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High temperature superconductivity in diamond

Steven Prawer
UNIVERSITY OF MELBOURNE
GRATTAN ST
PARKVILLE, 3052
AU

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14. ABSTRACT
Professor Steven Prawer and his research team have taken a pioneering approach to the problem of high temperature superconductivity in diamond through two distinct avenues high energy ion implantation, and growth via chemical vapor deposition. By appropriately tuning the experimental parameters of our CVD growth, they have produced superconducting diamond in their lab for the first time. Previous studies have generally compared several samples grown under different plasma conditions, or on substrates having different crystallographic orientations in order to vary the incorporation of boron into the lattice. Instead, they have performed a study of a single sample with unchanging boron concentration, and modified the charge carrier concentration by introducing compensating defects via high energy light ion irradiation. Superconductivity is completely suppressed when the number of defects is sufficient to compensate the hole concentration to below threshold. Furthermore, they show that it is possible to recover the superconductivity by annealing the sample in vacuum to remove the compensating defects. This novel approach to the understanding of superconductivity in boron doped diamond has enabled the demonstration of the strong link between hole concentration and superconductivity in this material. To their knowledge, this is the first study which shows the ability to directly alter the superconducting properties through ion irradiation.
Professor Prawers group also advanced their work on implantation of boron to create deeply buried layers of heavily doped diamond having hole concentrations exceeding the metal insulator transition (MIT). The use of MeV implantation allows the heavily doped layers to be isolated from the confounding influences of impurities and surfaces and provides an ideal platform on which to test the underlying theory. Despite the use of advanced t

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PI and Co-PI information:

Professor Steven Prawer
School of Physics, University of Melbourne
David Caro Building (192)
Parkville VIC 3010
Australia

s.prawer@unimelb.edu.au
T: (+61 3) 8344 5460 F: (+61 3) 9347 4783

Professor Marvin Cohen
Department of Physics, University of California
366 LeConte Hall MC 7300
Berkeley, CA, 94720-7300
USA

mlcohen@berkeley.edu
T: +1 510 642 4753

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Summary: Short summary of most important research results that explain why the work was done, what was accomplished, and how it pushed scientific frontiers or advanced the field. This summary will be used for archival purposes and will be added to a publicly searchable DoD database.

Diamond, a wide band-gap semiconductor, can be engineered to exhibit superconductivity when doped heavily with boron. The phenomena has been demonstrated in samples grown by the high pressure high temperature (HPHT) and chemical vapor deposition (CVD) methods where the hole density due to boron doping exceeds the critical concentration for the metal-to-insulator transition. By extending density functional theory to model the phonon-electron coupling strength in carbon polymorphs doped with light atoms, Marvin Cohen has predicted that the remarkably strong coupling strengths in these materials gives the potential for critical temperatures as high as 290 K. We wish to push experiment, where the current state of the art is T_c ~ 10 K, further towards this theoretical prediction.

The basic model suggested by existing theoretical and experimental results is that the critical temperature T_c in diamond should scale monotonically with increasing boron concentration. Given that equilibrium processes for growth such as HPHT are limited by the solubility of boron in diamond (approximately 2.8%) it is clear that non-equilibrium fabrication methods such as chemical vapor deposition and ion implantation must be pursued. However, there is not a straightforward dependence of T_c on boron concentration, with experimental data in the literature showing significantly different T_c for samples having nominally the same boron concentration. Our understanding of superconductivity in diamond is clearly not complete.

We have taken a pioneering approach to the problem of high temperature superconductivity in diamond through two distinct avenues – high energy ion implantation, and growth via chemical vapor deposition. By appropriately tuning the experimental parameters of our CVD growth, we have now been able to produce superconducting diamond in our lab for the first time. Previous studies have generally compared several samples grown under different plasma conditions, or on substrates having different crystallographic orientations in order to vary the incorporation of boron into the lattice. We have instead performed a study of a single sample with unchanging boron concentration, and instead modified the charge carrier concentration by introducing compensating defects via high energy light ion irradiation. Superconductivity is completely suppressed when the number of defects is sufficient to compensate the hole concentration to below threshold. Furthermore, we show it is possible to recover the superconductivity by annealing the sample in vacuum to remove the compensating defects. This novel approach to the understanding of superconductivity in boron doped diamond has allowed us to demonstrate the strong link between hole concentration and superconductivity in this material. To our knowledge is the first study which shows the ability to directly alter its superconducting properties through ion irradiation.

We have also continued our work in implantation of boron to create deeply buried layers of heavily doped diamond having hole concentrations exceeding the metal insulator transition. The use of MeV implantation allows the heavily doped layers to be

isolated from the confounding influences of impurities and surfaces and provides an ideal platform on which to test the underlying theory. In order to reach the high boron concentrations required for superconductivity, the implantations were performed at high temperatures to prevent graphitization and preserve the important property of high atomic order critical for high temperature superconductivity. Despite the use of this technique and a comprehensive post-implant annealing study, the boron implanted diamond with carrier concentration well above the MIT has still not been made to superconduct.

However, using this high quality, high boron density material, we have now performed preliminary investigations into using a pulsed laser annealing technique to induce superconductivity. Recent studies of novel non-diamond phases of carbon such as “Q-carbon”, an amorphous quenched allotrope of carbon, have resulted in high temperature superconductivity at critical temperatures up to 55K. Fabricating this material relies on rapid nanosecond laser melting of multilayered boron/carbon films in a super undercooled state, and subsequent quenching. We have now created multilayered boron implants in diamond, with the goal of using nanosecond laser melting of the buried layers to create single-crystal material with high boron incorporation. We anticipate that this technique may allow sufficient repair of ion implantation related damage, and allow the observation of superconductivity. This technique would allow the direct writing of superconducting circuits in diamond, with possible applications in single photon detectors.

Introduction: Include a summary of specific aims of the research and describe the importance and ultimate goal of the work.

The goal of this research was to investigate the potential of diamond as a high temperature superconductor. Given that intrinsic diamond is also an electrical insulator, has an exceptionally high dielectric strength, and conducts heat even more effectively than copper, a diamond based superconductor would be very robust and versatile. This unique combination of properties make it an ideal material for future electronics, superconducting quantum devices, integrated photonic circuits, or sensitive detectors. Engineering diamond with high critical temperature is expected to lead to concrete practical applications in these fields.

The specific aims of the research as described in the original proposal were:

- Elucidation of the mechanism of superconductivity in diamond.
- Critical tests of the theory of high temperature superconductivity as proposed by Marvin Cohen.
- Evaluation of the properties of superconducting diamond based devices
- Training of research students, both post-graduate and on post-doc level

Marvin Cohen's theory has predicted that new superconducting phases exist with remarkably strong coupling strengths leading to the potential for very high critical temperatures. In particular, the theory predicts boron doped diamond should display superconductivity at temperatures perhaps as high as 290 K. If this theory can be proved to be correct, we will have established a robust method for predicting new superconducting phases, with obvious important practical implications. However, despite more than a decade of work since its discovery, the physical mechanism of superconductivity in diamond is not fully understood and the highest recorded critical temperatures are still on the order of only 10 K.

In pursuit of these goals we have investigated the development of a process to implant boron ions into diamond plates to create superconducting, sub-surface layers. These layers hold great promise for the emergence of superconductivity at relatively high temperatures provided the carrier density can be made high enough and the crystal damage is minimized through in-situ dynamic annealing, and post implant high-temperature annealing techniques. The short-term goal of is to show that the critical temperature of boron-doped diamond increases with hole concentration. To this end we have developed and refined experimental protocols to fabricate such samples via both boron implantation and chemical vapour deposition. We have analyzed their crystal integrity using Raman spectroscopy, and developed the software and techniques to electronically characterize these conducting layers as a function of both temperature and magnetic field.

The ultimate goal of the work is to develop superconducting diamond technology and expertise to create robust, useful devices that can operate in high-magnetic fields and at relatively high temperatures.

Experiment: Description of the experiment(s)/theory and equipment or analyses.

A summary of the main experimental investigations carried out follows below:

MeV energy ion implantation with In-Situ Dynamic Annealing

Boron ions were implanted into single crystal diamond plates of both optical and electronic grade, supplied by Element6. The diamond plates are high purity type-IIa samples made via a commercial chemical vapor deposition process (CVD), with the optical grade containing nitrogen impurities at a parts per million (ppm) concentration, and electronic grade at a parts per billion (ppb) concentration. A/Prof. Jeffrey McCallum implanted a number of 4x4x0.5 mm diamond plates at the National Collaborative Research Infrastructure Strategy (NCRIS) Heavy Ion Accelerator facility at the Australian National University in Canberra. The implant used an ion energy of 1 MeV and a fluence of $1x10^{17}$ B/cm^2. An isotope enriched 99% pure boron-10 powder, purchased from Trace Sciences International, was used as the ion source. This isotope is lighter than natural boron and aims to take advantage of the isotope effect in superconductors, where lighter isotopes have higher critical temperatures.

A challenge for the implantation of diamond, which is metastable at standard temperature and pressure, is the likelihood of relaxation to graphite under strain. The destructive ion implantation process causes significant damage to the crystal lattice, increasing the likelihood of graphitization. Room temperature implantation above the critical dosage, ~2.95 g/cm^3 or 10^{22} vacancies/cm^3, causes irreversible graphitization, even after high pressure high temperature (HPHT) annealing. To reduce the formation of structural damage, phase relaxation, and charge traps, in-situ dynamic annealing (i.e. “implanting hot”) was used which has been shown to prevent graphitization for implant temperatures above 700 K. Previous studies of multiple low energy implantation at high temperatures have shown an absence of superconductivity, however MeV ion implantation is advantageous as it maintains an undamaged diamond cap. In combination with shadow masking techniques, ion implantation of boron into diamond forms an embedded thin film under lateral and longitudinal pressure, an essential feature for an elevated electronic spring constant, potential two-dimensionality, and higher T_c.

Annealing study for lattice repair and dopant activation

Thermal annealing is a common process used to repair crystal damage and activate electrical conduction after ion implantation. Boron implanted diamond requires high temperature thermal annealing to electrically activate the implanted ions due to its high internal pressure and density. Lattice vacancies become mobile at approximately 600 C, and implantation damage is healed around 1200 C, however this is not hot enough to activate B ions. The presence of oxygen whilst annealing may cause the diamond to burn, hence a high vacuum furnace is required to activate implanted boron and repair the diamond lattice. High temperature annealing of the implanted diamond plates was performed using the electron beam of a Thermionics metal evaporator, which was used to indirectly heat the sample through a graphite crucible. The vacuum in this system could be maintained to $5x10^{-5}$ mbar throughout the anneal process. An annealing study was performed where five samples implanted with boron at identical energy and fluence were each processed with different annealing temperature. The effect on the sample was determined through Raman spectroscopy and direct electrical measurements in a dilution refrigerator.

CVD Growth of Samples

Given the challenges involved with fabricating superconducting samples from boron implanted diamond, we began an investigation of CVD growth of this material and subsequently produced superconducting diamond for the first time in our lab.

The heavily boron-doped diamond samples were mostly fabricated at the Melbourne Centre for Nanofabrication (MCN) using substrates sourced from Element Six. The substrates are single-side polished to have nucleation sites for reactions at the sample surface, with four laser-cut edges with <100> orientation. The surface orientation is also in the <100> direction, and with correct tuning of the plasma parameters, the growth layer is expected to form epitaxially with <100> orientation. The diamond substrates are standard grade Type-Ib diamonds, having low nitrogen content of < 200 ppm.

Growth of superconducting diamond in a highly dense CVD plasma

A Seki diamond tool 6300 at the MCN was used for fabricating diamond films. The microwave assembly consists of 1.5 kW power supply, a symmetric plasma coupler, a dummy load for absorbing reflected power, a rectangular waveguide propagating TE_{10} EM mode which is connected to the reactor chamber and magnetron head, a three stub tuner for minimising reflected power and making the plasma power approximately the same as the forward power. The three stub tuner was used especially when changing plasma density by tuning pressure or pedestal size. The forward power is used for activating the gas molecules near the substrate stage. The cavity itself consists of a tunable-height cylindrical sample stage which is made of molybdenum in order to survive the high temperature environment during growth. One can control the temperature by tuning the plasma pressure and power. In general, higher plasma density concentrated into a small region results in high substrate temperature. By balancing between the hydrogen plasma pressure and power, one can create optimal growth conditions, which avoids graphitization of the diamond substrate and enables the growth of high-quality single crystalline homo-epitaxial diamond.

The sample substrate is placed on two 2.93 mm thick circular or square molybdenum pedestals to provide a further degree of freedom for substrate height adjustment relative to the plasma ball. In addition, the actual dimensions of the pedestals modify the cavity boundary conditions and help to confine the plasma to a region of that size on top of the pedestal itself, ensuring the sample is sitting in a small, dense plasma. A large dependence of T_c was found on the dimensions of this pedestal. A circular molybdenum puck is placed underneath the pedestals for defining boundary conditions of the cylindrical reaction chamber.

It takes 100 sccm of H_2 for initial plasma ignition, under the condition of 10 Torr chamber pressure and 400 W of microwave plasma. The plasma power is generally ramped up along with increased hydrogen flow rate and plasma pressure. Further adjustments are done by looking at the temperature of the substrate and plasma conditions, to accommodate for the desired plasma pressure and power.

The first half of the growth runs for 18 hours in order to grow a buffer layer, which is an unintentionally boron doped layer that fits between diamond lattice and the heavily boron doped lattice, acting as a quality control for producing single crystalline diamond successfully in the following heavily doped growth. We have also grown samples without a buffer layer.

Irradiation Study

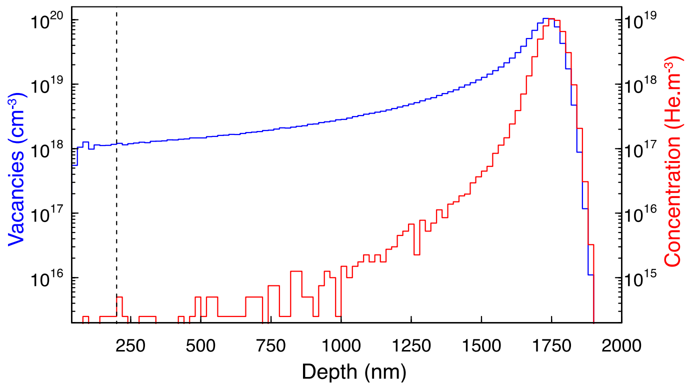
The absence of superconductivity in boron implanted samples despite our best efforts made it increasingly clear that the presence of even small amounts of damage, nanoscale disorder, or point defects could quench the superconductivity. In order to gain further insight into the mechanism for superconductivity in boron doped diamond, and to determine its robustness to damage and the effect on critical temperature, an irradiation damage study of a superconducting sample grown by CVD was performed. The aim was to systematically introduce disorder and damage into a known-good superconducting system with fixed boron concentration to investigate its effect, rather than what is typically done in the literature – a study of a large number of samples grown under different CVD plasma conditions.

A sample was grown homoepitaxially on a 3x3 mm Type-Ib <111> oriented substrate via microwave plasma assisted CVD using the method of Prof. Hiroshi Kawarada of Waseda University, a world leader in superconducting diamond growth. The substrate was held at 850ºC with a microwave power of 400 W and chamber pressure of 110 Torr consisting of a dilute gas mixture of methane and trimethylboron (TMB) in hydrogen. The methane concentration was 5% in hydrogen with a [TMB]/[CH_4] ratio of 20,000 ppm, and growth was carried out for 20 minutes resulting in a superconducting BDD cap layer of 200 nm thickness.

The as-grown sample demonstrated p-type conduction, with a hole concentration of $3.8x10^{21}/cm^3$ at ambient temperature, and was measured to have a superconducting critical temperature of T_c = 8.0 K and critical field in excess of 9 T. We define T_c as the temperature at which the resistivity of the sample was reduced to 50% of its normal-state resistivity at 15 K.

After growth and initial electrical characterisation, a systematic study was carried out in which the sample was repeatedly subjected to irradiation with a 1 MeV helium ion beam, followed by electrical characterisation at cryogenic temperatures. The fluence of the ion beam was increased with each irradiation and measurement cycle, ranging between 1x10^{12}/cm^2 and 5x10^{16}/cm^2, at which point superconductivity was completely quenched. In each irradiation, the ion beam was raster scanned over a 4x4 mm^2 region, ensuring the whole sample was uniformly irradiated. The irradiation was performed with the sample held at room temperature 295 K, and under vacuum of 4x10^{-6} Torr, oriented ‘face on' to the beam at a small misalignment angle of 3° to avoid ion channelling. During the irradiation, the sample was glued and wire-bonded into a ceramic chip carrier. Wire-bonds were made to evaporated Ti/Au electrical contact pads of thickness 100 nm and 20 nm respectively, with the bonds reinforced using a generous thickness of silver paste (~300 µm). The contact pads were evaporated in a typical van der Pauw configuration at the edges of the sample, having a diameter more than an order of magnitude smaller than the sample dimensions.

The choice of helium as the implant species was made in order to ensure the damage distribution was nominally uniform throughout the boron doped top layer, with the end-of-range of such light ions lying deep inside the substrate, well beyond the doped region. This was confirmed by modelling the *Stopping and Range of Ions in Matter* (SRIM) software. The heavy damage and amorphization of the lattice from the ions was thus placed deep in the insulating, unmeasured substrate, and only point defects from ion track damage were introduced into the superconducting surface layer. The effect of ion irradiation damage in the contact pad regions is limited to the very surface of the thick reinforcing silver paste layer, effectively shielding the evaporated ohmic contact pads and the superconducting diamond region directly underneath them. The sub-contact regions remaining unirradiated does not affect the electrical measurements, as the path of the current in the van der Pauw measurement is across the bulk irradiated sample region.



Vacancy density and end of range as modelled by SRIM

Each resultant vacancy acts as a donor which will compensate the hole introduced by a single substitutional boron atom. Thus, without changing the concentration or distribution of boron in the sample, it becomes possible to progressively compensate more and more holes until the superconductivity is quenched.

After each irradiation, the sample underwent standard electrical and Hall measurements at room temperature and magnetic fields up to 0.7 T to determine resistivity, mobility, and charge carrier density. The sample was then mounted in a dilution refrigerator and cooled to approximately 50 mK while undergoing four-terminal resistance measurement using standard low noise lock-in amplifier techniques. All measurements were made in a four-terminal van der Pauw configuration using the same pair of contacts for driving current and measuring voltage each time.

Preliminary investigation of pulsed laser annealing

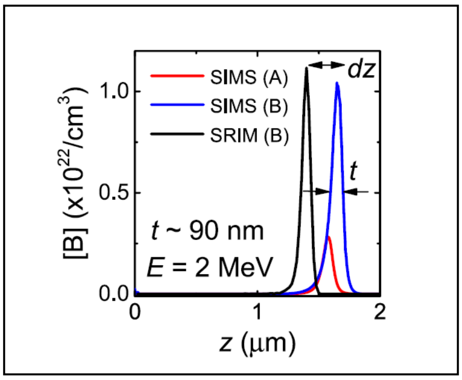
Recent studies of novel non-diamond phases of amorphous carbon such as “Q-carbon” have resulted in high temperature superconductivity at critical temperatures up to 55 K. Motivated by these results, which relied on nanosecond laser melting of alternating thin films of boron and carbon, we began preliminary investigations into pulsed laser melting of our boron implanted samples. The goal of the pulsed laser annealing is to successfully incorporate the boron into the diamond lattice through the formation of the necessary boron-carbon bonds that are seen to directly cause superconductivity. Rapid melting and super-undercooled quenching effectively allow ‘solute trapping’ of boron in the diamond lattice, allowing highly non-equilibrium concentrations of boron to be incorporated.

We have utilised our 20ns pulse length 532nm Laser Micro Cutting System (Alpha) from Oxford Lasers to undertake a preliminary study of the laser power and focus required for pulsed annealing in our boron implanted samples. Raman spectroscopy was performed of the buried layer after laser treatment to search for the presence of strong boron peaks, or damage from amorphization.

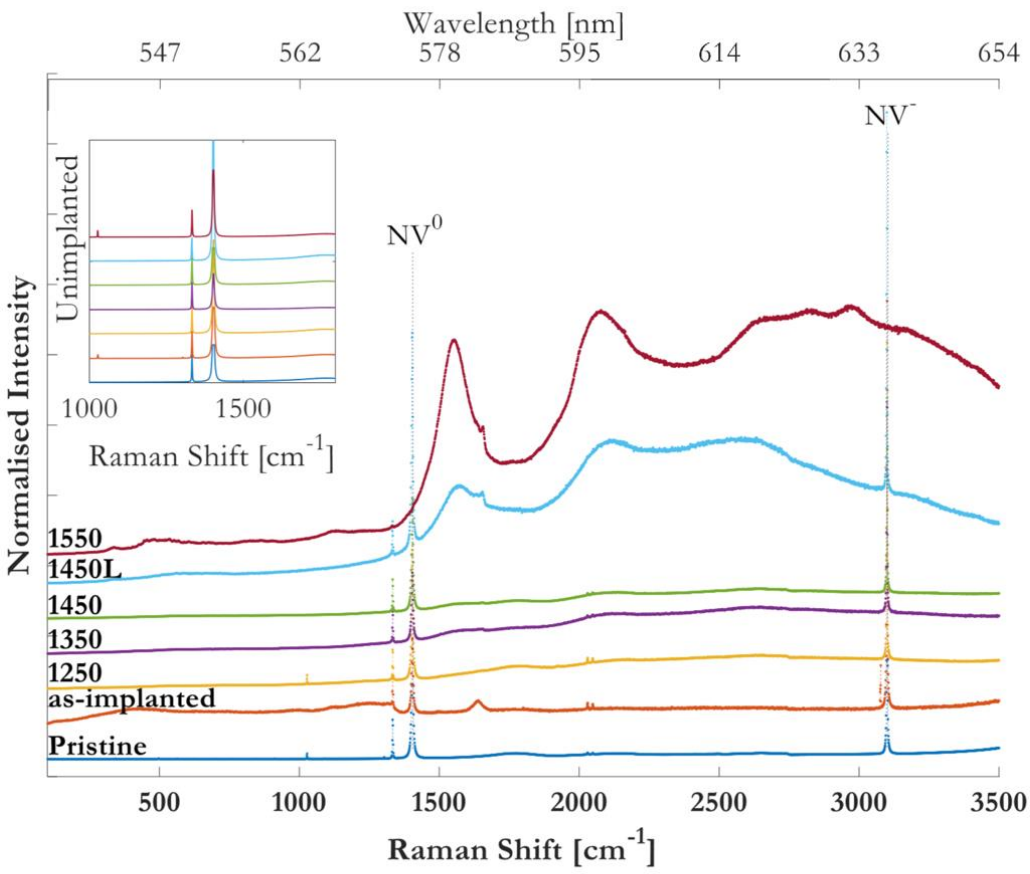
Results and Discussion: Describe significant experimental and/or theoretical research advances or findings and their significance to the field and what work may be performed in the future as a follow on project. Fellow researchers will be interested to know what impact this research has on your particular field of science.

In-situ dynamic annealing, and post implant annealing results

High energy boron implants were performed at elevated temperatures of 600ºC to take advantage of the in-situ dynamic annealing. Post-implant annealing was also performed for the repair of the diamond lattice. We show using spectroscopic measurements clear evidence of lattice repair above 1200ºC, but electronic measurement of the samples at low temperature showed no evidence of a superconducting transition.



Following the irradiation, SIMS measurements (see panel to the left) showed that a peak B concentration of 1.0 x 10^{22} B/cm^3 or 6 at.%. This is far in excess of the solubility limit for B in diamond, and far in excess of the boron concentration required to reach the metal insulator transition. It is also far in excess of the level of damage which usually causes

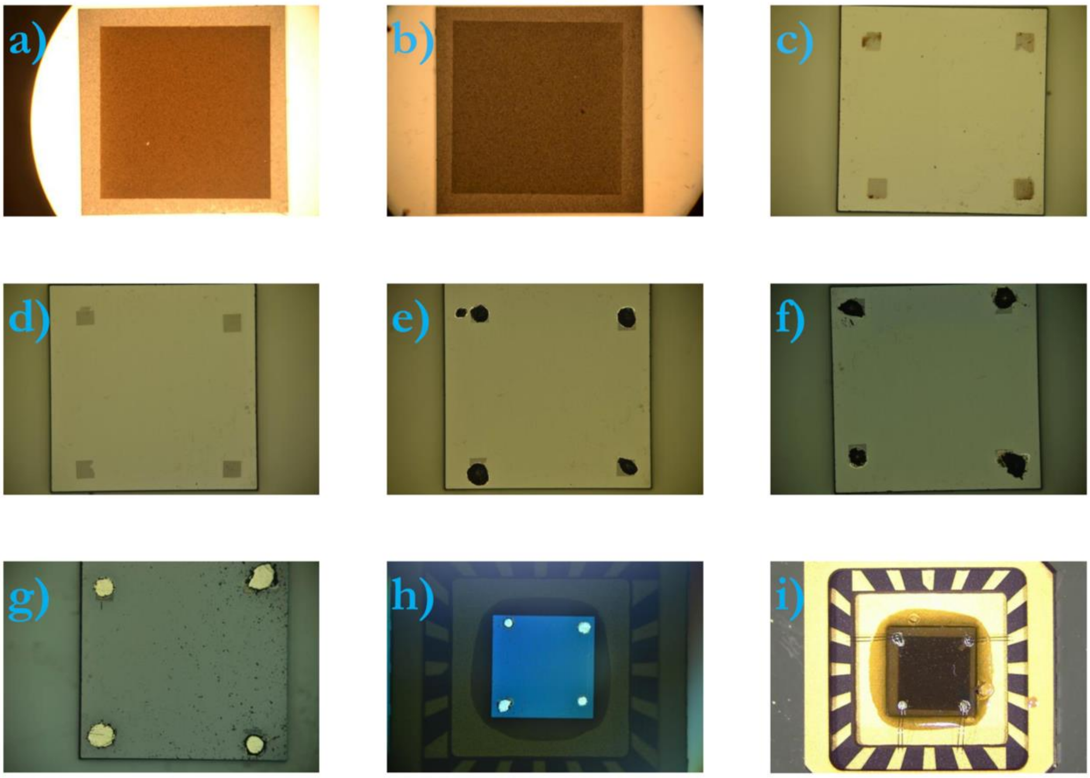


Low temperature Raman spectra of heavily B doped samples annealed at different temperatures.

amorphization and graphitization of the diamond lattice. But because the diamond was held at an elevated temperature during the implantation, we were able to avoid the graphitization to produce a very heavily B doped layer that is still intact diamond.

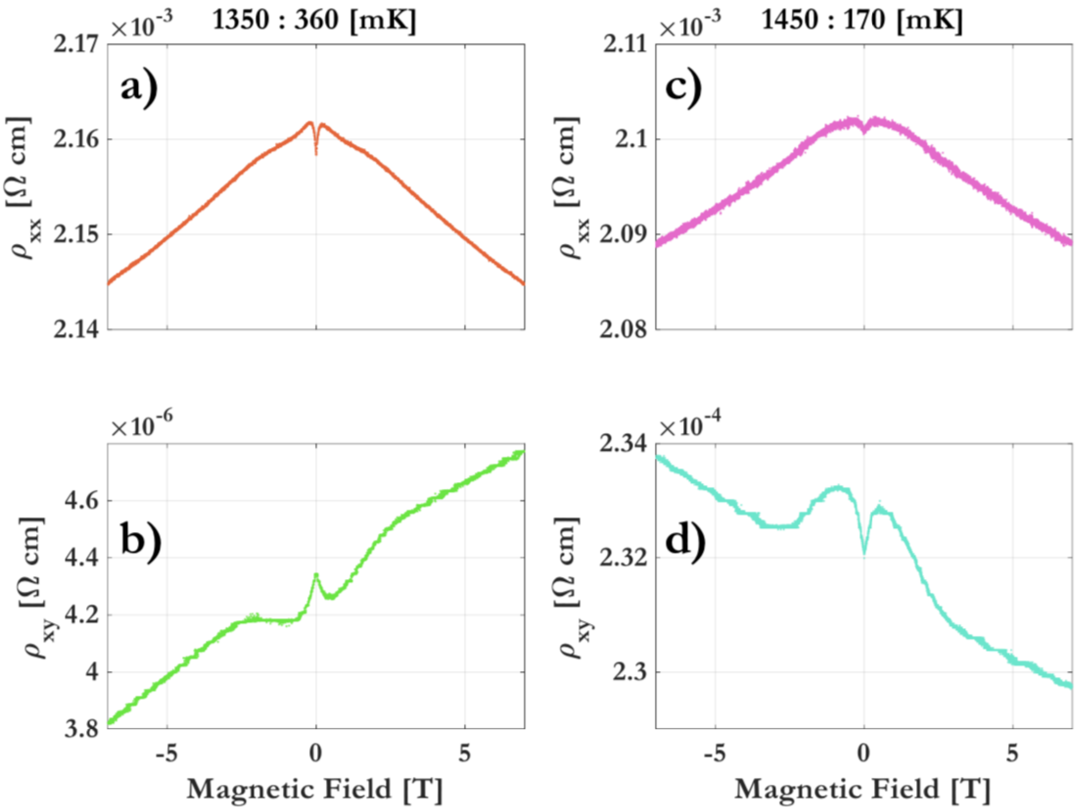
Raman spectroscopy was used to assess the degree of residual damage as implanted, and after annealing. The Raman measurements shown above demonstrate that an annealing temperature of 1450C is optimal for removal of residual defects. Higher temperatures result in graphitization and lower temperatures left many defects (mainly vacancies and interstitials) unannealed.

The fabrication process for the samples placed the contact pads in a van der Pauw configuration to allow accurate electrical characterization, and is described in the figure below:



Schematic of the fabrication procedures involved in the development of subsurface conducting devices. a) Transmitted light upon the as-implanted diamond with edges masked by a Mo holder. b) Transmitted light upon a sample annealed at 1450° C. c) Reflected light upon laser percussion holes with ablation damage and d) reflected light upon plasma cleaned percussion holes with ablation removed. e) Ag-ABA placed atop the diamond pre-alloy and f) Ag-ABA melted atop diamond. g) Reflected light upon Au-ABA alloyed and polished. h) Reflected light using a half-wave plate and optical polariser to illuminate the implanted region post-processed. h) Reflected white light illuminating Al wires bonded atop the Au-ABA and in a Spectrum Semiconductor Materials Inc. 20 lead chip carrier..

Sadly, detailed electrical measurements at low temperature did not reveal superconductivity in any of the annealed samples. Whilst hole conduction is expected in boron doped diamond, which would be indicated by a positive Hall slope when measured under magnetic field, both positive and negative hall slopes were observed for different annealing temperatures. The origin of the apparent n-type conduction has not been determined. Additionally, large low-field scattering effects similar to weak-localisation are seen. It is clear that disorder and defects are present, despite the evidence from Raman spectroscopy of excellent annealing. This prompted a different approach as outlined in the next section.



Comparisons of the 1350ºC (a,b) and 1450ºC (c,d) sample measured at 361 mK and 170 mK respectively. We clearly show negative magnetoresistance for a) the 1350C and c) the 1450C samples whilst observing b) a positive Hall voltage for 1350ºC and d) a negative Hall voltage for the 1450ºC sample.

Sample Anneal [°C]	Temperature [mK]	n_s [cm^{-2}]	μ_H [$cm^2V^{-1}s^{-1}$]	μ_{GMR} [$cm^2V^{-1}s^{-1}$]
1250	40	$8.183(5) \times 10^{15}$	1.437(60)	0.057(2)
1350	41	$7.03(7) \times 10^{15}$	2.46(1)	0.0389(12)
	90	$7.28(7) \times 10^{15}$	2.44(3)	0.0143(1)
	361	$2.18(1) \times 10^{16}$	0.618(2)	0.0154(3)
1450	38	$9.71(89) \times 10^{15}$	2.46(10)	0.041(1)
	170	$6.74(2) \times 10^{15}$	2.64(1)	0.0171(1)
1550	38	$4.06(9) \times 10^{16}$	10.88(23)	0.016(1)

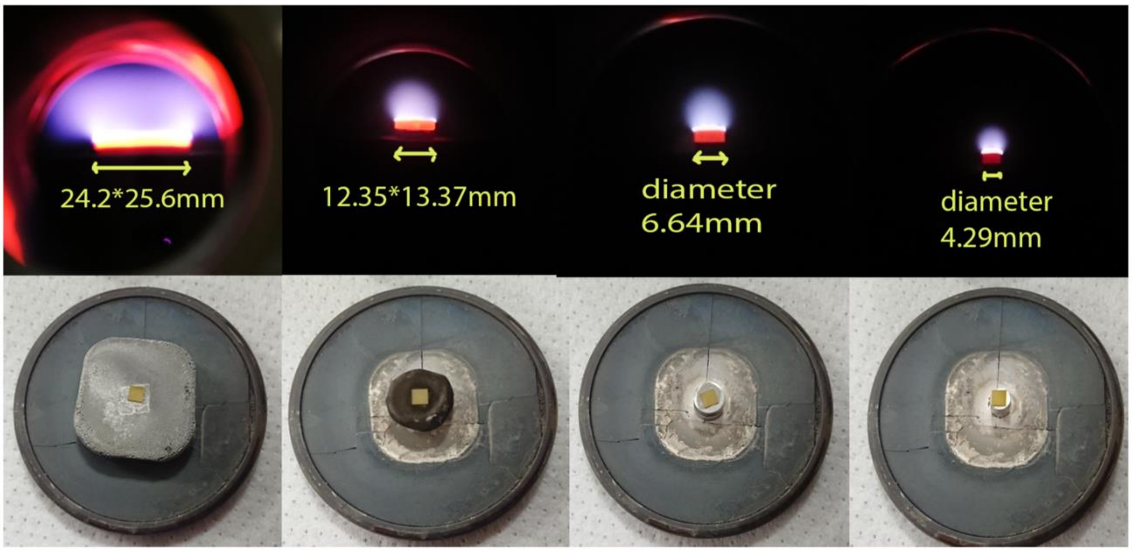
Summary of carrier density and mobility as a function of measurement temperature and annealing temperature

Results of CVD Growth of Superconducting Samples

After a fruitful collaboration with Professor Hiroshi Kawarada of Waseda University, we have been now been able to successfully grow superconducting diamond in our lab via CVD for the first time. Much work was done to determine and optimize the best plasma parameters and growth conditions. After growth, the samples were characterized via Raman spectroscopy and via electrical measurements in a Hall effect system and dilution refrigerator to determine their carrier density and critical temperature and field.

We provide some pertinent details here of the growth conditions: these details are often not provided in publications but prove to be essential for obtaining superconductivity

The growth conditions that are tunable with the Seki 6300 diamond tool used for growth are the flow rate of hydrogen, methane, oxygen and TMB, and the chamber pressure and microwave power. These parameters correspond to gas flow rate, plasma size and temperature. Further tuning can be done by adjusting the gap between the puck and the graphite susceptor underneath, however this feature was not changed throughout our experiments. We found that growth recipes are highly dependent on the vagaries of an individual CVD reactor and the geometry of the sample stage upon which the diamond substrate is placed. Exploration of the parameter space is essential for optimising growth conditions in one's own system.



Side to side comparison of pedestals used for diamond growth. From left to right: L, M, S, and XS size

Perhaps the most important parameter we found for increasing the hole density in the CVD boron doped layer, and thus achieving superconductivity, was the diameter of the sample stage and thus the plasma density. A small, dense plasma is essential in order to produce superconducting material. We used four different sizes of pedestal (XS, S, M, and L), but the height of the pedestals remained the same during all growth runs in order to keep the position of the diamond substrate at the centre of the plasma ball. The effect on the plasma sizes achievable by varying the diameter of the pedestal is readily seen by inspection. Note that the first and second pedestals were made in a quick manufacturing process as they are not perfectly cylindrical.

Pedestal size	Pedestal dimension	Plasma volume (mm^3)	Microwave power density (W/mm^3)	Carrier concentration ($cm^{-}3$)
L	24.2×25.6 mm	8440	0.107	4.167×10^{20}
M	12.35×13.37 mm	1650	0.303	2.407×10^{21}
S	⌀6.64mm	469	0.533	6.601×10^{21}
XS	⌀4.29mm	77.07	2.790	-

Despite the chamber pressure being different from recipe to recipe, the plasma volume is mainly defined by the pedestal size. Essentially, when one uses smaller pedestal the main parameter that changes is the boundary condition for the TM resonance mode in the cylindrical cavity through the impedance matching system, and hence the plasma size and plasma density. Growth with the M size, S size and XS size pedestals all resulted in samples having a superconducting transition above 50 mK, the lower limit of measurement in our dilution refrigerator.

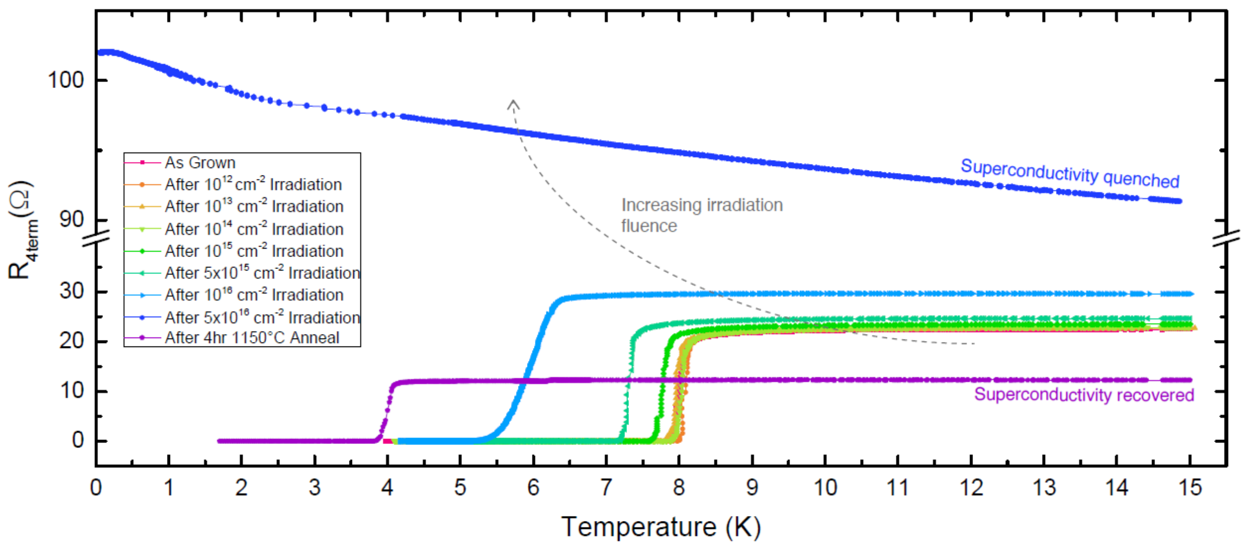
Using the pedestal to concentrate the plasma we were able to obtain films with a Tc of 3-4K and a critical field of circa 9T. However, the results of measurements on our samples revealed that in the future, the growth needs to be done on <111> oriented diamond substrates as this always results in higher T_c than <100> diamond.

Irradiation study results

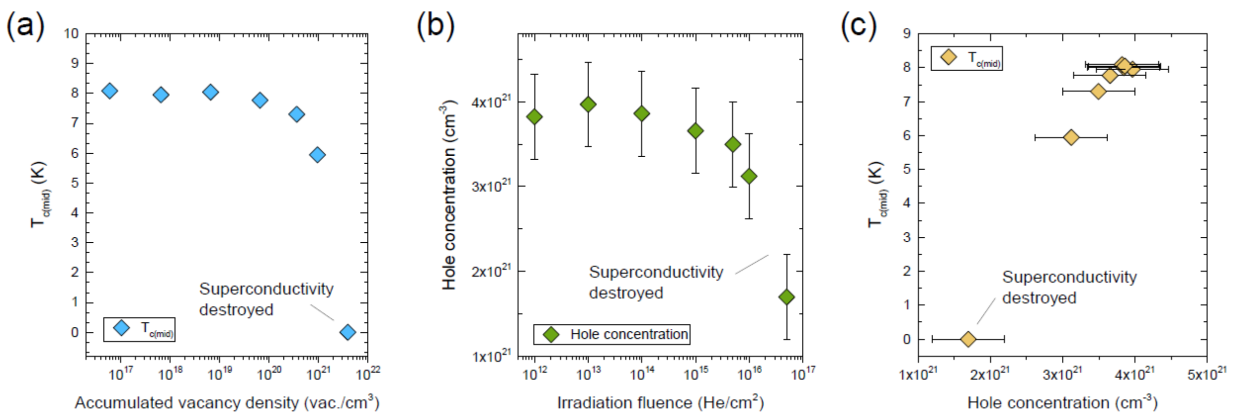
Whereas previous work has compared CVD boron doped diamond layers of differing thickness, boron concentration, crystallographic orientation, and almost certainly differing local disorder at the nanoscale, we have instead studied a single sample of fixed boron concentration. Irradiation with high energy light ions was used to systematically compensate boron acceptors through the introduction of vacancies, with one single vacancy capable of compensating one single substitutional boron atom. Thus, the density of states at the Fermi level E_F is reduced, and correspondingly the T_c also decreases. Our data shows good agreement with this simple picture, with the measured concentration of acceptors (holes from substitutional boron) reduced by the accumulated number of donors (vacancies as modelled by SRIM) with each iteration of the irradiation and measurement process. At the point where the hole concentration is compensated beyond the threshold for superconductivity near the metal-to-insulator transition, superconductivity is quenched as expected. After annealing, we show that superconductivity can be recovered by way of removing the introduced point defects.

The figure below shows the four-terminal resistance of the sample below 15 K as a function of helium ion irradiation fluence, and the table shows parameters such as irradiation fluence, defect concentration in the 200 nm superconducting cap layer as modelled by SRIM, superconducting critical temperature, and the hole concentration and mobility determined from electrical measurements. To within the error of the measurement, no change in T_c was seen for an irradiation fluence up to $1x10^{14}/cm^2$. At fluences above this level, three general trends were observed:

• The bulk resistivity of the sample (measured cryogenically, above Tc) increased with increasing fluence,
• The superconducting Tc decreased, as well as the charge carrier (hole) concentration nH
• The width of the superconducting transition, i.e. the difference between the onset of superconductivity and the offset (zero resistance) was broadened.



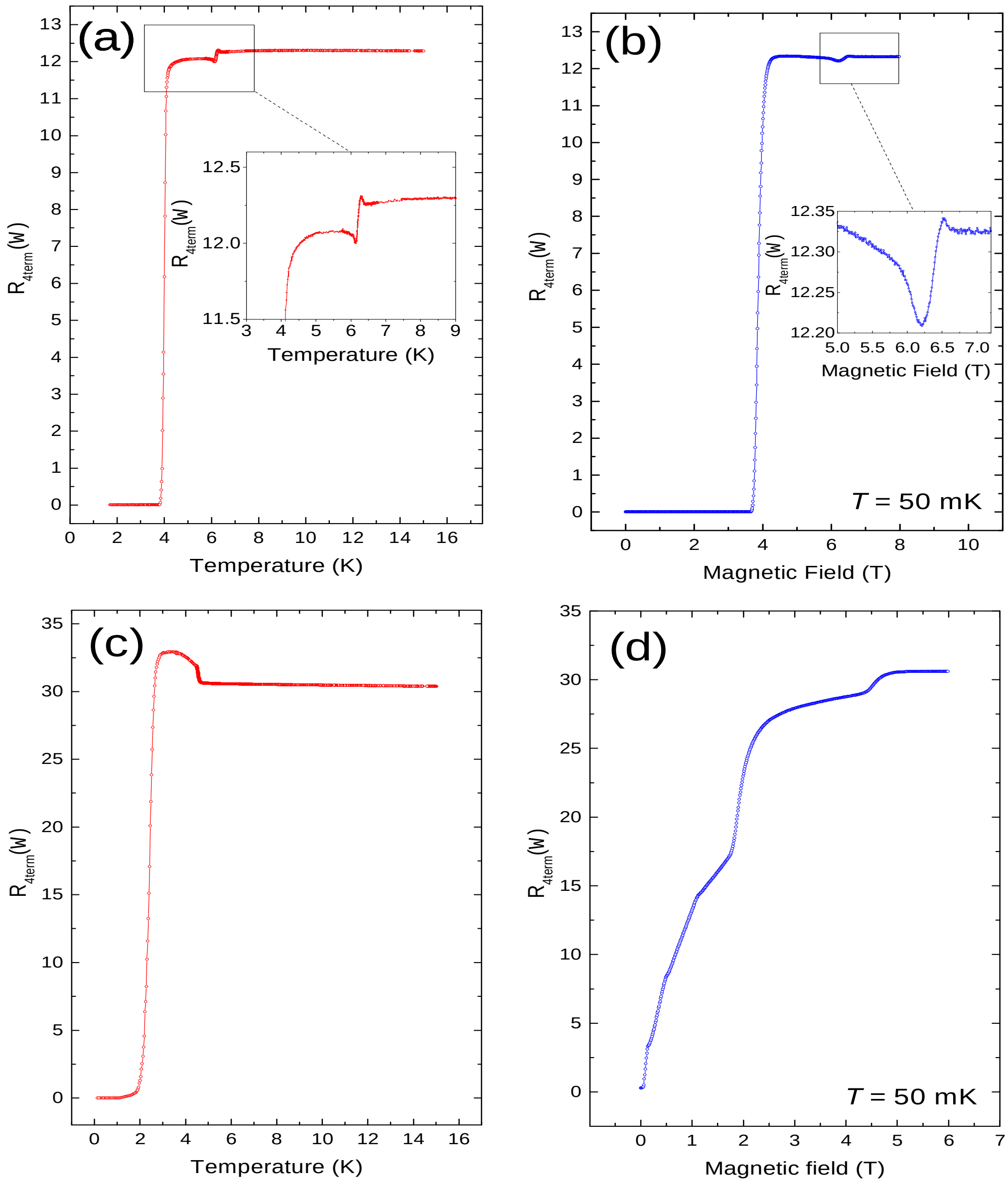
Four-terminal resistance measurement performed after each irradiation of the sample. The dashed line is a guide to the eye showing that the normal-conducting sample resistivity generally increases as a function of irradiation fluence, while the superconducting critical temperature decreases. Note the break in the vertical axis due to the significantly higher R4term after superconductivity was quenched at the highest fluence of 5x10^{16} /cm^2



These plots show that the superconductivity in diamond is destroyed when the hole concentration is reduced below 1.5 x 10^{21} holes.cm^{-3}.

This experiment thus demonstrates the critical concentration for superconductivity in diamond is 1.5 x 10^{21} holes/cm^3. Indeed as Cohen predicted if we can raise this hole concentration we can also raise Tc.

Annealing after irradiation: It has been shown previously that annealing diamond is an effective method of removing compensating point defects. To attempt to remove the point defects introduced by helium ion irradiation, the sample was annealed in vacuum at 1150ºC for four hours, with a slow ramp up and ramp down from this temperature of approximately 10 hours each. After annealing, electrical measurements revealed the successful recovery of superconductivity in the sample, albeit at a lower T_c.



Recovery of superconductivity by annealing after quenching by light ion implantation

An anomalous preliminary transition before the bulk of the material becomes superconducting was also observed. This behaviour, which was not observed at any point during the irradiation study prior to annealing, suggests that the annealing strategy may have catalysed the separation of the material into two discrete regions with differing T_c. At such a low annealing temperature, boron is not mobile and will not diffuse in diamond, so the redistribution of boron into higher concentration areas is unlikely. We are left to conclude that domains or percolation paths through the material have had compensating defects annealed out with higher efficiency than the bulk, leading to part of the material undergoing a superconducting transition at a higher T_c due to the resultant non-uniform hole density.

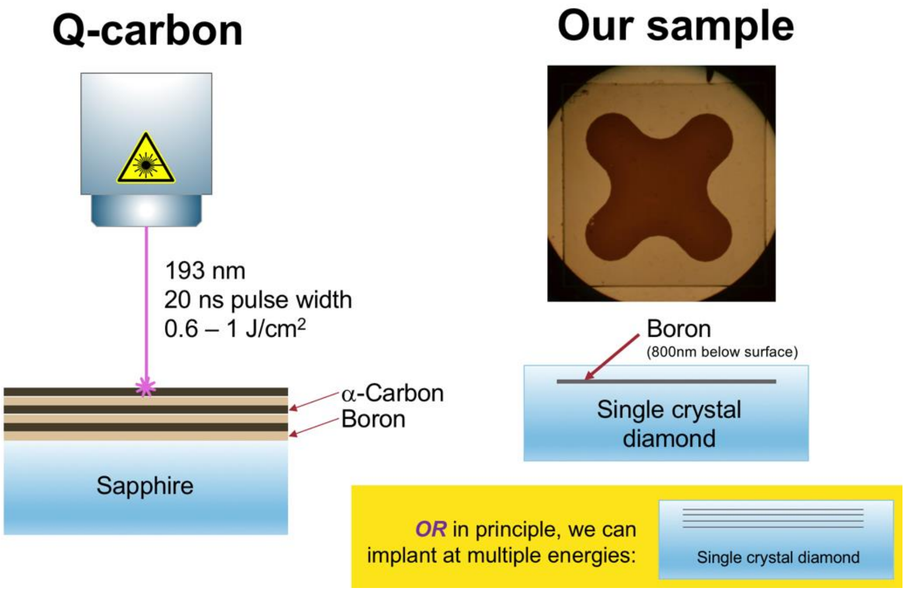
Nevertheless, the fact that superconductivity can be recovered in samples of boron doped diamond which have suffered heavy irradiation damage is promising, and the parameters of the recovered sample suggest that localised disorder in superconducting boron doped diamond has a strong effect on the density of states at the Fermi level and thus the T_c. Future work can now seek to optimise the hole concentration in the quest for higher Tc. We also demonstrate for the first time the ability to quench superconductivity via ion implantation in this material, which we hope has significant implications in providing a simple path to device fabrication. For instance, a focused ion beam could be used to selectively 'write' well-defined channels or regions of normal-conducting diamond into a superconducting wafer, or create the 'weak links' required for SQUID devices. The exceptional promise of superconducting diamond for application to devices is clear given its extremely high upper critical field (up to 30.1 T reported in the literature), and potential for very high critical temperatures which we hope the result of the present work may help realize in the future.

New approaches to annealing.

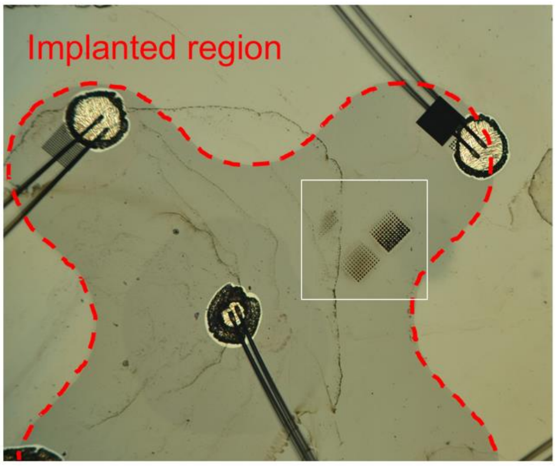
Preliminary pulsed laser annealing

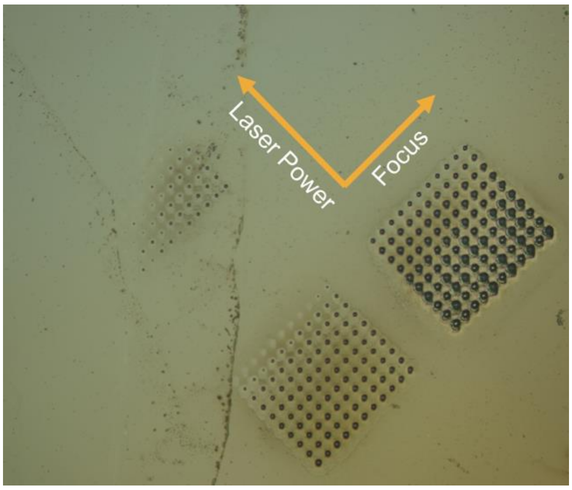
As mentioned above, recent studies of novel non-diamond phases of amorphous carbon such as "Q-carbon" have resulted in high temperature superconductivity at critical temperatures up to 55 K. Motivated by these results, which relied on nanosecond laser melting of alternating thin films of boron and carbon, we began preliminary investigations into pulsed laser melting of our boron implanted samples.

An electronic grade diamond sample 4x4x0.5 mm was implanted with 1 MeV boron-10 ions, followed by a standard 1400ºC anneal for 15 minutes under vacuum. The result according to SRIM modelling is a 60 nm thick implanted boron layer approximately 1μm below the diamond surface. Akin to the results seen in boron doped Q-carbon, we then attempted pulsed laser annealing of the implanted boron layer.

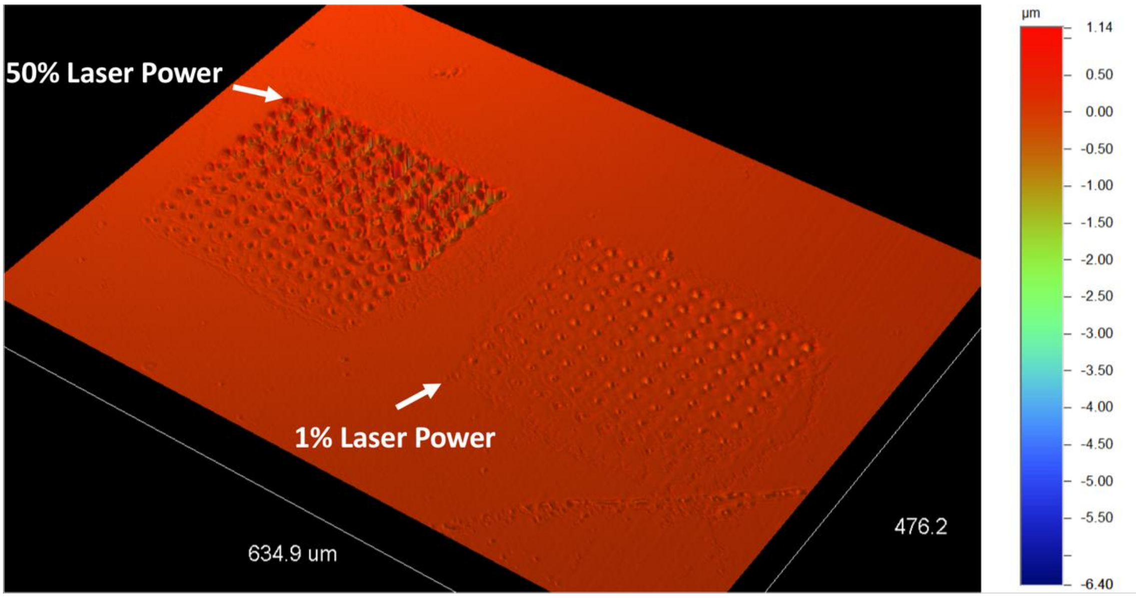


The optical images below show the resulting impact of a preliminary study of pulse energy and focus. Each spot was formed by a single 20ns laser pulse with power ranging from 50% down to 0.2% of the full 45mW power. Several 11x11 grids of laser annealing points were created to explore the parameter space and determine if pulsed laser annealing could be successfully applied to boron implanted diamond. Inspection under a microscope readily shows that at higher energy levels the laser simply ablated the top surface resulting in amorphization and relaxation to graphite. At lower energies the laser has shown to have a lower impact on the structural integrity of the boron doped diamond region.

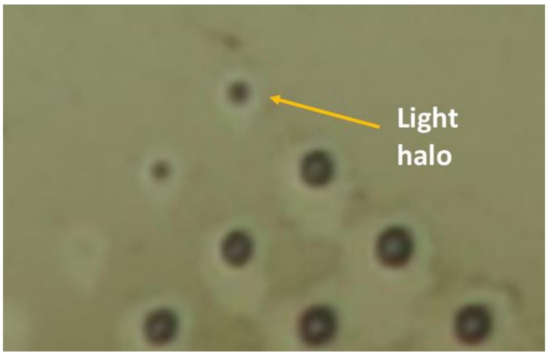




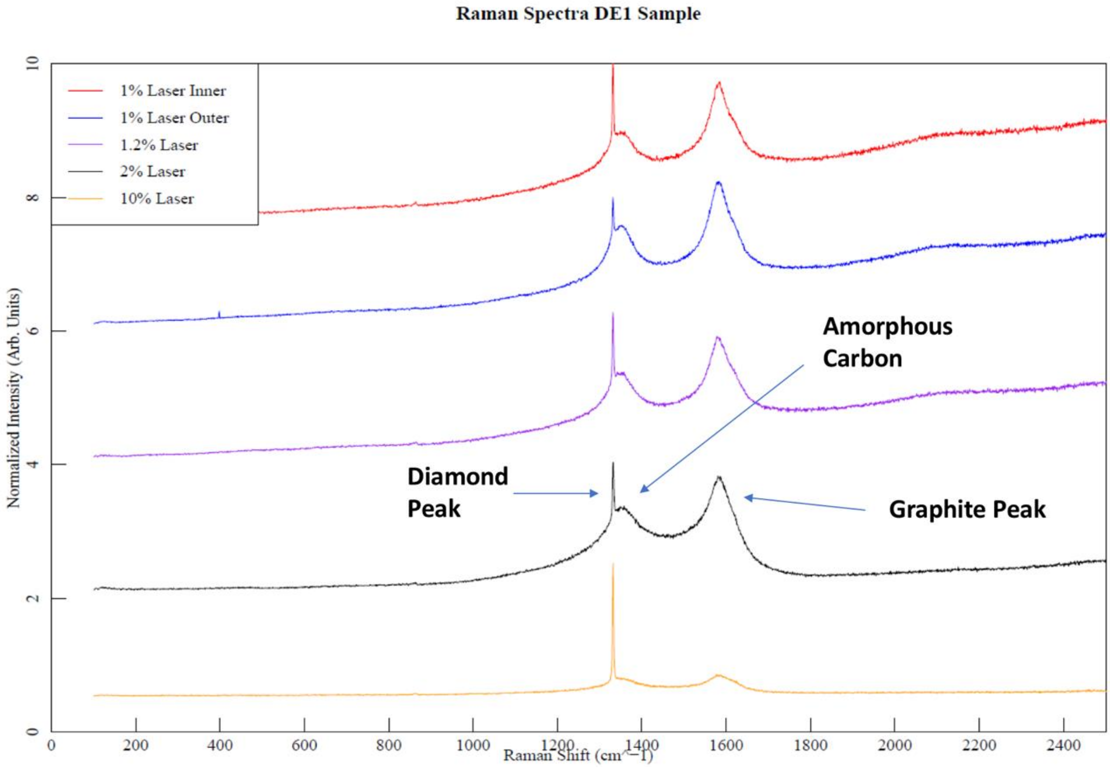
The large difference in reflectivity of our sample compared to the Q-carbon layered source material means that we must determine the laser power appropriate to our system. Optical profilometry imaging was used to gain a better picture of the structural damage to the laser surface as a result of the laser pulses. Only the lowest laser powers used were found to prevent ablation of diamond material and relaxation to graphite at the surface.



To gain a deeper understanding of the resulting effects of the pulsed laser anneal on the boron implanted layers, Raman spectroscopy techniques were employed to examine the resultant spots.



The Raman measurements were initially made on the region annealed at 10% laser power, where severe damage and the formation of a crater is seen. The regions of highest interest are laser power between 1 and 2%, where in the optical images a light halo is visible surrounding a small black dot. High spatial resolution Raman measurements were made on the dark central area of the laser annealed spots (herein referred to as 'inner') as well as the light outer halo ('outer') of the spots. The Raman shows several distinct peaks but also fails to show any evidence of boron being incorporated into the lattice (viz, the boron dimer peak located around 450-550 cm^{-1} and the peak corresponding to boron-carbon bonds located near 1214-1230 cm^{-1}) Amorphous carbon and graphite peaks were clearly visible, indicating that much lower laser energies are required in future tests.



These preliminary data are encouraging, and we hope that with further modelling and simulation, and potentially moving to a laser system of shorter wavelength and large beam area, we may be able to successfully transform highly conducting boron implanted diamond into superconducting diamond through super undercooled rapid quenching.

List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:
a) papers published in peer-reviewed journals,
b) papers published in non-peer-reviewed journals or in conference proceedings,
c) conference presentations,
d) manuscripts submitted but not yet published, and
e) provide a list any interactions with industry or with Air Force Research Laboratory scientists or significant collaborations that resulted from this work.

Published:

L. H. Willems van Beveren, R. Liu, H. Bowers, K. Ganesan, B. C. Johnson,J. C. McCallum, and S. Prawer: (2016) "Optical and electronic properties of sub-surface conducting layers in diamond created by MeV B-implantation at elevated temperatures", Journal of Applied Physics, 119, 223902 (2016).

Following a visit in 2017 to the lab of the world leader in superconducting diamond synthesis, Professor Hiroshi Kawarada (Waseda University, Japan), members of our team returned to Australia with the detailed recipe of how to grow high quality superconducting B doped diamond films. The Kawarada group have previously fabricated superconducting diamond films with the highest critical temperature recorded in the literature. This visit has resulted in a significant collaboration with the Kawarada group which we expect will continue into the future. The Kawarada group furnished us with a high quality superconducting diamond grown via their CVD process on <111> oriented diamond, which we have had great difficulty purchasing due to worldwide availability issues. This sample was used for our irradiation study of boron doped diamond.

The result of this work has been a manuscript submitted to the journal Physical Review Applied, titled "Irradiation induced modification of the superconducting properties of heavily boron doped diamond". This is currently awaiting editorial approval after addressing referee comments, and we expect it should be accepted for publication shortly. Postdoc Daniel Creedon will present a talk on this work at the International Workshop on Superconducting Sensors and Detectors (IWSSD 2018) to be held from the 24th to 27th July 2018 in Sydney, Australia.

Publications under review:
D.L. Creedon, Y. Jiang, K. Ganesan, A. Stacey, T. Kageura, H. Kawarada, J.C. McCallum, B.C. Johnson, S. Prawer, and D.N. Jamieson (2018) "Irradiation induced modification of the superconducting properties of heavily boron doped diamond", Physical Review Applied, *Under Review*