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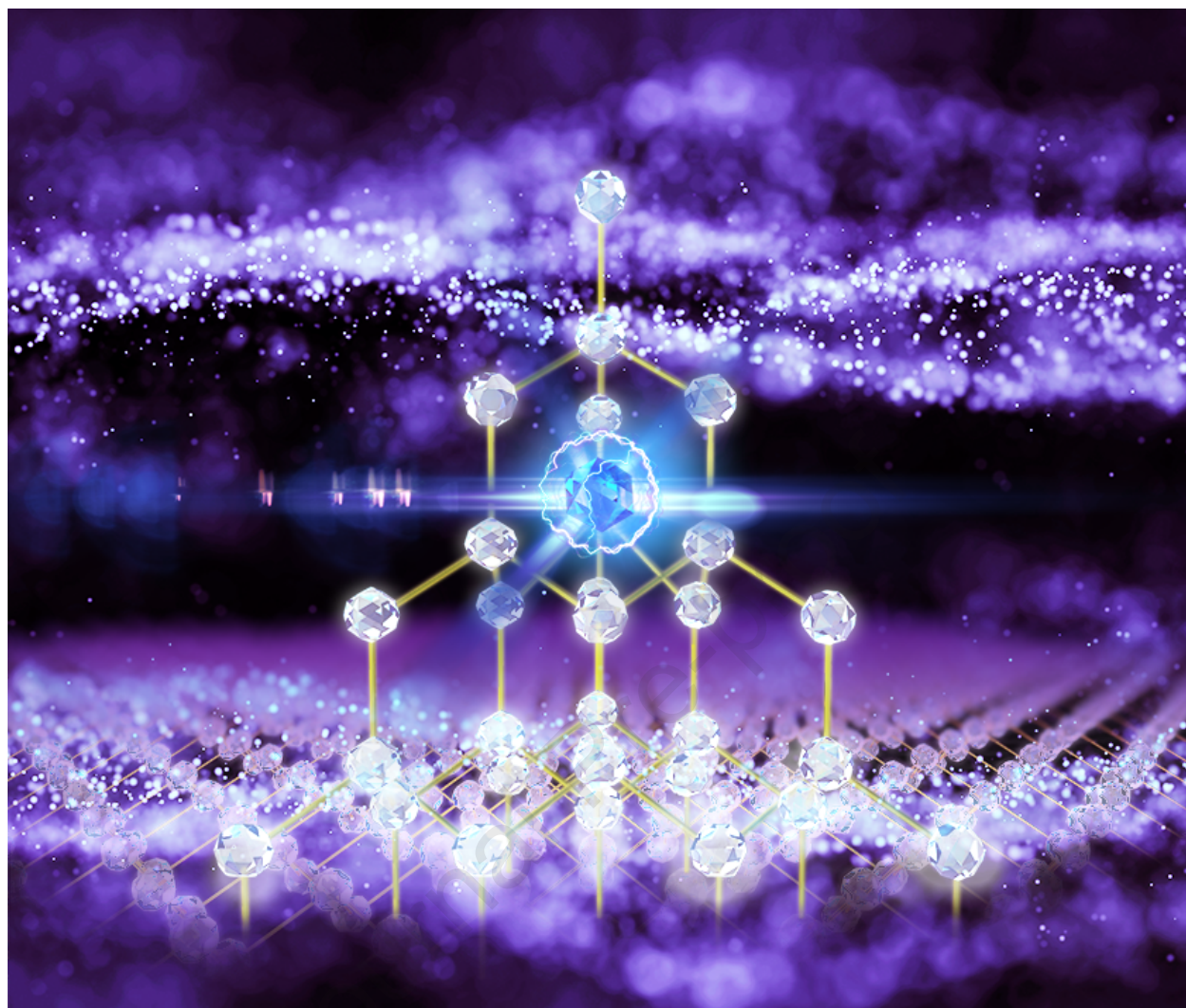
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Controlled Boron Content in Lightly B-doped Single Crystal Diamond Films by Variation of Methane Concentration

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Abstract

Obtaining desirable electrical properties from B-doped single crystal diamond (SCD) films hinges on precise control of boron incorporation into the crystal lattice structure. In this study, the impact of methane concentration during plasma deposition on boron incorporation of lightly B-doped SCD films is investigated. SCD layers are grown successively by microwave plasma enhanced chemical vapor deposition (CVD) at different methane-to-hydrogen concentrations (1%, 2%, and 3%), with residual boron atoms present in the CVD reactor. An increase in methane concentration leads to surface defects such as unepitaxial crystallites and pyramidal hillocks. The charge carrier mobility, electrical conductivity, and boron content of samples are evaluated and discussed. The temperature-dependent mobility is analyzed through

22 theoretical modeling, revealing dominant scattering mechanisms at different temperatures. At
23 300 K, the maximum hole mobility reached $1200 \text{ cm}^2/\text{V}\cdot\text{s}$ for the 1% methane concentration
24 sample, transitioning to hopping conduction at lower temperatures. An increase in
25 boron-doping level with rising methane concentration is detected by Fourier transform infrared
26 spectroscopy, cathodoluminescence spectroscopy, Hall effect, and X-ray photoelectron
27 spectroscopy measurements. These findings highlight the potential of methane concentration
28 in plasma feedgas to control boron concentration in CVD diamond and open avenues for
29 crafting efficient high-power electronic applications using *p*-type SCD films.

30 **Keywords:** Boron doped single crystal diamond, methane concentration dependence, residual
31 boron, CVD diamond growth.

32 Introduction

33 Boron doped single crystal diamond (SCD) is a well-known candidate material for the next
34 generation power electronic devices, and controlling the boron incorporation in its structure is
35 one of the most laborious challenges. In recent years, the growth of lightly B-doped SCD with
36 boron concentrations below 10^{16} cm^{-3} and hole mobility above $2200 \text{ cm}^2/\text{V}\cdot\text{s}$ have gained
37 attention for the fabrication of high-power diamond Schottky diodes.¹⁻⁴ One of the promising
38 method to achieve high crystalline quality of B-doped SCD films is through crystallization
39 from a carbon solution in metal melts at high pressure and high temperature (HPHT). However,
40 it has been observed that synthetic HPHT single crystals of diamond can exhibit various crystal
41 forms with different predominate faces, which strongly depends on the growth conditions such
42 as temperature, pressure, and used metals for catalysis and inhibition.^{5,6} Therefore, B-doped
43 HPHT diamonds have a non-uniform distribution of boron, dependent on the growth sector,
44 potentially impacting the performance diamond-based electronic devices.^{6,7} On the other hand,
45 microwave plasma enhanced chemical vapor deposition (MW PE CVD) is an appropriate
46 method to have a good control of diamond electrical conductivity by the uniform incorporation
47 of boron atoms in the crystal lattice structure for electronic devices,⁸⁻¹⁴ even if it is still a
48 challenge to reach a low boron doping ($< 5 \times 10^{15} \text{ cm}^{-3}$).¹⁵ Another crucial factor is the ability
49 of growing a high crystalline quality of B-doped SCD film with a low density of dislocations
50 and surface defects, because several growths are required to resume in order to fabricate the
51 drift layer of electronic devices such as Schottky diodes.^{8,11,16,17}

52 The effect of methane concentration on the crystalline quality of homoepitaxial diamond films
53 has been extensively studied.^{8,18-21} A low concentration ratio ($\leq 0.5\%$) of methane-to-hydrogen
54 ($[\text{CH}_4]/[\text{H}_2]$) in the plasma feedgas mainly resulted in the high crystalline quality of SCD
55 films.¹⁶ However, obtaining the required thickness (a few tens of micrometers) of diamond

56 films needed for power electronics, e.g. vertical Schottky barrier diodes becomes both
57 time-consuming and cost-prohibitive with such a low $[\text{CH}_4]/[\text{H}_2]$ ratio ($\leq 0.5\%$), primarily due
58 to a low deposition rate ($\leq 0.4 \mu\text{m/h}$).^{22,23} In order to obtain higher growth rates, which reduces
59 the fabrication cost, it is required to increase the methane concentration. Nevertheless, the
60 increase of methane concentration may cause the appearance of several types of surface defects
61 such as unepitaxial crystallites.^{8,18,24,25} These defects are known to increase the leakage current
62 and reduce the breakdown field in high power electronic devices, due to the fact that the leakage
63 current is likely to flow through these defects and provide alternative conduction
64 pathways.^{16,26,27} Hence, an optimized CVD growth condition is demanded to deposit a SCD
65 layer with a low density of surface defects at reasonably high growth rate.

66 In our previous study,²³ the impact of methane concentration in the plasma feedgas on the
67 electrical properties of heavily boron doped SCD films was investigated. The results revealed
68 that by increasing the methane concentration, the B-doping level in the films was also
69 increased. *Ab initio* density-functional theory calculations showed that the presence of CH_2
70 sites has no significant impact on the binding energy of an adsorbed boron atom. However, the
71 presence of CH_2 sites increases the chance of H-defect site formation, *i.e.* places where the
72 diamond lattice is not terminated with a hydrogen atom, providing additional binding sites for
73 boron. These results have great potential to provide a route to understand impurity
74 incorporation in diamond on a general level, of great importance for doping but also colour
75 center formation.²⁸

76 The purpose of the current work is to develop a new protocol allowing coupling methane
77 concentration and boron incorporation to reach lightly B-doped SCD grown layers with an
78 improvement of the surface quality with a low density of surface defects. Along these lines, a
79 series of experiments that varied the methane concentration in the plasma feedgas have been
80 carried out in this study.

81 Materials and Methods

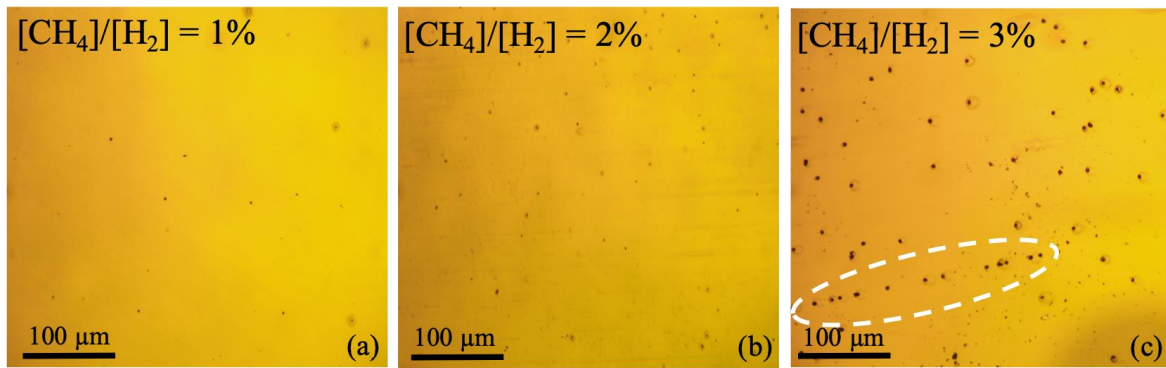
82 Unintentionally boron doped diamond was homoepitaxially grown on 3 mm × 3 mm type Ib
83 HPHT SCD substrates provided by Sumitomo Electric. A 2.45 GHz MW PE CVD homemade
84 metal chamber reactor containing a 4.5 cm inside diameter fused silica tube was used for the
85 deposition.²⁹ The orientation of diamond substrate surfaces was less than 1° off of the (100)
86 crystallographic orientation, as measured by X-ray diffraction. Prior to being loaded into the
87 CVD reactor, diamond substrates were acid cleaned, as described in our previous work.²³ The
88 base pressure in the reactor was $\approx 3 \times 10^{-7}$ mbar before igniting the hydrogen plasma. A
89 hydrogen plasma treatment was performed on the substrates using a temperature of 800°C, a
90 gas flow of 500 sccm, a microwave power of 315 W, and a pressure of 200 mbar (20 kPa) for
91 approximately 45 min. A new fused silica tube, which was not contaminated by boron, was
92 used for this series of experiments.³⁰ Unintentionally B-doped diamond films were then grown
93 with 1%, 2%, and 3% of [CH₄]/[H₂] ratios in the plasma feedgas, sequentially. The boron atoms
94 source was related to the memory effect of metal chamber used previously for the growth of
95 heavily B-doped SCD films with trimethylboron. These growths were performed at a pressure
96 of 200 mbar (20 kPa) and a total gas flow of 500 sccm. Microwave power was varied between
97 315 W and 320 W to maintain a constant substrate temperature at 780–800°C. The temperature
98 was measured every 20 min during the 2 h deposition time by a Minolta/Land Cyclops 52
99 Infrared Thermometer in the peak measuring mode with emissivity set to 0.6. This pyrometer
100 is designed to operate within wavelength range of 3.4 μm to 3.9 μm, minimizing errors arising
101 from emissivity, ensuring maximum accuracy in temperature measurements. Sample thickness
102 was measured by a Mitutoyo Linear Gage (Model EH-101P) at the center of the sample,
103 avoiding surface defects, nine times and given as an average over all measurements.²³ The
104 grown films were characterized by optical microscopy and atomic force microscopy (AFM) to

105 identify the main topological defects. AFM scans were performed on a Bruker Multimode 8 in
106 tapping mode. The Fourier transform infrared (FTIR) transmission spectrum was measured by
107 a Bruker Tensor 27 FTIR spectrometer. For each sample, a spectrum of the HPHT diamond
108 substrate was measured prior to growth, and then for the grown diamond layer on the substrate
109 after deposition. Hence, any variation in the transmission spectrum is due to the grown diamond
110 films, signifying that any newly observed absorption feature occurs exclusively within the
111 thickness of the grown layer. Hall effect measurements were carried out in a Transient Signal
112 Technologies vacuum chamber at temperature ranges from 90 K to 700 K using the van der
113 Pauw method.²³ All of the diamond surfaces were chemically oxidized by acid cleaning prior
114 to metal deposition. Four Ti/Au (20 nm/50 nm) Ohmic contacts with a 250 μm diameter were
115 deposited at the corners of the samples by a homemade dual magnetron sputtering system,
116 without breaking the vacuum between the depositions. The Ohmic nature of the contacts was
117 confirmed at several temperatures between 90 K to 700 K by the observation of linear
118 current-voltage characteristics for each contact pair. For cathodoluminescence (CL)
119 spectroscopy, an electron beam generated by a FEI Quanta 200 scanning electron microscopy
120 gun was focused on the sample (0.2-30 kV acceleration voltage) in order to generate
121 electron-hole pairs. The sample was located on a cold stage GATAN using the liquid helium
122 to set the temperature (5 K to 300 K). The detection system was composed of a parabolic mirror
123 collecting the light generated and focusing it on the lens and entrance slit of a Jobin Yvon
124 HR460 monochromator. The monochromator was associated with a photomultiplier or charge
125 coupled device, placed at the exit of the spectrometer, to analyze the emitted light and generate
126 a spectrum. To measure the samples of this study at 5 K, the entrance slit size of
127 monochromator was chosen to be 0.2 mm, and the acceleration voltage was fixed to 30 kV.
128 X-ray photoelectron spectroscopy (XPS) measurements on the diamond samples were
129 performed in the beamline U41-PEAXIS at the BESSY II synchrotron.³¹ The XPS analyzer

130 was a commercial PHOIBOS 150 EP hemispherical analyzer from SPECS.³² Photoelectrons,
131 emitted from the sample after the photon absorption, were collected by the electron analyzer
132 mounted at the sample chamber. The excitation (1000 eV) and the pass (20 eV for C1s and 100
133 eV for B1s) energies of the analyzer were kept constant whereas the kinetic energy of the
134 electrons was varied. The energy resolution of the analyzer was constant throughout the scan.
135 During the measurements, the pressure inside the experimental chamber was $\approx 10^{-8}$ mbar.

136 Results and Discussion

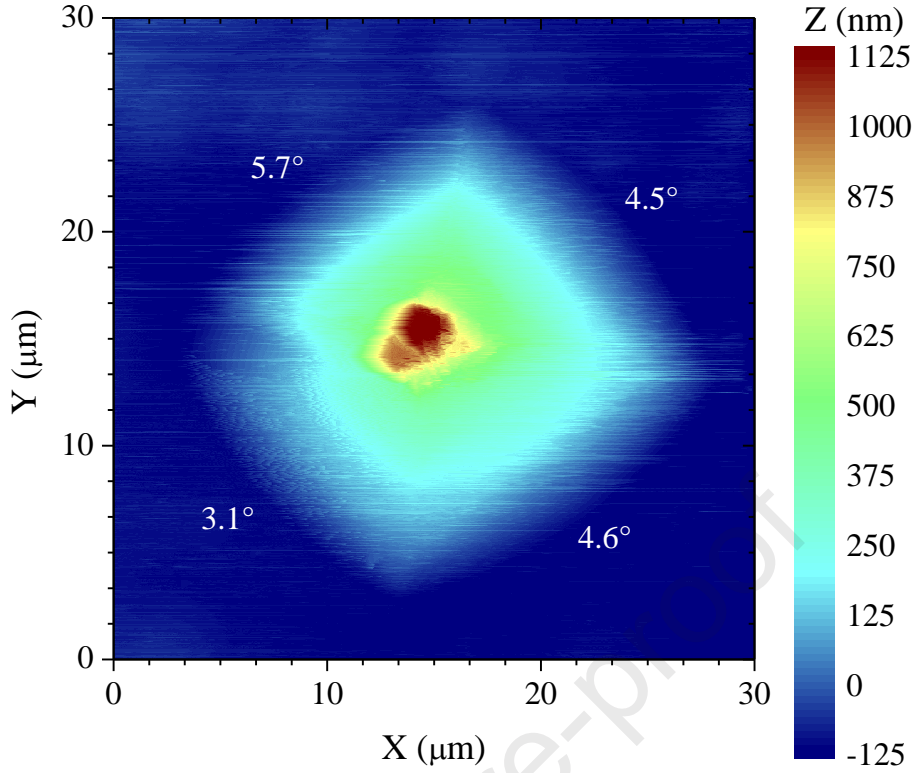
137 The homoepitaxial CVD diamond grown film morphologies, observed by optical microscope,
138 are compared in Figure 1. For the sample with 1% methane concentration, a high surface
139 quality was achieved exhibiting very few visible surface defects such as small hillocks and
140 unepitaxial crystallites on the grown surface. When the methane concentration was increased
141 to 2%, the number of unepitaxial crystallite defects (dark dots in Fig. 1) increased, which leads
142 to a degraded surface quality of the film. Moreover, the SCD film grown at 3% methane
143 concentration contains an even higher number of surface defects like unepitaxial crystallites
144 and hillock defects compared to the previous two samples grown at lower methane
145 concentrations (1% and 2%). This can be a consequence of the high growth rate at 3% methane
146 concentration (see Table 1) and/or bad polishing of the as-received HPHT substrate. The latter
147 is proposed due to the appearance of some defects along what appears to be a polishing line
148 (Fig. 1(c)).



149

150 Figure 1: Optical micrographs show the surface morphology of SCD samples grown with: (a) 1%, (b) 2%, and
 151 (c) 3% methane concentration in the plasma feedgas. (c) The white dashed oval marks surface defects created
 152 along a polishing line.

153 In order to define the identity of the defects on the sample grown with 3% methane
 154 concentration, its surface morphology was investigated by AFM (Fig. 2). Figure 2 shows one
 155 of the pyramidal hillocks that consists of four-fold symmetry defects, featuring inclination
 156 angles between 3.1° to 5.7° , and truncated by an unepitaxial crystallite on the top. These
 157 pyramidal hillocks have sizes up to $30\ \mu\text{m}$ in lateral dimension. Lloret *et al.*³³ reported that
 158 high methane concentrations result in the generation of the $\mathbf{b}=\frac{1}{2}\langle 011 \rangle$ family of threading
 159 dislocations. When it is energetically favourable, in undoped or lightly doped SCD samples,
 160 such threading dislocations tend to dissociate into partial $\mathbf{b}=\frac{1}{6}\langle 211 \rangle$ Burgers vectors by a
 161 Shockley mechanism.³⁴ This process changes the Burgers vector family and introduces
 162 stacking faults which may form micro $\{111\}$ disoriented planes that favour the generation of
 163 penetration twins. In addition to the mechanism governing the formation of such defects, it is
 164 believed that hillock formation may arise due to stacking faults or dislocations that originate at
 165 the interface between the surface and the CVD grown layer from lattice defects or suboptimal
 166 substrate polishing (Fig. 1(c)), or propagate from the substrate into the CVD layer.^{35,36}
 167 Furthermore, it was reported that these regions consist of agglomerated impurities, primarily
 168 composed of Fe, Mo, and amorphous carbon.^{36,37} These metals are present as impurities in
 169 HPHT substrates, as well as within the growth chamber and substrates holder.



170

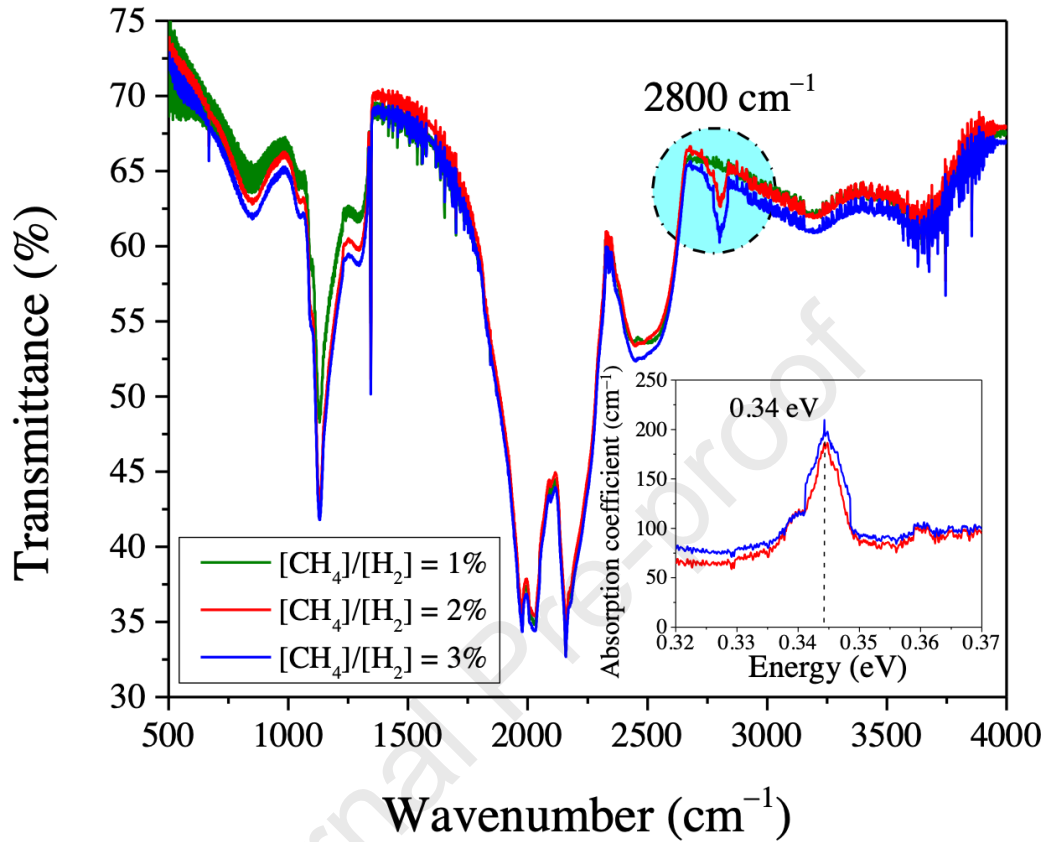
171 Figure 2: AFM image of a pyramidal hillock exhibiting an unepitaxial crystallite in its centre, observed in the
 172 sample grown at 3% methane concentration. The inclination angle of each side of the hillock is also provided.

173 The analysis of the FTIR transmission spectrum focused on the absorption feature at 2800 cm^{-1}
 174 (Fig. 3), which is attributed to the second excited state electronic transition of the neutral boron
 175 acceptor.^{38,39} This peak has been correlated with the boron content in diamond to estimate
 176 doping levels in the range of 10^{16} cm^{-3} to 10^{18} cm^{-3} .³⁸⁻⁴¹ The uncompensated acceptor
 177 concentration ($N_a - N_d$) can be evaluated using the equation given by Collins and Williams for
 178 the peak at 2800 cm^{-1} .⁴² The inset of Figure 3 shows a plot of absorption coefficient vs. energy,
 179 which can give the integrated area of the 2800 cm^{-1} absorption peak, I_{2800} . Fitting a baseline to
 180 these data, enables the use of a relationship between I_{2800} and $N_a - N_d$:

$$N_a - N_d = 8 \times 10^{17} I_{2800} (\text{cm}^{-3}) \quad (1)$$

181 The uncompensated acceptor concentrations of films prepared at methane concentrations of
 182 2% and 3% were estimated to be $4.5 \times 10^{17}\text{ cm}^{-3}$ and $5.6 \times 10^{17}\text{ cm}^{-3}$, respectively. While the
 183 spectrum of the sample with 1% methane concentration has no obvious FTIR peak at

184 2800 cm^{-1} , this simply demonstrates a SCD film without visible evidence of a boron
 185 incorporation higher than 10^{16} cm^{-3} .⁴²



186

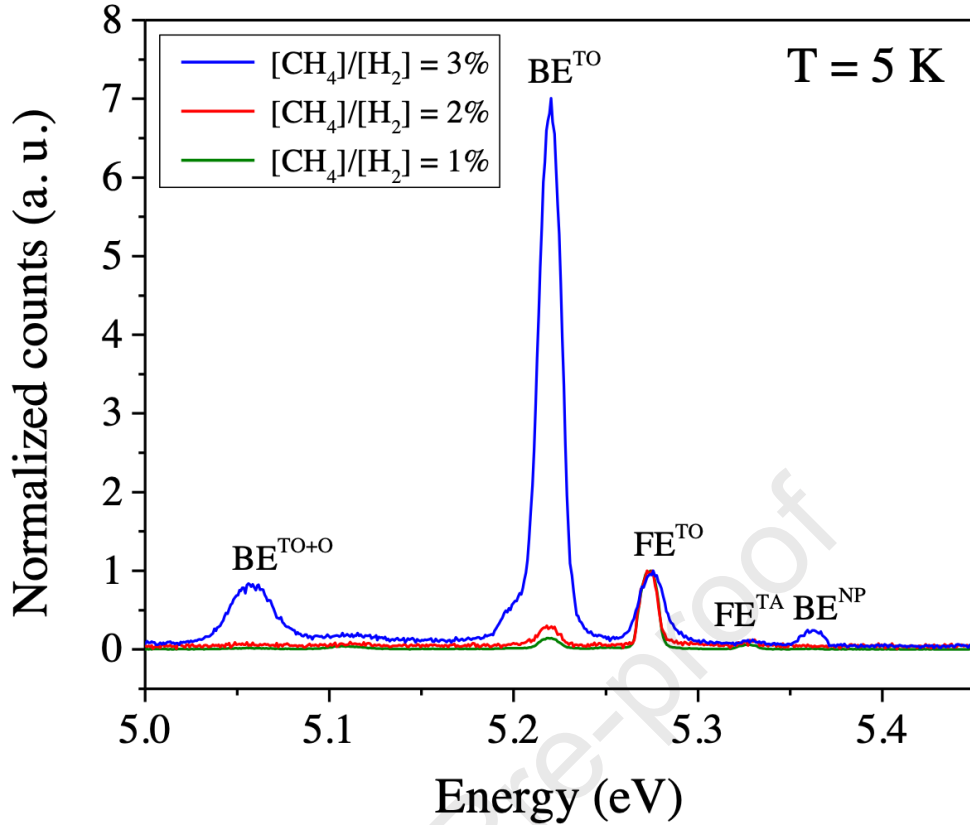
187 Figure 3: FTIR transmission spectra of diamond films grown at 1%, 2%, and 3% methane concentrations. The
 188 inset shows the corresponding absorption coefficient vs. energy plots of the samples deposited at 2% and 3%
 189 methane concentrations.

190 Figure 4 displays the details of the CL spectra (normalized with respect to the free exciton (FE)
 191 at 5.27 eV) of the B-doped SCD layers grown with 1%, 2%, and 3% methane concentration in
 192 the excitonic energy range at 5 K . These spectra exhibit two dominant peaks: the peak at
 193 5.27 eV corresponds to the recombination of the FE assisted by a transverse optical (TO)
 194 phonon (FE^{TO}), and the peak at 5.22 eV corresponds to the neutral-boron bound exciton (BE),
 195 also assisted by a TO phonon (BE^{TO}). The boron acceptor concentration was calculated from
 196 the ratio between the BE^{TO} and FE^{TO} recombination intensities, as given in Eq. (2):⁴³

$$[B] = 3.5 \times 10^{16} \frac{I_{\text{BE}^{\text{TO}}}}{I_{\text{FE}^{\text{TO}}}} \text{ (cm}^{-3}\text{)} \quad (2)$$

197 To ensure the collection of CL signals are from the CVD grown layer, the sample deposited at
198 1% methane concentration was additionally measured at 10 and 20 kV (not shown here). The
199 ratio between BE^{TO} and FE^{TO} intensities showed consistency with that measured at 30 kV,
200 confirming that the acquired signal indeed mostly originated from the CVD doped layer. The
201 boron content in diamond samples was found to be 5×10^{15} , 1×10^{16} , $2 \times 10^{17} \text{ cm}^{-3}$ for the
202 samples grown at 1%, 2%, and 3% of methane concentrations, respectively.

203 The full width at half maximum (FWHM) of the FE^{TO} peak is directly related to the crystalline
204 quality of the film.⁴⁴ The lower the defect density, the lower is the FWHM of FE^{TO} peak.⁴⁴ The
205 samples grown at 1% and 2% methane concentrations exhibit narrower peaks (FWHM
206 $\approx 10 \text{ meV}$) of the FE^{TO} peak than the sample grown with 3% methane concentration (FWHM
207 $\approx 15 \text{ meV}$). This is explained by the presence of unepitaxial crystallites and pyramidal hillock
208 defects observed on this sample by optical micrographs and AFM measurements, causing the
209 degradation of crystalline quality.



210

211

Figure 4: CL spectra of B-doped SCD films grown at 1%, 2%, and 3% methane concentrations.

212

The energy and FWHM of the BE^{TO} exciton show good agreement with the results achieved

213

by other studies (Fig. 5).⁴⁴⁻⁴⁷ In all three samples of this work, the peak position of BE^{TO} peak

214

is neither red- nor blue-shifted from its position reported in the literature.⁴⁴ This indicates that

215

there is no residual strain in the samples that could be caused by interstitial boron atoms in the

216

diamond lattice structure. In the work of Ghodbane *et al.*,⁴⁴ a downward shift (0.033 eV) of the

217

peak position of the BE^{TO} peak was reported for the B-doped SCD sample with a boron

218

concentration of $6.2 \times 10^{17} \text{ cm}^{-3}$, whereas the sample with a boron content of $3.3 \times 10^{15} \text{ cm}^{-3}$

219

showed no shift. Another possible reason for this shift would be the formation of the boron

220

impurities energy level and the narrowing of the diamond bandgap. Here, this origin is ruled

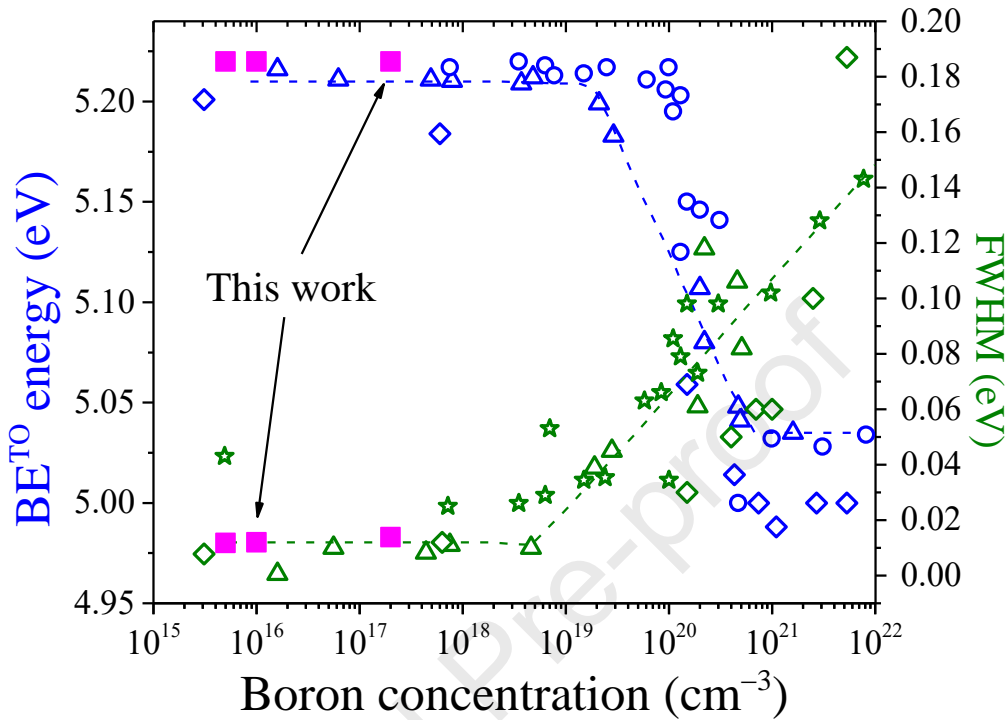
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out as the boron concentration of the samples in this work is estimated to be below the

222

minimum limitation of formation of this impurity level in diamond ($1.5 \times 10^{19} \text{ cm}^{-3}$).⁴⁸ The

223 FWHM of the BE^{TO} peak remains very low reflecting a low density of imperfections in the
 224 lattice structure of the films.



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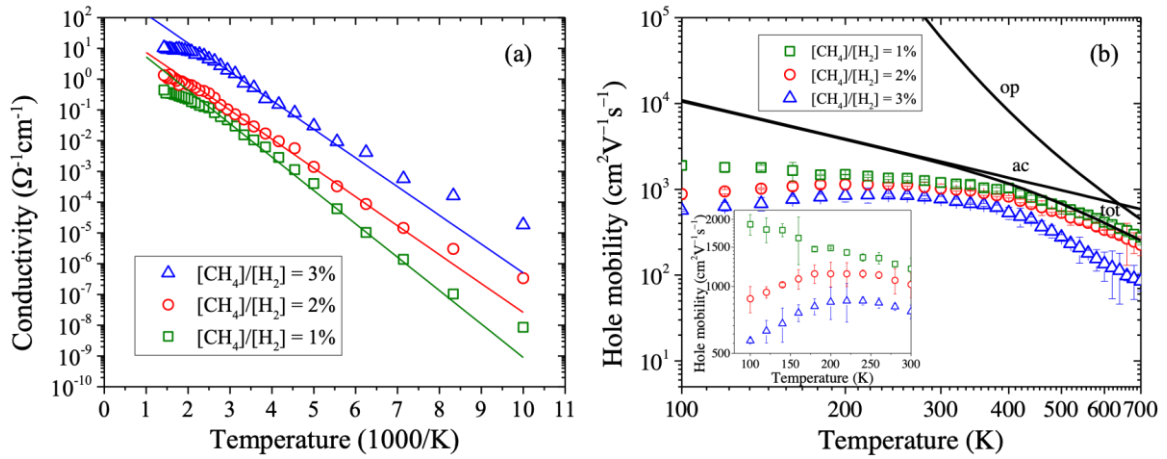
226 Figure 5: Peak position and FWHM of BE^{TO} as a function of boron concentration for B-doped SCD films of this
 227 study compared with previous results reported in literature: \diamond —Ref. (44), Δ —Ref. (45), \circ —Ref. (46), \star — Ref.
 228 (47), and \blacksquare — this work.

229 Figure 6 shows the temperature dependence of electrical conductivity and hole mobility as
 230 determined by the Hall effect. All the samples showed *p*-type conductivity, which indicated
 231 that holes are the majority carriers in the films. The electrical conductivity increased with
 232 increasing temperature in all the samples, which is typical for semiconductors (Fig. 6(a)). The
 233 increase in methane concentration from 1% to 3% in the plasma feedgas resulted in the higher
 234 electrical conductivity of samples, from $15 \text{ m}\Omega^{-1}\cdot\text{cm}^{-1}$ to $0.74 \text{ }\Omega^{-1}\cdot\text{cm}^{-1}$ at room temperature,
 235 respectively. This correlates with the increase of acceptor concentration, as seen in CL and
 236 FTIR results. For B-doped SCD films grown at 1%, 2%, and 3% methane concentrations, the
 237 hole concentrations measured by Hall effect at room temperature were 8×10^{13} , 3×10^{14} , and
 238 $6 \times 10^{15} \text{ cm}^{-3}$, respectively.

239 The hole mobility decreased with increasing the methane concentration, as shown in
240 Figure 6(b). B-doped SCD grown at 1% methane concentration reaches a Hall mobility of
241 $(1200 \pm 140) \text{ cm}^2/\text{V}\cdot\text{s}$ at 300 K, which corresponds to the higher range of the experimental
242 values reported in boron doped layers.^{15,49,50} Such a high value of Hall mobility can be
243 attributed to the low degree of compensation and good crystalline quality of this sample.⁵¹
244 Samples grown with a methane concentration of 2% and 3%, exhibit lower values of
245 $(1020 \pm 130) \text{ cm}^2/\text{V}\cdot\text{s}$ and $(770 \pm 54) \text{ cm}^2/\text{V}\cdot\text{s}$ at room temperature, respectively. For these two
246 B-doped SCD samples, the Hall mobility values were relatively smaller in the lower
247 temperature range below 200 K (Fig. 6(b) inset), and decreased with increasing temperature
248 above 500 K. The observed rapid increase in the Hall mobility of the samples grown at 2% and
249 3% methane concentration with temperature from 90 K to 200 K can be attributed to the
250 contribution of hopping conduction, which has been reported in the other studies
251 extensively.^{15,52-54} Tsukioka *et al.*⁵² showed that if the Hall coefficient, calculated by $K_s = \mu/\sigma$,
252 decreases due to the effect of hopping conduction, mobility also decreases proportionally to
253 K_s .

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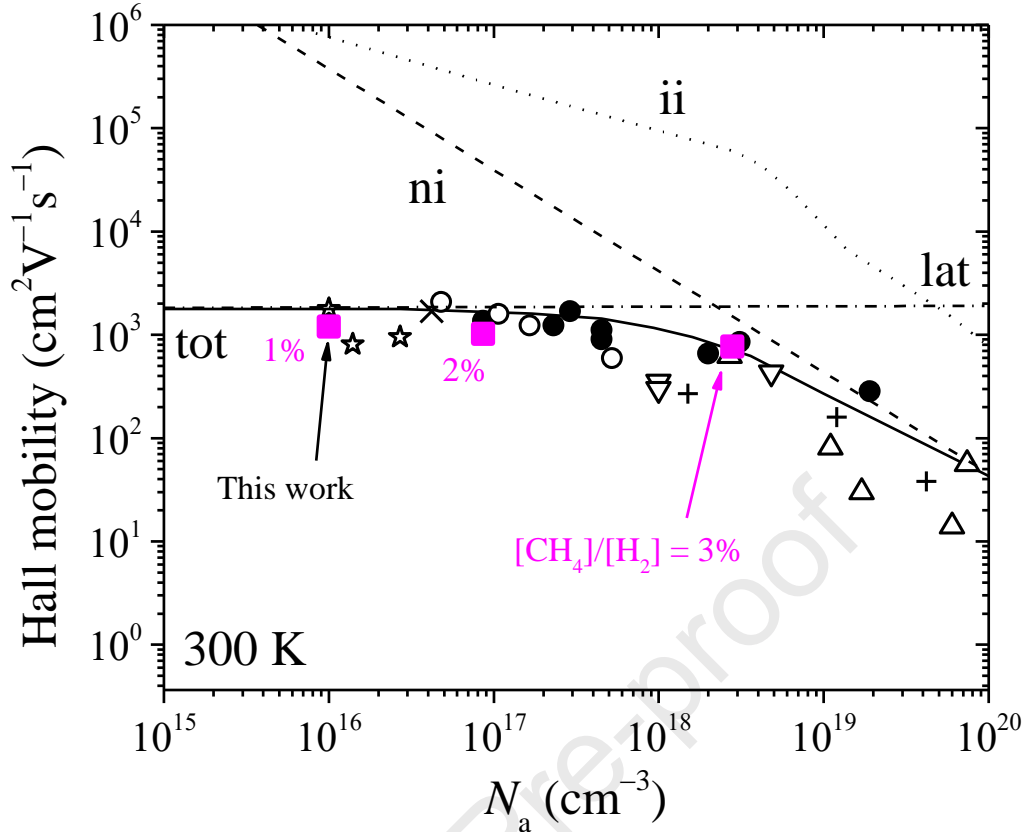
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256

257 Figure 6: Temperature dependence of (a) bulk electrical conductivity and (b) hole mobility of B-doped SCD
 258 samples grown with 1%, 2%, and 3% methane concentration in the plasma feedgas. (a) The solid lines are the
 259 exponential fitting data.⁵³ The disparities between the fitting and experimental data at low temperatures are
 260 attributed to the hopping mechanism. (b) The solid lines show the theoretical contribution of optical phonon
 261 (op) and acoustic phonon (ac) scattering modes and the total mobility (tot), calculated from Ref. (51). Ionized
 262 and neutral impurity scattering are not included here. According to Ref. (51), their contribution at elevated
 263 temperatures (above 400 K) is considered negligible, whereas at lower temperatures (below 400 K), the data
 264 lacks the reliability necessary for fitting. The inset shows a zoom-in perspective of temperature (plotted in a
 265 linear scale) dependence of hole mobility of samples below 300 K.

266 The scattering mechanisms of B-doped SCD samples in Figure 6(b) were deduced from
 267 mobility temperature dependence using the model, explained in details in Ref. (51). The
 268 calculations took into account acoustic phonon (ac), and optical phonon (op) scattering
 269 mechanisms (Fig. 6(b)). In these calculations, both acoustic phonon (ac) and optical phonon
 270 (op) scattering are intrinsic to diamond and hence are assumed to be the same for all samples.⁵¹
 271 Once the temperature is below 400 K, the hopping mechanism assumes control over hole
 272 mobility, as discussed above, rendering fitting impossible below this temperature range. In
 273 addition, the hole mobility as a function of doping level of this study shows a good agreement
 274 with the summation of the theoretical contribution of various scattering modes,⁵¹ together with
 275 the results of previous studies, as shown in Figure 7.^{50,52,55-59}



276

277 Figure 7: Room temperature Hall hole mobility as a function of N_a , calculated from Eq. (3), for lightly doped
 278 SCD films of this study compared with previous results reported in literature: +—Ref. (55), ☆—Ref. (50), ∇—
 279 Ref. (56), Δ—Ref. (57), ●—Ref. (52), ○—Ref. (58), and ×—Ref. (59). The theoretical contribution of various
 280 scattering modes is illustrated by dashed and dotted line for lattice (lat), dotted line for ionized impurities (ii)
 281 mode, dashed line for neutral impurities (ni) mode, and solid line for their combination (tot).⁵¹

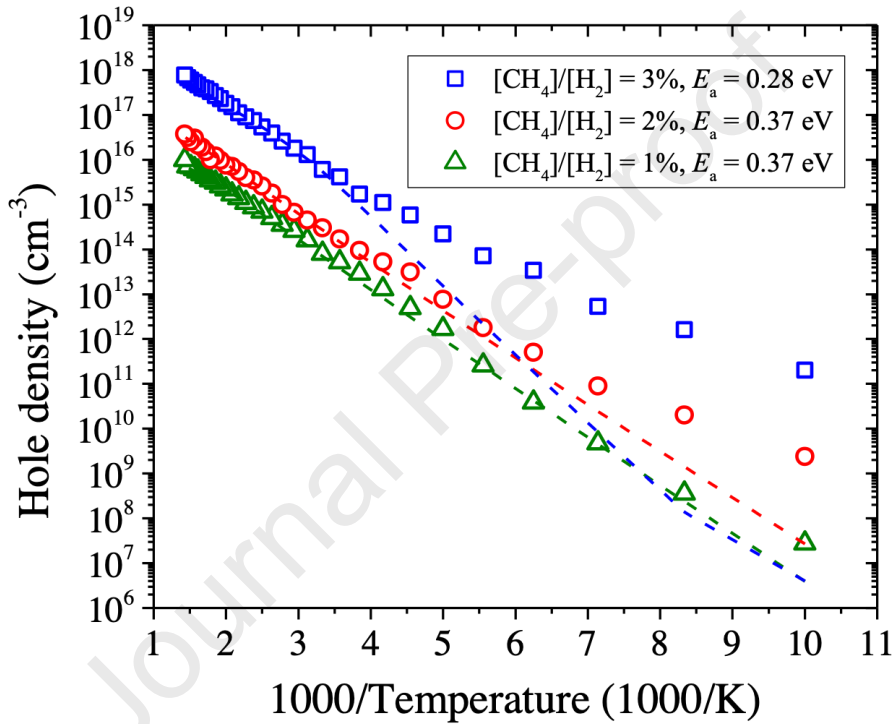
282 The temperature dependence of free hole concentration, $p(T)$, was fitted using neutrality
 283 equation.⁶⁰

$$\frac{p(p+N_d)}{(N_a - N_d - p)} = \frac{N_v}{g_a} \exp\left(-\frac{E_a}{k_B T}\right) \quad (3)$$

284 where N_a and E_a are the density and activation energy of the acceptor, respectively, N_d is the
 285 density of compensating donors, N_v is the density of states in the valence band, k_B is the
 286 Boltzmann's constant, T is the absolute temperature, and g_a is the ground-state degeneracy
 287 factor for acceptor level. Taking into the account the spin-orbit coupling in diamond, the
 288 following expression for the degeneracy factor can be used:^{56,61}

$$g_a = 4 + 2\exp\left(-\frac{\Delta}{k_B T}\right) \quad (4)$$

289 with $\Delta = 6$ meV the split off by the energy as experimentally determined.⁵¹ In these
 290 calculations, the total density-of-state mass (m^*) was taken as $0.919m_0$,^{51,62} with m_0 the free
 291 electron mass. Figure 8 shows the variation of the hole concentration in the grown diamond
 292 films as a function of temperature.



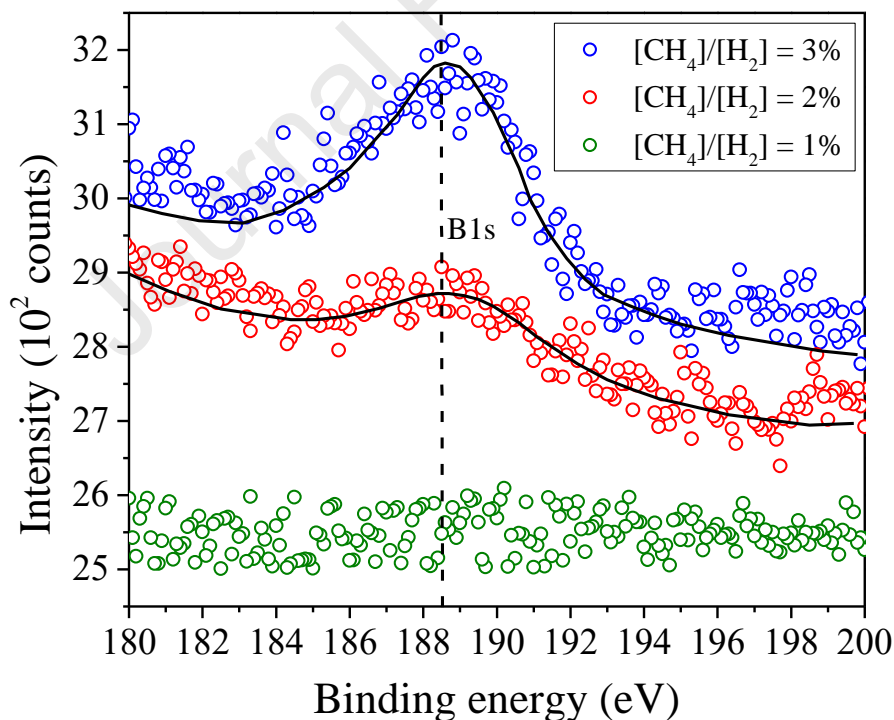
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294 Figure 8: Hole density as a function of temperature of the B-doped diamond layers grown at different methane
 295 concentrations. The fitting data calculated by using Eq. (3), are plotted as the dashed lines.

296 The results of the hole concentration fitting by the neutrality equation (Eq. (3)) are presented
 297 in Table 1. These findings align with the results obtained through other methods (FTIR and CL
 298 spectroscopy), which also demonstrated that an elevated methane concentration in the CVD
 299 plasma corresponds to an increased level of boron incorporation in the grown layers. During
 300 the fitting process, the domination of hopping conduction at low temperatures hinders reliable
 301 estimation of compensation based on hole density data, and therefore there is deficiency in

302 available data for fitting. Nonetheless, based on the fitting variability on the available reliable
 303 data, the compensation ratio of the sample is assumed to be no higher than 7%.

304 XPS measurements were carried out to evaluate and compare the boron content of the surface
 305 bonds of the B-doped SCD films of this study, and to investigate the C 1s core level
 306 components and their change with B-doping. The XPS B1s spectra from the surface of the
 307 samples are shown in Figure 9. The peak at ≈ 188.5 eV is assigned to a bond of boron at a
 308 substitutional position with carbon in the diamond lattice.⁶³⁻⁶⁵ The intensity of this peak
 309 drastically increased with increasing the methane concentration from 2% to 3% in plasma
 310 feedgas. This peak was not observed in the sample grown at 1% methane concentration. The
 311 presence of B1s peak at ≈ 188.5 eV has been mostly reported in heavily B-doped diamond
 312 films ($\geq 10^{20}$ cm⁻³).⁶⁴⁻⁶⁶

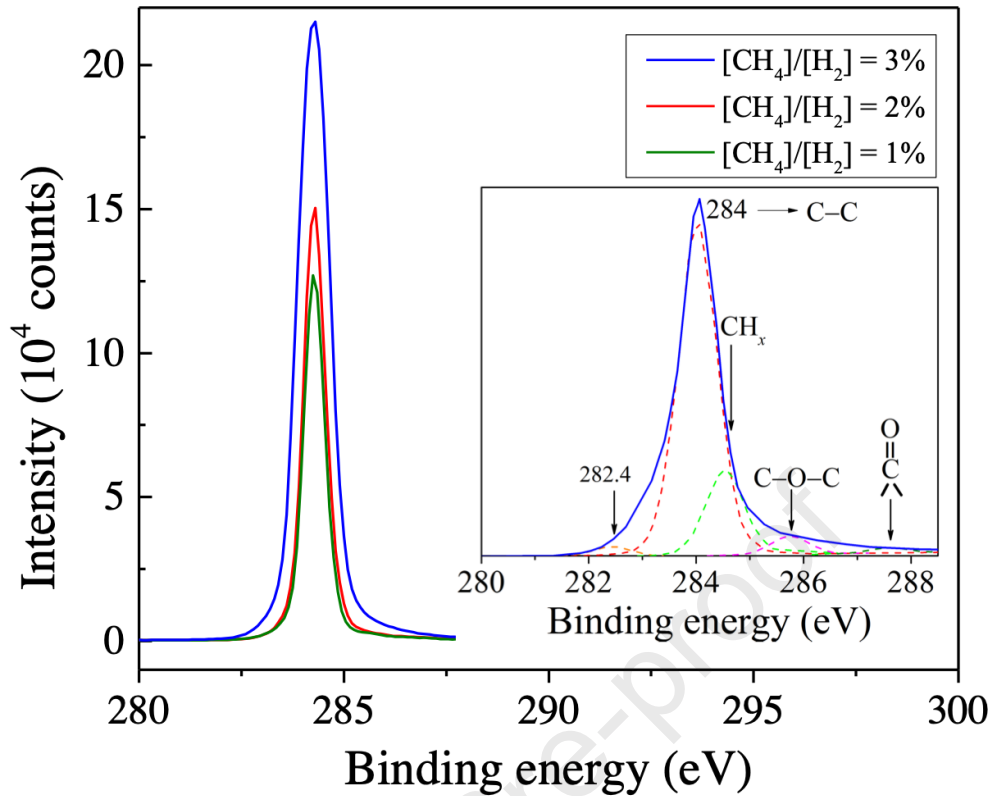


313

314 Figure 9: The XPS B1s spectra of B-doped SCD films grown at 1%, 2%, and 3% methane concentrations in the
 315 plasma feedgas.

316 Figure 10 shows the C1s core level spectra of the films grown with 1%, 2%, and 3% methane
 317 concentration in the plasma feedgas. The C1s peaks are centered on ≈ 284 eV in all the films.

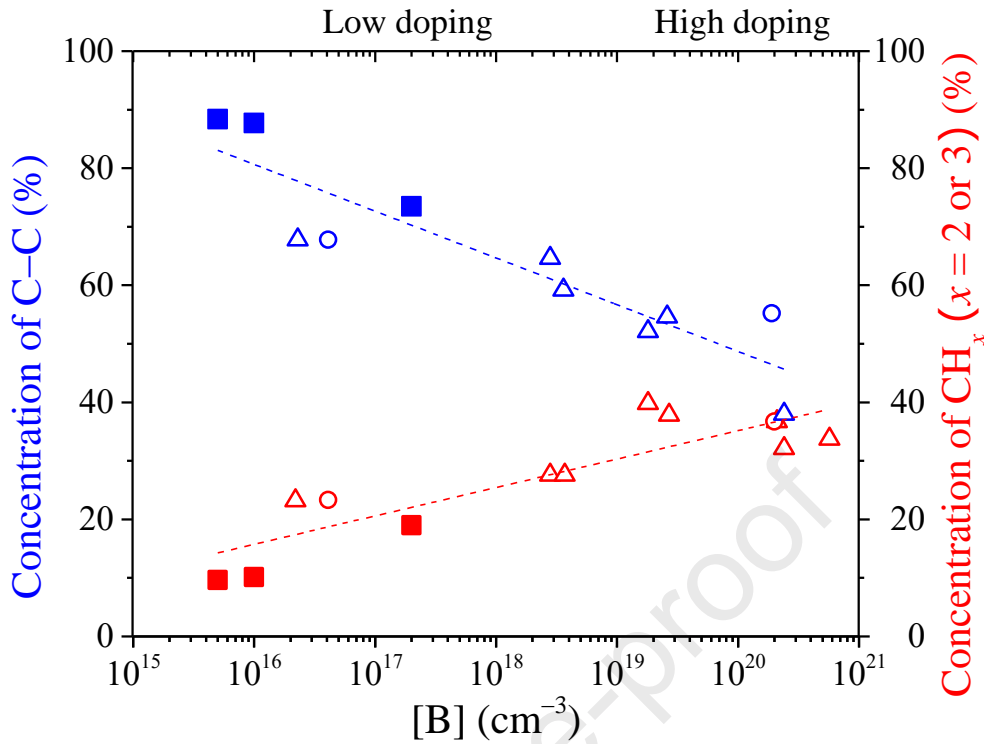
318 A slight widening of the C1s is observed as the methane concentration increases. The FWHM
319 of C1s peak increased from 0.59 eV to 0.88 eV by increasing the methane concentration from
320 1% to 3% in the plasma. Ghodbane *et al.*^{67,68} reported the same broadening of C1s peak by
321 increasing the boron incorporation in their samples. This widening of the C1s peak is also
322 accompanied by an increase of its components' intensities mostly at the higher energy side.
323 This is particularly visible for the sample grown with 3% methane concentration, as shown in
324 the inset of Figure 10. The main component is attributed to the carbon σ bond (C–C) core level
325 of diamond surface.^{67,69,70} The second important component is associated to CH_x bounds with
326 ($x = 2$ or 3), which results from carbon-hydrogen bounds at the diamond surface and
327 subsurface.^{67,69,70} Two oxygenated groups (C–O–C and $>\text{C}=\text{O}$) were also found in the
328 samples.^{68,70} The component at 282.4 eV is usually referred to the carbon double bond (C=C)
329 and can be assigned to the residual dimers at the diamond surface.^{67,68}



330

331 Figure 10: The XPS C1s spectra of B-doped SCD films grown at 1%, 2%, and 3% methane concentrations in
 332 the plasma feedgas. The inset shows the fit of the C1s energy range for the sample grown at 3% methane
 333 concentration.

334 Finally, Figure 11 illustrates the evaluation of concentration of C-C and CH_x ($x = 2$ or 3) groups
 335 as a function of boron concentration determined by CL spectroscopy, and compares it with
 336 other studies.^{67,68} In the low doping range, where the samples of this study are located, the C-C
 337 concentration decreases with increasing [B] concentration while that of CH_x group increases.
 338 The increase of CH_x concentrations might be ascribed to the increase of C-C bond length
 339 occurring when there is higher [B] concentration, as described by Ghodbane *et al.*⁶⁸



340

341 Figure 11: Comparisons of the concentrations of C–C and CH_x ($x = 2$ or 3) according to the boron concentration
 342 with previous results reported in the literature: \circ —Ref. (67), Δ —Ref. (68), and \blacksquare —this study.

343 The XPS results are in reasonable agreement with the FTIR, CL, and Hall effect results shown
 344 in Table 1, revealing a strong positive correlation of the boron level with the methane
 345 concentration in the plasma feedgas, that is, higher methane concentrations lead to higher boron
 346 content. Moreover, as the growth with 3% methane concentration was performed as the last
 347 and no intentional boron-containing gas precursor added, a reduced boron concentration in the
 348 deposition chamber can be ruled out.

349 The variation in boron concentration determined by different techniques is an issue, which has
 350 been also previously reported by other research groups, like Demlow *et al.*⁷¹ that shows the
 351 overestimation of boron content calculated by FTIR compared to the result of secondary ions
 352 mass spectroscopy, due to the imperfect transmission through the grown samples and/or the
 353 presence of defects such as dark colored unepitaxial defects in FTIR spectroscopy. The

354 inhomogeneity of the boron concentration in the CVD grown layers may also be one possible
 355 cause of the variation in the measured boron content by different methods.

356 Table 1: Summary of the doping concentrations of samples measured by different techniques.

| [CH ₄]/[H ₂] (%) | Growth rate at sample center (μm/h) | [N _a - N _d] by FTIR (cm ⁻³) | [B] by CL (cm ⁻³) | N _a by Hall effect (cm ⁻³) |
|---|--|---|----------------------------------|---|
| 1 | 1 [§] | - [‡] | 5 × 10 ¹⁵ | (1.0 ± 0.5) × 10 ¹⁶ |
| 2 | 2.1 ± 0.1 [†] | 4.5 × 10 ¹⁷ | 1 × 10 ¹⁶ | (8.6 ± 1.0) × 10 ¹⁶ |
| 3 | 2.8 ± 0.1 [†] | 5.6 × 10 ¹⁷ | 2 × 10 ¹⁷ | (2.8 ± 0.7) × 10 ¹⁸ |

357 § - Determined via transmission electron microscopy.

358 ‡ - No measurable data.

359 † - Measured by Mitutoyo linear gage.

360 Conclusions

361 Unintentionally boron doped SCD (100)-oriented films were deposited by MW PE CVD using
 362 a [CH₄]/[H₂] range from 1% to 3% in the plasma feedgas. For the samples grown at 1% and
 363 2% methane concentrations, a high surface quality was observed by means of a low density of
 364 surface defects. With increasing the methane concentration to 3%, the appearance of superficial
 365 defects on the grown diamond layers as well as the increase of the FWHM free-exciton FE^{TO}
 366 peak in the CL spectra were observed, most likely due to the higher growth rate. The electrical
 367 conductivity of samples increased from 15 mΩ⁻¹·cm⁻¹ to 0.74 Ω⁻¹·cm⁻¹ at room temperature
 368 with increasing the methane concentration from 1% to 3% in the plasma feedgas. The hopping
 369 conduction mechanism at low temperatures (90 K ≤ T ≤ 200 K) was discussed by the electrical
 370 conductivity, mobility, and hole concentration results. The mobility analysis shows the
 371 dominant role of acoustic phonon (ac) and optical phonon (op) scattering mechanisms for all
 372 used methane concentrations samples. In addition, the doping dependence of the Hall hole
 373 mobility of this study showed a good agreement with the calculations and the previously
 374 reported results. The results of FTIR, CL, Hall effect, and XPS measurements showed that by

375 increasing the methane concentration, the B-doping level increased. This study sheds light on
376 the important role of methane concentration in controlling the B-doping levels of lightly *p*-type
377 SCD films, a *sine qua non* requirement for the fabrication of high power electronic applications
378 and low concentration colour center creation.

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Declaration of interests

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