Structural and optical properties of micro-diamonds with SiV− color centers

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Abstract
Isolated, micro-metre sized diamonds are grown by micro-wave plasma chemical vapour deposition technique on Si(001) substrates. Each diamond is uniquely identified by markers milled in the Si substrate by Ga+ focused ion beam. The morphology and micro-grain structure analysis, indicates that the diamonds are icosahedral or bi-crystals. Icosahedral diamonds have higher (up to $\sigma_h = 2.3$ GPa), and wider distribution ($\Delta\sigma_h = 4.47$ GPa) of hydrostatic stress built up at the micro-crystal grain boundaries, compared to the other crystals. The number and spectral shape of SiV− colour centres incorporated in the micro-diamonds (MDs) is analysed, and estimated by means of temperature dependent photoluminescence measurements, and Monte Carlo simulations. The Monte Carlo simulations indicates that the number of SiV− colour centres is a few thousand per MD.

Keywords: optical, micro-diamonds, silicon-vacancy, colour centre, structure

(Some figures may appear in colour only in the online journal)

1. Introduction

Colour centres in diamond have become well established architectures for quantum technologies [1]. In particular, the negatively-charged silicon vacancy (SiV−) centre has proven to be an excellent single photon source [2, 3] and quantum-optical platform [4–6]. For many quantum information applications it is important to achieve isolated single defects in fabricated structures and nano-diamonds [7–10]. There have been successful demonstrations of single SiV− centres in nano-beam waveguides [4], and bottom-up engineering of complex quantum systems from nano-diamonds has been proposed [8]. The SiV− centre has exhibited stable fluorescence in molecular-sized meteoric nanodiamonds as small as 1.6 nm [11], and reliable fabrication of similarly ultrafine SiV− nanodiamonds has been demonstrated [12]. However, other applications demand high densities of SiV− centres in confined geometries [13, 14]. Microdiamonds (MDs) can host ensembles of SiV− centres, although surface effects can be important to control for optimal colour centre properties [15, 16]. The spectral stability and strong zero-phonon line of SiV− centres makes them attractive for exploring cooperative effects such as superradiance [17]. Emerging techniques for optical
trapping have applications in particle sorting and inertial sensing, but demand high concentrations of optical dipoles [18].

Here we report a novel approach to fabricate MDs with large ensembles of SiV\(^{−}\) colour centres, and to calculate their number density. Firstly, isolated and high crystal quality MDs, are grown by micro-wave plasma chemical vapour deposition (MWCVD) technique on silicon. Each MD is uniquely identified and addressed by micrometre-wide markers milled in the Si substrate by focused ion beam (FIB) technique in the scanning electron microscope (SEM) chamber. The microstructure and morphology of individual MDs is investigated by a combination of SEM, atomic force microscopy (AFM) and polarized confocal Raman spectroscopy. Finally, the number density and spectral shape of SiV\(^{−}\) ensembles in MDs is investigated and calculated by temperature dependent photoluminescence (PL) spectroscopy, and Monte Carlo simulations. These simulations qualitatively reproduce the ensemble spectra by realistically simulating individual SiV\(^{−}\) spectra for a given number of SiV\(^{−}\) centres ranging in axial strain, transverse strain, and temperature. It is possible to estimate the number of SiV\(^{−}\) centres to be a few thousand per MD.

2. Results

2.1. Growth and morphology of MDs on Si

Micrometre-sized diamonds, were grown by MWCVD with CH\(_4\) and H\(_2\) as precursor gases, directly on Si(001) substrates without any seeding procedure. The MDs nucleate on the defects of the SiC/Si(001) thin layer which is formed during the CH\(_4\) plasma process, with a density below 1 mm\(^{−2}\). The x-ray photoelectron spectroscopy (XPS) analysis (see supporting material) clearly indicates the formation of a SiC layer both in the C 1s and Si 2p signals. The atomic concentration of the SiC layer is 26% ± 1% calculated from the integral peak intensities (see section 4), considering that the XPS penetration depth ranges between 5–10 nm, it corresponds to a few SiC monolayers. The formation of a SiC interlayer enables the nucleation, and crystal growth of diamonds without any seeding procedure [19, 20].

The growth process (see section 4) has been optimized to form MDs with well defined crystal facets, having the so-called crystal quality (intensity ratio between the Raman signal of C sp\(^{3}\) and sp\(^{2}\)) higher than 99.5% measured by Raman spectroscopy [21–23], and a crystal size of about 2 \(\mu\)m.

In order to measure and to correlate the structural and optical properties of specific diamond crystals, six different MDs, with various morphology and structure, were identified by SEM and labelled by FIB milled markers. Figures 1(a) and (b) report perspective view SEM images of the Si(001) substrate after the MWCVD MD growth, and FIB milling of markers. The FIB markers (dark grey) are 2 \(\mu\)m deep and 30 \(\mu\)m wide with unique shapes. These aspects make the markers easily addressable by AFM, and confocal optical spectroscopy techniques. In figure 1(b), a single MD, labelled as MD3, is clearly visible in the middle of the FIB marked area.

The morphology of six different MDs, labelled as MD1–MD6 is investigated by perspective view SEM and AFM, the results are displayed in figures 1(c)–(h), and (i)–(n), respectively.

Both SEM and AFM analysis shows a similar crystal size of \(\sim 2\ \mu\)m for every MDs, indicating that all crystals nucleated in a similar stage of the CVD process. Each MD presents well-defined \{100\} and \{111\} crystal facets, but the overall crystal shape and morphology are different. Indeed, the diamond crystal shape is determined by the growth velocity parameter \(\alpha = \sqrt{3v_{100}}/v_{111}\), where \(v_{100}\) and \(v_{111}\) are the growth velocity of the \{100\} and \{111\} surfaces, respectively [24]. If \(\alpha < 1.5\), the \{111\} facets are the fastest growing, and therefore the crystal will be predominantly \{111\} textured. On the contrary, if \(\alpha > 1.5\) the \{100\} facets are the fastest growing, and therefore the crystal will be predominantly \{100\} textured. The parameter \(\alpha\) strongly depends on the local plasma and gas mixture conditions, typically it increases with high methane concentrations, and it decreases with high growth temperatures. The overall MD shape does not depend on the parameter \(\alpha\) only, but also on the formation of multiple crystal twins separated by grain boundaries [25, 26].

The SEM and AFM images in figure 1 of MD2, MD3, MD5 and MD6 indicate that the crystals are constituted by two different crystal grains, and they are bounded by \{100\} and \{111\} facets.

Differently, the SEM and AFM images in figures 1(a), (f) and (i), (l) of MD1 and MD4, indicate that these diamonds are dimpled icosahedral crystals, formed out of \{111\} facets with 5-fold pseudo symmetry axes [24, 27]. The five-fold crystal symmetry originates from the formation of five neighbouring \(\Sigma 3\) twins. Even though this crystal structure lacks of 7.33° to a full 360° closure, the mismatch is compensated by internal strain at the grain boundary regions [25]. If the parameter \(\alpha = 1.5\), the five-fold symmetric structure results in a perfect icosahedral crystal. As the growth conditions change towards higher values of \(\alpha\), dimples form on the top of the symmetry axes.

In order to get more insights into the diamonds’ microstructure, the crystal height profile along the two orthogonal Si[100] and Si[010] directions, together with the stereographic map of the crystal facets distribution [28], are extracted from the AFM data for each MD. Figure 2 reports the crystal profile and stereographic map for MD1; all MDs are analysed analogously. AFM data are flattened with respect to the Si(001) substrate surface. The crystal height profile of MD1 along the Si[100] (black) and Si[010] (red) directions, is reported in figure 2(a). Here, the different \{111\} facets of the icosahedron are clearly visible in both crystal directions. In the stereographic map of figure 2(b), the bright central spot corresponds to the Si(001) substrate, while the different groups of \{111\} facets forming the icosahedral crystal shape, are marked by: one red dashed circle, three green dashed circles, and six blue dashed circles. The corresponding \{111\} crystal facets are marked in red, green and blue in figures 2(c), (d) and (e), respectively.
A summary of the facet distribution for MD1–6, obtained by AFM and stereographic map analysis, is reported in figures 3(a)–(f), respectively. The {100} and {111} facets are distinguished by the facet symmetry, as explained in [24]. In figure 3, the facet inclination angle represents how steep the crystal facet is with respect to the Si(001) substrate surface. This angle is determined by the radial distance between a point and the centre in the stereographic map (e.g. see figure 2(b)). The probability indicates the normalized ratio between the number of points belonging to a {111} (black histograms) or {100} (red histograms) diamond facet with a specific inclination angle, and the total number of points. Figure 3 indicates that MD1, MD4 and MD6 present {111} facets only, while MD2, MD3 and MD5 exhibit also {100} facets. The {100} surface coverage is maximum 30% for MD2, thus indicating that the value of the growth parameter is $\alpha \geq 1.5$.

### 2.2. Polarized Raman spectroscopy

Confocal Raman spectroscopy is a very powerful technique to analyse the micro-structural properties of diamonds, such as crystal quality, twins formation and lattice stress [23]. Diamond is a face centred cubic Bravais lattice with $O_h$ point group symmetry. The Raman scattering effect in diamond is characterized by a triply degenerate optical phonons belonging to the $F_{2g}$ symmetry group, whose scattering tensors $R_{1,2,3}$ are described by equation (1)

$$R_1 = \begin{bmatrix} 0 & 0 & 0 \\ 0 & d & 0 \\ 0 & 0 & d \end{bmatrix}, \quad R_2 = \begin{bmatrix} 0 & 0 & d \\ 0 & 0 & 0 \\ d & 0 & 0 \end{bmatrix},$$

$$R_3 = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

In equation (1), $d$ represents the Raman tensor element which depends on the crystal electrical polarizability. The Raman tensors $R_1$ and $R_2$ are associated to transverse optical (TO) phonon modes along the [100] and [010] crystal directions, respectively. Differently, $R_3$ relates to the longitudinal optical (LO) phonon mode along the [001] crystal direction. The overall measured Raman scattering intensity $I_{\text{measured}}$ is a combination of the three different phonon modes, and it can be expressed by equation (2)

$$I_{\text{measured}} \propto \sum_{n=1}^{3} |e_i R_n e_s|^2,$$  

In equation (2), $e_i$ and $e_s$ are the linear polarization vectors of the incident laser beam and scattered light, respectively. Thus, the Raman scattered intensity strongly depends on the
by CVD growth. The diamond scattered Raman signal was negligible, corroborating the good crystal quality obtained from amorphous and sp
scattering transition around 1332 cm

ν

relaxed value of stress

function of

ity dependence on

perpendicular to the crystal facets, the Raman scattered intensity for different crystal facets can be found in [23, 29, 30]. In summary, the Raman intensity for backscattered measurements normal to the diamond (001) and (111) facets is

I(001) = d^2 \cos^2(\phi - \phi_{\text{max}}),

and

I(111) = 2d^2/3, respectively. The angle \phi_{\text{max}} indicates the tilt of the investigated crystal with respect to the Si substrate [010] and [100] directions. If the incident and scattered beams are not perpendicular to the crystal facets, the Raman scattered intensity dependence on \phi becomes more complicated, and \nu(111) is function of \phi [31]. If the diamond lattice is under hydrostatic stress \sigma_0, the Raman peak position \nu is shifted by \Delta\nu from the relaxed value of \nu_0 = 1332 cm\(^{-1}\), according to the equation

\nu = \nu_0 + \Delta\nu, where \sigma_0 = 0.34 (GPa cm) \Delta\nu [23, 32].

A typical Raman spectrum obtained from the MDs is reported in figure 4(a). It clearly presents the sharp diamond Raman scattering transition around 1332 cm\(^{-1}\), while the contribution from amorphous and sp\(^2\) C at higher wavenumbers is almost negligible, corroborating the good crystal quality obtained by CVD growth. The diamond scattered Raman signal was mapped at different X–Y positions as a function of the incident light beam polarization angle \phi. This revealed the micro-structure of the MDs. Figure 4(b) represents a 3D colour coded map of the diamond Raman peak intensity around 1332 cm\(^{-1}\) as a function of the X–Y sample position (in steps of 200 nm), and the angular rotation \phi (0 \leq \phi \leq 120\(^{\circ}\)) of the laser polarization. The 3D map is sliced along the two orthogonal directions Si[100] and Si[010], through the centre of MD3. The high intensity Raman peak regions come from scattering of the MD3 crystal, while the dark blue region at low intensities corresponds to the Si(001) substrate (the Raman mode of Si is around 520 cm\(^{-1}\) [33]). Interestingly, the modulation of the diamond Raman intensity [23, 29, 30] as a function of the laser polarization angle \phi is not uniform throughout the entire MD surface, as it is expected for a single-crystal diamond.

In order to analyse the micro-structure of the MDs, Raman spectra are recorded at different laser light polarizations (0 \leq \phi \leq 360\(^{\circ}\), in steps of 3\(^{\circ}\)), in five different diamond positions, labelled in figure 4(a) inset as 1–5 in blue, red, cyan, orange, and magenta, respectively. Position 3 is set at the MD centre, the other positions are spaced by 600 nm along the X–Y ortho-
gonal directions. As an example, figure 4(c) presents polar plots of the Raman peak intensity for the Si(001) substrate (black) as a reference, and MD3 at two opposite positions: 1

Figure 2. (a) Height profile of MD1 taken through the crystal centre along the Si [100] (black) and Si[010] (red) directions.

(b) Stereographic map of the MD1 crystal facets obtained by AFM analysis. The high-intensity central peak is related to the Si(001) substrate. The red, green and blue dashed circles indicate the family of (111) crystal facets marked in (c)–(e).

(c)–(e) AFM images of MD1 with [111] facets marked in red, green and blue, according to the stereographic map reported in (b).

Figure 3. (a)–(f) Probability distribution of the (001) (red) and {111} (black) facet inclination angle with respect to the Si(001) substrate, for MD1, MD2, MD3, MD4, MD5 and MD6, respectively. The facet inclination angle is measured by calculating the stereographic map from the AFM data as illustrated in figure 2(b).
The micro structural results, obtained from Raman scattering of the icosahedral crystals, are summarized in figure 5. Figure 5(a) shows the Raman spectrum of MD4 measured at position 4, close to the dimpled corner where 5 different [111] facets are joining (see the inset schematic diagram). The diamond Raman signal (orange solid line), recorded in the $z(yyyyzz)$ configuration, is clearly split in two distinct components, and it is fitted by the sum of two Gaussian curves (grey solid line). The first Gaussian component C1 (dashed orange curve) is centred around 1324 cm$^{-1}$, while the second one C2 (dotted orange curve), is centred around 1334 cm$^{-1}$. Presumably, the significant difference in Raman peak position between the C1 and C2 crystal components of MD4, is ascribed to large stress built at the five-fold grain boundary [34] because of lattice mismatch and C sp$^2$ defects [35]. Raman peak intensities as a function of the incident laser light polarization angle $\phi$, for the Si(001) substrate, MD4 C1 and C2 crystal components, are reported in figure 5(b) in black spheres, orange triangles, and orange spheres, respectively. The Si Raman peak intensity has a clear polarization dependence as described above, with the maximum along the Si[100] direction. Differently, the Raman peak intensity of the two diamond crystal components C1 and C2 is almost independent from the incident laser light polarization angle $\phi$. This result may be attributed to the weak dependence of the Raman signal on the angle $\phi$ for [111] crystal facets [29], and to the Raman scattering contribution of differently oriented, and distorted crystal grains.

Analogously, all MDs have been analysed by Raman spectroscopy with the procedure reported in figures 4 and 5. A summary of the micro-crystal properties obtained for each MD at position 1–5 (marked in different colours as indicated in figure 4(a) inset) is summarized in figure 6. Clearly, the crystal properties of the icosahedral diamonds MD1 and MD4 differ from those of the others. The diamond Raman peak centre, see figure 6(a), of MD1 and MD4 varies significantly between 1339 to 1324 cm$^{-1}$, while it ranges between 1332.8 and 1333.8 cm$^{-1}$ only, for the other crystals. Analogously, the calculated hydrostatic diamond stress $\sigma_h$ follows the same trend, ranging from 2.3 to $-3.3$ GPa for MD1 and MD4, and varying between 0.3 and 0.5 GPa only, for the other crystals. The large difference of diamond Raman peak centre and $\sigma_h$ for icosahedral MD1 and MD4 is ascribed to the significant lattice deformation and high density of defects formed at the multiple grain boundaries regions.

The presence of several crystal grains, with different orientation, causing the large stress in MD1 and MD4 is clearly elucidated in figure 6(b). Here, the values of $\phi_{\text{max}}$, measured at different crystal positions, of MD1 and MD4, significantly scatter between $80^\circ$ and $-10^\circ$, $20^\circ$ and $-87^\circ$, respectively. The large error bar, and poor spatial consistency of $\phi_{\text{max}}$ as a function of the different (1–5) crystal positions,
indicate that MD1 and MD4 are constituted by several micro-
crystals forming highly-stressed and defective grain bound-
aries. Differently, for MD3, MD5 and MD6, the values of
$\phi_{\text{max}}$ at different crystal positions, can be grouped in two dis-
tinct sub-ranges, around $-60^\circ$ and $-40^\circ$, around $-60^\circ$ and
$-50^\circ$, around $20^\circ$ and $-55^\circ$, respectively. The presence of
two distinct sub-ranges of $\phi_{\text{max}}$ values at different crystal
positions, indicate that MD3, MD5 and MD6 are formed by
two crystal grains with different crystallographic orientations.
Interestingly, the value of $\phi_{\text{max}}$ for MD2 is $11^\circ \pm 3^\circ$ for every
crystal position, suggesting that it is a single diamond crystal.
On the other hand, by comparing the MD2 $\phi_{\text{max}}$ Raman re-
sults, with the AFM image of figure 1(j), it is clear that MD2 is
formed by two crystal grains with similar crystallographic orientations.

In summary, in this section we have demonstrated that a
combination of AFM, SEM and Raman spectroscopy is a very
powerful approach to address the diamond structural proper-
ties, such as crystal stress and grain boundary distribution.

2.3. SiV$^-$ PL spectroscopy

PL spectra were recorded for numerous MDs under 514 nm
excitation, which is known to efficiently excited SiV$^-$ centres
despite being far detuned. The characteristic SiV$^-$ PL band
was observed in all of the MDs, and the zero-phonon line at 737 nm was investigated in high resolution. At room temper-
ature there is considerable thermal broadening of this optical
transition, and so features were difficult to identify. However, a
range of SiV$^-$ fluorescence intensities were observed. Figure 7
reports room temperature, polarization resolved PL measure-
ments taken for MD3 at position 4.

2.4. Monte Carlo simulation of SiV ensembles for size estimation

The sample was cooled to liquid-helium temperatures (below
10 K), and the cryogenic PL spectra exhibited a stable and
repeatable pattern of sharp peaks across the ZPL. Typical
examples are shown in figure 8. The SiV$^-$ ZPL is known
to consist of four separate transitions that can be resolved
at low temperature, and they can approach the lifetime lim-
ited linewidth of about 100 MHz [2]. This is well below the
measurement resolution, and it is interpreted that the spiky
structure of the measured spectra is due to individual SiV$^-$
transitions. For large ensembles of many SiV$^-$ centres the
individual lines average out and the expected spectrum would
be a smooth band shaped by the inhomogeneous distribution
(predominantly strain variation), whereas for small ensembles
of only a few SiV$^-$ centres the spectrum would be dominated
by individual transition lines and a very spiky spectrum would
be expected. This observation provides a way to estimate the
number of SiV$^-$ centres present in the MDs.
Figure 8. Monte Carlo simulated cryogenic spectra to estimate number of SiV\(^-\) centres in MDs. (a) The SiV\(^-\) ZPL consists of four transitions between orbitally-split ground and excited states. Axial strain and temperature can alter the central energy of these transitions. Transverse strain alters the orbital splitting in each state, which in turn alters the thermalization in the excited state that leads to a change in relative intensity between the two sets of optical transitions indicated by different line thicknesses. (b) The cryogenic (below 10 K) PL spectrum (blue) for a MD showed a band-like shape with reproducible spikes superimposed. (c) A set of 200 simulated spectra were generated for a given estimate of the total number of SiV\(^-\) centres in the MD. The spikiness was calculated for each simulated spectrum, producing the distribution shown in the shaded histogram. This was repeated for a range of SiV\(^-\) numbers, and the spikiness distribution from the Monte Carlo simulation compared with the value obtained for the measured spectrum. Smaller ensembles (lower numbers of SiV\(^-\) centres) produced spectra with higher spikiness as expected. (d) The 'intersection' of each normalized histogram with the measured spikiness distribution gives a probability distribution over the number of SiV\(^-\) centres. An ‘optimum’ simulated spectrum is shown in orange in (a) for easy comparison with the measured data.

The spikiness of each MD spectrum was calculated by first taking a moving-window average of 50 points to obtain the smoothest ‘band shape’. The area between the measured spectrum and this smooth band shape was divided by the area under the band (for normalization) to produce a quantitative description of the spikiness. Spikiness values of 5.8 × 10\(^{-2}\), 9.5 × 10\(^{-2}\), and 1.2 × 10\(^{-1}\) were obtained for the three MD spectra shown in figure 8.

The SiV\(^-\) transition energies are predominantly influenced by the presence of strain. Axial strain (along the (111) SiV\(^-\) symmetry axis) shifts the overall transition energy, and transverse strain increases the splitting between the four ZPL components. At cryogenic temperatures the splitting of the excited-state spin–orbit doublet is enough to cause thermalization of the excited-state population, and this leads to the higher-energy (blue-shifted) peaks decreasing in intensity relative to the lower-energy peaks. Thermal broadening of the ZPL components also alters the shape of the SiV\(^-\) spectrum. Using detailed parameters for these effects from the literature, a SiV\(^-\) spectrum simulator was created capable of producing the expected spectrum given information about temperature and strain.

The running-average smoothed spectral data was used as a probability distribution for randomly sampling the ZPL central position for each SiV centre, and transverse strain was sampled from an exponential distribution to represent the majority of centres having low strain but some high-strain outliers. Temperature was set to match the 8 K measurement temperature, and each simulated SiV\(^-\) centre was scaled by a brightness factor sampled from a flat distribution (not all colour centres are in the confocal microscope focal spot). Summing the individual simulated SiV\(^-\) spectra provided Monte Carlo ensemble simulations of the measured MD spectra. For a chosen number of SiV\(^-\) centres, 200 simulated ensemble spectra were generated and their spikiness calculated. The histograms in figure 8(b) show examples of the resulting spikiness distributions, which are compared to the single value obtained for the experimental data (vertical line). As anticipated, increasing the ensemble size (more SiV\(^-\) centres) tends to produce MD spectra with reduced spikiness.

A probability distribution of the number of SiV\(^-\) centres contributing to the measured MD spectrum was obtained by comparing the heights of these histograms at various ensemble sizes with the experimental spikiness. The MD spectrum featured in figure 8(a) produced the distribution illustrated in figure 8(c), suggesting this MD contained 7700 ± 850 SiV\(^-\) centres (standard deviation as uncertainty). This process is summarized in figures 9(a) and (b) for two other MDs, which had more spikiness in their spectra and were
estimated to have $2100 \pm 270$ and $1700 \pm 180$ SiV$^-$ centres respectively.

This Monte Carlo simulation of the ensemble spectrum is a novel method for estimating the number of colour centres in medium-sized ensembles. There is no accessible technique to verify the estimates obtained, but it seems reasonable that MDs grown on silicon substrates would have quite high concentrations of SiV$^-$ defects. A few thousand SiV$^-$ centres per MD corresponds to a few parts-per-million concentrations, which is in line with other SiV$^-$ samples produced by CVD with silicon etched into the plasma [36].

3. Conclusions

In summary, we demonstrate the fabrication of MDs with large ensemble of SiV$^-$ centres by MWCVD on Si(001) substrates. The morphology and micro-structure of the diamond crystals are fully investigated and correlated to the stress formed at the grain boundary regions. We have demonstrated a novel Monte Carlo simulation technique to evaluate the number of SiV$^-$ centres in each MD, based on temperature dependent PL measurements. The fabrication of MDs with a large density of SiV$^-$ centres represents a viable solution for numerous applications. Bio-marking can benefit from the bright fluorescence within a biological transparency window. Spatially confined colour centre ensembles are also of interest for fundamental investigations including optical trapping and a recent proposal for strong light–matter coupling in cavities [14]. The MDs presented here are valuable materials for quantum technologies.

4. Experimental methods

MDs were grown on Si(001) substrates consisting of $15 \times 15$ mm$^2$ chips cleaved from a 4 inch, 500 $\mu$m thick, and n-type (1–10 $\Omega$ cm) wafer. Si(001) chips were rinsed in acetone and isopropanol, followed by piranha etching for 15 minutes, and finally cleaned by RF oxygen plasma. CVD growth was performed using the MWCVD Seki 6500 reactor at a chamber pressure of 70 Torr, with a CH$_4$ to H$_2$ ratio of 1.5%, at a substrate temperature of 900 $^\circ$C for 120 min.

The SEM analysis was performed using a ZEISS Auriga electron microscope (acceleration voltage 5 kV, aperture size 30 $\mu$m) equipped with a FIB gun. The markers were fabricated by FIB using 30 kV Ga$^+$ ions and 1 nA current, they are about 2 $\mu$m deep and 30 $\mu$m wide, to be easily addressed by optical microscopy.

AFM measurements were carried out by a Bruker Dimension ICON SPM microscope at 256 samples/line and 0.3 Hz. The data are analysed with the open-source software Gwydion [37].

Room temperature confocal Raman spectroscopy and SiV$^-$ PL were performed with a Renishaw inVia system equipped by a green laser (514 nm), 2400 lines mm$^{-1}$ monochromator, 50x 0.9 NA objective, and CCD camera detector. Polarized measurements are obtained by using a motorized (3$^\circ$/step) rotating $\lambda/2$ waveplate on the laser beam, and a polarizer on the scattered beam.

Low temperature PL measurements were performed on a galvo mirror home-built confocal set up, operated using the Qudi software suite [38]. The silicon substrate was clamped on to the side of an x-y Attocube nano-positioner stack mounted inside a Montana Instruments s200 closed cycle cryostat, with the cold finger at ~8 K. Off resonant excitation was achieved with a 532 nm Coherent OBIS laser set to 135 mW for spectra measurements. PL spectra were taken using a prototype Redback Systems echelle spectrometer, similar in design to the RHEA [39] spectrometer built for astronomical applications.

XPS analysis was performed using an AXIS Ultra DLD spectrometer (Kratos Analytical Inc. Manchester, UK) with a monochromated Al K$\alpha$ source at a power of 180 W (15 kV, 12 mA) at a pressure of $\sim 1 \times 10^{-9}$ mbar, a hemispherical analyser operating in the fixed analyser transmission mode and the standard aperture (analysis area: 0.3 mm $\times$ 0.7 mm). To obtain more detailed information about chemical structure, high resolution spectra were recorded from individual peaks at 20 eV pass energy. The specimen was analysed at an emission angle of 0$^\circ$ as measured from the surface normal. Assuming typical values for the electron attenuation length of relevant photoelectrons, the XPS analysis depth (from which 95% of the detected signal originates) ranges between 5–10 nm for a flat surface.

XPS data processing was performed using CasaXPS software version 2.3.15 (Casa Software Ltd Teignmouth, UK). All elements present were identified from survey spectra. The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. Binding energies were referenced to the Si 2p$_{3/2}$ peak at 99.4 eV for Si(100). The accuracy associated with quantitative XPS is about 10%–15%.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Author contributions

Experiments were conceived by F I, L R, A B, and T V. F I performed the diamond CVD growth, SEM, FIB and Raman measurements. M J, L R and F I performed the spectroscopic measurements. NHH performed the AFM analysis. BW and F I performed the diamond CVD growth, SEM, FIB and Raman measurements. M J, L R and F I performed the Monte Carlo simulation of SiV− centres. The manuscript was written by F I and L R, and all authors discussed the results and commented on the manuscript.

Conflict of interest

The authors declare no competing financial interests.

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