

Origin of the 1150-cm⁻¹ Raman mode in nanocrystalline diamond

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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 H₂, 17.5 sccm CH₄, and 2.5 sccm CO₂ 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.*⁸ 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.^{9–15} 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*≈2π/*d*, where *d* is the grain size. Grains of 5–100 nm would still favor modes quite close to Γ, 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

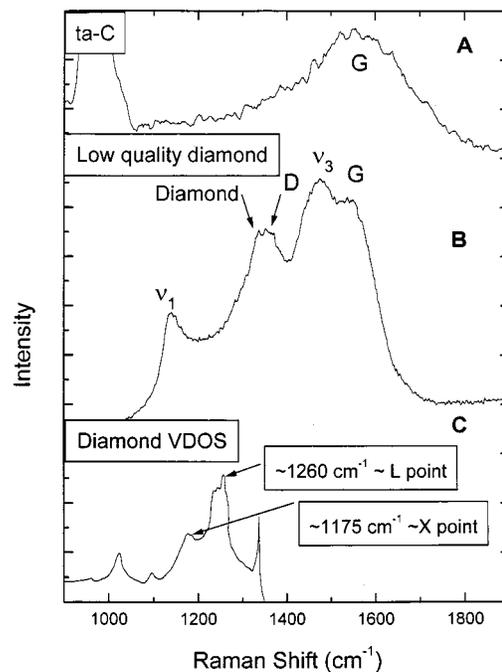


FIG. 1. Raman spectrum of (a) tetrahedral amorphous carbon and (b) a low quality CVD diamond at 514 nm. (c) The VDOS of diamond, from Ref. 16 for comparison; showing a maximum at 1260 cm⁻¹ and a kink at 1175 cm⁻¹. The peak at ~970 cm⁻¹ in (a) is due to Si second order.

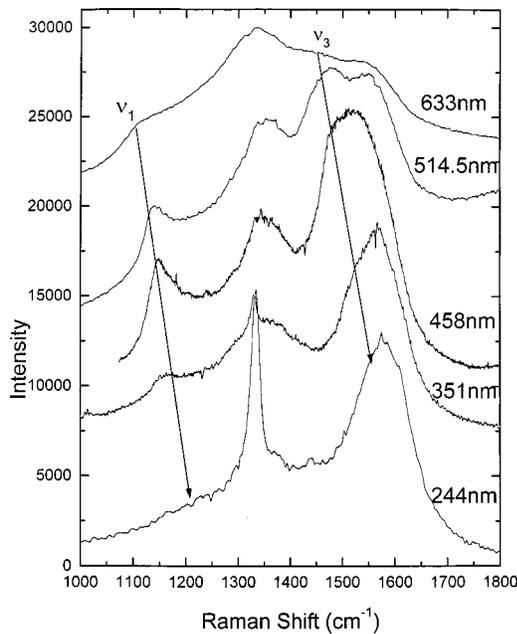


FIG. 2. Raman spectra of nanodiamond excited at different wavelengths. Unpolarized Raman spectra were acquired in back-scattering geometry. A Renishaw micro-Raman system modified for UV excitation was used to record spectra at 244 and 325 nm, from a frequency-doubled Ar-ion laser and a He-Cd laser. Another Renishaw system was used for 514.5 and 633 nm spectra from Ar-ion and He-Ne lasers. A Dilor XY system was used for spectra at 351 and 458 nm from an Ar-ion laser.

than the amorphous carbon phase and crystalline diamond phase [Fig. 1(b)]. 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. A decrease in intensity of the 1150 cm^{-1} mode compared to the 1332 cm^{-1} mode suggests that the 1150 cm^{-1} mode is due to sp^2 sites of some type.

It has been suggested that the 1150 cm^{-1} mode may be

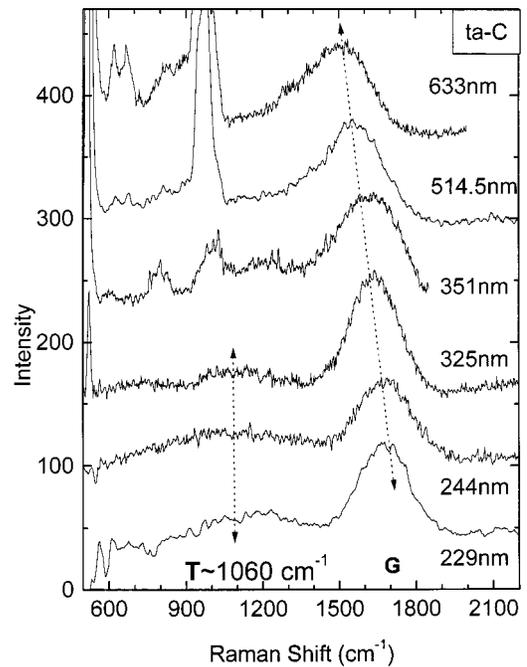


FIG. 3. Raman spectra of *ta*-C as a function of excitation wavelength. The *T* peak at $\sim 1050 \text{ cm}^{-1}$ seen for UV excitation is labeled. The low-frequency peaks for visible excitation are the first and second orders of the Si substrate (Ref. 27); note the combination modes of Si between 600 and 700 cm^{-1} (Ref. 27), which are clearly seen at 633 nm, due to the low absorption of the sample at this wavelength. The peak at $\sim 800 \text{ cm}^{-1}$, seen at 351 nm excitation wavelength, is a spurious peak due to the optics of the 351 nm Raman system.

caused by hexagonal diamond.^{8,10} However, it is now known³ 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 is seen in Fig. 2, but it is sometimes obscured by the tail of the *G* peak of the disordered carbon phase at 1560 cm^{-1} . It has been suggested that the 1450 cm^{-1} mode could be due to SiC in the films.⁸ This can be ruled out, as it is still seen in diamond on non-silicon substrates.¹³ It has also been attributed to some form of sp^3 bonding.^{8,11,14,13} This can be ruled out because sp^3 bonding can only give modes up to about 1350 cm^{-1} , the band limit of diamond.¹⁶

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.²¹ The high excitation energy allows sp^3 sites to be excited with a cross section

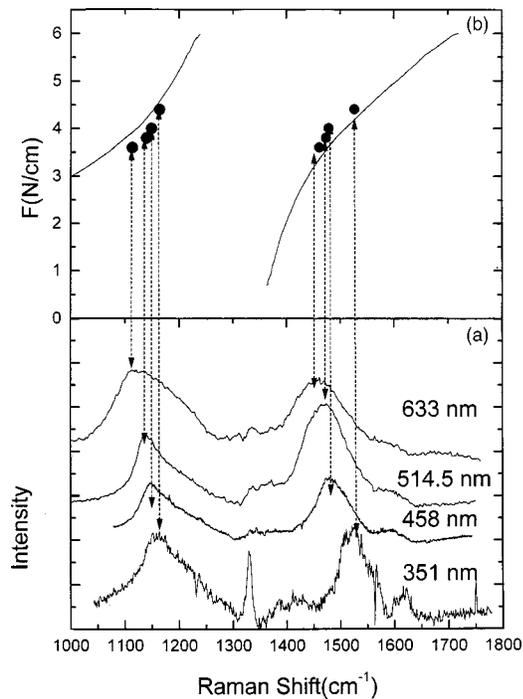


FIG. 4. (a) Raman spectra of Fig. 2 after removal of G and D peaks near 1550 and 1350 cm^{-1} of the $a\text{-C}$ phase. This leaves the zone-center mode at 1332 cm^{-1} (nondispersive) and two new modes at ~ 1150 and 1450 cm^{-1} labeled ν_1 and ν_3 . (b) Comparison of the ν_1 and ν_3 modes to the theoretical dispersion relation for transpolyacetylene (Refs. 22 and 23).

comparable to sp^2 sites. 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 ν_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 the ν_1 and ν_3 modes of transpolyacetylene (trans-PA) (explaining our terminology).^{22,23} These modes are roughly sum and difference combinations of $\text{C}=\text{C}$ chain stretching and CH wagging modes. Trans-PA is an alternate chain of sp^2 carbon atoms, with a single hydrogen bonded to each C . The possibility of trans-PA in CVD diamond has been suggested previously from a surface-enhanced Raman scattering (SERS) study.²⁴

The dispersion of the ν_1 and ν_3 modes arises naturally in this model. The dispersion arises because the conjugated π bonding along the PA chain is broken into segments of different conjugation lengths. The local band gap of each segment increases as the length decreases. Varying the excitation energy selectively tunes into a segment with that length and excites it. The vibrational frequency of the segments also varies with the conjugation length, so the mode wave number increases as the segment length decreases. The conjugation length can be represented by an average force constant

F . F is smaller for longer conjugation lengths. Figure 4(b) plots the calculated ν_1 and ν_3 against F for trans-PA itself.^{22,23} The observed positions of the ν_1 and ν_3 peaks in our low-quality diamond are seen to lie close to these reference lines. The observed ν_1 and ν_3 follow the same trend as the reference curves, which confirms our assignment of these two peaks. The F vs ν plot also allows one to derive the effective conjugation length of the trans-PA chains. We find a length of 6–15 $\text{C}=\text{C}$ 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.²⁴ SERS also enhanced a small peak at $\sim 1240\text{ cm}^{-1}$, which was attributed to nanocrystalline diamond, due to its negligible dispersion.²⁴ 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 ν_2 at this frequency,^{22,23} with smaller intensity than ν_1 and ν_3 , and a very small dispersion with excitation energy.^{22,23} We did not observe ν_2 in our spectra, due to its small intensity and the dominance of the D peak at that frequency.

The ν_1 and ν_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 ν_1 and ν_3 modes to disappear,¹¹ which is consistent with the loss of hydrogen. The need for hydrogen also accounts for why the ν_1 and ν_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.^{11,17}

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} .^{25,26} 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 $\text{C}-\text{C } sp^3$ 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.²⁷

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