Insight into boron-doped diamond Raman spectra characteristic features

Vincent Mortet, Z. Vlčková Živcová, A. Taylor, O. Frank, P. Hubík, David Trémouilles, François Jomard, Julien Barjon, L. Kavan

To cite this version:


HAL Id: hal-01643027
https://hal.laas.fr/hal-01643027
Submitted on 21 Nov 2017

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
Insight into boron-doped diamond Raman spectra characteristic features

V. Mortet a, b, *, Z. Vlčková Živcová c, A. Taylor a, b, O. Frank c, P. Hubík d, D. Trémouilles e, F. Jomard f, J. Barjon f, L. Kavan c

a Institute of Physics of the Czech Academy of Sciences, Na Slovance 1999/2, 182 21, Prague 8, Czech Republic
b Czech Technical University in Prague, Faculty of Biomedical Engineering, Sítná 3105, 272 01, Kladno, Czech Republic
c J. Heyrovsky Institute of Physical Chemistry of the Czech Academy of Sciences, Dolejškova 3, 182 23, Prague 8, Czech Republic
d Institute of Physics of the Czech Academy of Sciences, Cukrovarnická 10, 162 00, Prague 6, Czech Republic
e LAAS-CNRS, Université de Toulouse, CNRS, 7, avenue du Colonel Roche, 31031, Toulouse Cedex 4, France
f Groupe d’Etude de la Matière Condensée, Université Versailles St Quentin, 45, avenue des Etats Unis, 78035, Versailles Cedex, France

 Article info

Article history:
Received 9 December 2016
Received in revised form
5 January 2017
Accepted 8 January 2017
Available online 9 January 2017

ABSTRACT

Characteristic Raman features of boron-doped diamond layers with metallic conduction are studied experimentally and discussed in comparison with an extensive selection of literature data. Despite evidence that the main Raman bands are mostly characteristic features of carbon atom vibration modes, their position is found to be proportional to boron concentration. While the origin of the Raman bands located at c.a. 500 cm\(^{-1}\) remains unclear, the band centred at c.a. 1200 cm\(^{-1}\) is attributed to a maximum of phonon density of states due to softening of the Raman wave vector conservation rule. The downshift and broadening of the diamond line are attributed, primarily, to the domain size effect caused by scattering on boron impurities, secondly to the Fano effect due to electronic Raman interaction, and finally to lattice expansion due to the boron doping.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Boron-doped diamond with metallic conduction is a promising material for various electronic and electrochemical applications. It is a basic building block for the fabrication of ohmic contacts [1] in diamond electronic devices. It is also recognized as one of the best working electrochemical electrodes with high chemical stability, low capacitive current and a large potential window [2]. Diamond electrodes can be used for fabrication of chemical and biological sensors [3], water treatment systems [4], super capacitors [5], dye sensitized solar cells [6–9], etc. Measurement of boron concentration is an important feedback parameter and is usually determined by Secondary Ions Mass Spectroscopy (SIMS) and Hall effect measurements with the assumption that the acceptor concentration is equal to the hole concentration. While Raman spectrum of pure diamond is unmistakably simple, it becomes more and more complex with an increasing concentration of non-diamond carbon species and other impurities. More specifically, Raman spectra of boron-doped diamond are not fully understood. However, Raman spectroscopy is a simple and non-destructive technique which has been reported to enable the determination of boron concentration [10]. In this work, we analyse characteristic features in Raman spectra of boron-doped diamond with metallic conductivity in order to deepen the understanding of their origin and their dependence with boron concentration.

2. Experimental

Epitaxial (111) diamond layers were grown in a 1.5 kW resonance cavity microwave plasma enhanced chemical vapour deposition system AX5010 from Seki Diamond Systems with a base pressure below 2 \(\times\) 10\(^{-6}\) mbar. Substrates are high-pressure high-temperature synthetic Ib diamond crystals from Sumitomo ELECTRIC Hartmetall GmbH, polished as described in Ref. [11]. Prior to CVD deposition, diamond substrates were cleaned in hot sulphuric acid with potassium nitrate for 10 min, rinsed in hot deionized water, acetone and alcohol in an ultrasonic bath for 10 min. Epitaxial layers were grown at high temperature (c.a. 1000 °C) in
diluted methane in hydrogen (0.1%) with the addition of a boron precursor (trimethylborane) with variable boron to carbon (B/C) ratio in the gas phase. The thickness of deposited layers was estimated by double mass measurement using a high precision ME5 microbalance (Sartorius). Electrical properties of deposited layers were measured by the van der Pauw method at room temperature and 100 °C using a Keithley 6221 current source and Keithley 2182A nano-voltmeter. Secondary-ion mass spectrometry was measured with Cs+ primary ions accelerated at 10 keV using a Cameca IMS 4f apparatus on layers grown with a B/C ratio in the gas phase of 20,000 ppm to determine its boron atoms depth distribution. The concentration of boron was quantified using implanted standards. Raman spectroscopy measurements were carried out using a Labram HR spectrometer (Horiba Jobin-Yvon) interfaced to an Olympus microscope (objective 100×) equipped with a 50 μm confocal hole and a He–Ne laser 633 nm (1.96 eV) with 8 mW power. The spectrometer was calibrated using the silicon $F_{1g}$ peak at 520.2 cm$^{-1}$. Raman spectra were corrected for the spectrometer spectral response.

3. Results and discussion

Van der Pauw Hall-effect measurements revealed hole concentrations above the Mott transition concentration (i.e. above $\approx 2–3 \times 10^{20}$ cm$^{-3}$) [12,13] in all samples. This fact together with the minute variation in resistivity with temperature indicates that all studied layers have metallic type conduction. Deposition rate ($r_d$), resistivity ($\rho$), acceptor concentration ($N_a$, assumed equal to the hole concentration), and mobility ($\mu$) of deposited layers with variable B/C ratio are reported in Table 1.

![Raman spectra of epitaxial (111) boron-doped diamond layers grown with various B/C ratios in the gas phase.](image)

Fig. 1. Raman spectra of epitaxial (111) boron-doped diamond layers grown with various B/C ratios in the gas phase. (A colour version of this figure can be viewed online.)

Table 1: Deposition rate ($r_d$); room temperature resistivity ($\rho$), acceptor concentration ($N_a$), and mobility ($\mu$); and Fano line-shape fitting parameters of doped diamond zone centre phonon line: peak frequency ($\omega_0$) and width ($\Gamma$) and asymmetry parameter ($q$) as function of B/C ratio in the gas phase during CVD deposition process.

<table>
<thead>
<tr>
<th>B/C (ppm)</th>
<th>$r_d$ (μm/h)</th>
<th>$N_a$ (cm$^{-3}$)</th>
<th>$\rho$ (mΩ cm)</th>
<th>$\mu$ (cm$^2$ V$^{-1}$ s$^{-1}$)</th>
<th>$\omega_0$ (cm$^{-1}$)</th>
<th>$\Gamma$ (cm$^{-1}$)</th>
<th>$q$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>1.02</td>
<td>2.6 $10^{25}$</td>
<td>13</td>
<td>1.8</td>
<td>1329</td>
<td>7.73</td>
<td>-1.72</td>
</tr>
<tr>
<td>10,000</td>
<td>1.14</td>
<td>4.6 $10^{25}$</td>
<td>5.8</td>
<td>2.3</td>
<td>1320</td>
<td>17.18</td>
<td>-1.31</td>
</tr>
<tr>
<td>20,000</td>
<td>0.8</td>
<td>1.8 $10^{25}$</td>
<td>2.3</td>
<td>1.8</td>
<td>1320.7</td>
<td>15.43</td>
<td>-1.26</td>
</tr>
<tr>
<td>40,000</td>
<td>0.04</td>
<td>1.5 $10^{21}$</td>
<td>2.07</td>
<td>2.62</td>
<td>1323</td>
<td>16.25</td>
<td>-1.75</td>
</tr>
<tr>
<td>100,000</td>
<td>0.02</td>
<td>2.5 $10^{21}$</td>
<td>0.96</td>
<td>2.59</td>
<td>1320</td>
<td>17.26</td>
<td>-1.98</td>
</tr>
</tbody>
</table>
the position of the L2 and RD lines despite both peaks being clearly identified as pure C–C vibration modes. Calculated linear equation coefficients and corresponding zero values, i.e. X values at Y equal to zero, are also reported in Table 1. These zero values correspond to the estimated line positions of undoped diamond. The calculated value of the diamond Raman line: ω_{RD}(B = 0) ~1326.9 cm⁻¹ is remarkably very close to the diamond Raman line position. Corrected for the Fano effect (c.a. 4-5 cm⁻¹, see below), this zero value is perfectly consistent with the known position of the intrinsic diamond zone centre phonon line. Similarly, the zero value of the L2 line: ω_{L2}(B = 0) ~1230.9 cm⁻¹ is interestingly very close to the diamond phonon density of state maximum located at c.a.1250 cm⁻¹ [20], supporting its assignment to the phonon density of states maximum due to the high concentration of boron defects and the consequent softening of Raman wave-vector conservation rule.

Superimposed onto the L2 line is the diamond line with its characteristic Fano line-shape for boron concentrations higher than the Mott transition. This line-shape results from the interaction of the discrete zone centre phonon Raman line with continuous electronic Raman band and was first reported by Cerdeira, Fjeldly and Cardona in highly doped silicon[24]. In the particular case of constant electronic Raman, the resulting Fano line-shape is analytically described by equation (1).

\[ F(\sigma) = \frac{(q + \epsilon)^2}{1 + \epsilon^2} \]  

with \( \epsilon(\omega) = \frac{\sigma - \sigma_0}{\Gamma} \)  

Table 2
Fitting parameters of linear empiric laws (Y = a + X + b).

<table>
<thead>
<tr>
<th>( \omega_{L1} ) (cm⁻¹)</th>
<th>a (unit)</th>
<th>X (unit)</th>
<th>b (unit)</th>
<th>Zero (unit)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \omega_{RD} ) (cm⁻¹)</td>
<td>1.40</td>
<td>( \omega_{RD} ) (cm⁻¹)</td>
<td>-1335.4 (cm⁻¹)</td>
<td>-</td>
</tr>
<tr>
<td>( [B]_{SIMS} ) (cm⁻³)</td>
<td>0.77</td>
<td>( \omega_{RD} ) (cm⁻¹)</td>
<td>212 (cm⁻¹)</td>
<td></td>
</tr>
<tr>
<td>( \omega_{L2} ) (cm⁻¹)</td>
<td>-6.99 \times 10^{19} (cm⁻²)</td>
<td>( \omega_{RD} ) (cm⁻¹)</td>
<td>3.57 \times 10^{19} (cm⁻²)</td>
<td>510.4 (cm⁻¹)</td>
</tr>
<tr>
<td>( \omega_{L2} ) (cm⁻¹)</td>
<td>-1.28 \times 10^{20} (cm⁻²)</td>
<td>( \omega_{RD} ) (cm⁻¹)</td>
<td>1.57 \times 10^{20} (cm⁻²)</td>
<td>1230.9 (cm⁻¹)</td>
</tr>
<tr>
<td>( [B]_{SIMS} ) (cm⁻³)</td>
<td>-9.81 \times 10^{19} (cm⁻²)</td>
<td>( \omega_{RD} ) (cm⁻¹)</td>
<td>1.30 \times 10^{19} (cm⁻²)</td>
<td>1326.9 (cm⁻¹)</td>
</tr>
<tr>
<td>( [B]_{Hall} ) (cm⁻³)</td>
<td>-1.29</td>
<td>( \omega_{RD} ) (cm⁻¹)</td>
<td>1726.6 (cm⁻¹)</td>
<td>-</td>
</tr>
</tbody>
</table>
function possesses two extrema: a resonant peak at \( q(q_0) = -q \) and an anti-resonant peak at \( q(q_0) = q^{-1} \). Consequently, a red-shift of the resonant peak corresponds to a negative value of the asymmetric coefficient. Indeed, reported values of asymmetry coefficient in doped diamond are negative with a value \( -2 \pm 0.4 \) [22,25–29].

The variation of the Fano line shape with the negative asymmetry coefficient \( q \) is illustrated in the supplementary data. Fitting parameters \( (q, q_0 \text{ and } \Gamma) \) of the diamond Fano line-shape can be quickly estimated using a simple analytical method knowing the resonant \( (q_0) \), anti-resonant \( (q_0) \) and wavenumber at half maximum \( q(1/2) \) between \( q_0 \) and \( q_0 \). Estimated fitting parameters of epitaxial layers used in this study are reported in Table 1. Values of the line width \( \Gamma \) are also reported as function of the peak position in Fig. 4 and they are compared to data available from literature. The observed linearity of diamond Raman line broadening and its downward shift (fitting parameters are reported in Table 2) is characteristic of a decrease in domain size and phonon confinement effects. In 1988, Fauchet and Campbell demonstrated that silicon Raman linewidth varies linearly with the frequency shift in microcrystalline silicon with variable domain size [30]. Later, LeGrice et al. reported that the same linear relation applies to silicon [31] based on a comparison of silicon and diamond phonon dispersion curves. However, the determined proportionality between diamond’s line maxima and full width at half maximum is c.a. 2.5 times smaller than the one calculated for silicon. Another reason for the downshift of the doped diamond Raman mode is lattice expansion, which inevitably occurs upon doping. Following the study of Wojewoda et al. [32], we estimate the upper limit of the maximum line shift for the maximum doping presented in our data to be \(-0.25–0.3\%\) [32]. With the Grüneisen parameter of the zone centre phonon of \(-1\) [33], the maximum Raman shift for \([B] \sim 5 \times 10^{21} \text{ cm}^{-3}\) reaches 6.6–8 cm\(^{-1}\).

The effect of domain size on full width at half maximum \( \Gamma \) and position of the diamond Raman line have been studied by several groups of researchers [20,31,34,35]. A noticeable down shift and an inversely proportional line broadening with domain size has been reported by Zaitsev [20] and Yoshikawa [35]. Experimental data from Refs. [31,34–36] of domain size \( L \) as a function of \( \Gamma \) of undoped diamond nano-crystals, reported in Fig. 5, more closely follow Zaitsev’s model in comparison to Yoshikawa’s model.

Average boron-to-boron atom distance \( \langle dB-B \rangle \) is also reported on Fig. 5 as a function of the Fano fitted \( \Gamma \), i.e. diamond Raman line width determined from literature. Average boron-to-boron atom distance \( \langle dB-B \rangle \) is calculated from the boron concentration using:

\[
d_{B-B}(nm) = 10^2 \sqrt[3]{|B|/(cm^3)}
\]

Boron concentration is estimated from the diamond line position using the aforementioned linear relation. Fig. 5 clearly shows that the average boron-to-boron atom distance follows the same variation with the diamond line width as domain size varies, though with a factor of c.a. 5 difference. This result further designates that the diamond line broadening and red-shifting are due to a domain size effect by phonon scattering on boron impurities. This result is not too surprising as impurities are known to strongly reduce semiconductors’ thermal conductivity by two effects: carrier-phonon scattering (for electrically active impurities) and phonon-impurity scattering (due to the impurities’ mass and radius differences) [37].

In an attempt to conceive the relation between the domain size and the boron concentration in doped diamond, we calculated the radial distribution function of boron atoms (RDFB) in doped diamond (see Fig. 6). The RDFB has been computed using a supercell of \( I \) (being an integer) elementary cubic cells with a randomly positioned boron atom (see Fig. 6a–b). The size of the elementary cubic cell is arbitrary set to unity but can also be defined as the average boron-to-boron atom distance \( a \). The boron atom position in each elementary cell was randomly positioned around the cube’s centre using a normal distribution with the variance \( \sigma^2 = 1/(2\pi) \) [38]. The RDFB was determined by computing the number of boron atoms as a function of distance \( r \) to the origin \( (O) \) of the supercell and normalized to the surface of the sphere of the same radius. The RDFB has been calculated on 1/8 of the space due to the system symmetry. Fig. 6b shows the doped diamond can be locally seen as a quasi-perfect crystal encapsulated by discontinuous layers of spherical shells with a variable concentration of boron atoms. The first defective spherical shell is located at

![Fig. 4](image_url)  
**Fig. 4.** Variation of fitted diamond’s zone centre phonon line width (\( \Gamma \)) as a function of fitted line position \( \omega_0 \) using Fano function from various reports [18,27,28,42–46] for various types of CVD diamond layers: polycrystalline diamond (circles), [100] epitaxial diamond layers (squares) and [111] epitaxial diamond layers (diamond), and Raman laser excitation wavelength: 633 nm (red), 514 nm (green) and 488 nm (blue). Black stars correspond to results of this study. (A colour version of this figure can be viewed online.)

![Fig. 5](image_url)  
**Fig. 5.** Diamond domain size (left scale) compared to average boron-to-boron distance (right scale) as a function of zone centre phonon Raman line width. Black line: Zaitsev’s model [20]; red line: Yoshikawa’s model [35]; full circles: experimental values from Ref. [31] (black) [34], (red) and [35] (green); open circle: average boron-to-boron distance extracted from Refs. [10,22,26–29,43,45] and this work. (A colour version of this figure can be viewed online.)
4. Conclusion

Epitaxial diamond layers with variable boron concentrations and metallic conductivity were prepared by microwave plasma enhanced chemical vapour deposition and characterized by Raman spectroscopy. Despite evidence that the main Raman bands are mostly characteristic features of carbon atom vibration modes in diamond, their position is proportional to the boron concentration. Analysis of Fano fitting parameters indicates that the downshift and broadening of the diamond line are primarily due to phonon confinement, secondly to electronic Raman interaction and finally to lattice expansion due to the boron doping. Analysis of boron atoms radial distribution function supports this assertion, as it shows that doped diamond can be considered as nanometre sized domains encapsulated in a highly defective matrix.

Acknowledgements

The work was financially supported by the project 13-31783S of Czech Science Foundation, the French-Czech Project Barrande 35785SC of the Czech Ministry of Education, Youth and Sports and the J.E. Purkyne fellowship awarded to V. Mortet by the Czech Academy of Sciences. We also acknowledge Ing. Lucie Holasová and Ing. Jaroslava Hnilíčková of the Institute of Organic Chemistry and Biochemistry CAS, v.v.i. for mass measurements and Ing. Lukáš Kaderávek and Ing. Lucie Drbohlavová of Institute of Physics CAS, v.v.i. for their contribution in the preparation of the manuscript.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.carbon.2017.01.022.

References
