Diamond-Like Carbon Bonds

A report by G. T. Visscher *et al.* (*1*) describes the synthesis of transparent and hard carbon solids by an uncommon chemical route. From a downshift of 7 cm^{-1} of the disorder-induced vibrational band, observed by Raman spectroscopy, Bianconi and her co-workers (*1*) conclude that the synthesized material contained diamond-like carbon. I would like to comment on the discussion and the designation of the vibrational band at 1336 cm^{-1}.

The Raman spectra of most graphite-related materials show a disorder-induced vibrational band that has been reported to appear in an energy range of 1343 to 1360 cm^{-1}, which lies close to the expected vibrational mode of crystalline diamond (1332 cm^{-1}). Raman spectra of closed-shell carbon particles and nanotubes have shown curvature-induced downshifts of the phonon spectrum by about 10 cm^{-1} (*2*). It has been calculated that bond-angle bending of a few degrees in a graphitic structure can downshift the optical phonon spectrum by 10 to 25 cm^{-1} (*2*). The Raman-allowed phonon band at 1582 cm^{-1} for graphite shifts to larger energies with increasing disorder. The appearance (*1*) of the downshifted band at 1336 cm^{-1} and a band at 1582 cm^{-1}, therefore, could also be explained by disorder- and strain-induced effects in a graphitic structure.

Diamond-like bonding is considered to be present when the Raman spectrum shows an intense and sharp band at 1332 cm^{-1}. However, broader and weaker spectral features in the same spectral range and a graphite-like band in the energy range of 1570 to 1620 cm^{-1} ought not be designated to a mixed phase that contains diamond-like bonding. Such a spectrum is too close to that of disordered forms of graphite, although diamond-like bonding cannot be excluded as the Raman cross section for diamond is much smaller than for graphite.

Other experimental probes could give indications for diamond-like bonding. Visscher *et al.* mention having used nuclear magnetic resonance (NMR) measurement for the precursor material, but it is not clear why they did not report using NMR on the synthesized material. MicroRaman spectroscopy, which could be used to obtain spectra from the transparent regions, and other methods such as scanning electron (SEM) and transmission electron microscopy (TEM), might provide evidence for the purported diamond-like carbon. Direct evidence of diamond-like hardness is not given in the report and furthermore, x-ray diffraction is difficult to interpret in disordered materials.

I conclude that, although the vibrational band at 1336 cm^{-1} is downshifted by at least 7 cm^{-1} as compared to most graphitic materials and is close to the diamond vibrational band, the observed Raman spectrum is also consistent with highly disordered and strained graphite, and therefore no conclusions as to whether the material contains diamond-like carbon should be drawn from the reported Raman spectrum (*1*). Results of experimental probes such as NMR, Micro-Raman, SEM, and TEM might be more useful and give evidence for the purported diamond-like bonding.

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Response: Our identification of this carbon as diamond-like is based not only on its Raman spectrum, which is characteristic of diamond or highly sp^3 diamond-like carbon, but also on the material's crystallinity, transparency, hardness, morphology, and resistance to oxidation, all of which combined are characteristic only of diamond or diamond-like carbon (*1*).

The Raman spectra of the carbon materials shown in figure 3 of (*1*) were acquired using microfocus techniques, as we stated in note 29 of (*1*). The Raman band we report at 1336 cm^{-1} is not shifted down in frequency by 7 cm^{-1} from the usual position in sp^2 carbons: The lowest frequency at which the *D* band of these materials has ever been reported [at this laser irradiation wavelength (*2*)] is 1343 cm^{-1}, but it usually appears at 1355 to 1362 cm^{-1} (*3*, *4*).

We know of no study that has attributed a Raman band at 1336 cm^{-1} or below (at this laser wavelength) solely to the *D* band of sp^2 carbon structures; bands at frequencies below 1343 to 1362 cm^{-1} have been attributed both to the presence of some four-coordinate carbon and to bond-angle bending disorder (*5*, *6*). Also, in Raman spectra of disordered carbons (both hydrogen-free amorphous carbon and graphite) in which the *D* band is downshifted by bond-angle bending, the G band is also downshifted (*5–10*). Bacsa reports this downshift in closed-shell carbon particles: "The Raman spectrum . . . shows additional changes . . . : the Raman-allowed peak and the disorder-induced scattering at the higher energy edge is downshifted by 10 cm^{-1} from that observed in graphite (1582 cm^{-1}). The induced peak at 1350 cm^{-1} is also downshifted . . ." (*7*, p. 347). The band arising from nondiamond carbon in our Raman spectrum, however, is not downshifted, but is located at 1582 cm^{-1}. This frequency is also within the region identified by Yarbrough and Messier as characteristic of the nondiamond or graphitic carbon found in many diamond and diamond-like carbon films [1500 to 1590 cm^{-1} (*3*)]. The 1336 cm^{-1} band in our Raman spectrum is therefore not likely to arise from downshifting of the *D* band of a strained disordered graphitic structure, because the G band of the material is not similarly downshifted.

The 1336 cm^{-1} Raman band of our transparent carbon is, however, in the reported frequency range (1324 to 1345 cm^{-1}) for diamond or diamond-like carbon (*3*, *11–13*). The upward shift of the Raman bands of diamond materials from the 1332 cm^{-1} band of natural diamond is reported to arise from compressive stress in the lattice (*11–13*); calculations indicate that stress-induced upward shifts of up to 25 cm^{-1} are possible (*12*, *14*). Diamond deposited on hard substrates, in which the mismatch of thermal expansion between the substrate and the diamond particles is great, displays Raman lines between 1336 and 1345 cm^{-1} [figure 10 and table 4 in (*11*); (*12*)]. The substrates we use for pyrolysis of poly(phenylcarbyne) are necessarily hard, high-temperature materials; some degree of stress would therefore be likely in the diamond-like carbon formed from the polymer.

A sharp band at 1332 cm^{-1} is not the only Raman spectral feature that indicates diamond-like bonding. Nanocrystalline diamond powders and some diamond-like carbons show broad Raman spectral features identical to ours (*15–19*), which appear to be characteristic of these materials. The Raman spectra of vapor-deposited diamond powders consist of a broad (80 cm^{-1} at half-height) band at 1332 cm^{-1} and a band at 1582 cm^{-1} [figure 4 in (*15*)]. No band in the region of the *D* band of sp^2 carbon (1362 to 1343 cm^{-1}) is seen. These spectral features are also seen in the Raman spectra of other nanocrystalline diamond powders (*16–18*) and in some diamond-like carbons [figure 2 in (*19*)] and are characteristic of multiple-phase nanosize diamond and diamond-like powders. The band in the ~1330 cm^{-1} region is reported to arise from sp^3 carbon and the band at 1582 to 1608 cm^{-1} to arise from sp^2 carbon (*15*, *18*, *19*); we gave this interpretation to our identical Raman spectrum results (*1*). The unusual width of the ~1330 cm^{-1} region-bands in the Raman spectra of nanocrystalline diamond and diamond-like powders has been interpreted as arising from the materials being powders, not films, with far greater surface areas and surface defects (*15*); from many polytypes of diamond and amorphous carbon being present (*11, 15, 18–20*); from possible overlap of the *D* band of sp^2 carbon with the 1330-region band of the sp^3 carbon present (*21*); and from reduction of the photon lifetime by an increase in the density of defects in the diamond phase (*19, 22*). Our transparent carbon is also a powder, and its XRD patterns indicate that many phases of crystalline carbon are present (*1*). The width of our 1336 cm^{-1} band (70 cm^{-1} at half-height) is identical to those reported for 50- to 150-nm diamond powders (*11, 15, 17, 18*). Also, the Raman spectra of the black carbon formed by our method shows a band at 1140 cm^{-1} (*1*), which is seen only in diamond samples, many of them nanocrystalline, and which has been attributed to small crystallite size or disorder in the tetrahedral carbon (*3*), regions of amorphous or microcrystalline diamond, or precursors to crystalline diamond (*4*).

Although our Raman spectra are consistent only with those reported for nanocrystalline diamond or diamond-like powders, Raman spectroscopy does underestimate the presence of sp^3 carbon phases, both amorphous and crystalline (*3–5, 11, 23*). We found (*1*), however, that other experimental probes also gave evidence for diamond-like bonding. Our transparent carbon displays XRD patterns that show it to be highly crystalline (*1*), which cannot arise from any form of glassy carbon or other amorphous sp^2 carbon, and in which no XRD pattern characteristic of graphite is seen. Also, the *d*-spacings in our XRD patterns correspond to those reported for cubic diamond and polytypes of hexagonal diamond and diamond-like carbon, which suggests possible similarities in structure between our crystalline carbon phases and these known phases. We also reported that, in addition to being optically transparent at thicknesses of ~38 μm (a characteristic only of sp^3 carbon), this carbon easily scratches agate, and is therefore harder than any known graphitic phase (*1*).

Scanning electron microscopy of our carbon shows crystalline morphology (Fig. 1) that is characteristic of that of some vapor-synthesized diamond films [figure 5 in (*24*)], and is not seen in any sp^2 phase. Of the carbon char (both black and transparent), we reported that 67% is resistant to oxidation by concentrated perchloric acid at 200°C after 5 hours (*1*). Wet etching with hot perchloric acid, a standard method of purifying diamond and highly sp^3 diamond-like carbon, removes sp^2 carbon as CO or CO_2 (*15, 17, 25*). We have found similar resistance to dry etching with oxygen plasma in our transparent carbon; the black carbon, but not the transparent, is removed by the plasma. Graphitic and glassy carbon and other forms of all-sp^2 carbon, especially highly strained forms, are quickly and quantitatively oxidized by dry etching treatments (*26*).

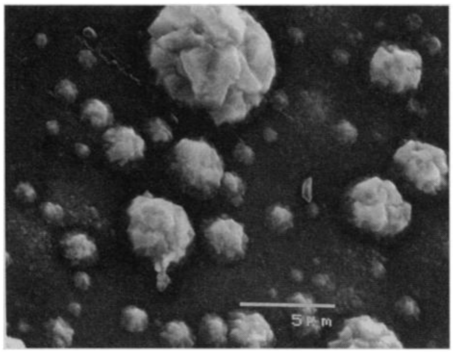

Fig. 1. Scanning electron micrograph of carbon produced by pyrolysis of $[PhC]_n$.

For this carbon material, ^{13}C NMR and TEM are not viable experimental probes. TEM can be performed only on samples thin enough to allow transmission of the electron beam; we reported (*1*) that our transparent carbon is ~38 μm thick, which exceeds the limit of transmission thickness for a TEM beam, and we then had no method to control the thickness of the carbon our system produced. We reported ^{13}C CPMAS NMR on our polymer precursor (*1*) because, as it contains hydrogen, the combination of cross-polarization and slight ^{13}C enrichment provided enough enhancement to obtain a signal. We also reported (*1*) that our solid carbon product contains no detectable H, so cross-polarization cannot be used to enhance the signal in ^{13}C NMR of this material (*27*). ^{13}C NMR of diamond or solid carbon is reported only at higher levels of ^{13}C enrichment (*27*) because enhancement of the signal by some method is required. Because ^{13}C-labeled trichlorotoluene is available only in limited quantities by custom synthesis, our solid carbon products cannot be ^{13}C-enriched to the necessary level.

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