

# Fano interference of the Raman phonon in heavily boron-doped diamond films grown by chemical vapor deposition

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A series of boron-doped polycrystalline diamond films grown by direct current and microwave plasma deposition was studied with Raman and infrared (IR) absorption spectroscopy. A Fano line shape is observed in the Raman spectra for films with a boron concentration in a narrow range near  $10^{21} \text{ cm}^{-3}$ . The appearance of the Fano line shape is correlated with the disappearance of discrete electronic transitions of the boron acceptor observed in the IR spectrum and the shift of the broadened peak to lower energy. The Fano interaction is attributed to a quantum mechanical interference between the Raman phonon (0.165 eV) and transitions from the broadened impurity band to continuum states composed of excited acceptor and valence band states. © 1995 American Institute of Physics.

The use of diamond as a wide-band gap semiconductor with attractive electrical and mechanical properties has been reviewed recently.<sup>1,2</sup> Construction of practical devices requires methods to make *n*- and *p*-type material. Boron is a *p*-type dopant in diamond and there is interest in making B-doped diamond for semiconductor applications. Due to its small covalent radius, B is easily incorporated into the diamond lattice; B concentrations in excess of  $10^{21} \text{ cm}^{-3}$  are possible. However, the activation of the acceptor site is limited by the large activation energy of substitutional B, 0.37 eV, such that at moderate doping levels only ~0.2% of the sites are ionized at room temperature.<sup>3</sup> At boron concentrations below  $10^{17} \text{ cm}^{-3}$  (or at low temperatures), conduction occurs through holes in the valence band contributed by ionized substitutional B, and  $E_A$  of 0.37 eV is measured. At higher doping levels conduction occurs by nearest neighbor and variable range hopping of holes between ionized B sites.<sup>4</sup> This is accompanied by a drop in mobility.<sup>5</sup> At very high doping levels, an impurity band is formed and a metalliclike conductivity is observed. Also at very high doping levels B complexing effects are observed.<sup>6</sup>

Fano line shapes occur when a discrete transition undergoes quantum mechanical interference with a continuum.<sup>7</sup> The Fano line shape is asymmetric with an enhancement of one flank of the line and a decrease or a minimum (antiresonance) of the other. The Raman phonon of Si has a Fano line shape in heavily doped *n*-type<sup>8</sup> and *p*-type<sup>9</sup> material. In this case, the Raman phonon (discrete) interferes with intersubband transitions that occur when the Fermi level moves into the valence (conduction) band in heavily doped material. Fano line shapes have also been reported in the Raman spectra of intercalated graphites<sup>10,11</sup> and doped  $\text{C}_{60}$ .<sup>12</sup>

Diamond films were grown on unscratched *n*- and *p*-doped Si substrates. Microwave plasma chemical deposi-

tion (CVD) was used to deposit films with a boron concentration of  $10^{18} \text{ cm}^{-3}$  or less. Direct-current (dc) plasma CVD was used to deposit films with higher boron concentrations.<sup>13</sup> The dc plasma films are 40 nm thick and polycrystalline. One thick (50  $\mu\text{m}$ ) microwave plasma CVD had the substrate chemically removed to create a freestanding film. Boron incorporation was measured by SIMS for some of the films and ranges from  $1 \times 10^{18}$  to  $5 \times 10^{21} \text{ cm}^{-3}$ .

Raman measurements were performed with a Raman spectrometer described in detail previously.<sup>14</sup> Measurements were made with the 488 (2.54 eV) and 514.5 (2.41 eV) lines of an Ar ion laser at a laser power of 8 mW. The laser light was incident at 65° from the surface normal; scattered light was collected normal to the surface. Most measurements were made at 1  $\text{cm}^{-1}$  resolution; some high resolution measurements were made with 0.5  $\text{cm}^{-1}$  resolution. Low temperature measurements were made with an ultrahigh vacuum chamber equipped with Raman optics and capable of cooling samples to 12 K.<sup>15</sup>

Fourier transform infrared (FTIR) measurements were made at room temperature and 4 K with a Bomem spectrometer (0.2  $\text{cm}^{-1}$  resolution) equipped with a KBr beamsplitter and a MCT detector. Spectra were obtained from the freestanding microwave film and on some of the dc plasma films grown on *p*-type Si. Films grown on *n*<sup>+</sup> epi Si substrates could not be measured due to free-carrier absorption. Background-subtracted spectra were obtained by using a Si substrate that had been exposed to the dc plasma under conditions that did not grow diamond. The spectra shown here consist of 256 co-added scans at 2  $\text{cm}^{-1}$  resolution.

Raman spectra of a series of films with increasing boron concentration measured at 488 nm are shown in Fig. 1. Raman spectra (not shown) obtained with the 514.5 nm laser line are essentially identical, which confirms that all the observed peaks are due to Raman scattering. In addition to the relatively sharp Raman phonon at 1332  $\text{cm}^{-1}$ , most of the spectra have a broad peaks at 1500 and 1200  $\text{cm}^{-1}$ . The

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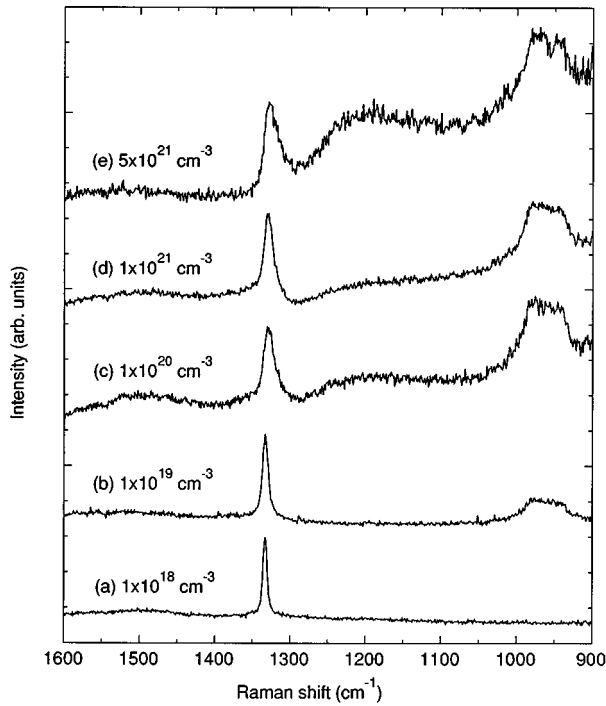


FIG. 1. Room-temperature Raman spectra of a series of B-doped CVD diamond films at 488 nm. The spectra were collected at a laser power of 8 mW and an integration time of 100 s. The feature at  $975\text{ cm}^{-1}$  in (b)–(e) is a second-order phonon from the Si substrate. The diamond phonon appears near  $1330\text{ cm}^{-1}$ ; a Fano line shape is observed in (d). Some line asymmetry is observed in (c) and (d). The broad features in some of the spectra at  $\sim 1500$  and  $1200\text{ cm}^{-1}$  are attributed to amorphous carbon impurities and disordered diamond, respectively.

broad peak centered at  $970\text{ cm}^{-1}$  in Figs. 1(b)–1(e) is second-order scattering from the Si substrate. The weak, broad peak at about  $1500\text{ cm}^{-1}$  is attributed to a small amorphous carbon impurity. The relative height of the broad feature at  $1200\text{ cm}^{-1}$  peak increases with increasing B concentration. This peak may be related to the feature observed at  $1147\text{ cm}^{-1}$  in intrinsic CVD diamond and attributed to disordered  $sp^3$  bonding.<sup>16</sup> The  $50\text{ cm}^{-1}$  shift to higher frequency could be caused by the incorporation of the lighter boron into the disordered phase.

The diamond phonon observed at  $1332\text{ cm}^{-1}$  is a symmetric Lorentzian at low boron concentration, cf. Figs. 1(a) and 1(b). At boron concentrations of  $10^{21}\text{ cm}^{-3}$  the distinctive, asymmetric Fano line shape is observed [Fig. 1(d)]. There is some asymmetry at  $[B]=1\times 10^{20}\text{ cm}^{-3}$ , Fig. 1(c). In the most heavily doped sample, Fig. 1(e), overlap of the  $1200\text{ cm}^{-1}$  peak may partially obscure a Fano line shape.

The IR spectra of four films with a range of boron concentrations corresponding to the Raman measurements are shown in Fig. 2 (an IR spectrum was not available at the highest B concentration). Spectra obtained at 4 K were nearly identical to the room temperature spectra. The IR spectrum of the free-standing microwave film ( $[B]=10^{18}\text{ cm}^{-3}$ ) is Fig. 2(a). The peak at  $1280$  is assigned to defect-activated phonon absorption, which is observed in natural diamond;<sup>17</sup> this peak is also found in Fig. 2(b). The relatively

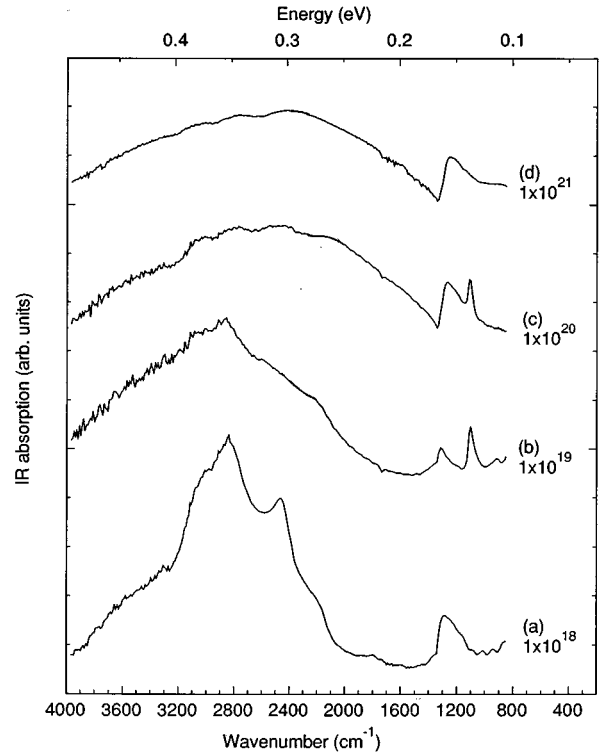


FIG. 2. IR spectra of a series of boron-doped, CVD-grown, diamond films. The spectra have been offset and normalized for clarity. A linear background term has been subtracted from all spectra. Peaks below  $1350\text{ cm}^{-1}$  are assigned to lattice vibrations. The relatively sharp features in (a) peak at  $2450$  and  $2840\text{ cm}^{-1}$  and a shoulder at  $3060\text{ cm}^{-1}$  are assigned to bound states of the boron acceptor. At higher boron concentrations, individual states cannot be distinguished and the peak broadens and shifts to lower energy.

sharp peak at  $1100\text{ cm}^{-1}$  in Figs. 2(b) and 2(c) is assigned to nitrogen in the B form.<sup>17</sup> The peaks at  $2450\text{ cm}^{-1}$  ( $304\text{ meV}$ ) and  $2840\text{ cm}^{-1}$  ( $352\text{ meV}$ ), and the shoulder at  $3060\text{ cm}^{-1}$  ( $379\text{ meV}$ ) are assigned to transitions between bound states of the boron acceptor. The peak positions are in excellent agreement with previous measurements on natural type IIb semiconducting diamond<sup>17</sup> and on boron-doped CVD diamond ( $[B]=1\times 10^{19}\text{ cm}^{-3}$ ) by Mort *et al.*<sup>18</sup> In the spectra shown in Figs. 2(b)–2(d), the relatively sharp boron transitions broaden and a shift of the peak to lower energy is observed.

The Fano line shape describes a quantum mechanical interference between a discrete state and a continuum.<sup>7</sup>

$$I(\omega) = \frac{(q + \epsilon)^2}{(1 + \epsilon^2)} + C, \quad (1)$$

where  $\epsilon$  is a reduced frequency,  $\epsilon = (\omega - \omega_0 - \Delta\omega_0)/\Gamma$ .  $q$  is the asymmetry parameter,  $\Gamma$  is a width parameter,  $C$  is the background, and  $\Delta\omega_0$  is the shift of the diamond Raman phonon from the intrinsic value of  $\omega_0 = 1332.5\text{ cm}^{-1}$ . Small values of  $q$  produce asymmetric lines and the Fano line shape becomes Lorentzian as  $q \rightarrow \infty$ . The film whose Raman spectrum is shown in Fig. 1(d) has the most prominent asymmetric Fano line shape of the films studied here. Figure 3

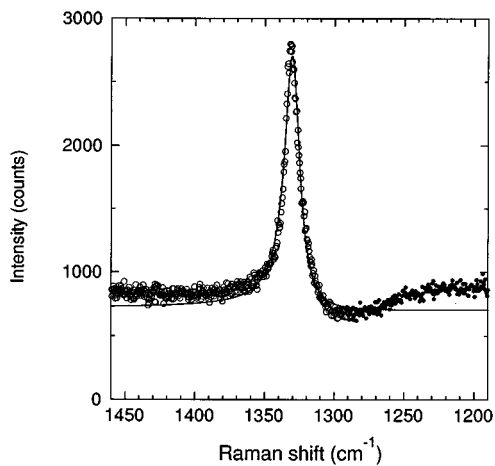


FIG. 3. Fit of the Fano line shape (line), Eq. (1), to the high resolution Raman spectrum of a film with  $[B]=10^{21} \text{ cm}^{-3}$  (open circles). Fit parameters are  $\Delta\omega_0=-2.3$ ,  $q=15.5$ , and  $\Gamma=6.0$ . The deviation from the fit at below  $1300 \text{ cm}^{-1}$  (closed circles) is caused by overlap of the  $1200 \text{ cm}^{-1}$  peak, which was not included in the fit.

shows the fit of a high-resolution, room-temperature spectrum of this film to the Fano line shape. There is good agreement of the Fano line shape and the observed peak. The slight discrepancies away from the line center are attributed to the overlap of the  $a$ -C peak and the  $1200 \text{ cm}^{-1}$  band. The peak center is shifted by  $2.3 \text{ cm}^{-1}$  to lower frequency. This may be caused by a combination of the self-energy shift expected for a Fano interaction and tensile stress in the lattice from the incorporation of substantial quantities of boron.

In heavily B-doped Si ( $4 \times 10^{20} \text{ cm}^{-3}$ ), the Fano interaction is caused by intersubband transitions from filled to empty states within the valence band.<sup>9</sup> This explanation is unlikely for B-doped diamond, because of the large ionization energy of the B acceptor. If empty valence band states were involved in diamond, one would expect that the complete freezing out of the carriers expected at 15 K would lessen the interaction, leading to a more symmetric line at low temperature. However, the high-resolution Raman spectra of the film with the most distinctive Fano line shape, cf. Fig. 1(d), at 295 and 15 K (not shown) are identical to within experimental uncertainty, except for an expected shift of the Raman phonon to higher frequency in the 15 K spectrum due to thermal contraction of the lattice.

It is possible that the Raman phonon (0.165 eV) is interacting with a continuum of transitions either: (1) within the impurity band that is formed at high doping levels or (2) between the impurity band and states formed from mixtures of excited acceptor level and valence band states, or both. Massarani *et al.*<sup>4</sup> estimated an impurity bandwidth of 200 meV for  $[B]=10^{20} \text{ cm}^{-3}$  using simple Coulomb repulsion model and assuming 50% compensation. Thus, at the doping levels at which Fano line shapes are found in this work,

$\sim 10^{21} \text{ cm}^{-3}$ , the impurity bandwidth is larger than the energy of the Raman phonon, which would make a Fano interaction possible with intrapurity band transitions. Alternatively, transitions between the broadened impurity band and states formed from mixing excited acceptor states and valence band states might also form a continuum, which could overlap the energy of the Raman phonon.

These two possibilities are evaluated by examining the IR spectra. In the IR spectrum of the film with the strongest Fano line shape [Fig. 2(d)] the tail of main IR peak does overlap slightly with the position of the Raman phonon, indicating that the broad IR peak might be the source of the Fano interaction. It is also significant that the broad IR feature centered at 360, 320, and 290 meV in Figs. 2(b)–2(d) (eV units are indicated on the upper axis) shifts to lower energy with increasing boron concentration. We would expect an absorption due to intrapurity band transitions to shift to higher energy with increasing B concentration, as the band broadens. Therefore we consider the second of the above mechanisms more likely and assign the Fano interference of the Raman phonon in heavily B-doped diamond to an interaction with a continuum formed from mixtures of excited acceptor level and valence band states.

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