“Knock-on doping”: A universal method to direct-write dopants in a solid state host

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Abstract

Modifying material properties at the nanoscale is crucially important for devices in nanoelectronics, nanophotonics and quantum information. Optically active defects in wide band gap materials, for instance, are vital constituents for the realisation of quantum technologies. Yet, the introduction of atomic defects through direct ion implantation remains a fundamental challenge. Herein, we establish a universal method for material doping by exploiting one of the most fundamental principles of physics - momentum transfer. As a proof of concept, we direct-write arrays of emitters into diamond via momentum transfer from a Xe⁺ focused ion beam (FIB) to thin films of the group IV dopants pre-deposited onto a diamond surface. We conclusively show that the technique, which we term “knock-on doping”, can yield ultra-shallow dopant profiles localized to the top 5 nm of the target surface, and use it to achieve sub-50 nm lateral resolution. The knock-on doping method is cost-effective, yet very versatile, powerful and universally suitable for applications such as electronic and magnetic doping of atomically thin materials and engineering of near-surface states of semiconductor devices.
Much of solid-state science revolves around modification of materials at the atomic scale, where site-selective control over the incorporation and formation of defects within a host lattice enables control of physical, chemical and optoelectronic properties. Ion implantation has become a key tool in this regard, allowing for the modification of material properties for nanoelectronics, spintronics and quantum photonics.\textsuperscript{1-4} Of particular interest is the generation of optically-addressable qubits such as color centres in diamond, silicon carbide (SiC) or yttrium orthovanadate (YVO$_4$) which are considered prime candidates for scalable quantum technologies.\textsuperscript{5-8} Examples include the nitrogen vacancy (NV) centre\textsuperscript{9} and more recently the group IV elements\textsuperscript{10-15} in diamond that exhibit excellent optical and coherence properties suitable for quantum circuitry.\textsuperscript{16-18}

Indeed, significant efforts over the last few decades have been dedicated to ion implantation of color centres.\textsuperscript{19-26} However, the technique is inherently problematic. Firstly, ion implanters are expensive, cumbersome and hard to maintain. Hence, they are sparse and not readily available for end-users. Secondly, ion implantation is generally applicable only for relatively deep implants due to the minimum accelerating voltage of the ions and are not suitable for direct-write nanoscale patterning due to their large beam size. Yet, many applications require focused and very shallow ($\lesssim 10$ nm) implants that are challenging to achieve using commercial implanters.\textsuperscript{27,28} Thirdly, co-implantation of numerous elements, as well as dose series are practically impossible due to their need for long pumping times and the large spot size of the beam.

Herein, we establish a cost-effective method to direct-write ultra-shallow dopants by momentum transfer\textsuperscript{29,30} from a nanoscale ion beam that we term “knock-on doping”. The “knock-on” concept is schematically depicted in Figure 1a and it mitigates many of the shortfalls of commercial ion implanters. We employ a readily-available, unmodified dual beam system comprised of coincident scanning electron microscope and a focused ion beam (SEM - FIB) with a xenon (Xe) ion source. The knock-on doping is performed by site-selective irradiation of a target coated with a thin film of the desired dopant species using the inert Xe$^+$ ion beam. On an atomic scale, momentum transfer from xenon (purple circles in Figure 1a) to the target atoms of the thin film (red circles) causes the latter to be implanted into the underlying target. The process can yield ultra-shallow implant profiles (eg: sub-$5$ nm using a $30$ keV Xe$^+$ beam, as is demonstrated below), which is desirable for many applications.

As a benchmark for the versatility of this technique, we choose diamond and a range of group IV elements in the periodic table (Fig. 1b): silicon (Si), germanium (Ge), tin (Sn) and lead (Pb). The reasons for the choice of host and dopants are as follows: first, diamond is available as an ultra-pure material with a wide bandgap and exceptional chemical inertness, making it an ideal platform for investigations of extrinsic dopants. Second, color centres in
diamond, particularly the group IV-related negatively charged vacancy complexes, are currently front runners for a plethora of quantum photonic and quantum sensing applications. Hence, a robust method to create these centres is needed. Finally, these defects in diamond are optically active and can be imaged at a single photon level. This, in turn, allowed us to establish the efficacy of the proposed technique in the extreme case of advanced material systems which require engineering of individual, isolated atomic point defects.

To perform knock-on doping, the aforementioned group IV elements were deposited onto diamond using a standard sputtering technique (15-nm thickness). Then, a 30 keV, focused Xe$^+$ ion beam was used to pattern the University of Technology Sydney logo, and the acronym “UTS” into the thin film sections. After irradiation, the thin film was stripped using chemical processes and the diamond was annealed to activate the fabricated emitters (i.e. vacancy complexes of Pb, Sn, Ge and Si). Further specifications are given in the Methods section and in the Supplementary Information 1. Figure 1c shows the photoluminescence (PL) map of the implanted area. The UTS emblem and the letters U, T, and S are clearly visible. Importantly, the emblem and each of the letters consist of a different dopant - Pb, Sn, Ge, and Si, respectively - implanted using the same inert Xe$^+$ ion beam. We stress that the doping is achieved by momentum transfer from the xenon beam to the abovementioned elements in the thin films deposited atop the diamond. The pattern is formed by electrostatic scanning of the ion beam with no additional lithography steps. Moreover, the process is performed using a dual FIB-SEM system. All imaging and spatial alignments are therefore performed using the electron beam which is coincident with the ion beam at the diamond surface and serves as a passive imaging tool free from undesired implantation. Figure 1d shows photoluminescence spectra from the respective areas, featuring characteristic emissions of the four color centres with zero phonon lines (ZPLs) at ~ 550 nm (PbV), ~ 620 nm (SnV), ~ 600 nm (GeV), and ~ 740 nm (SiV). Remarkably, the color centres are optically active and bright, despite the fact that the dopant profiles are ultra-shallow, as is discussed below.
Figure 1. Creation of color centres in a diamond target by knock-on doping. a) Schematic illustration of the process inside a standard electron-ion dual beam microscope. The inset shows an atomic picture of the process - momentum is transferred from inert primary ions to the atoms of a thin film comprised of the dopants, resulting in implantation of the latter into the underlying target. (b) Extract from the periodic table highlighting the versatility of this technique. The dopants used in this work are shaded red, and the xenon ion beam species that we used is lavender. (c) Photoluminescence map of a pattern fabricated in a single region of diamond using four dopant species that were implanted by momentum transfer from an electrostatically scanned Xe\(^+\) beam. The emblem is patterned in Pb, and the letters U, T and S in Sn, Ge, and Si, respectively. The scale Bar corresponds to 5 μm. (d) Photoluminescence spectra recorded from the implants in (c), showing characteristic emissions from defect complexes that contain the Pb (green), Ge (orange), Sn (red) and Si (maroon) dopants.

We now turn to an in-depth analysis of the technique and the fabricated dopants, starting with the photophysical properties of the emitters. For this purpose, spot arrays (10 x 10) were patterned as a function of Xe\(^+\) dose, which was varied logarithmically for each of the aforementioned dopants. Analysis of the implanted areas was then conducted at room temperature using a confocal setup with an oil immersion objective. A representative map of a dose-dependent implantation series is shown in Figure 2a. The image refers specifically to the case of silicon-vacancy (SiV) emitters, but identical arrays were also patterned for the other three elements (GeV, PbV and SnV). For all four elements, we observe the emergence of the related color centre emission above a distinctive threshold dose (specified in Figure 2a as the number of Xe\(^+\) ions per spot exposure). That is, a minimum number of primary Xe\(^+\) ions is required to fabricate color centres. The threshold for observable emission, specific to the
15-nm dopant film thickness used in our experiments, is on the order of 600, 1500, 3000, and 3000 xenon ions for Si, Ge, Sn, and Pb respectively. This trend with atomic weight is intuitive given that the Xe\(^+\) ions mill the 15 nm films via sputtering and simultaneously implant the dopants into the underlying diamond via momentum transfer. More details about modelling of the ion-solid interactions and further characterisation (AFM and PL) are presented and discussed in the Supplementary Information 2 and 3, respectively.

Throughout the implanted arrays (fabricated as a function of Xe\(^+\) ion dose), prominent ZPLs are observed at 738 nm (SiV), 602 nm (GeV), 620 nm (SnV) and 550 nm (PbV), as is shown in Figure 2b, which are characteristic of the respective color centers. We note that an additional broad peak at 630 nm that appears in some of the spectra is the Raman signal of the immersion oil (Supplementary Information 4), and in the case of SnV an additional peak at 595 nm is present, associated with intermediate defect configurations.\(^{31}\) To confirm the quantum nature of the emitted light at the threshold implantation doses, a second order autocorrelation function, \(g^{(2)}(\tau)\), was recorded from each of the emitters. The background-corrected \(g^{(2)}(\tau)\) curves are shown as insets in Figure 2b. A clear dip below 0.5 at zero-delay time is observed for GeV, SnV, and PbV-related emitters, confirming the single photon nature of the implanted color centres. We did not observe anti-bunching from the fabricated SiV color centres, most likely due to their very low quantum efficiency.

The excited state lifetimes of the created defects are in accord with previously reported values—1.5 ns, 4.7 ns, 3.9 ns, 3.5 ns, for SiV, GeV, SnV, and PbV centres, respectively (Supplementary Information 5).\(^{10}\) Furthermore, resonant excitation at cryogenic temperatures was performed on some of the emitters. Narrowband linewidths on the order of 5 GHz were observed for the GeV and the SiV color centres, which is promising for practical applications (Supplementary Information 6).

We further analysed the ZPL positions of the ultra-shallow emitters. Interestingly, the ZPL distribution width increases with the atomic weight of the dopant species, under the exact same annealing conditions. For instance, the SiV ZPL is almost always at the same location of \(\approx 738\) nm, while the PbV and SnV ZPL vary over several nm. Furthermore, additional spectral lines (tentatively attributed to intermediate defect states) appear with a greater extent and frequency for heavier implants, as is discussed in the Supplementary Information 7.\(^{14,31,32}\) Whilst some of these characteristics can be attributed to an increase in strain associated with dopant size, these results warrant further investigation, in particular towards optimisation of the annealing process.\(^{31,33}\) Nonetheless, our technique is robust and can produce color centres on demand, as is demonstrated here with the group IV family in diamond.
Figure 2. Spot arrays of dopants implanted into diamond as a function of Xe$^+$ dose. a) Photoluminescence map of a representative array, here shown for Si dopants. The framed area shows the threshold Xe$^+$ dose that yielded an unambiguous observable array in this case. The number above each array specifies the Xe$^+$ dose per spot exposure. (b) Photoluminescence spectra measured for the threshold dose of SiV (maroon), GeV (orange), SnV (red), and PbV-related emissions (green). An additional peak at 630 nm corresponds to the Raman signal of the utilized immersion oil. Insets show second order correlation measurements (background corrected), illustrating the quantum nature of the color centres. (c) Histograms showing variability in ZPL positions in spot arrays of the color centre ensembles.

Next, we analyse the dopant depth profiles and the lateral resolution of the knock-on technique. Lateral precision was determined using PL maps of spot-arrays of low dose GeV ensembles. The ensemble locations were determined by local fits of the PL signal at the nominal implantation sites to 2D gaussian functions. To minimise the influence of setup-related aberrations (e.g. due to large map areas), as well as distortions due to drift, several subarrays of 4 x 4 points were considered. Horizontal and vertical lines were fitted through these points, with the constraint of equivalent slopes and equidistant line offsets for
individual subarrays. Gridline intersections are taken as the nominal implantation sites. The distance of the nominal position to the centre of the gaussian fit was calculated, yielding a rayleigh distribution of the relative ensemble position, as shown in Figure 3a, whereas the extracted relative position did not show any skewness in x or y direction (inset). A fit to a Rayleigh distribution, yields a mode of $(44 \pm 4)$ nm, representative of the precision of the technique. This value is better than the required threshold for engineering of quantum emitters within photonic devices, e.g. in the high field of a 2D photonic crystal cavity. Further, this value has to be considered in the context of the ion beam diameter of the utilised FIB, which in our case is $\approx 30$ nm. See Supplementary Information 8 for a more detailed analysis. Despite the inherently larger spot size of a Plasma FIB ion beam, the precision is on par with values from sources with fundamentally smaller spot sizes. The reason for comparable values lies in the shallowness of the implant, which leads to virtually no lateral straggling within the host material. Improvements in the plasma source and the ion beam focusing optics can lead to more precise placement of the implanted species, potentially beyond the current limits of other implantation techniques. Moreover, in terms of accuracy, interpreted as the implantation at a particular target site (e.g. a cavity hotspot), we emphasize that the FIB is integrated with a coincident high resolution SEM in the same tool. This allows for high accuracy localisation of the implantation site using the SEM which will not lead to any unwanted implantation or alteration of the material.

We now discuss one of the most peculiar characteristics of this technique, namely the ultra-shallow implantation. Stopping and Range of Ions in Matter (SRIM)$^{34}$ modelling suggests that the technique yields dopants within the top 2 nm of the target surface. In fact, as is shown in Figure 3b, over 90% of the implanted species are located within a depth of 1 nm. At the same time the depth distribution of the co-implanted xenon is broader, ranging from the surface up to a depth of $\approx 15$ nm with a subtle maximum at $\approx 5$ nm (Fig. 3b, inset). Figure 3b is plotted for the Ge dopants, but simulations of all other species show analogous behaviour (Supplementary Information 2).

We cannot conclusively confirm by direct optical imaging that the emitters are $\leq 5$nm from the interface. Therefore, to verify the depths of the implanted emitters experimentally, we employed Electron Beam Induced Etching (EBIE) in an environmental SEM with H$_2$O vapour as the etch precursor. EBIE enables to locally remove the top material of the implanted areas, without damaging the underneath material. During EBIE the electron beam locally induces a chemical reaction with the environmental species (H$_2$O) forming a volatile complex that desorbs spontaneously or is removed by electron beam induced desorption. $^{35}$ The rationale for the deployment of this technique is given by the fact that no further physical alteration of the implanted species is expected, as the etching process is chemically driven.

Using EBIE, a wedge-shaped feature was etched along a square implanted area, schematically shown in Figure 3c. In the following, we correlated the depth (AFM scan, shown in Figure 3d) to the local fluorescence intensity (PL map, shown in Figure 3e). Using three etched spots (white circles) to correlate both maps, an averaged depth profile and PL profile of the wedge were extracted (Fig. 3f). In particular, we observe an emission maximum from a
mean depth of less than $(1 \pm 1)$ nm in the section—along the x-axis—between 11 μm and 13 μm. An initial increase seen the PL line profile may be caused by an increase in surface roughness, which leads to an increase of luminescence scattered towards the objective, effectively increasing the collection of light. The assumption of increase in PL signal due to scattering is underlined by the observation that the increase in PL stems primarily from spot-like features observed in the PL map in Figure 3e.

Consequently, as the mean depth drops below 1.5 nm, the PL intensity decreases sharply to less than 50 %, in the section along the x-axis, $x \approx 13 \, \mu m$ - 14 μm and down to 20 % at about $(5 \pm 2)$ nm at $x \approx 15 \, \mu m$. However, a residual PL signal is still present at a depth of $(8 \pm 2)$ nm, in contrast to what is predicted by the simulation. We assume that ion channeling is the main factor responsible for the increased luminescence at this depth. As the etched wedge finishes, at $x \approx 22 \, \mu m$, the luminescence is restored. The fluorescence then drops again to zero at the edge of the implanted area ($x \approx 25 \, \mu m$).

**Figure 3.** Spatial distribution of the dopants. (a) Distribution of the ensemble position relative to the implantation site, fitted by a Rayleigh function with a mode of $(44 \pm 4)$ nm. The inset shows directly the relative ensemble position. (b) Monte Carlo Simulations (performed using SRIM) of the depth distribution of Ge in diamond from a Xe$^+$ knock-on implantation process.
and of the co-implanted Xe (inset). (c) Schematic of the wedge edge to access the implantation profile of an area with the implanted species. (d) AFM map of the wedge prepared by EBIE. (e) PL map of the same area. The position of both maps was correlated by the 3 marked spots. Scale bars in (d) and (e) correspond to 2.5 μm. (f) Average profile of depth (blue) and PL (red) along the wedge feature. The shaded areas present the standard deviation.

To conclude, we presented a universal and cost-effective method to create shallow implants in a solid-state host that we term “knock-on doping”. This is achieved by utilizing momentum transfer from a Xe⁺ FIB to atoms of a thin target film deposited on top of a target of choice. We demonstrated the technique by a controlled engineering of all group IV-related color centres in diamond. An intriguing aspect of the developed knock-on technique is the ability to achieve ultra-shallow implants. We provided direct evidence that the majority of the emission stems from within the top 5 nm of the diamond surface. The latter, in combination with the quantum nature of the engineered defects, marks a major leap in applications for quantum sensing and quantum photonics.

Whilst our immediate demonstration was focused on the creation of group IV color centres in diamond, the underlying experiments pave the way to doping using a wide range of elements and a readily-available, commercial focused ion beam system. We note that even elements heavier than the employed ion can be implanted, as is demonstrated in our case of Pb implantation using a Xe⁺ beam. Thus, the technique is relevant to discovery of novel color centres in both diamond, and other materials such as YAG, SiC or hBN and will accelerate research in quantum photonics. Beyond the field of quantum technologies, our knock-on technique is appealing for shallow doping of single electron transistors, deterministic direct writing of near surface dopants or controlled introduction of magnetic elements in order to control magnetism at the nanoscale. Finally, one of the biggest advantages of this technique is the ability to engineer selected defects in atomically thin materials, that by definition require ultra-shallow implants.

Methods
Sample Preparation
A CVD-grown electronic grade diamond (< 1ppb Nitrogen) was purchased from Element Six. Before all subsequent experiments the sample was cleaned in hot (150 °C) Piranha Acid (H₂SO₄:H₂O₂ (30%) 2:1) for at least 2 hours. All thin film depositions were carried out in a lab-built magnetron sputter deposition chamber, pumped to a pressure of 1×10⁻⁵ Torr or lower before deposition. For deposition, argon was introduced with a pressure of 1.5×10⁻³ Torr and a plasma was ignited, for which the power was adjusted to yield a deposition rate of 0.5 Å s⁻¹. Sputter targets were purchased from Changsha Xinkang Advanced Materials Co., Ltd with a purity of 99.99 % or higher. For the implantation experiments discussed in Figure 2 and Figure 3 the diamond was coated at 4 different corners with the respective thin films, whilst being masked during subsequent deposition steps to avoid cross deposition of different materials. For the patterning of the UTS logo, thin films were deposited on rectangular sections,
lithographically defined using EBL as described in Supplementary Information 1. After deposition, sample irradiations were performed within a day or less.

**Focused Ion Beam Irradiation**

All ion beam irradiations were carried out in a ThermoFischer Scientific Helios G4 PFIB with exchangeable plasma ion source. For irradiation a xenon beam was used with an acceleration voltage of 30 kV and current of 10 pA. For irradiation of spot arrays and the UTS logo, custom patterning files (stream files) were created, defining the time per spot for individual spots (pixels). Box irradiations as discussed in the Supplementary Information 3 were performed, defining squares with 4 μm length and increasing the number of passes during the irradiation, using the built-in pattern generator.

**Post Irradiation treatment**

After irradiation with the Xe⁺ FIB, the coated thin films were chemically stripped. We used subsequently 2 cycles of various solutions with intermittent water rinsing in between. First, the sample was held in KOH (30 min., 50 °C, 30 wt. %), then HCl (30 min., 75 °C, 37 wt. %), followed by Piranha Acid (30 min, 150 °C H₂SO₄:H₂O₂ (30%) 2:1) to efficiently eliminate any residue of thin film coating on the substrate surface. After the chemical treatments the sample was annealed in a tube furnace (Lindberg Blue Mini-mite) under high vacuum with pressure lower than 2×10⁻⁶ Torr for the entire annealing cycle. The temperature was ramped up to 950 °C and held for 2 hours. Then furnace was cooled down to room temperature before breaking vacuum. After annealing the sample was again cleaned in hot (150 °C) Piranha Acid (H₂SO₄:H₂O₂ (30%) 2:1) for at least 2 hours and stored in a desiccator in between experiments.

**PL measurements**

All PL measurements were performed on lab-built confocal setups. The UTS logo was characterised using a 405 nm/ 1mW cw laser as the excitation source, which was directed through an arrangement of a dichroic mirror, scanning mirror and lens relay system and focused on the sample surface by a 0.9 NA objective. Photoluminescence from the sample was collected from the same objective and directed into a multimode fiber guiding the signal either to an APD (excelitas) for mapping or to a spectrometer (Princeton Instruments). Lifetime measurements were conducted on the same configuration using either a 512 nm (for Si, Ge, Sn) or 405 nm (for Pb) pulsed laser diode as the excitation source. The fluorescence was correlated to the laser pulse using a pico harp 300 picoquant. Characterisation of spot arrays and second order correlation measurements were done on a different setup. A 532 nm laser (cw, 2 mW) was used as the excitation source, and focused onto the sample by using an oil immersion objective (1.25 NA). Photoluminescence was collected through the same objective and coupled into a single mode fiber. The signal was either guided to a Spectrometer (Andor), or a 50/50 fiber splitter with the respective outputs connected to an APD. Their signals were then correlated by a time correlator (Swabian Instruments).
Electron Beam Induced Etching
Electron beam induced etching of the diamond was done in a Zeiss EVO, under 15 keV, 2 nA, 100 mTorr H₂O vapour. A rectangular area (16 μm length, 10 μm width) was irradiated (5 μs dwell time, 20 nm point pitch) in a raster scan. The length of the rectangle was reduced in subsequent steps by 2 μm, whilst the time/ area (≃ 1 s·μm⁻¹) for each rectangle was held constant, thus achieving a linear fluence gradient resulting in the shown etch profile. After etching the diamond was again cleaned in hot (150 °C) Piranha Acid (H₂SO₄:H₂O₂ (30%) 2:1).

AFM measurement
AFM measurements were done on a Park XE-7 AFM. Post-processing of AFM data was done in XEI and Gwyddion to remove artefacts of the scan and to extract height profiles.

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