Origin of the 1150-cm\(^{-1}\) Raman mode in nanocrystalline diamond

A. C. Ferrari* and J. Robertson

Department of Engineering, University of Cambridge, Cambridge, CB2 1PZ, United Kingdom

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The peak near 1150 cm\(^{-1}\) in the visible Raman spectra of poor quality chemical-vapor-deposited diamond is often used as the signature of nanocrystalline diamond. We argue that this peak should not be assigned to nanocrystalline diamond or other sp\(^3\)-bonded phases. Its wave number disperses with excitation energy, its intensity decreases with increasing excitation energy, and it is always accompanied by another peak near 1450 cm\(^{-1}\), which acts similarly. This behavior is that expected for sp\(^2\)-bonded configurations, with their smaller band gap. The peaks are assigned to transpolyacetylene segments at grain boundaries and surfaces.

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The chemical-vapor deposition (CVD) of diamond is an important route in the production of this unique material.\(^1\);\(^2\) Generally, the aim is to maximize the crystalline quality of CVD diamond. A single, sharp peak at 1332 cm\(^{-1}\) in the Raman spectrum is frequently used as a signature of high crystalline quality.\(^3\) However, diamond grown under non-optimum conditions, such as lower temperature or higher carbon activity in the plasma, gives films with small grain size. This material is often called nanocrystalline diamond, even if the grain size is actually 5–100 nm. Recently, nanodiamond was grown intentionally under specific conditions,\(^4\);\(^5\) because smaller grains give films with valuable tribology and field-emission properties.\(^6\) The appearance of a 1150 cm\(^{-1}\) Raman peak is very widely used as a simple signature of such nanocrystalline diamond. This paper argues that the 1150 cm\(^{-1}\) Raman peak in fact cannot originate from a nanodiamond or related sp\(^3\)-bonded phase, but must arise from a coexisting sp\(^2\) phase, which we suggest is transpolyacetylene. Figure 1(b) shows a Raman spectrum of a typical low-quality CVD diamond, grown by microwave CVD at 1300-W, 780 °C, 180-sccm H\(_2\), 17.5 sccm CH\(_4\), and 2.5 sccm CO\(_2\) at 45 mbar.\(^7\) Similar spectra were seen by many groups (e.g., Refs. 1, 5, and 8–15). In addition to a small diamond peak at 1332 cm\(^{-1}\), the spectrum has four extra features at 1150, 1350, 1450, and 1550 cm\(^{-1}\). The peaks at 1350 and 1550 cm\(^{-1}\) are the D and G modes of disordered carbon.\(^3\) The peak at 1150 cm\(^{-1}\) has been attributed to nanocrystalline diamond.\(^1\);\(^8\) We refer to this peak as v\(_1\), and to the 1450 cm\(^{-1}\) peak as v\(_3\).

Nemanich et al.\(^9\) proposed that the 1150 cm\(^{-1}\) peak arises from nanocrystalline or amorphous diamond. A small grain size would be expected to relax the q = 0 selection rule and allow phonon modes with q ≠ 0 to contribute. Subsequent workers always supported this assignment.\(^9\);\(^10\);\(^11\);\(^12\);\(^13\);\(^14\);\(^15\) This is largely because this wave number corresponds roughly to a maximum in the vibrational density of states (VDOS) of diamond. We argue against this assignment for the following reasons. First, the idea that this peak is due to q ≠ 0 phonons activated by disorder is ruled out because the grains are too large to observe a zone boundary peak at ~1150 cm\(^{-1}\). Phonon confinement allows the participation of phonons with a wave vector q = 2\(\pi d\), where d is the grain size. Grains of 5–100 nm would still favor modes quite close to \(\Gamma\), rather than modes nearer the zone boundary at \(L\), which contribute most to the VDOS maximum,\(^16\) seen in Fig. 1(c). Even if the grains were truly 1 nm or less, the VDOS maximum is near 1260 cm\(^{-1}\), not 1150 cm\(^{-1}\), so a single peak at 1150 cm\(^{-1}\) would not be seen. The phonons in small grains could be softer than in bulk diamond. However, the Raman spectra of diamond nanocrystals from shock synthesis, with a fairly uniform distribution of grain sizes of 4–6 nm, were measured by Yoshikawa et al.\(^17\) and Obratsova et al.\(^11\) They saw only the main diamond peak broadened and downshifted by ~12–13 cm\(^{-1}\), consistent with phonon confinement,\(^18\) confirming that bulk-phonon dispersion curves are valid for nm-size grains.

Second, sp\(^2\) sites have a much larger cross section for visible Raman than sp\(^3\) sites, about 50–230 times,\(^19\) but the intensity of v\(_1\) is sometimes comparable to or even higher

![FIG. 1. Raman spectrum of (a) tetrahedral amorphous carbon and (b) a low quality CVD diamond at 514 nm. (c) The VDOS of diamond, from Ref. 16 for comparison; showing a maximum at 1260 cm\(^{-1}\) and a kink at 1175 cm\(^{-1}\). The peak at ~970 cm\(^{-1}\) in (a) is due to Si second order.](image)
than the amorphous carbon phase and crystalline diamond phase. If the nanocrystalline diamond is located in rather wide grain boundaries, for example, where is the much larger signal from the $sp^2$ graphitic sites, which are also in the grain boundaries? In low-quality diamond, one expects the Raman signal from $sp^2$ sites to dominate that from $sp^3$ sites.

The third and fourth reasons are the key ones, and can be understood from Fig. 2. This shows Raman spectra taken at various laser excitation energies on a region of suboptimal CVD diamond film. We see that the $v_1$ and $v_3$ peaks in fact disperse by 50–100 cm$^{-1}$ with excitation energy. This is not possible for a density-of-states feature, which should remain fixed as the excitation energy varies. Fourth, the intensity of the $v_1$ and $v_3$ peaks decreases compared to the 1332 cm$^{-1}$ diamond peak, as the excitation energy is raised. If the two modes were both due to $sp^3$ sites, they would both increase in intensity as the excitation energy is raised. This is because $sp^3$ sites have a wide, 5.5 eV band gap. Raising the excitation energy allows the $sp^3$ bonds to be excited more strongly. In contrast, $sp^2$ sites have a low band gap and are easily excited by visible light. We see that the 1150 cm$^{-1}$ mode is in fact absent at 244 nm excitation, where $sp^3$ sites have their highest cross section. This can be ruled out because $sp^3$ sites have a low band gap and are easily excited by visible light. The peak at 244 nm excitation, seen at 351 nm excitation wavelength, is a spurious peak due to the optics of the 351 nm Raman system.

It has been suggested that the 1150 cm$^{-1}$ mode may be caused by hexagonal diamond. However, it is now known that hexagonal diamond has a Raman mode at 1323 cm$^{-1}$, just below that of cubic diamond.

A further reason is that the 1150 cm$^{-1}$ mode usually has a companion mode around 1450 cm$^{-1}$. This can be ruled out, as it is still seen in diamond on non-silicon substrates. It has also been attributed to some form of $sp^3$ bonding. This can be ruled out because $sp^3$ bonding can only give modes up to about 1350 cm$^{-1}$, the band limit of diamond.

The final argument against assigning the 1150 cm$^{-1}$ peak in the visible Raman spectrum to $sp^3$ sites, is the Raman spectrum of tetrahedral amorphous carbon (ta-C). This is an amorphous carbon with about 85–90% $sp^3$ bonding. Figure 3 shows its Raman spectra for increasing excitation energy. It is seen that at visible excitation (e.g., 514 nm), the spectra is dominated by a very broad $G$ peak at around 1560 cm$^{-1}$ (Ref. 20); see Fig. 1(a). There is no mode near 1150 cm$^{-1}$. The spectra change with increasing excitation energy. Only at deep UV excitation, 244 nm or 5.1 eV, does the spectrum have a broad peak centered on 1050 cm$^{-1}$. This is a VDOS feature of the random $sp^3$ network. The high excitation energy allows $sp^3$ sites to be excited with a cross section...
spolyacetylene ~ sp is an alternate chain of carbon atoms. However, this 1050 cm$^{-1}$ peak is not present for visible or near-UV excitation. The 1050 cm$^{-1}$ peak only appears in UV excitation, so its intensity has the opposite dependence with excitation to $v_1$, so these peaks cannot be related.

The spectra of Fig. 2 were fitted with four Lorentzians, with all parameters free. We then subtracted the $D$ and $G$ peaks to give the residual intensity, shown in Fig. 4(a). This clearly shows the dispersion of these peaks. We assign the 1150- and 1450 cm$^{-1}$ peaks to $v_1$ and $v_3$. (b) Comparison of the $v_1$ and $v_3$ modes to the theoretical dispersion relation for transpolyacetylene (Refs. 22 and 23).

$F, F$ is smaller for longer conjugation lengths. Figure 4(b) plots the calculated $v_1$ and $v_3$ against $F$ for trans-PA itself. The observed positions of the $v_1$ and $v_3$ peaks in our low-quality diamond are seen to lie close to these reference lines. The observed $v_1$ and $v_3$ follow the same trend as the reference curves, which confirms our assignment of these two peaks. The $F$ vs $v$ plot also allows one to derive the effective conjugation length of the trans-PA chains. We find a length of 6–15 C–C units, as the excitation changes from 325 to 633 nm.

In a previous SERS study of trans-PA in CVD diamond, the sample showed only the 1332 cm$^{-1}$ diamond peak in normal Raman. SERS also enhanced a small peak at ~1240 cm$^{-1}$, which was attributed to nanocrystalline diamond, due to its negligible dispersion. Although its position agrees with the maximum in the diamond VDOS, we disagree with this assignment. Indeed, this peak is further evidence of trans-PA as trans-PA normally has a third peak $v_2$ at this frequency, with smaller intensity than $v_1$ and $v_3$, and a very small dispersion with excitation energy.

We did not observe $v_2$ in our spectra, due to its small intensity and the dominance of the $D$ peak at that frequency.

The $v_1$ and $v_3$ modes of trans-PA are clearly connected to the presence of hydrogen. Indeed, a post-deposition anneal of low-quality CVD diamond causes the $v_1$ and $v_3$ modes to disappear, which is consistent with the loss of hydrogen. The need for hydrogen also accounts for why the $v_1$ and $v_3$ modes are not seen in nanocrystalline diamonds prepared by shock synthesis. The Raman spectra of such diamonds shows a broadening and lowering of the 1332 cm$^{-1}$ mode, expected from phonon confinement, but not of the 1150 cm$^{-1}$ mode.

Finally, we note that fitting broad visible Raman spectra of amorphous carbons with a set of Gaussians can sometimes give a peak around 1150 cm$^{-1}$. This should not be taken as evidence of $sp^3$ bonding, but that a multi-Gaussian fit may be inappropriate.

In summary, the suggestion that peaks near 1150 and 1450 cm$^{-1}$ in the Raman spectra of low quality CVD diamond are due to nanocrystalline or amorphous diamond is critically examined. It is found not to be possible to link these peaks to $C—C sp^3$ vibrations. The peaks are assigned to transpolyacetylene lying in grain boundaries. The origin of such polyacetylene must be related to the deposition mechanism. The amount of polyacetylene is probably very small, as it has a large Raman cross section.

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