

## RAMAN SCATTERING IN HEAVILY BORON-DOPED SINGLE-CRYSTAL DIAMOND

G. FAGGIO,<sup>a\*</sup> G. MESSINA,<sup>a</sup> S. SANTANGELO,<sup>a</sup> D. ALFIERI,<sup>a</sup>  
G. PRESTOPINO,<sup>b</sup> I. CIANCAGLIONI,<sup>b</sup> M. MARINELLI<sup>b</sup>

**ABSTRACT.** A series of boron-doped homoepitaxial diamond films grown by Microwave Plasma Enhanced Chemical Vapor Deposition at the University of Rome “Tor Vergata” have been investigated with Raman spectroscopy. As the boron content increases, we observed systematic modifications in the Raman spectra of single-crystal diamonds. A significant change in the lineshape of the first-order Raman peak as well as a wide and structured signal at lower wavenumbers appeared simultaneously in samples grown at higher boron content.

### 1. Introduction

Thanks to its exceptional electronic and thermal properties, diamond is an attractive material for electronic devices working at high temperature and in harsh chemical environment [1, 2]. Semiconducting p-type diamond films can be grown when boron is introduced into the film. Heavy boron incorporation induces metallic diamond. Boron-doped (B-doped) diamond has attracted considerable attention for its applications such as solid state photovoltaic Schottky diodes able to detect x-ray and ultraviolet radiation [3]. In this paper, B-doped homoepitaxial diamond films have been analyzed by Raman spectroscopy. The measurements have been performed at room temperature on films with different boron content. The resistivity of the samples has been also measured to evaluate the activation energy as a function of boron content.

### 2. Experimental

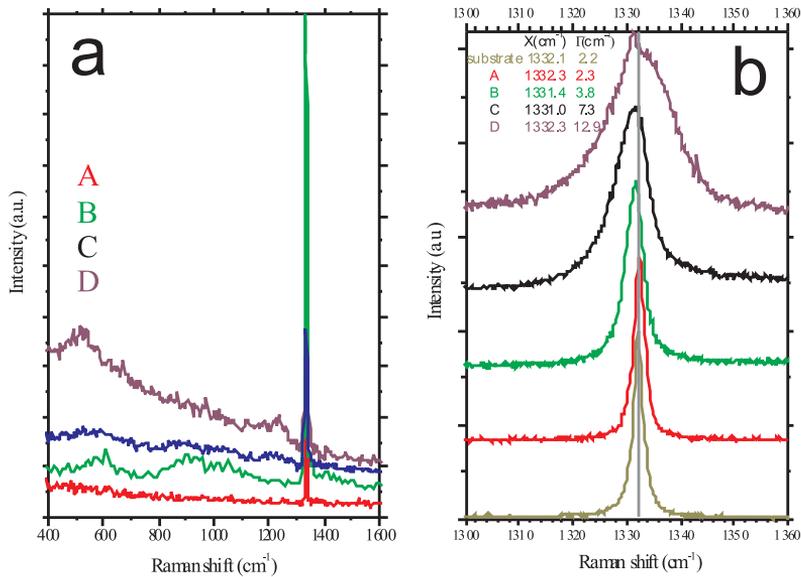
The B-doped homoepitaxial diamond films used in this study have been grown at the University of Rome “Tor Vergata” by Microwave Plasma Enhanced Chemical Vapor Deposition (MWPECVD) on a commercial low cost synthetic type Ib 100 HTHP single crystal diamond substrates. The samples (A, B, C, D) are listed in order of increasing boron content in the grown layers. The four films were grown at different concentrations of a 100 ppm dyborane-hydrogen gas mix added to a methane-hydrogen source gas. The grown samples were electrically characterized by means of electrically conductivity vs. temperature measurements obtaining activation energies from 0.28eV to 0.03 eV. From these values, boron concentrations from  $10^{18}$  to  $10^{20}$  cm<sup>-3</sup> were estimated [4, 5].

The Raman scattering measurements have been carried out at room temperature with an Instrument S.A. Ramanor U1000 double monochromator, equipped with a microscope Olympus BX40 for micro-Raman sampling and with an electrically cooled Hamamatsu R943-02 photomultiplier for photon-counting detection or with a CCD detector. The 514.5 nm (2.41 eV) line of an Ar<sup>+</sup> ion laser (Coherent Innova 70) has been used to excite Raman scattering. Using a X100 objective, the laser beam was focused to a diameter of approximately 1 mm. A depth resolution of approximately 4 mm was obtained with a confocal aperture of 200 mm.

### 3. Results and Discussions

Raman spectroscopy is a powerful technique to investigate the structure and the properties of doped diamond. Figure 1a shows typical Raman spectra measured on the surface of the samples synthesized at various B-doping level. At low boron content, the spectrum of the sample A is very similar to that of the substrate, exhibiting only the characteristic peak at 1332 cm<sup>-1</sup>. Two wide bands at approximately 500 cm<sup>-1</sup> and 1225 cm<sup>-1</sup> and another one of low intensity at approximately 1000 cm<sup>-1</sup> are added on the low frequency side of the spectrum of the samples grown at higher boron content (samples B, C and D). These bands are commonly observed in the Raman spectra of heavily boron polycrystalline and homoepitaxial diamond films [6, 7], although their origin is still a matter of controversy. The phonon density of states of diamond presents a main asymmetric maximum around 1250 cm<sup>-1</sup> and secondary maximum around 550 cm<sup>-1</sup> and hence their origin has been attributed to the relaxation of selection rules induced by the high boron content [8]. Later, Bernard et al [6] proposed that 500 cm<sup>-1</sup> band originates from local vibration modes of boron pairs. Figure 1b shows the line shape of the first-order Raman peak for the samples investigated. The spectra have been recorded by carefully focusing the laser spot at the sample surface. As the boron content increases, the thickness of the grown films gradually decreases and then it becomes increasingly difficult to exclude the contribution of the substrate. With the exception of the sample with lower boron content (sample A), all the peaks exhibit a downshift and a broadening with respect to the Raman peak of the undoped substrate. The position, X, and the full width at half maximum, G, of the peaks are reported in Fig. 1b. The asymmetric broadening and the downshift of the one-phonon Raman line of B-doped diamond, observed both in polycrystalline and in homoepitaxial samples [6, 7, 9, 10] have been explained as the result of a Fano-type discrete-continuum interaction between the discrete zone-centre phonon state and the continuum of the electronic states induced by the presence of the dopant [9, 10, 11, 12]. Moreover, dopant incorporation at substitutional or interstitial sites can produce stress that generally depends on the doping level. Therefore, it is possible that the changes observed in first-order Raman peak (Fig. 1b) reflect both a Fano-type interaction and the presence of tensile stress. At the doping levels used in this work, lower than the critical threshold of  $\sim 3 \cdot 10^{20}$  cm<sup>-3</sup> [13] to clearly observe a strong Fano deformation of the Lorentzian Raman line, it is difficult to distinguish between the two mechanisms [14, 15].

Boron doping makes the diamond films conductive. The acceptor level lies rather deep into the band-gap with an activation energy of about 0.37 eV from the valence band [16, 17]. In order to evaluate the activation energy, the resistivity of the samples has been



**Figure 1.** (a) Raman spectra of the B-doped homoepitaxial diamond films at different boron concentration. (b) First-order Raman peaks of the B-doped homoepitaxial diamond films at different boron concentration.

measured between room temperature and 800 K. Activation energies of 0.28 eV, 0.16 eV, 0.07 eV and 0.03 eV have been obtained for samples A, B, C and D, respectively, from the best fit of the Arrhenius plot of the measured data in the temperature range 500-700 K. From the activation energy values, the acceptor densities  $N_a$  were roughly estimated by the model developed by Pearson and Bardeen [4] for silicon:

$$E_a = E_0 - \alpha N_a^{1/3} \quad (1)$$

where  $E_0$  is the ionization energy of an isolated dopant and  $\alpha$  is a material dependent constant, whose value for diamond is about  $6.7 \times 10^{-8}$  eVcm. From this model, for activation energies ranging between 0.28 and 0.03 eV, boron concentrations from  $\sim 10^{18}$  to  $\sim 10^{20}$  cm<sup>-3</sup> are evaluated. Such values are approximate, due to the low accuracy in the activation energy measurements and the simplified model used for their determination. The decrease of the values of the activation energy at increasing boron content highlights the gradual change of conductivity of the samples from p-type semiconductor to metallic diamond. This gradual change of the sample conductivity is in agreement with the structural modifications pointed out by Raman measurements.

#### 4. Conclusions

Heavily boron-doped MWPECVD single-crystal diamonds grown with various boron contents have been investigated by Raman scattering. At low doping level, the Raman spectrum exhibited only the characteristic diamond peak at  $1332 \text{ cm}^{-1}$ . With increasing doping

level, the first-order Raman peak appeared broadened and shifted at lower wavenumbers with respect to the Raman peak of the undoped substrate. In the same samples, two wide bands at approximately  $500\text{ cm}^{-1}$  and  $1225\text{ cm}^{-1}$  and another one of low intensity at approximately  $1000\text{ cm}^{-1}$  were observed on the low frequency side of the spectrum. Complementary measurements of resistivity have shown a gradual change of sample conductivity from semiconducting p-type to metallic diamond.

## References

- [1] D. Alfieri, S. Almaviva, A. De Sio, M. G. Donato, G. Faggio, A. Giannini, G. Messina, S. Morgante, E. Pace, S. Santangelo, S. Scuderi, P. Tripodi, *Radiation Effects and Defects in Solids* **165**, 737 (2010).
- [2] S. Almaviva, M. Marinelli, E. Milani, G. Prestopino, A. Tucciarone, C. Verona, G. Verona-Rinati, M. Angelone, D. Lattanzi, M. Pillon, R. M. Montereali, and M. A. Vincenti, *J. Appl. Phys.* **103**, 054501 (2008)
- [3] S. Almaviva, M. Marinelli, E. Milani, G. Prestopino, A. Tucciarone, C. Verona, G. Verona-Rinati, M. Angelone, M. Pillon, I. Dolbnya, K. Sawhney, and N. Tartoni, *J. Appl. Phys.* **107**, 014511 (2010).
- [4] G.L. Pearson and J. Bardeen, *Phys. Rev.* **75**, 865 (1949)
- [5] K. Thonke, *Semicond. Sci. Technol.* **18**, S20 (2003)
- [6] M. Bernard, C. Baron, A. Deneuve, *Diam. Rel. Mater.* **13**, 896 (2004).
- [7] F. Pruvost, E. Bustarret, A. Deneuve, *Diam. Rel. Mater.* **9**, 295 (2000).
- [8] E. Gheeraert, P. Gonon, A. Deneuve, L. Abello, G. Lucazeau, *Diam. Rel. Mater.* **2**, 742 (1993).
- [9] S. Prawer, R. J. Nemanich, *Philos. Trans. R. Soc. London Ser. A* **362**, 2537 (2004).
- [10] F. Prouvost, A. Deneuve, *Diam. Relat. Mater.* **10**, 531 (2001).
- [11] M. Roy, A.K. Dua, J. Nuwad, K.G. Girija, A.K. Tyagi, and S.K. Kulshreshtha, *J. Appl. Phys.* **100**, 124506 (2006)
- [12] F. Cerdeira, T.A. Fjeldly, and M. Cardona, *Phys. Rev. B* **8**, 4734 (1973)
- [13] F. Brunet, P. Germi, M. Pernet, A. Deneuve, E. Gheeraert, F. Laugier, M. Burdin, G. Rolland, *J. Appl. Phys.* **83**, 181 (1998)
- [14] W.L. Wang, M.C. Polo, G. Sanchez, J. Cifre, and J. Esteve, *J. Appl. Phys.* **80**, 1846 (1996)
- [15] H. Li, T. Zhang, L. Li, X. L. B. Li, Z. Jin, G. Zou, *J. Crystal Growth* **312**, 1986 (2010)
- [16] A. T. Collins, A. S. W. Williams, *J. Phys. C Solid State Phys.* **4**, 1789 (1971).
- [17] A. Deneuve, C. Baron, S. Ghodbane, C. Agnes, *Diam. Relat. Mater.* **16**, 915 (2007).

---

<sup>a</sup> Università "Mediterranea" di Reggio Calabria  
Dipartimento di Meccanica e Materiali  
I-89122 Reggio Calabria, Italy

<sup>b</sup> Università di Roma "Tor Vergata"  
Dipartimento di Ingegneria Meccanica  
I-00133 Roma, Italy

\* To whom correspondence should be addressed | Email: gfaggio@unirc.it

Paper presented at the ELS XIII Conference (Taormina, Italy, 2011), held under the APP patronage; published online 15 September 2011.

© 2011 by the Author(s); licensee *Accademia Peloritana dei Pericolanti*, Messina, Italy. This article is an open access article, licensed under a [Creative Commons Attribution 3.0 Unported License](https://creativecommons.org/licenses/by/3.0/).