Raman spectroscopy study of heat-treated and boron-doped double wall carbon nanotubes

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We performed Raman spectroscopy experiments on undoped and boron-doped double walled carbon nanotubes (DWNTs) that exhibit the “coalescence inducing mode” as these DWNTs are heat treated to temperatures between 1200 °C and 2000 °C. The fact that boron doping promotes DWNT coalescence at lower temperatures allowed us to study in greater detail the behavior of first- and second-order Raman modes as a function of temperature with regard to the coalescence process. Furthermore, by using various excitation laser energies we probed DWNTs with different metallic (M) and semiconducting (S) inner and outer tubes. We find that regardless of their M and S configurations, the smaller diameter nanotubes disappear at a faster rate than their larger diameter counterparts as the heat treatment temperature is increased. We also observe that the frequency of the G band is mostly determined by the diameter of the semiconducting layer of those DWNTs that are in resonance with the laser excitation energy. Finally, we explain the contributions to the G’ band from the inner and outer layers of a DWNT.

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I. INTRODUCTION

The mechanical and electronic properties of carbon nanotubes are not only highly dependent on nanotube diameter and chirality, but also on the number of concentric layers.1 Adding layers to a single wall nanotube gives rise to charge transfer effects2 and also enhances its chemical, mechanical, and thermal stability.3 Since double wall carbon nanotubes (DWNTs) can possess desirable electrical properties characteristic of single wall carbon nanotubes (SWNTs) while being more mechanically robust, they are good candidates for building blocks in electronic devices,3 where relatively large amounts of energy need to be transferred without compromising the lifetime of the device. In this context, besides controlling the length and diameter of carbon nanotubes, researchers are now making an effort to control the number of layers and numerous attempts have been made to fabricate high quality DWNTs.5–10

In this work we study a DWNT material where previous Raman spectroscopy studies have revealed the presence of the “coalescence inducing mode” (CIM).11 The CIM has been identified as a novel resonant Raman mode related to the vibration of one-dimensional carbon chains (3–5 atoms long) that are created in DWNTs by heat treatment. The appearance of these linear carbon chains by Raman spectroscopy was correlated with the coalescence of the DWNTs, as observed by high resolution TEM measurements.11 In this early study,11 Raman spectra for these DWNTs were only studied at 2.33 eV.

Herein we present a detailed study of the comparison in behavior between boron-doped and undoped DWNT samples with regard to heat treatment to various temperatures, in general, and with regard to further exploration of what Raman spectroscopy tells us about the role of boron in the coalescence process of DWNTs. Special emphasis is given to whether the inner and outer walls are metallic (M) or semiconducting (S) and comparisons are also made to recent studies of DWNTs carried out at the individual isolated DWNT level.12 In Sec. II experimental procedures are summarized, while Sec. III is devoted to the results and discussion of these results. In Sec. III A an overview of the Raman studies in these DWNTs is presented while in Secs. III B–III E more detailed results are presented for RBM, D band, G band and G’ band Raman spectra, respectively. Finally, Sec. IV presents a summary and concluding remarks relevant to our findings.

II. EXPERIMENTAL PROCEDURES

We used a catalytic chemical vapor deposition (CCVD) method to synthesize the double walled carbon nanotubes used in this study. As reported elsewhere,5,13 the buckypaper made with the resulting DWNTs is extremely flexible and macroscopic, and its high purity relative to residual catalyst particles has been confirmed by diamagnetic susceptibility experiments. Its purity relative to SWNTs (single wall carbon nanotubes) has been probed by Raman spectroscopy.14 In order to dope the DWNTs with boron and to study the effect of boron doping on DWNT coalescence, elemental boron was mixed (0.05 wt %) with the highly purified DWNTs and thermally annealed at various temperatures (T0) between 1000 and 2000 °C for 30 minutes in a high purity argon atmosphere. Since we dope DWNTs with elemental boron and all our heat treatments are performed in an argon...
atmosphere, we only expect to have partial substitution reactions where only a small fraction of carbon atoms in the CNT lattice are substituted by B atoms. Two batches of samples were fabricated using the same synthesis method but on different experimental runs. The first batch contains three samples that we used for undoped experiments (Pristine, \( T_{\text{ht}} = 1500 \), \( T_{\text{ht}} = 2000 \) °C) and the second batch contains nine samples that we used for B-doping experiments (Pristine, \( T_{\text{ht}} = 1200 \), \( T_{\text{ht}} = 1300 \), \( T_{\text{ht}} = 1400 \), \( T_{\text{ht}} = 1500 \), \( T_{\text{ht}} = 1600 \), \( T_{\text{ht}} = 1700 \), \( T_{\text{ht}} = 1800 \), \( T_{\text{ht}} = 2000 \) °C). In this work the word “Pristine” indicates no boron doping and no heat treatment. Two different pristine samples were used in this work, neither of which have been heat treated nor boron doped.

Resonance Raman spectra with three different excitation laser energies \( E_{\text{laser}} \) were taken on the macroscopic mats of the buckypaper described above. Every Raman measurement was conducted at room temperature and the laser power levels were kept below 0.5 mW to avoid excessive heating. A 100× objective lens was used to focus the laser beam on a spot within a 1 μm diameter region and the acquisition times were varied from 5 seconds to 1 minute depending on how strong the Raman signal was. Scattered light was collected through the 100× objective using a backscattering geometry. An Ar\(^+\) ion laser was used to generate \( E_{\text{laser}} = 2.41 \) eV, a dye laser containing Rhodamine 6 G dye was pumped by an Ar\(^+\) ion laser to generate \( E_{\text{laser}} = 1.92 \) eV, and a Kr\(^+\) ion laser generated \( E_{\text{laser}} = 1.58 \) eV. A thermoelectrically cooled Si charge coupled device (CCD) detector operated at \(-75 \) °C was used to collect the spectra. Every spectrum was normalized to the intensity of the \( G \) band and line shape analyses were performed using linear baselines and Lorentzian functions.

III. RESULTS AND DISCUSSION

A. Diameter \((d)\) distribution and metallic/semiconducting nature of the resonantly excited layers of DWNTs

In this work, special emphasis was given to the fact that DWNTs can consist of any of the four \( S@S \), \( S@M \), \( M@S \), or \( M@M \) configurations, where \( S@M \) denotes, for example, a semiconducting \((S)\) inner tube within a metallic \((M)\) outer tube. Figure 1 shows a theoretical Kataura plot based on the extended tight-binding (ETB) model.\(^{15,16}\) The laser energies marked on this figure with horizontal lines were chosen to excite different configurations of DWNTs. The shaded regions indicate the diameter distribution of the inner and outer tubes in our DWNT samples.\(^{5,13}\) Such a Kataura plot, based on prior studies on SWNTs, is accurate enough for the qualitative identification of the \((n,m)\) for small diameter tubes within DWNTs.

By comparing the information provided by the theoretical Kataura plot,\(^ {15,17}\) with our experimental results, we can see that the inner tubes that are in resonance with \( E_{\text{laser}} = 2.41 \) eV are \( M \) tubes with \( E_{11}^M \) transitions,\(^ {18}\) while most of the outer tubes that are in resonance with \( E_{\text{laser}} = 2.41 \) eV are \( S \) tubes with \( E_{11}^S \) transitions. The corresponding tube diameters \( d \) are expected to be in resonance with \( E_{\text{laser}} = 2.41 \) eV are 0.87 nm and 1.4 nm, based on the relation \( \omega_{\text{RBM}} = 218.3/d + 15.9,^{11} \) where \( \omega_{\text{RBM}} \) is in units of \( \text{cm}^{-1} \).

On the other hand, if the sample is excited with \( E_{\text{laser}} = 1.58 \) eV, the nanotubes that are in resonance are those whose inner (outer) tubes are \( S \) (M) with \( d \) around 0.82 nm (1.56 nm) for \( E_{\text{laser}} = 1.58 \) eV. However, the actual inner (outer) tube configurations present in the sample include all four of the possibilities mentioned above. Therefore, it is important to keep in mind that the inner \( S \) tubes that are in resonance with a given laser energy may also have outer \( M \) or \( S \) layers that may be in resonance with the same laser line, but with a much higher probability that the outer tube forming a given DWNT will not be in resonance with that \( E_{\text{laser}} \). Moreover, likewise for an inner resonant \( M \) tube, its outer tube can be an \( S \) or \( M \) tube that in general will not be in resonance with the same \( E_{\text{laser}} \) as the inner tube. Our Raman experiments were performed on bundled samples. It is only by carrying out systematic studies at the individual DWNT level using multiple laser lines that the explicit correlation between the inner and outer tubes of the \( M@S, S@M, S@S \) and \( M@M \) configurations can be studied in detail.\(^ {12}\)

The \((n,m)\) integers that define the particular structure of a carbon nanotube have been assigned to each nanotube group present in our pristine DWNT (undoped and without heat treatment) sample by relating the measured \( \omega_{\text{RBM}} \) to the theoretical Kataura plot (see Fig. 1). Our \((n,m)\) assignments for the strongest RBM peaks \((8,5)\) for \( E_{\text{laser}} = 2.41 \) eV and \((11,0)\) for \( E_{\text{laser}} = 1.58 \) eV are in agreement with previous Raman characterization studies performed on the same kind of DWNT sample by Souza Filho et al.\(^ {19}\) We observed that most of the inner nanotubes present in the DWNT samples when using \( E_{\text{laser}} = 2.41 \) eV and \( E_{\text{laser}} = 1.58 \) eV, re-
If we excite the sample with $E_{\text{laser}}=1.58$ eV or most likely would be outside the resonant window (equivalent to fixing a value or range of values for the outer tube diameter and moving vertically along the Kataura plot in Fig. 1 to find other tubes that are present in the sample but not in resonance with the $E_{\text{laser}}=1.58$ eV).

RBM measurements with $E_{\text{laser}}=1.58$ eV reveal that there are also tubes with diameters ranging from $\sim 1.0$ to $\sim 1.37$ nm that also remain intact at temperatures as high as $T_{\text{ht}}=2000$ °C. Measurements with $E_{\text{laser}}=2.41$ eV gives similar results, confirming the great thermal stability of the undoped DWNTs in an inert atmosphere. These results are in good agreement with measurements at $E_{\text{laser}}=2.33$ eV in Ref. 11.

2. Boron doped DWNT samples

Figure 3(a) depicts the RBM region of the spectra (using $E_{\text{laser}}=1.58$ eV) from samples that were heat treated at various temperatures in the presence of elemental boron. When compared to the pristine (undoped and not heat treated) samples, the boron-doped DWNT samples start showing structural disorder at much lower $T_{\text{ht}}$ than their undoped counterparts. We show in this section that this effect is also found at the other $E_{\text{laser}}$ values that were investigated. Also, the behavior of the RBM Raman intensities as a function of $T_{\text{ht}}$ ($I_{\text{RBM}}$) in Fig. 3(a), suggests that the smaller $d_{t}$ (S) tubes disintegrate at a faster rate than their large diameter (M) counterparts. Other weaker RBM features [follow the circles and triangles in Fig. 3(b)] corresponding to tubes with 1.0 $<d_{t}<1.37$ nm, show RBM intensities that become undetectably small at $T_{\text{ht}}=1400$ °C.

Figure 3(b) shows that the most prominent RBM features (e.g., $\sim 267$ and $\sim 159$ cm$^{-1}$) correspond to inner tubes (with $E_{22}^{S}$ in resonance with $E_{\text{laser}}=1.58$ eV) that have $d_{t}\sim 0.88$ nm and to outer tubes (with $E_{11}^{M}$ in resonance with $E_{\text{laser}}=1.58$ eV) that have $d_{t}\sim 1.55$ nm. As discussed above for the undoped samples, it is possible that some inner semiconducting (S) and outer metallic (M) tubes might belong to the same DWNT, both being in resonance with $E_{\text{laser}}=1.58$ eV and having an interlayer distance of $\sim 0.34$ nm. At $T_{\text{ht}}=1700$ °C, the boron-doped samples showed no RBM signal, thus indicating that the DWNTs were destroyed and that their carbon atoms either formed other carbon-based structures or left the system.

It is reasonable to expect that boron doping and heat treatment might affect M and S tubes in different ways. In order to investigate these differences, we switched the laser excitation energy to $E_{\text{laser}}=2.41$ eV (see Fig. 1) and excited M inner walls and S outer walls that may or may not correspond to the same DWNTs. Figure 3(c) shows the RBM region of the spectra thus obtained at 2.41 eV as a function of increasing $T_{\text{ht}}$ for the boron-doped samples. The same general behavior as depicted in Fig. 3(a) is also observed in this case as $T_{\text{ht}}$ increases, the small diameter tubes corresponding to inner tubes of the DWNTs [for example, with family $p=21$, (8,5) for $E_{\text{laser}}=2.41$ eV] disappear at a faster rate than their large diameter counterparts, especially for $1400<T_{\text{ht}}<1600$ °C. Independent of whether the tubes are M or S, we also observe that the intensity of the RBM first increases

d$_{t}=1.56$ nm, and this outer tube might be in resonance with $E_{\text{laser}}=1.58$ eV or most likely would be outside the resonant window (equivalent to fixing a value or range of values for the outer tube diameter and moving vertically along the Kataura plot in Fig. 1 to find other tubes that are present in the sample but not in resonance with the $E_{\text{laser}}=1.58$ eV).

B. Radial breathing mode as a function of $T_{\text{ht}}$

1. Undoped DWNT samples

When undoped, our DWNT sample shows exceptionally good structural stability up to high $T_{\text{ht}}$ (2000 °C). The Raman intensities (Integrated area of a feature normalized to the integrated area of the G band) of the RBM features for these undoped tubes decrease with increasing $T_{\text{ht}}$ (approx. a 50% decrease in intensity when going from the pristine sample to the one for $T_{\text{ht}}=2000$ °C) but these Raman intensities remain relatively high even at $T_{\text{ht}}=2000$ °C (see Fig. 2). The structural stability at high $T_{\text{ht}}$ of similar undoped DWNT samples has also been confirmed by previous high-resolution transmission electron microscopy (HRTEM) and Raman studies.

For Raman spectra taken at $E_{\text{laser}}=1.58$ eV, the strongest RBM features correspond to inner tubes (in resonance with $E_{22}^{S}$) that have a $d_{t}=0.88$ nm and to outer tubes (in resonance with $E_{11}^{M}$) that have a $d_{t}=1.55$ nm. Previous HRTEM studies on this kind of DWNT bundled samples have reported an intertube spacing of $\sim 0.34$ nm. Considering an intertube spacing of $0.34\pm0.01$ nm between the inner and outer tubes of DWNTs, it is possible that we are exciting the inner and outer layers of the same DWNT because $1.55$ nm $-0.88$ nm $=0.67$ nm, consistent with an intertube separation of $0.34$ nm. This inner semiconducting tube could also be paired up with either an M or S outer tube with a
with \( T_{\text{ht}} \) as defects are annealed (Pristine to \( T_{\text{ht}} = 1200 \, ^\circ\text{C} \)), it then reaches a maximum which coincides with the appearance of the CIM (Ref. 11) (\( T_{\text{ht}} = 1300 \) and \( 1400 \, ^\circ\text{C} \)), and then the intensity decreases sharply as the tubes start to coalesce or to transform to other carbon forms such as noncylindrical structures (\( T_{\text{ht}} \geq 1500 \, ^\circ\text{C} \)).

Regardless of whether they are metallic or semiconducting [follow squares and rotated triangles in Fig. 3(d)], when subjected to heat treatment, the inner tubes always tend to disappear at \( T_{\text{ht}} \) between 1400–1600 \( ^\circ\text{C} \) and the outer tubes disintegrate as 1600 \( ^\circ\text{C} \) is reached. Therefore, from the RBM data taken with two laser lines (1.58 and 2.41 eV) that excite the (M inner, S outer) and (S inner, M outer) tube configurations, respectively, we conclude that the metallic or semiconducting nature of the outer layers of a DWNT does not change the temperature at which the coalescence process starts. However, one must keep in mind that the \( T_{\text{ht}} \) steps used for our set of heat treated samples might be too large to

FIG. 3. (Color online) The RBM region of the Raman spectra of boron-doped DWNTs taken with (a) \( E_{\text{laser}} = 1.58 \) eV and (c) \( E_{\text{laser}} = 2.41 \) eV for samples exposed to various heat treatment temperatures. (b) and (d) show the frequency of the various observed RBM features (\( \omega_{\text{RBM}} \)) and their corresponding tube diameters (\( d_t \)) as a function of heat treatment temperature (\( ^\circ\text{C} \)) for both undoped and boron-doped DWNT samples. The shaded regions in (b) and (d) mark the corresponding metallic or semiconducting nature of the nanotubes according to their location on the Kataura plot shown in Fig. 1. Note that the RBM signal becomes very weak for \( T_{\text{ht}} \geq 1600 \, ^\circ\text{C} \) (blue shaded region) indicating that most of the DWNTs in the sample have, as has been previously observed using HRTEM, 11 either coalesced or become a mixture of complex tubular structures and of more disordered carbon.
detect small differences in the coalescence onset temperatures between DWNTs with different metallicities.

C. D band as a function of \(T_{ht}\) and boron doping

As for the case of the RBM feature, the behavior of the disorder-induced D band is very different for the undoped and the boron-doped DWNT samples, for various heat treatments, as discussed below.

1. Undoped DWNT samples

The D band intensity is very weak \(I_D/I_G = 0.1\) at 2.41 eV and 0.29 at 1.58 eV in the Raman spectra from the pristine (undoped) samples that did not receive any heat treatment. This observation, along with previous scanning electron microscopy (SEM), TEM, and magnetic susceptibility experiments,\(^5\) corroborates the good quality and high purity of our DWNT buckypaper samples.

The pure (undoped) DWNT samples in Fig. 4(a) show only a weak increase in the D-band intensity with increasing \(T_{ht}\). The low D band intensity at \(T_{ht} = 2000\ °C\) \(I_D/I_G = 0.22\) at 2.41 eV and 0.39 at 1.58 eV) is consistent with the RBM results indicating that only a small portion of the DWNTs in the sample has been transformed into non-nanotube carbon-based material. The low D band intensity is also consistent with previous HRTEM studies\(^1\) concluding that in the absence of elemental boron, the structure of the DWNTs remains relatively undamaged, even at \(T_{ht} = 2000\ °C\). Figure 5(a) shows the \(I_D/I_G\) ratio for different \(E_{laser}\) values because the D band intensity depends on \(E_{laser}\) as \(E_{laser}^{-3}\) or \(E_{laser}^{-4}\) depending on the type of sample under consideration.\(^2\) Thus improved spectral resolution for studying D band properties is achieved when using lower...
TABLE I. D-band doublet parameters from undoped and B-doped DWNT samples that were heat treated at \(T_{\text{ht}}=1500\,^\circ\text{C}\). The \(I_D/I_G\), \(I_{DL}/I_{DH}\), and \(I_{DH}\) values correspond to the integrated area of the Lorentzian peaks that were fitted to the D and G band spectral regions after choosing adequate linear baselines (see Fig. 6).

<table>
<thead>
<tr>
<th>(T_{\text{ht}}) (1500 °C)</th>
<th>(E_{\text{laser}}) (eV)</th>
<th>(I_D/I_G)</th>
<th>(I_{DL}/I_{DH})</th>
<th>FWHM(_{DH}) (cm(^{-1}))</th>
<th>FWHM(_{DL}) (cm(^{-1}))</th>
<th>(\omega_{DH}) (cm(^{-1}))</th>
<th>(\omega_{DL}) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>1.58</td>
<td>0.30</td>
<td>2.2</td>
<td>22.08</td>
<td>27.45</td>
<td>1312.5</td>
<td>1292.4</td>
</tr>
<tr>
<td></td>
<td>1.58</td>
<td>0.45</td>
<td>1.24</td>
<td>25.6</td>
<td>26.28</td>
<td>1306.8</td>
<td>1288.5</td>
</tr>
<tr>
<td>B doped</td>
<td>2.41</td>
<td>0.45</td>
<td>1.15</td>
<td>23.77</td>
<td>29.88</td>
<td>1351.3</td>
<td>1330.4</td>
</tr>
<tr>
<td>Undoped</td>
<td>2.41</td>
<td>0.18</td>
<td>3.19</td>
<td>21.22</td>
<td>29.7</td>
<td>1350.9</td>
<td>1333.5</td>
</tr>
</tbody>
</table>

\(E_{\text{laser}}\) values. The results of Fig. 5(a) show that the D band intensity for the undoped samples remains low for all \(T_{\text{ht}}\) values and all \(E_{\text{laser}}\) values that were investigated.

2. Boron-doped DWNT samples

Figure 4(b) shows the Raman spectra taken with \(E_{\text{laser}}=1.58\ eV\) from boron-doped samples that received heat treatments at various temperatures. As shown by comparison of the D band intensity in Figs. 4(a) and 4(b), the presence of elemental boron during heat treatment enhances the development of structural disorder (and thus the appearance of a more intense D band) at lower \(T_{\text{ht}}\) (starting at \(T_{\text{ht}}=1500\,^\circ\text{C}\) when compared to undoped samples.

On the basis of the experimental results shown in Fig. 4(b), the spectral behavior for the boron-doped samples with respect to \(T_{\text{ht}}\) can be divided into two regimes: regime I corresponds to \(T_{\text{ht}}<1500\,^\circ\text{C}\) where the spectral profile is dominated by DWNTs and regime II corresponds to \(T_{\text{ht}}>1500\,^\circ\text{C}\) where the spectral profile is consistent with the increasing domination by non-DWNT structures such as noncylindrical tubules, which are seen in the HRTEM measurements previously reported.11

It is important to keep in mind that boron addition has two separate effects on DWNTs: it dopes the nanotubes, changing their Fermi level and boron addition also lowers the \(I_D/I_G\) ratio because of the integral area of the Lorentzian peaks that were fitted to the D and G band spectral regions after choosing adequate linear baselines (see Fig. 6).

a. Regime: \(T_{\text{ht}}\approx 1500\,^\circ\text{C}\). The bottom half of the shaded region in Fig. 4(b) shows the Raman spectra (using \(E_{\text{laser}}=1.58\ eV\)) from boron-doped samples that were heat treated at \(T_{\text{ht}}=1500\,^\circ\text{C}\) and below. The corresponding values of the \(I_D/I_G\) and \(I_{DL}/I_{DH}\) intensity ratio of the D band and G band features in this \(T_{\text{ht}}\) regime are plotted as a function of heat treatment temperature (\(T_{\text{ht}}\)) in Fig. 5(a). Figures 4(b) and 5(a) show that the \(I_D/I_G\) range remains low over the whole range of \(T_{\text{ht}}\) in regime I and no significant changes in \(\omega_{DH}\), \(I_D/I_G\), or the full width of half maximum (FWHM\(_D\)) linewidth are observed. The low D band intensity in this regime indicates that the DWNTs in our sample can withstand \(T_{\text{ht}}\) below 1500 °C without major structural damage even when doped with boron. The onset of D band intensity occurs between 1400 (\(I_D/I_G=0.29\)) and 1500 °C (\(I_D/I_G=0.45\)), in agreement with prior studies at \(E_{\text{laser}}=2.33\ eV\).11 It is only at \(T_{\text{ht}}=1500\,^\circ\text{C}\) that a significant D-band feature appears for both the undoped and B-doped samples [see Table I and Figs. 4(a) and 5(b)].

In order to fully characterize a DWNT one needs to know not only the \((n,m)\) indices of its inner and outer tubes but also the relative atomic positions of the constituents of each tube with respect to one another. The layers of a double wall carbon nanotube are weakly coupled in order to minimize the total energy of the system. Therefore, the electronic structure of a DWNT can be interpreted as the addition of two electronic structures coming from each of its constituents with only a weak modification due to interlayer interactions. The asymmetric line shape of our D band suggests that the spectral profile should be fitted with two Lorentzians and the D band has a well-documented diameter dependence,18 so we assign the origin of the lower frequency component \(D_L\) and higher frequency component \(D_H\) to the inner and outer layers, respectively. This assignment is justified by the measurements on isolated individual DWNTs which have very weak D bands (too weak for line-shape analysis), but they have strong \(G^*\) bands which involves the same phonons as the D band in a double resonance process. The experimental results for the isolated individual DWNTs show only two peaks, both with large intensities with the lower frequency component associated with the inner tube, and the upper frequency associated with the outer tube.12

If DWNT coalescence is catalyzed by boron doping and if the inner tubes start disappearing at a lower heat treatment temperature than the outer tubes due to their higher curvature, it would be reasonable to expect the D band intensity of the inner tubes (\(D_L\)) to be greater than that of the outer tubes (\(D_H\)). The same principle should apply for both undoped and B-doped samples at a given \(T_{\text{ht}}\) value but the effect would be more pronounced for B-doped samples where the D-band intensities are higher, as can be seen by comparing the D-band spectra for \(T_{\text{ht}}=1500\,^\circ\text{C}\) (see Table I and Fig. 6).

In order to study the \(D_H\) and \(D_L\) spectral features we used the samples that were heat treated at 1500 °C because they are the only ones where both the intensities of the D band and the RBM are large enough to allow for adequate line-shape analysis. This means that at \(T_{\text{ht}}=1500\,^\circ\text{C}\) the D band intensity is large enough for an accurate line-shape analysis to be carried out, while there are still enough DWNTs present in our sample. This is not the case for \(T_{\text{ht}}=1400\,^\circ\text{C}\) where the RBM intensities are large enough to be analyzed but the D band intensity is too weak to be analyzed in as much detail. This is also not the case for \(T_{\text{ht}}\).
=1600 °C where the D band intensity is large enough to be analyzed, but most of the DWNTs have been destroyed by the coalescence process and the RBM intensity is too weak to analyze.

Figure 6 shows the decomposition of the D-band Raman spectra for a B-doped sample with $T_{\text{ht}}=1500$ °C into two Lorentzian components with the low-frequency D band component $I_{DL}$ being more intense than its high-frequency counterpart $I_{DH}$ for $E_{\text{laser}}=1.58$ and 2.41 eV and the results are summarized in Table I. The results show that $I_{DL}/I_{DH}>1$ for both undoped and B-doped samples at both values of $E_{\text{laser}}$. However, if we look carefully, we observe that when using 1.58 eV (2.41 eV), the ratio $I_{DL}/I_{DH}$ decreases (increases) with B doping. This complex behavior is a probable indicator that different mechanisms are in play for different DWNT configurations and this complex behavior needs to be researched further preferably at the individual DWNT level.

Those DWNTs with an outer metallic layer (DWNTs excited with 1.58 eV) show a larger overall intensity of the D band (ratio) than those DWNTs (DWNTs excited with 2.41 eV) that have an outer semiconducting layer. Even though the doping effect is subtle and mixed with the $E_{\text{laser}}$ dependence of $I_D/I_G$, the S or M character of the constituent tubes plays a role in the increase of the $I_D/I_G$ ratio because the metallicity (M or S) of the outer tube affects the degree of interaction that the outer layer has with the dopant. A higher degree of interaction of the outer tube with the dopant would imply a faster insertion of foreign atoms into the tube wall and a greater increase in the D band intensity at lower $T_{\text{ht}}$. From a theoretical standpoint this increased interaction of the M outer layer with a dopant is reasonable because the D-band intensity depends on the electron-phonon matrix element and metallic nanotubes have an increased carrier concentration and these carriers are available for increasing the electron-phonon coupling.

b. Regime II: $T_{\text{ht}}>1500$ °C. In this $T_{\text{ht}}$ regime we observe [in Figs. 4(b), 5(a), and 5(b)] a rapid increase in the $I_D/I_G$ intensity ratio as $T_{\text{ht}}$ increases from 1600 to 2000 °C for boron-doped tubes. In addition to the structural destabilization processes that occur for $T_{\text{ht}}=1500$ °C and above, boron appears to enter the outer tubes and gives rise to point defect disorder scattering as suggested by structural HRTEM studies. As $T_{\text{ht}}$ keeps rising, increased disorder is induced in the sample and various kinds of defects are expected to appear and accumulate. Besides being a probe for the defect density in the sample, the $I_D/I_G$ ratio may also provide a
means to estimate the dopant concentration in the boron-doped DWNT samples. This approach for sample characterization is especially valuable when the doping level is too low to be measured by other commonly used structural characterization techniques such as HRTEM operating in the EELS mode.25

The power-law dependence of the $I_D/I_G$ band with varying laser energy is observed in various sp$^2$ carbon materials and has its origin in a dependence of the electron-photon, electron-phonon, and elastic scattering matrix elements on $E_{\text{laser}}$.22–24 In the $1600< T_{\text{htt}} <1800 \degree \text{C}$ region we observe that decreasing the laser excitation energy increases the overall $I_D/I_G$ ratios. The laser energy dependence of the $I_D/I_G$ ratio for samples with $T_{\text{htt}}>1500 \degree \text{C}$ is shown in Fig. 5(b). The figure also contains the best fit of the experimental $I_D/I_G$ data to the functional form $cE_{\text{laser}}^\alpha$, where $c$ is a constant and $\alpha$ defines the power-law dependence of $I_D/I_G$ as a function of $E_{\text{laser}}$. The behavior of the D-band Raman intensity as a function of $E_{\text{laser}}$ depicted in Fig. 5 is qualitatively consistent with previous experimental and theoretical reports on nanographite and SWNTs.26 In the cited works the dominant effects of increasing the heat treatment temperature were a reduction in the D-band intensity through an increase in crystallite size and a concomitant elimination of defects, as opposed to the heat treatment induced disorder that is studied in our work. However, our experimental trend is similar to previous works regarding the marked increase in the intensity of the $I_D/I_G$ ratio as $E_{\text{laser}}$ is decreased.23

Whereas Fig. 5(b) shows a power-law dependence of the form $I_D/I_G=cE_{\text{laser}}^\alpha$, where $\alpha$ varies from $\sim -2.5$ to $\sim -3$ with increasing $T_{\text{htt}}$, a value of $\alpha=-4$ was reported for systematic studies on nanographite for both experiment23 and theory.24 Values for the magnitude of $\alpha$ less than $-4$ and in a similar range were observed experimentally for graphitic foams where both two-dimensional (2D) and 3D graphite regions are present.21

D. G band as a function of $T_{\text{htt}}$ and boron doping

The G band contains contributions from all the tubular, graphitic, and sp$^2$ carbon material in the sample.18 In particular, for semiconducting tubes, the G$^+$ feature is generated when carbon atoms vibrate in the axial direction (LO phonon mode) of the nanotube and the G$^-$ feature comes from atoms vibrating along the circumferential direction of the nanotube (TO phonon mode). If the excited nanotube is metallic (semiconducting), the line shape of the G$^+$ is expected to show a Breit-Wigner-Fano (Lorentzian) line shape arising from the conduction electrons interacting with phonons and the Kohn Anomaly causes a large downshift of the LO mode.22 Charge donors (acceptors) coming from dopants or impurities also modify the Breit-Wigner-Fano line shape and can upshift (downshift) the frequency of the G$^+$ band.18 Finally, the configuration of the M or S layers of a DWNT also has an effect on the details of the observed line shape of the G band. Taking these considerations into account, the following trends were observed in the G-band region of the spectra as a function of $T_{\text{htt}}$ and boron doping.

1. Undoped DWNT samples

Figure 4(a) shows the G-band region of the Raman spectra of a pristine (no doping and no heat treatment) DWNT sample taken with $E_{\text{laser}}=1.58 \text{ eV}$. The G$^+$ feature is relatively sharp and although the inner tubes that are excited by $E_{\text{laser}}=1.58 \text{ eV}$ are predominantly semiconducting, a weak BWF tail appears in the G$^+$ region. We first discuss the G$^-$ feature and then the G$^+$ feature. The observed BWF line shape of the G$^+$ feature suggests a contribution coming from outer metallic tubes whose $E_{\text{g}}$ could be in resonance with $E_{\text{laser}}=1.58 \text{ eV}$. Keep in mind that the inner tubes excited by $E_{\text{laser}}=1.58 \text{ eV}$ may also have outer semiconducting layers that are out of resonance with $E_{\text{laser}}=1.58 \text{ eV}$. At $T_{\text{htt}}=2000 \degree \text{C}$, the G$^-$ region loses some of its original BWF shape and a sharper G$^+$ feature than the one observed in the nonheat treated sample is noticeable. If we ignore a possible increase in the average $d$, due to the high $T_{\text{htt}}$, the observed change towards a more semiconducting line shape at $T_{\text{htt}}=2000 \degree \text{C}$ could suggest that the sample’s ratio of metallic to semiconducting tubes decreases because metallic tubes might be more sensitive to heat treatment than semiconducting nanotubes and thus more readily destroyed. The change in the metallic/semiconducting ratio is expected to be subtle because, regardless of their metallic or semiconducting nature, undoped tubes can withstand high heat treatment temperatures without showing significant structural damage.

Figure 7(c) shows the dependence of $\omega_{G^+}$ on $T_{\text{htt}}$ for undoped samples using three different laser excitation energies. As can be appreciated from the left-hand side of Fig. 7(c), the undoped DWNT samples did not show significant changes in the frequency of G$^+$ (FWHM line width of G$^+$ also remained constant) as $T_{\text{htt}}$ was increased. This observation, along with the fact that the G$^+$ feature remains sharp at all $T_{\text{htt}}$, is yet another confirmation that, in the absence of boron, pure DWNTs are stable under heat treatments to temperatures up to $2000 \degree \text{C}$.11

So far we have described the behavior of the G band as observed by using $E_{\text{laser}}=1.58 \text{ eV}$. As previously mentioned in the RBM section, if we switch to $E_{\text{laser}}=2.41 \text{ eV}$, we excite DWNTs whose inner walls are metallic and outer walls are semiconducting, keeping in mind that the inner M layers in resonance with this laser energy may also be contained inside nonresonant M outer walls. The overall behavior of the G$^+$ band using $E_{\text{laser}}=2.41 \text{ eV}$ as a function of $T_{\text{htt}}$ is similar to its $E_{\text{laser}}=1.58 \text{ eV}$ counterpart, but there is one important difference that should be noted, the $\omega_{G^+}$ is upshifted by $\sim 8 \text{ cm}^{-1}$ for all $T_{\text{htt}}$ in regime I relative to the data at $1.58 \text{ eV}$ [see Fig. 7(c)]. We attribute this offset in $\omega_{G^+}$ to the change in the excited DWNT configuration from DWNTs with M inner tubes when using $E_{\text{laser}}=2.41 \text{ eV}$ to DWNTs with S inner tubes when using $E_{\text{laser}}=1.58 \text{ eV}$. Alternatively, we could also expect this upshift to have its origin in the $d_i$ dependence of $\omega_{G^+}$ for S tubes. According to Pailler,20 the $\omega_{G^+}$ for S tubes tends to downshift as $d_i$ decreases. Also, from Raman studies on isolated SWNTs,18 it is known that S tubes show sharper and more intense G band features than M tubes. In this context, we could be observing how S constituents in our DWNTs dominate the G-band signal and tend to
determine the $\omega_{G^+}$, since different $E_{\text{laser}}$ lines excite S tubes with different $d_j$ values. Figure 7(d) shows the behavior of $\omega_{G^+}$ as a function of $E_{\text{laser}}$ for an undoped DWNT sample that did not receive heat treatment. The two $\omega_{G^+}$ regimes of behavior may suggest that we are switching from S inner tubes/M outer tubes to M inner tubes/S outer tubes as we increase the laser excitation energy. This explanation of the observed upshift in $\omega_{G^+}$ which is seen in Fig. 7(d) is consistent with observations on individual, isolated DWNTs where $\omega_{G^+}$ for M@S configurations is also found to be upshifted with respect to the S@M and S@S configurations.\textsuperscript{12}

2. Boron-doped DWNT Samples

The simultaneous effects of boron intercalation between DWNTs, boron incorporation into the nanotube lattice, and heat treatment-induced disorder with increasing $T_{\text{ht}}$, are all reflected in the $G$-band region of the spectra. We discuss the results in terms of the two regimes of heat treatment temperatures and the results for $G^+$ and $G^-$.\textsuperscript{12}

\textbf{a. Regime I: $T_{\text{ht}} \leq 1500$ °C.} In this regime no large shifts in the frequency of the G band are observed as a function of increasing $T_{\text{ht}}$ for constant laser energy. However, doping and boron incorporation into the nanotube lattice are ex-
pected to generate large shifts in the frequency of the G band. The lack of a large G band shift in this regime indicates that the boron doping levels generated in regime I are low and that most of the atoms contributing to the Raman signal are due to C-C vibrations.

Nevertheless, if we do a careful line-shape analysis, small G band shifts close to the noise level can be seen to follow the same two trends. First, when outer M tubes and inner S tubes are excited with \( E_{\text{laser}} = 1.92 \text{ eV} \) or \( 1.58 \text{ eV} \) [follow the circles and triangles in Fig. 7(c)], a slight \( \sim 2 \text{ cm}^{-1} \) \( \omega_G \) downshift is observed for increasing \( T_{\text{ht}} \). The observed BWF features at \( T_{\text{ht}} \) below 1500 °C are generated mainly by outer metallic tubes [see Fig. 7(a)], with \( d_t \sim 1.56 \text{ nm} \) [see the squares for the RBM in Fig. 3(b)] which are in resonance with \( E_{11}^{\text{M}} \) for \( E_{\text{laser}} = 1.58 \text{ eV} \).

Second, when outer S tubes and inner M tubes are excited with \( E_{\text{laser}} = 2.41 \text{ eV} \) [follow the squares in Fig. 7(c)] we find that, in regime I, an arguably small frequency upshift of the \( G^* \) peak (by \( \sim 2 \text{ cm}^{-1} \)) occurs as \( T_{\text{ht}} \) reaches 1600 °C. These two opposite shifts of \( \omega_G \), with increasing \( T_{\text{ht}} \) suggest that when the outer shell of a DWNT is semiconducting \( (E_{\text{laser}} = 2.41 \text{ V}) \), the dominant effect is that of boron acting as an acceptor, which reduces the C-C distance and upshifts \( \omega_G \).

On the other hand, when the outside layer is metallic, as for the lower \( E_{\text{laser}} \) values, boron incorporation into the lattice seems to be the dominant effect because the binding energies of B-C bonds are weaker than those of C-C bonds and a downshift of the \( G^* \) phonon frequency is then expected. This result is consistent with the work of Yang et al. on nitrogen and boron-doped coaxial nanotubes,\(^{29}\) where they observe downshifts in the \( G^* \) band as the boron/carbon fraction was increased in their nanotube samples. Thus the observed dependence of \( \omega_G \) on \( T_{\text{ht}} \) is consistent with the coalescence process.

b. Regime II: \( T_{\text{ht}} > 1500 \text{ °C} \). The effects of boron doping are magnified in this temperature regime. We observe a significant broadening of the G band [see Figs. 7(a) and 7(b)] that has its origin from two simultaneous phenomena, defects and doping as described below. The destruction of carbon nanotubes at high \( T_{\text{ht}} \) values (above 1600 °C) gives rise to complex Raman spectra.

For \( T_{\text{ht}} \geq 1600 \text{ °C} \) the sample loses crystallinity as linear carbon chains form and trigger nanotube coalescence. In this process carbon nanotubes are destroyed\(^{11}\) noncylindrical structures form, and other sp\(^2\) and amorphous carbons start to dominate the G band spectra above \( T_{\text{ht}} = 1600 \text{ °C} \) for all \( E_{\text{laser}} \) values studied. As \( T_{\text{ht}} \) rises, the contributions to the Raman spectra from complex and heterogeneous sp\(^2\) carbons become more and more important, broaden the G-band line shape dramatically, and downshift the central frequency. These structural changes are correlated with the appearance of a strong D band at \( T_{\text{ht}} \) above 1500 °C (see Fig. 5) and have been confirmed by complementary studies using HRTEM.\(^{41}\)

As stated above, boron doping in this regime plays two roles, forming B-C bonds which lowers \( \omega_G \) and adding hole carriers which increases \( \omega_G \) and both effects are seen in the spectra. The broadening is more pronounced for the \( E_{\text{laser}} = 2.41 \text{ eV} \) which is resonant with DWNTs with M@S configuration.

### E. G’ band as a function of \( T_{\text{ht}} \) and boron doping

The G’-band feature has its origin from a two phonon second-order Raman resonance process that is observed at a frequency of approximately twice \( \omega_G \). When using \( E_{\text{laser}} = 2.41 \text{ eV} \), SWNTs with \( d_t \) values comparable to that of the outer semiconducting tubes in resonance with this \( E_{\text{laser}} \) show \( \omega_{G'} \approx 2700 \text{ cm}^{-1} \) (Ref. 18) and their G’ band can be fit with a single Lorentzian showing a dispersion of \( \omega_{G'} d \approx 106 \text{ cm}^{-1}/\text{eV} \). The G’ band of single layer graphene can also be fit with one Lorentzian but if a second layer is added to the system, the electronic bands split, and four peaks are observed in the G’ region.\(^{30}\) Unlike bilayer graphene, the layers of a DWNT are likely to be incommensurate and weakly coupled so the observed splitting of the G’ in DWNTs could be generated by a phonon softening effect due to the differences in curvature between the inner and outer layers. Since the two diameter distributions of the inner and outer tubes can be further subdivided into metallic and semiconducting categories, in this section we fit the G’ band with four Lorentzians. The independent behavior of each Lorentzian is complex and some overlapping between these categories exists. We however expect the two lower frequency Lorentzians to have their origin coming from inner M or S layers and the two higher frequency Lorentzians to come from outer M or S layers.

#### 1. Undoped DWNT samples

The G’ band region of the undoped DWNT samples reveals four Lorentzian peaks that we have identified as G’1, G’2, G’3, and G’4 [see Fig. 9(a)]. As shown in Fig. 8, the heat treatments (up to \( T_{\text{ht}} = 2000 \text{ °C} \)) of the undoped samples do not have a significant effect on the line shape of the G’ region for all \( E_{\text{laser}} \) values, indicating again that the DWNTs can withstand high temperatures in the absence of boron. At \( T_{\text{ht}} = 2000 \text{ °C} \) the intensity of the G’ band is slightly decreased, but the RBM features corresponding to the inner diameter tubes are still present and the G’1–G’4 features do not disappear. The spectrum in Fig. 8(a) taken at \( E_{\text{laser}} = 2.41 \text{ eV} \) for the pristine undoped DWNTs has also been fit by other authors with four peaks.\(^{31,32}\)

If we decrease the laser excitation energy, the overall FWHM of decreases and the G’1–G’4 features tend to merge into a single peak located at \( \omega_{G'} = 2582 \text{ cm}^{-1} \) for \( E_{\text{laser}} = 1.58 \text{ eV} \) [see Figs. 8(a)–8(c)]. Also, each G’ component has a different dispersion value (see Table II and, in particular, the G’4 feature shows the closest agreement (within 8%) with the dispersion of SWNTs.

In order to assign the G’1–G’4 features to the inner and/or outer walls of our DWNTs, we can compare their diameter dependence to that of SWNTs \( \omega_{G'} = \omega_{G'} + c/d_t \), where \( \omega_{G'} \) is the frequency of the G’ feature associated with 2D graphite and \( c \) is a constant that accounts for laser excitation energy and type of sample.\(^{33}\) Interestingly, only the
2. Boron-doped DWNT samples

Since boron acts as a catalyst for DWNT coalescence and for the structural destabilization of DWNTs at a lower $T_{\text{int}}$ than in their undoped form, the change in the structure of boron-doped DWNTs as $T_{\text{int}}$ is increased provides further insights into the origins of the $G'$ features.

G’3 feature at $\omega_{G'}=2663$ cm$^{-1}$ [see Fig. 9(a)] shows a reasonable agreement with SWNTs when using $E_{\text{laser}}=2.41$ eV and a $d_i=0.88$ nm corresponding to the most prominent inner diameter tube in our DWNT sample in resonance at 2.41 eV. When using $E_{\text{laser}}=1.58$ eV the agreement of $G'$–$G'$4 with the $\omega_{G'}$ dependence on $d_i$ for SWNTs is also limited. Therefore, comparisons to SWNT $\omega_{G'}(d_i)$ functions can only be qualitative and a new DWNT $\omega_{G'}(d_i)$ relation has to be developed from experiments on DWNTs with various laser excitation energies. The next section describes how boron doping provided an alternative procedure to investigate the origins of the $G'$–$G'$4 features.

FIG. 8. (Color online) G’ band region of the Raman spectra of undoped and boron-doped DWNT samples for different $T_{\text{int}}$ using (a, d) $E_{\text{laser}}=2.41$ eV, (b, e) $E_{\text{laser}}=1.92$ eV, and (c, f) $E_{\text{laser}}=1.58$ eV. The DWNT schematics mark the metallic or semiconducting nature of the inner tubes that each $E_{\text{laser}}$ predominantly excites. The shaded (A) region in (d) marks the low-frequency components of the G’ band (G’1 and G’2) corresponding to the inner diameter tubes. The shaded (B) region for DWNTs corresponds to the G’3 and G’4 features mostly associated with the outer tubes and is observed at all $T_{\text{int}}$. The predominant excited DWNT configuration for $E_{\text{laser}}=2.41$ eV consists of inner metallic (M) tubes and outer semiconducting (S) tubes.
insight into the relationships between the G’1–G’4 features and their identification with the inner and the outer walls of our DWNTs. The G’ band analysis for the boron-doped samples with respect to T_{ht} has also been divided into two regimes: regime I corresponds to T_{ht} ≤ 1500 °C and regime II corresponds to T_{ht} > 1500 °C.

a. Regime I: T_{ht} ≤ 1500 °C. In the T_{ht} range of regime I, the inner and the outer walls of our DWNTs remain in most cases structurally stable. The frequency, intensity, and dispersion of the G’1–G’4 features show a similar behavior to that of the boron free samples. The dispersion of the G’4 feature (100 cm⁻¹/eV) is again close to the expected 106 cm⁻¹/eV of the G’ band in SWNTs (Ref. 18) and the dispersions of G’1–G’3 are considerably below that value (See Table II column T_{ht}=1400 °C).

Figure 8(d) presents the G’ region of the Raman spectra from pristine (no heat treatment and no boron doping) and heat treated boron-doped DWNTs for increasing T_{ht} using E_{laser}=2.41 eV laser excitation. Since the laser energy is E_{laser}=2.41 eV, we know from the Kataura plot that we are exciting DWNTs whose inner tubes are metallic. Also, increasing the laser excitation energy increases the fourfold splitting of the G’ band, so we select E_{laser}=2.41 eV to observe the changes in the four components (G’1 to G’4) of the G’ as T_{ht} is increased. The shaded region marked with an A (B) corresponds to the G’1 and G’2 (G’3 and G’4) features and is expected to come from the inner (outer) layers of the DWNTs.\[1\]

A slight increase in the A/B intensity ratio (I_A/I_B) is observed for T_{ht}=1200–1400 °C when compared to the pristine sample. Since the D band is still very weak at T_{ht} ≤ 1400 °C, the change in I_A/I_B suggests that the heat treatment anneals possible defects in the inner layer of the DWNT structure and enhances the contribution to the G’ signal from the inner layers (G’1 and G’2).

The correlation between the A/B intensity ratio (I_A/I_B) and the intensity of the RBM peaks from inner layers and the D band can be used to assign the G’1–G’2 (G’3–G’4) features to the inner (outer) layers of our DWNTs. As shown in Fig. 8(d), at T_{ht}=1400 °C the intensity ratio I_A/I_B is greater than 1 while at T_{ht}=1500 °C, I_A/I_B approaches 1 and at T_{ht} > 1500 °C I_A/I_B < 1. At T_{ht}=1500 °C, the onset of the decrease in the intensity of the A region (G’1–G’2) exactly


table II. G’ band dispersion values from pristine (no boron doping and no T_{ht}) and B-doped DWNT samples that were heat treated at T_{ht}=1400 °C and T_{ht}=1600 °C.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Pristine</th>
<th>T_{ht}=1400 °C (Boron doped)</th>
<th>T_{ht}=1600 °C (Boron doped)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G’1</td>
<td>86.2</td>
<td>86.4</td>
<td>41.28</td>
</tr>
<tr>
<td>G’2</td>
<td>65.04</td>
<td>63.43</td>
<td>47.04</td>
</tr>
<tr>
<td>G’3</td>
<td>85.1</td>
<td>73.67</td>
<td>82.4</td>
</tr>
<tr>
<td>G’4</td>
<td>98.3</td>
<td>100</td>
<td>85.4</td>
</tr>
</tbody>
</table>

FIG. 9. (Color online) Lineshape analysis for the G’-band region of the Raman spectra at E_{laser}=2.41 eV into four components for the cases of (a) pristine (second batch) and (b) heat-treated boron-doped DWNTs at T_{ht}=1600 °C. (c) A plot of ω_{G’1} for G’1 through G’4 as a function of T_{ht}. All the spectra were taken with E_{laser}=2.41 eV which excites DWNTs whose inner tubes are metallic (M). Notice the generalized ω_{G’} upshift for T_{ht} above 1600 °C.
coincides with the onset of DWNT coalescence, the increase in intensity of the D band and with the onset of the intensity decrease in the RBM peak corresponding to the inner tubes [see \( \omega_{\text{RBM}} \approx 265 \text{ cm}^{-1} \) in Fig. 3(e)]. This observation allows us to confirm the assignment of G’1–G’2 to the inner layers of the DWNTs that are in resonance with \( E_{\text{laser}} = 2.41 \text{ eV} \). On the other hand, at \( T_{\text{htt}} = 1500 \text{ °C} \), the intensity of the B region and the intensity of the RBM peak corresponding to the outer layer [see \( \omega_{\text{RBM}} \approx 165 \text{ cm}^{-1} \) in Fig. 3(c)] remain unchanged, so we can confirm the assignment of G’3–G’4 to the outer DWNT tubes.

b. Regime II: \( T_{\text{htt}} > 1500 \text{ °C} \). In this \( T_{\text{htt}} \) regime, the required energy for boron-doped DWNT structural destabilization is reached and significant changes occur to the line shape of the G’ band. At \( T_{\text{htt}} = 1600 \text{ °C} \) all the RBM signal is lost, the D band intensity increases considerably [see Fig. 5(a)] and the intensity of the G’3 peak decreases [see Fig. 5(b)]. A similar effect is observed when using \( E_{\text{laser}} = 1.92 \text{ eV} \). The marked decrease in the intensity of the G’1–G’3 features, the overall broadening of the G’ region, and the generalized loss of a nanotubelike dispersion \( (dQ/dE_{\text{laser}}) \) all suggest that for \( T_{\text{htt}} \approx 1600 \text{ °C} \), our sample is mainly composed of a mixture of defective tubular structures and disordered sp² carbon materials. Increasing \( T_{\text{htt}} \) above 1600 °C also results in the alteration of the dispersion of the G’1–G’4 peaks as shown in Fig. 9(b). As presented in Table II, the dispersion of the G’4 feature goes below that of SWNTs \( (\sim 106 \text{ cm}^{-1}/\text{eV}) \) (Ref. 18) and in fact goes down all the way to 85.4 cm⁻¹/eV. As a reference, at 2.54 eV the G’ for HOPG has two peaks, a weak one at \( \sim 2690 \text{ cm}^{-1} \) and a much higher intensity one at \( \sim 2740 \text{ cm}^{-1} \) that has a dispersion of \( \sim 99 \text{ cm}^{-1}/\text{eV} \).

**IV. CONCLUSIONS**

We have analyzed the Raman spectra from DWNT bundles that were annealed in the presence and in the absence of elemental boron. An early study of the Raman spectra for such heat treated samples was carried out previously using \( E_{\text{laser}} = 2.33 \text{ eV} \) excitation. In the present work, we observe, in agreement with the earlier study at heat treatment temperatures between 1200 and 2000 °C that the addition of elemental boron both enhances DWNT coalescence and lowers the onset of structural destabilization to \( T_{\text{htt}} = 1500 \text{ °C} \). In this context, the RBM region of the spectra indicates that smaller diameter tubes disintegrate more readily upon heat treatment than larger diameter tubes, and this disintegration effect is strongly amplified in the boron-doped tubes. Also, we did not detect a difference in the structural destabilization temperature for DWNTs with different metallic and semiconducting configurations. Such a distinction was evaluated using multiple laser excitation energies and different metallic-semiconducting inner/outer tube configurations.

We observe that the D band in DWNT bundles can be fit with two Lorentzians which have their origin in the inner and outer layers of a DWNT as is also observed at the single isolated DWNT level. The overall dependence of the D band intensity on \( E_{\text{laser}} \) is qualitatively consistent with previous experimental reports and theoretical reports on nanographite and SWNTs. We find that the \( I_D/I_G \) ratio has a power-law dependence on \( E_{\text{laser}} \) (in the range 1.6–2.41 eV) of the form \( I_D/I_G = cE_{\text{laser}}^{-\alpha} \), where \( \alpha \) varies from \( \sim 2.5 \) to \( \sim 3 \) with decreasing \( T_{\text{htt}} \) similar to the behavior of graphitic foams.

Both the inner and outer tube constituents of a DWNT contribute to the characteristic line shape of the G band but the semiconducting tubes and the outer tubes have a stronger effect on the overall lineshape. By using various laser lines to excite DWNTs with different configurations, we found that the line shape of the G band is dominated by the outer DWNT layers, regardless of the metallic or semiconducting nature of the inner layers. If the outer tube is metallic, the G band shows a noticeable BWF tail, but if the outer tube is semiconducting, the G” band is clearly visible. The effect of boron doping is to increase the frequency of the G” feature indicating that boron behaves as an acceptor dopant for DWNTs.

Finally, by comparing the intensity of the G’ band to the intensity of the corresponding RBM peaks as a function of heat treatment temperature and as the DWNTs reach coalescence with increasing \( T_{\text{htt}} \), we observe that its four components (G1–G4) can be assigned to the inner (G’1 and G’2) and the outer tubes (G’3 and G’4) of the DWNTs present in our sample, consistent with but complementary to the behavior of the G’ band in graphene, and consistent with the behavior of the G’ band in individual isolated DWNTs.

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