most popular method to etch the graphite layer is electrochemical etching.

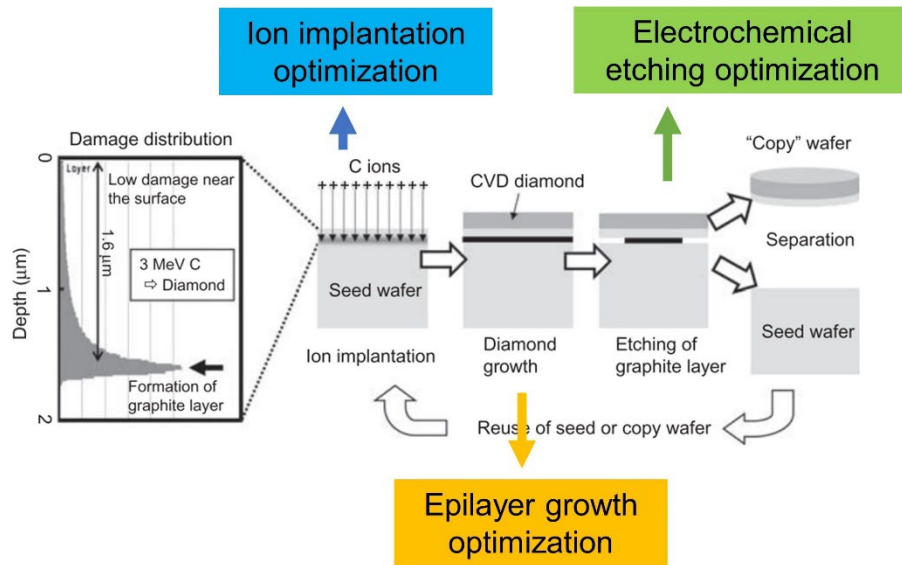


Fig. 12 Ion implantation and lift-off process

We performed ion implantation on two samples from Element Six, a PCD and a regular-grade SCD. After ion implantation, it can be clearly seen from Fig. 13a that the surface contrast has changed. The SCD became nontransparent. Raman spectra in Fig. 13b show that the diamond peak turns broad and weak, while graphite peaks arise. Then the PCD was broken into pieces, and epilayer growth was conducted on a piece of them. Based on the weight gain, the grown film thickness is around 16.7 μm . The sample was then immersed in electrolyte $\text{K}_2\text{SO}_4/\text{H}_2\text{SO}_4$, while a DC source supplies approximately 30 V through Pt wire electrodes. Unfortunately, the lift-off process was not successful. Instead, a small area of epilayer on the sample disappeared, making the original substrate exposed (Fig. 13c). The edge of the epilayer can be seen in the SEM image in Fig. 13d, where the original substrate exhibits low surface roughness. The AFM height profile in Fig. 13e reveals that the

thickness of the epilayer is approximately 14–18 μm , which is in good agreement with the previously calculated thickness from weight gain. Raman spectra collected on the epilayer and substrate show similar features. The results demonstrate the feasibility of lifting off the epilayer from the substrate. More optimization needs to be performed in the electrochemical etching process.

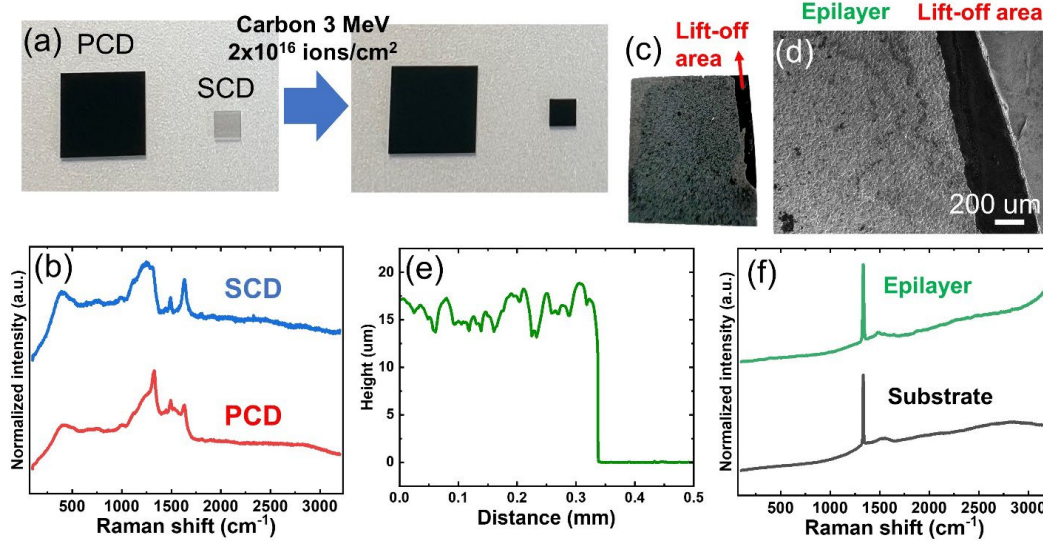


Fig. 13 (a) Optical images of polycrystalline diamond and single crystal diamond before and after ion implantation. (b) Raman spectra of diamond substrates after ion implantation. (c) Optical image and (d) SEM image of a piece of polycrystalline diamond with a lift-off area. (f) Raman spectra collected on the epilayer and the substrate.

3.7 Growth of Cubic Boron Nitride/Diamond by Pulsed Laser Deposition

UWBG semi-conductors lie at the heart of next-generation high-power RF electronics, owing to their high chemical, thermal, and mechanical stability. According to the Baliga figure of merit (BFOM) of power loss (Fig. 14a), UWBG diamond and cubic boron nitride (c-BN), the two strongest materials, show great potential for devices with very high breakdown voltage (~ 1000 V) and low power loss, suitable for RF electronics.¹⁴

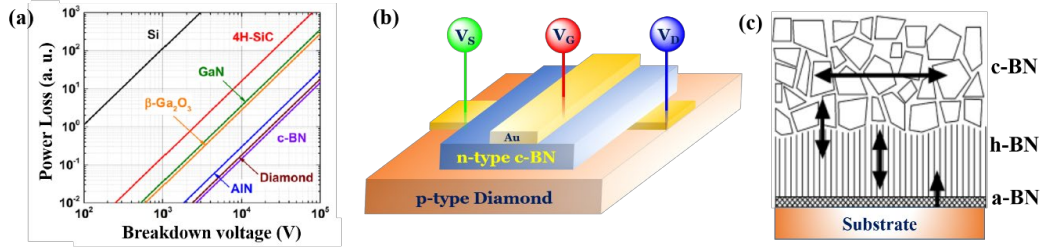


Fig. 14 (a) Wide and ultrawide-bandgap semiconductors with Baliga figure of merit (BFOM). (b) Schematic of the field-effect transistor with c-BN and diamond. (c) Growth of various phases of BN while growing the c-BN phases.

Diamond and c-BN are structurally, chemically, thermally, optically, and electrically compatible to each other (Table 1).¹⁵ The only difference is that while c-BN can be doped with both p- and n-type dopants, diamond can only be p-type doped. Therefore, an ideal high-mobility transistor could be produced by making the electronic-quality interface between n-type c-BN and p-type diamond, forming the FET devices with very high mobility (Fig. 14b).

Table 1 Property comparison of bulk c-BN and diamond

Property	c-BN	Diamond
Lattice constant (Å)	3.61	3.56
Bond length (Å)	1.57	1.54
Band gap (eV)	6.36	5.55
Density (gm/cm ³)	3.45	3.51
Refractive index	2.1	2.42
Thermal conductivity (W m ⁻¹ K ⁻¹)	1200	2000
Electrical resistivity (Ω-m)	10 ⁸	10 ⁹
Doping ability	Both p and n-type	Only p-type
Oxidation resistance (°C)	> 1200	> 700
Corrosion resistance	Yes	Yes
Baliga figure of merit (Power loss in vertical device)	600	1100
Johnson figure of merit (Power at high frequency)	8200	5800
Keyes figure of merit (For thermal limitation)	32	31

The growth of electronic quality (i.e., single crystalline, defect-free, and ultra-smooth) pure (and doped) (001) c-BN thin films on (001) diamond substrates are of the utmost importance for device scientists. The growth of electronic-quality c-BN thin films by using any growth method remains challenging, as B and N form a very rich and nontrivial pressure-temperature phase diagram.¹⁶ Depending on pressure and temperature, BN forms various phases (e.g., h-BN, c-BN, r-BN, and

w-BN). For the device fabrication, our aim is to grow metastable epitaxial c-BN thin films on (001) SCD substrates with atomically smooth interfaces.

In terms of growth, some effort has been put forth to deposit c-BN thin films on various substrates (e.g., sapphire, Si, and diamond) by CVD and molecular beam epitaxy, with little success. In most cases, an interfacial defective BN layer (turbostratic or amorphous BN) forms during the growth due to the minimization of the interfacial energy (Fig. 14c).¹⁷ Therefore, the interface was found to be defective, hindering its usefulness for high-performance RF devices, as it causes a lot of scattering centers at the interface, hence reducing the carrier mobility. Therefore, the goal is to grow electronic-quality c-BN/diamond heterostructures with atomically sharp defect-free ultra-smooth interface to fabricate RF devices.

3.8 Pulsed Laser Deposition Thin Film Growth Facility at Rice University

For the c-BN thin film growth, we are using the pulsed laser deposition (PLD) growth facility at Rice University. As stated in the literature, c-BN thin films can only be grown at very high temperature and pressure, thus requiring a high amount of kinetic energy to the B and N radicals during growth. Based on this information, we adopted a more advanced and highly energetic thermally nonequilibrium PLD growth process (Fig. 15a). The advantages of PLD over the other deposition process is that we use a highly dense stoichiometric single or polycrystalline target for the ablation by high-energy UV-pulsed laser, in either high-vacuum or in the presence of a partial gas pressure (mostly inert atmosphere) environment.¹⁸ This is an ultra-clean film growth process that does not form residue onto the film during the deposition. Moreover, the process shows the faithful transfer of elements from the target to the substrate surface, producing a film with a stoichiometric ratio and epitaxial in nature. Also, the film-substrate lattice mismatch plays a crucial role, and the deposition process is endowed with the transfer of high-energy radicals and ions ($\sim 10\text{--}100$ eV) in the form of a dense plasma, which travels to the substrate within a few microseconds and coalesces together, resulting in the epitaxial BN film growth.

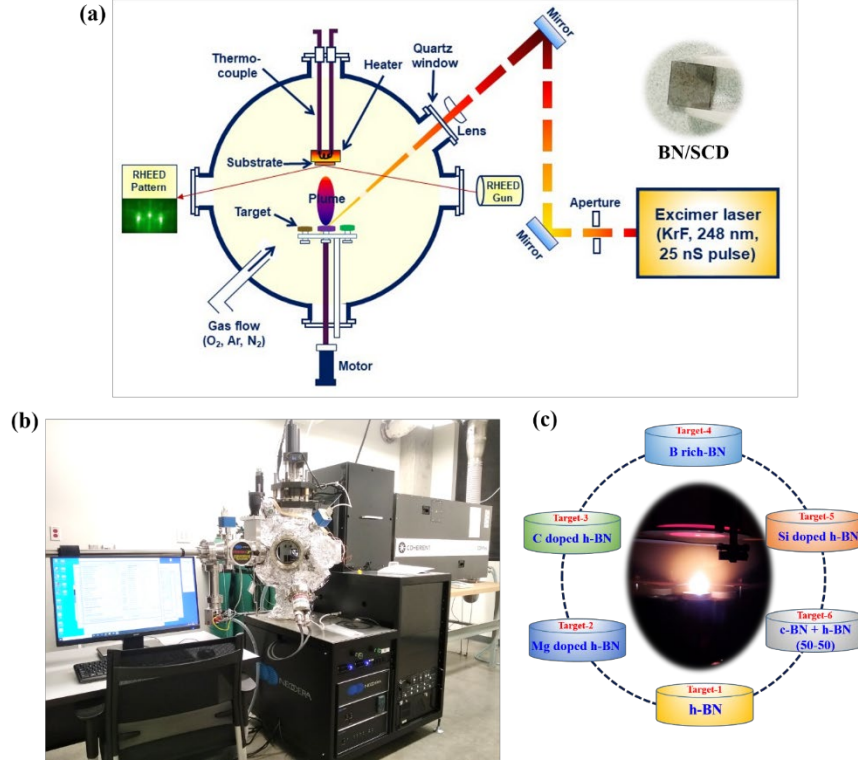


Fig. 15 (a) Schematic of a PLD process in which pulsed laser ablates the target surface and generates plasma impinging onto the substrate and deposits as a film. (b) PLD facility installed at Rice University. (c) Typical image of BN films with multiple targets mounted in the PLD chamber.

An advanced ion-beam-assisted PLD chamber (Pioneer 180 PLD) installed at Rice University is shown along with the formation of plasma during the real-time BN thin film growth (Figs. 15b,c). The KrF excimer laser has a wavelength of 248 nm (photon energy ~ 5 eV, with pulse width of 25 nS). The chamber is equipped with a substrate load-lock (base vacuum $\sim 5 \times 10^{-8}$ Torr). It has a multitarget carousel with a target raster/rotation facility (six targets can be mounted at a given time for the multilayer growth) (Fig. 15c). We also have a target raster and a software-controlled target selection facility, needed for multilayer and superlattice growth. The base vacuum of the chamber can go down to $\sim 2 \times 10^{-9}$ Torr, and the maximum achievable growth temperature of 800 °C. The typical substrate size for the growth must be $\sim 10 \times 10$ mm² or lower, limited by the plume shape and size. We use nitrogen partial pressure (1–500 mTorr) for the growth, controlled by the mass flow controllers. The chamber is also equipped with the ion-beam-assisted growth facility, where we can supply additional high-energy Ar⁺ ions at high-acceleration voltage (300–800 V), generated by an RF ion source, to provide additional energy to the ablated species.

Since various factors play pivotal roles during the film deposition, we needed to optimize all the growth parameters in order to obtain high-quality c-BN thin films (e.g., growth temperature, laser energy, pulse repetition rate, partial gas pressure, and substrate quality). For depositing approximately 20-nm c-BN thin films, we used normal-grade (100) SCD substrate (Fig. 15a) and optimized the growth parameters. The number of laser pulses per second calibrates the thickness of the film.

3.9 Single Crystal Diamond Substrate Characterizations

To grow c-BN thin films, we used normal-grade single crystal (001) SCD substrates (purchased from Element Six). First, we characterized the crystallinity of SCD substrates by using several characterizations (Fig. 16). We performed XPS, both survey and elemental scans, showing the presence of an intense carbon peak (Fig. 16a) with small traces of Si impurity, possibly due to the mechanical polishing effect. We also performed in-situ annealing, which shows improved quality with the reduction of oxygen and Si peaks on the surface (Fig. 16b). This shows the necessity of pre-annealing the SCD substrates prior to c-BN growth. High-resolution XRD shows only the (004) peak of diamond throughout the scan range, indicating the single crystallinity (Fig. 16c). The FWHM of the rocking curve is approximately 0.3° , indicating high-crystalline quality. The surface topography was obtained through AFM, showing a smooth surface, with some dips (~ 10 nm) (Fig. 16c). We measured the miscut angle of the substrate by doing the rocking curve analysis at different azimuthal angles (Fig. 3d). From the azimuthal scans, we found the miscut angle to be approximately 1.54° (Fig. 3e). In the Raman spectra, we can see the intense D-band peak (~ 1333 cm^{-1}) from the diamond, along with several nitrogen vacancy-related peaks (Fig. 16f).

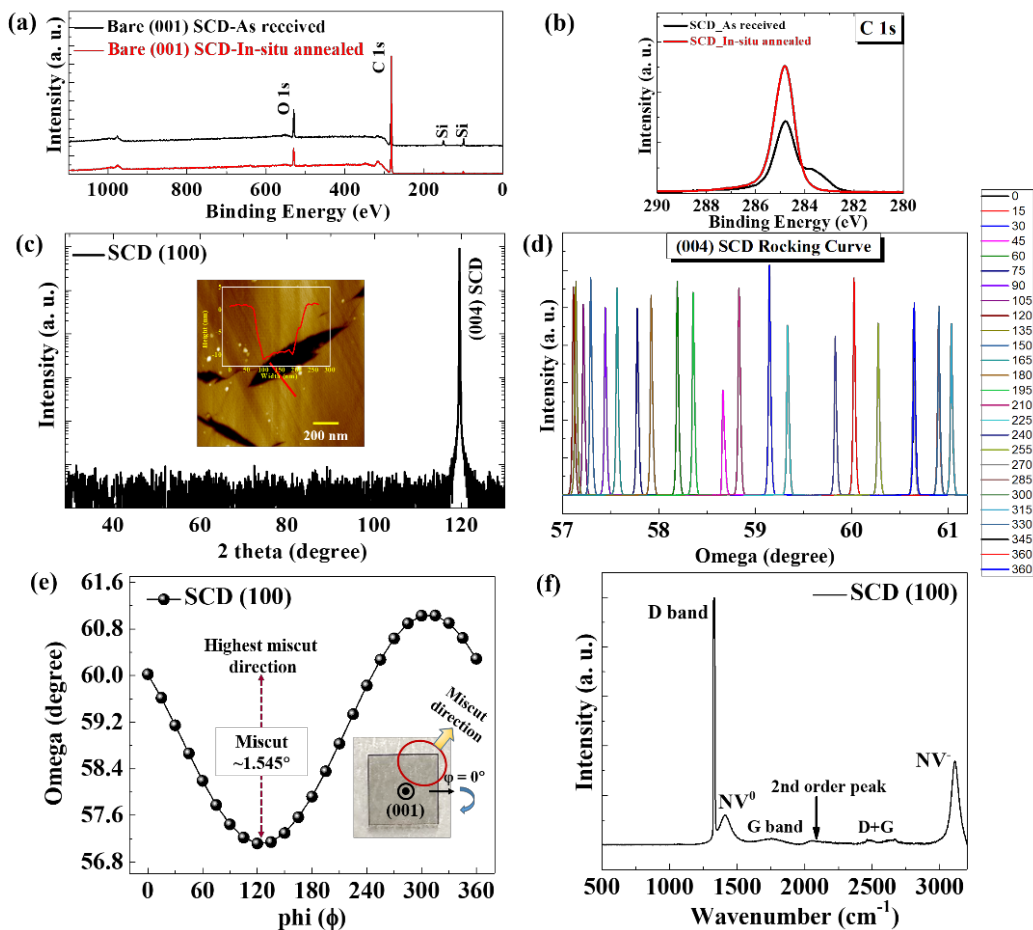


Fig. 16 (a,b) X-ray photoelectron spectroscopy, (c) X-ray diffraction, (d) omega rocking curve, (e) azimuthal angle dependence omega scan to measure the miscut angle, and (f) Raman spectra of the normal-grade single crystal (001) diamond substrates

3.10 Room Temperature Growth and In-situ Annealing

Considering the complex c-BN phase diagram, we first deposited the BN films on SCD at room temperature and at 100 mTorr N₂ partial pressure. Although it showed the growth of BN in Raman, we do not see any BN-related peaks. Therefore, we performed the in-situ annealing of the grown BN films at approximately 750 °C in 100 mTorr N₂ atmosphere for several hours and optimized the annealing time to improve the quality of the BN films. Optimized annealing for 30 min at 750 °C improves the quality, and in Raman, one can now see the c-BN-related peak at 1060 cm⁻¹ (Fig. 17a). Grazing angle X-ray diffraction (GIXRD) shows the c-BN (111) diffraction peak, with FWHM of approximately 0.35°, which gives an estimated crystal size of approximately 24.4 nm (Fig. 17b). AFM surface topography shows an improved surface quality of BN after a 30-min anneal. This annealing process results in a lower surface roughness than that found on as-grown or longer time-annealed samples (Fig. 17c). In the XPS, we can see that for longer time annealing,

we started losing B and N from the surface, the reason for which remains puzzling. Remarkably, the refractive index (n) measurement in the visible to NIR wavelength range of the 30-min annealed BN/SCD film shows $n \sim 2.3$, similar to the refractive index reported for c-BN² (Fig. 17d).

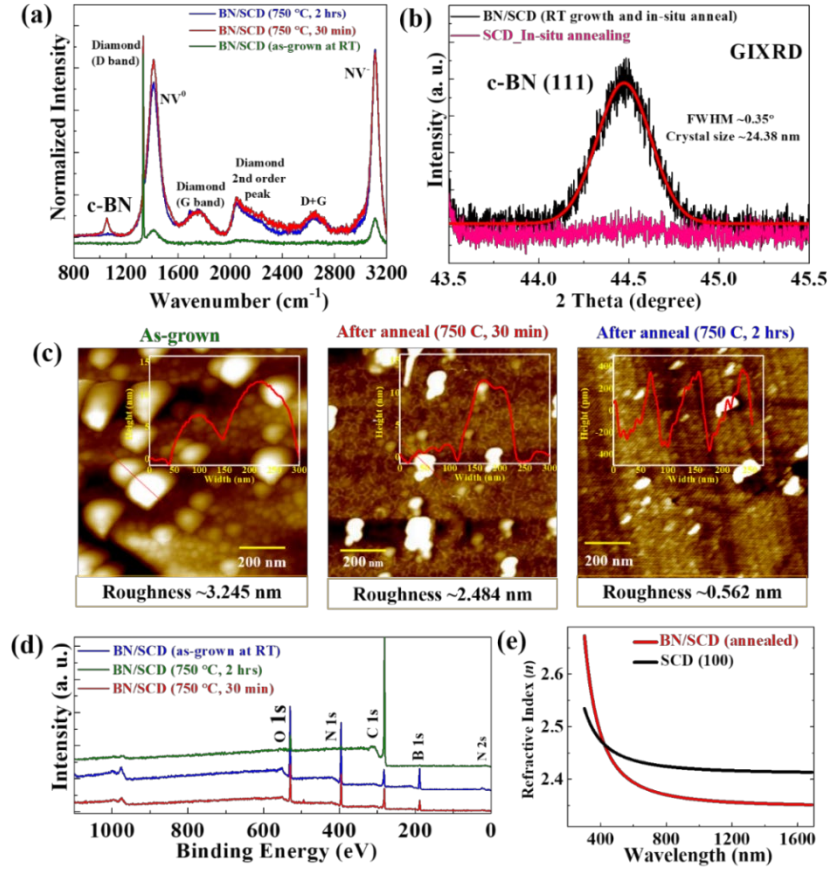


Fig. 17 (a) Raman spectra, (b) grazing-angle X-ray diffraction, (c) surface topography, (d) X-ray photoelectron spectroscopy, and (e) refractive index of the BN films grown at room temperature with subsequent high-temperature annealing

3.11 High-Temperature Growth and In-situ Annealing

After room temperature growth, we grew BN thin films on SCD at high temperature (at ~ 750 °C) and subsequently annealed them at the same temperature after growth. We also compared these BN films with the BN films grown at high temperature, but not annealed after growth. GIXRD of the annealed film showed that the XRD peak is more profound (Fig. 18a). In comparison, a pristine annealed SCD or only a high-temperature grown BN film does not show a significant peak in XRD. This better crystalline quality of BN is also reflected in the Raman spectra, showing c-BN-related peaks at approximately 1050 cm^{-1} (Fig. 18b). Moreover, the optical

refractive index measurement shows the value of $n \sim 2.4$ in the visible to NIR wavelength range (Fig. 18c).

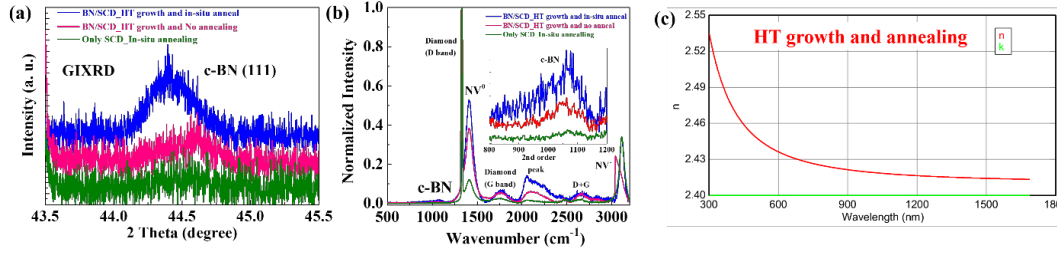


Fig. 18 (a) Grazing-angle X-ray diffraction, (b) Raman spectra, and (c) refractive index of the BN films grown at high temperature with subsequent annealing at the same growth temperature

3.12 Comparison in Room Temperature vs. High-Temperature Growth and Annealing

We then compared the crystalline quality of BN films on SCD for the room temperature growth and high-temperature (at 750 °C) growth cases. As seen, both in the XRD and Raman, the high-temperature growth and annealing cases show much better resultant peaks than RT (Fig. 19). This clearly indicates that to obtain better crystalline quality of c-BN, one needs to grow films at high temperature with subsequent annealing for 30 min.

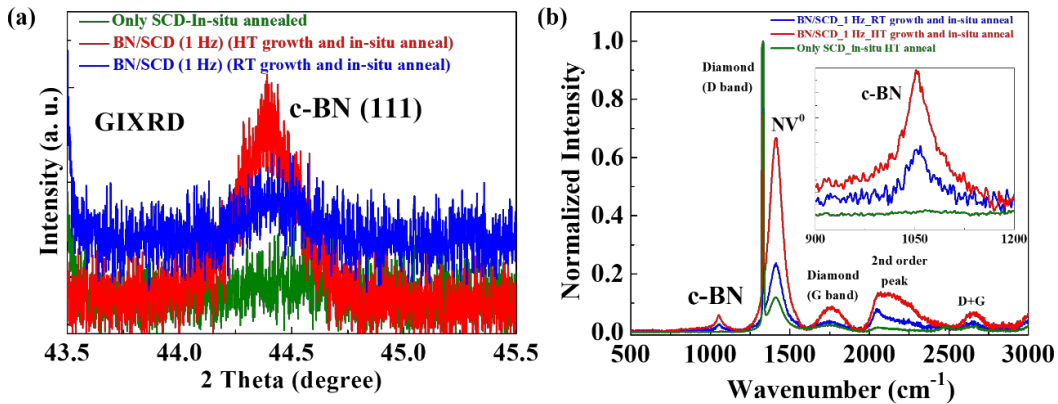


Fig. 19 Comparison of (a) grazing-angle X-ray diffraction and (b) Raman spectra of the BN films grown at high and low temperature with subsequent high-temperature annealing

3.13 Pressure-Dependent BN Growth on SCD at High Temperature

Since higher growth temperature (~ 750 °C) is crucial for the better crystalline c-BN, we tried to optimize the partial nitrogen pressure (P_{N_2}) during growth, as it always affects the film quality. By keeping the other conditions similar, we varied

the supplied N₂ partial pressure from 1 to 500 mTorr. Although the target contains B and N with a 1:1 ratio, there is a propensity for a loss of N during growth that results in N vacancies in the grown film. Supplying additional N₂ during the growth compensates the N vacancies. As seen from XRD and XPS, films grown at higher partial pressure show better crystalline quality. In XPS, we do not see the B-B and/or B-C related peaks when we grow films at higher partial pressure; however, we do see them for films grown at lower partial pressure (Fig. 20a). This clearly shows that supplying additional N₂ pressure compensates the N vacancies during growth. This is also clearly reflected in the XRD, for films grown at higher partial pressure show better crystalline peak of c-BN in comparison to films grown at lower partial pressures (Fig. 20b). Overall, these observations indicate that for better c-BN quality, along with high-temperature growth and post-annealing, we also need high partial pressure.

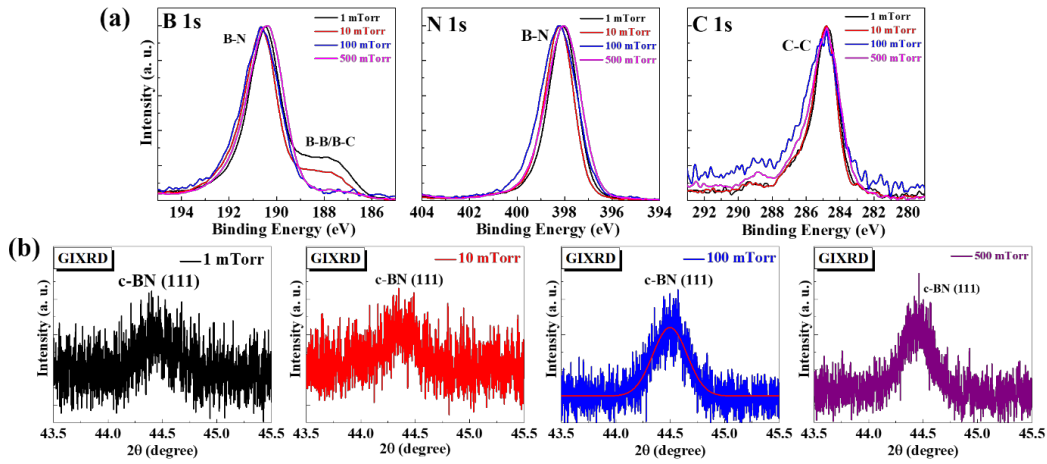


Fig. 20 (a) X-ray photoelectron spectroscopy and (b) grazing-angle X-ray diffraction of the pressure-dependent BN thin films growth

3.14 Frequency-Dependent BN Growth on SCD at High Temperature

After optimizing the temperature and pressure for the better c-BN growth, we also performed the frequency-dependent growth (at 5 and 1 Hz). We changed the number of laser pulses per second that impinge onto the target. Considering that both B and N are light elements, a higher repetition rate might have a scattering issue. However, in some cases a higher repetition rate can reduce impurity incorporation (mainly oxygen species) and is due to the resulting increase in film growth rate. Considering that annealing is a crucial factor for the growth, a slow growth rate would also provide additional time for the B- and N-related species to mobilize and thereby improve the crystalline quality. As seen, the slower growth process does moderately improve the crystalline quality of the films, as slightly

higher intensity is shown in the GIXRD as well as in the Raman spectra for c-BN (Fig. 21). The crystallite sizes are found to be slightly smaller for the slower deposition process.

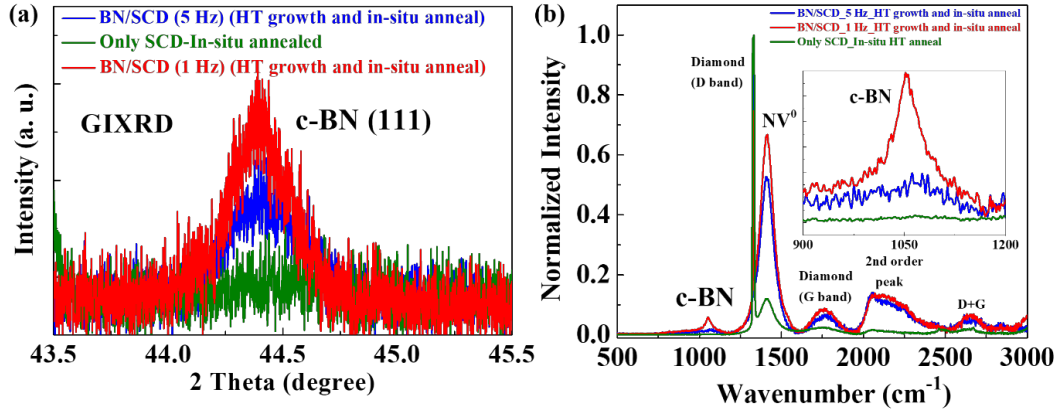


Fig. 21 Comparison of (a) grazing-angle X-ray diffraction and (b) Raman spectra of the repetition rate-dependent BN films grown at high temperature

3.15 Doping-Dependent BN Growth on SCD at High Temperature

In the literature, it has been shown that for c-BN growth, the catalyst (magnesium [Mg], silicon [Si], and possibly beryllium [Be]) plays an important role for c-BN nucleation, as it possibly reduces the high-energy barrier of the c-BN formations.⁴ We tried to perform the growth, not by supplying Mg or Si from separate sources, but by making BN targets by doping approximately 1 at% Mg or Si. By performing this procedure, we can supply Mg or Si during growth and see how the c-BN nucleation changes. It should be mentioned that we kept all growth conditions the same (growth temperature 750 °C, nitrogen partial pressure of 100 mTorr, repetition rate of 5 Hz, and pre-annealing and post-annealing of ~30 min). After the growth, we checked that the films contained B and N by using XPS, which showed the presence of B and N in equal ~1:1 ratio for both the cases (Fig. 22a). In the GIXRD, we see the c-BN (111) peak, but interestingly, the Mg-doped case shows a more profound peak in the XRD (Fig. 22b). In Raman spectra, we can also see the peak around approximately 1050 cm⁻¹, which corresponds to the c-BN transverse optical modes⁴ (Fig. 22c). In addition, we also varied the repetition rate during growth for both films and performed Fourier transform infrared (FTIR) (Figs. 22d,e). Clear c-BN peaks were shown between 1000 and 1100 cm⁻¹, but they were better resolved for the Mg-doped cases, further providing evidence of formation of c-BN on SCD.

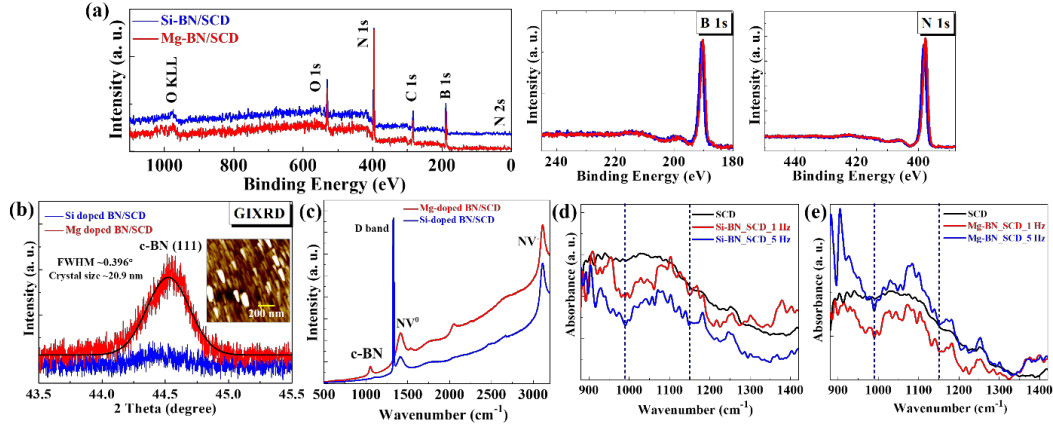


Fig. 22 (a) X-ray photoelectron spectroscopy, (b) grazing-angle X-ray diffraction, (c) Raman spectra, and (d,e) FTIR of the BN thin films grown by using the Mg- and Si-doped BN as a target

3.16 Pressure-Dependent Mg-Doped BN Thin Film Growth on SCD

Since Mg-doped BN cases show slightly better crystalline quality, we also performed several growth experiments by varying the nitrogen partial pressure during the Mg-doped BN growth case (mainly at 100 and 500 mTorr) and performed several characterizations. As seen in the GIXRD and Raman spectra, both cases show similar features (Fig. 23). From the Debye–Scherrer equations, we can estimate that the particle sizes are approximately 23.82 nm (for the 100 mTorr case) and 24.38 nm (for the 500 mTorr case) (Figs. 23a,b). In addition, the Raman spectra showed similar peaks, slightly better for the 100 mTorr growth case. Interestingly, for the higher partial pressure, the nitrogen vacancy–related peaks were suppressed (Fig. 23c).

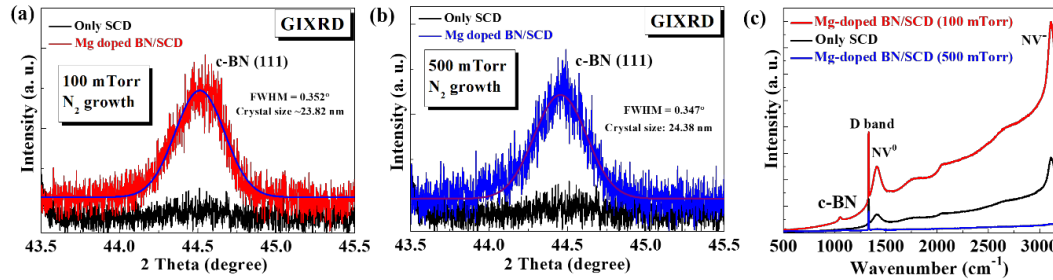


Fig. 23 (a,b) Grazing-angle X-ray diffraction and (c) Raman spectra of Mg-doped BN thin film growth at different pressures

3.17 Temperature-Dependent Mg-Doped BN Growth on Functionalized SCD

Functionalization of the diamond surface seems to play a crucial role in breaking the surface reconstruction, which facilitates the c-BN formations,⁴ affecting the first few layers of BN growth on the de-reconstructed diamond surface. Therefore, we investigated the c-BN growth by using the nitrogen-functionalized SCD surface (N-SCD). We implemented nitrogen onto the diamond surface by using the dry-chemistry approach. The nitrogen concentration on the N-SCD surface upon functionalization is approximately 2%–3%. By using N-SCD, we have grown several thin films at different temperatures. The limitation with the functionalized N-SCD surface is that we cannot grow films at a higher temperature of 750 °C, as we have been doing until now for BN growth showing optimized quality, because the functional groups evaporate from the surface above approximately 500 °C. Therefore, we have grown BN films at 300 and 500 °C on N-SCD. As shown in XPS, both B and N are present; however, at lower growth temperature the B:N elemental ratio is significantly reduced, whereas the films show approximately 1:1 B and N ratio when grown at 500 °C (Fig. 24a). Interestingly, in the GIXRD comparison, the BN films on N-SCD show that N-groups on the SCD surface promote the c-BN growth (Fig. 24b). In Raman spectra, BN films on N-SCD show the c-BN peak (at 1050 cm⁻¹) (Fig. 24c). However, in FTIR, all the films show the presence of both c-BN and h-BN phases, indicating the formation of mixed phase of BN on N-SCD substrates (Fig. 24d).

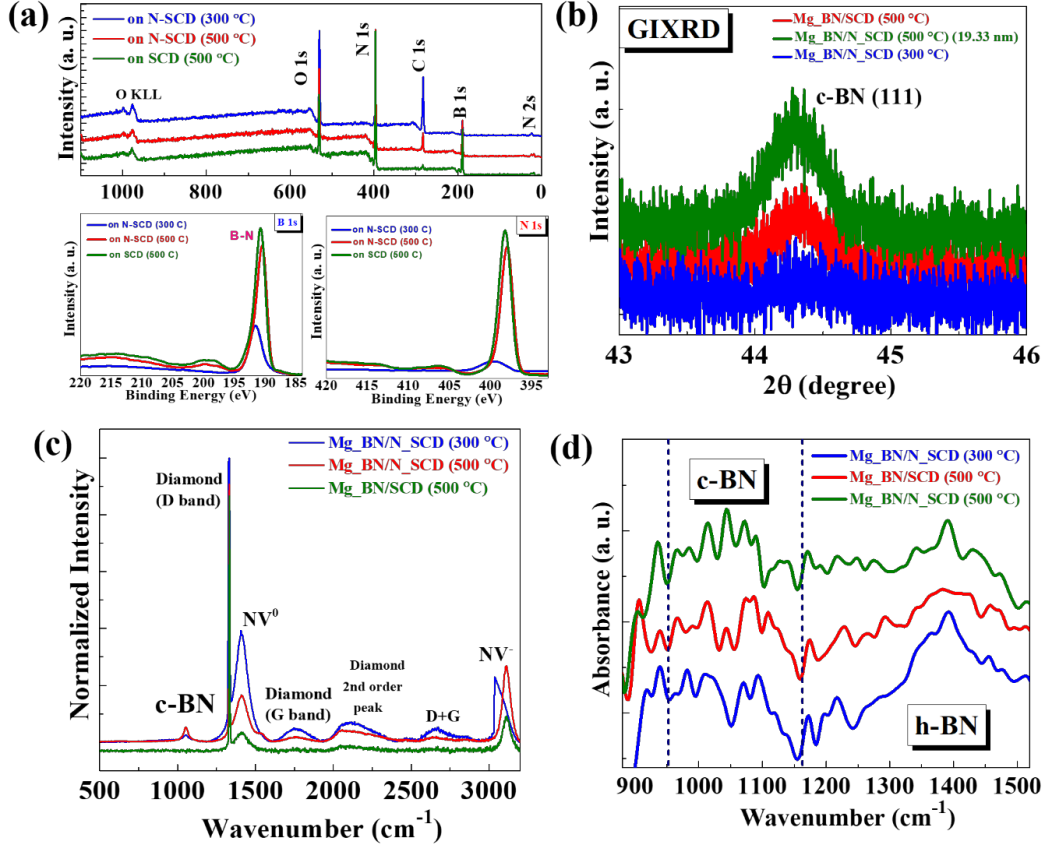


Fig. 24 (a) X-ray photoelectron spectroscopy, (b) grazing-angle X-ray diffraction, (c) Raman spectra, and (d) FTIR of Mg-doped BN thin films grown on N-functionalized (001) SCD substrates at different growth temperatures

3.18 Energy-Dependent Growth of Intrinsic BN

We have grown intrinsic BN films by varying the laser energy (which changes the energy density of the ablated species) to see what impact it would make on the film. We used three different laser energies to grow BN films (220, 400, and 600 mJ) and performed various characterizations. In all three cases, we observed the peak related to c-BN in the GIXRD, and the intensity of this peak was observed to increase with the laser energy (Fig. 25a). The crystal sizes are typically around 17–18 nm (from the Debye–Scherrer equation). Raman spectra show similar behavior (Fig. 25b). We also performed FTIR on the films and compared them with the Mg-doped BN cases. Interestingly, in FTIR we can see both the c-BN and h-BN related phases when we apply the high laser power, whereas in the lower-energy case, we see a better c-BN related peak, with a minimal amount of h-BN (Figs. 25c,d). We also performed the elemental depth-profile analysis by secondary ion mass spectrometry (SIMS) for Mg-doped BN films. It shows that rather than acting as a catalyst, Mg or Si is doped throughout the BN film. We have not studied further for

the c-BN growth optimization, as our goal is to grow the pure c-BN thin films on diamond. However, Mg is a p-type dopant for c-BN, so it would be interesting to explore the p-type c-BN/diamond-based RF devices in the future.

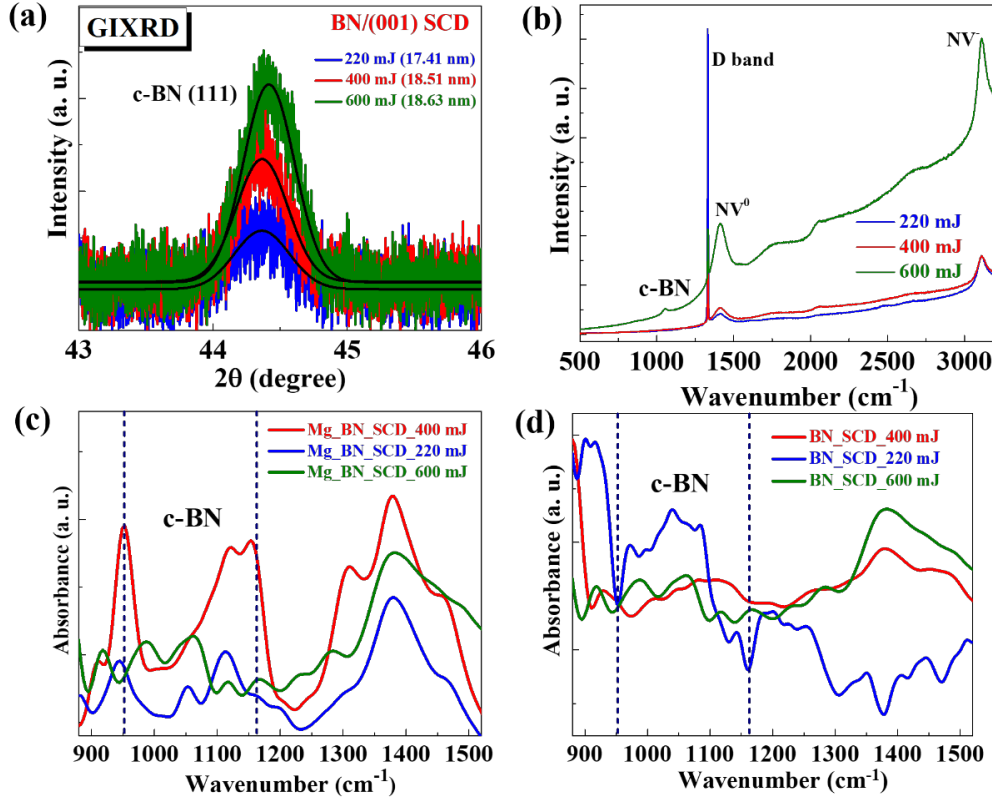


Fig. 25 (a,b) Grazing-angle X-ray diffraction, (b) Raman spectra, and (c,d) FTIR spectra of pure and Mg-doped BN thin films grown at different laser energies

3.19 BN Growth on N-Functionalized Hydrogenated SCD Substrates

We now move to the pure c-BN thin film growth on functionalized SCD (i.e., on N-SCD). We have grown films on hydrogenated SCD (H-SCD) and nitrogen-functionalized hydrogenated SCD surfaces (N-H-SCD). In XPS, we can see the presence of both B and N in the films with an approximate 1:1 elemental ratio (Figs. 26a,b). In Raman spectra, we can clearly see the c-BN peak at approximately 1050 cm^{-1} , which is not seen either for pristine SCD or for c-BN film grown on H-SCD surfaces (Fig. 26c). FTIR spectra show the presence of both h-BN and c-BN, but one can see the more profound peak for h-BN (Fig. 26d). Thus, we need to optimize the growth conditions further for the c-BN film growth on N-H-SCD.

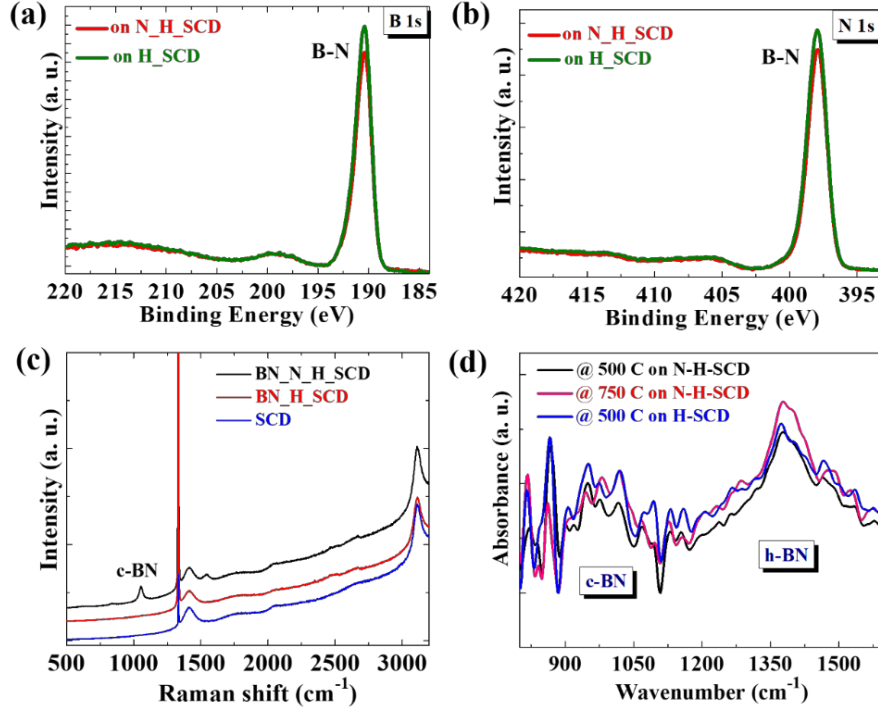


Fig. 26 (a,b) X-ray photoelectron spectroscopy, (c) Raman spectra, and (d) FTIR of BN thin film grown on N-functionalized hydrogenated SCD surface at different temperatures

3.20 BN Growth on Implanted SCD Surface

To gain additional insight and optimize the c-BN grown by trying to break the surface reconstruction, we have used various cations implanted in the SCD surface. By using ion implantations (in Dresden, Germany), we have implanted B, N, and both B and N onto the diamond surface and grown BN films to investigate the quality of grown c-BN films. We have also used B implantations on the SCD surface, which is subsequently annealed at 200 °C. Prior to the growth, we annealed the implanted SCD surfaces in a nitrogen atmosphere for an hour at approximately 500 °C inside the PLD chamber to remove the unwanted adsorbates or contaminations. We then grew BN films on the implanted SCD surfaces by using similar growth conditions (at 500 °C, 100-mTorr nitrogen pressure, 5 Hz) and compared them with the only implanted diamond surface. After the growth, we performed the GIXRD, Raman, and FTIR of BN films. Although we see the GIXRD peaks, they are not very strong compared with earlier cases (Fig. 27a). In Raman spectra, we do see the c-BN peaks at approximately 1050 cm^{-1} for the BN films on implanted SCD surfaces, which were absent for the only implanted SCD surface (Figs. 27b,c). In FTIR, we can see peaks from both c-BN and h-BN for all cases; however, N-implanted SCD shows a better c-BN percentage than the films

on the other implanted SCD surface (Fig. 27d), illustrating the importance of nitrogen on the SCD surfaces.

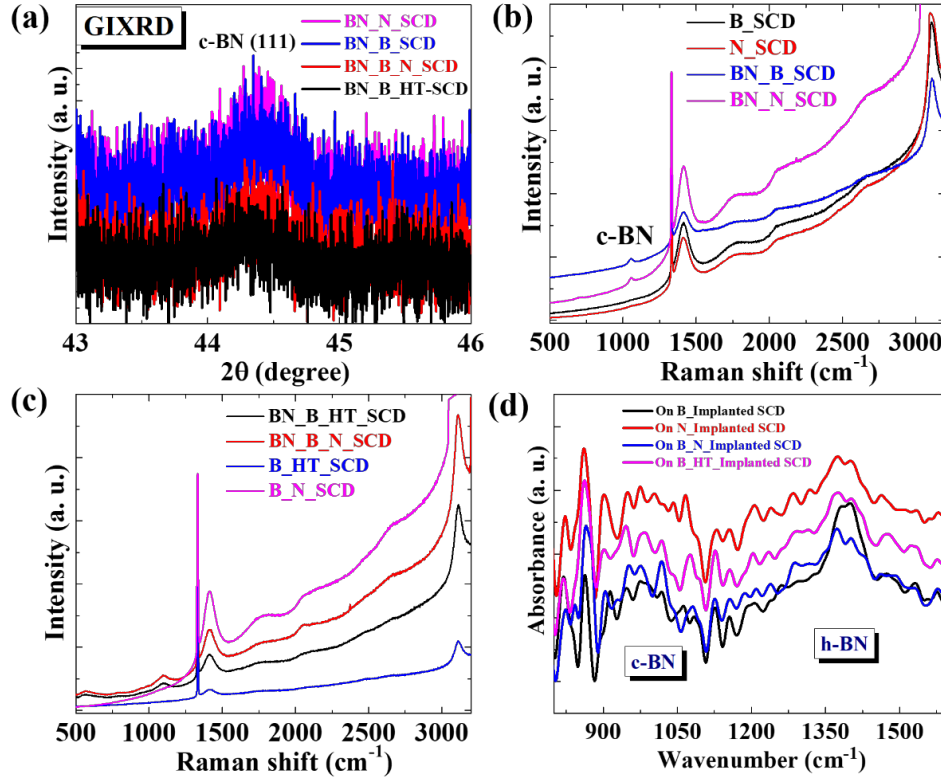


Fig. 27 (a) Grazing angle X-ray diffraction, (b,c) Raman spectra, and (d) FTIR of BN thin films grown on implanted SCD substrate at different growth temperatures

3.21 c-BN/SCD Growth Summary and Future Plans

In summary, we attempted to optimize and grow high-quality c-BN thin films on SCD substrates. We used various growth temperatures, partial pressures, laser energy, repetition rates, elemental doping, and N-functionalized and cation-implanted diamond surfaces to understand and optimize the growth of c-BN thin films. We found that to grow better crystalline c-BN (001) thin films, we needed to use high growth temperatures (> 500–700 °C) with a nitrogen pressure of approximately 100 mTorr (Fig. 28). However, we observed that c-BN (111) is the more stable phase under these growth conditions. Furthermore, N-functionalization of the SCD surface does impact the c-BN growth. We also used various dopants to induce the p- or n-type carrier in c-BN, which is important for device fabrication. Considering that the surface of SCD is very important for BN growth, in the fourth year we plan to investigate the (de)reconstruction of the SCD surface by using a reflection high-energy electron diffraction (RHEED) setup prior to BN growth. With the RHEED facility, we can also monitor the real-time layer-controlled c-BN

film growth. In addition, we would like to vary the nitrogen concentration on the SCD surface (by using a wet and dry chemistry approach to break the diamond surface reconstruction) to promote c-BN growth. With these optimized parameters and better growth controls, we hope to achieve the highest-quality atomically smooth defect-free pure and doped (001) c-BN thin films on (001) diamond surfaces, which would be pivotal for future diamond-based RF devices.

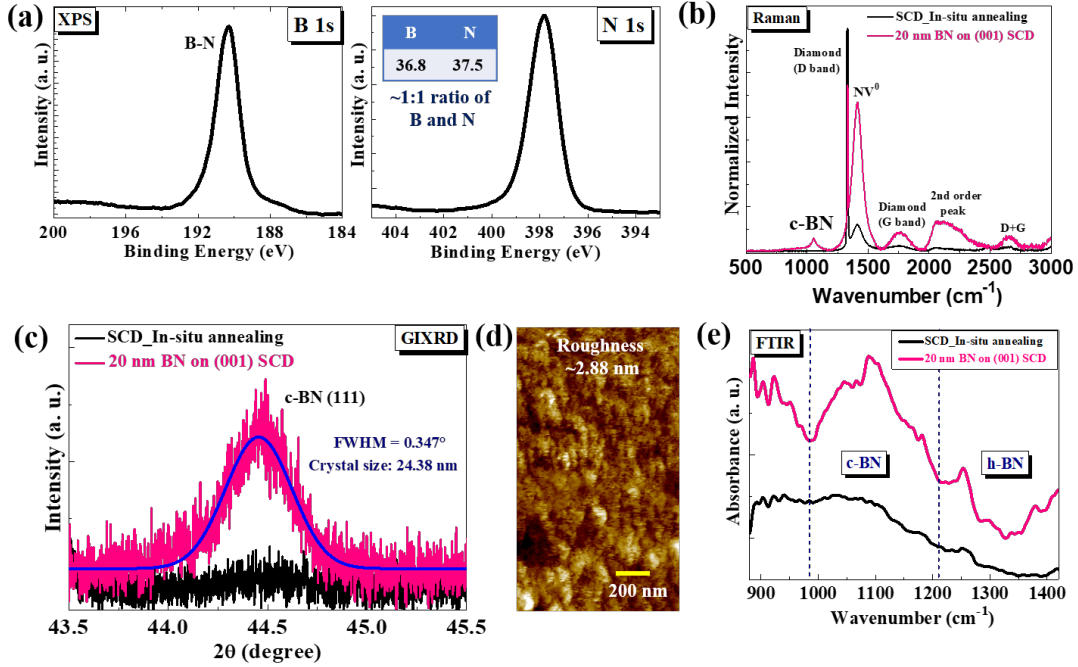


Fig. 28 Summary of c-BN/diamond thin film heterostructures: (a–e) XPS, Raman spectra, grazing incident angle XRD, atomic force surface topography, and FTIR spectra showing the growth of (111) c-BN thin films on (001) diamond substrates

4. State-of-the-Art Metrology Approaches: Microscopy and Spectroscopy of BN-Diamond Heterostructures

Since the prime objective of the research is to synthesize high-quality single crystalline diamond and diamond-BN heterostructures, it is vital to study their morphology, crystal structure, and phase purity at the bulk and atomic levels. Here, we are employing a Titan transmission electron microscope (TEM) (FEI Titan Themis3) at an acceleration voltage of 300 kV for performing electron microscopy. The unit is capable of performing TEM, scanning transmission electron microscopy (STEM), energy dispersive spectroscopy (EDS), and electron energy loss spectroscopy (EELS). The samples of interest are home-grown diamond and different phases of BN materials grown at various temperature conditions and substrates. The following samples are bulk and need TEM specimen preparation (FIB) and microscopy analysis:

- Diamond (MPCVD) BN (PLD) heterointerfaces
- PLD-deposited BN structures on various substrates
- BN deposited at room temperatures
- As-synthesized c-BN crystals
- H-BN–c-BN composites
- Boron-implanted diamond wafers
- Low-energy-implanted diamond wafers

4.1 BN Grown at Room Temperatures

As we are studying and experimenting with the phase diagram of BN materials, understanding the nucleation and growth and phase selection at a wide range of growth and annealing temperatures, including room temperature, is vital. In this study, we have deposited BN onto a TEM holey carbon grid at room temperature via PLD. The number of laser shots attempted here are 50 and 100. Later, deposited samples were analyzed under a microscope. The schematic showing the growth approach and the results of microscopy analysis is provided in Fig. 29. Note that the BN crystalline phases are being deposited even at room temperature within 50 laser shot deposition, and BN flakes/sheets were grown when the laser shot is increased to 100 shots.

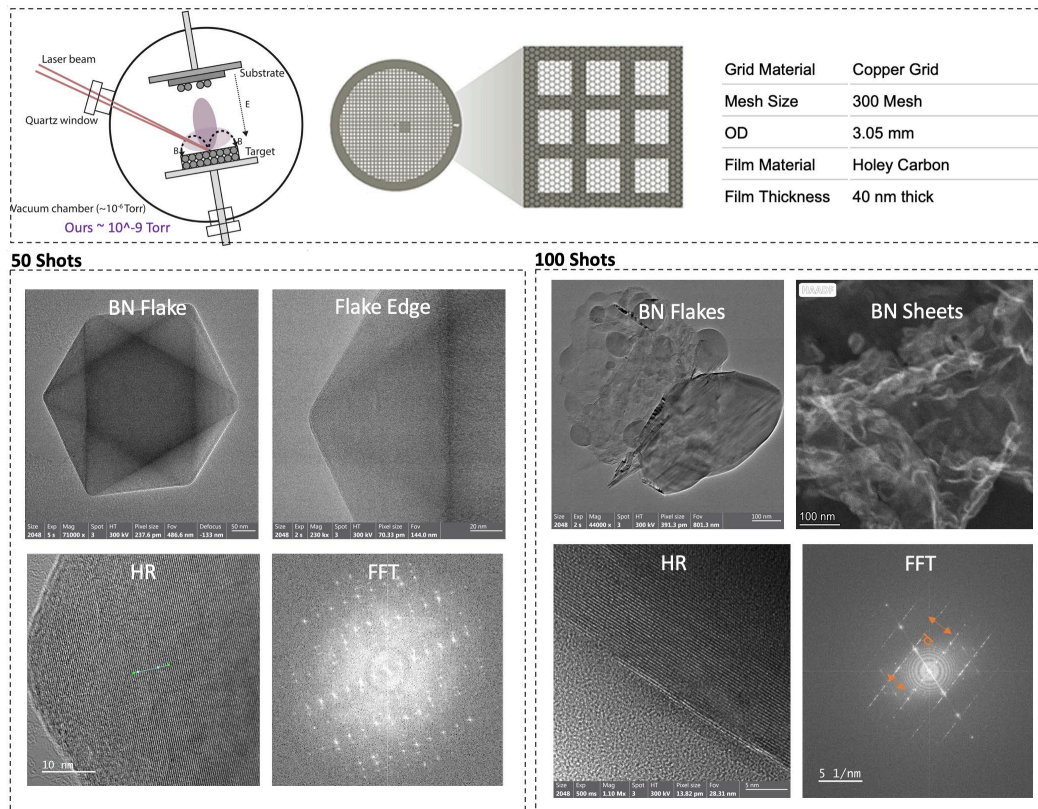


Fig. 29 (top) Schematic showing the BN deposition onto a TEM grid at room temperature; specifications of the grid are provided in the inset. (bottom) The morphology, crystallinity, and diffraction patterns of BN flakes (left)/sheets (right) deposited with 50 and 100 laser shots, respectively.

4.2 BN Structures Deposited on Single Crystalline Diamond

One of the prime objectives of the ongoing research is the synthesis of BN diamond heterointerfaces for high-power electronic applications. Here, attempts were made to epitaxially grow a cubic phase of boron nitride (c-BN) on single crystalline diamond. The growth conditions were detailed in the BN growth section. A post-annealing approach is also attempted to improve the crystallinity of deposited films. To investigate the diamond-cBN interface, cross-sectional lamella is prepared with the help of focused ion beam (FIB) milling and imaged under a microscope in STEM mode. Diamond lattice is perfectly crystalline without any ordering issues at the interface; however, the BN layer deposited shows no or very poor crystallinity with no epitaxial relationship. The scenario remains the same even after the post-annealing approach for 4 h at 800 °C. The schematic of the heterointerface and the low- and high-magnification images of the diamond lattice, amorphous BN layer, and very thin nanocrystalline layers of BN immediate to the diamond surface are displayed in Fig. 30.

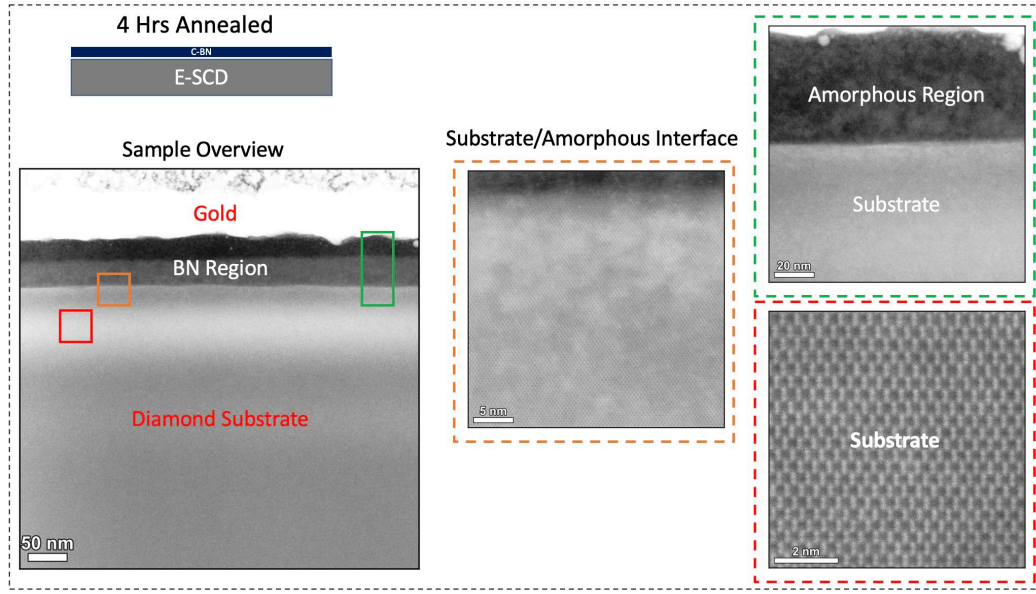


Fig. 30 (top) Schematic showing the interface of diamond and BN layer. (bottom) Low-magnification STEM image of cross section prepared via FIB and the high-magnification images of the interface, amorphous BN layer, and diamond substrate.

4.3 BN Structures Deposited on Al_2O_3

Since the direct deposition of cubic boron nitride on (100) diamond surface is not very successful, we have attempted to deposit BN on various single crystalline substrates such as sapphire, GaN, and SiC to study the possibility of growth of BN with epitaxial relation and a high order of crystallinity. In order to study the BN growth and crystalline quality, a cross-sectional lamella is prepared with the help of FIB and the sample is investigated under STEM mode. The low-magnification image of the lamella is shown in Fig. 31. In order to obtain atomic resolution images, the lamella is thinned down to less than 40 nm thick by graded thinning and polishing. The image of the interface at moderate magnification and atomic resolution images are also displayed in Fig. 31. As observed for the case of BN deposited on diamonds, crystalline BN layers were absent under the Au protection layer. If BN is present, it is limited to the immediate proximity of the Al_2O_3 surface. The plan is to grow at least 50- to 100-nm-thick highly ordered and crystalline BN layers, but the growth that took place is still far from expectations. In order to identify the elemental composition of the BN layer deposited onto the sapphire, EELS is performed. Although the EELS core loss peaks correspond to the carbon, oxygen is well evident. The spectrum edge corresponding to either boron or nitrogen is very weak in intensity or absent (Fig. 31 bottom), further indicating that the crystalline order of BN is lacking. This leads us to postulate that if BN layers have been grown, they have a nanocrystalline structure.

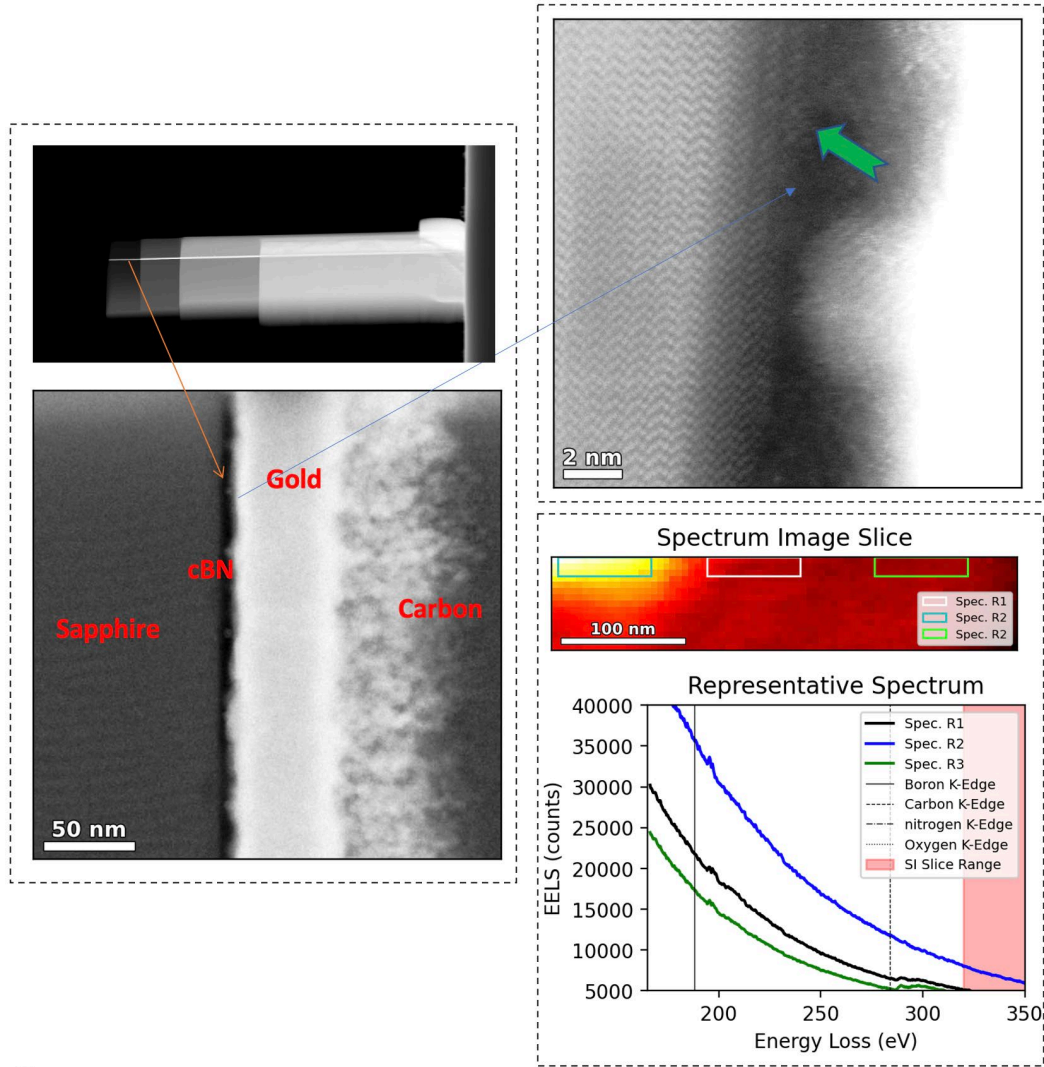


Fig. 31 (top) Cross-sectional lamella of BN deposited on Al_2O_3 substrate. (bottom) Moderate magnified image of the area of interest and atomic resolution images of the interface region and EELS spectra collected from different BN-containing regions as shown in the color mapped image.

4.4 BN Structures Deposited on GaN

Although the crystallinity of the BN layer deposited is not very high, the presence of a nanocrystalline BN layer, possibly a mix of cubic and hexagonal phases of BN on the single crystalline substrates, is promising. We have attempted to deposit BN phases on GaN crystal to study the growth possibilities and device properties with BN as a gate and electronic material, respectively. The device properties are described elsewhere.¹⁹ When it comes to the structural and microscopic properties, an approximately 15-nm-thick BN layer is deposited on the GaN substrate and is nanocrystalline in nature with spherical-like morphology. The schematic and

STEM low-mag and atomic resolution images of the cross-sectional lamella, GaN-BN interface, and GaN lattice structures are provided in Fig. 32.

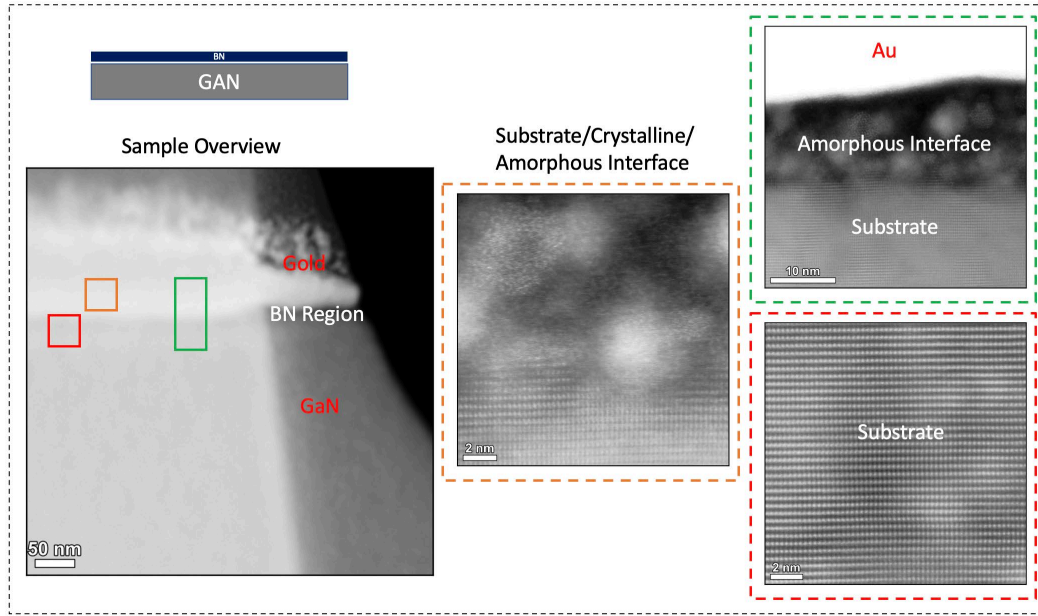


Fig. 32 (top) Schematic of BN deposited on GaN substrate. (bottom) Low-magnification STEM image of the cross-sectional lamella, GaN-BN interface, and atomic resolution images of GaN and BN nanocrystals, respectively.

Unlike the deposited BN structure on diamond and sapphire substrates, the presence of nanocrystalline BN layers is evident and reflected in the atomic resolution STEM images, FFT patterns and d-spacing values, the EELS spectra, and the map generated based on EELS spectra and machine learning (Figs. 33 and 34).

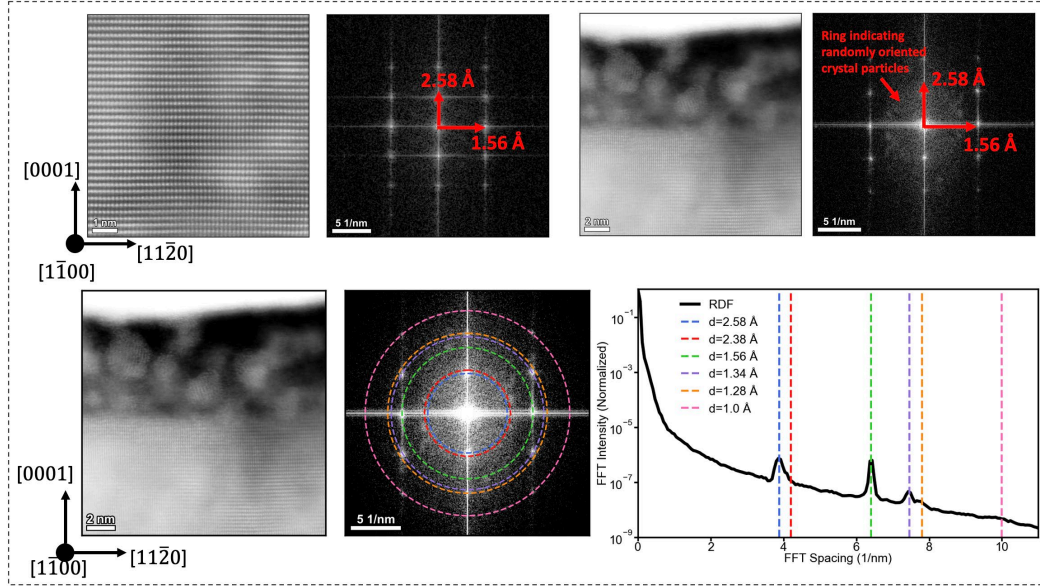


Fig. 33 The lattice constants of GaN lattice and BN nanocrystal are computed from the fast Fourier transform (FFT) pattern based on the intensity variation from the center to outward regions

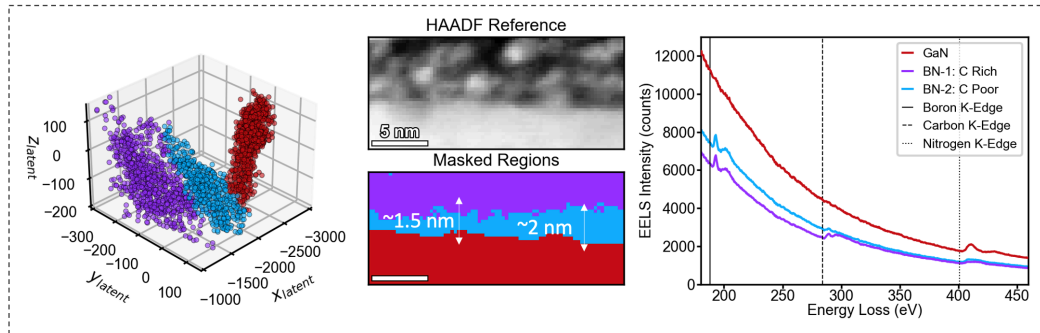


Fig. 34 The distribution of BN (C-rich and C-poor regions) and the GaN regions were mapped based on the EELS spectra and machine learning approach

4.5 BN Structures Deposited on SiC

Similar to BN deposited onto GaN crystal substrate, the BN layer deposited onto SiC crystal also shows promise as a thick layer of approximately 50 nm yet a nanocrystalline BN layer is observed when a cross-sectional lamella is prepared and imaged under bright- and dark-field TEM modes. The TEM, STEM images, diffraction patterns, EELS spectra, and mapping of each layer in the lamella are displayed in Fig. 35. The quality of the SiC substrate is confirmed, and the crystalline nature of the BN layer deposited is studied with the help of atomic resolution imaging and EELS spectrum. Several nanocrystalline regions of BN phases were observed with lattice constants matching more with the hexagonal

phase and a very little region to the cubic phase. EELS spectra confirmed the presence of boron and nitrogen in the BN layer; a mapping of the BN layer is attempted based on the B-K-edge intensity and is provided in Fig. 35 (bottom right). The BN layer is quite uniform and displayed a uniform thickness across the whole lamella.

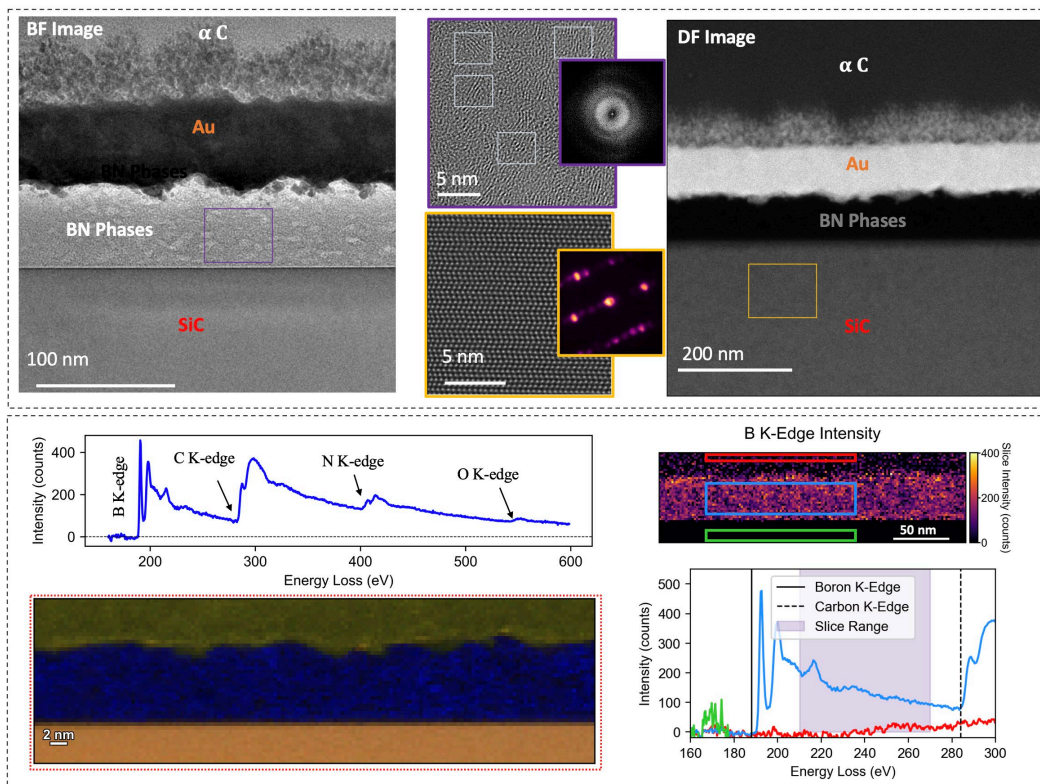


Fig. 35 (top) Low-magnification bright field image of the BN deposited on SiC lamella and atomic resolution images of the SiC and BN layers, corresponding to the FFT and dark-field image. (bottom) EELS spectra and mapping of the BN region.

4.6 Cubic Boron Nitride Microcrystals

Being that the growth of the cubic phase of BN is challenging, to study the microscopic nature of the cBN crystal, we have purchased cBN microcrystals from vendors and investigated the same under microscope. The cBN microcrystals with average particle sizes on the order of 1–1.5 μm are found to be highly crystalline with sharp edges without any impurities or contaminants and inhomogeneity. The low-magnification images, atomic resolution images, and corresponding fast Fourier transform (FFT) patterns are shown in Fig. 36, as are EDS and mapping, which correspond to the boron and nitrogen elements. The density functional theory (DFT) modelled structure of the cBN crystal is also provided in the inset. The signal strength of boron and nitrogen is strong in the EDS spectrum; we find a uniform

distribution of B and N elements in the EDS mapping, indicating further purity and homogeneity (free from oxides, etc.) of the microcrystalline samples.

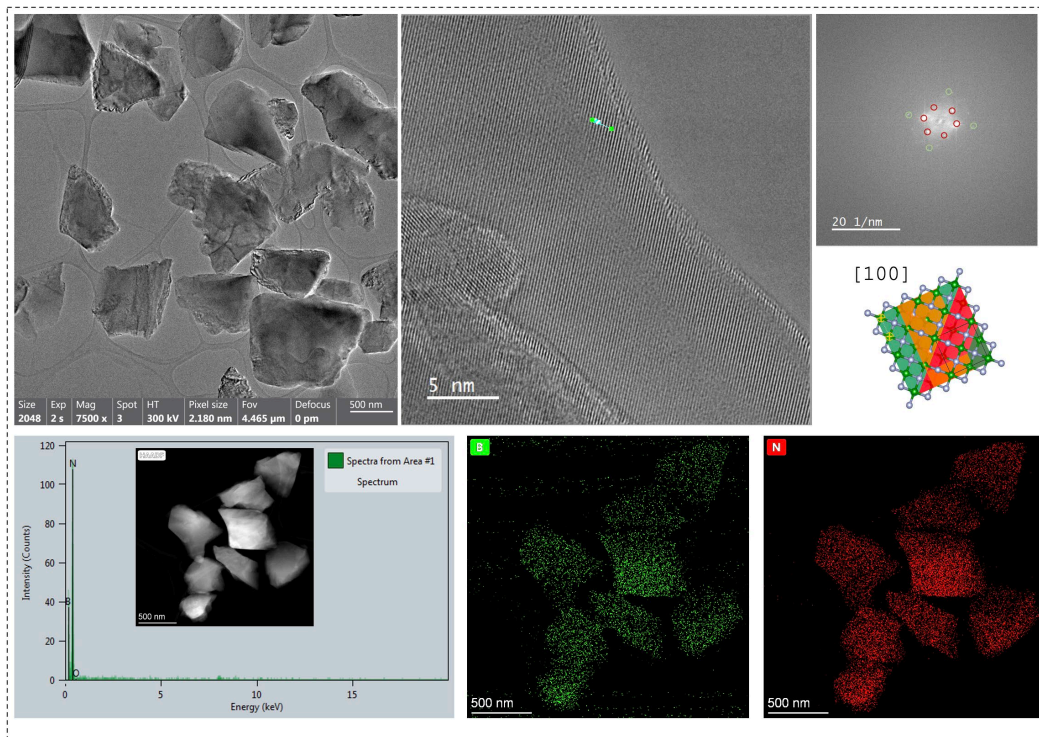


Fig. 36 (top) Low-magnification and atomic resolution images of the cBN crystal and corresponding diffraction pattern. The DFT-modelled cBN structure with zone axis [100] is also provided in the inset. (bottom) EDS spectra and EDS mapping of B and N elements. The region from the EDS spectra where mapping of B and N is performed is appended in the inset.

4.7 h-BN and c-BN Composite Structures as Annealed

To study the phase stability of hexagonal and cubic BN crystals, we synthesized the composite of the h-BN and cBN microcrystal by solid-state mixing (weight ratio 1:1) both phases and performed annealing thereafter under vacuum conditions. The annealed samples were transferred to the TEM grid and the morphology and crystalline nature studied with the help of electron microscopy. Note that both cBN and hBN phases are observed in the annealed composite sample with some intricate interfaces between the phases. The schematic showing the pellet made out of hBN-cBN microcrystalline powder, and the low-magnification and atomic resolution images of the composite structure and corresponding FFT patterns, are provided in Fig. 37.

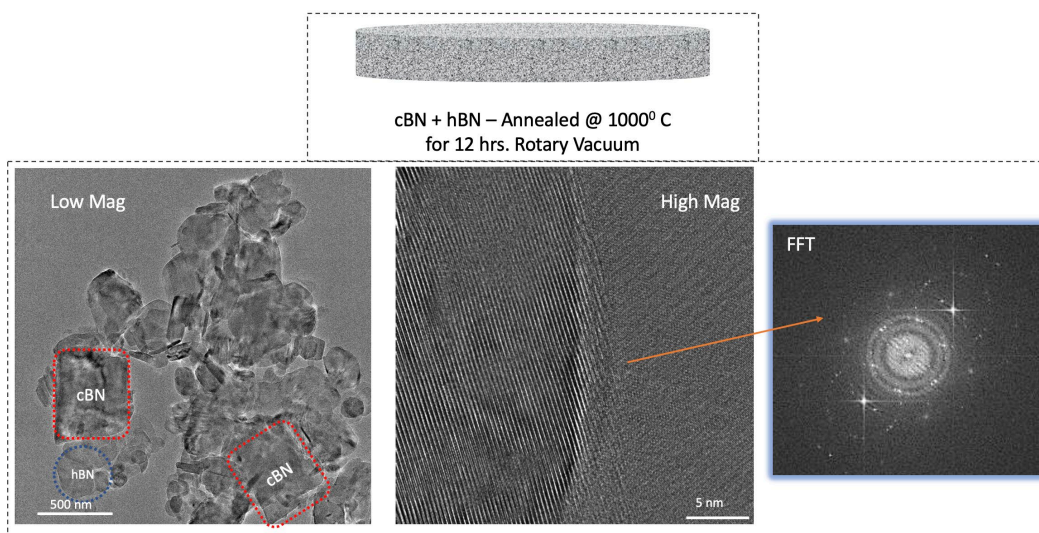


Fig. 37 (top) Schematic showing the pellet made of cBN and hBN microcrystalline powders. (bottom) Low-magnification and atomic resolution images of the cBN-hBN composite after the annealing treatment and corresponding diffraction pattern showing the presence of both cubic and hexagonal phases.

4.8 h-BN and c-BN Composite Structures after Plasma Sintering

Since the vacuum annealing treatment option in the tube furnace is limited by the unavailability of very high temperature ranges ($>1200\text{ }^{\circ}\text{C}$), other than vacuum annealing, we have also attempted spark-plasma sintering where the maximum temperature of annealing can be reached above $2000\text{ }^{\circ}\text{C}$. The cBN-hBN sample after plasma sintering is transferred to the TEM grid, and its microscopic properties are analyzed. Unlike the vacuum-annealed sample, there were no traces of cBN phase found in the spark plasma-annealed sample. It can be concluded that all the cBN-phased samples were converted to the hBN phase during the spark plasma sintering, which could be inferred on the basis of the metastable nature of the cBN phase and higher stability of the hBN phase under the given temperature and pressure conditions. The high-resolution TEM and STEM images, EDS spectra, and mapping correspond to B, N, O, and C in Fig. 38.

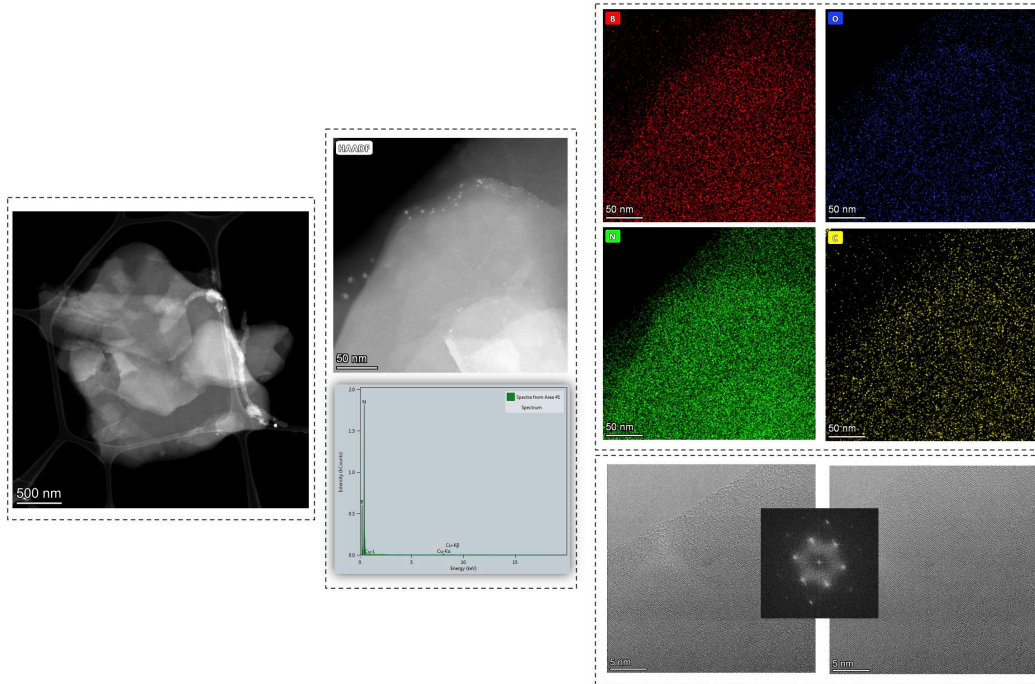


Fig. 38 (Left to right) STEM image of spark plasma-sintered BN crystal. EDS spectrum and EDS mapping correspond to B, O, N, and C. (bottom) Atomic resolution images of the sample showing the pure hexagonal crystal nature of the sintered sample.

4.9 B-Implanted SCD

The bulk doping of diamond is achieved by either introducing dopants like B (p-type doping) or P (n-type doping) during growth or by ion implantation procedures. Here we have studied the impact of B implantation into the single crystalline diamond wafer with the help of electron microscopy and detailed EELS spectrum analysis. The B-implanted sample is annealed, and the top layer is etched off before preparing the TEM lamella employing FIB. Upon analyzing the microscopy data, a thin graphitic layer (~ 20 nm) is found on the surface, and the implanted B species is found in both the graphitic layer and in the first few nanometers of the diamond layer. EELS spectra were collected from three different regions of the lamella top—the protection layer-Au (red), graphitic layer (blue), and diamond layer (green)—and the presence of implanted B species is detected both in the graphitic layer and the diamond layer, but not in the protective layer. A series of EELS spectra collected across the graphitic and diamond interface is taken to pinpoint the interface of sp^2 and sp^3 carbon layers as both of these phases have distinctive EELS peaks. The STEM images (low mag and atomic resolution) and EELS spectra and mapping are provided in Fig. 39. The variation of B density across the sp^2 - sp^3 interface is also mapped based on the B curve intensity. It can be found that the

implanted B density is more on the sp² phase and sharply decreased upon moving from the sp² to sp³ phase (Fig. 40).

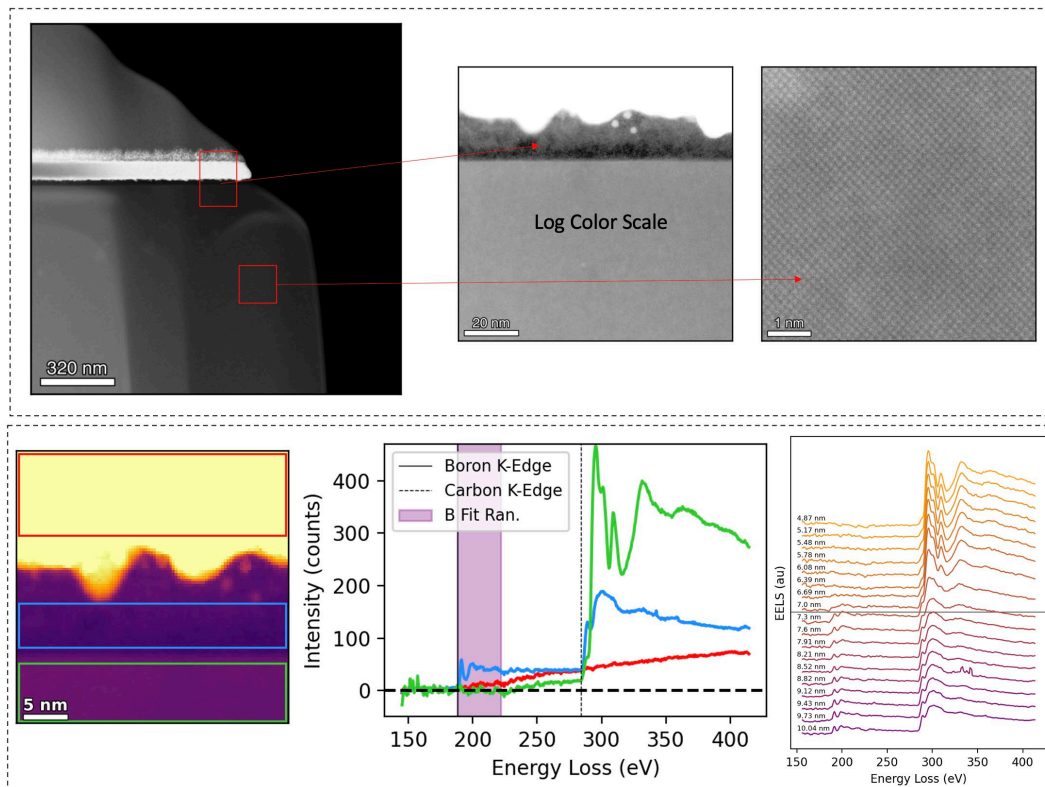


Fig. 39 (top) Low-mag and high-resolution STEM images of the cross-sectional lamella of treated B implanted sample. (bottom) Intensity variation across the different regions of the lamella, EELS spectra from three different regions, and line scans of EELS spectra across the sp² and sp³ region of the implanted diamond wafer.

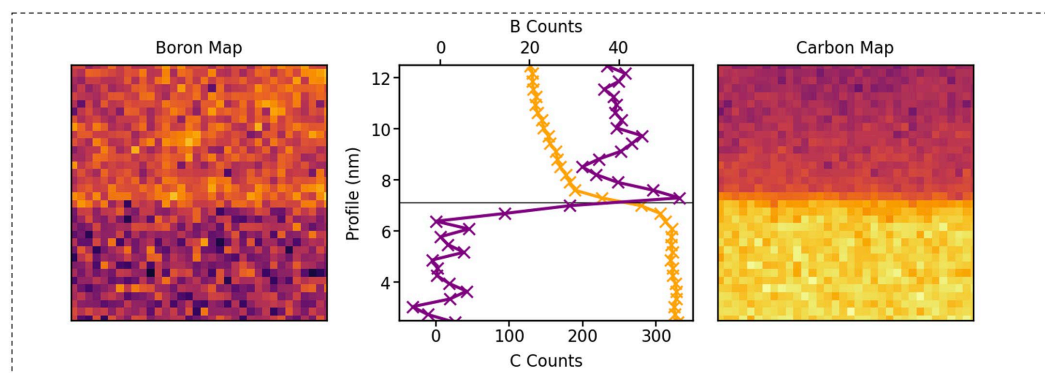


Fig. 40 Mapping of B and C density across the sp²-sp³ interface: (left) boron map and (right) C map. The implanted B density is found to be higher in the sp² region than the sp³ region.

4.10 Electrical Conductivity Evolution of SCD vs. Hydrogenation Conditions

As we pursue the terahertz time domain spectroscopy to optically read out the electrical properties of diamond, where a highly conducting sample of sheet resistance $< 10 \text{ Ohm}/\square$ is required, we tried to optimize the H-termination coverage on the SCD surface through a series of hydrogenation steps employing an MPCVD setup (SEKI). Although conductivity is improved with a slight modification in the sample surface roughness, the required level of sheet resistance to study a sample under terahertz spectroscopy is yet to be achieved; experiments are underway to achieve the same. The surface morphology variation of the diamond surface and sheet resistance variation on hydrogenation are displayed in Fig. 41.

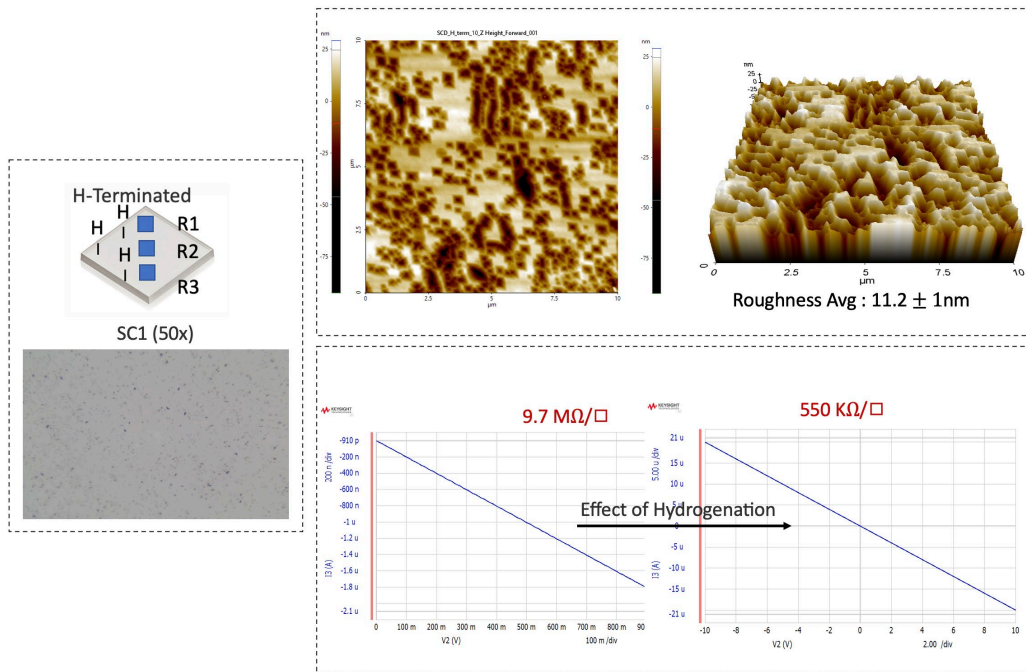


Fig. 41 (left) Schematic showing the hydrogenated diamond surface and the optical microscopy image (50x) of the sample surface. (right) AFM height image showing the modification of the diamond surface on H termination treatment and the IV curves showing the change in sheet resistance (high to low).

4.11 Cathodoluminescence Studies on Pristine, Doped, and Functionalized Diamond Surfaces

Cathodoluminescence (electron beam excited optical emission) is an interesting phenomenon and can be used for powerful imaging and as a spectroscopy tool to characterize the samples with a luminescent center in a sample/crystal. This can be employed to analyze diamond wafers for the presence of impurities and structural variations as both will leave traces in the cathodoluminescent image and fetched

spectra. For example, the presence of nitrogen vacancy (NV) centers will clearly show up in a cathodoluminescence spectra while the variation in the structure of diamond will result in the variation of the contrast in a cathodoluminescent-based image. Here we have employed an electron probe microanalyzer (JEOL) system with cathodoluminescent imaging capability to study the diamond wafers, where half of the sample surface is hydrogenated and half is oxygen terminated. The schematic showing the sample under study and the results of cathodoluminescent imaging under 15-kV electron excitation energy are appended in Fig. 42. Both the gray scale and false color images are provided; the H-terminated region and oxygen termination can be clearly differentiated. Hence, cathodoluminescent imaging is a powerful tool to differentiate and study the effect of surface termination and functionalization as well as to scan and detect the impurities present in the diamond wafer.

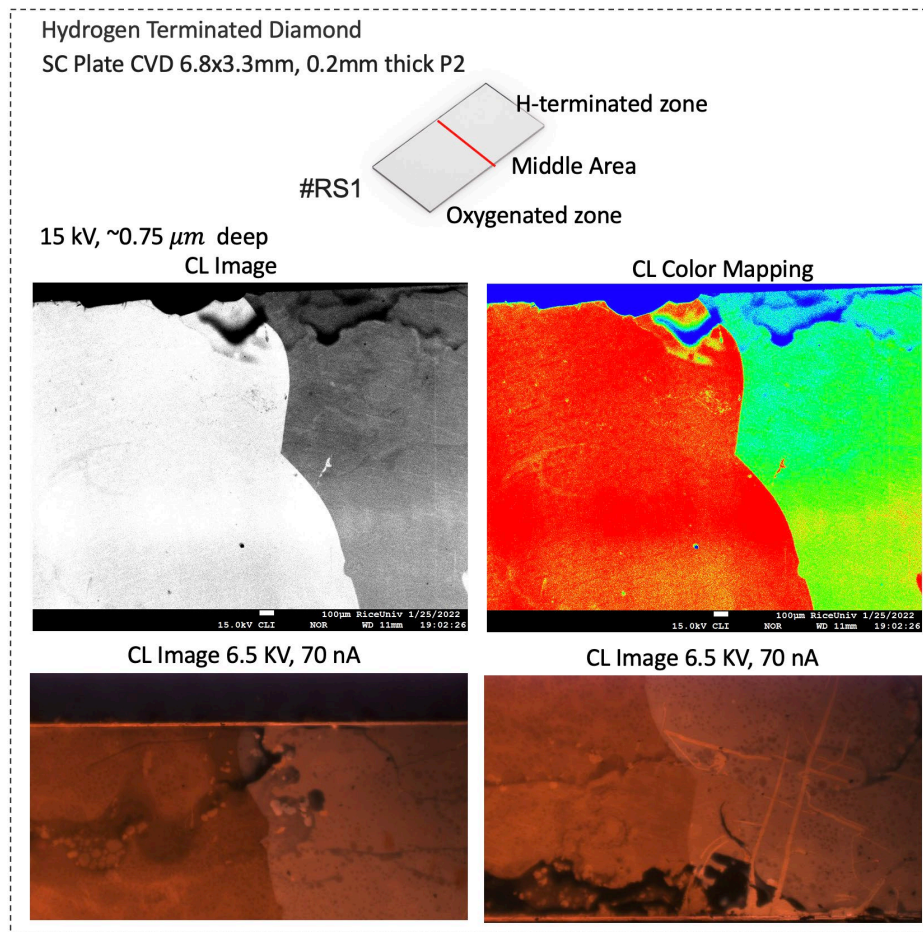


Fig. 42 (top) Schematic showing the diamond wafer sample understudy where half of the geometric surface area is H terminated and half is oxygen terminated. (Bottom) Gray scale and false color cathodoluminescent images of the sample clearly differentiating the H- and O-terminated surfaces.

5. Diamond Doping and Surface Modification

5.1 Low-Energy Ion Implantation: An Approach to Develop RT n-type Diamond Wafers

Diamond is a promising material for semiconductor technologies given its UWBG, excellent thermal conductivity, and high carrier mobility. It has been previously shown that p-type diamond semiconductors can be achieved with B doping; however, n-type diamond semiconductors have yet to be synthesized with sufficient electronic properties to outclass currently available n-type semiconductors. Although multiple elements such as N, P, Li, and Na have been shown to have potential in the development of n-type diamond semiconductors, it has not been a trivial task experimentally due to the low diffusivity of the doping elements in the diamond lattice and damage that is incurred in the diamond crystals during the doping process. Thus, there still exists a need to develop a method of synthesis to produce n-type diamond with sufficient quality and dopant concentrations for room temperature applications.

Multiple methods of doping diamond have been developed over the years since the realization of its high potential in electronic devices, with CVD and ion implantation being some of the most prominent methods. Specifically, P and N have received considerable attention with these methods; however, synthesizing n-type semiconductor diamond still currently suffers from activation energies too high for room temperature application (1.7 eV for N and 0.57 eV for P) and comparatively low carrier mobility, leading to the consideration of other elements such as Li, Na, and more recently, As.²⁰ It has been predicted that Li, Na, and As can achieve activation energies as low as 0.1, 0.3, and 0.4 eV, respectively (Table 2), making them ideal candidates.²¹ Unfortunately, the attempts at doping Li and Na have been met with difficulties such as low solubility, and As has received much less experimental investigation. Thus, the results have been inconsistent, and P remains to be the most successful doping element thus far. Ion implantation in particular is already widely used in the semiconductor industry, with attractive features such as precise concentration control in selective areas. But in the case of diamond, the high-energy ions often lead to lattice damage and amorphization in the crystal, consequently causing adverse effects for semiconductor applications.⁷ While some of this damage can be rectified by thermal annealing after doping, it often leads to the formation of graphite, and careful optimization is necessary. Low-energy ion implantation is expected to introduce n-type dopants to desired depth levels (Fig. 43) without damaging the diamond structure and realize n-type diamond with competing electronic properties compared to the widely explored p-type diamond.

Table 2 The ionization energy of various elements in the diamond lattice and the maximum achievable doping levels in the diamond lattice

Dopants	Ionization energy (eV)	Achievable levels (cm ⁻³)
Li	0.17	10 ^[21]
B	0.37	10 ^[21]
P	0.6	10 ^[20]
N	1.7	10 ^[19]

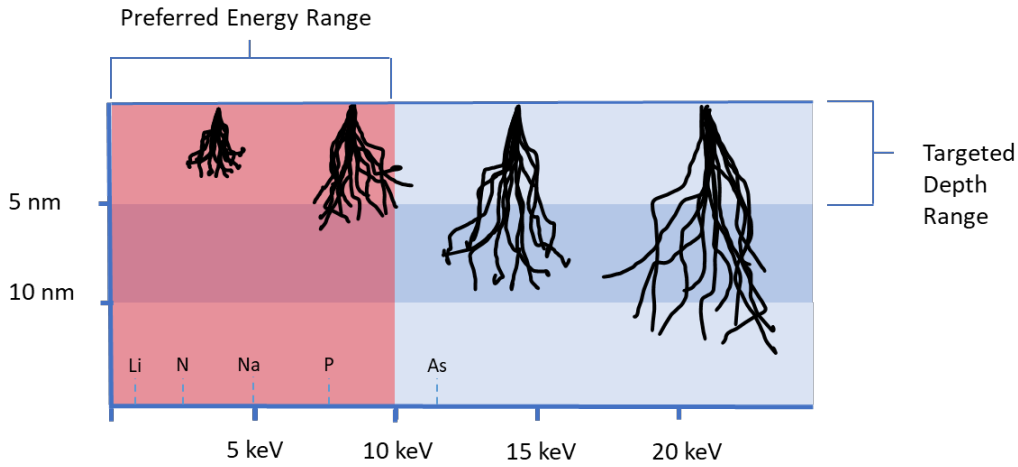


Fig. 43 Schematic showing the proposed low-energy implantation process where the ions can be placed to the very surface region without damaging the parent lattice

Low-energy ion implantation was carried out for multiple dopant elements on $3.0 \times 3.0 \times 0.25$ -mm single crystalline samples under the given parameters summarized in Table 3. The implantation conditions were identified based on the stopping and range of ions in matter (SRIM) calculations, and the calculation outputs are appended in Fig. 44. Previous studies have shown that increasing the temperature of the substrate to be implanted can reduce the amount of amorphization in the sample.⁸ Since B-doped diamond is already well established with results to compare it to from previous works, it was chosen first to test the effects of substrate heat on the amorphization of the diamond substrate. Two samples were prepared, one at room temperature and one at 200 °C, with all other conditions kept the same. Raman spectroscopy and PL was used for the initial characterization of the resulting B-doped diamond. As seen in Fig. 45, the peak between 1400 and 1500 is significantly reduced for the sample implanted at 200 °C, which can be a significant indication of reduced amorphization during implantation. A similar trend is observed in the PL spectra as well, where the defects related to (NV center) PL intensity are reduced for the sample implanted at 200 °C. Based on this result, the remainder of the samples were implanted at 200 °C.

Table 3 Low-energy implantation parameters

Ion	Implantation energy (KeV)	Fluence (cm ⁻²)	Flux (cm ⁻² /s)	Implantation temperature (°C)	Expected implantation depth (nm)
Li	1.2–1.5	1 x 10 ¹⁵	1–2.2 x 10 ¹¹	RT – 200	5–10
N	1.4	1 x 10 ¹⁵	1–2.2 x 10 ¹¹	RT – 200	5–10
B	1	1 x 10 ¹⁵	1–2.2 x 10 ¹¹	RT – 200	5–10
Na	1.6	1 x 10 ¹⁵	1–2.2 x 10 ¹¹	RT – 200	5–10
P	2.5	1 x 10 ¹⁵	1–2.2 x 10 ¹¹	RT – 200	5–10
As	20	1 x 10 ¹⁵	1–2.2 x 10 ¹¹	RT – 200	5–10

Note: RT = room temperature.

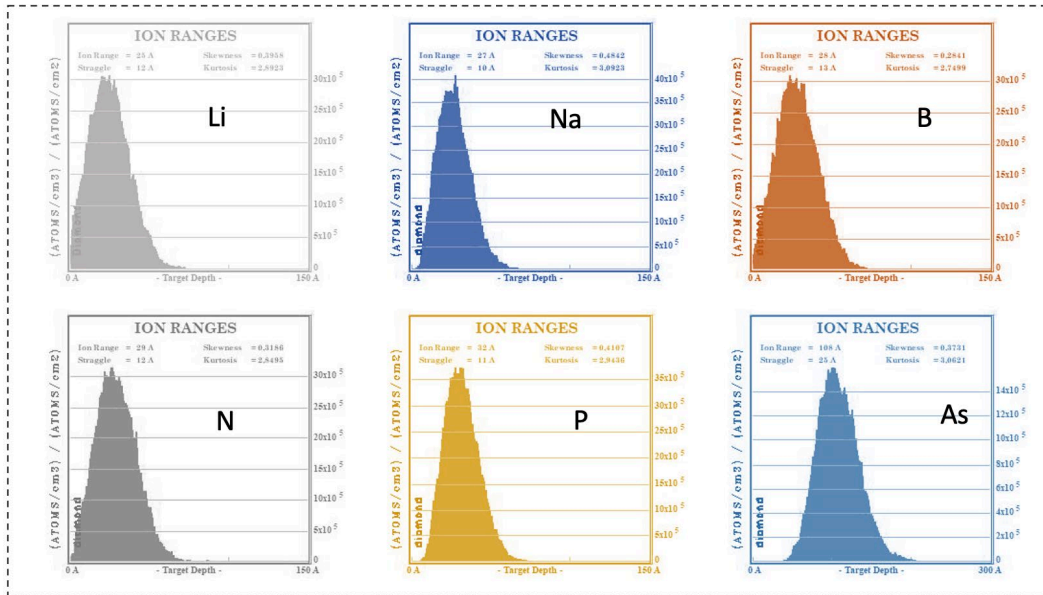


Fig. 44 SRIM modelling output for Li, Na, B, N, P, and As. The implantation energy is computed based on the required depth of implantation, which is within the first 10 nm for the diamond wafer.

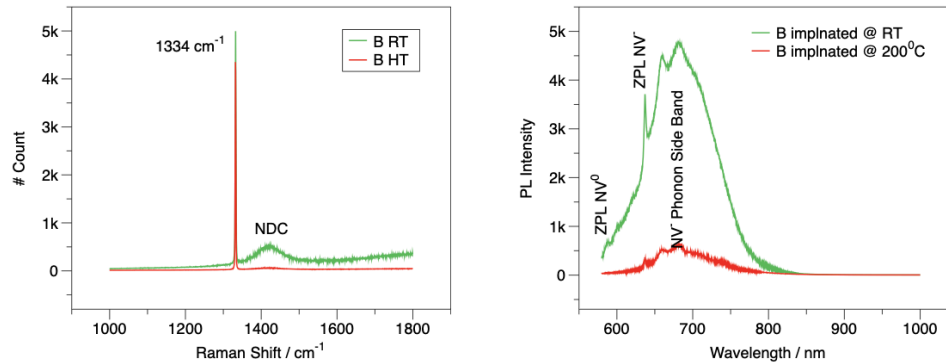


Fig. 45 The Raman and PL spectra of B-implanted diamond sample with and without substrate temperature

We plan to perform several measurements and evaluate the implanted samples for any structural and chemical changes, as well as verify the presence of the dopants in the samples. This includes Raman (Fig. 46), PL (Fig. 47), XPS, time-of-flight (ToF) SIMS (Fig. 48), AFM, and conductivity/resistance tests, as well as any other measurements that may be needed during this stage. Once the first round of measurements is completed, the samples will be subjected to thermal annealing to help recrystallize any amorphous carbon and activate the dopants. Then, the measurements will be repeated to determine any changes in the structural and electrical properties of the samples.

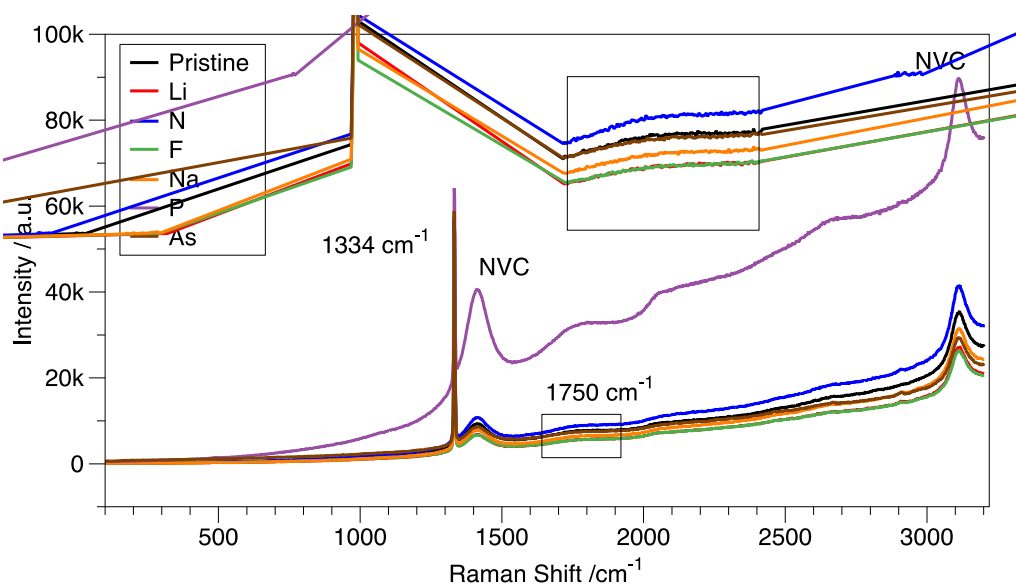


Fig. 46 The Raman spectra of pristine and low-energy implanted samples with Li, N, F, Na, P, and As

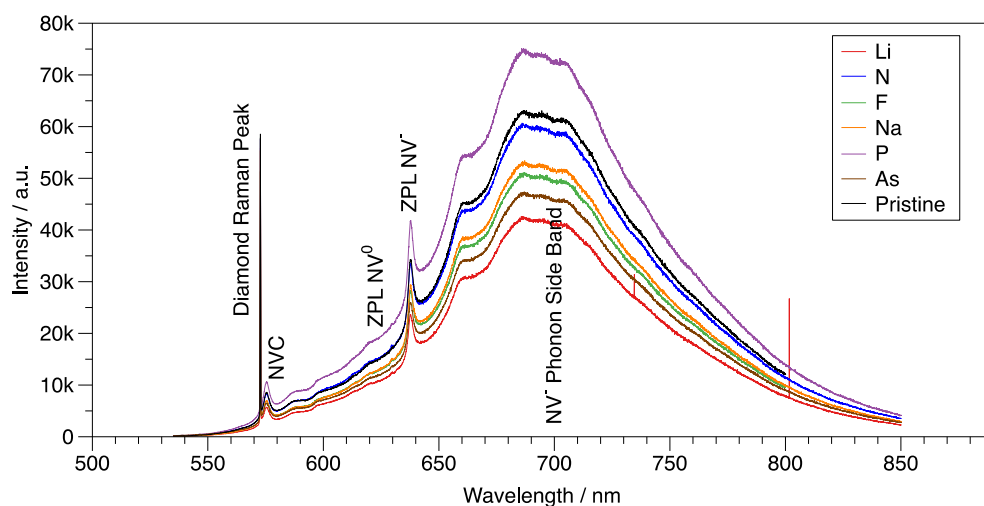


Fig. 47 The photoluminescence spectra of pristine and low-energy implanted samples with Li, N, F, Na, P, and As

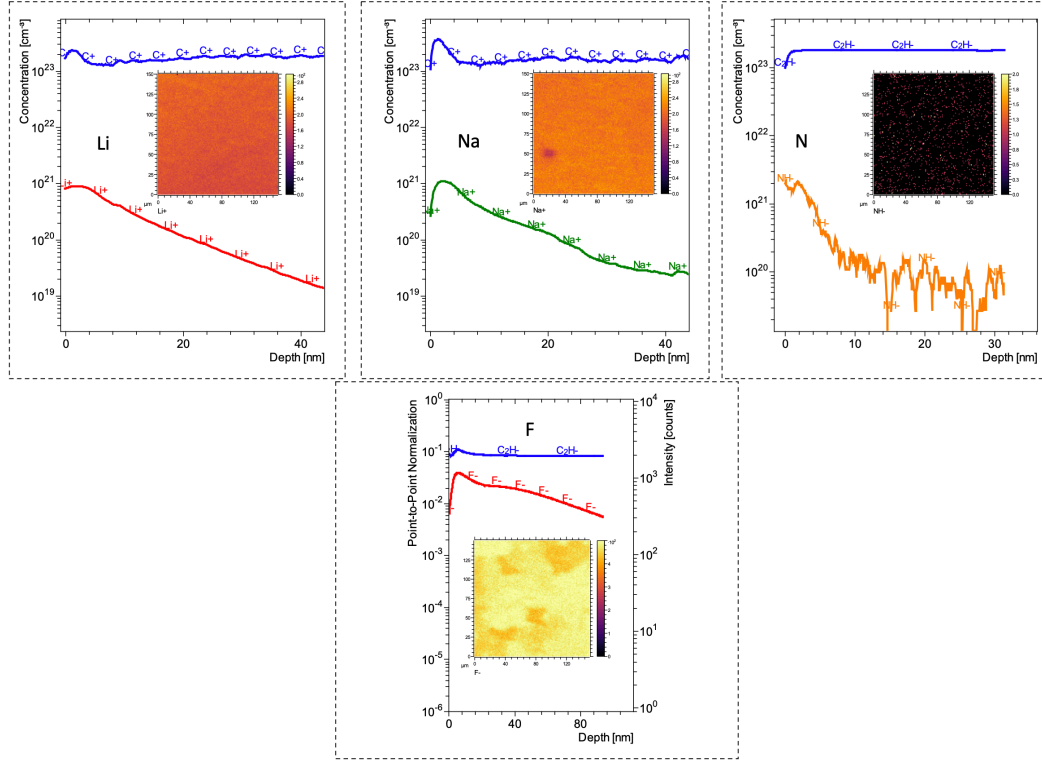


Fig. 48 ToF SIMS results showing the concentration of implanted species with respect to the depth from the surface and the homogeneity of the implanted species on the diamond surface (inset) for Li, Na, N, and F

5.2 Reactive Ion Etching Toward Clean and Roughness-Free Diamond Surfaces

With an UWBG of approximately 5.5 eV and electrical properties that rival that of the prominent existing semiconducting materials (GaN and 4H-SiC), diamond is of great interest for next-generation power electronics, optical, quantum, and biosensing applications. Namely, the high thermal conductivity, breakdown voltage, and carrier mobility suggest its promise to perform especially well in devices in extreme conditions. Today, diamond can be artificially grown via CVD and interfaced with 2D materials such as hexagonal boron nitride for application in FETs, microelectromechanical systems, and other unique electronic device structures. However, reducing the defect density, enhancing the growth rate, and controllably tuning its properties remain challenges to the consistent growth of high-quality, large-area SCD wafers and the widespread realization of diamond-based devices.²²

To grow high-quality homoepitaxial layers of diamond, smooth substrates with low surface defects must be used. These defects, which can either be inherent to the bulk material or the result of polishing-induced damage, are suspected to extend

well below the surface of the material, acting as charge traps and scattering centers that can negatively impact the electrical performance of the grown material.²³ To address this, we explored the use of inductively coupled plasma–reactive ion etching (ICP-RIE) as a pre-growth treatment that could remove layers of the substrate and create a smooth, defect-free surface prior to growth.

The ICP-RIE system uses RF to excite one or more gaseous species into a plasma that etches away at the surface at room temperature. Unlike traditional RIE, ICP-RIE has two coils that enable separate control of the ion energy and density for more precise etching. Compared to materials such as Si, the influence of the parameters of the ICP-RIE process on diamond are not well understood. Furthermore, only minimal consideration has been given to the quality of growth on the ICP-RIE treated substrates in literature thus far.²⁴ Therefore, through this work we aimed to systematically optimize the conditions of ICP-RIE treatment for the preparation of smooth diamond substrates that can be used for high-quality CVD growth and future device applications.

We used the Oxford Plasmalab 180 ICP system, located in the Rice Nanofabrication Cleanroom to systematically test the parameters of the etching process (gas mixture, ICP and bias power, gas flow rate, and pressure) on PCD substrates purchased from the company Element Six. In terms of characterization, we gathered data from SEM, Raman spectroscopy, AFM, and XPS. This enabled us to analyze the surface roughness, morphology, elemental composition, and formation of features such as etch pits on the surface. We also performed pre- and post-etch mass and thickness analyses to determine the etch rate of each process.

As shown in Fig. 49, we successfully reduced the roughness of the pristine PCD substrates from Element Six from a root-mean-square value of 3.318 to 0.943 nm with a with CF_4+O_2 (50:50 sccm) etch at 5 mTorr, 200-W bias, and 400-W coil power for 10 min. Interestingly, our XPS data (Fig. 50) has revealed the presence of oxygen and fluorine bound to the diamond surfaces as a result of the plasma treatment from various gaseous species. This indicates the potential for using ICP-RIE as an alternative means of fluorinating the surface.

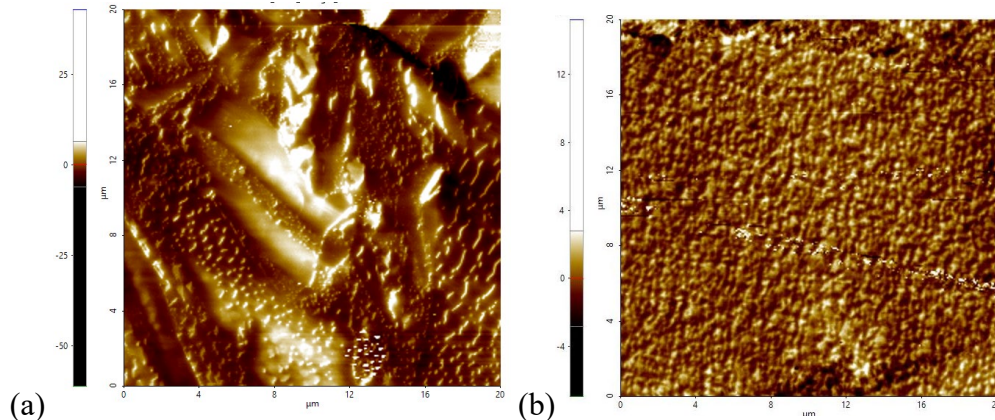


Fig. 49 AFM measurements for both (a) the pristine PCD sample and (b) an ICP-RIE treated PCD sample with $\text{CF}_4 + \text{O}_2$ (50:50 sccm) at 5 mTorr, 200-W bias, and 400-W coil for 10 min

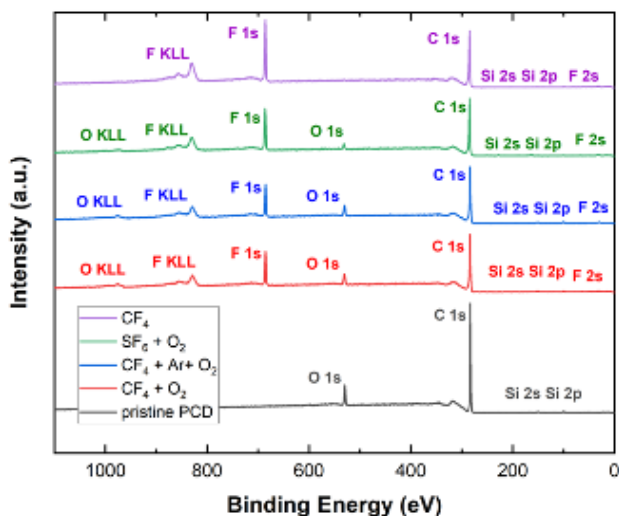


Fig. 50 XPS spectra for various fluorinated diamond substrates treated via ICP-RIE

With the recent update of our facility's ICP-RIE tool, we explored the use of $\text{Ar} + \text{Cl}_2$ plasma etching. A clear morphological difference between the rough pristine PCD and the etched samples can be observed in the SEM images shown in Fig. 51.

Our next steps will involve exploring the ability of the $\text{Ar} + \text{Cl}_2$ -based ICP-RIE process to smooth and reduce the subsurface damage on SCD substrates. These, as compared to PCD, are more expensive but preferable for future electronic device applications. Furthermore, after preparing optimally smooth SCD substrates via ICP-RIE, we will utilize them for the homoepitaxial growth of diamond layers via microwave plasma CVD.

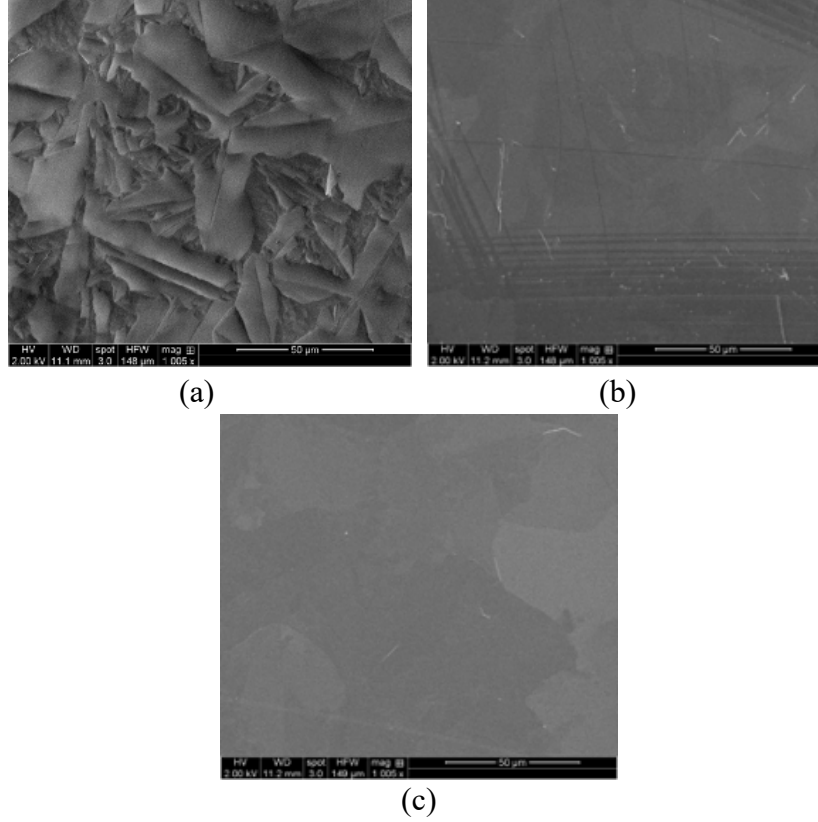


Fig. 51 SEM measurements for (a) pristine PCD sample, (b) PCD sample etched with Ar+Cl₂ (10:40 sccm) at 200-W bias, 400-W coil, 5 mTorr for 10 min, and (c) PCD sample etched with Ar+Cl₂ (25:40 sccm) at 200-W bias, 400-W coil, 5 mTorr for 10 min

5.3 Heteroatom Functionalization of Diamond Surfaces for Improved Transfer Doping

Diamond is a promising UWBG semiconductor material for high-power RF communication device applications.^{25,26} Hydrogen termination is attractive in the sense that it endows the diamond surface with the negative electron affinity effect due to the upward bending of the valence and conduction bands. The surface is then exposed to adsorbates (H₂O, NO₂), or the metal oxides (Al₂O₃, V₂O₅), for the charge transfer from the hydrogenated diamond surfaces to the transfer dopants to generate p-type semiconducting behavior.^{27,28} Nevertheless, the employment of expensive facilities and complicated procedures in the transfer doping processes inevitably lowers the cost-efficiency of broad productions and applications. In contrast, surface functionalization via the wet and dry chemical routes is known for its low operating cost and mild reactivity²⁶ and may serve a similar purpose.^{29–32}

Here we introduce heteroatoms on hydrogenated polycrystalline diamond (HPCD) surfaces via wet and dry chemical approaches. Surface characterization of post-functionalized diamond surfaces shows that these groups are uniformly distributed

and covalently bonded to diamonds. Four chemical functional groups (-SH, -S-S-, -S-O, and -S=O) were found on the sulfur-modified diamond surface, and two groups (-NH₂ and =NH) upon amination. We also report a co-functionalized surface with N and S (N-S), where sulfurization promotes sequential amination efficiency with reduced exposure time. Electrical measurement shows that hetero-atom-modified diamond surfaces possess higher conductivity compared to H-terminated diamonds.

The heteroatom functionalization of diamonds involves multiple steps as shown in Fig. 52. The amination of diamonds was conducted according to our previous report.³³ In short, the HPCD was first heated with the hydrobromic acid solution under 85 °C in a regular three-neck boiling flask for 24 h. The film was then taken out by an acid-resistant twister, rinsed with deionized water, and dried with a nitrogen gun. Next, the amination (N-HPCD) was carried out by UV-irradiating the film with ammonia gas for 8 h (UV lamp, GPX 13, 13.4 W, 254 nm) in a quart tube. Finally, the tube was purged with argon for 5 min to clean off all the residual ammonia gas. The quartz-made two-neck boiling flask was used for the sulphuration reaction because of its UV-transparent nature. Elemental sulfur (40 mg) in carbon disulfide/hexane (4 mL, 3:1) was irradiated with a UV lamp in the presence of diamond films (4 × 4 mm) under argon atmosphere with stirring for 4 h (S-HPCD-1) and 8 h (S-HPCD-2), respectively.³⁴ After finishing the photoreaction, the diamond film was washed with 10 mL carbon disulfide and 5 mL methanol to remove all the unreacted materials and contaminations. The nitrogen (N) and sulfur (S) co-functionalized samples were prepared based on the pre-sulphurated PCD film. Specifically, the films were placed in the quart tube and further irradiated with UV light in ammonia gas for 4 h. After the reaction, the tube was again purged with argon for 5 min. The resultant films were respectively coded as N-S-HPCD-1 and N-S-HPCD-2.

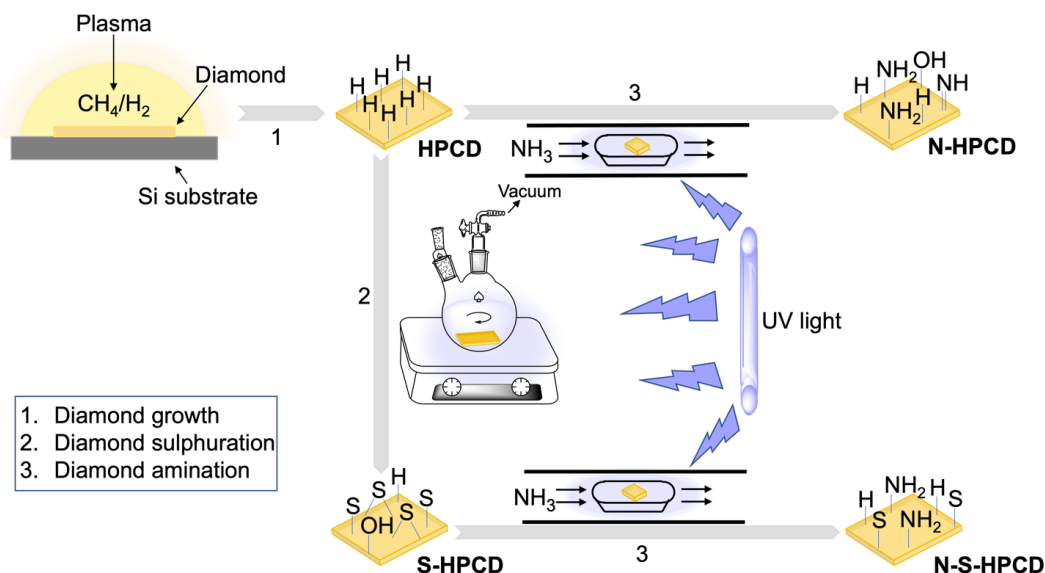


Fig. 52 The PCD film was grown and passivated with H plasma (HPCD) inside the MPCVD system. The UV-irradiation process in NH_3 medium was utilized to aminate the HPCD surface (N-HPCD). The sulphuration of HPCD (S-HPCD) was conducted with the same process in dissolved S powder. S-HPCD was subjected to amination to acquire a co-functionalized surface (N-S-HPCD).

Attenuated total reflectance–FTIR was employed to investigate the chemical compositions of diamond surfaces. As shown in Fig. 53a, we did not observe any other peaks on the HPCD surface beside the one at $2800\sim3000\text{ cm}^{-1}$, demonstrating the C-H_x group's stretching mode.³⁵ This observation indicates that H plasma treatment fully hydrogenated the PCD surface. After amination, new peaks at $1235\sim1245\text{ cm}^{-1}$ and $3050\sim3490\text{ cm}^{-1}$ were identified on the N-HPCD surface, suggesting the stretching vibrations of the C-N and N-H groups, respectively. Meanwhile, the peak intensity of the C-H_x group was decreased. In our previous work, we explored that during the UV-irradiation process, the H atom on the diamond surface is substituted by the nitrogen species disassociated from ammonia gas. This process was accompanied by mild oxidation on the surface, as the features, representative of the bending mode of the C-O group and the stretching mode of the C=O group, were detected at $1043\sim1140\text{ cm}^{-1}$ and $1320\sim1370\text{ cm}^{-1}$, respectively. Diamond sulphuration shared the similarity. While the peak height of the C-H_x group declined, two distinctive peaks at $845\sim865\text{ cm}^{-1}$ and $2650\sim2680\text{ cm}^{-1}$ were raised, standing for the C-S and S-H groups, respectively. As for the N-S-HPCD, it revealed a stronger feature based on the nitrogen-bonded moieties (N-H and C-N groups) compared with N-HPCD. This result suggests that the sulphurated surface's nitrogenation efficiency might be enhanced.

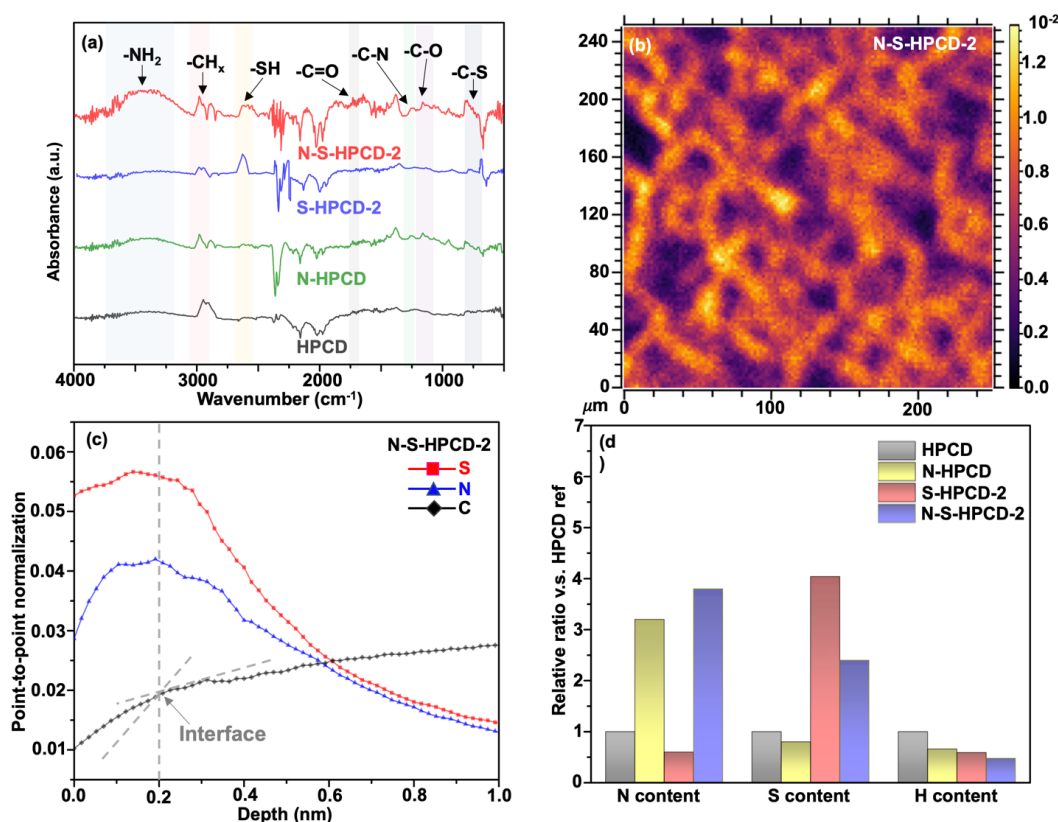


Fig. 53 Attenuated total reflectance–FTIR (a) spectra revealed the surface composition of functionalized diamond surfaces. The ionized mapping of nitrogen groups (b) and depth profile analysis (c) were accomplished by ToF-SIMS on the N-S-HPCD-2 surface. The elemental ratios (d) of N, S, and H on functionalized samples were also examined by ToF-SIMS. To be noted, the larger-ranking sequence indicates the higher atomic coverage on the diamond surface (e.g., N-S-HPCD-2 has a higher N-S ratio than that of N-S-HPCD-1).

ToF-SIMS measurement was carried out to understand functionalized diamond surfaces further. The N-S-HPCD-2 sample was chosen for analysis. Ionized imaging was conducted by sputtering the surface with an ion beam, and the feature is listed in Fig. 53b. The scale bar on the right directs the magnitude of the ionized mass of attached nitrogen on the surface. The light features, indicative of higher weight, are evenly scattered across the region, which suggests that the functional groups are uniformly distributed on the PCD surface. A depth profile was performed after that to measure the thickness of the functionalized layer. As can be seen in Fig. 53c, there are three curves representing the depth profile of carbon (C-, black), nitrogen (N-, blue), and sulfur (S-, red) elements on the PCD surface, respectively. A well-defined slope is observed until roughly 0.2 nm for the C- layer, after which the curve gradually flattens as the etching process going deeper into the surface. Meanwhile, the counts of N- and S- species decline rapidly after 0.2 nm. This tendency implies that the interface between the functionalized layer and bulk diamond could be established around 0.2 nm beneath the surface, corresponding to

one carbon layer of diamond.³⁶ Analysis of the elemental ratio was also implemented for all samples (Fig. 53d). Compared to HPCD, the surface coverages of the H atom decreased upon functionalization. Co-functionalization of N-S moieties consumed most H atoms on the diamond surface. The contents of N and S were raised after surface treatments, where for N-S-HPCD-2, the surface coverage of N gained more than that of S. Additionally, the ratio of N to S was found to be greater than that observed for S-HPCD-2. These variations manifest that amination on the sulphurated surface causes partial dissociation of S bonds.

Analyses of XPS S 2p spectra disclose the bonding components of S groups on surfaces. The S 2p peak was curve-fitted with two components by a doublet, $2p^{1/2}$, and $2p^{3/2}$, owing to the spin-orbit coupling. In Figs. 54a,b, four significant features can be found, and they are representing C-S-H (162.79/163.97 eV), C-S-C (164.21/165.39 eV), C-S-O (165.31/166.49 eV), and C-S=O (168.59/169.77 eV), respectively.^{37,38} In contrast to S-HPCD-2, N-S-HPCD-2 presents an 11.9% higher ratio than the S-H group. On the other hand, a decrease (49.9%, as compared to S-HPCD-2) is noticed in the feature indicative of the C-S-C group after amination, possibly due to mild oxidation of such during the UV process. Correspondingly, oxidized S groups, like C-S-O and C-S=O, respectively, gain 31.2% and 6.7% and primarily exist on the N-S-HPCD-2 surface. The following reaction mechanism is proposed: Under the UV light activation in wet chemistry, the S ring is first broken into a chain with two free radicals on dual sides. One of them substitutes H termination on the diamond surface. After this, the S chain is further cleaved by the UV-irradiation and leaves the surface with S radical in the gas-phase reaction. Per bonding with oxygen, it turns to oxidative S groups. On the other hand, the disassociation of NH_3 under UV light generates N radicals and H radicals coming as by-products. This by-product partially bonds with the above-mentioned S radical to form a thiol group.

The deconvolutions of XPS N 1s spectra are carried out as well. Figures 54c,d show that two major peaks can be found on N-HPCD and N-S-HPCD-2, which are contributed by the C-NH₂ (399.5 eV) and C=NH (400.8 eV) group, respectively.^{39,40} The integrated area of those two peaks is roughly in the ratio of 3:1 for the N-HPCD surface. With pre-sulphuration, the feature corresponding to the C-NH₂ group is in the majority (up to ~92%). This observation indicates that amination on the pre-sulphurated diamond surface primarily results in C-NH₂ group attachment.

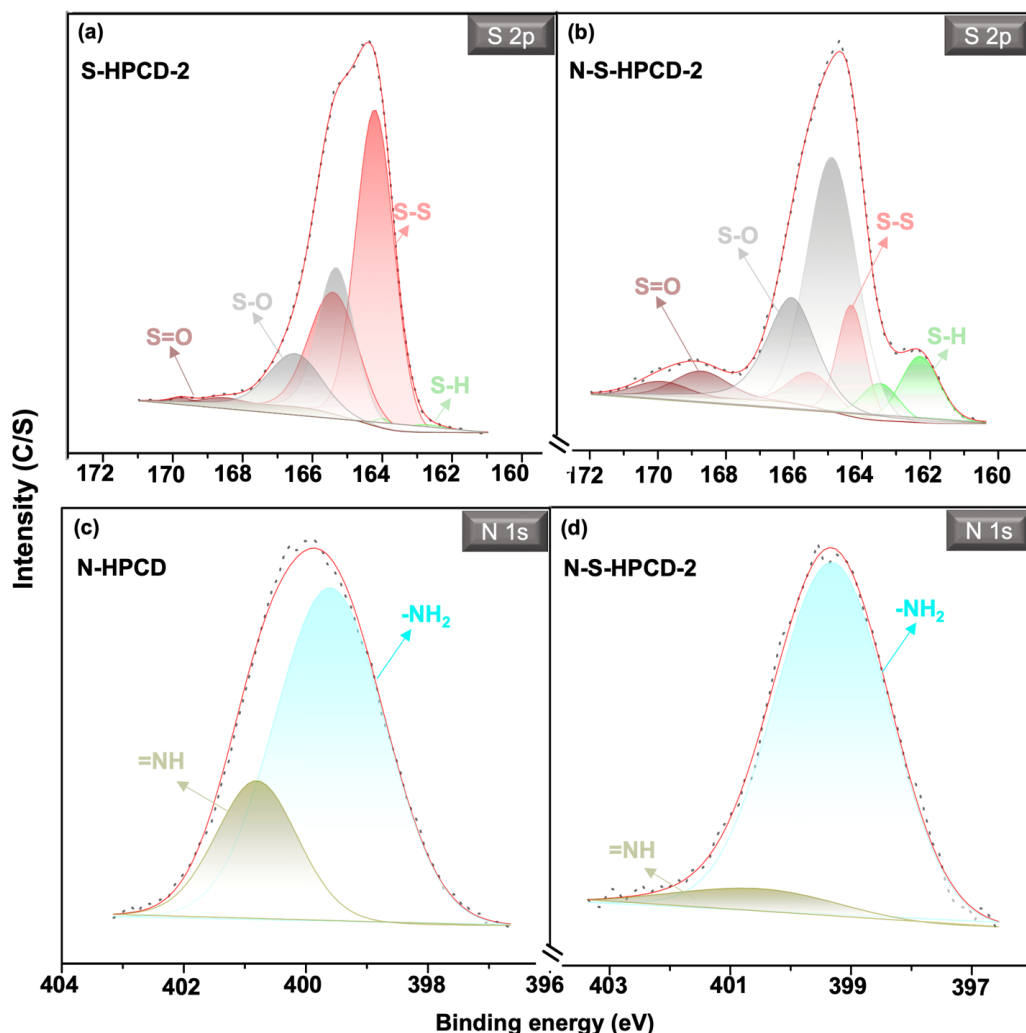


Fig. 54 The deconvolution of XPS S 2p spectra of S-HPCD-2 (a), and N-S-HPCD-2 (b); XPS N 1s spectra of N-HPCD (c), and N-S-HPCD-2 (d). The featured peaks from each spectrum were highlighted with distinct colors. All spectra under the same core analyses were plotted in the same scales.

Having the heteroatom functional groups substituted to the H-terminated diamond surface, the next property to explore is the electrical characteristics of the functionalized diamond surfaces. It has been reported that the treatment of NH₃ downshifts the position of valence band maximum on the PCD surface. We expect such a manner to modulate the electrical conductivity by introducing more hole carriers into the diamond surface via the transfer doping induced by the heteroatoms, which, like surface adsorbates or metal oxides, will attract electrons from the valence band. This assumption is confirmed in the theory section as one could observe the downshift of the Fermi level in contrast to the fully hydrogenated surface. Henceforth, the measurements of I-V characteristics were performed at room temperature. The two-terminal device was fabricated by forming metal

contacts (gold, 100 nm thick) on a diamond surface as schematically shown in Fig. 55a. The electrode sizes were deposited in such a way that the channel dimensions (4.0×3.5 mm) remain the same for all the samples, which helps to compare the behaviors of pristine and functionalized diamond surfaces. Before the measurement, the channel regions were examined by XPS to ensure their cleanliness and preclude the presence of trace amounts of Au that may be deposited during the masked deposition of Au electrodes. The current-voltage (I-V) characteristics displayed from Figs. 55a–c reveal the dependences of current densities versus potential sweeps on functionalized PCD surfaces. A close inspection of I-V characteristics from each sample demonstrates an almost linear curve representative of “Ohmic-like” contact.

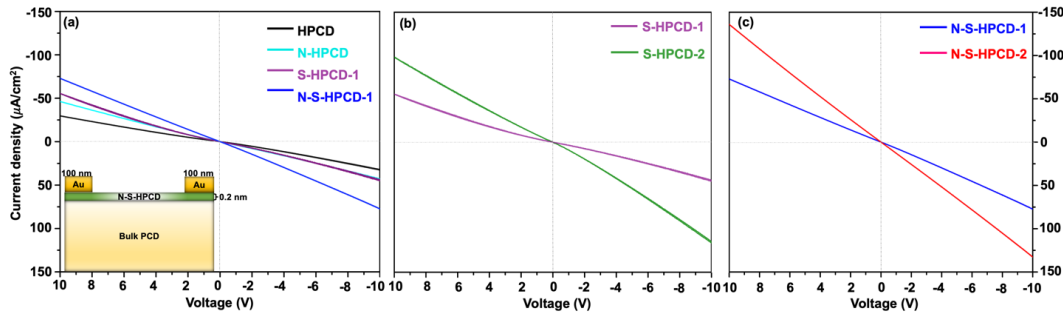


Fig. 55 Schematic view (a) of fabricated device; values stand for the thickness of layers. The I-V characteristics of functionalized diamond surfaces: (a) HPCD (black), N-HPCD (cyan), S-HPCD-1 (violet), and N-S-HPCD-1 (blue); (b) S-HPCD-1 (violet), and S-HPCD-2 (olive); (c) N-S-HPCD-1 (blue), N-S-HPCD-2 (red). The forward and backward voltage sweeps were from +10 V to −10 V with 200-mV step.

As compared to HPCD (Fig. 55a), the heteroatoms-terminated surfaces reveal higher current density at 10-V bias voltage from $27 \mu\text{A}/\text{cm}^2$ (HPCD) to $49 \mu\text{A}/\text{cm}^2$ (N-HPCD), $53 \mu\text{A}/\text{cm}^2$ (S-HPCD-1), and $74 \mu\text{A}/\text{cm}^2$ (N-S-HPCD-1), respectively. These observations suggest that resultant surfaces have better electrical performances by substituting the H atoms with heteroatoms than HPCD. As such, the S atom is expected to perform better in the doping process than the N atom because N-HPCD and S-HPCD-1 share a similar ratio of N (3.4%) and S (3.0%) on the diamond surfaces, respectively. Interestingly, after S-HPCD-1 is terminated with N, N-S-HPCD-1 shows higher current density at 10-V bias voltage even if the S concentration is compromised a bit by 0.9%. The plausible reason might be that despite N-S-HPCD-1 having a lower S ratio, there is a gain in N-related groups by roughly 2.4%, leading to the concentration of total conductive species being 2.3% higher than that of S-HPCD-1. This is consistent with what was observed in Fig. 54b. As surface coverage of S increases by 3.8% on S-HPCD-2 than that of S-HPCD-1, current density increases by $47 \mu\text{A}/\text{cm}^2$ at 10 V. Meanwhile, after subsequent amination in Fig. 54c, N-S-HPCD-2 lowers the ratio of S by 1.8% as

compared to S-HPCD-2, but 4.8% gain for N-related species with majorly -NH₂ group. This variation gives rise to higher current densities, accounting for 64 and 38 $\mu\text{A}/\text{cm}^2$ higher than N-S-HPCD-1 and S-HPCD-2, respectively. In short, our measurement here could imply that the Ohmic-like contact has been established on the interface between the functionalized layer and electrode, where heteroatoms, like N and S, are found to promote conductive behavior more than that of H termination on the diamond surface. The co-functionalized (N-S) surface demonstrates the best conductivity, which may suggest an alternative to modifying the electrical properties of the diamond surface.

In the future, we are planning to extend our research into diamond device fabrication based on the N-and-S-terminated surfaces and to measure how those functional groups will affect the surface resistance as well as the carrier concentration. Diamond FETs will also be fabricated to investigate the gate effect.

5.4 Fluorination of Diamond Surfaces and the Study of Fluorine Color Centers

The growing interest in diamond-based semiconductor applications hinges fundamentally on its versatility as a material with a large bandgap of 5.47 eV, a superior breakdown voltage of 10 MV/cm, and a thermal conductivity of over 22 $\text{W}\cdot\text{cm}^{-1}\text{K}^{-1}$, apart from the very high carrier mobility. This paves the way for next-generation power devices and is well reported. Additionally, another parallel area of interest within the materials-chemistry purview of diamond has been in quantum optics and quantum information processing applications arising from the optically rich defect centers, also known as the negatively charged nitrogen-vacancy (NV⁻) centers.⁴¹ To that extent, as a follow-up to the previous works on diamond functionalization using rigorous wet-chemistry approaches, fluorinating diamond is of interest. Over the years, fluorinating diamond has particularly unraveled deeper areas of study and applications consistently. These areas range from surface cleaning to removing surface adsorbates, surface smoothening arising from the etching and the pertinent work in tribology, followed by wet chemistry applications.⁴² Recently, more advanced device engineering work, particularly that of Schottky barrier diode based on the fluorine termination, has been achieved due to the increased work function aiding in reducing reverse current.⁸ Although these areas already serve as a roadmap to a variety of techniques available to fluorinate diamond, there is a necessity to pursue a morphological and optical defect focused study within the context of an extremely facile approach. We have therefore adopted a simple non-plasma gas phase approach to fluorinate PCD surfaces.

In order to realize the incorporation of fluorine atoms to the diamond surface, a lab-built Monel reactor was used as the reaction chamber given its nonreactivity and noncorrosive nature when exposed to the harsh fluorine environment. Gas cylinders with a 10% fluorine-helium mixture and helium were separately used as a part of the reaction setup. Helium served as a purging agent to evacuate ambient air in the absence of a vacuum pump. The downstream gas line was connected to the vent through a sodium hydroxide trap. In short, the experimental procedure involved solvent-washing and vacuum-drying the commercially purchased Element Six PCD substrate to remove surface adsorbates with acetone and isopropyl alcohol before starting the experiment. The PCD sample is manually loaded to the reaction chamber as shown in Fig. 56. At a minimum of 1 h, helium was allowed to purge the chamber prior to the fluorination. The temperature was controlled using a hot plate and was strictly increased till thermal equilibrium was achieved, only during the purging stage. The boundary conditions for temperature and time varied from ambient room temperature and 30 min to 350 °C and 6 h. Within these condition limits, several experiments were designed, varying time and temperature to study the effect of temperature and time on the fluorination of the diamond surface. The functionalized surface was then characterized using XPS, Raman spectroscopy, AFM to study the surface morphology, and PL measurements for the study of the optical defect centers.

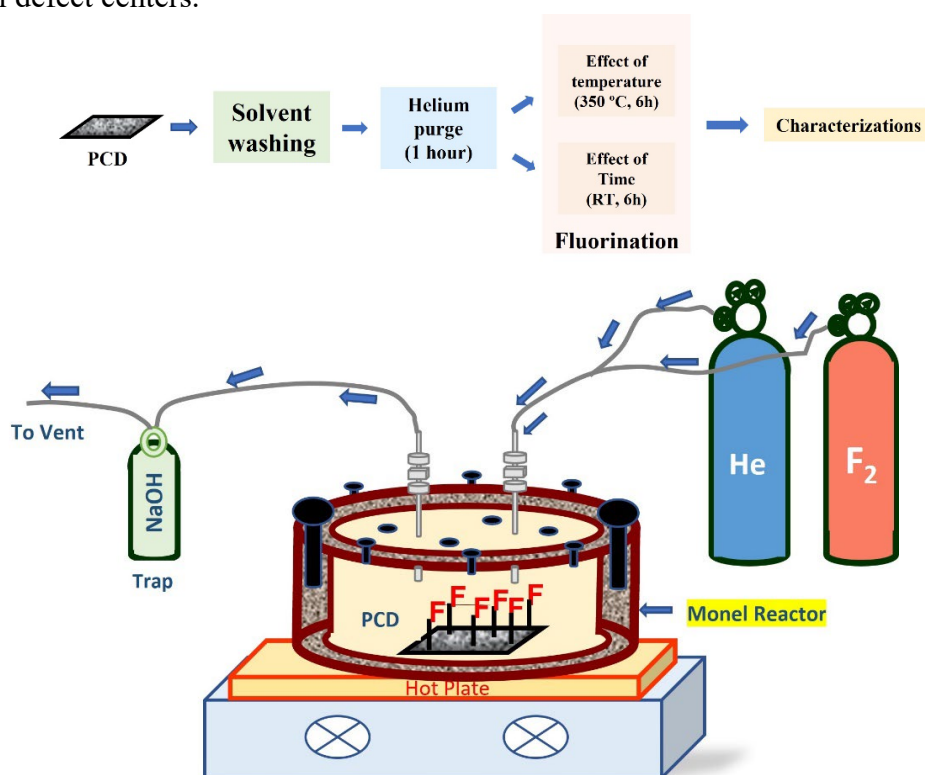


Fig. 56 Schematic depicting the experiment design (top) and illustration of the reaction setup (bottom)

The XPS measurements pertaining to the survey spectra confirm the anchoring of fluorine atoms covalently to the diamond surface as shown in Fig. 57. The effect of temperature depicts increasing the fluorine coverage ranging from over 6% to as high as 8.8%, directly affecting the rate kinetics.

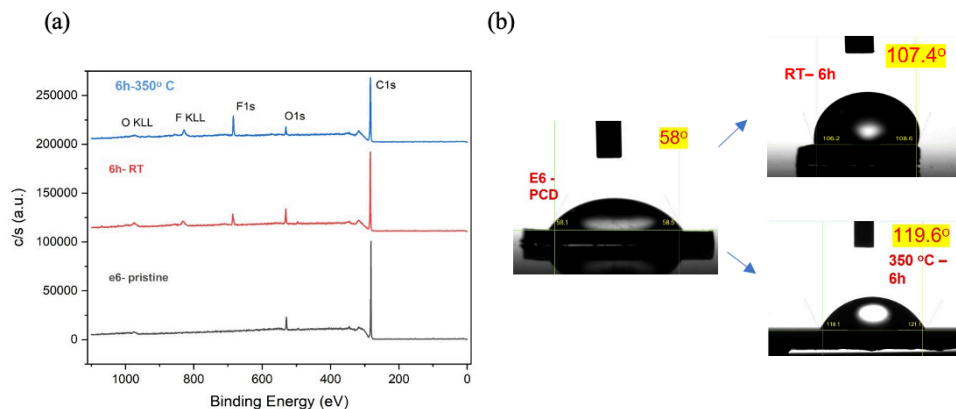


Fig. 57 (a) XPS data confirming the functionalization of diamond with fluorine group and (b) contact-angle data corroborating the higher coverage of fluorine on the surface as a function of temperature and the resulting increased hydrophobicity arising from the higher contact angle

This coverage of fluorine atoms is expected to create a hydrophobic layer due to the dangling fluorine bonds; this was validated by contact-angle measurements done on the sample (Fig. 58).

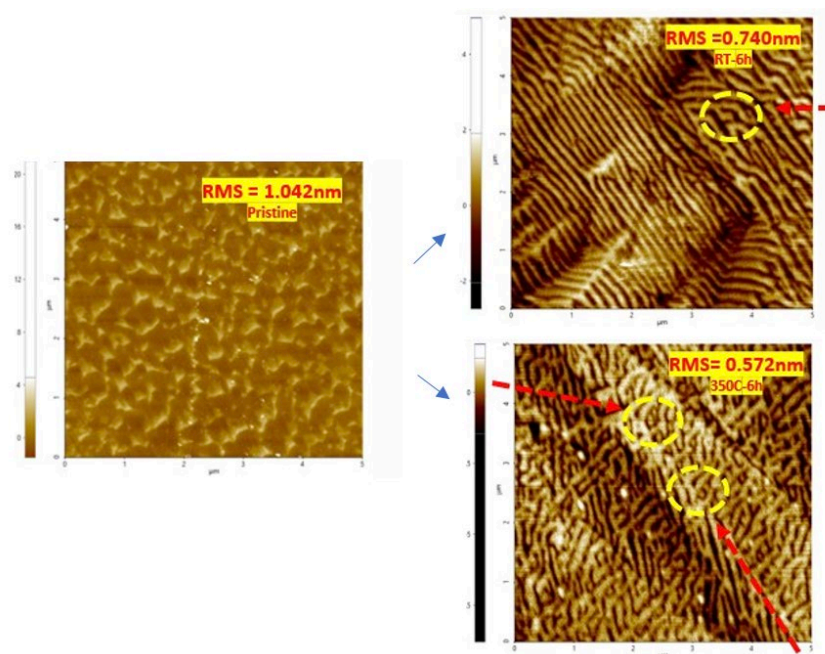


Fig. 58 AFM measurements done to validate the decrease in surface roughness while depicting nano-hill-like symmetrical features arising from the surface etching

From a morphological standpoint, surface roughness measurements done by AFM consistently showed a reduction in surface roughness compared with the pristine sample in line with works done before. Interestingly, the reactivity of fluorine on the diamond substrate showed the Marangoni effect and Coffee-Ring effect, suggesting the desorption of the unreacted fluorine and the formation of trace CF_4 gas species etching the surface in symmetrical patterns. We believe that this will pave the way to a realistic mechanism of understanding the etching process taking place on the diamond surface. Raman spectroscopy data of the functionalized diamond surface did not affect the diamond peak at approximately 1333 cm^{-1} (Fig. 59). However, the consistent feature of the fluorescence validated the etching mechanism previously observed from the AFM measurements, thus opening the possibility of changes in the optical defect centers (considering the functionalizing gas used is a highly electronegative species like fluorine).

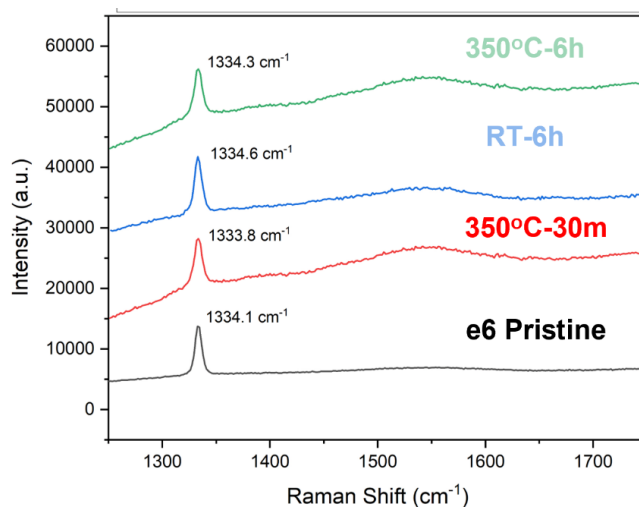


Fig. 59 Raman spectroscopy corroborated the increased fluorination and posited the possibility of increased density of vacancy centers from the increased surface etching compared to the pristine surface

This motivated us to explore the luminescence behavior of the sample comparing the pristine and functionalized surface at greater depth. The low-temperature PL spectroscopy was measured using a collaborator's lab-built confocal microscopy system. The pumping wavelength was 480 nm using a monochromatic pulsed laser with approximately 1- μm beam size at 0.5-mW laser power. The range of the PL data was collected from 500 to 950 nm (1.3–2.4 eV) under cryogenic conditions of approximately 6.2 K under a vacuum of 10^{-5} Torr.

At 6.2 K, there is a broad emission observed within the 530–950 nm spectral region (1.3–2.3 eV) centered around 700 nm from the pristine sample, as shown in Fig. 60. This is attributed to the nominal concentrations of substitutional nitrogen present from the commercially obtained PCD substrate within the range of 5–100

ppb. Interestingly, while investigating the emission spectra from the 6-h fluorinated sample at room temperature under the same conditions, new additional features were observed across a few regions that can possibly be attributed to fluorine defect or vacancy centers (F-V). The single narrow emission lines centered at 693 nm from Location 1 as shown in Fig. 61 (right) are to be noted. These findings are congruent to previously reported works that incorporate the fluorine into the diamond lattice by ion implantation.⁴³ This also clearly differs from the conventional defect centers such as silicon-vacancy (Si-V) and NV centers. The single narrow emission lines centered at 693 nm from Location 1 and multiple sharp lines observed from Location 2 at 620, 625, 630, and 642 nm (2.00, 1.98, 1.97, and 1.93 eV, respectively) are within the permissible range of possible generation of F-V centers.

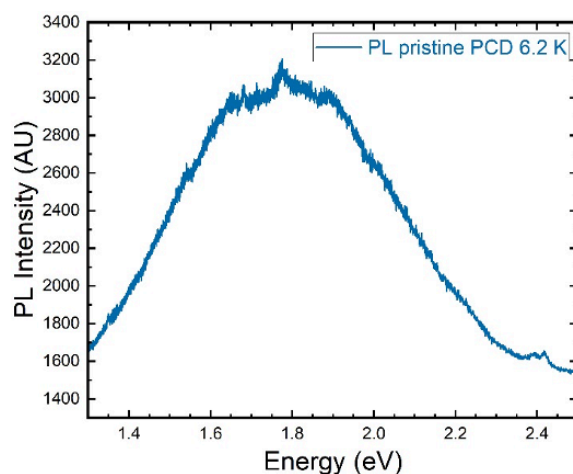


Fig. 60 PL spectra of a pristine PCD sample showing broad spectral emission

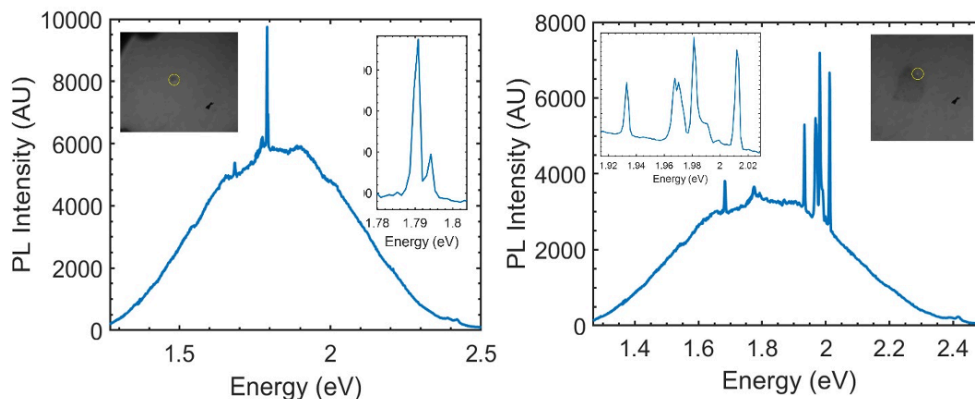


Fig. 61 PL spectra of fluorinated diamond under 6 h, and room temperature conditions on Location 1 (left) and Location 2 (right) under similar conditions

To that end, this work demonstrates creating a newer dopant-rich color center that can pave the way for studying the single photon emission and related autocorrelation function. Moreover, a comparative analysis of all the fluorinated

samples under different conditions of time and temperature can confirm the creation of non-NV-based color centers in this work.

6. Theoretical Studies Performed with Classical and Quantum Theory Levels

6.1 Amination of Diamond Surfaces

To understand the experimental results regarding the nitrogen-related groups found on our samples, we performed a theoretical analysis using DFT/PBE (Perdew–Burke–Ernzerhof)/ PAW (Projector Augmented Wave) on bare, hydrogenated, and partially oxidized (110) diamond surfaces to determine the possible nitrogenated groups found on the diamond surface. Here we will present only the main conclusions of this work. (For more details, see Li et al.³³)

The experimental observations on more C-NH₂ groups than the C=NH group on the surface could be explained with the following theoretical observations: (1) Diamond surface presents a lower number of defects, which decreases the number of surface carbon atoms with two or more dangling bonds, (2) during the hydrogenation or amination process, these defects are more efficiently hydrogenated, making C-H bonds more stable than C-NH₂ or C=NH bonds, and (3) the amination process may produce fewer C=NH groups than other nitrogen-related species. In addition, the amination process leads to a decrease in the sp² carbon concentration, which can further lower the number of carbon atoms with two or more dangling bonds, as well as the related defects. Considering regions on the surface without hydrogen or oxygen atoms (bare surface), the absence of a considerable number of carbon atoms with at least two dangling bonds makes the formations of C-NH₂/O=C-NH₂ groups more favored than C=NH groups. In summary, the theoretical simulation results are consistent with the overall experimental observations on the low concentration of the C=NH group on the aminated diamond surface, as compared to the C-NH₂/O=C-NH₂ groups.

6.2 Stability of Oxygenated Groups in Diamond Surfaces

To investigate the stability of the oxygenated groups at specific diamond surfaces, we evaluated, through fully atomistic reactive (ReaxFF force field) molecular mechanics simulations, the formation energies of the C=O, C–O–C, and C–OH groups on pristine and defective diamond surfaces (110), (111), and (311) (Fig. 62). Here we will present only the main conclusions of this work. (For more details, see Oliveira et al.⁴⁴)

According to our findings, the C–OH group has the lowest formation energy on a perfect (110) surface, while the C–O–C is favored on a defective surface. As for the (111) surface, the C–O–C group is the most stable for both pristine and defective surfaces. Similarly, the C–O–C group is also the most stable one on the defective/perfect (311) surface. In this way, our results suggest that if, in a diamond film, the (110) surface is the major exposed facet, the most adsorbed oxygen group could be either C–OH or C–O–C, in which the C–O–C would depend on the level of surface defects.

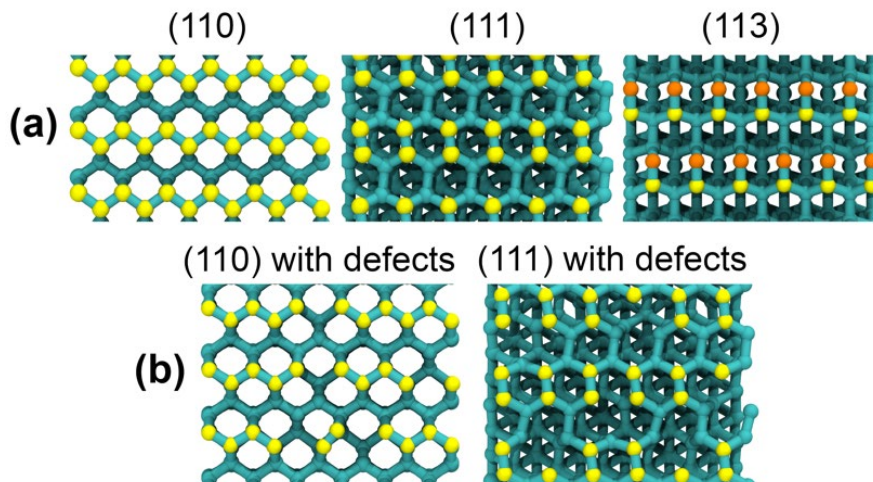


Fig. 62 (a) Pristine bare (110), (111), and (311) diamond surfaces in top and perspective views. (b) Defective (110) and (111) diamond surfaces. In (113) surface, the yellow and orange atoms represent the ones with one and two dangling bonds, respectively. For the other cases, the yellow atoms represent the most exposed carbon atoms.

7. Collaborations between Rice University and ARL

The Rice team and ARL team have been working closely since the project started. In addition to having biweekly meetings, both teams had many interactions, discussions, and specimen exchanges. Table 4 lists some of the samples exchanged between the two teams.

Table 4 Samples exchanging between Rice and ARL

Exchanged samples	Number of samples	Purposes	Rice→ ARL	ARL→ Rice
c-BN/diamond	2	Raman measurement	P	...
Epilayer grown on E6 diamond	1	Raman measurement	P	P
E6 electronic grade diamond	2	...	P	...
Polycrystalline diamond pattern	1	Display	P	...
c-BN powders	1	Raman measurement	P	...
Cu film on sapphire	1	h-BN growth	P	P
Transferred h-BN on E6 diamond	2	Electrical measurement	P	P
E6 SCD	2	Hydrogenation	P	P
E6 polycrystalline diamond	1	Hydrogenation	P	P
B-implanted SCD	1	Microscopy analysis		P
B-doped SCD	1	Microscopy analysis		P

8. Conclusions

This report assembles various research activities as part of the cooperative agreement between Rice University and ARL. These efforts focus on the joint collaborative work between the two institutions in developing diamond as the next-generation UWBG material for electronic devices. The Rice University team has excellent experience in the growth and development of high-quality materials, and the ARL team has outstanding experience in developing diamond-based devices. The synergies were developed during the first year of the project, and a strong collaborative team has been formed.

With the help of ARL and significant investment from Rice University, a state-of-the-art diamond growth facility was built and is ready for use at Rice University. During the third year of the program, we expect rapid progress in the preparation of high-quality samples for use by the ARL team in building devices. Growth of SCD substrates was attempted, as was heteroepitaxial growth of diamond and c-BN, both of which are considered a significant advancement in the field. Considerable work was done during the first two years to optimize the growth of high-quality h-BN and transfer these onto H-terminated diamond substrates. These samples have been sent to ARL for device fabrication.

Creation of diamond-based hetero-interfaces is the core of the project, and several such heterostructures have been synthesized and characterized. For the BN thin film

growth, we installed the advanced-level load-lock and ion-beam-assisted PLD growth chamber. Since the PLD thin film growth process involves several growth parameters, in the first phase we tried to optimize and understand the evolution of BN thin film growth on various substrates (SCD, Al_2O_3 , GaN, SiC) and various growth conditions (by varying all the possible growth parameters). Films were characterized by several techniques (e.g., XRD, AFM, XPS, FTIR, Raman, and HRTEM). As observed, BN films grown on sapphire and other substrates at high-temperature and pressure show nice crystalline quality. Furthermore, we found that in-situ annealing improves the surface quality. We then adopted the same growth conditions to grow BN films on GaN substrates, and finally on both commercially purchased and home-grown PCD and SCD substrates. In some cases, we also performed in-situ annealing of films to improve the surface quality. From our in-depth characterizations, films on SCD substrates show the formation of possible nanocrystalline c-BN, without any long-range atomic ordering.

Considering the complex phase diagram of BN and related growth kinetics, to obtain highly crystalline c-BN/SCD films in the future, we need to adjust and optimize the growth parameters to grow epitaxial c-BN thin films on SCD substrates by PLD. One important parameter would be to grow films at a much higher temperature, possibly at 1000 °C, as high growth temperature is important for c-BN to form. Another parameter would be to change the substrate crystalline facets, as different facets form different formation energy. Furthermore, in-situ or ex-situ high-temperature annealing (≥ 1000 °C) might be needed to obtain the pure phase c-BN. Our aim is to grow c-BN films not only along (001)-oriented SCD substrates, but also along different facets of SCD (e.g., (111), (113)) with different miscut angles and surface roughness; this will allow us to better understand the interfacial relationship between c-BN and SCD, and consequent device potentials of c-BN/diamond heterostructures, with the ultimate goal of making high-mobility FET devices. Strong theoretical effort was used to support several of the experimental activities including growth, surface modification, and doping in diamond.

Development of specific metrology for diamond-based structures has been another highlight during the second- and third-year efforts. Various new techniques such as terahertz spectroscopy, cathodoluminescence imaging, second harmonic generation techniques, scanning probe techniques, and others, have been explored to enable fast and efficient characterization of diamond surfaces in addition to conventional imaging and spectroscopy methods. Characterization of materials has been done in synergy with ARL researchers and facilities. Some of the device structures fabricated at ARL are being characterized in detail at Rice using FIB slicing and high-resolution transmission microscopy. More importantly, the FIB

milling procedure to prepare TEM specimens of as-grown diamond wafers, diamond-BN hetero interfaces, and diamond-based FET devices is now optimized, and state-of-the-art microscopy methods are employed to characterize these systems with sub-nanometer resolution. The details revealed from these studies will enable further optimization of the device architectures being developed at ARL.

A strong collaborative team has been formed between Rice and ARL. Interactions included bimonthly discussions via Microsoft Teams, phone calls, specimen exchanges, joint publications (several in the pipeline), and facility sharing at both sites. The third-year interactions have been equally strong, as the diamond substrates being grown at Rice will be used by ARL in device fabrication. The collaboration will extend to other DoD labs (Air Force and Naval Research Laboratories) during the fourth and fifth years. The work done during the third year lays the foundation for a long-term collaboration between Rice and ARL toward developing diamond-based UWBG electronic devices for areas such as high-power and RF electronics. The facility established at Rice for diamond growth will also enable other applications of diamond-based materials, such as quantum sensing and computing. The diamond devices built as part of this effort will also enable new opportunities in the network platforms that are being developed as part of the same cooperative agreement.

9. List of Publications

- Biswas A, Xu M, Fu K, Zhou J, Xu R, Puthirath AB, Hachtel JA, Li C, Iyengar SA, Kannan H, et al. Properties and device performance of BN thin films grown on GaN by pulsed laser deposition. *Appl Phys Lett*. 2022;121:092105.
- Biswas A, Ruan Q, Lee F, Li C, Iyengar SA, Puthirath AB, Zhang X, Kannan H, Gray T, Birdwell AG, et al. Unidirectional domain growth of hexagonal boron nitride thin films. *Applied Materials Today*. 2023;30:101734.
- Biswas A, Maiti R, Lee F, Chen CY, Li T, Puthirath AB, Iyengar SA, Li C, Zhang X, Kannan H, et al. Unravelling the room temperature growth of two-dimensional h-BN nanosheets for multifunctional applications. Revised version submitted to *Nanoscale Horizons*. 2023.
- Biswas A, Xu R, Alvarez GA, Christiansen-Salameh J, Zhang J, Puthirath AB, Burns K, Hachtel JA, Li T, Li C, et al. Twisting related structure property correlations in h-BN/SiC heterostructures. To be submitted to *Adv. Mater*. 2023.
- Biswas A, Xu R, Christiansen-Salameh J, Jeong E, Alvarez GA, Li C, Puthirath AB, Gao B, Garg A, Gray T, et al. Synthesis, properties and phase transformation of 2D/3D h-BN/c-BN nanocomposite. To be submitted to *ACS Nano*. 2023.
- Biswas A, Li C, Puthirath AB, Gray T, Kannan H, Zhang X, Elkins J, Vajtai R, Birdwell AG, Neupane MR, et al. Exploring bulk c-BN phase diagram via spark plasma synthesis. In preparation, 2023.
- Li C, Zhang X, Oliveira EF, Puthirath AB, Neupane MR, Weil JD, Birdwell AG, Ivanov TG, Kong S, Gray T, et al. Systematic comparison of various oxidation treatments on diamond surface. *Carbon*. 2021;182:725.
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- Oliveira E, Li C, Zhang X, Puthirath A, Neupane MR, Weil J, Birdwell AG, Ivanov T, Kong S, Grey T, et al. Stability of oxygenated groups on pristine and defective diamond surfaces. *MRS Advances*. 2022;7:543–546.
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- Puthirath AB, et al. Superior FET characteristics with Al₂O₃ dielectric gate layer on transfer doped diamond. In preparation.
- Roy S, Zhang X, Puthirath AB, Meiyazhagan A, Bhattacharyya S, Rahman MM, Babu G, Susarla S, Saju SK, Tran MK, et al. Structure, properties and applications of two-dimensional hexagonal boron nitride. *Adv Mater*. 2021;33:2101589.
- Zhang X, Biswas A, Puthirath AB, Vajtai R, Ajayan PM, Ruzmetov DA, Birdwell AG, Ivanov TG. Growth of carbon – boron – nitrogen heterostructures. *GOMACTech*. 2022.
- Zhang X, et al. Low-temperature deposition of boron nitride thin films on arbitrary substrates by microwave-plasma assisted chemical vapor deposition. In preparation.
- Zhang X, et al. A novel and simple method for polycrystalline diamond patterning. In preparation.

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List of Symbols, Abbreviations, and Acronyms

2D	two-dimensional
AFM	atomic force microscopy
Al ₂ O ₃	alumina/sapphire
Ar	argon
ARL	Army Research Laboratory
B	boron
BCN	boron carbon nitride
BDD	B-doped diamond
BE	beryllium
BFOM	Baliga figure of merit
BN	boron nitride
C	carbon
CA	cooperative agreement
c-BN	cubic boron nitride
CL	cathodoluminescence
Cu	copper
CVD	chemical vapor deposition
DC	direct current
DEVCOM	US Army Combat Capabilities Development Command
DFT	density functional theory
DOD	Department of Defense
EDS	energy dispersive spectroscopy
EELS	electron energy loss spectroscopy
ESCD	electronic-grade single crystal diamond
FET	field-effect transistor
FFT	Fourier transform

FIB	focused ion beam
FTIR	Fourier transform infrared
FWHM	full width at half maximum
GaN	gallium nitride
GIXRD	grazing angle X-ray diffraction
H/H ₂	hydrogen
H ₂ O	water
H ₂ O ₂	hydrogen peroxide
h-BN	hexagonal BN
HD	hydrogenated diamond
HPCD	hydrogenated polycrystalline diamond
HRTEM	high-resolution TEM
ICP-RIE	inductively coupled plasma–reactive ion etching
Mg	magnesium
MPCVD	microwave-plasma chemical vapor deposition
N	nitrogen
NEA	negative electron affinity
NIR	near infrared
NV	nitrogen vacancy
O	oxygen
OES	optical emission spectrometer
P	phosphorus
PCD	polycrystalline diamond
PL	photoluminescence
PLD	pulsed laser deposition
RF	radio frequency
RHEED	reflection high-energy electron diffraction

S	sulfur
Si	silicon
SiC	silicon carbide
SCD	single crystal diamond
SEM	scanning electron microscopy
SIMS	secondary ion mass spectrometry
SRIM	stopping and range of ions in matter
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
ToF	time of flight
UV	ultraviolet
UWBG	ultrawide bandgap
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction

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