



ARL-TR-9414 • MAR 2022



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

**by Pulickel M Ajayan, Robert Vajtai, Xiang Zhang,
Anand B Puthirath, Eliezer Oliveira, Chenxi Li,
Harikishan Kannan, Tia Gray, Tony Ivanov, A Glen Birdwell,
Dmitry Ruzmetov, Mahesh Neupane, Pankaj Shah,
Sergey Rudin, James Weil, Leonard De La Cruz,
Derwin Washington, Stephen B Kelley, and Bradford B Pate**

Approved for public release: distribution unlimited.

NOTICES

Disclaimers

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorized documents.

Citation of manufacturer's or trade names does not constitute an official endorsement or approval of the use thereof.

Destroy this report when it is no longer needed. Do not return it to the originator.



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

**Pulickel Ajayan, Robert Vajtai, Xiang Zhang, Anand B Puthirath,
Eliezer Oliveira, Chenxi Li, Harikishan Kannan, and Tia Gray**
Materials Science and NanoEngineering, Rice University

**Tony Ivanov, A Glen Birdwell, Dmitry Ruzmetov, Mahesh Neupane,
Pankaj Shah, Sergey Rudin, James Weil, Leonard De La Cruz,
Derwin Washington, and Stephen B Kelley**
DEVCOM Army Research Laboratory

Bradford B Pate
*Nanomaterial Interfaces and Devices, Chemistry Division,
Naval Research Laboratory*

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188		
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) March 2022		2. REPORT TYPE Technical Report		3. DATES COVERED (From - To) August 2019–October 2020	
4. TITLE AND SUBTITLE Development of Diamond-Based Materials Systems for High-Power RF Electronics: First-Year Report			5a. CONTRACT NUMBER		
			5b. GRANT NUMBER		
			5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) Pulickel M Ajayan, Robert Vajtai, Xiang Zhang, Anand B Puthirath, Eliezer Oliveira, Chenxi Li, Harikishan Kannan, Tia Gray, Tony Ivanov, A Glen Birdwell, Dmitry Ruzmetov, Mahesh Neupane, Pankaj Shah, Sergey Rudin, James Weil, Leonard De La Cruz, Derwin Washington, Stephen B Kelley, and Bradford B Pate			5d. PROJECT NUMBER		
			5e. TASK NUMBER		
			5f. WORK UNIT NUMBER		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Rice University 6100 Main St. Houston, TX 77005			8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) DEVCOM Army Research Laboratory ATTN: FCDD-RLS-ER 2800 Powder Mill Rd, Adelphi, MD 20783-1138			10. SPONSOR/MONITOR'S ACRONYM(S) DEVCOM ARL		
			11. SPONSOR/MONITOR'S REPORT NUMBER(S) ARL-TR-9414		
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release: distribution unlimited.					
13. SUPPLEMENTARY NOTES ORCID IDs: A Glen Birdwell, 0000-0001-5235; Tony Ivanov, 0000-0002-1472-788X					
14. ABSTRACT The report details the first-year research effort that is part of the Cooperative Agreement between Rice University and US Army Combat Capabilities Development Command Army Research Laboratory. The project aims to develop diamond and diamond-based heterostructures for the next generation of ultra-wide-bandgap electronic devices, with performances far exceeding existing diamond devices as well as other wide-bandgap-material-based devices. The Rice team focuses on the growth of high-quality, single-crystal diamond substrates and heterostructures of diamond and boron nitride, and the DEVCOM Army Research Laboratory team 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 diamond and heterostructures. First-year work has included growth and transfer of boron nitride on commercially available diamond substrates, doping using ion implantation, development of unique metrology tools to characterize diamond surfaces, surface modification using hydrogenation and oxygenation, and development of theoretical models to understand the growth and surface characteristics of diamond. The synergy between the two institutions establishes a close working relationship leading to the synthesis of controlled diamond materials and their utilization in high-power devices.					
15. SUBJECT TERMS diamond, hexagonal boron nitride, interface characterization, surface modification, hydrogenation simulation					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 96	19a. NAME OF RESPONSIBLE PERSON Pulickel M Ajayan/Tony Ivanov
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) 713-348-5904/301-394-3568

Contents

List of Figures	v
List of Tables	x
Acknowledgments	xi
1. Introduction	1
2. Events	2
3. Setup of State-of-the-Art Facilities for Fabrication of Diamond Single Crystals and Heterostructures	3
4. Growth and Preparation of H-BN–Diamond Heterostructures	9
4.1 Introduction	9
4.2 Optimizing h-BN Growth	11
4.3 Optimizing h-BN Transfer	14
4.4 Direct Growth of h-BN on Diamond	18
4.5 Exploration of Other Related Materials Growth	19
5. Development of Characterizations Techniques for Diamond Interfaces	21
5.1 Terahertz Spectroscopy	21
5.1.1 Introduction	21
5.1.2 THz Spectroscopy System (Operating Principle of THz-TDS)	22
5.1.3 Materials Properties	24
5.1.4 THz Measurements on Pristine and Hydrogenated Single-Crystalline Diamond Wafers	25
5.2 Focused Ion Beam (FIB) Processing of Diamond Wafers	28
5.3 Aberration-Corrected Electron Microscopy	29
5.4 Piezoelectric Force Microscopy Mapping of Hydrogenated Diamond Surfaces	31
5.5 Magnetic Force Microscopy	32

5.6	Second-Harmonic Generation on Diamond Surface	33
6.	Diamond Surface Modification and Doping	34
6.1	Surface Conduction in Diamond via Transfer Doping	34
6.2	Functionalization of the Diamond Surface with Hexagonal Boron Nitride	40
6.2.1	Experimental Work	40
6.2.2	Theoretical/Modeling Work	42
6.3	Oxygenation of Diamond Microcrystals and Polycrystalline Wafer through Hummers' Method	47
6.4	Oxygenation of Diamond through Acid Mixture	53
6.5	Oxygenation of Diamond through UV Ozone and O ₂ Plasma	56
6.6	Diamond Doping by Ion Implantation	58
7.	On the Hydrogenation of Diamond Surfaces: A Reactive Molecular Dynamics Study	60
7.1	Methodology	61
7.2	Results and Discussions	62
7.2.1	Bare Surfaces	62
7.2.2	Hydrogenation of Different Diamond Surfaces	67
7.3	Continuing Simulation Work	70
8.	Collaborations between the Rice Team and DEVCOM ARL Team	71
9.	Conclusions	72
10.	References	74
	List of Symbols, Abbreviations, and Acronyms	79
	Distribution List	83

List of Figures

Fig. 1	Timeline for the establishment of RUNSRA lab in Dell Butcher Hall. This includes state-of-the-art diamond growth facility and characterization.	4
Fig. 2	Blueprint of the RUNSRA center (left) and the diamond and diamond-based heterostructures laboratory (right)	5
Fig. 3	Office space at the center under construction	5
Fig. 4	Infrastructure installation underway; gas safety cabinets for H ₂ , methane, and ammonia storage (left), and a segment of the infrastructure rack at the ceiling, carrying electrical, gas, coolant, and compressed air lines	6
Fig. 5	Diamond growth MPCVD systems, SEKI SDS6350 (left) and Plassys SSDR-150 (right), being installed at the facility	7
Fig. 6	The Pioneer 180 PLD equipment and the COMpex 205 excimer laser have been acquired and will be located in the dedicated lab space at the center	8
Fig. 7	MTI dual-sliding tube furnace and HQ Graphene nanomaterials transfer setup are located in the satellite lab at the center.....	8
Fig. 8	a) h-BN lattice structure; b, c) diamond FETs with h-BN as a gate dielectric.....	10
Fig. 9	Two types of potential h-BN–diamond FET structures	10
Fig. 10	a) Cu (111) single-crystal film. b) h-BN single crystals grown on Cu film. c) Wafer-scale h-BN single crystal transferred on a Si wafer....	11
Fig. 11	a) Photo and b) illustration of the dual-furnace CVD system for h-BN growth. c) Schematic of the main steps involved in substrate preparation and h-BN growth.	11
Fig. 12	a) Optical image and b) SEM image of a Cu film after high-temperature annealing. c) SEM image of a thicker Cu film after annealing. d, e) Optical images of Cu films after annealing at approximately 100 and 300 Torr, respectively.	12
Fig. 13	a) Optical image of a Cu film after annealing, b) XRD patterns of the sapphire substrate, c) as-deposited Cu film on sapphire, and d) annealed Cu film on sapphire	13
Fig. 14	a) Optical image and b) SEM image of the h-BN film grown on Cu. XPS spectra of c) B 1s and d) N 1s. e) Optical image of h-BN film transferred on SiO ₂ –Si. f) Raman spectra of h-BN film. g, h) AFM measurement of h-BN film.	14
Fig. 15	Schematic illustration of the PMMA-assisted transfer process flow..	15
Fig. 16	Schematic illustration of the PDMS-assisted transfer process flow ...	16

Fig. 17	Schematic illustration of the TRT-assisted transfer process flow	17
Fig. 18	a) Optical image and b) Raman spectra of h-BN transferred on SiO ₂ -Si using the PMMA-assisted transfer method. c) Optical image and d) AFM measurement of h-BN transferred on diamond using the PMMA-assisted transfer method. e) Optical image and f) Raman spectra of h-BN transferred on SiO ₂ -Si using the PDMS-assisted transfer method. g) Optical image and h) AFM measurement of h-BN transferred on diamond using the PDMS-assisted transfer method.	17
Fig. 19	a) PMMA-h-BN transferred on a hydrogenated diamond. b) XPS spectra of h-BN transferred on a hydrogenated diamond. c) XPS spectra of transferred h-BN on diamond after hydrogenation.	18
Fig. 20	a) Schematic illustration of a CVD system. b) Surface morphology and c) Raman spectra of a pristine ESCD. d) Surface morphology, e) Raman spectra, f) XPS spectra, and g, h) AFM thickness measurement of the ESCD after h-BN growth.....	19
Fig. 21	a) Optical image, b) SEM image, c) Raman spectra, and d, e) element mappings of MoS ₂ grown on PCD. f) Cross-sectional TEM image of MoS ₂ and diamond interface.....	20
Fig. 22	a) SEM image and b) XPS spectra of h-BN-graphene heterostructure grown on Cu. c) Optical image of h-BN-graphene heterostructure transferred on SiO ₂ -Si. d, e) Raman spectra collected on the red spot and green spot, respectively.....	20
Fig. 23	Electromagnetic spectrum highlighting THz	21
Fig. 24	Standard characterization techniques to measure the doping profiles in semiconductors (image courtesy of Tulsyan ²⁵).....	22
Fig. 25	THz-TDS experimental setup	23
Fig. 26	THz spectroscopy: the signal pathway and processing.....	24
Fig. 27	The relation connecting the contributions charge carriers and crystal structure toward the total conductivity plotted against frequency	25
Fig. 28	Thin-film THz-time-domain experimental setup.....	26
Fig. 29	Electric-field variation recorded for a reference signal, SCD, and H-terminated SCD wafer.....	27
Fig. 30	Preliminary results of a) refractive index, b) absorption coefficient, and c) real and d) imaginary conductivity values for pristine single diamond (plotted against the frequency). e) Since the pristine SCD wafers are insulating without any charge carriers, a negligible conductivity value is observed on SCD wafers.	27
Fig. 31	a) The refractive index, b) absorption coefficient, and c) real, and d) imaginary conductivity values for H-terminated diamond (plotted against the frequency). e) Since H- terminated SCD wafers with atmospheric adsorbates are conducting with the formation of 2DHG, a reasonable conductance value is observed on H-terminated SCD wafer.	28

Fig. 32	Schematic of FIB unit showing the sample stage and various ion and electron guns and a micromanipulator (left) and instrumentation (right)	29
Fig. 33	FIB processing stages starting from PCD wafer to processed ultra-thin wafer attached to the TEM grid	29
Fig. 34	EDS mapping of various elements (C, Ga) on the FIB-milled PCD samples.....	30
Fig. 35	Electron microscopy image and selected area diffraction patterns of PCD wafers. The identified planes are given in the inset. Also shown is the crystallographic perspective of a SCD showing different planes and facets.	30
Fig. 36	From left to right: topography, piezo amplitude, and phase maps of the pristine PCD surface. A contrast variation is observed in the piezoelectric mapping (amplitude and phase) indicating the piezo active centers on the surfaces.....	31
Fig. 37	From left to right: topography, MFM amplitude, and phase maps of a pristine PCD surface. A contrast variation is MFM mapping (amplitude and phase) indicating the magnetically active centers on the surfaces.	32
Fig. 38	SHG intensity mappings of a) pristine PCD and b) hydrogenated PCD. c) BSE image of PCD. SHG intensity mappings of d) pristine SCD and e) hydrogenated SCD.....	33
Fig. 39	Band diagram with key material parameters. E_C , E_{VAC} , E_F , E_V , and χ denote the energy level of the conduction band, vacuum level, Fermi level, valance band, and electron affinity, respectively. KP and PES positions, E_F and E_V , are respectively relative to E_{VAC}	35
Fig. 40	$E_F - E_V$ vs. 2DHG density for H-terminated diamond	36
Fig. 41	PES data taken on an H-terminated diamond surface for four different measurement conditions. Electronic transitions listed in the spectra (labeled 1, 2, and 3) are illustrated in the band diagrams. The measurement conditions and key for the color-coding scheme is provided in the text.	37
Fig. 42	Diamond electronic and phononic band structure with PES measured transitions.....	38
Fig. 43	$E_F - E_V$ vs. 2DHG density for H-terminated diamond. Uncertainty in the measurement of $E_F - E_V$ is estimated to be approximately 0.050 eV.....	38
Fig. 44	The stability of the parameters of the electrical conduction of diamond with MoO_3 transfer dopant layer and capped with a SiO_2 (150-nm) protective layer.....	40
Fig. 45	Process of lattice-matched 2-D-H-D (100) heterostructure design. Blue, red, and gray (light) atoms represent B, N, and C atoms, respectively.	43

Fig. 46	Details on heterostructure design: (Top left to right) unstrained 2X5 h-BN (graphene) layer and strained and rotated 2X5 h-BN (graphene) layer and (bottom right to left) 2X1 H-D (100) substrate and lattice-matched 2-D–H-D (100) heterostructure	43
Fig. 47	Optimized 2-D–H-D (100) heterostructures (left) h-BN–H-D (100) heterostructure and (right) graphene–H-D (100) heterostructures.....	44
Fig. 48	The sDOS plots for 2-D–H-D (100) heterostructures: (left) graphene/H-D (100) heterostructures and (right) h-BN–H-D (100) heterostructure.....	44
Fig. 49	Effective potential profile of h-BN–H-D (100) and graphene–H-D (100) heterostructures. Inset highlights band-alignment characteristics between the 2-D layers and H-D (100) system in 2-D–H-D (100) heterostructures	46
Fig. 50	Steps involved in the MHM process to create O-terminated diamond surfaces	48
Fig. 51	FTIR spectrum comparing the pristine and MHM-process-modified O-terminated samples. A stark difference is observed in terms of vibrational bands that correspond to C–O vibrations	50
Fig. 52	EDS of microcrystalline diamond powder samples and the EDS showing the elevated O concentration in MHM-processed diamond samples.....	51
Fig. 53	Survey XPS of pristine and MHM-treated diamond powders for three different pass energies.....	51
Fig. 54	High-resolution C1s spectra of pristine and microcrystalline diamond powders	52
Fig. 55	MD calculations on the effect of surface geometry on the percentage of oxygenation via MHM. The excess surface to volume ratio predicts the powder samples are more prone to oxidation compared to a PCD wafer.	53
Fig. 56	a) The setup for web-chemistry treatments on diamond powder a PCD. Normalized XPS survey spectra of diamond powder treated by b) H ₂ SO ₄ /HNO ₃ at 195 and 360 °C, and c) various methods including aqua regia, Fenton solution, and piranha solution. d) Normalized attenuated total reflectance–FTIR spectra of diamond powder treated by various methods.	54
Fig. 57	High-resolution core-level O 1s spectrum of PCD: a) pristine sample, b) H ₂ SO ₄ /HNO ₃ 5:1 at 360 °C, c) aqua regia, d) Fenton solution, and e) piranha solution. f) The quantified results of O-related groups for each of treated samples calculated based on the whole elements of PCD surface	55
Fig. 58	Normalized Raman spectra of PCD treated by H ₂ SO ₄ /HNO ₃ at a) 195 and 360 °C, and b) various methods. The images of AFM spectroscopy of PCD: c) untreated (0.134 nm) and d) H ₂ SO ₄ /HNO ₃ 1:1 at 360 °C (0.077 nm) treated samples	56

Fig. 59	a) Schematic illustration of dry-chemistry treatments on PCD. b) Normalized XPS survey spectra of PCD treated by UV ozone and O ₂ plasma.	56
Fig. 60	High-resolution core-level O 1s spectrum of PCD: a) O ₂ plasma and b) UV ozone. c) The quantified results of O-related groups for each of treated samples calculated based on the whole elements of PCD surface.	57
Fig. 61	Normalized Raman spectra of PCD treated by a) UV ozone and b) O ₂ plasma. The images of AFM spectroscopy of PCD treated by c) UV ozone (0.120 nm) and d) O ₂ plasma (0.170 nm).	58
Fig. 62	1) pristine SCD, 2) 40-keV B-implanted SCD, and 3) 60-keV B-implanted SCD.	59
Fig. 63	Optical image of a) pristine PCD, b) 20-keV B-implanted PCD, and c) 40-keV B-implanted PCD. d) Raman spectra of pristine PCD. e) Raman spectra and g) diamond peak intensity mapping of 20-keV B-implanted PCD. f) Raman spectra and h) diamond peak intensity mapping of 40-keV B-implanted PCD.	60
Fig. 64	Diamond surface (001) a) before and b) after a thermal equilibration at 900 °C. c) Representative bond lengths between C atom at the surface.	62
Fig. 65	Diamond surface (013) a) after a thermal equilibration at 900 °C. b) Representative bond lengths between C atoms at the surface.	63
Fig. 66	Diamond surface (110) a) after a thermal equilibration at 900 °C. b) Representative bond lengths between C atom at the surface.	64
Fig. 67	Diamond surface (113) a) after a thermal equilibration at 900 °C. b) Representative bond lengths between C atoms at the surface.	65
Fig. 68	Potential energy per atom in relation to the elapsed time of MD simulation at room temperature	66
Fig. 69	a) Snapshots of the initial configuration of each tested diamond surface in contact with the atmosphere of H atoms. b) Snapshots of the resulting hydrogenated diamond surfaces at 900 °C after the H incorporation saturation.	68
Fig. 70	Number of H atoms per nm ² incorporated in each tested diamond surface in relation to the elapsed time of simulation	69
Fig. 71	a) Total number of H atoms that are incorporated in each surface in relation to the temperature. b) Percentage of the initial dangling bonds per nm ² that a H atom is incorporated in relation to the temperature in each surface.	69

List of Tables

Table 1	Electron affinity (χ), work function (ϕ), and the Fermi level position are relative to the valance band ($E_F - E_V$) measured on a hydrogenated diamond surface. Units are in eV.....	37
Table 2	Calculated device-related parameters for the bare H-D (100) surface and 2-D–H-D (100) heterostructures. All the numerical values are given in eV.....	45
Table 3	Ion implantation diamond sample list.....	59
Table 4	Number of dangling bonds at different diamond surfaces in relation to the temperature. These data were collected according to the results presented in the previous sections.....	67
Table 5	Samples exchanging between Rice and DEVCOM ARL.....	71

Acknowledgments

The following people were involved and are thanked:

- **Rice University:** Dr Pulickel Ajayan, Dr Robert Vajtai, Dr Xiang Zhang, Dr Anand B Puthirath, Dr Eliezer Oliveira, Chenxi Li, Harikishan Kannan, and Tia Gray
- **DEVCOM ARL:** Dr Tony Ivanov, Dr A Glen Birdwell, Dr Dmitry Ruzmetov, Dr Mahesh Neupane, Dr, Pankaj Shah, Dr Sergey Rudin, James Weil, Leonard De La Cruz, Derwin Washington, and Stephen B Kelley
- **Naval Research Laboratory:** Dr Bradford B Pate
- **Collaborators:** Dr Di Chen (University of Houston), Dr Hanyu Zhu (Rice), Dr Aditya Mohite (Rice), and Dr Junichiro Kono (Rice)

1. Introduction

With the increasing demand for silicon (Si) 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 ultra-wide-bandgap (> 5 eV) material, has significant advantages compared to GaN or SiC if implemented in high-power devices.⁵ With 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 an easy electron emitter 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 generate 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, the drivers of the semiconductor industry. The high thermal conductivity⁸ of diamond also allows excellent intrinsic thermal management, so far a bottleneck with Si 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 polycrystalline films over areas ranging from a few millimeters to several centimeters.¹⁰ For the dielectric layer over diamond, several oxide films have been explored (e.g., alumina, molybdenum trioxide [MoO₃], and so on) with varying degrees of success based on the interface structure, epitaxy, and charges present. For the doping part, various approaches have enabled p- and n-type structures to be produced with dopants such as boron (B) and diamond.¹¹ However, uniform and controlled doping has been challenging, leading to techniques that alter diamond surface terminations (hydrogen [H] or oxygen [O]). These surface modifications, termed 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.

The specific objectives of the project are the following:

- 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–hexagonal-boron carbon nitride (h-BCN), 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, selecting metals and alloys, and integrating and testing these in field-effect transistor (FET) diamond devices.
- Developing close collaborations with the US Army Combat Capabilities Development Command Army Research Laboratory to develop device architectures for the diamond–BN heterostructures grown at Rice University, and fabricating and testing these devices both at Rice and the DEVCOM Army Research Laboratory. The goal is to achieve far better device performance compared to existing diamond wide-bandgap devices, based on well-defined device metrics.
- Exploring, 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

The following events were part of the first-year project:

- The kick-off event, 10/31/2019, Rice University
- Materials Research Society Fall Meeting, 12/1/2019–12/6/2019, Boston
- Dr Tony Ivanov seminar, 2/20/2020, Rice University

- Rice University National Security Research Accelerator (RUNSRA) lab ribbon-cutting event, 10/30/2020, Rice University
- The 6-month review meeting, 5/8/2020, online
- Second Workshop on Diamond Electronics, 10/19/2020–10/22/2020, online
- The annual review meeting, 11/6/2020, online
- Biweekly meeting, 10/21/2019 to present, online

3. Setup of State-of-the-Art Facilities for Fabrication of Diamond Single Crystals and Heterostructures

Rice invested a substantial amount of funds and energy into establishing the laboratories and the related office space used in this project. In the process of selecting the location of the new lab from several options, premium space in Dell Butcher Hall has been renovated into the new diamond growth facility. The advantage of this choice is the environment: this building is on Rice campus, in the engineering quad, and close to the cleanroom, the main characterization facilities, and peer labs. The newly established Welch Foundation Materials Center will also be located in the same building.

The process from location selection to the creation of a state-of-the-art facility is illustrated in Fig. 1. In the first stage, we established a project management team from Rice, including a project manager, safety officer, and planning representative. The predesign process started at the end of October 2019 and was finished by December 6, 2019, and as the budget exceeded its threshold, it needed to be approved by Rice upper management. The design team was selected in early January 2020 and after the usual steps of design, permissions, and pricing, the construction began in the middle of April 2020. The substantial construction work on the labs and offices is now finished and the final part of the research facility installation is progressing. The final installation time and initiation for the equipment was estimated to be early 2021.

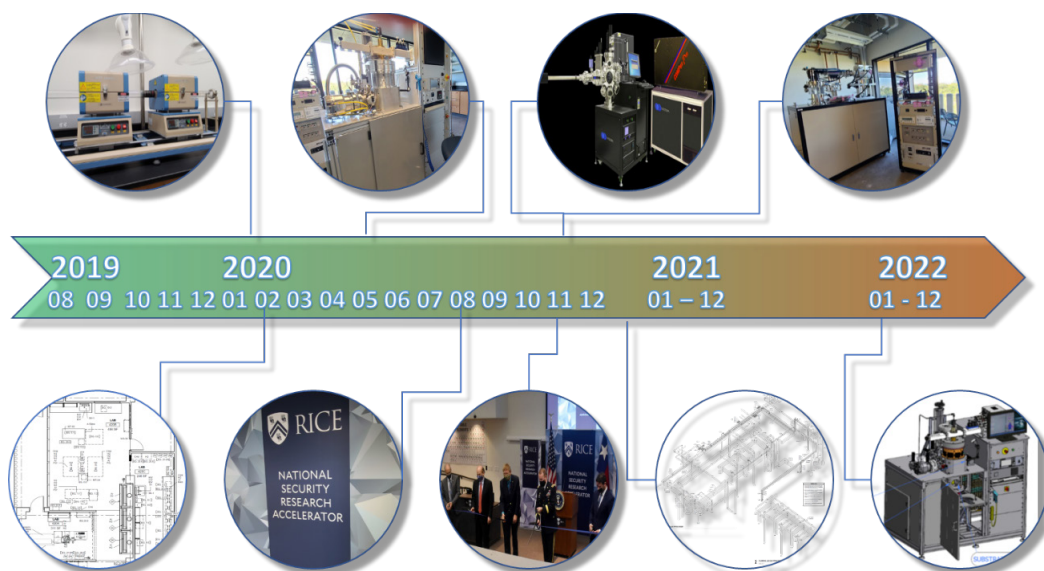


Fig. 1 Timeline for the establishment of RUNSRA lab in Dell Butcher Hall. This includes state-of-the-art diamond growth facility and characterization.

The main parameters of the center (Fig. 2) include a 1050-ft² lab space for the development of diamond and related materials (Thrust I), a 700-ft² lab space for characterization and other related research, a space for approximately 10 student/postdocs working at RUNSRA, the center director's office, accommodation for four senior scientists, and a conference room. The "Diamond" lab has three partially separated spaces: the main hall (420B), where the diamond growth equipment will be located; a laser lab/pulsed laser deposition (PLD) (420A); and a satellite lab (420C), where the thermal CVDs and several small pieces of equipment will be installed and located.

For developing the lab space for the unique equipment needs, we needed to consider the need for ultra-high purity gases. For providing the highest possible quality and at the same time maintaining high-level confidence, we decided to use an H₂ generator (Proton OnSite G4800) as a primary H₂ source, and gas cylinders and an H₂ purifier (SAES PS7-PD05) as a backup system. As many of the CVD processes take long periods of operation, this design seems to be the safest solution. For a carbon (C) source, methane cylinders was used with the highest purity level of gas; however, to maintain parts per billion-range contaminant level, a methane purifier (Entegris PS4-MT3) was also included in the infrastructure. To address the quality, temperature, and level of cooling, the house cooling system needed to be expanded with four high-quality heat exchangers. During this design and development stage, several key safety issues needed to be addressed, such as H₂ safety, handling of the exhaust gases that also contain H₂, storage, the use of highly corrosive solvents and acids, and the high-intensity laser. At this point, most of the infrastructure is installed (Fig. 4), and the ultra-high purity gas handling system is being installed in the coming weeks.



Fig. 4 Infrastructure installation underway; gas safety cabinets for H₂, methane, and ammonia storage (left), and a segment of the infrastructure rack at the ceiling, carrying electrical, gas, coolant, and compressed air lines

Presently, diamond substrates are purchased from the company Element Six. The goal is to transition to homegrown diamond substrates with better control of the parameters. The purpose of our diamond growth facility is twofold: we need to grow electronic-grade pristine diamond wafers and we also need to carry out in-situ doped diamond growth. Beyond growth, we need to consider surface treatment of samples, especially hydrogenation of the wafers. Accordingly, we selected two microwave-plasma CVD (MPCVD) reactors with very high-quality but somewhat different features to match the high-reproducibility and high-flexibility needs of these processes. Both of the systems are equipped to handle the process gases at the required precision, and they have the appropriate microwave power inputs and both work with the 2.45-GHz frequency, which serves a 2-inch sample holder. The main differences are in the chamber consisting of the sample holder; while the SEKI setup has an electro-polished metal enclosure, the Plassys works with a quartz-bell

system. The former is less prone to impurities originating from the chamber, while the latter is easier to clean, which is an important factor for removing contaminants that remain from prior experiments. This equipment has been delivered and is located in the main lab space. Installation is planned as soon as the gas lines are ready and the installation and training will be done soon after that. Figure 5 shows the two systems during installation.



Fig. 5 Diamond growth MPCVD systems, SEKI SDS6350 (left) and Plassys SDR-150 (right), being installed at the facility

Another key element of the project is the growth and characterization of atomically precise diamond–dielectric and diamond–metal interfaces. To deposit hexagonal and cubic BN (h-BN and c-BN) or other nanostructures, we plan to use a PLD system, which has an electro-polished ultra-high-voltage (UHV) 304 stainless steel 18-inch-diameter spherical chamber with numerous ports for PLD, high-pressure reflection high-energy electron diffraction (RHEED), RF sputtering, a DC ion source, a substrate load-lock, a six-target carousel, a rotating 2-inch sample holder, and a substrate load-lock with a magnetically coupled linear feed through (Fig. 6). This is a powerful excimer laser setup filled with krypton fluoride as the active medium, with a wavelength of 248 nm and a pulse duration of 25 ns; the maximum pulse energy is 700 mJ and the repetition rate is 50 Hz. The setup consists of a DC ion gun that is needed for molecular-beam epitaxy–level deposition; it has maximum kinetic energy (argon [Ar] ions) of 1200 eV and beam current of 120 mA.



Fig. 6 The Pioneer 180 PLD equipment and the COMPex 205 excimer laser have been acquired and will be located in the dedicated lab space at the center

In summary, the lab space has been renovated and a substantial part of the construction is finished. The installation of the gas delivery system was expected by the end of 2020. The large equipment purchased in Year 1 has been acquired and is ready to be installed, and most of the smaller equipment is installed and in use. Further equipment planned for subsequent years, contingent upon availability of funds, includes another diamond growth MPCVD chamber for B doping, RHEED mounted on the PLD setup, an electrical probe station, and a diamond polishing facility. Figure 7 shows the equipment located in the satellite lab.

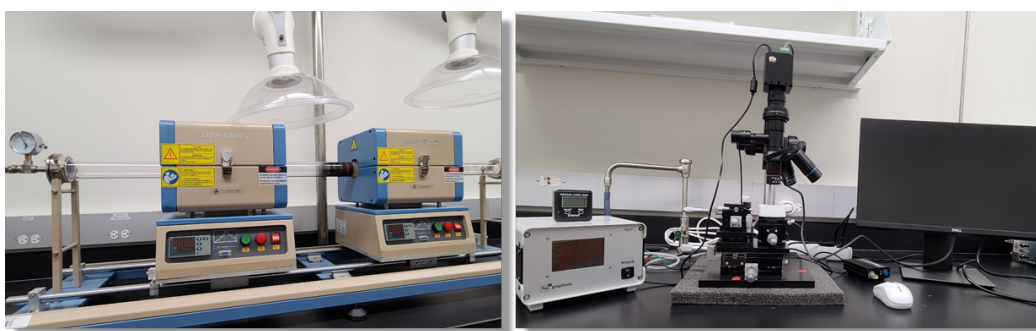


Fig. 7 MTI dual-sliding tube furnace and HQ Graphene nanomaterials transfer setup are located in the satellite lab at the center

4. Growth and Preparation of H-BN–Diamond Heterostructures

4.1 Introduction

BN is an inorganic chemical compound consisting of equal numbers of B and nitrogen (N) atoms. BN is isostructural to C and exists in various crystalline forms, including amorphous form (a-BN), hexagonal form (h-BN), cubic form (c-BN), and wurtzite form (w-BN). The crystalline h-BN in its honeycomb hexagonal structure is also known as “white graphite” as it is similar to graphene, consisting of atomically flat layers of alternating sp^2 hybridized and strongly covalent B and N atoms held together by van der Waals (vdW) interactions between the layers. But unlike graphene, the B–N covalent bond is strongly polarized with electronegative N atoms, giving rise to possible anisotropic properties. h-BN has been suggested as an ideal insulating material for 2-D electronic devices due to its excellent properties. It has a wide direct bandgap (5.9–6.1 eV), high mechanical hardness and resilience, high thermal conductivity, high breakdown electric field, and excellent chemical inertness without surface dangling bonds.

Diamond FETs have potential applications in power electronics and high-output, high-frequency amplification. However, high carrier mobility has been difficult to realize in diamond FETs, especially when the carrier density is high. The reported mobilities of H-terminated diamond FETs in the literature range between 3 and 300 $\text{cm}^2/\text{V s}$, which are much lower than the maximum hole mobility reported in bulk diamond (2000 $\text{cm}^2/\text{V s}$). It can be attributed to the charge impurities existing in the gate insulator. For example, a sapphire film deposited by atomic layer deposition contains O point defects and aluminum vacancies.

Sasama et al.¹² reported diamond FETs with monocrystalline h-BN as a gate dielectric and obtained excellent mobilities ($>300 \text{ cm}^2/\text{V s}$) for moderately high carrier densities ($>5 \times 10^{12} \text{ cm}^{-2}$) (Fig. 8). This work shows that h-BN is promising as an alternative gate dielectric for diamond FETs because of its high crystallinity, few charged impurities, and a flat surface with no dangling bonds. Recent theoretical work suggests if the negative charges are confined too close to the interface between gate dielectric and diamond, any increase in the carrier concentration will be counterbalanced by a decrease in the mobility.¹³ h-BN can repel the negative charges from the 2-D hole gas (2DHG), thereby the 2-D hole carrier mobility will be enhanced to higher values.

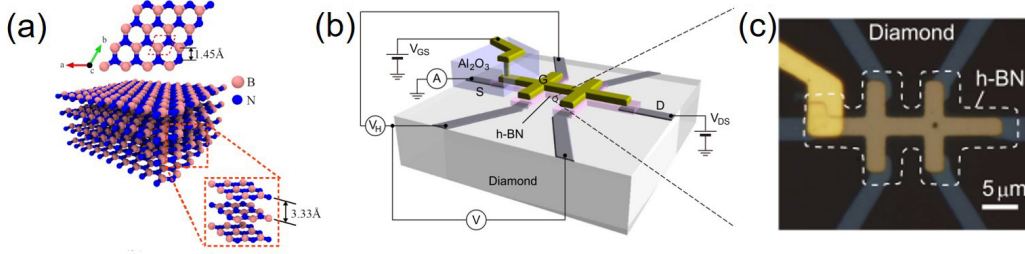


Fig. 8 a) h-BN lattice structure; b, c) diamond FETs with h-BN as a gate dielectric reported by Sasama et al.¹²

Inspired by these reports, we have considered h-BN–diamond FETs with transfer doping, as shown in Fig. 9. To fabricate these FETs, high-quality, single-crystal h-BN with atomic thickness is required. The synthesis methods of h-BN can be mainly categorized into two approaches: the top-down approach, such as mechanical and chemical exfoliation, and the bottom-up approach, such as CVD and physical vapor deposition. Among all the methods, CVD has been deemed as the most effective method to grow large-scale h-BN film with controllable atomic thickness. The Ajayan group at Rice has reported pioneering work of growing monolayer and few-layer h-BN film on a copper (Cu) foil.^{14–22} Despite such accomplishments, there still exist many challenges for h-BN synthesis. For example, the reported grain size of an h-BN single crystal is usually smaller than graphene crystals. The h-BN growth mechanism is more complicated than graphene growth, as B and N show different diffusion behavior on a Cu substrate. The precursors for h-BN growth are usually solid and liquid, such as ammonia borane and borazine. They often undergo several decomposition steps at different temperatures before forming h-BN films.

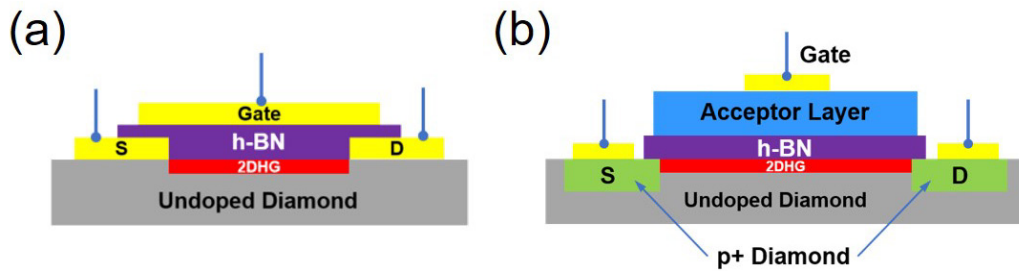


Fig. 9 Two types of potential h-BN–diamond FET structures

Chen et al.²³ reported the wafer-scale epitaxial growth of single-crystal monolayer h-BN on a Cu (111) thin film across a c-plane sapphire wafer. A Cu (111) surface with step edges was found as the key to achieving single-crystal h-BN growth. Inspired by this work, we have optimized the h-BN growth in our lab (Fig. 10).

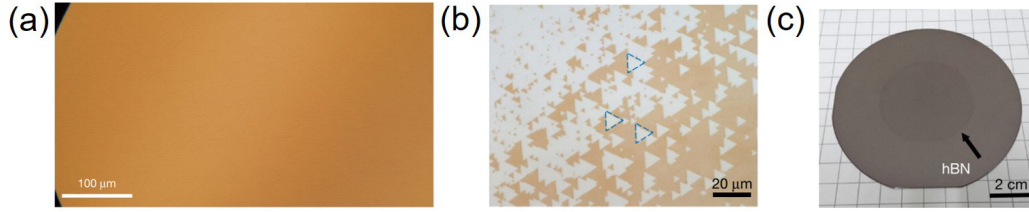


Fig. 10 a) Cu (111) single-crystal film. b) h-BN single crystals grown on Cu film. c) Wafer-scale h-BN single crystal transferred on a Si wafer, reported by Chen et al.²³

4.2 Optimizing h-BN Growth

Figure 11a and b shows the dual-furnace CVD system we use for h-BN growth. The maximum heating temperature we use is 1200 °C. The carrier gases are ultra-high-purity H_2 and Ar. Ammonia borane is used as the precursor and placed in the upstream furnace. The Cu film on a sapphire substrate is placed in the downstream furnace. A needle valve is installed between a vacuum pump and the quartz tube so the working pressure can be adjusted between 1 mTorr to 1 atm. Figure 11c illustrates the main procedures for substrate preparation and h-BN growth. The Cu film is deposited on a clean single-crystal c-plane sapphire before inserting into the quartz tube for high-temperature annealing. While the ammonia borane is heated, the h-BN growth starts. After performing more than 100 experiments, we have found many parameters that play important roles in h-BN growth, including the orientation, roughness, cleanliness, and termination of sapphire substrate; the deposition method, deposition rate, substrate temperature, and film thickness during Cu film deposition; annealing temperature; pressure; gas flow rate and time duration during high-temperature annealing; substrate temperature; precursor temperature; and gas flow rate, pressure, and time duration during h-BN growth.

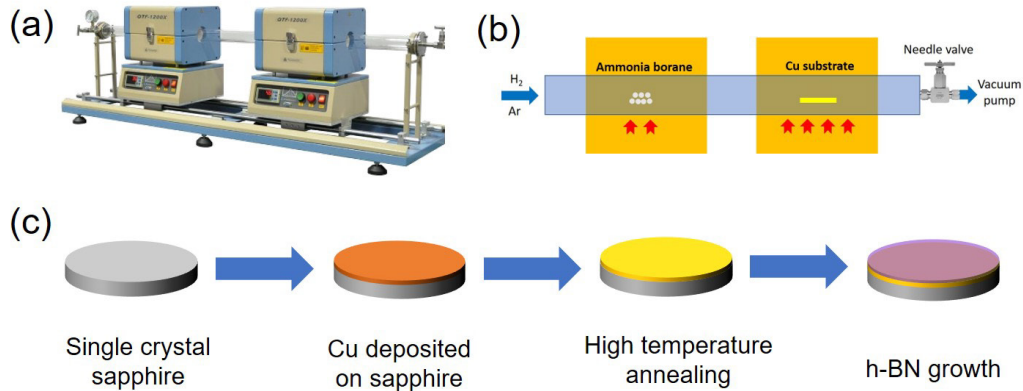


Fig. 11 a) Photo and b) illustration of the dual-furnace CVD system for h-BN growth. c) Schematic of the main steps involved in substrate preparation and h-BN growth.

One of the biggest challenges we have encountered during the optimization is the Cu film de-wetting after annealing. Figure 12a and b shows the optical image and scanning electron microscopy (SEM) image of an annealed Cu film on sapphire. A lot of holes can be observed in the film. To solve the problem, we first tried to increase the Cu film thickness to increase the melting point of the Cu film. However, this still had challenges. Figure 12c still shows a lot of holes in a thicker Cu film. Next, to suppress the Cu evaporation, we increased the annealing pressure from approximately 1 Torr to approximately 100 Torr, and then to hundreds of torr. It seems that the number of holes decreases with the increasing pressure, but a certain number of holes can still be observed. After several experiments, we learned that the sapphire surface or the interface between sapphire and Cu is extremely important to Cu wetting. A sapphire substrate with low surface roughness and high cleanliness is desired. And a more critical requirement is having O- or OH- termination, which helps form a Cu oxide layer at the initial stage of Cu deposition and therefore greatly improves the Cu film adhesion. To meet these requirements, we conducted a very careful pretreatment on sapphire. After sonication in ethanol, the sapphire is cleaned by three types of acid mixtures. Then it is immersed in ultrapure water to form O- or OH- termination.

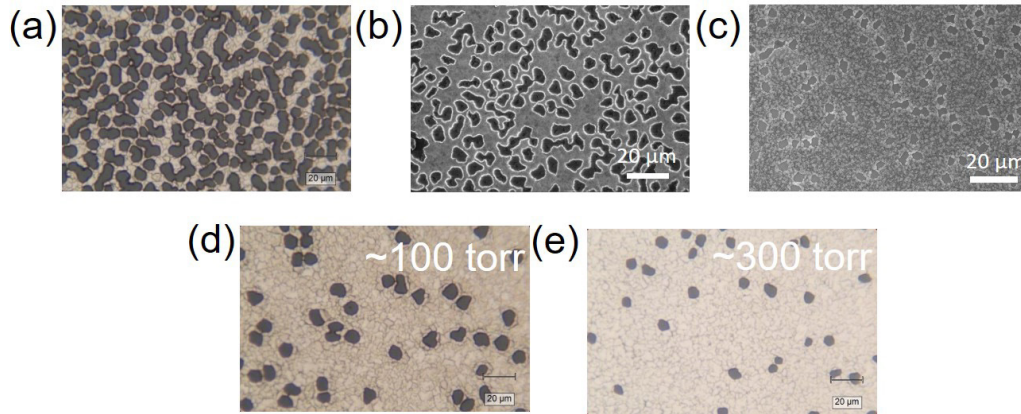


Fig. 12 a) Optical image and b) SEM image of a Cu film after high-temperature annealing. c) SEM image of a thicker Cu film after annealing. d, e) Optical images of Cu films after annealing at approximately 100 and 300 Torr, respectively.

After combining all the techniques, we successfully prepared a Cu film without holes on a large scale, as shown in Fig. 13a. X-ray powder diffraction (XRD) measurement was performed on sapphire and Cu on sapphire to analyze their crystallinity and orientation. The XRD pattern in Fig. 13b–d indicates the single crystallinity of the sapphire substrate. The Cu film forms in (111) orientation when deposited on sapphire, whose crystallinity is further improved after annealing.

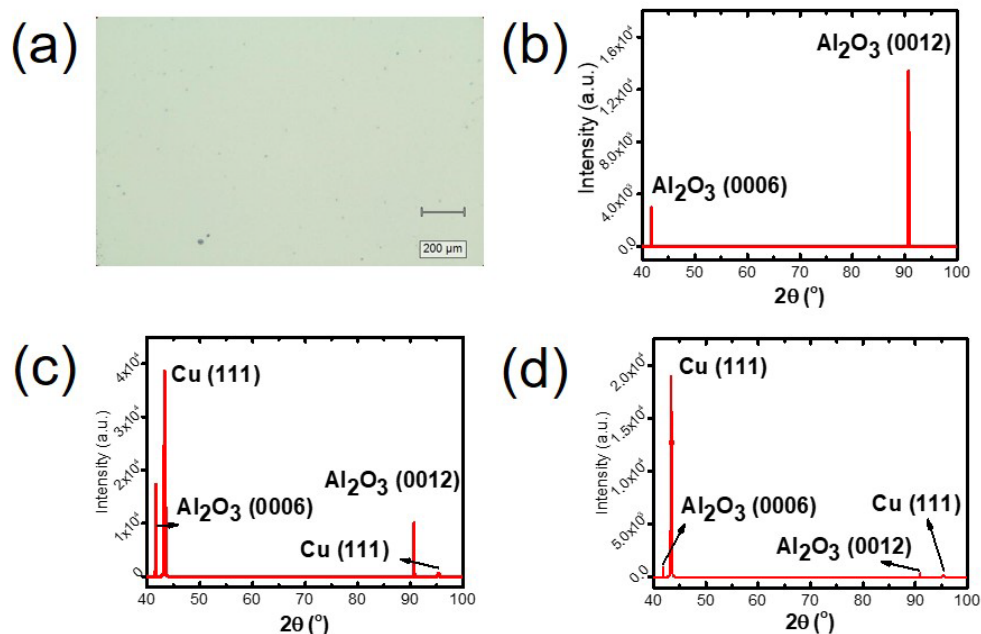


Fig. 13 a) Optical image of a Cu film after annealing, b) XRD patterns of the sapphire substrate, c) as-deposited Cu film on sapphire, and d) annealed Cu film on sapphire

Figure 14a and b shows the optical image and an SEM image of a typical h-BN film grown on Cu. It shows good uniformity, not only on a large scale, but also at smaller scales. Intense B and N peaks are detected in the X-ray photoelectron spectroscopy (XPS) spectrum. Since the contrast of thin h-BN on Cu is very low, we transferred h-BN onto silicon dioxide (SiO_2)–Si. A clear border of the h-BN film can be observed in Fig. 14e. Raman spectrum in Fig. 14f shows the h-BN E_{2g} peak. Atomic force microscopy (AFM) measurement was performed at the edge of the h-BN film and the confirmed film thickness is less than 2 nm. Through these optimization protocols, we successfully grew large-area h-BN thin film on a Cu–sapphire substrate.

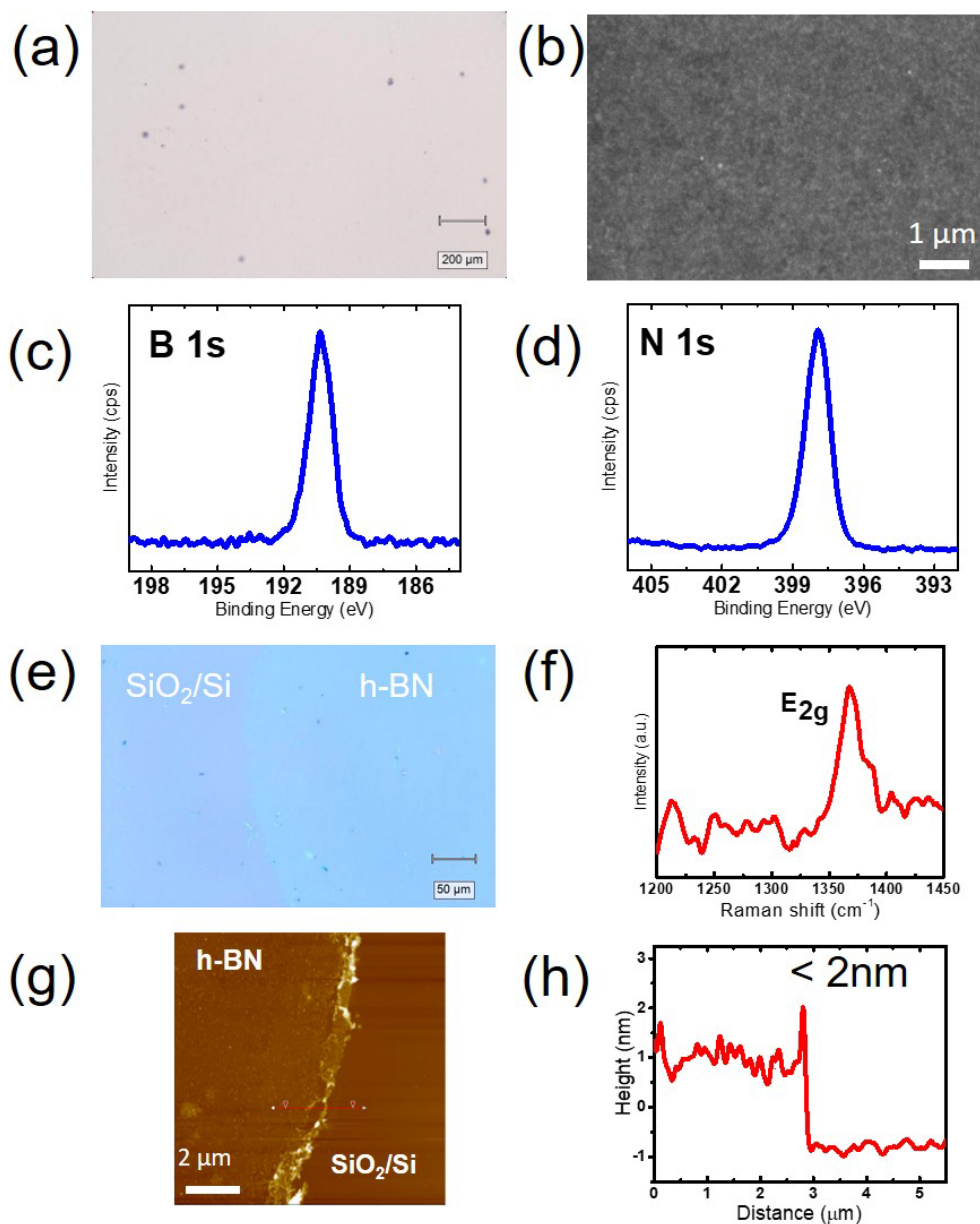


Fig. 14 a) Optical image and b) SEM image of the h-BN film grown on Cu. XPS spectra of c) B 1s and d) N 1s. e) Optical image of h-BN film transferred on SiO₂-Si. f) Raman spectra of h-BN film. g, h) AFM measurement of h-BN film.

4.3 Optimizing h-BN Transfer

Figure 15 shows the most widely used transfer technique for 2-D materials, poly(methyl methacrylate) (PMMA)-assisted transfer. A thin PMMA layer is first spin-coated on an h-BN-Cu sample. The sample is left in Cu etchant, usually ferric chloride or ammonium persulfate solution, for a couple of hours. After deionized water rinsing, the sample is scooped by the target substrate, diamond in this case.

Finally, PMMA is dissolved by acetone and isopropyl alcohol (IPA). This method is relatively simple. However, one major drawback is the transfer position cannot be precisely controlled.

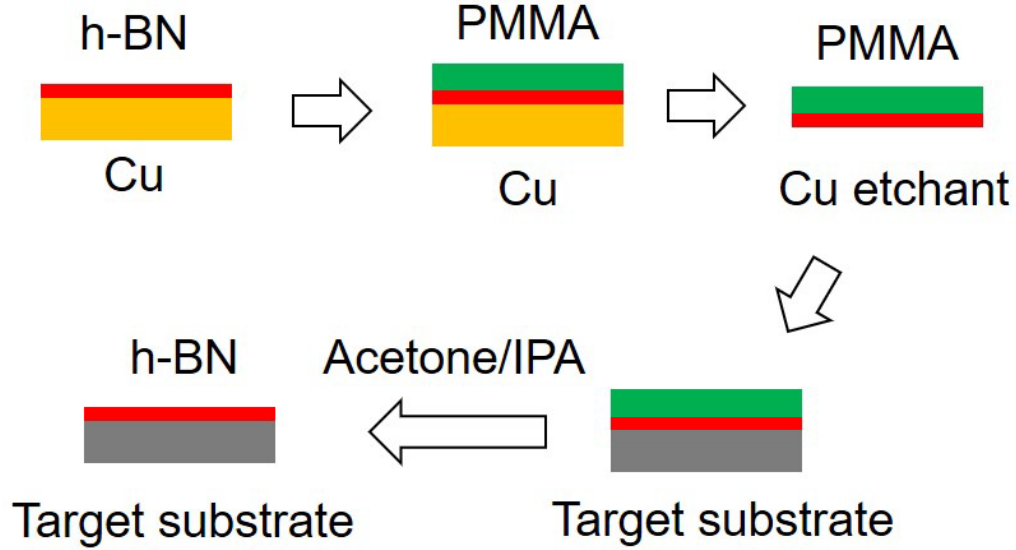


Fig. 15 Schematic illustration of the PMMA-assisted transfer process flow

To control the transfer position, we developed a polydimethylsiloxane (PDMS)-assisted transfer method, as shown in Fig. 16. The commercial PDMS film is thicker than PMMA and can be made to be double-sided sticky. After attaching the PDMS film onto h-BN and etching Cu, we attached the other side of the PDMS film to a glass slide. The glass slide with PDMS–h-BN can be inserted into the 2-D materials transfer system, which provides precise control of the x, y, z movement and title angle during transfer. As a result, the h-BN film can be transferred to the desired position on the target substrate, which is greatly beneficial to subsequent device fabrication.

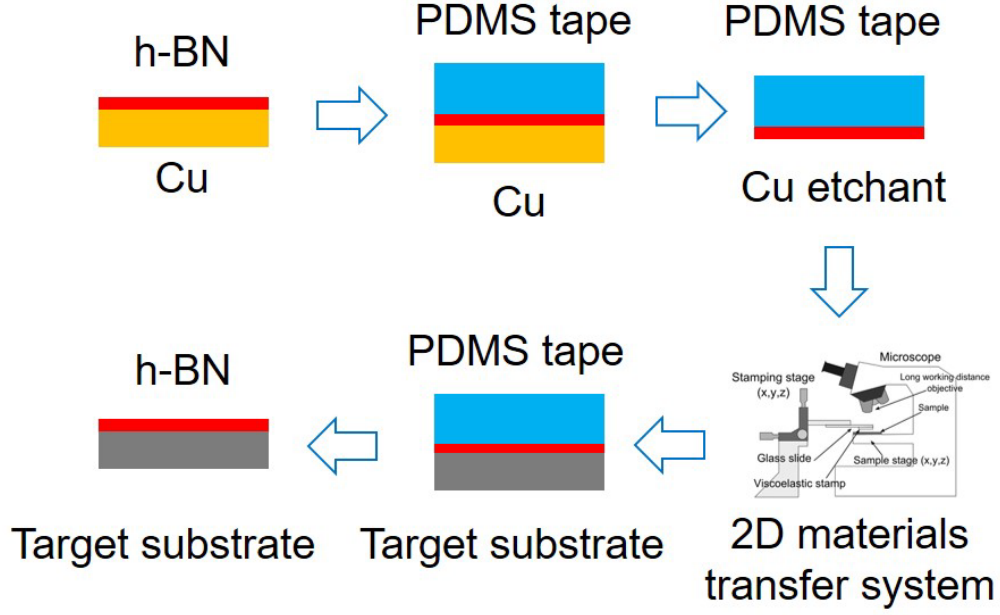
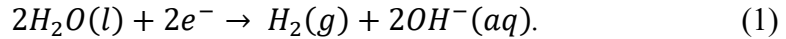


Fig. 16 Schematic illustration of the PDMS-assisted transfer process flow

Recently, we have tried another transfer method utilizing thermal release tape (TRT) and electrochemical delamination (Fig 17). After spin-coating PMMA on h-BN/Cu, TRT is attached onto PMMA. The TRT–PMMA–h-BN–Cu and a platinum (Pt) foil are dipped into sodium hydroxide solution, working as a cathode and an anode of an electrolysis cell, respectively. Once a voltage is applied, a water reduction reaction takes place to produce H_2 . The reaction can be represented as follows:



A large number of H_2 bubbles formed between Cu and h-BN help make h-BN detach from the Cu substrate very quickly. Similar to PDMS-assisted transfer, we can also use the 2-D materials transfer system to control the position precisely. Then, the TRT can be peeled off by placing the sample on a hot plate at approximately 120 °C. Acetone and IPA are used to dissolve the PMMA.

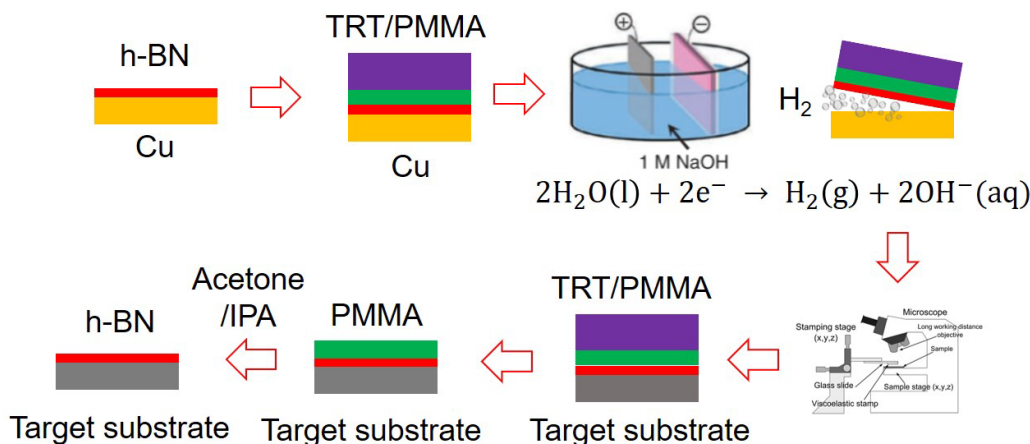


Fig. 17 Schematic illustration of the TRT-assisted transfer process flow

Figure 18 shows the optical image, Raman spectra, and AFM measurement of h-BN transferred on SiO_2 -Si and diamond using PMMA- and PDMS-assisted methods. Both methods successfully transfer large-area h-BN film, showing a similar thickness approximately 2 nm. A video recording is used to visualize h-BN detaching from Cu in about 10 s during the TRT-assisted electrochemical delamination.

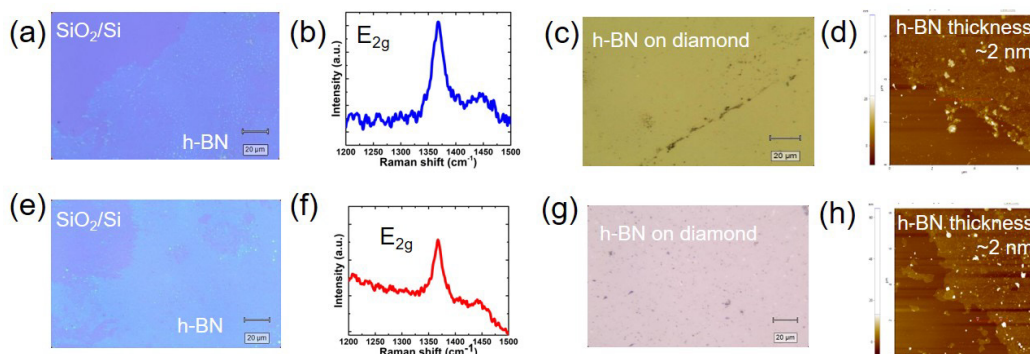


Fig. 18 a) Optical image and b) Raman spectra of h-BN transferred on SiO_2 -Si using the PMMA-assisted transfer method. c) Optical image and d) AFM measurement of h-BN transferred on diamond using the PMMA-assisted transfer method. e) Optical image and f) Raman spectra of h-BN transferred on SiO_2 -Si using the PDMS-assisted transfer method. g) Optical image and h) AFM measurement of h-BN transferred on diamond using the PDMS-assisted transfer method.

With the optimization of h-BN growth and transfer, the Rice team and DEVCOM ARL team have been exchanging samples and collaborating on h-BN-diamond device fabrication. Figure 19a shows a picture of a transferred h-BN film on a hydrogenated diamond. The hydrogenated diamond from DEVCOM ARL has a hydrophobic surface, which can be challenging for h-BN transfer. After dissolving

the PMMA layer, XPS measurement was performed, showing the B and N peaks in Fig. 19b. This indicates the h-BN transfer is successful.

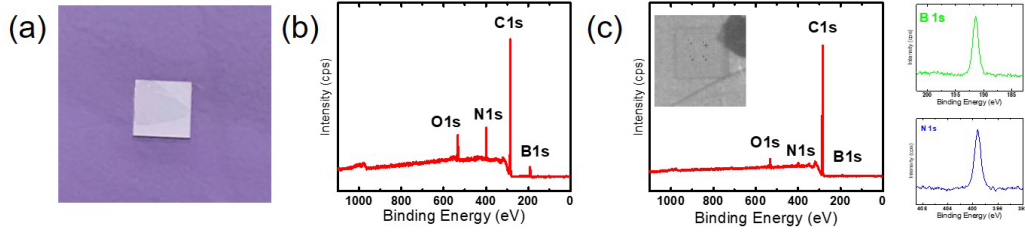


Fig. 19 a) PMMA–h-BN transferred on a hydrogenated diamond. b) XPS spectra of h-BN transferred on a hydrogenated diamond. c) XPS spectra of transferred h-BN on diamond after hydrogenation.

In addition, the transferred h-BN on diamond sample prepared at Rice was sent to DEVCOM ARL for hydrogenation. After the hydrogenation, XPS measurement was conducted on the sample. Figure 19c shows B and N peaks in the XPS spectra, implying h-BN can sustain the hydrogenation. These two examples not only show the close collaborations between Rice and DEVCOM ARL, but also pave the way for h-BN–diamond device fabrication.

4.4 Direct Growth of h-BN on Diamond

In addition to growing h-BN on a Cu substrate and transferring to diamond, we also studied growing h-BN directly on diamond. Figure 20a shows the CVD system, where boric acid and ammonia gas are used as precursors and H_2 is the carrier gas. An H-terminated electronic-grade single-crystal diamond (ESCD) was received from DEVCOM ARL, showing very low surface roughness and a sharp Raman peak, as shown in Fig. 20b and c. After h-BN growth, the surface roughness increased. The h-BN E_{2g} peak is not observed in Fig. 20e because it is too weak compared to the diamond peak. However, the XPS spectra in Fig. 20f clearly show B and N peaks. The atomic ratio is calculated as 1.04:1. The h-BN film thickness turns out to be approximately 6 nm according to the AFM measurement (Fig. 20g and h). All the characterization confirms the successful growth of h-BN on diamond.

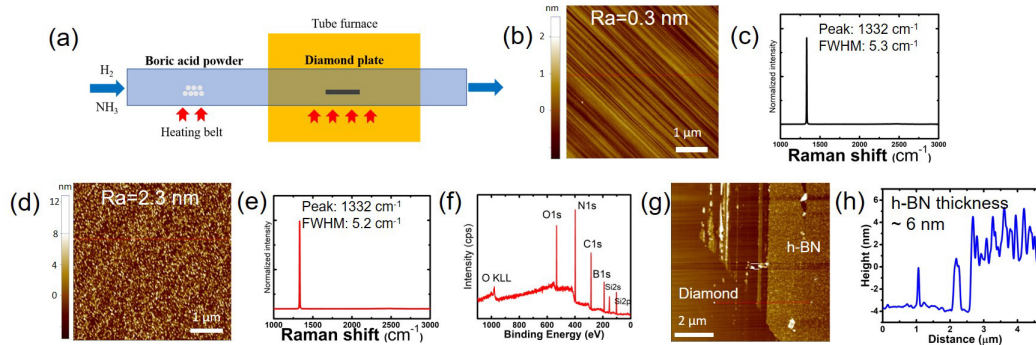


Fig. 20 a) Schematic illustration of a CVD system. b) Surface morphology and c) Raman spectra of a pristine ESCD. d) Surface morphology, e) Raman spectra, f) XPS spectra, and g, h) AFM thickness measurement of the ESCD after h-BN growth.

Dr Dmitry Ruzmetov at DEVCOM ARL performed the electrical characterization on the ESCD sample before and after h-BN growth. The hydrogenated ESCD showed a sheet resistance of 12.2 k Ω /sq before h-BN growth. After h-BN growth, the sheet resistance increased to 58 k Ω /sq. The sample was then subjected to another hydrogenation. After that step, the sheet resistance was still high, 47.6 k Ω /sq. These results not only confirm the dielectric property of h-BN, but also imply that h-BN can sustain the hydrogenation.

4.5 Exploration of Other Related Materials Growth

In addition to h-BN, we have also explored the growth of other related materials. Molybdenum disulfide (MoS₂) is an n-type 2-D material that has the potential to form the p-n junction with hydrogenated diamond or act as the transfer doping layer in a diamond device. Figure 21a and b shows an optical image and an SEM image of MoS₂ flakes directly grown on polycrystalline diamond (PCD). MoS₂ flake keeps its triangular shape similar to the growth on other substrates. Raman spectra in Fig. 21c show the E_{2g}¹ and A_{1g} peaks. The element mappings of molybdenum (Mo) and sulfur (S) are illustrated in Fig. 21d and e. Figure 21f shows cross-sectional transmission electron microscopy (TEM) images of the interface between diamond and MoS₂. Amorphous Pt coating, MoS₂ layered lattice, and diamond cubic structure, and so on can be observed in the image (from top to bottom).

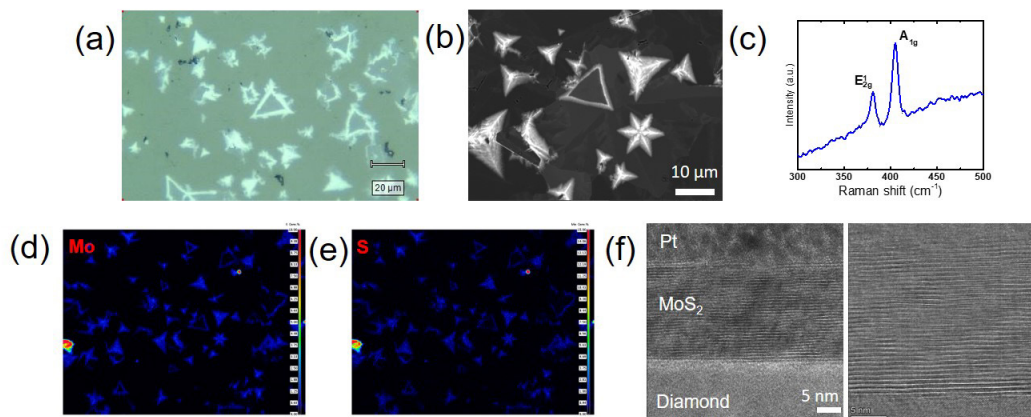


Fig. 21 a) Optical image, b) SEM image, c) Raman spectra, and d, e) element mappings of MoS₂ grown on PCD. f) Cross-sectional TEM image of MoS₂ and diamond interface.

Another heterostructure we studied is the h-BN–graphene heterostructure. Figure 22a demonstrates an SEM image of h-BN–graphene heterostructure grown on a Cu film. The XPS spectra in Fig. 22b reveal N, C, and B peaks. The h-BN–graphene heterostructure was transferred to a SiO₂–Si substrate and the structure is seen in Fig. 22c. Raman spectra collected at the red spot shows graphene peaks, while the green spot shows an h-BN peak. These results confirm the successful growth of h-BN–graphene heterostructure, which could further be converted to diamond–h-BN.

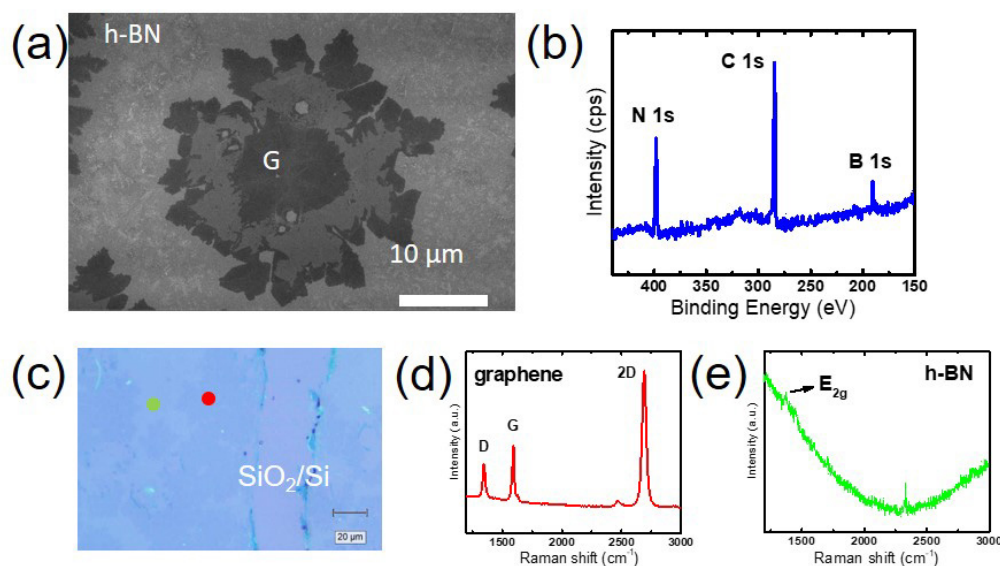


Fig. 22 a) SEM image and b) XPS spectra of h-BN–graphene heterostructure grown on Cu. c) Optical image of h-BN–graphene heterostructure transferred on SiO₂–Si. d, e) Raman spectra collected on the red spot and green spot, respectively.

5. Development of Characterizations Techniques for Diamond Interfaces

5.1 Terahertz Spectroscopy

5.1.1 Introduction

Terahertz (THz) radiation ($1 \text{ THz} = 10^{12}$ cycles per second, T-rays) lies in the frequency gap of the microwave and IR region of the electromagnetic spectrum, typically in the frequency range from 0.1 to 30 THz. Previously, due to low photon energies and long wavelengths, THz spectroscopy's primary use was to characterize the thermal emission lines of simple molecules and spectral characterization of the vibrational and rotational resonances. Recently, the THz bands are being used in a wide range of applications such as information and communications technology, nondestructive evaluation, homeland security, global environmental monitoring, ultrafast computing, and so on. Development of THz imaging, THz-time domain spectroscopy (THz-TDS), and high-power THz generation by nonlinear effects are the few areas to push THz exploration into the forefront. Such tools have proven to be interesting in examining a wide variety of materials compared to using existing conventional tools for characterization.²⁴ Figure 23 illustrates where THz lies on the electromagnetic spectrum.

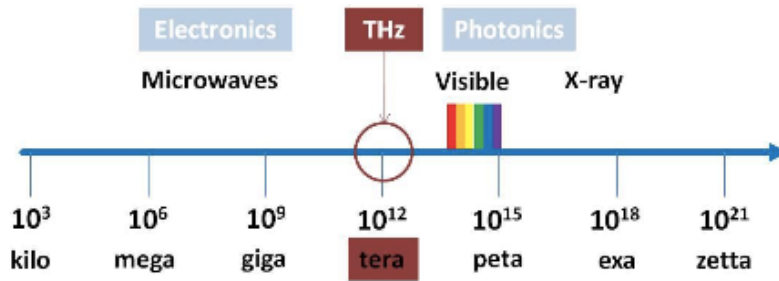


Fig. 23 Electromagnetic spectrum highlighting THz

The energy that corresponds to THz radiation is equivalent to the energy of free carriers in semiconductors and metallic conductors. Hence, the use of THz has shown success in measuring the electrical conductivity and carrier densities in Si semiconductors. The motivation here is to design metrology to predict the electrical doping profiles in semiconductor devices such as transfer-doped diamond utilizing THz frequencies. The mainstream characterization techniques to map conductivity, doping profiles, and so on are designed as stand-alone systems and are most often destructive with the application of contacts, and so on, which make it hard to obtain feedback measurements in a timely manner. Examples of such characterization

techniques are shown in Fig. 24. However, the THz-TDS system enables us to consider a virtually non-contact option, used here for the first time for diamond devices. THz-TDS utilized as optical metrology to attain a doping profile with several advantages as listed²⁵:

- Non-contact technique
- High sensitivity to carrier concentrations
- High spectral resolution
- Measures both amplitude and phase shift and additional information (mobility, the lifetime of carriers, etc.)
- Rapid measurement with high accuracy

Such non-contact metrology would open new exciting areas to increase the throughput production through in-situ process control with real-time feedback. Therefore, the THz technique motivates us to develop alternative metrology to map doping profile and other structure–electronic property correlations in diamond devices.^{26,27}

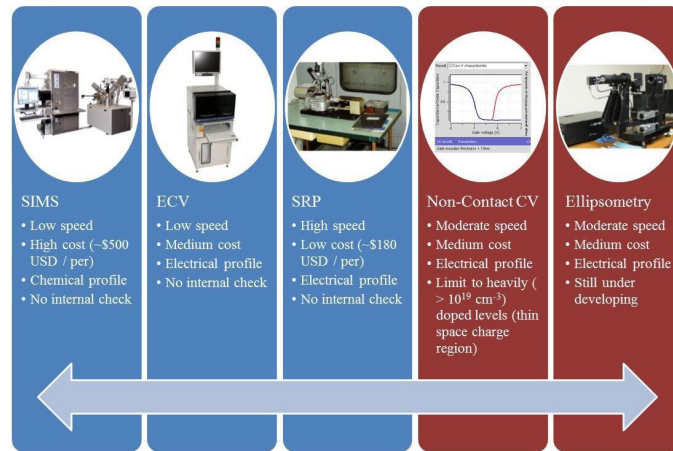


Fig. 24 Standard characterization techniques to measure the doping profiles in semiconductors (image courtesy of Tulsyan²⁵)

5.1.2 THz Spectroscopy System (Operating Principle of THz-TDS)

THz spectroscopy facilitates a material's far-IR optical properties to be determined as a function of frequency. This optically read out information can provide an understanding of the material characteristics for a range of applications. THz-TDS can be designed either as transmission or reflection mode. So far, we have employed transmission mode to obtain preliminary results.

A typical THz-TDS setup is shown in Fig. 25, based on a photoconductive antenna to generate and detect THz radiation. The principle of THz-TDS starts with a femtosecond laser producing an optical pulse train (~ 250 fs, 835 nm) by a mode lock achieved titanium (Ti)-sapphire laser. The generated optical pulse divides into two paths. One part (Path A) reaches the THz emitter (i.e., photoconductive antenna, semiconductor wafer, or nonlinear crystal), where the optical pulses are transformed into THz radiation (ultrashort electromagnetic pulses). This excited THz pulse is collimated by a high-resistivity hemispherical Si lens and travels in free space (purged with N_2 or compressed air to decrease the humidity) before reflecting from a parabolic mirror. A couple of parabolic mirrors, as shown in the diagram, are used to focus the THz waves onto an ultrafast THz detector (for example, a low-temperature-grown gallium arsenide photoconductive switch or an electro-optic crystal). The other part (Path B) of the pulse from the beamsplitter is also delivered onto the detector as a reference signal after passing through a delay stage. A sample holder is located for the reference and sample measurements between the two parabolic mirrors, which causes a time delay and a reduction in the magnitude of the THz pulse. The reference THz pulse is measured considering air as a reference or can be measured without the sample (only substrate).²⁸ We determine both magnitude and phase information of the spectra (the absorption and refractive index [and therefore σ of the sample]) without using Kramers–Kronig relations. The signal pathway and processing sequence are schematically presented in Fig. 26.

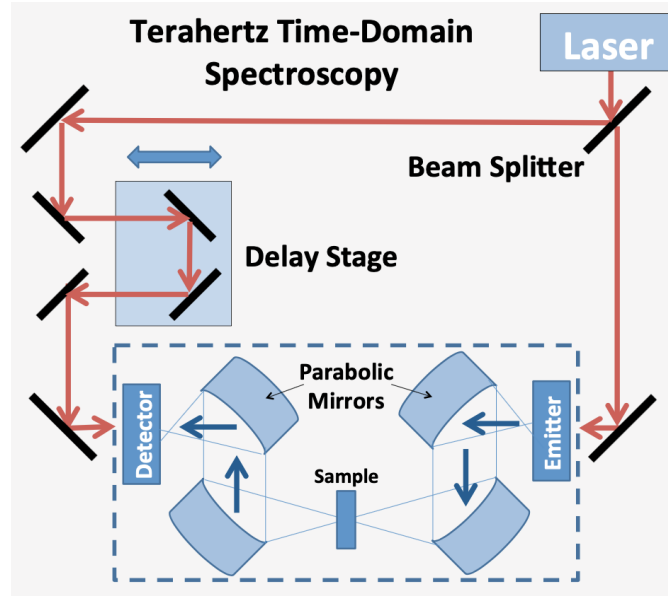


Fig. 25 THz-TDS experimental setup

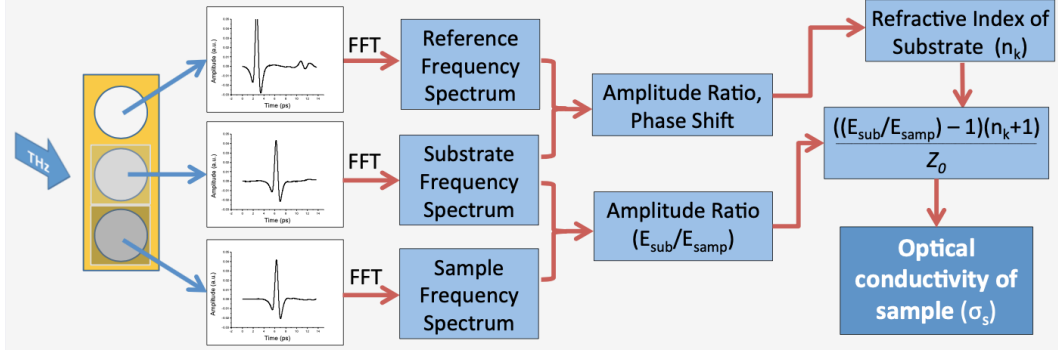


Fig. 26 THz spectroscopy: the signal pathway and processing

THz-TDS has numerous advantages over incoherent techniques²⁵:

- Able to extract the complex optical properties (refractive index) of material without doing theoretical calculations using the Kramers–Kronig relationship.
- Capable of removing Fabry–Perot reflections in thick substrates by windowing the time-domain data.
- Able to measure the time-resolved photoconductivity on picosecond timescales in a non-contact way.
- The time-gated detection of THz pulses allows all spectrometer components to be used at room temperature.

However, there are disadvantages of the THz-TDS setup, which includes the high cost of an ultrafast laser. Apart from it, the bandwidth is not as broad as the commercially available Fourier transform IR (FTIR). The other drawback includes the position of the reference mirror, which needs to be precisely determined to avoid phase errors to calculate optical properties. Even though the THz technique is becoming well established, its application to very thin film samples remains particularly difficult.

5.1.3 Materials Properties

As reported by Ulatowski et al.,²⁹ the complex refractive index of a material $\tilde{n}$ depends on its polarisability, which can be described by the complex dielectric function $\tilde{\epsilon}_r = \epsilon_1 + i\epsilon_2$. The relation between the refractive index and the dielectric function is given by

$$\tilde{n}^2 = \tilde{\epsilon}_r = \epsilon_1 + i\epsilon_2. \quad (2)$$

For conductive samples, one can further distinguish the individual contributions to the dielectric function from the crystal structure (through phonon modes, lattice

polarization), $\tilde{\epsilon}_L$, as well as the charge carriers (movement of free charge carriers, polarization of excitons), $i\tilde{\sigma}_{cc}/\omega\epsilon_0$. Here, $\tilde{\sigma}_{cc}$ is the complex conductivity of the charge carriers, which could be present in the semiconductor as a result of either photoexcitation or doping. An apparent conductivity, $\tilde{\sigma} = \sigma_1 + i\sigma_2$, can be then defined, which encompasses both these contributions to the overall dielectric response of the material,

$$\tilde{\epsilon}_r = \tilde{\epsilon}_L + \frac{i\tilde{\sigma}_{cc}}{\omega\epsilon_0} = 1 + \frac{i\tilde{\sigma}}{\omega\epsilon_0}. \quad (3)$$

The relation between these quantities is illustrated in Fig. 27, which shows how the charge-carrier conductivity (column A) and the dielectric function of the crystal (column B) contribute to the overall polarizability of the sample (column C), here presented as the apparent complex conductivity $\tilde{\sigma}$. The conductivity of charge carriers with number density n , mobility μ , and charge q was assumed to be Drude-like,

$$\tilde{\sigma}_{cc} = \frac{\sigma_{DC}}{1-i\omega\tau} = \frac{n\mu q}{1-i\omega\tau} \quad (4)$$

with the scattering rate of charge carriers $1/\tau$ comparable to THz frequencies.^{27,29}

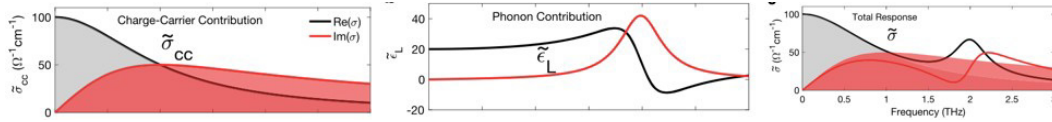


Fig. 27 The relation connecting the contributions charge carriers and crystal structure toward the total conductivity plotted against frequency, as reported by Ulatowski et al.²⁹

5.1.4 THz Measurements on Pristine and Hydrogenated Single-Crystalline Diamond Wafers

As the free carriers are confined to the wafer surface, around 5 nm, the thin-film THz-TDS approach²⁶ (Fig. 28) can be used to differentiate pristine 2DHG containing H-terminated single-crystalline diamond (SCD) surfaces and the rest of the samples.

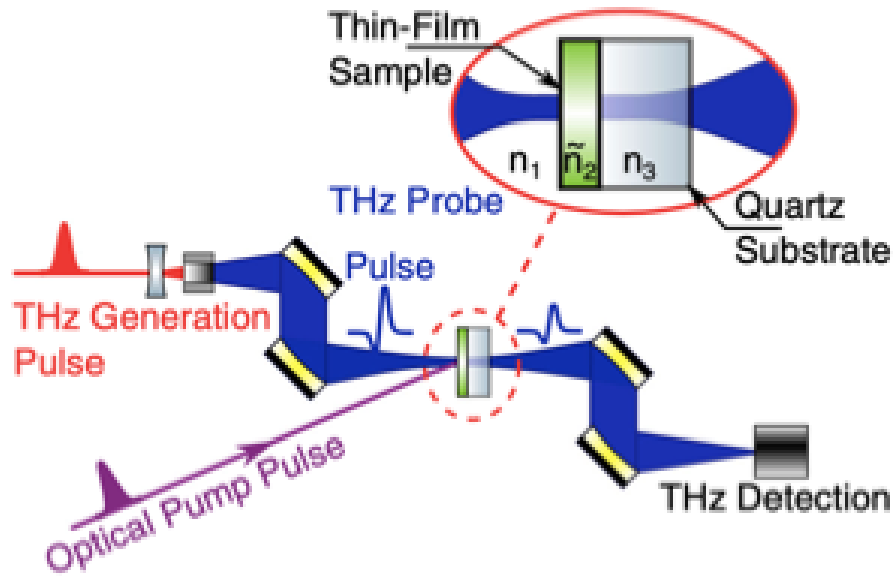


Fig. 28 Thin-film THz-time-domain experimental setup, as reported by Ulatowski et al.²⁹

From the variation of generated intensity to the reference beam, refractive indices and extinction coefficient can be deduced from which the real and imaginary conductivity values can be estimated, as well as the free-carrier concentrations such as carrier density, mobility, and so on. The as-obtained readout signals are given in Fig. 29 and the corresponding conductivity measurements are provided afterward. The refractive indices, absorption coefficient, and real and imaginary part of the conductivity values are provided in Figs. 30 and 31, respectively, for pristine single-crystal and H-terminated SCD. Our preliminary results suggest that using the THz technique one could obtain fast semi-quantitative information of the carrier density in diamond structures. More work is being done to better understand the data and compare pristine, H-terminated, and doped diamond substrates.

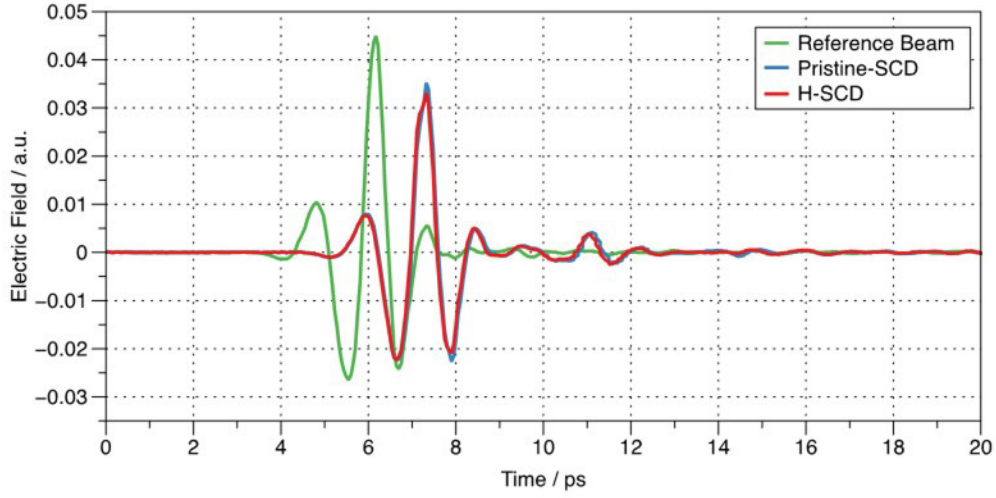


Fig. 29 Electric-field variation recorded for a reference signal, SCD, and H-terminated SCD wafer

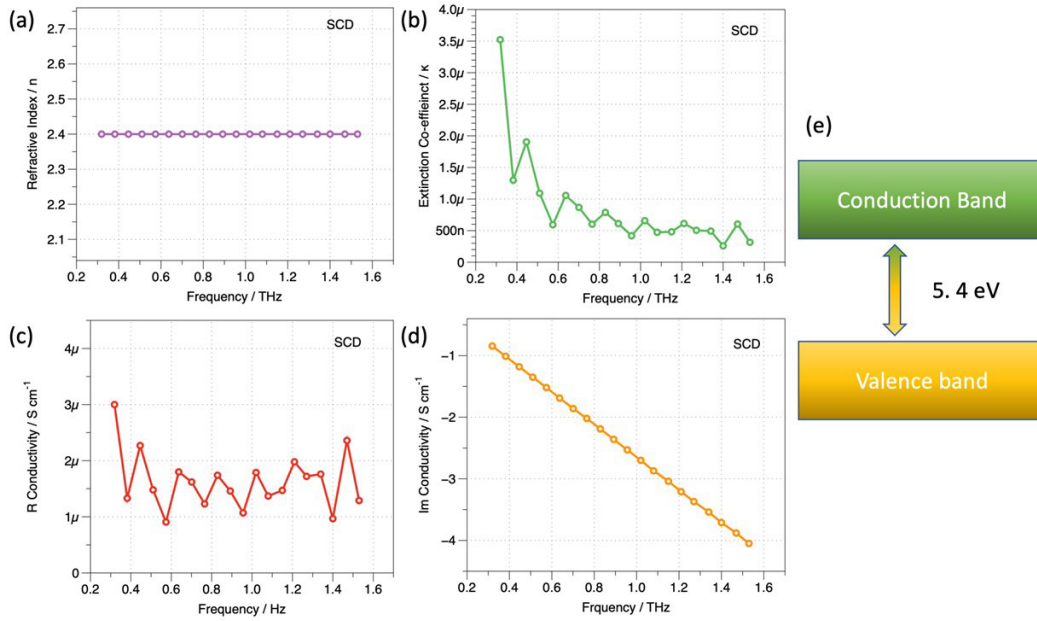


Fig. 30 Preliminary results of a) refractive index, b) absorption coefficient, and c) real and d) imaginary conductivity values for pristine single diamond (plotted against the frequency). e) Since the pristine SCD wafers are insulating without any charge carriers, a negligible conductivity value is observed on SCD wafers.

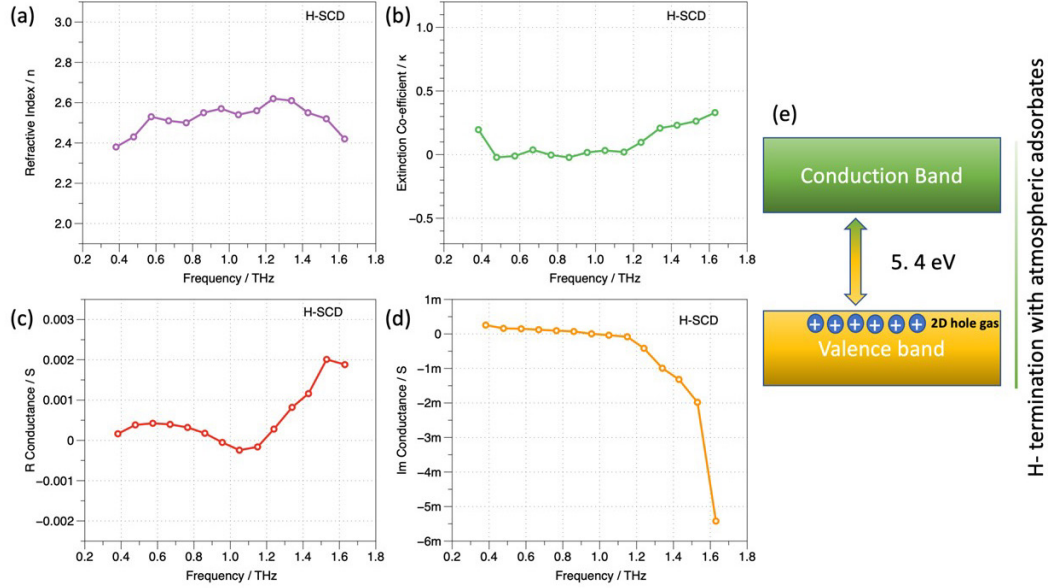


Fig. 31 a) The refractive index, b) absorption coefficient, and c) real, and d) imaginary conductivity values for H-terminated diamond (plotted against the frequency). e) Since H-terminated SCD wafers with atmospheric adsorbates are conducting with the formation of 2DHG, a reasonable conductance value is observed on H-terminated SCD wafer.

5.2 Focused Ion Beam (FIB) Processing of Diamond Wafers

An ion is an atom or molecule where the total number of electrons is not equal to the total number of protons, providing net negative or positive electrical charges. The smallest ion has almost 2000 times the mass of an electron, and bigger ions can be even 250 times as massive. In a SEM, the comparatively low-mass electrons interact with a sample surface nondestructively and generate secondary electrons, which, when collected and processed, provide very high image resolution down to the subnanometer range. A focused ion beam (FIB) instrument almost matches an SEM but employs a beam of ions instead of electrons (Fig. 32). The FIB can transform the sample through either deposition of metals or C through e-beam and ion beam depositions or milled using the ion beam with nanometer precision. By judiciously controlling the ion beam's intensity and energy, it is feasible to execute very precise nanomachining to create minute components or remove unnecessary materials. It is certainly possible to image the sample surface through ion beam, but one must take care to use the lowest possible energy and intensity as imaging with ion beam could mill the samples away. Besides, electron- or ion-beam-assisted CVD can be used to deposit materials with a level of precision similar to FIB milling. A small quantity of a selected precursor in gaseous form is brought into the vicinity of the beam, where the beam disintegrates it, depositing the nonvolatiles on the sample surface while the volatile disintegrates are extorted by the vacuum system.³⁰

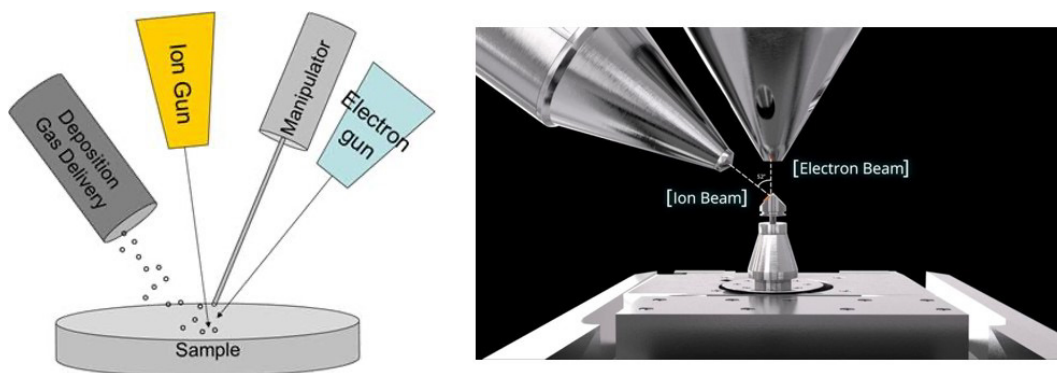


Fig. 32 Schematic of FIB unit showing the sample stage and various ion and electron guns and a micromanipulator (left) and instrumentation (right) (Schematic courtesy: Materials Research Institute, Pennsylvania State University.)

FIB becomes even more powerful when combined with a SEM, as in the Thermo Scientific DualBeam system available at the shared equipment center of Rice. In a dual-beam instrument, the electron and ion beams intersect at a 52° angle at a coincident point near the sample surface, enabling immediate, high-resolution SEM imaging of the FIB-milled surface. Such systems combine the benefits of both the SEM and FIB, and provide complementary imaging and beam chemistry capabilities. We have prepared several TEM specimens, from DEVCOM ARL samples of diamond wafers and devices, as shown in Fig. 33.

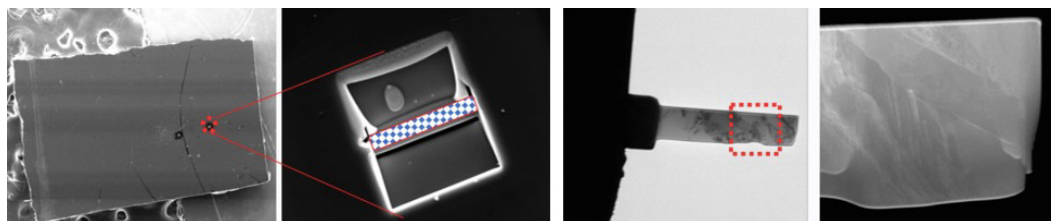


Fig. 33 FIB processing stages starting from PCD wafer to processed ultra-thin wafer attached to the TEM grid

5.3 Aberration-Corrected Electron Microscopy

The unique possibilities of aberration-corrected scanning transmission electron microscopy (STEM) can be extremely useful in imaging interfaces and we will be making use of the Rice STEM facility in imaging diamond-based heterostructures.³¹ The small probe size gives improved single-atom sensitivity, both for imaging and spectroscopy, facilitating light elements to be detected in a Z-contrast image and giving much-improved phase contrast imaging using the bright field detector with pixel-by-pixel correlation with the Z-contrast image. Additionally, the augmented probe-forming aperture brings significant depth

sensitivity and the possibility of optical sectioning to fetch information in three dimensions.

Rice hosts a state-of-the-art, aberration-corrected TITAN electron microscopy and a few energy dispersive spectroscopy (EDS) mapping images (Fig. 34) and microscopy images of the PCD wafers are appended in Fig. 35. In addition, one can study the various interfaces of miniaturized devices such as source–drain interfaces over the semiconducting wafer, dielectric–semiconducting wafer interfaces, transfer dopant interfaces over the diamond wafer, and so on.

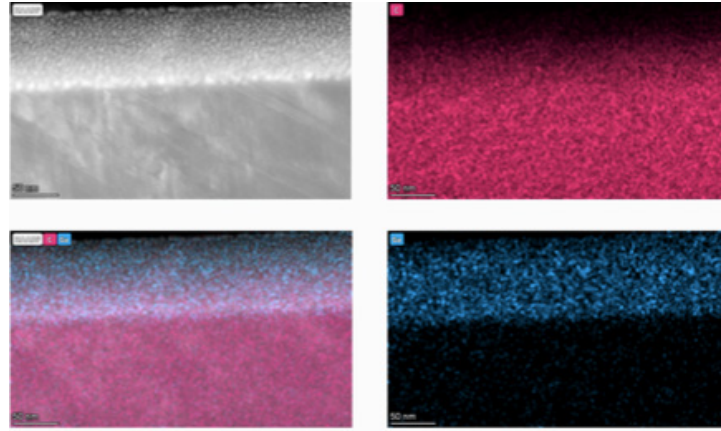


Fig. 34 EDS mapping of various elements (C, Ga) on the FIB-milled PCD samples

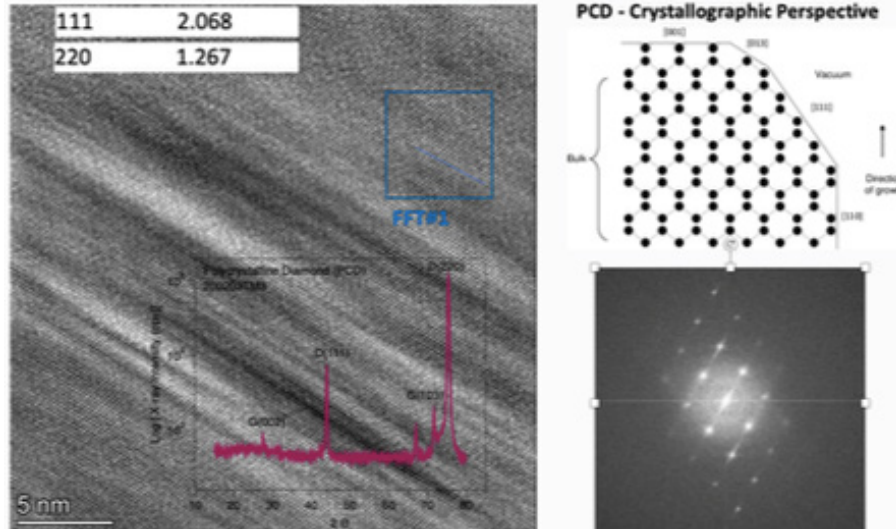


Fig. 35 Electron microscopy image and selected area diffraction patterns of PCD wafers. The identified planes are given in the inset. Also shown is the crystallographic perspective of a SCD showing different planes and facets.

5.4 Piezoelectric Force Microscopy Mapping of Hydrogenated Diamond Surfaces

Piezoelectric force microscopy (PFM) is a scanning probe microscopy method that utilizes the piezoelectric effect of materials to generate contrast. Piezo-response force microscopy has shown to be a powerful tool for the characterization of piezoelectric materials at the nanoscale. Alignment of electric dipoles in a piezoelectric material due to the application of an external electric field physically shows up as material elongation or contraction. In PFM, the surface electromechanical deformation is detected as the first-harmonic component of a conductive tip deflection, oscillating in contact with the surface. The deflection amplitude is proportional to the converse piezoelectric coefficient and the phase yields information about polarization direction below the tip.^{32,33} Here, PFM was done with ASYLUM Research probe model “ASYELEC-01-R2” (MFP-3D origin+ Asylum Research AFM by Oxford Instruments with an Si tip coated with Ti/iridium [Ir] (5/20)). The probe spring constant and lever air resonance frequency are 2.8 N/m and 75 kHz, respectively. The resonance frequency of the tip during measurement was 360 kHz on average.

The hydrogenated diamond surface is expected to be a little rough, and the hydrogenation could potentially break the center of symmetry and makes inherent dipoles on the surface. The broken center of symmetry and the presence of aligned dipoles are otherwise the basic requisites for a material to be ferroelectric or piezoelectric. Here the pristine and hydrogenated diamond wafers are scanned through PFM techniques and we could observe a contrast difference in the hydrogenated diamond wafer. Hence such a surface probe microscopy could be potentially used to differentiate an H-terminated diamond wafer from the pristine sample and at the same time with the remarkable spatial resolution, the coverage of hydrogenation could also be studied. As the preliminary result, piezo scan results of a PCD wafer are provided in Fig. 36. Work is in progress to evaluate pristine and H-terminated SCD.

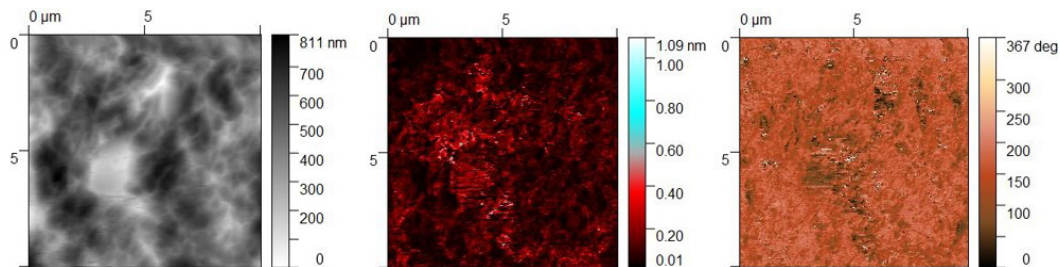


Fig. 36 From left to right: topography, piezo amplitude, and phase maps of the pristine PCD surface. A contrast variation is observed in the piezoelectric mapping (amplitude and phase) indicating the piezo active centers on the surfaces.

5.5 Magnetic Force Microscopy

Magnetic force microscopy (MFM) images the spatial variation of magnetic forces on a sample surface with the magnetized tip coated with a ferromagnetic thin film. Here, surface topography is obtained in tapping mode. At the same time, the MFM profiles are fetched by computing the amplitude or the phase change of the cantilever oscillations from the magnetic force between the surface and the ferromagnetic cantilever tip. MFM profiles/images carry information of the magnetic domain allocations/distributions on the sample surface. MFM facilitates the imaging of atomically smooth (roughness-free surfaces) naturally occurring and intentionally written domain structures in magnetic materials.³⁴ Two forces are acting on the tip in MFM measurements: magnetic and vdW forces. Therefore, the MFM signal contains both the information of surface magnetic properties and surface topography generated by magnetic and vdW forces, respectively. The dominating force depends on the distance between the tip and the sample surface. The inter-atomic magnetic force persists for greater tip-to-sample separations than the vdW force.

MFM was done with ASYLUM Research probe model “ASYELEC-01-R2” (MFP-3-D origin+ Asylum Research AFM by Oxford Instruments with a 30-nm-thick chromium [Cr]Pt coating). The probe spring constant and lever air resonance frequency are 2.8 N/m and 75 kHz, respectively. The resonance frequency of the tip during measurement was around a few tens of kilohertz on average.

The hydrogenated diamond wafer surface is expected to be weakly magnetic due to the unsaturated C–H bonding and free spins that exist in the surface. There are several reports on the magnetism in hydrogenated C allotropes.³⁵ Hence attempts were done to differentiate hydrogenated and non-hydrogenated samples through the MFM technique. As the preliminary result, we have provided the MFM scan of PCD samples in Fig. 37. More work is in progress.

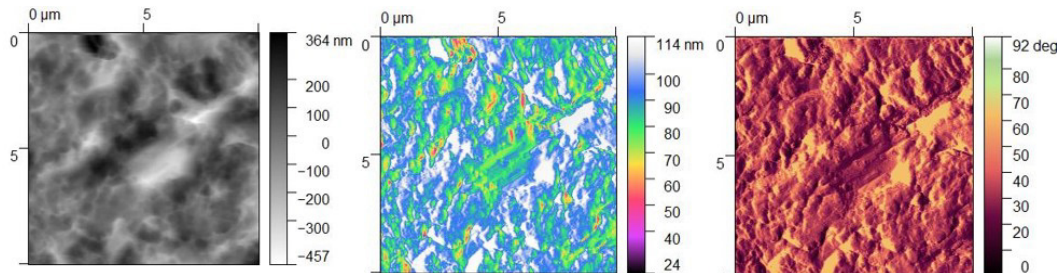


Fig. 37 From left to right: topography, MFM amplitude, and phase maps of a pristine PCD surface. A contrast variation is MFM mapping (amplitude and phase) indicating the magnetically active centers on the surfaces.

5.6 Second-Harmonic Generation on Diamond Surface

Second-harmonic generation (SHG) is a nonlinear optical process in which photons interacting with a nonlinear material effectively combine to form new photons having twice the frequency of initial photons. It is only allowed in a material with inversion symmetry breaking. For centrosymmetric materials, SHG is zero and forbidden. The pristine diamond has a cubic structure and therefore shows zero SHG. However, when the diamond surface has certain terminations or roughness, the symmetry would break, leading to nonzero SHG.

Figure 38a shows SHG intensity mapping on a pristine PCD. High SHG intensity is detected in some areas and can be attributed to the relatively high surface roughness of PCD. After hydrogenation, PCD still shows high SHG intensity, as can be seen in Fig. 38b. A backscatter electron (BSE) image of PCD shown in Fig. 38c exhibits similar surface morphology corresponding to SHG intensity maps. The SHG intensity mapping on a pristine SCD demonstrated in Fig. 38d indicates an overall low intensity due to SCD's low surface roughness. However, when the SCD has the H terminations, the SHG intensity is greatly enhanced by about 1000 times. We observed a blue spot during the measurement due to the SHG wavelength of 400 nm (the laser wavelength is 800 nm). Work is in progress to better understand H-terminated diamond surfaces using SHG techniques.

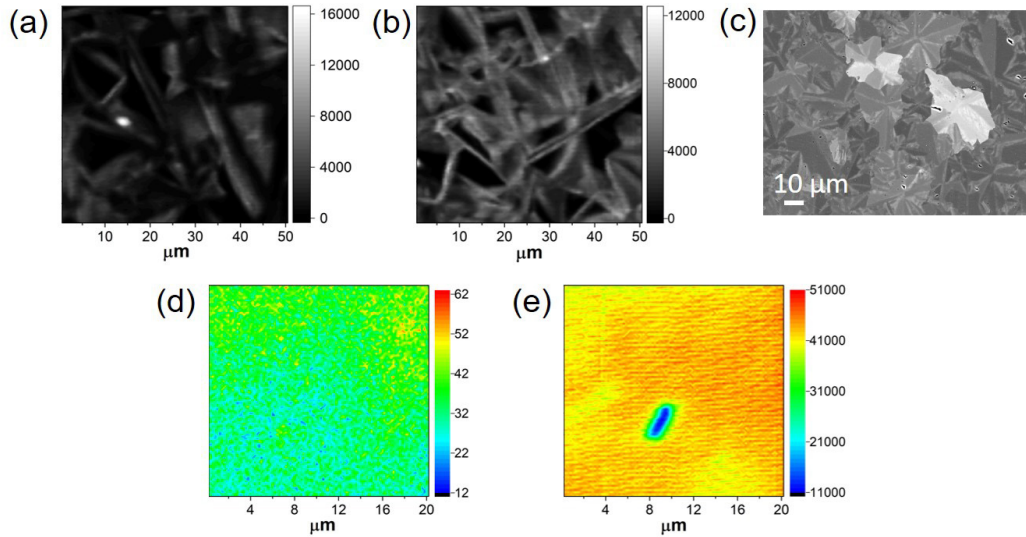


Fig. 38 SHG intensity mappings of a) pristine PCD and b) hydrogenated PCD. c) BSE image of PCD. SHG intensity mappings of d) pristine SCD and e) hydrogenated SCD.

6. Diamond Surface Modification and Doping

6.1 Surface Conduction in Diamond via Transfer Doping

Diamond is an ultra-wide-bandgap crystal and has been historically considered an excellent insulator. Since semiconducting electrical properties are desired for electronics applications, a considerable amount of effort has been done to dope diamond with electrically active impurities. Due to the very dense atomic lattice of diamond, there are only a few doping impurities of similar masses, such as B and N, and at low concentrations that can enter the diamond without significantly distorting the host crystal lattice. And importantly, the available dopants create rather deep states, which remain mostly unoccupied at room temperature. Specifically, the activation energies for B and N are 0.37 and 1.7 eV, respectively.^{36,37}

A recent advance with the doping of diamond is to employ transfer doping at the diamond surface, which will create surface conduction. Then, electronic devices, such as FETs, can be created on the diamond surface.³⁸ The first step in the transfer doping technique is to hydrogenate the diamond surface so that the valence band will move upward and will allow for the electrons in the valence band of the diamond to fall down into the lower conduction band of the transfer doping material at the diamond surface.³⁸ Once diamond hydrogenation is achieved, exposing the diamond surface to ambient air will result in a layer of atmospheric adsorbates to adhere to the diamond surface. These air adsorbates will act as a transfer doping material to diamond and accept the electrons from the diamond surface, leaving a surface layer of hole carriers in the top several nanometers of the diamond crystal.³⁹

To obtain diamond plates with hole carrier surface conduction suitable for RF diamond transistors, DEVCOM ARL has established a collaboration with Dr Bradford Pate at the US Naval Research Laboratory (NRL). Dr Pate used a MPCVD reactor to perform hydrogenation of the diamond plates provided by the DEVCOM ARL researchers. A series of optimization experiments were performed together with Dr Pate on ESCD (100) plates purchased from Element Six. As a result, DEVCOM ARL established a source of electrically active diamond with typical surface sheet resistivities of the air-doped diamond (100) plates in the range between 7 and 10 k Ω /Y.

Increasing the charge density made available by transfer doping is a metric of primary interest. As such, we are engaged in research to achieve this end that will require metrologies that can provide valuable insight. Here we briefly review how the nondestructive metrologies of Kelvin probe (KP) and constant final state yield spectroscopy (CFSYS; shortened here to just photoemission spectroscopy, i.e.,

PES) can be used to characterize the robustness and charge-transferring efficiency of the H-terminated diamond surface by quantifying the density of the 2DHG. The results obtained by KP and PES are compared to those obtained by Hall measurements.

KP and PES are well-established techniques used to characterize H-terminated diamond.^{40,41} KP provides the work function (ϕ) and PES the ionization energy (IE). Together, given the well-established bandgap (E_G) values of diamond as a function of temperature, they provide the full band structure of this surface (Fig. 39). Combining these techniques into one measurement chamber provides several advantages. One in particular is that the same tip is used as the sensing element for both techniques and can be calibrated in situ without the need for a separate standard.⁴²

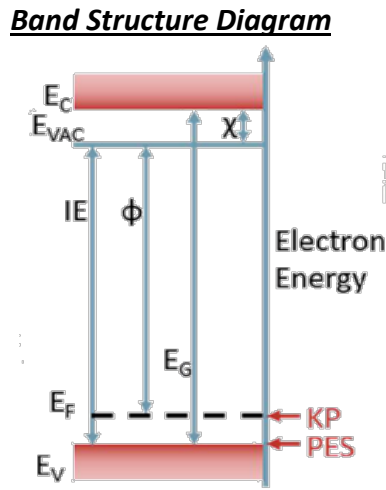


Fig. 39 Band diagram with key material parameters. E_C , E_{VAC} , E_F , E_V , and χ denote the energy level of the conduction band, vacuum level, Fermi level, valance band, and electron affinity, respectively. KP and PES positions, E_F and E_V , are respectively relative to E_{VAC} .

In an attempt to extract charge density via KP and PES, we make use of the work by Edmonds and coworkers.⁴³ In particular, their positioning of the Fermi level relative to the valance band ($E_F - E_V$) versus hole density results obtained by curve-fitting experimental data, as illustrated in Fig. 40.

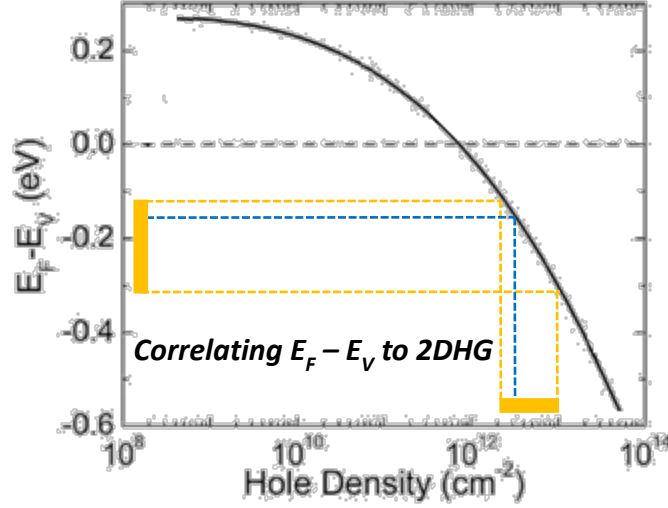


Fig. 40 $E_F - E_V$ vs. 2DHG density for H-terminated diamond. Data curve is taken from Edmonds et al.⁴³

Our experimental approach for this effort is simple. First, we established a hydrogenation process with our NRL colleague. After hydrogenation, the diamond plates were exposed to room air for several days. Then, Hall effect measurements were performed to verify carrier type and obtain charge density. After this initial Hall effect measurement, KP and PES were performed on the as-received material (i.e., atmospheric doped surface) during a 350 °C in-situ heating step used to remove atmospherics and then on the post-annealed surface after cooling to room temperature under high vacuum (HV). The sample was removed from the chamber and exposed to air for several days and later reinserted and measured under the HV environment. Finally, Hall effect measurements were repeated.

The outlined approach is implicit to the use of a color-coding scheme used to display the results in Fig. 41. Green represents the as-received room-temperature condition, orange the 350 °C measurement, light blue the post-anneal room-temperature condition, and purple the remove, expose, re-insert case. Simple band structure diagrams using the same color-coding scheme are included for clarification. Using established values for the bandgap of diamond as a function of temperature and the measured values for work function and ionization potential, one can calculate the electron affinity and the Fermi level position (i.e., $E_F - E_V$ values).

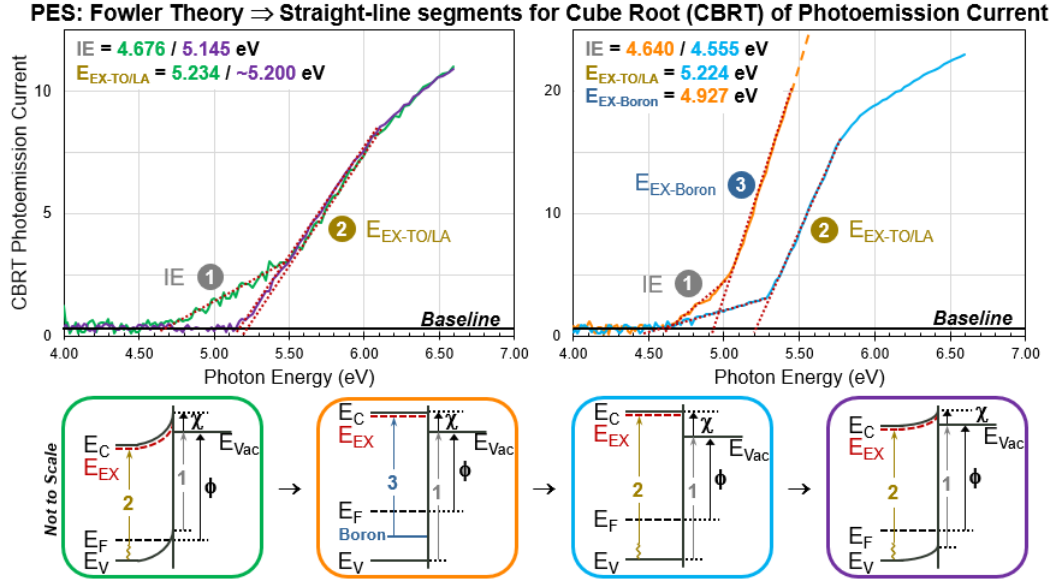


Fig. 41 PES data taken on an H-terminated diamond surface for four different measurement conditions. Electronic transitions listed in the spectra (labeled 1, 2, and 3) are illustrated in the band diagrams. The measurement conditions and key for the color-coding scheme is provided in the text.

Based on Fowler Theory, the photoemission spectra can be fit using straight-line segments for the cube root of the photoemission current.⁴⁴ This method yields a few different transitions. First, the transition (with an onset at the lowest energy) is attributed to the valence band-to-vacuum level occurring at the surface. Next is a phonon-assisted excitonic transition observed on all room-temperature measurements. Finally, an excitonic transition originating from the B acceptor level appears at 350 °C. This analysis yields the key material parameter of electron affinity, work function, and $E_F - E_V$ values that are presented in Table 1. However, one should note the considerable changes that occurred in these parameters as a result of the measurements (i.e., compare the as-received room-temperature condition values to that of the remove, expose, re-insert case).

Table 1 Electron affinity (χ), work function (ϕ), and the Fermi level position are relative to the valance band ($E_F - E_V$) measured on a hydrogenated diamond surface. Units are in eV.

Condition	χ	ϕ	$E_F - E_V$
As-received room temperature	-0.794	4.720	-0.044
350 °C anneal	-0.745	3.875	0.765
Post-anneal room temperature	-0.915	3.961	0.594
Remove, expose, re-insert case	-0.325	4.805	0.340

To build confidence in the PES transition assignments, a comparison was made between measured and expected values deduced from the literature for bandgap,

exciton, phonon, and B acceptor level energies. An excellent agreement between inferred and measured values was observed for the average values of the phonon-assisted excitonic transition and the excitonic transition originating from the B acceptor level. These transitions are illustrated in the band structure diagram in Fig. 42.

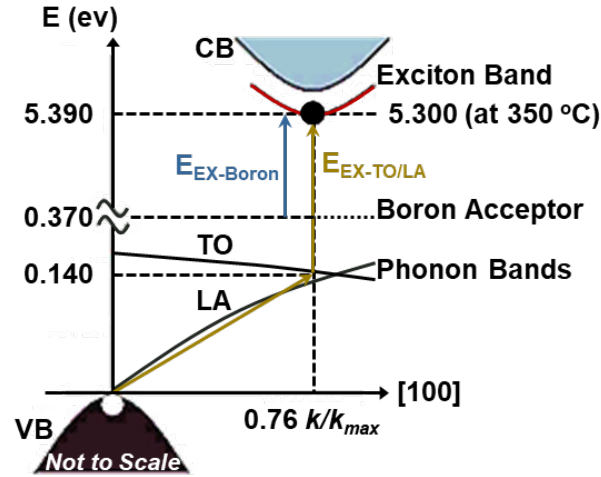


Fig. 42 Diamond electronic and phononic band structure with PES measured transitions

Finally, an attempt was made to correlate the measured $E_F - E_V$ values to the Hall effect results using the results of Edmonds and co-workers shown in Fig. 43. In the end, we found that KP combined with PES underestimates the 2DHG charge density vis-à-vis the Hall effect, but it is “in the ballpark”.

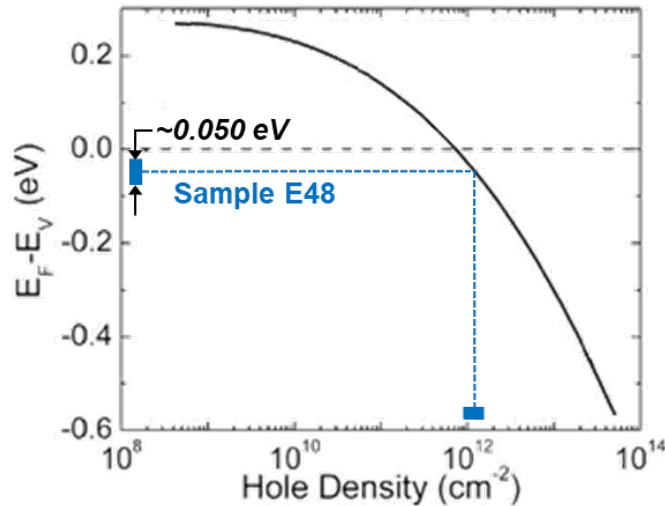


Fig. 43 $E_F - E_V$ vs. 2DHG density for H-terminated diamond. Uncertainty in the measurement of $E_F - E_V$ is estimated to be approximately 0.050 eV. Data curve is taken from Edmonds et al.⁴³

In conclusion, a combined KP and PES system was used to clarify the details in the surface band structure of H-terminated diamond. The full band structure information was obtained, yielding $E_F - E_V$ values that were correlated to a 2DHG charge density using literature results and compared to Hall effect data. These preliminary experiments revealed a significant decrease in charge density post-anneal and/or UV light exposure that is possibly due to loss of H that would result in partial oxidation. Moving forward, we plan to continue with experiments. In particular, we will work to obtain results on multiple samples and separate the effects of annealing and UV light exposure. In addition, we plan to improve the signal-to-noise and chamber environment by various system upgrades.

The drawbacks of the air-doped diamond are the variability of the carrier density in the diamond depending on the environment and the history of the exposure to the ambient. Using a solid-state material for transfer doping can reduce the dependence of the carrier density on the environment and provide higher doping efficiency, thus higher carrier density and lower sheet resistance. DEVCOM ARL has employed transition metal oxides (TMOs), such as MoO_3 and vanadium pentoxide (V_2O_5), to dope diamond because those oxides possessed high electron affinity, which aligned the conduction band in the TMO below the valence band in diamond allowing the electron transfer from diamond to TMO.⁴⁴ The DEVCOM ARL team has found that the MoO_3 transfer dopant is poorly compatible with the semiconductor microfabrication techniques used in our team to fabricate the RF diamond FETs. Also, our Raman investigation showed evidence of a chemical reaction between the MoO_3 and diamond leading to the presence of the sp^2 -bonded C on the diamond surface. For these reasons, we adopted the V_2O_5 as the material of choice for TMO transfer dopant.

The V_2O_5 was thermally evaporated for us at the Blue Wave Semiconductors (Baltimore, Maryland). We measured the improvement of the surface conduction in ESCD plates covered with V_2O_5 from $R_{\text{sheet}} = 7.3 \text{ k}\Omega/\text{Y}$, $\mu = 126 \text{ cm}^2/\text{V s}$, and $p_{\text{sheet}} = 6.8 \times 10^{12} \text{ cm}^{-2}$ to $R_{\text{sheet}} = 4.8 \text{ k}\Omega/\text{Y}$, $\mu = 86 \text{ cm}^2/\text{V s}$, and $p_{\text{sheet}} = 1.5 \times 10^{13} \text{ cm}^{-2}$. Though a sheet resistances down to $0.7 \text{ k}\Omega/\text{Y}$ have been obtained by other techniques,⁴⁵ the strength of DEVCOM ARL-developed V_2O_5 transfer doping method is that it is compatible with the semiconductor microfabrication technique used to produce RF FETs. Thus, DEVCOM ARL has reported diamond transistors with world record-breaking values for TMO-enhanced FETs output current up to $700 \text{ mA}/\mu\text{m}$.³⁸

One issue with the TMO transfer dopants is their stability. The electrical properties of diamond covered with MoO_3 were shown to degrade with time, probably due to the reaction of MoO_3 with air. V_2O_5 was shown to be more stable in air than MoO_3 , but even V_2O_5 -capped diamond still suffered a similar degradation of conductivity.

DEVCOM ARL has explored the electrical stability in the time of diamond that was covered with TMO doping layers and has developed a process of capping the diamond–TMO structure with a SiO₂ protective layer cap. Importantly, the process was compatible with the FET device fabrication, which put stringent requirements on the thicknesses of TMO (40 nm) and SiO₂ (150 nm). The SiO₂ capping layer improved the electrical stability of diamond plates in time, as shown in Fig. 44.

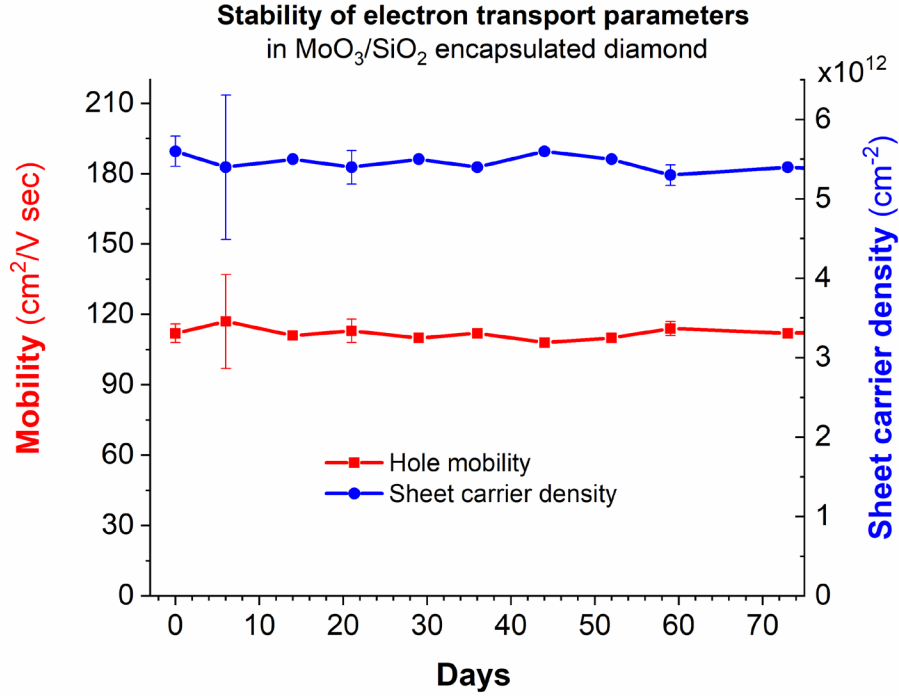


Fig. 44 The stability of the parameters of the electrical conduction of diamond with MoO₃ transfer dopant layer and capped with a SiO₂ (150-nm) protective layer

6.2 Functionalization of the Diamond Surface with Hexagonal Boron Nitride

6.2.1 Experimental Work

Diamond is a promising ultra-wide-bandgap material with unmatched thermal conductivity and high bulk charge carrier mobility in the range of 3800 and 4500 cm²/V·s.^{46,47} The difficulty with doping diamond can be overcome by employing surface transfer doping. The latter can be achieved after surface hydrogenation, which results in a raising of the valence band that promotes hole doping. However, the achieved mobilities for near-surface holes are reported to be in the range of 10 to 300 cm²/V·s,¹² which are much lower than the mobilities in the bulk diamond. One of the reasons for this reduction in mobility is due to charge carrier scattering at traps and defects in the gate dielectric and the diamond–

dielectric interface.⁴⁸ As mentioned in Section 4.1, to mitigate this problem, Sasama et al.¹² employed monocrystalline h-BN as a gate dielectric in a diamond FET. In this case, a monocrystalline h-BN flake was cleaved using the “Scotch tape technique” and transferred onto a type IIa diamond (111) surface. The thicknesses of the h-BN in these devices ranged between 7 to 16 nm. Unusually high hole carrier mobilities were achieved in these diamond–h-BN FETs.¹² In this application, h-BN was used as an optimal ultra-thin and pinhole-free insulating material, and for its unique 2-D crystal properties. Namely, the h-BN surface is atomically flat, has no dangling bonds, and possesses very few electrically active defects resulting in fewer scattering events and thus higher mobility.

One of the limitations of utilizing h-BN in the FETs as fabricated by Sasama et al.¹² is the use of the exfoliation technique and mechanical transfer of h-BN onto the diamond surface. This process is difficult to automate and apply on a wafer-scale area, thus reducing the number of produced devices to a few individually made ones. Growing h-BN on diamond may circumvent this limitation. Researchers at Rice were able to grow h-BN directly on diamond (100) substrate by means of CVD at a temperature of 1000 °C. Preliminary analysis indicates polycrystalline h-BN on diamond (100) with an h-BN thickness in the range of a few nanometers. Similarly, a recent report by Yang et al.⁴⁸ describes a disordered growth of h-BN on diamond (100) and highly oriented growth on diamond (111) by means of metalorganic vapor phase epitaxy at 1380 °C.

The Rice group in collaboration with DEVCOM ARL used an SCD plate that was hydrogenated prior to the h-BN growth. The hydrogenated diamond substrate had surface conduction of 30 k Ω /Y prior to the h-BN growth. After the CVD growth of an h-BN layer of approximately 6 nm, the surface conduction was significantly diminished, most likely due to the loss of H from the diamond surface at the elevated temperature (1000 °C) during the growth. Since the hydrogenation is crucial for FETs developed on diamond with the conductive channel at the diamond surface, the researchers attempted a re-hydrogenation of the h-BN/diamond heterostructure in a microwave CVD reactor setup for diamond growth. It was discovered that the hydrogenation did not reinstate the surface conduction of the diamond substrate, most likely due to the diffusion barrier encountered by the H molecules.

This observation was corroborated by first-principle calculations of H diffusion through an h-BN–diamond heterointerface.⁴⁸ A diffusion potential barrier of approximately 10 eV was calculated that is an order of magnitude higher than that encountered in the graphene–diamond heterointerface, rendering it experimentally impracticable to achieve hydrogenation through the h-BN layer in h-BN–diamond heterostructure. These results suggest that the mechanical transfer of

monocrystalline h-BN onto hydrogenated diamond remains the most promising route for the introduction of h-BN into diamond FETs. That is, until a suitable process of fabricating a high-quality monocrystalline, atomically thin h-BN overlayer on hydrogenated diamond is developed.

6.2.2 Theoretical/Modeling Work

Due to the doping limitations imposed by the strong C–C bonds, low dopant solubility limit, and deeper doping energy, traditional doping techniques such as substitutional and delta doping techniques are extremely hard to achieve in diamond. To overcome material-specific limitations and use it as a base material for RF applications, a novel chemistry-driven doping technique known as surface-induced transfer doping was recently employed.^{49,50} This novel, high-efficient doping technique is used to invoke p-type surface conductivity of intrinsic diamond. In this process, a thin-film acceptor layer with high electron affinity (EA) is interfaced with the hydrogenated diamond surface with a negative electron affinity (NEA). Initial surface-doped device designs used atmospheric molecules as the acceptor layer.⁵¹ In recent times, TMOs have attracted considerable attention due to their large EA and potential for improved robustness in devices.^{38,52} However, TMOs' tendency to exhibit stoichiometry degradation makes them vulnerable to the device fabrication process.

Motivated by this and recent encouraging experimental device works, as discussed in the previous section, our theoretical efforts have focused on performing bottom-up design of novel acceptor layers (e.g., monolayer 2-D materials) for diamond-based devices using first-principles density functional theory (DFT).⁵³ The heterostructure between the 2-D layer (graphene and h-BN) and reconstructed H-terminated—(2X1) H-D (100)—is constructed by minimizing interfacial strain. The process of heterostructure construction involves three key steps: strain, rotate, and rotation of the 2-D layer, as illustrated in Fig. 45. The 2-D layer is compressed 10% in the x-plane direction and 3.5% stretched in the y-plane direction. Finally, the modified 2-D layer is rotated and shifted to minimize the strain. The detailed information on the heterostructure design can be found in Mirabedini and et al.⁵⁴ The process flow of heterostructure design is illustrated in Fig. 46.

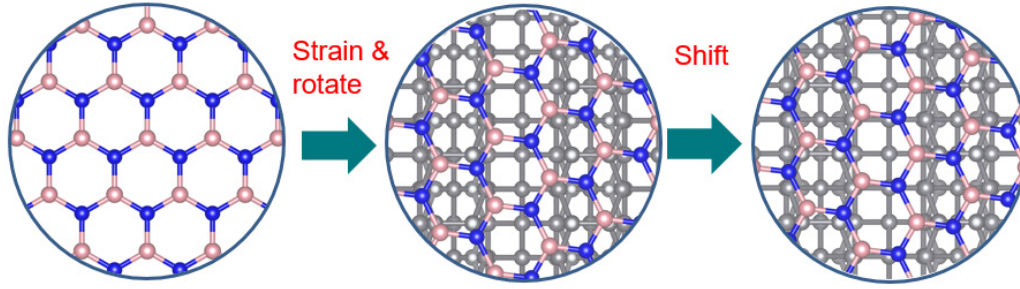


Fig. 45 Process of lattice-matched 2-D-H-D (100) heterostructure design. Blue, red, and gray (light) atoms represent B, N, and C atoms, respectively.

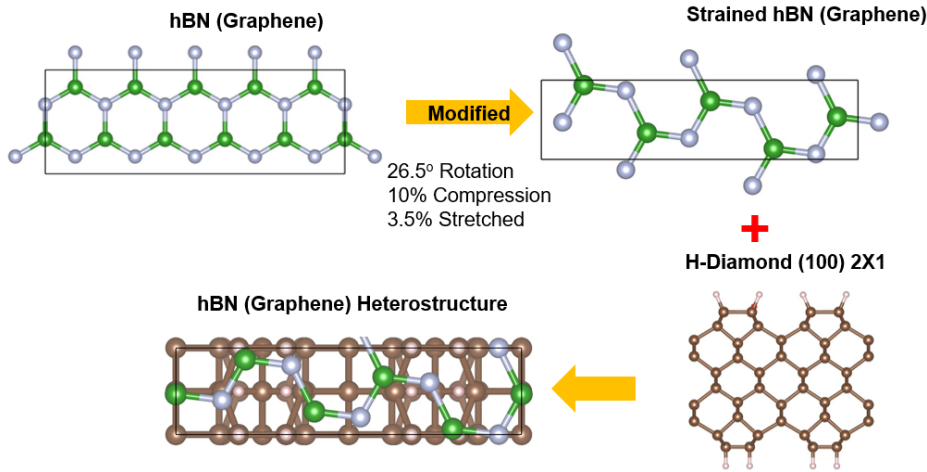


Fig. 46 Details on heterostructure design: (Top left to right) unstrained 2X5 h-BN (graphene) layer and strained and rotated 2X5 h-BN (graphene) layer and (bottom right to left) 2X1 H-D (100) substrate and lattice-matched 2-D-H-D (100) heterostructure

Due to interfacial strain, when 2-D layers are allowed to relax on top of the (2X1) H-D (100) surface, they buckle or ripple around the reconstructed (2X1) H-D (100) surface. The observed optimized vdW distance between the 2-D layer and (2X1) H-D (100) surface is approximately 3 Å, which is approximately 30% smaller than the intralayer distance in a bilayer graphene. The optimized rippled 2-D layers on 2-D-H-D (100) heterostructures are illustrated in Fig. 47.

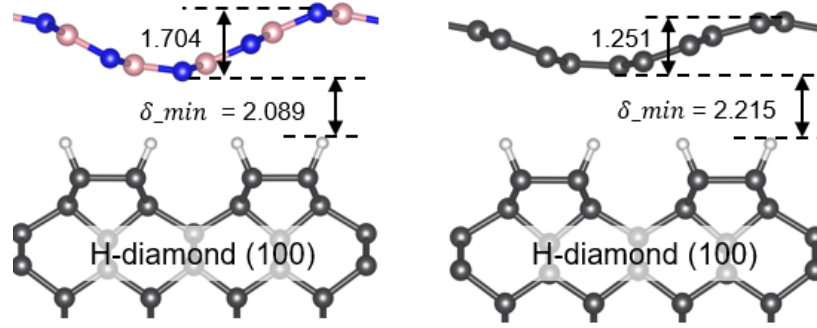


Fig. 47 Optimized 2-D-H-D (100) heterostructures (left) h-BN-H-D (100) heterostructure and (right) graphene-H-D (100) heterostructures

Following the structural properties calculation, the electronic properties such as band structure, surface-resolved density of states (sDOS), and projected density of states (pDOS) were calculated for 2-D-H-D (100) heterostructures. The sDOS plots for the heterostructures are plotted in Fig. 48.

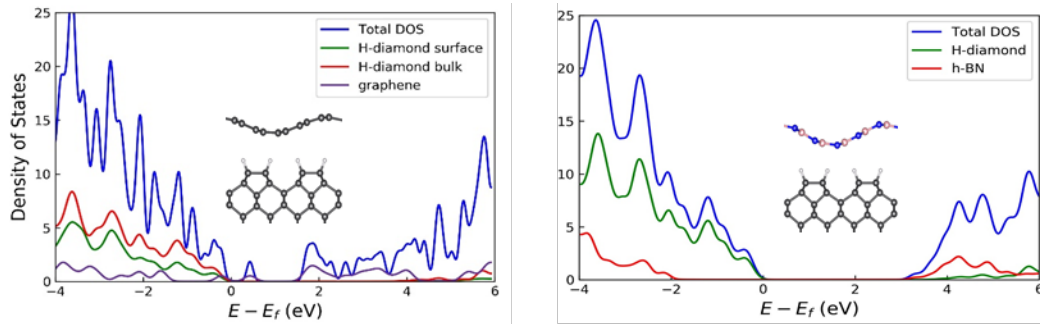


Fig. 48 The sDOS plots for 2-D-H-D (100) heterostructures: (left) graphene/H-D (100) heterostructures and (right) h-BN-H-D (100) heterostructure

One can obtain further insight into the roles proximal 2-D layers play in modifying the device-related properties of H-D (100) from the sDOS. In this analysis, the contributions from the surface states in the band alignment between the 2-D layers and H-D (100) are determined by isolating the contributions from the surface atoms in total density of states and plot them together. Here, the first three C layers and the H atoms, from the top and bottom, are identified as the surface layers of the H-D (100), whereas the central two layers are identified as bulk atoms. Here, all energies are relative to the Fermi level of the system. This approach is first proposed in Sque et al.⁵⁵ and is commonly adopted by numerous follow-up theoretical studies. In the case of graphene-H-D (100) heterostructure, the states from the graphene Dirac cone contribute to the mid-gap states within the diamond energy gap and leads to semi-metallicity behavior. In contrast, for the h-BN-H-D (100) heterostructure, the system retains the gapped properties of the bulk diamond with

the gap of 3.55 eV, an approximately 15% reduction in the bare H-D (100) surface gap. All the relevant band parameters from our calculations are tabulated in Table 2.

Table 2 Calculated device-related parameters for the bare H-D (100) surface and 2-D–H-D (100) heterostructures. All the numerical values are given in eV.

System	$E_f - E_{vb}$	E_{cb} (surf)	E_{cb} (bulk)	E_g (surf)	E_g (bulk)	WF	IP	EA (surf)	EA (bulk)
H-D (100)	0.1509	4.032	5.748	4.183	5.89	4.63	4.855	0.672	-1.045
Graphene/H-D (100)	0.117	1.721	4.032	1.838	5.89	4.424	4.821	2.983	-0.929
h-BN/H-D (100)	0.192	3.35	5.761	3.55	5.95	4.5	4.896	1.346	-1.056

Notes: E_f = Fermi level, E_v = valence band energy, E_{cb} = conduction band energy, E_{vb} = valence band energy, E_g = energy gap, WF = work function, IP = ionization potential, and EA = electron affinity.

For application as a FET, it is necessary to obtain interface carrier confinement properties of these heterostructures by determining the band alignments between the constituent systems. In the 2-D–H-D (100) heterostructures, both the charge accumulation and depletion occur at the interface, which results in the electron wave function being polarized, leading to the formation of interface dipoles, which further modifies band alignment at the interface. We identify the band alignments and band offsets between the interfacing 2-D layers and H-D (100) system by further analyzing the sDOS and plotting them against the vacuum level as a common reference energy level. To gain confidence in our numerical values of the band energies extracted from the sDOS, we also evaluated the band lineup using the “band alignment” method⁵⁵ by utilizing the microscopic and macroscopic averages of the electrostatic local potentials for the isolated 2-D layers and 2-D–H-D (100) heterostructures, as shown in Fig. 49. Since the band parameters obtained from both these methods were quantitatively similar (within 10%), here, we only discuss the results from the latter method. This method is also a relatively direct approach that incorporates the atomistic changes in the band alignment due to the interfacial strain-induced lattice deformation within the heterostructure.⁵⁵ Schematics of the band alignment characteristics in the graphene–H-D (100) and h-BN–H-D (100) heterostructures is illustrated in the inset figure of Fig. 49, and a detailed discussion on the band offsets and work functions (ψ) in these systems is presented in Mirabedini et al.⁵⁴

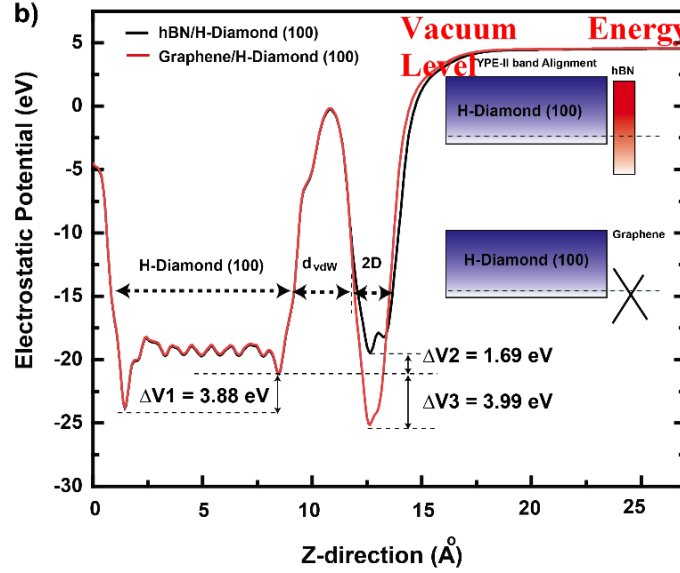


Fig. 49 Effective potential profile of h-BN–H-D (100) and graphene–H-D (100) heterostructures. Inset highlights band-alignment characteristics between the 2-D layers and H-D (100) system in 2-D–H-D (100) heterostructures

As seen in Fig. 49, the potential fluctuations along the H-D (100) surface for both the heterostructures are quite similar, but the vacuum level for the h-BN–H-D (100) system is lower in energy than the graphene–H-D (100) system by 80 meV. However, the work function difference, $\Delta\psi$, between these systems is around 70 meV, resulting in a potential energy difference of 0.15 eV. According to the Helmholtz equation, the $\Delta\psi$ is defined as $\Delta\psi = \Delta\sigma \cdot (A \cdot \epsilon_0)^{-1}$, where $\Delta\sigma$ is a charge parameter, A is the surface area, and ϵ_0 is vacuum dielectric constant. Since both the systems have equivalent A at the interface, the bulk of the contributions to the $\Delta\psi$ (by the corollary to the potential drop $[\Delta V]$) should come from $\Delta\sigma$, which includes changes in the surface dipoles, vdW interaction, and charge transfer due to heterogeneity.⁵⁶ Since the charge transfer between the 2-D layers and H-D (100) is minimal, as suggested by the Bader charge analysis, surface dipoles and vdW interaction collectively contribute to the $\Delta\psi$. This reduction of work function due to the adsorption of the 2-D layers on the H-terminated diamond surface is consistent with the molecule adsorption on Si (100)⁵⁷ and adsorption of organic semiconductor on diamond (100) surface.⁵⁸

Due to the nonionic vdW interaction, the interfacing 2-D layers modify the surface-related electronic properties, such as IP and EA, of H-D (100) surface through charge transfer and modulation of the C–H dipoles. In order to understand the proximity effect of the 2-D layers on the NEA and IP, we analyzed the band alignments of these heterostructures and compared them to the intrinsic H-D (100) surface. The graphene–H-D (100) system exhibit semi-metallic behavior, whereas

h-BN–H-D (100) system exhibits insulating characteristics. These values are tabulated along with other electronic properties in Table 2. Even though the surface gap of the H-D (100) system is reduced from 4.183 eV to 1.838 (3.55 eV) due to graphene (h-BN) layer, the bulk gap remains within the 5.90 ± 0.5 eV. This suggests that the electronic states from the 2-D layers interact strongly and modify C–H dipoles at the surface. Consequently, the NEA, one of the critical parameters that define the magnitude of the accumulated hole channel in the vicinity of the C–H bonds on the diamond surface, gets modified by the 2-D layers. The value of NEA decreases by approximately 10% due to graphene, whereas h-BN increases slightly this materials parameter ($\sim 1\%$). The h-BN layer not only preserves the NEA of the diamond surface, but also maintains the ultra-wide gap characteristics of the H-D (100) surface, making it an ideal candidate material as capping layer for H-D (100) surface. Due to its extremely high dielectric constant, planner structure, and potential for very low intrinsic charge impurities, h-BN could also minimize interfacial defects between the oxide-based acceptor layer and the H-D (100) surface.

Due to the noncovalent, non-interacting bonding, the h-BN layer preserves bulk-like properties of the diamond surface making it a fascinating candidate for a spacer layer between the hydrogenated diamond surface and the acceptor layer in surface-doped diamond transistor applications.⁵² Even though the observed charge transfer is minimal across the vdW gap, the electrons and holes in this heterostructure are predicted to be spatially separated and confined in the h-BN layer and diamond surface, respectively, resulting in Type-II band alignment. This predicted band alignment was validated in recent experimental work.⁵⁹ The spatially separated electrons and holes are tightly bound and long-lived, and form indirect excitons. These intriguing electrical neutral quasiparticles are of considerable interest in current research on next-generation electronic and optical devices.^{60,61} In conclusion, our atomistic modeling supports the feasibility of using the 2-D layers, particularly an h-BN layer, as an interfacial layer between the H-D (100) surface and acceptor layer, while leveraging their layer-dependent tunable electronic properties.

6.3 Oxygenation of Diamond Microcrystals and Polycrystalline Wafer through Hummers' Method

Modified Hummers' method (MHM) is used to convert graphite powders into graphene oxide (GO) through three-step oxidation reactions. On addition of sulfuric acid (H_2SO_4) and sodium nitrate (NaNO_3), an acid oxidative environment is created and the first reaction intermediate formed is acid intercalated graphite structure (GIC), and through the addition of oxidizing agents such as potassium

permanganate (KMnO_4) and hydrogen peroxide (H_2O_2), the reaction progresses into the second step by the oxidation into pristine graphite oxide (PGO) followed by the third step, the completion into GO.⁶² Considering the extreme oxidizing nature of the MHM, we have treated 10-N-methylcarbamoyl-3,7-bis(dimethylamino)phenothiazine (MCDP) with MHM and studied the efficacy of this method on oxidizing the diamond surfaces. The chemical used and reaction sequence remains the same and the reactants such as H_2SO_4 , NaNO_3 , KMnO_4 , and H_2O_2 were purchased from Sigma Aldrich and used as such without any further dilution. The various stages of MHM in oxidizing the diamond surfaces are depicted in Fig. 50.^{63,64}

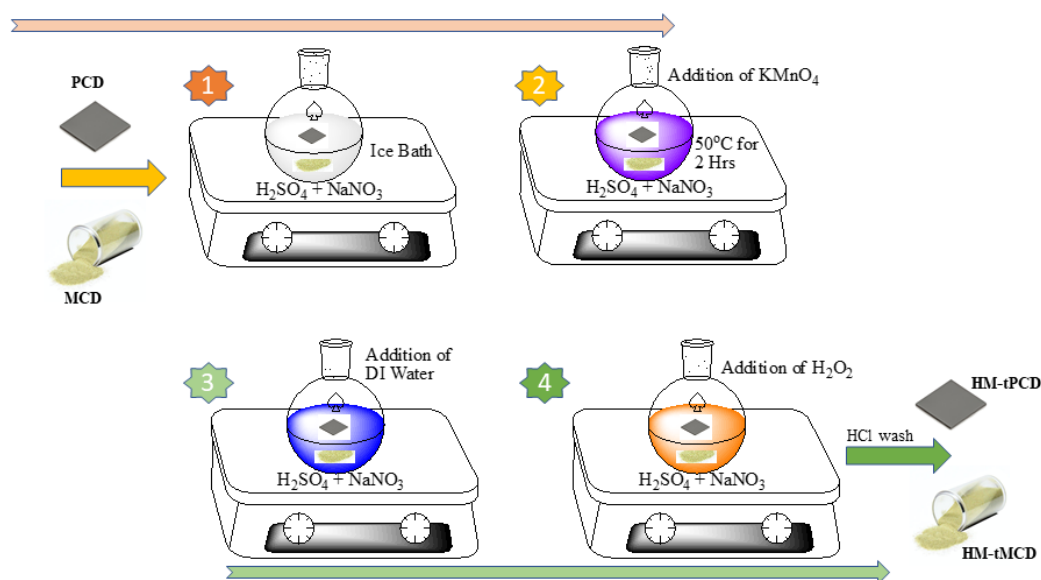


Fig. 50 Steps involved in the MHM process to create O-terminated diamond surfaces

The most widely used approaches to study diamond surfaces are XPS, which reveals the binding energy (BE) states inside a 15-nm-thick layer at the surface, and Kelvin force microscopy (KFM), where the surface potential with respect to the scanning probe is deduced.⁶⁵ In XPS, the expected peaks on the diamond surface are sp^3 (about 284.5–285 eV), polyhydride carbon species (285 eV), and hydroxyl and ether groups (about 286.5 eV). The peak at about 283.5 eV is generally assigned to π -bonded C atoms. Several authors assign the contribution at about 280–281 eV to the emission from surface atoms missing the nearest neighbor or caused by the non-monochromatic sources. On the other hand, oxidation processes produce several kinds of C–O bonds. As reported in the literature, –C–OH or –C–O–C– bond bonds appear at a BE of 286.5 eV. At about 288 eV, –O–C–O– bond or carbonyl groups are assigned and –(O=C)–O– carboxyl groups are found at about 289 eV. In

this study, FTIR, TEM, and XPS were employed to characterize the MHM-treated microcrystalline samples.

When it comes to the FTIR spectra, the IR region is extremely difficult to interpret on the microcrystalline diamond because many contributions from the diamond core and surface groups are overlapping. Diamond core features are mainly associated with C–C lattice vibrations and various types of defects.⁶⁴ N-induced defects may appear with diverse contributions in the spectra, especially as detonation product diamond powders have a large amount of N in the core but also a highly defective structure when compared to bulk diamond. A broad feature in the 1100–1500 cm^{-1} region is ascribed to N impurities. The other vibrational modes reported for N-based defects are 1180, 1260, and 1360 cm^{-1} . Being polar, surface groups are contributing considerably to the IR fingerprint region. The main contribution from O-related groups is usually attributed to C–O–C bending modes of ether-like groups, acid anhydrides, or lactones around 1100–1140 cm^{-1} ; however, C–O stretching modes of hydroxyl groups are also generally detected in this region. C–O bending modes of ether group or epoxy structure are reported at 1260 cm^{-1} , and acid anhydride-related vibrations at 940, 1290, and 1370 cm^{-1} on oxidized diamond powders. Amide III bands and C–N stretching also contribute to the 1210–1320 cm^{-1} region for monocrystalline diamonds having high N content or aminated surface. Finally, C–H bending modes around 1460 cm^{-1} are seen when hydrogenated groups are present on the microcrystalline diamond surfaces.⁶⁶ When comparing the IR spectrum of pristine and MHM-processed diamond powder samples (Fig. 51), the IR bands corresponding to C=O vibrations are intensified in MHM-treated samples also the signals of C=C. The bands C–OH and C–O are present they are not as intense as C=O proves the preferential O termination reaction to just the O functionalization of various kinds.

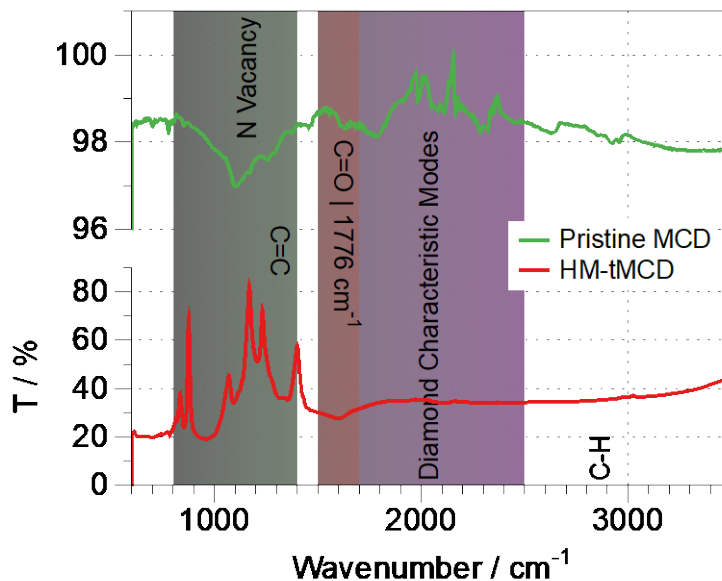


Fig. 51 FTIR spectrum comparing the pristine and MHM-process-modified O-terminated samples. A stark difference is observed in terms of vibrational bands that correspond to C–O vibrations

The size and morphology of the microcrystalline diamond samples are investigated through TEM, and the low- and high-magnification images are provided in Fig. 52a–c. The crystals are a few micrometers in size and uniformly distributed. The EDS before and after the MHM process is displayed in Fig. 52d and e, respectively. It is obvious that the net O content in the MHM-treated samples are around 16% compared to 4% in the pristine samples. TEM EDS is not as sensitive as XPS; still, the increment in the O content is an indication of surface oxygenation.

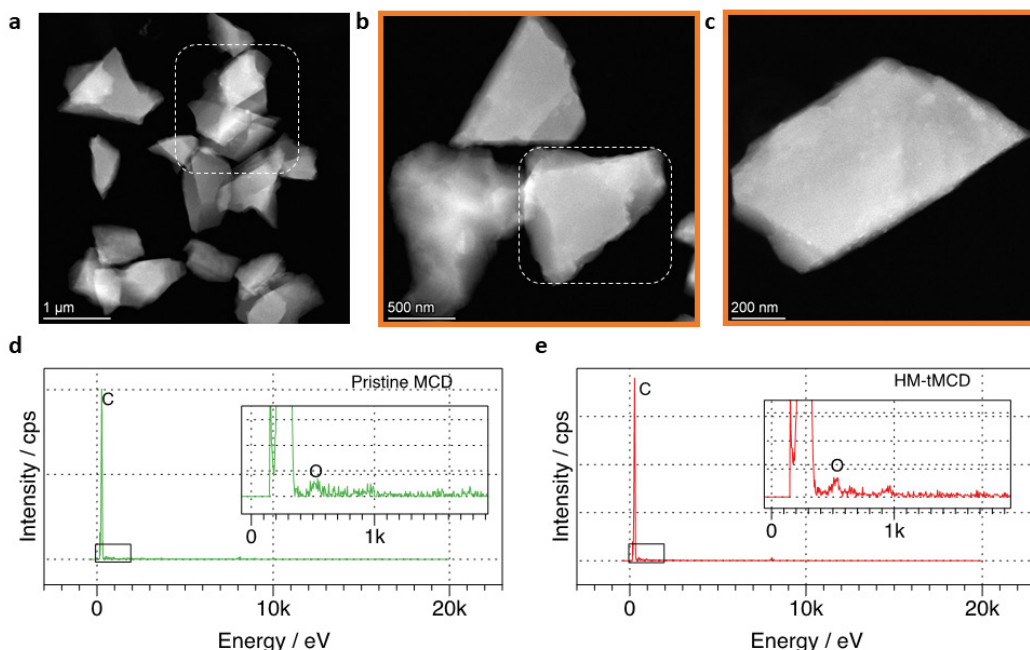


Fig. 52 EDS of microcrystalline diamond powder samples and the EDS showing the elevated O concentration in MHM-processed diamond samples

An elemental scan was obtained for pristine and MHM-treated microcrystalline diamond powders for three different pass energies and the results are displayed in Fig. 53. The difference in the O content between pristine and MHM-treated diamond powder is readily visible and the increment is approximately 20% quantitatively. This is a remarkable increment though the contribution from small impurities and surface adsorbed O still needs to be accounted for.

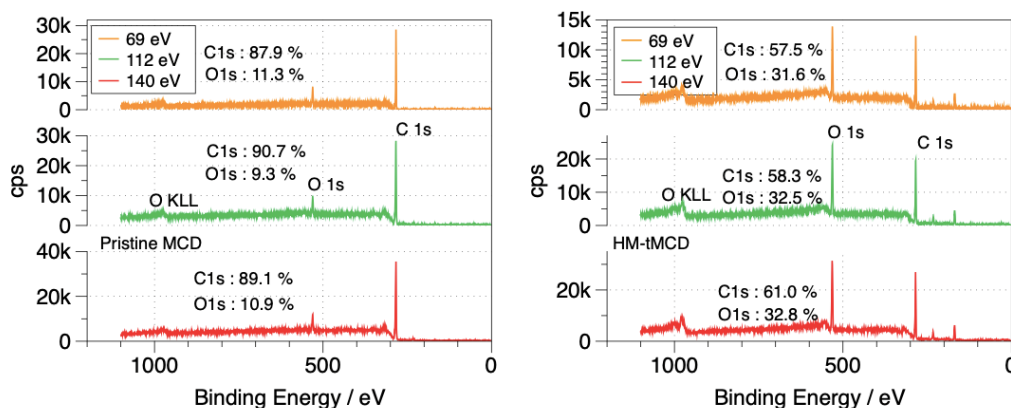


Fig. 53 Survey XPS of pristine and MHM-treated diamond powders for three different pass energies

To study the chemical environment of C on the powder surface, high-resolution C1s spectra are fetched (pass energy 26 eV) for pristine and MHM-treated samples

and are displayed in Fig. 54. The C 1s core-level spectra of samples were fitted by phi lab software with the following reference peaks: 284.5-eV BE assigned to sp^2 hybridized C atoms in microcrystalline diamond (graphite-like structure) and 285.4-eV BE assigned to sp^3 hybridized C atoms (diamond structure) also could be due to the formation of C–H and the C–C bonds in the microcrystalline diamond. Other components including C–O (286.3 eV), C=O (287.6 eV), and COOH (288.6 eV) with much higher BEs, which usually originated from functionalized–terminated interface states and ambient O and moisture.⁶⁷

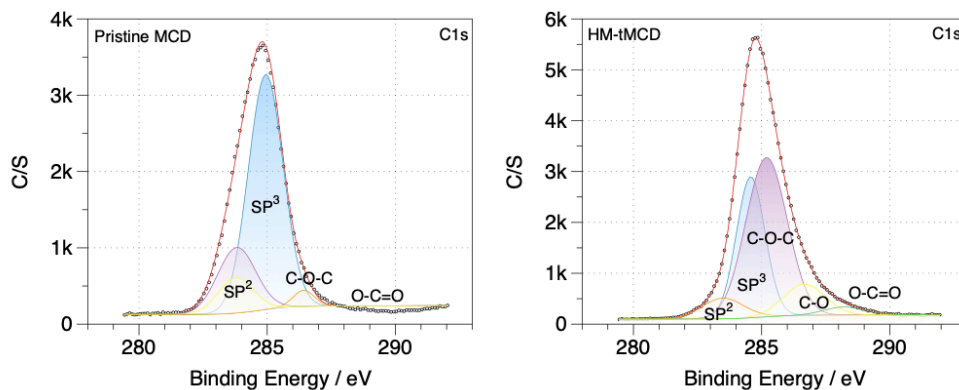


Fig. 54 High-resolution C1s spectra of pristine and microcrystalline diamond powders

Hence the XPS spectra of pristine and MHM-treated samples can be deconvoluted to either of the abovementioned species and fitted as appropriate. On comparing the high-resolution XPS, one can see that the contribution of C–O–C species is much higher for MHM-treated samples compared to the pristine samples and indicates a successful O termination. The contribution of other species such as C–O, O–C=O, C=O also needs to be taken into account along with C–O–C carbon structures.

We have also tried to simulate the feasibility of oxygenation on a spherical as well as slab-like sp^3 C structure through molecular dynamics (MD) calculations. Due to the presence of different facets and excess surface to volume ration, spherical-shaped diamond samples are found to be more fertile for O termination compared to the wafer/slab like diamond structures. The simulated structures and the percentage of oxygenation predicted are displayed in Fig. 55.

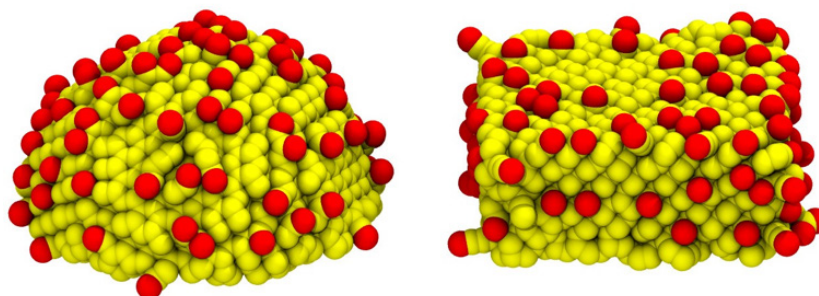
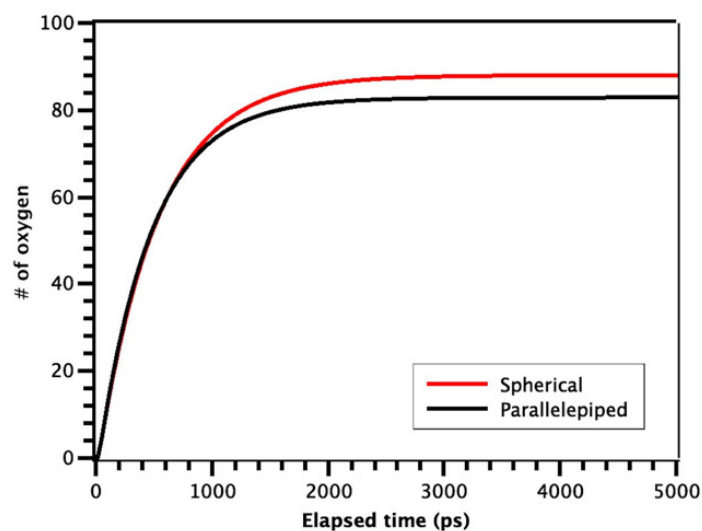


Fig. 55 MD calculations on the effect of surface geometry on the percentage of oxygenation via MHM. The excess surface to volume ratio predicts the powder samples are more prone to oxidation compared to a PCD wafer.

6.4 Oxygenation of Diamond through Acid Mixture

The monocrystalline diamond powder and PCD, respectively, were oxidized by various wet-chemistry treatments, using H_2SO_4 /nitric acid (HNO_3) mixture, aqua regia, Fenton, and piranha solution. For each of the methods, the reactions were carried on using the setup shown in Fig. 56a.

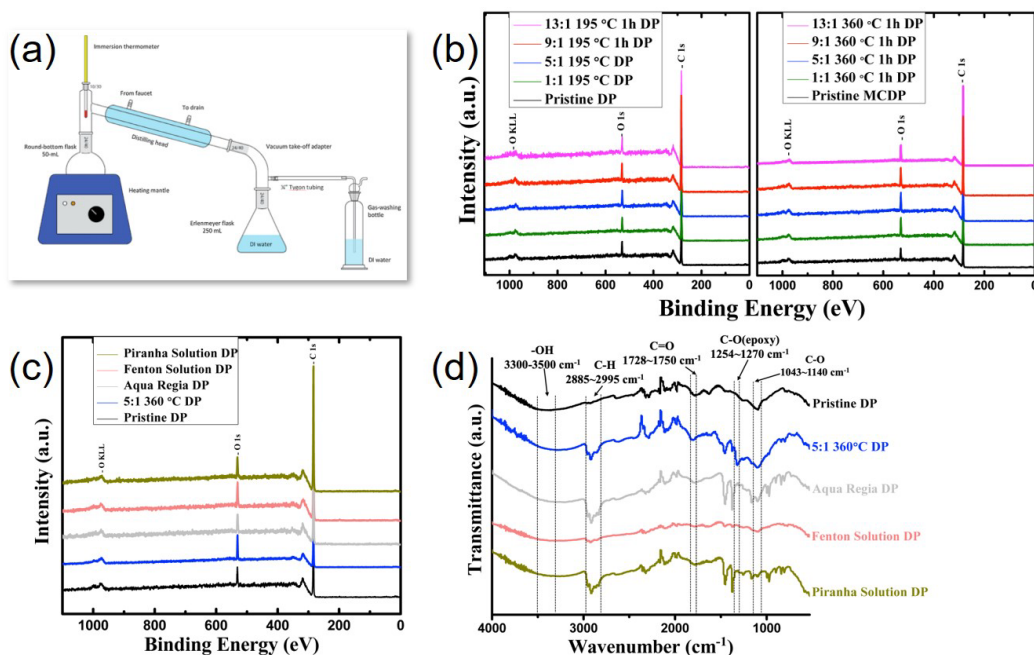


Fig. 56 a) The setup for web-chemistry treatments on diamond powder a PCD. Normalized XPS survey spectra of diamond powder treated by b) H₂SO₄/HNO₃ at 195 and 360 °C, and c) various methods including aqua regia, Fenton solution, and piranha solution. d) Normalized attenuated total reflectance-FTIR spectra of diamond powder treated by various methods.

To investigate the oxidation behaviors brought by each wet-chemical route, the XPS measurement was first employed on the oxidized diamond powder. From the intensities of O 1s peaks demonstrates in Fig. 56b and c, the O content of diamond before and after all treatments can be estimated. The H₂SO₄/HNO₃ acid mixture with a ratio of 5:1 under 360 °C presents the highest O 1s peak, implying the greatest oxidation performance on diamond powder via wet-chemical treatment.

To realize the surface component of diamond powders treated by different methods, the FTIR analysis was carried out. In Fig. 56d, five functional groups can be detected: methyl/methane (–CH₃/CH₂, 2885~2996 cm⁻¹), single-bonded C/O atom (C–O, 1043~1140 cm⁻¹), epoxy (C–O–C, 1254~1270 cm⁻¹), carbonyl (C=O, 1728~1750 cm⁻¹), and hydroxyl (–OH, 3300~3500 cm⁻¹) groups. Among those, three of them are the O-related groups (C–O–C, –OH, and C=O), and their peak intensities are varied depending on the reaction route.

As it is shown that each treatment gives rise to three kinds of oxygenation groups, their compositions on diamond surface were further analyzed by the high-resolution O 1s spectra of XPS. From Fig. 57a and b, we can observe three O-related peaks: carbonyl (C=O), hydroxyl (–OH), and epoxy (C–O–C). Among those, the PCD oxidized by H₂SO₄/HNO₃ acid mixture with ratio 5:1 under 360 °C (Fig. 57b) gives the highest epoxy peak among three kinds, while the pristine PCD (Fig. 57a) and

one treated by aqua regia (Fig. 57c), Fenton (Fig. 57d), and piranha solution (Fig. 57e) present the highest hydroxyl peaks. This observation demonstrates that most of the wet-chemical treatments are capable to imparting hydroxyl group as the major surface component, while the $\text{H}_2\text{SO}_4/\text{HNO}_3$ acid mixture (5:1, 360 °C) presents epoxy as the alternative. The quantified results for each treatment are plotted in Fig. 57f.

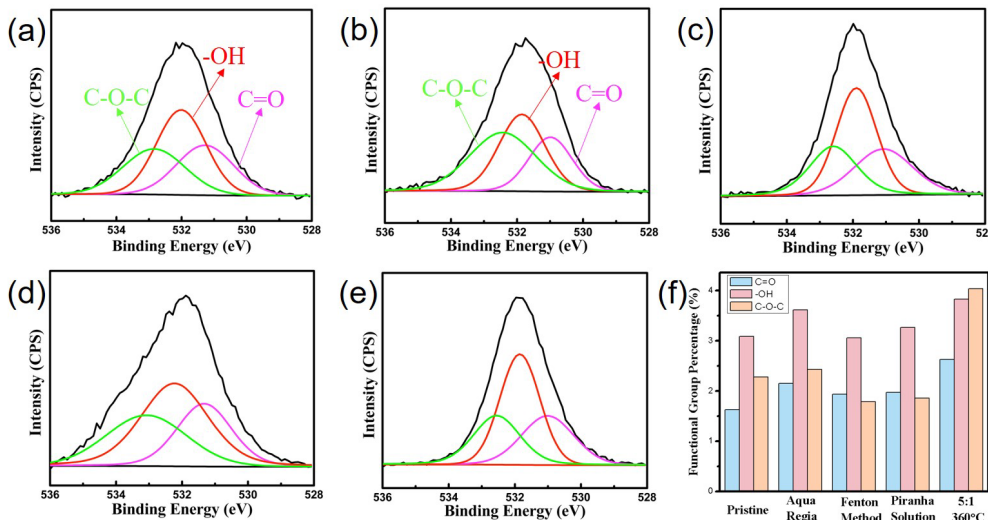


Fig. 57 High-resolution core-level O 1s spectrum of PCD: a) pristine sample, b) $\text{H}_2\text{SO}_4/\text{HNO}_3$ 5:1 at 360 °C, c) aqua regia, d) Fenton solution, and e) piranha solution. f) The quantified results of O-related groups for each of treated samples calculated based on the whole elements of PCD surface

In order to realize the residual sp^2 C after wet-chemistry treatments on PCD, the Raman spectroscopy was performed. Fig. 58a and b present the Raman spectrum of oxidized diamond that exhibits a sharp sp^3 peak at approximately 1332 cm^{-1} , while graphene has four Raman peaks, including D band ($\sim 1349\text{ cm}^{-1}$), G band ($\sim 1592\text{ cm}^{-1}$), 2-D band ($\sim 2687\text{ cm}^{-1}$), and S3 peak ($\sim 2865\text{ cm}^{-1}$). The G band is chosen as the criterion to judge the degree of residual sp^2 C. As can be seen, the $\text{H}_2\text{SO}_4/\text{HNO}_3$ acid mixture with ratio 1:1 under 360 °C gives the lowest intensity of G band, indicating the best sp^2 C cleaning effect among wet-chemical treatments.

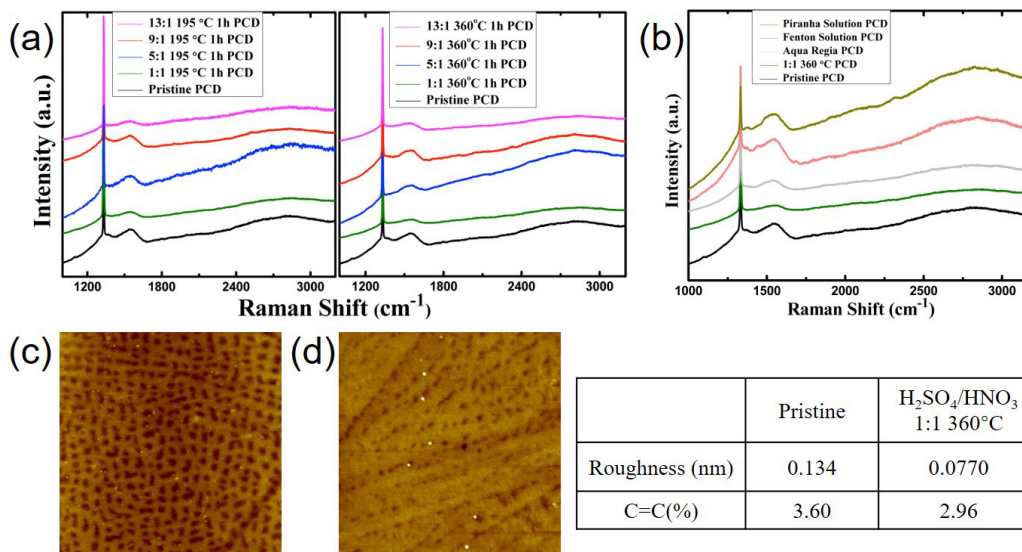


Fig. 58 Normalized Raman spectra of PCD treated by H₂SO₄/HNO₃ at a) 195 and 360 °C, and b) various methods. The images of AFM spectroscopy of PCD: c) untreated (0.134 nm) and d) H₂SO₄/HNO₃ 1:1 at 360 °C (0.077 nm) treated samples

Furthermore, the AFM spectroscopy was performed to characterize the roughness of diamond material treated by wet-chemical routes. In Fig. 58c and d, the surface roughness of PCD declines, against pristine one, after the treatment of acid mixture (1:1, 360 °C), implying it can smoothen the surface of diamond material.

6.5 Oxygenation of Diamond through UV Ozone and O₂ Plasma

In light of the oxidizing performances of wet-chemistry methods on diamond material, the PCD was further chosen as the substrate to demonstrate the oxygenating behavior of dry-chemical routes, UV ozone, and O₂ plasma. The process depicted in Fig. 59a was used during the procedures.

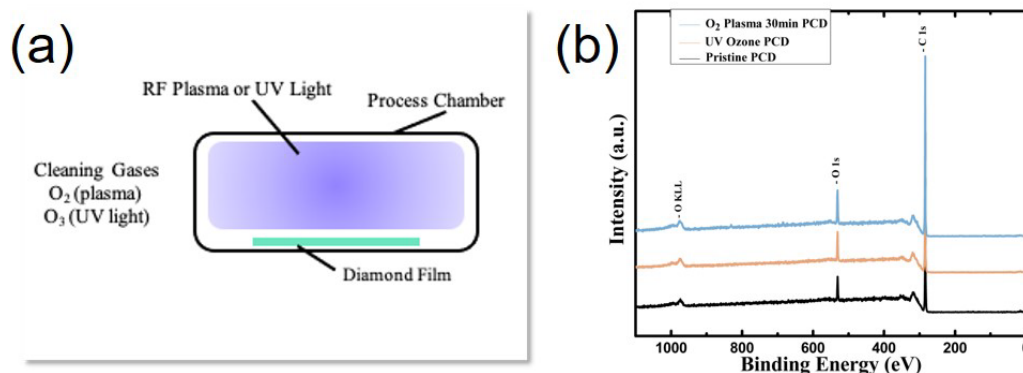


Fig. 59 a) Schematic illustration of dry-chemistry treatments on PCD. b) Normalized XPS survey spectra of PCD treated by UV ozone and O₂ plasma.

The XPS measurement was first employed on the oxidized PCD to learn the oxidation behaviors of dry-chemical treatments. From the intensities of O 1s peaks present in Fig. 59b, the oxygenation abilities of UV ozone and O₂ plasma on PCD are estimated. The O₂ plasma gives the topmost O 1s peak, implying the higher oxidation performance than UV ozone has.

As found before, each oxidizing treatment brings three kinds of O-related group, their compositions on dry-chemical-oxidized PCD surface were further analyzed by the high-resolution O 1s spectra of XPS. From Fig. 60a and b, three O-related groups can be found: carbonyl (C=O), hydroxyl (–OH), and epoxy (C–O–C). The O₂ plasma and UV ozone, respectively, demonstrate the topmost peaks of epoxy and hydroxyl groups among the three kinds. The quantified results for each treatment are plotted in Fig. 60c.

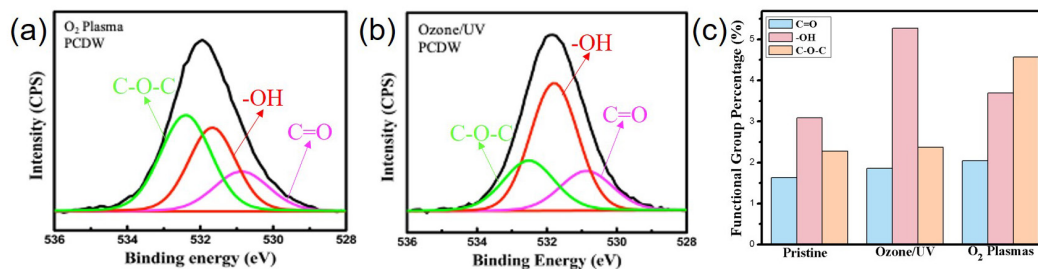


Fig. 60 High-resolution core-level O 1s spectrum of PCD: a) O₂ plasma and b) UV ozone. c) The quantified results of O-related groups for each of treated samples calculated based on the whole elements of PCD surface.

The Raman spectrum was also performed to realize residual sp² C after dry-chemistry treatments on PCD. In Fig. 61a, both O₂ plasma and UV ozone show a lower G band than the pristine diamond has, which indicates the sp² C cleaning effect.

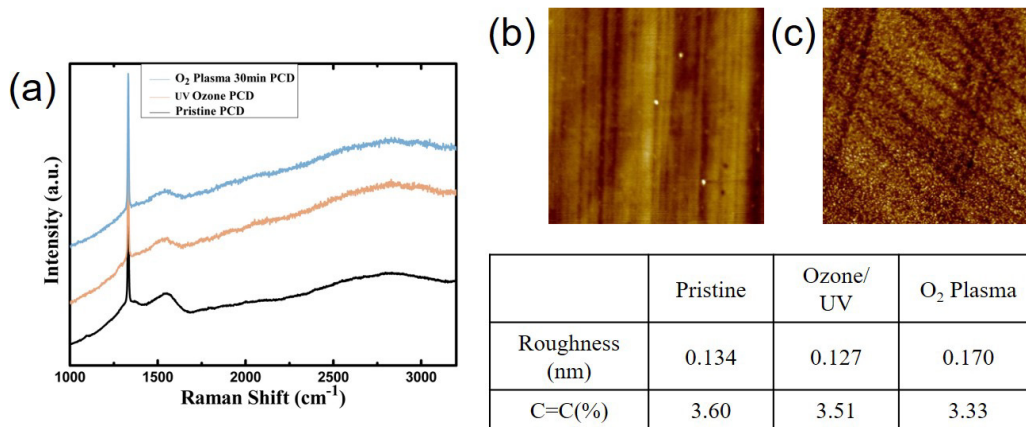


Fig. 61 Normalized Raman spectra of PCD treated by a) UV ozone and b) O₂ plasma. The images of AFM spectroscopy of PCD treated by c) UV ozone (0.120 nm) and d) O₂ plasma (0.170 nm).

Moreover, from the AFM spectroscopy in Fig. 61b and c, we can observe that the UV ozone can smoothen the diamond surface while the O₂ plasma roughens it.

6.6 Diamond Doping by Ion Implantation

Ion implantation is a process whereby ions of one element are accelerated into a solid target, thereby changing the physical or chemical properties of the target. This technique has been widely applied in the semiconductor industry, doping or otherwise modifying Si and other semiconductor wafers. A major advantage of ion implantation is the capability of precisely controlling the number of implanted dopant ions. The selection of dopant ion species and control of dose amount and implantation energy allows selective doping, to fabricate a proper conduction type and resistivity. Besides, the depth distribution of the injected dopants is directly related to the implantation energy and the masses of the target material and ion, which can be simulated and predictable. Ion implantation has already applied on diamond for various purposes, including graphitization, p- and n-type doping, creation of ohmic contacts, and creation of a nitrogen-vacancy (NV) center.

After discussion with the DEVCOM ARL team and the collaborator Dr Di Chen at the Texas Center for Superconductivity at the University of Houston, two ion implantation plans were selected (Table 3). The first one is the p-type doping of diamond by B implantation with low energy (20–60 keV). The low-energy ions would form a heavily doped layer close to the diamond surface less than 100 nm, which is used for creating ohmic contacts. Another one is n-type doping of diamond by phosphorus (P) implantation with high energy (1.5 MeV). It is expected to form an n-type layer approximately DEVCOM ARL. The B-implanted layer on #5

ESCD was found and removed after annealing and acid cleaning. Therefore the implantation energies were increased for the subsequent diamond samples.

Table 3 Ion implantation diamond sample list

Diamond	Implanted ion	Energy	Dose (ion/cm ²)	Expected implantation depth (nm)	Status
#1 PCD	B	20 keV	2.5E15	37 ± 11	Finish
#2 PCD	B	40 keV	3.7E15	69 ± 16	Finish
#3 PCD	P	1.5 MeV	2.5E13	707 ± 66	Pending
#4 PCD	P	1.5 MeV	2.5E13 or higher	707 ± 66	Pending
#5 ESCD	B	20 keV	2.6E15 at 60°	20 ± 10	Finish/sent to DEVCOM ARL
#6 SCD	B	40 keV	3.7E15	69 ± 16	Finish/sent to DEVCOM ARL
#7 SCD	B	40 keV	3.7E15	69 ± 16	Finish/sent to DEVCOM ARL
#8 SCD	B	60 keV	4.3E15	97 ± 20	Finish/sent to DEVCOM ARL
#9 SCD	B	60 keV	4.3E15	97 ± 20	Finish/sent to DEVCOM ARL

Figure 62 shows the picture of a pristine standard-grade SCD, a 40-keV B-implanted SCD, and a 60-keV B-implanted SCD. It can be clearly observed that the optical contrast of the implanted diamond is different from the pristine diamond. A similar phenomenon has been found on PCD. Figure 63a–b shows optical images of a pristine PCD, a 20-keV B-implanted PCD, and a 40-keV B-implanted PCD. Scattered patches with dark contrast can be observed on implanted PCD samples. Raman spectra in Fig. 63d–f indicate the dark area and bright area have different intensities of the diamond peak. On the 20-keV B-implanted PCD, the diamond peak is more intense on dark area than that on the bright area. In contrast, the intensity of the diamond peak is higher on the bright area than that on the dark area on the 40-keV B-implanted PCD. These results are consistent with the diamond peak intensity mappings shown in Fig. 63g and h.

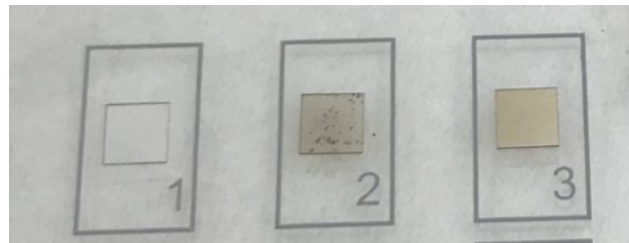


Fig. 62 1) pristine SCD, 2) 40-keV B-implanted SCD, and 3) 60-keV B-implanted SCD

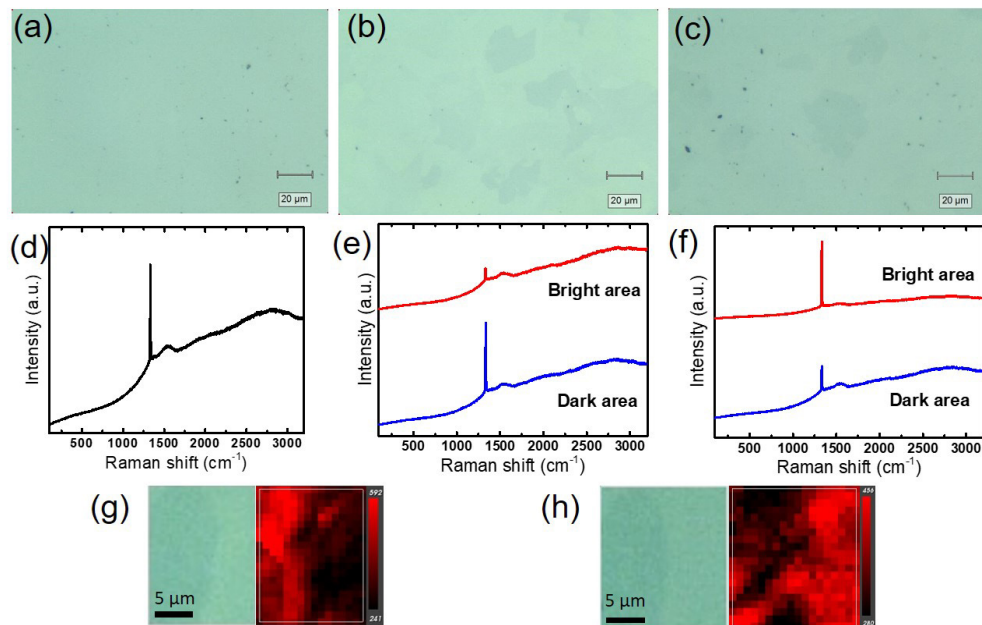


Fig. 63 Optical image of a) pristine PCD, b) 20-keV B-implanted PCD, and c) 40-keV B-implanted PCD. d) Raman spectra of pristine PCD. e) Raman spectra and g) diamond peak intensity mapping of 20-keV B-implanted PCD. f) Raman spectra and h) diamond peak intensity mapping of 40-keV B-implanted PCD.

7. On the Hydrogenation of Diamond Surfaces: A Reactive Molecular Dynamics Study

Recently, scientific research has shown that the use of diamond as a p-type material can be a relevant innovation for the next-generation FETs.^{68–70} Diamond has a high mobility of charge carriers and high thermal transport, and is extremely tolerant to high-voltage application, extreme heat, and even radiation.⁷¹ Along with this, the manufactured diamond has been showing a decreasing cost of production over the years.⁷² These qualities make diamond-based FETs ideal for the next generation of electronics that could equip RF devices, for example.

In the diamond-based FETs studied so far, hydrogenated diamond is used in order to eliminate the dangling bonds at the C atoms in the surface and avoid reactions with the material used as a gate. H also has the purpose to create a channel of holes that contributes to the conductivity of charge carriers in the diamond surface. Regarding the possible surfaces of the diamond that can be synthesized, depending on the distribution and number of dangling bonds of the C atoms, defects and reconstructions on the surface can occur. Thus, this also has a direct impact on how the hydrogenation of the surface will occur and the final properties of the surface. As it is known that the H layer influences the charge transport, it is important to use a surface with the least possible amount of dangling bonds and more H atoms.

As far as we know, there is no study that evaluates the quality and quantity of hydrogenation on different diamond surfaces. Then, our aim here is, using MD simulation, to perform studies of diamond hydrogenation in different surfaces, evaluating the resulting surface roughness, reduction of superficial dangling, as well as the electronic structure of the surfaces. From the obtained results, we hope to help the experimentalist to select the best diamond surface orientation to perform the hydrogenation that could bring improvements to FET application.

7.1 Methodology

Using MD simulation, our objective here is to evaluate the characteristics of different diamond surfaces and test the quality of the hydrogenation performed in each one. All MD simulations presented here were performed with the reactive force field (ReaxFF),⁷² as implemented in the computational code Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS).⁷³

To perform our study, we select four different diamond surfaces: (001), (013), (110), and (113). For these bare surfaces, it is interesting to evaluate the C dangling bonds available at each one, if there are reconstructions occurring at the surface, and also the surface stability. From this information, we can evaluate the number of H atoms that can be incorporated at each surface and also the groups formed at the surface ($-\text{CH}$, $-\text{CH}_2$, or $-\text{CH}_3$).

To evaluate the characteristics of each selected diamond surface, we build diamond slabs of approximately $5 \times 5 \text{ nm}^2$ and with eight layers for each one. Then, we performed thermal equilibration via MD to test their stability in room temperature, 500, 700, 900, and 1200 °C for 400 ps. These simulations were performed in an NVT ensemble and a timestep of 0.1 fs. The periodic boundary conditions (PBC) were applied in the x- and y-directions (reproduce the neighboring slabs) during the simulations.

After studying the properties of each bare surface, we performed hydrogenation in each one. To do so, we created an atmosphere of H atoms (randomly distributed) and put it in contact with each thermally equilibrated diamond surface. The number of hydrogenation atoms in contact with each diamond surface is equal to the initial number of dangling bonds + 20% of this value. We allowed the x- and y-directions to be periodic, but we confine the system along the z-direction adding an infinitely hard Lennard–Jones walls at the bottom and top of the box, respectively. Then, for each diamond surface, we carried out MD runs of 5.0 ns at 500, 700, 900, and 1200 °C in an NVT ensemble. The box size of the simulation was chosen to keep the internal pressure at 1 atm. The MD timestep used in these simulations was

0.1 fs. After each simulation, we evaluate the number of incorporated H atoms in each surface along the time.

7.2 Results and Discussions

Here we present the general results and conclusions of our studies. First, we briefly present the results obtained for each bare diamond surface and then follow with the hydrogenation studies results.

7.2.1 Bare Surfaces

7.2.1.1 Surface (001)

In Fig. 64, we present the snapshots of the (001) diamond surface in its initial configuration and after the thermal equilibration at 900 °C. The C atoms highlighted in red have initially two dangling bonds each one, which results in approximately 32 dangling bonds per nm² (Fig. 64a). These surface C atoms are distant approximately 2.5 Å each one.

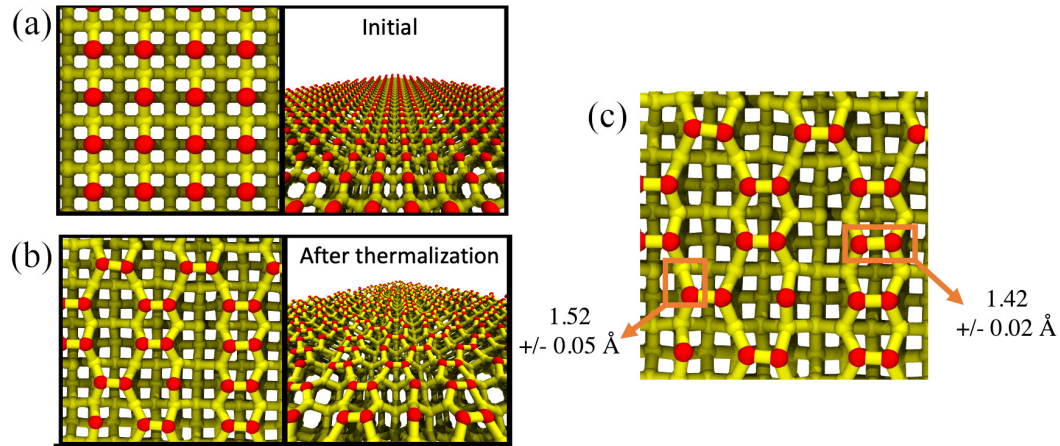


Fig. 64 Diamond surface (001) a) before and b) after a thermal equilibration at 900 °C. c) Representative bond lengths between C atom at the surface.

When we start to heat up the slab, reconstructions start to occur at the surface. As can be seen in Fig. 64b, which is the surface thermalized at 900 °C, the C atoms at the surface (the red one) will bond with its neighbor, decreasing the number of dangling bonds and generating a reconstruction (2x1). This is in good agreement with the experimental data and with some electronic structure simulations. However, our results indicate that the (2x1) reconstruction is temperature-dependent in (001) surface, in which we observed that the surface presents 10%, 75%, 80%, 85%, and 85% of reconstruction in, respectively, room temperature, 500, 700, 900, and 1200 °C. This corresponds with the approximately 30, 22, 19,

18, and 18 dangling bonds at the surface at room temperature, 500, 700, 900, and 1200 °C, respectively. These dangling bonds in each temperature indicate the places available to be hydrogenated.

Regarding the C bond length in the bulk and surface in our (001) slab, we observed some fluctuation on it at different temperatures. In the bulk part, at room temperature, the C–C bond length presents an average value of 1.55 ± 0.03 Å and increasing the temperature, this average value has a fluctuation of up to approximately 0.02 Å. This value is characteristic of the sp^3 – sp^3 bonds, as expected for diamond. At the surface, the reconstructed C atoms (dimer) present a bond length of 1.42 ± 0.02 Å at room temperature, as depicted in Fig. 64c, with a mix sp^2 – sp^2 and sp^3 – sp^2 character. As for the bond length of one of the C atoms that participate in the reconstruction and a C atom underneath of it (see Fig. 64c) present a bond length of 1.52 ± 0.05 Å, which corresponds to an sp^3 – sp^2 bond. Increasing the temperature, we also observed an increase of approximately 0.02 Å in the average values. Note these bond length values were obtained by doing an average along all elapsed time of simulation.

7.2.1.2 Surface (013)

In Fig. 65, we present the snapshots of the (013) diamond surface configuration. Different to the observed for the surface (001), the surface (013) did not present any surface reconstruction with respect to the temperature, keeping the same number of the dangling bonds at room temperature, 500, 700, 900, and 1200 °C. The C atoms highlighted in red (Fig. 65a) have two dangling bonds each and the green ones, one dangling bond each. Then, this surface presents approximately 29 dangling bonds per nm². The red surface C atoms are distant approximately 3.1 Å each one.

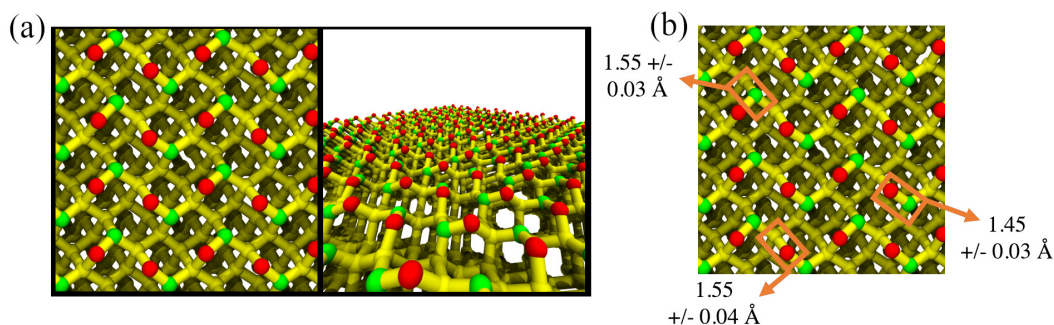


Fig. 65 Diamond surface (013) a) after a thermal equilibration at 900 °C. b) Representative bond lengths between C atoms at the surface.

Regarding the C bond length, in the bulk part the C–C bond length presents an average value of 1.55 ± 0.03 Å at room temperature, and increasing the temperature,

this average value changes up to approximately 0.02 Å. This value is characteristic of the sp^3-sp^3 bonds, as expected for diamond. At the surface, as depicted in Fig. 65b, the bond length between the green and red C atoms (the ones with dangling bonds) is 1.45 ± 0.03 Å, presenting an sp^2-sp^2 character. As for the bonds between the green and red C atoms with a C atom, which do not have dangling bond present, they both have a bond length of 1.54 ± 0.03 Å, which can fluctuate between an sp^3-sp^3 and sp^3-sp^2 character. Increasing the temperature, an increase of approximately 0.02 Å in the average values for the superficial atoms is observed. Again, these bond length values were obtained by doing an average along all elapsed time of simulation.

7.2.1.3 Surface (110)

In Fig. 66, we present the snapshots of the (110) diamond surface configuration. This surface did not also present any surface reconstruction with respect to the temperature. The C atoms highlighted in red (Fig. 66a) have one dangling bond each and they are distributed in a zig-zag configuration. This surface presents approximately 22 dangling bonds per nm², and as this surface do not reconstruct, this number remains the same at the tested temperatures (i.e., room temperature, 500, 700, 900, and 1200 °C).

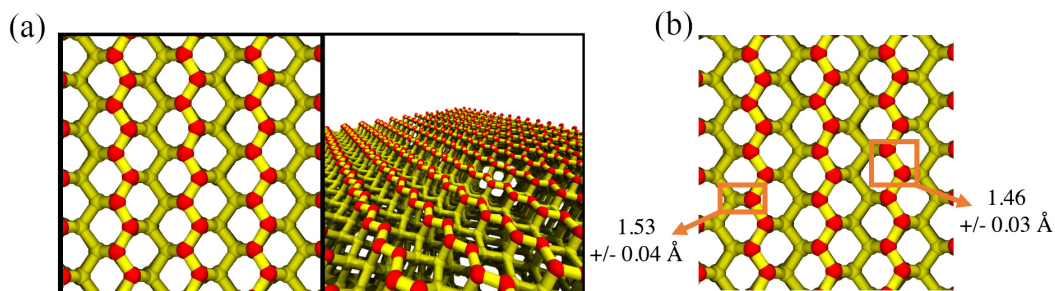


Fig. 66 Diamond surface (110) a) after a thermal equilibration at 900 °C. b) Representative bond lengths between C atom at the surface.

For this diamond surface, in the bulk part, the C–C bond length has an average value of 1.55 ± 0.04 Å at room temperature, representing an sp^3-sp^3 bond. Similar to the other studied surfaces, increasing the temperature, this average value can vary up to approximately 0.02 Å. At the surface, as depicted in Fig. 66b, the bond length between the red C atoms is 1.46 ± 0.03 Å, presenting an sp^2-sp^2 character. As for the bonds between the red C atoms and the ones underneath of them, they both present a bond length of 1.53 ± 0.03 Å, a characteristic that fluctuates between an sp^3-sp^3 and sp^3-sp^2 character. Increasing the temperature, an increase of approximately 0.02 Å in the average values for the superficial atoms is observed.

These bond length values were obtained by doing an average along all elapsed time of simulation.

7.2.1.4 Surface (113)

In Fig. 67, we present the snapshots of the (113) diamond surface configuration. The C atoms highlighted in red (Fig. 67a) have two dangling bonds each and the green ones, one dangling bond each. For this surface, we did not see surface reconstruction up to 900 °C, but at 1200 °C, a few amounts of reconstructions start to occur. According to this, this surface presents approximately 30 dangling bonds per nm² until 900 °C, and this number decreases slightly to 28 at 1200 °C. The red surface C atoms are distant approximately 2.5 ± 0.03 Å for each one.

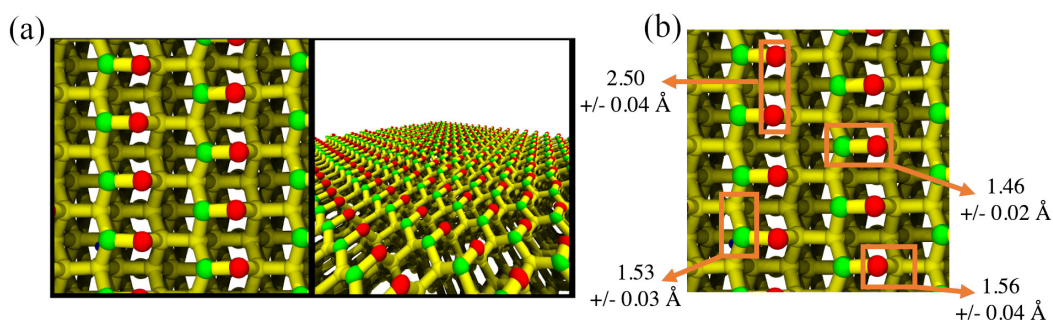


Fig. 67 Diamond surface (113) a) after a thermal equilibration at 900 °C. b) Representative bond lengths between C atoms at the surface.

As also observed for other surfaces, in the bulk part, the C–C bond length presents an average value of 1.55 ± 0.02 Å at room temperature, and this average value changes up to approximately 0.02 Å when the temperature is increased. This value is characteristic of sp^3 – sp^3 bonds, as expected for diamond. At the surface, as depicted in Fig. 67b, the bond length between the green and red C atoms (the ones with dangling bonds) is 1.46 ± 0.02 Å, presenting an sp^2 – sp^2 character. The bonds between the red C atoms with a C atom that do not have a dangling bond (see Fig. 67b) have a bond length of 1.56 ± 0.04 Å. As for the green one bonded to a C atom that does not have a dangling bond, a bond length of 1.53 ± 0.03 Å is observed. According to these bond lengths, we can consider that these bonds have an sp^3 – sp^3 character. As pointed out before, these bond length values were obtained by doing an average along all elapsed time of simulation.

7.2.1.5 Surface Stability

From our simulations, we can also evaluate the surface stability of each diamond surface studied here. This could give us an idea of the easier surface to be produced/synthesized. In Fig. 68, we present the potential energy per atom in relation to the elapsed time of MD simulation at room temperature. We did not

show the same data for the other tested temperatures as they present the same tendencies seen at room temperature. As we also observed a constancy in the potential energy after 60 ps of simulation, our graph presented in Fig. 68 shows the data obtained for 75 ps of simulation. As can be seen, the most stable surface is the (110), followed by the (013), (113), and (001). For the surface (001), we observed a decrease in the potential energy per atom up to approximately 55 ps of simulation, and this is due to the reconstructions that are happening on the surface; when the reconstruction ends, the energy remains constant (after ~55 ps). These data are in agreement with the literature, in which electronic structure simulation suggests that the surface (110) is the most stable one.^{74,75}

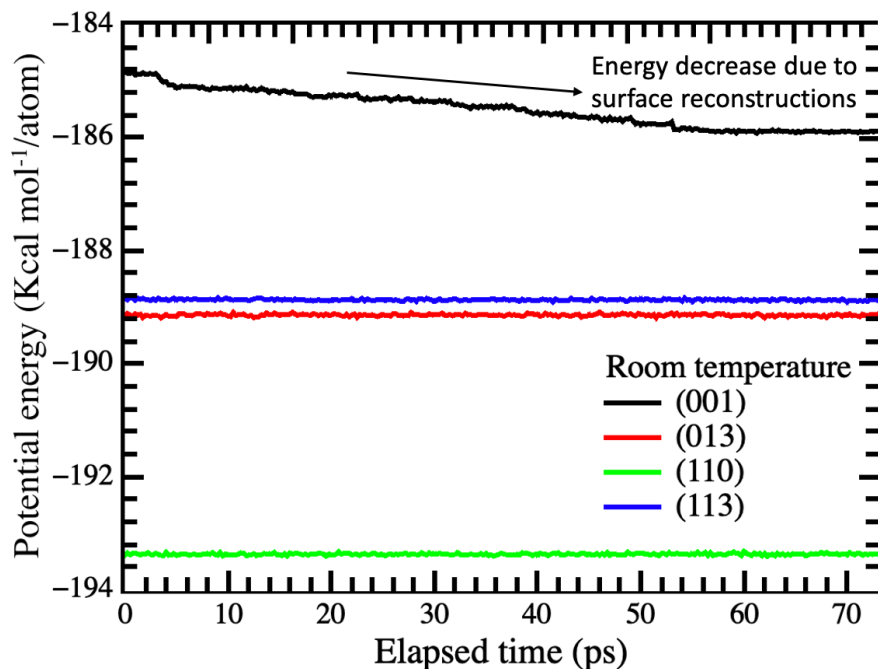


Fig. 68 Potential energy per atom in relation to the elapsed time of MD simulation at room temperature

7.2.1.6 Results for the Number of Dangling Bonds

According to the simulations performed for the bare diamond surfaces (001), (013), (110), and (113), we can now have an idea of how many spots available to hydrogenation each surface has. In Table 4, we present the available dangling bonds in each surface in relation to the temperature. As can be seen, only the surfaces (013) and (110) have a constant value of dangling bonds at the surface independent of its temperature. The (001) and (113) surfaces present some modification in the number of available dangling bonds with the temperature, but the last one presents some modification at only very high temperature (1200 °C). This information is

very relevant, since the temperature at which we want to perform the surface hydrogenation will influence the initial available dangling bonds.

Table 4 Number of dangling bonds at different diamond surfaces in relation to the temperature. These data were collected according to the results presented in the previous sections

Surface	Dangling bonds per nm ² in relation to the temperature				
	Room temperature	500 °C	700 °C	900 °C	1200 °C
(001)	30	22	19	18	18
(013)	29	29	29	29	29
(110)	22	22	22	22	22
(113)	30	30	30	30	28

7.2.2 Hydrogenation of Different Diamond Surfaces

After an extensive evaluation of the bare diamond surfaces and now having an idea of the number of available dangling bonds in each studied surface, we proceed to the hydrogenation simulations. Then, we put each diamond surface (previously thermalized in different temperatures) in contact with an atmosphere of H atoms and we tested the hydrogenation evolution in four different temperatures: 500, 700, 900, and 1200 °C. In Fig. 69a, we present snapshots of the initial configuration of each tested diamond surface in contact with the atmosphere of H atoms. Experimentally the most common temperatures in which the hydrogenation is performed are in the range of 700–900 °C using H plasma. Then, we decided to test other temperatures in order to have an idea of how much the hydrogenation changes when the process is done in different temperatures. To have an idea of the final results of each hydrogenation process, in Fig. 69b, we present the snapshots of the resulting hydrogenated diamond surfaces at 900 °C after the H incorporation saturation.

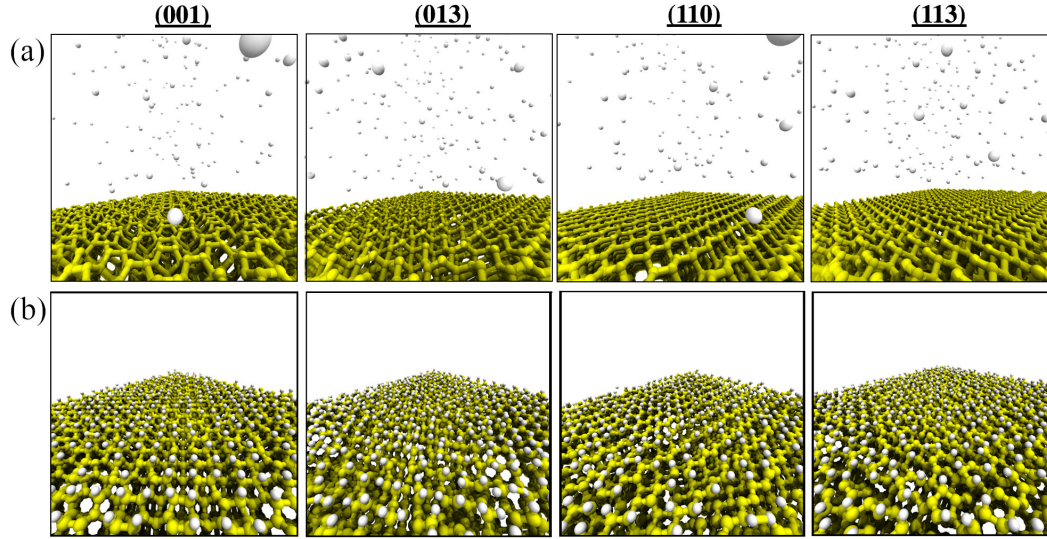


Fig. 69 a) Snapshots of the initial configuration of each tested diamond surface in contact with the atmosphere of H atoms. b) Snapshots of the resulting hydrogenated diamond surfaces at 900 °C after the H incorporation saturation.

In Fig. 70, we present the number of H atoms per nm^2 that are incorporated in each tested diamond surface in relation to the elapsed time of simulation. The data presented in Fig. 70 were fitted using an exponential function $\#H(t) = \#H0 - Ae(-t/B)$. $\#H(t)$ and $\#H0$ represent, respectively, the number of H atoms per nm^2 that are incorporated into the diamond surface in a time t (in ps) and the saturated one (when the incorporation saturates); A and B are adjusted parameters. As can be seen, it is clear the temperature effect and the contact with a different type of surface in the hydrogenation dynamics. All saturation curves suggest that independent of the temperature and type of surface, approximately 3 ps are necessary to reach the most possible H incorporation in each nm^2 of the surface.

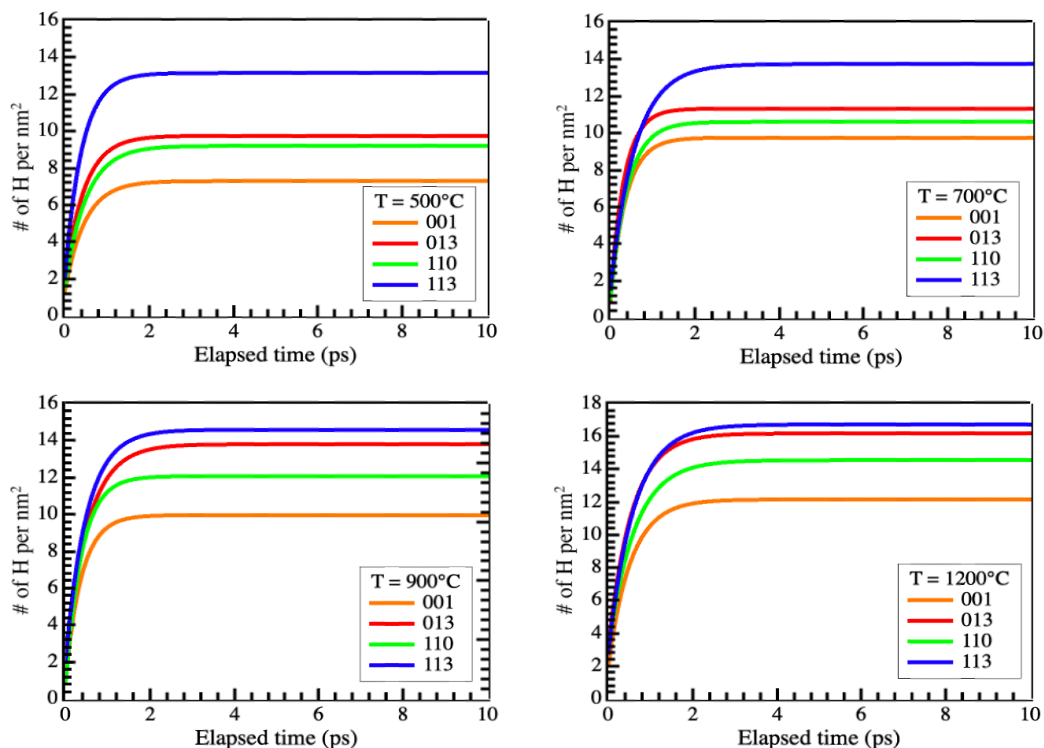


Fig. 70 Number of H atoms per nm² incorporated in each tested diamond surface in relation to the elapsed time of simulation

From the data of #H0 obtained for each curve in Fig. 70, we can evaluate the number of H atoms that can be incorporated into each surface in relation to the temperature. These data are shown in Fig. 71a. As can be seen in Fig. 71a, the number of H incorporation in relation to the temperature has an almost linear behavior for all studied diamond surfaces. The highest number of H atoms on the surface can be reached for surfaces (013) and (113); this is expected, as they have the highest number of dangling bonds (see Table 4).

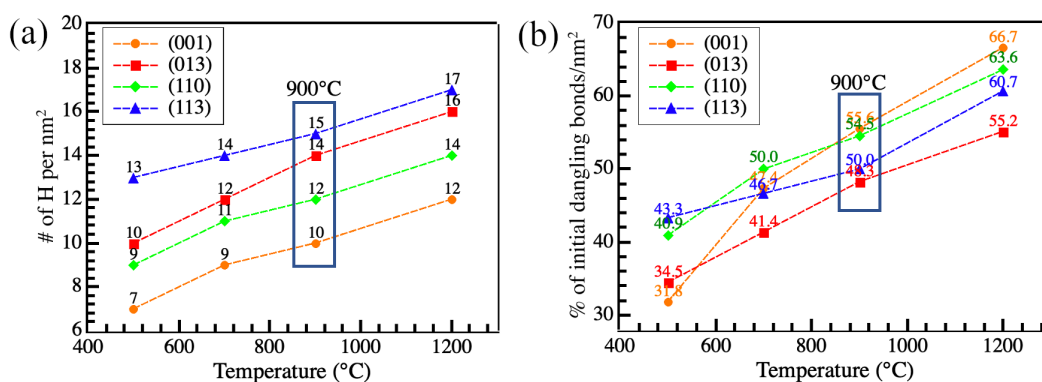


Fig. 71 a) Total number of H atoms that are incorporated in each surface in relation to the temperature. b) Percentage of the initial dangling bonds per nm² that a H atom is incorporated in relation to the temperature in each surface.

However, beyond the number of H atoms that can be incorporated at the surface, it is also important to verify which surface is most efficient in the hydrogenation process (i.e., the one in which the highest possible number of dangling bonds are consumed during the hydrogenation). To do such analysis, in Fig. 71b, we present the percentage of the initial dangling bonds per nm² that an H atom is incorporated in relation to the temperature on each surface. These percentages are based on the number of the initial dangling bonds in each temperature presented in Table 4 and the total number of H incorporations in each surface. As can be seen in Fig. 71b, the percentage of hydrogenation that can be done on the diamond surface can reach values around 60% at 1200 °C. This indicates that it is not possible to reach 100% of surface hydrogenation. From 700 °C to higher temperatures, we can see that the surfaces (001) and (110) are the most efficient surfaces to perform hydrogenation, reaching the highest percentages of the dangling bonds consumption. As the surfaces (013) and (113) present atoms with two and one dangling bonds at the surface (see the atoms highlighted in red and green in Figs. 72 and 67), the ones that have one dangling bond are less exposed (underneath) to the ones with two dangling bonds. Then, the atoms underneath the most exposed ones are less easy to reach, and this reflects in the number of hydrogenations that can be done at the surface. In conclusion, even though the surfaces (013) and (113) present the highest number of H atoms at the surface in comparison to the (001) and (110), they are not the most efficient to consume the highest possible number of dangling bonds.

7.3 Continuing Simulation Work

We have studied the characteristics of four different bare diamond surfaces—(001), (013), (110), and (113)—and the efficiency of the hydrogenation process in each one. Our results indicated that the number of dangling bonds at the surface is temperature-dependent for the (001) surface, but it has a less-pronounced effect for other tested surfaces. As the surfaces (013) and (113) have the highest number of dangling bonds (29 and 30 dangling bonds per nm², respectively), they will have the highest number of H at the surface (for example, 14 and 15 H atoms per nm² in comparison with the 10 and 12 H atoms per nm² found in surfaces (001) and (110), respectively, at 900 °C). However, as there are atoms with dangling bonds that are less easy to be reached by the H atoms in the surfaces (013) and (113), they are less efficient for hydrogenation in comparison with the surfaces (001) and (110). For example, while approximately 55% of initial dangling bonds can be consumed by the hydrogenation process at the surfaces (001) and (110), this number decreases to approximately 48% and 50% for the surfaces (013) and (113), respectively, at 900 °C. From these results, it is necessary to perform some electronic structure simulations in order to verify which condition is better: the highest number of H

atoms or the lowest number of dangling bonds at the surface. We are planning to do such simulations to clarify this point.

The future prospects for this project are to 1) evaluate the formed groups in different diamond surfaces (CH, CH₂, and eventually CH₃) after the hydrogenation process; 2) according to the results obtained from part 1, evaluate how the different hydrogenated groups at the diamond surface change the electronic properties; and finally, 3) evaluate the roughness and charge distribution before and after the hydrogenation process. After these evaluations, we could have a clear conclusion of the best conditions to perform the hydrogenation and which diamond surfaces will be recommended to be exposed to present the best performances in FET applications.

8. Collaborations between the Rice Team and DEVCOM ARL Team

The Rice team and DEVCOM ARL team have been working closely since the project starts. In addition to having biweekly meetings, both teams had a lot of interactions, discussions, and specimen exchanging. Table 5 lists some of the samples exchanged between the Rice team and DEVCOM ARL team.

Table 5 Samples exchanging between Rice and DEVCOM ARL

Exchanged samples	No. of samples	Purposes	Rice→ DEVCOM ARL	DEVCOM ARL→ Rice
Pristine PCD, SCD, ESCD	>13	Surface hydrogenation	Y	Y
Hydrogenated ESCD	3	Annealing and h-BN direct growth	Y	Y
h-BN transferred on diamond	4	Hydrogenation and electrical measurement	Y	Y
Boron implanted SCD, ESCD	5	N-type doping diamond	Y	
Diamond devices	2	Observing cross-section interfaces by FIB and TEM		Y
Oxidized diamond powder and PCD	>6	Characterizations	Y	
Patterned diamond devices	...	h-BN transfer		Y

9. Conclusions

This report assembles various research activities as part of the Cooperative Agreement (CA) between Rice and DEVCOM ARL. These efforts focus on the joint collaborative work between the two institutions in developing diamond as the next-generation, ultra-wide-bandgap material for electronic devices. The Rice team has excellent experience in the growth and development of high-quality materials and the DEVCOM ARL team has outstanding experience in developing diamond-based devices. The synergies have been developed during the first year of the project and a strong collaborative team has been formed.

With the help of the CA and significant investment from Rice, a state-of-the-art diamond growth facility has been created at the newly formed center at Rice. The facilities to grow high-quality diamond is now ready and the second year of the program will see rapid progress in the preparation of high-quality samples that will be used by the DEVCOM ARL team to build devices. Growth of SCD substrates, as well as heteroepitaxial growth of diamond and c-BN, will be a significant advance in the field. Considerable work was done during the first year to optimize the growth of high-quality h-BN and transfer these onto H-terminated diamond substrates. These samples have been sent to DEVCOM ARL for device fabrication. The creation of diamond-based heterointerfaces is the core of the project and several such heterostructures have been synthesized and characterized. Doping of diamond crystals with B has been attempted using ion implantation and this is being optimized is giving rise to new ways to dope diamond. Surface modification of both H- and O-terminated diamonds is important for device fabrication and these surface modification studies were rigorously followed to both understand the surface terminations as well as modify surface properties of diamond. The strong theoretical effort was used to support several of the experimental activities including growth, surface modification, and doping in diamond.

The development of specific metrology for diamond-based structures has been another highlight during the first-year effort. Various new techniques, such as THz spectroscopy, SHG techniques, scanning probe techniques, and so on, have been explored to enable the fast and efficient characterization of diamond surfaces in addition to conventional imaging and spectroscopy methods. Characterization of materials has been done in synergy with DEVCOM ARL researchers and facilities at DEVCOM ARL. Some of the device structures fabricated at DEVCOM ARL are being characterized in detail at Rice using FIB slicing and high-resolution transmission microscopy. The details revealed from these studies will enable optimization of the device architectures being developed at DEVCOM ARL.

A strong collaboration team has been built during the first year between teams at Rice and DEVCOM ARL. Interactions included bimonthly discussing via Microsoft Team, phone calls, specimen exchanges, joint publications (several in the pipeline), and use of the facilities at both sites. Second year will see strong interaction as the diamond substrates being grown at Rice will be directly used by DEVCOM ARL in device fabrication. The collaboration will extend to other Department of Defense labs (Air Force Research Laboratory, NRL) in the future. The work done during the first year lays the foundation for a long-term collaboration between Rice and DEVCOM ARL toward developing diamond-based, ultra-wide-bandgap electronic device 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 CA.

10. References

1. Neudeck PG; Okojie RS; Chen LY. *Proc IEEE*. 2002;90(6):1065–1076.
2. Takahashi K, Yoshikawa A, Sandhu A, Ishitani Y, Kawakami Y. *Wide bandgap semiconductors: fundamental properties and modern photonic and electronic devices*. Springer Berlin Heidelberg; 2007.
3. Davis RF, Sitar Z, Williams BE, Kong HS, Kim HJ, Palmour JW, Edmond JA, Ryu J, Glass JT, Carter CH. *Mater Sci Eng B*. 1988;1(1):77–104.
4. Chow TP, Tyagi, R. *IEEE Trans Electron Devices*. 1994;41(8):1481–1483.
5. May PW. *Sci*. 2008;319(5869):1490–1491.
6. Pau M. BW. *Phil. Trans R Soc Lond A* 2000;358:473–495.
7. Saslow W, Bergstresser TK, Cohen ML. *Phys Rev Lett*. 1966;16(9):354–356.
8. Wei L, Kuo PK, Thomas RL, Anthony TR, Banholzer WF. *Phys Rev Lett* 1993;70:3764.
9. Suzuki K, Sawabe A, Yasuda H, Inuzuka T. *Appl Phys Lett*. 1987;50(12):728–729.
10. Mokuno Y, Chayahara A, Yamada H. *Diam Relat Mater*. 2008;17(4–5):415–418.
11. Strobel P, Riedel M, Ristein J, Ley L. *Nature*. 2004;430(6998):439–441.
12. Sasama Y, Komatsu K, Moriyama S, Imura M, Teraji T, Watanabe K, Taniguchi T, Uchihashi T, Takahide Y. *APL Mater*. 2018;6(11):111105.
13. Daligou G, Pernot J. *Appl Phys Lett*. 2020;116(16):162105.
14. Song L, Liu Z, Reddy ALM, Narayanan NT, Taha-Tijerina J, Peng J, Gao G, Lou J, Vajtai R, Ajayan PM. *Adv Mater*. 2012;24(36):4878–4895.
15. Gong Y, Fei H, Zou X, Zhou W, Yang S, Ye G, Liu Z, Peng Z, Lou J, Vajtai R, et al. *Chem Mater*. 2015;27(4):1181–1186.
16. Gong Y, Shi G, Zhang Z, Zhou W, Jung J, Gao W, Ma L, Yang Y, Yang S, You G, et al. *Nat Commun*. 2014;5.
17. Song L, Ci L, Lu H, Sorokin PB, Jin C, Ni J, Kvashnin AG, Kvashnin DG, Lou J, Yakobson BI, et al. *Nano Lett*. 2010;10(8):3209–3215.
18. Liu Z, Song L, Zhao S, Huang J, Ma L, Zhang J, Lou J, Ajayan PM. *Nano Lett*. 2011;11(5):2032–2037.

19. Liu Z, Gong Y, Zhou W, Ma L, Yu J, Idrobo JC, Jung J, Macdonald AH, Vajtai R, Lou J, Ajayan PM. *Nat Commun.* 2013;4(1):1–8.
20. Ci L, Song L, Jin C, Jariwala D, Wu D, Li Y, Srivastava A, Wang ZF, Storr K, Balicas L, Liu F, Ajayan PM. *Nat Mater.* 2010;9(5):430–435.
21. Liu Z, Ma L, Shi G, Zhou W, Gong Y, Lei S, Yang X, Zhang J, Yu J, Hackenberg KP, et al. *Nat Nanotechnol.* 2013;8(2):119–124.
22. Shi G, Hanlunmyuang Y, Liu Z, Gong Y, Gao W, Li B, Kono J, Lou J, Vajtai R, Sharma P, et al. *Nano Lett.* 2014;14(4):1739–1744.
23. Chen TA, Chuu CP, Tseng CC, Wen CK, Wong HSP, Pan S, Li R, Chao TA, Chueh WC, Zhang Y, et al. *J Nature.* 2020;579(7798):219–223.
24. Hangyo M, Tani M, Nagashima T. *Int J Infrared Millimeter Waves.* 2005;26(12):1661–1690.
25. Tulsyan G. Doping profile measurements in silicon using terahertz time domain spectroscopy (THz-TDS) via electrochemical anodic oxidation [thesis]. Rochester Institute of Technology, 2015.
26. Ulatowski AM, Herz LM, Johnston MB. *J Infrared Millimeter Terahertz Waves,* 2020;1–19.
27. Neu J, Schmittenmaer CA. *J Appl Phys.* 2018;124(23):231101.
28. Baydin A, Makihara T, Peraca NM, Kono J. 2020.
29. Ulatowski AM, Herz LM, Johnston MB. *J Infrared Millimeter Terahertz Waves.* 2020;41(12):1431–1449.
30. Reyntjens S, Puers R. *J Micromech Microeng.* 2001 July 1;287–300.
31. Pennycook SJ, Chisholm MF, Lupini AR, Varela M, Borisevich AY, Oxley MP, Luo WD, van Benthem K, Oh S-H, Sales DL, et al. *Philos Trans R Soc A Math Phys Eng Sci.* 2009;367(1903):3709–3733.
32. Gruverman A, Alexe M, Meier D. *Nat Commun.* 2019.
33. Apte A, Mozaffari K, Samghabadi FS, Hachtel JA, Chang L, Susarla S, Idrobo JC, Moore DC, Glavin NR, Litvinov D, et al. *Adv Mater.* 2020;32(24):2000006.
34. De Lozanne A. *Microsc Res Tech.* 2006;69(7):550–562.
35. Eng AYS, Poh HL, Šaněk F, Maryško M, Matějková S, Sofer Z, Pumera M. *ACS Nano.* 2013;7(7):5930–5939.

36. Gildenblat GS, Grot SA, Badzian A. *Proc IEEE*. 1991;79(5):647–668.
37. Field J. *The properties of diamond*. Academic Press; 1979.
38. Crawford KG, Weil JD, Shah PB, Ruzmetov DA, Neupane MR, Kingkeo K, Birdwell AG, Ivanov TG. *IEEE Trans Electron Devices*. 2020;67(6):2270–2275.
39. Nebel CE. *New Diam Front Carbon Technol*. 2005.
40. Takeuchi D, Nebel CE, Yamasaki S. *Phys Status Solidi*. 2006;203(12):3100–3106.
41. Challinger SE, Baikie ID, Birdwell AG. In: *MRS Advances; Materials Research Society*. 2018;3:1937–1942.
42. Baikie ID, Grain A, Sutherland J, Law J. *Phys Status Solidi*. 2015;12(3):259–262.
43. Edmonds MT, Wanke M, Tadich A, Vulling HM, Rietwyk KJ, Sharp PL, Stark CB, Smets Y, Schenk A, Wu QH, et al. *J Chem Phys*. 2012;136(12):124701.
44. Fowler RH. *Phys Rev*. 1931;38(1):45–56.
45. Kasu, M. *Jpn J Appl Phys*. 2017;56:01AA01.
46. Geis MW, Wade TC, Wuorio CH, Fedynyshyn TH, Duncan B, Plaut ME, Varghese JO, Warnock SM, Vitale SA, Hollis MA. *Phys status solidi*. 2018;215(22):1800681.
47. Donato N, Rouger N, Pernot J, Longobardi G, Udrea F. *J Phys D Appl Phys*. 2020 Dec 17:38.
48. Yang Y, Koeck FA, Dutta M, Wang X, Chowdhury S, Nemanich RJJ. *Appl Phys*. 2017;122(15):155304.
49. Kohn E, Denisenko A. *Thin Solid Films*. 2007;515(10):4333–4339.
50. Kasu M, Ueda K, Kageshima H, Yamauchi Y. *Diam Relat Mater*. 2008;17(4–5):741–744.
51. Russell SAO, Sharabi S, Tallaire A, Moran DA. *J IEEE Electron Device Lett*. 2012;33(10):1471–1473.
52. Crawford KG, Cao L, Qi D, Tallaire A, Limiti E, Verona C, Wee ATS, Moran DA. *J Appl Phys Lett*. 2016;108(4):042103.
53. Perdew JP, Burke K, Ernzerhof M. *Phys Rev Lett*. 1996;77(18):3865–3868.

54. Mirabedini PS, Debnath B, Neupane MR, Greaney AP, Birdwell GA, Ruzmetov D, Crawford KG, Shah P, Weil J, Ivanov TG. *Appl Phys Lett*. 2020;117(12):121901.
55. Sque SJ, Jones R, Briddon PR. *Phys Rev B Condens Matter Mater Phys*. 2006; 73(8):085313.
56. Hofmann OT, Egger DA, Zojer E. *Nano Lett*. 2010;10(11):4369–4374.
57. Borriello I, Cantele G, Ninno D, Iadonisi G, Cossi M, Barone V. *Phys Rev B Condens Matter Mater Phys*. 2007;76(3):035430.
58. Qi D, Gao X, Wang L, Chen S, Loh KP, Wee ATS. *Chem Mater*. 2008;20(21):6871–6879.
59. Yang X, Pristovsek M, Nitta S, Liu Y, Honda Y, Koide Y, Kawarada H, Amano H. *ACS Appl Mater Interfaces*. 2020;12(41):46466–46475.
60. Liu Y, Dini K, Tan Q, Liew T, Novoselov KS, Gao W. *Sci Adv*. 2020;6(41):eaba1830.
61. Debnath B, Barlas Y, Wickramaratne D, Neupane MR, Lake RK. *Phys Rev B*. 2017;96(17):174504.
62. Dimiev AM, Tour JM. *ACS Nano* 2014.
63. Zaaba NI, Foo KL, Hashim U, Tan SJ, Liu WW, Voon CH. *Procedia Eng*. 2017;184:469–477.
64. Dimiev AM, Tour JM. *ACS Nano*. 2014;8(3):3060–3068.
65. Navas J, Araujo D, Piñero JC, Sánchez-Coronilla A, Blanco E, Villar P, Alcántara R, Montserrat J, Florentin M, Eon D, Pernot J. *Appl Surf Sci*. 2018;433:408–418.
66. Petit T, Puskar L. *Diamond Related Mater*. 2018 Oct 1:52–66.
67. Zhao F, Vrajitoarea A, Jiang Q, Han X, Chaudhary A, Welch JO, Jackman RB. *Sci Rep*. 2015;5(1):1–11.
68. Zhou CJ, Wang JJ, Guo JC, Yu C, He ZZ, Liu QB, Gao XD, Cai SJ, Feng ZH. *Appl Phys Lett*. 2019;114(6):063501.
69. Pham TT, Rouger N, Masante C, Chicot G, Udrea F, Eon D, Gheeraert E, Pernot J. *Appl Phys Lett*. 2017;111(17):173503.
70. Pierson HO. *Handbook of carbon graph diamonds fullerenes*. Noyes Publications; 1993. p. 43–69.

71. Koizumi S, Umezawa H, Pernot J, Suzuki M, eds. Power electronics device applications of diamond semiconductors. Elsevier; 2018.
72. Van Duin ACT, Dasgupta S, Lorant F, Goddard WA. J Phys Chem A. 2001;105(41):9396–9409.
73. Plimpton S. J Comput Phys. 1995;117(1):1–19.
74. Rivero P, Shelton W, Meunier V. Carbon 2016;110:469–479.
75. De La Pierre M, Bruno M, Manfredotti C, Nestola F, Prencipe M, Manfredotti C. Mol Phys. 2014;112(7):1030–1039.

List of Symbols, Abbreviations, and Acronyms

2-D	2-dimensional
2DHG	2-D hole gas
a-BN	amorphous BN
AFM	atomic force microscopy
Ar	argon
ARL	Army Research Laboratory
B	boron
BCN	boron carbon nitride
BE	binding energy
BN	boron nitride
BSE	backscatter electron
C	carbon
CA	Cooperative Agreement
c-BN	cubic BN
CFSYS	constant final state yield spectroscopy
Cr	chromium
CVD	chemical vapor deposition
Cu	copper
DC	direct current
DEVCOM	US Army Combat Capabilities Development Command
DFT	density functional theory
EA	electron affinity
E_{cb}	conduction band energy
EDS	energy dispersive spectroscopy
E_f	Fermi level
E_g	energy gap

ESCD	electronic-grade single-crystal diamond
E_v	valence band energy
E_{vb}	valence band energy
FET	field-effect transistor
FIB	focused ion beam
FTIR	Fourier transform IR
Ga	gallium
GaN	gallium nitride
GIC	graphite structure
GO	graphene oxide
H/H ₂	hydrogen
h-BCN	hexagonal BCN
h-BN	hexagonal BN
HNO ₃	nitric acid
H ₂ O ₂	hydrogen peroxide
H ₂ SO ₄	sulfuric acid
HV	high vacuum
IE	ionization energy
IPA	isopropyl alcohol
Ir	iridium
IR	infrared
KFM	Kelvin force microscopy
KMnO ₄	potassium permanganate
KP	Kelvin probe
LAMMPS	Large-scale Atomic/Molecular Massively Parallel Simulator
MCDP	10-N-methylcarbamoyl-3,7-bis(dimethylamino)phenothiazine
MD	molecular dynamics

MFM	magnetic force microscopy
MHM	modified Hummers' method
Mo	molybdenum
MoS ₂	molybdenum disulfide
MoO ₃	molybdenum trioxide
MPCVD	microwave-plasma CVD
N	nitrogen
NaNO ₃	sodium nitrate
NEA	negative electron affinity
NRL	Naval Research Laboratory
NV	nitrogen-vacancy
O	oxygen
PCD	polycrystalline diamond
PDMS	polydimethylsiloxane
pDOS	projected density of states
PES	photoemission spectroscopy
PGO	pristine graphite oxide
PLD	pulsed laser deposition
PFM	piezoelectric force microscopy
PMMA	poly(methyl methacrylate)
Pt	platinum
RF	radio frequency
RHEED	reflection high-energy electron diffraction
RUNSRA	Rice University National Security Research Accelerator
S	sulfur
SCD	single-crystal diamond
sDOS	surface-resolved density of states

SEM	scanning electron microscope
SHG	second-harmonic generation
Si	silicon
SiC	silicon carbide
SiO ₂	silicon dioxide
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
THz	terahertz
THz-TDS	THz-time domain spectroscopy
Ti	titanium
TMO	transition metal oxide
TRT	thermal release tape
UV	ultraviolet
UHV	ultrahigh vacuum
vdW	van der Waals
V ₂ O ₅	vanadium pentoxide
w-BN	wurtzite BN
WF	work function
XPS	X-ray photoelectron spectroscopy
XRD	X-ray powder diffraction

1 DEFENSE TECHNICAL
(PDF) INFORMATION CTR
DTIC OCA

1 DEVCOM ARL
(PDF) FCDD RLD DCI
TECH LIB

10 DEVCOM ARL
(PDF) FCDD RLS ER
T IVANOV
A G BIRDWELL
D RUZMETOV
M NEUPANE
P SHAH
S RUDIN
J WEIL
L DE LA CRUZ
D WASHINGTON
FCDD RLS ED
S B KELLEY