

uv Studies of Tetrahedral Bonding in Diamondlike Amorphous Carbon

V. I. Merkulov* and J. S. Lannin

Department of Physics, Penn State University, University Park, Pennsylvania 16802

C. H. Munro and S. A. Asher

Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260

V. S. Veerasamy and W. I. Milne

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

(Received 28 February 1997)

We report ultraviolet (uv) Raman scattering studies of hydrogen-free, diamondlike amorphous carbon thin films with a wide range of tetrahedral bonding. The uv Raman spectra are shown to provide direct evidence for the presence of sp^3 -bonded C atoms in these materials. The experimental results are found to be in excellent agreement with theoretical predictions and contribute to an improved understanding of the mechanism by which the diamondlike fraction develops within the amorphous carbon network. [S0031-9007(97)03420-0]

PACS numbers: 78.30.Ly, 61.43.Dq, 78.40.Pg

For over a decade, diamondlike amorphous carbon (DLC) has stimulated great interest from both scientific and industrial perspectives. Hydrogen-free DLC has interesting and useful properties [1], such as high hardness, chemical inertness, thermal stability, wide optical gap of ~ 2 eV, and negative electron affinity. Therefore, this material is important for coating technology and electronic device applications. Typically, it is produced by vacuum arc [2,3] or pulsed laser deposition [4] methods. In contrast to conventional amorphous carbon (*a*-C) prepared by evaporation or sputtering which consists mostly of threefold or sp^2 -bonded atoms, DLC contains significant fractions (up to 80 at. %) of fourfold or sp^3 -bonded C atoms.

In spite of extensive experimental work on DLC, evidence for the presence of sp^3 C atoms is somewhat indirect and measurements of the sp^3 C content tend to be empirical in nature. Although neutron [5] and electron diffractions studies [3] of DLC have been performed, information about the sp^3 C bonding cannot be readily extracted from the measurements. Estimates of the sp^3 C fraction in DLC are usually made by transmission electron energy loss spectroscopy (EELS) which relies on the loss of transitions from the $1s$ level to the empty π^* states [2,6] associated with the presence of sp^2 C atoms. While vibrational spectroscopies in principle can probe changes in bonding more directly, most of the available experimental techniques have not been successful in studies of DLC. Nuclear magnetic resonance (NMR) can detect sp^3 C atoms [7,8] but requires thick samples which are rather difficult to make in the case of DLC due to the high stress and consequent delamination. Inelastic neutron scattering also requires very thick samples. Typically, Raman scattering is a convenient tool for vibrational characterization of amorphous solids, in which case it represents the phonon density of states (PDOS), weighted by a coupling param-

eter [9,10]. However, Raman spectroscopy of DLC, obtained with photons in the visible range, does not appear to provide a good representation of the PDOS. First, the high frequency stretch modes of sp^2 C atoms are overemphasized due to the π - π^* transition resonance effect [11]. Second, and more importantly, the sp^2 C network exhibits resonance enhancement in the Raman cross section since the local sp^2 C energy gap of ~ 2 eV is comparable with the energy of incident photons. The sp^3 C atoms do not exhibit such a resonance effect because of the higher local gap of ~ 5.5 eV. As a result, the Raman spectra obtained with visible excitation are completely dominated by the sp^2 C atoms [1,12,13]. High resolution electron energy loss spectroscopy is not affected by resonance effects and has proven to be a useful tool for the characterization of DLC films [14]. However, it has a very low probe depth and therefore measures merely a few surface layers, whereas bulk characterization is preferable.

In contrast to other techniques, Raman scattering in the ultraviolet (uv) region appears to be more promising for vibrational studies of DLC. Advantages of using uv over visible photons include the suppression of previously dominant resonance Raman scattering from sp^2 C atoms and the possible increase in the signal from sp^3 C atoms, for which the resonance is expected to be attained. In addition, the overall Raman intensity is proportional to ω^4 , where ω is the frequency of incident photons; this makes utilization of uv excitation even more advantageous considering the weak Raman signal from thin DLC films.

DLC films containing 20, 30, and 75 at. % of sp^3 -bonded C atoms were prepared by the vacuum arc method and characterized using transmission EELS. Details of preparation and characterization can be found elsewhere [15]. Amorphous carbon consisting mostly of sp^2 C atoms was prepared by dc magnetron sputtering in an

ultrahigh vacuum chamber with base pressure of 2×10^{-10} Torr. For a similar sample NMR measurements yielded ~ 6 at. % sp^3 bonding [8].

For uv Raman scattering measurements, the 244 nm excitation wavelength of a Coherent Innova 300 intracavity frequency-doubled argon ion laser system was employed. Raman scattering was collected in a backscattering geometry via a microscope assembly [16] and imaged into a Spex 1701 single monochromator equipped with a 2400 groove/mm holographic grating, and an EG&G PARC 1456 blue intensified photodiode array and optical multichannel analyzer. Novel dielectric filters were used for rejection of stray light and Rayleigh scattering prior to the spectrograph [17]. Amorphous carbon samples were rotated using a microspinning assembly attached to the uv Raman microspectrometer sample stage. Consecutive replicate measurements were performed to ensure no photoalteration of the samples was induced during 244 nm excitation.

uv Raman spectra of DLC films with various sp^3 content and of sputtered amorphous carbon are shown in Fig. 1. The stray light background was subtracted using that of a Teflon calibration sample. The spectra consist of three main bands located at 400–900, 900–1400, and 1400–1800 cm^{-1} . The high frequency peak around 1600 cm^{-1} is associated with stretch modes of sp^2 -bonded C atoms. As the fraction of sp^3 C atoms increases, a significant shift of this peak from ~ 1580 to ~ 1620 cm^{-1} occurs, which may be explained by the stiffening of trigonal bonds by their tetrahedral neighbors. The width of the peak also increases due to the site-to-site variation in the number of next nearest neighbors, i.e.,

when sp^2 C atoms have sp^3 C neighbors, four different local configurations for the sp^2 C are possible. The low frequency peak at ~ 650 cm^{-1} corresponds mostly to the bending motion of sp^2 C atoms with some possible contribution from sp^3 C sites. The intensity of this peak relative to the high frequency band increases from the sputtered a -C to the arc-deposited DLC films which is associated with the presence of sp^3 C atoms within the network. Finally, the intermediate frequency peak at ~ 1180 cm^{-1} is attributed to sp^3 C atoms [18]. Present as a shoulder for the sample with 20 at. % sp^3 C bonding, it develops into a separate, well defined band for DLC films with higher sp^3 content.

As was mentioned above, the high frequency peak at ~ 1600 cm^{-1} is a consequence of the π - π^* transition resonance effect, and is highly overemphasized over the PDOS. Therefore, in order to better see changes in the intermediate frequency region for different samples and to compare the experimental results with theoretical PDOS, it seems reasonable to remove the high frequency peak by subtracting a best-fit analytical function, for example, a Lorentzian. The subtracted spectra are shown in Fig. 2. The spectra have two features: the previously discussed broad peak centered at 650 cm^{-1} and a band between 900 and 1550 cm^{-1} , resulting from subtraction of the sp^2 C atom stretch mode. The latter band evolves continuously with changes in sp^3 C content. Located at ~ 1400 cm^{-1} for the sputtered a -C with 6 at. % sp^3 C, atoms, it shifts downward in frequency to ~ 1300 cm^{-1} for the arc-deposited film with 20 at. % sp^3 C, and ~ 1150 cm^{-1}

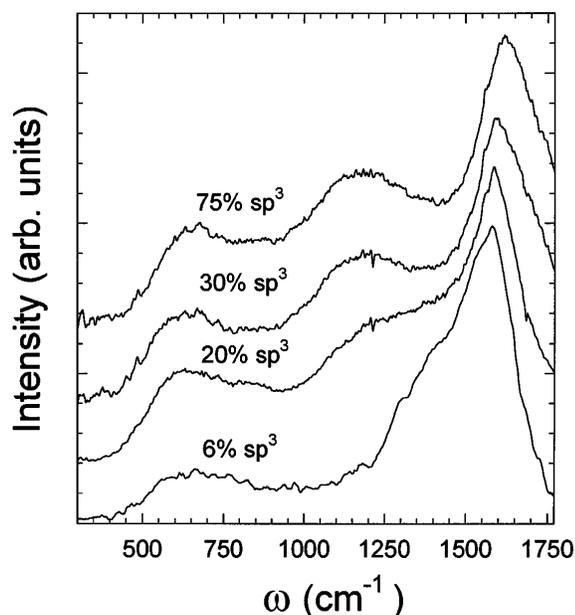


FIG. 1. uv Raman spectra of sputtered a -C containing ~ 6 at. % sp^3 C atoms and DLC with 20, 30, and 75 at. % sp^3 C atoms.

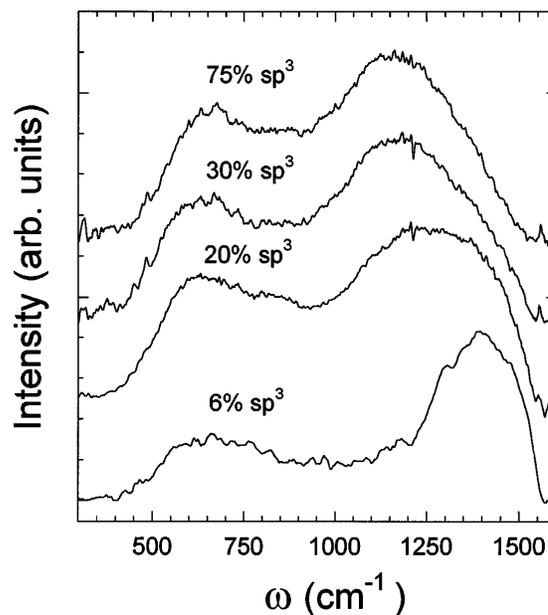


FIG. 2. Deconvoluted lower frequency uv Raman spectra of sputtered a -C (~ 6 at. % sp^3 C atoms) and DLC with 20, 30, and 75 at. % sp^3 C atoms. The spectra were obtained from those of Fig. 1 by subtraction of the high frequency peak using a fitted Lorentzian.

for the films with 30 and 75 at. % sp^3 C. The spectrum for the film with 20 at. % sp^3 C exhibits a broader peak (with additional scattering at lower frequency) compared to that of the film with 6 at. % sp^3 C. The spectra for the films with 30 and 75 at. % sp^3 C look similar, with the peak of the former having a slight shoulder at the higher frequency side. These observations can be explained as a result of two contributions to the spectra: an sp^2 C network with the scattering at ~ 1400 cm^{-1} and sp^3 C atoms yielding a peak at ~ 1150 cm^{-1} .

It is interesting to compare Raman spectra, which represent the experimental PDOS, to the results of theoretical calculations. Figure 3 shows such a comparison of the subtracted Raman spectra of the films with 6 and 75 at. % sp^3 C with the theoretical PDOS for a network with 74 at. % sp^3 -bonded C atoms [18]. One can see a strong resemblance of the theoretical total PDOS and the Raman spectrum of the film with 75 at. % sp^3 C. At the same time, the Raman spectrum for the film with 6 at. % sp^3 C exhibits no such resemblance. In fact, the latter spectrum shows greater similarity to the sp^2 C PDOS obtained with the same calculations, with the high frequency modes being enhanced in the Raman scattering response. The fact that the experimentally obtained phonon spectrum of the 75 at. % sp^3 C sample looks very similar to the predicted by theory shows that uv Raman scattering can directly probe the sp^3 -bonded C atoms, which is not the case for Raman scattering in the visible range [13].

Given the fact that the uv Raman spectra of DLC represent a superposition of scattering from sp^2 and sp^3 C

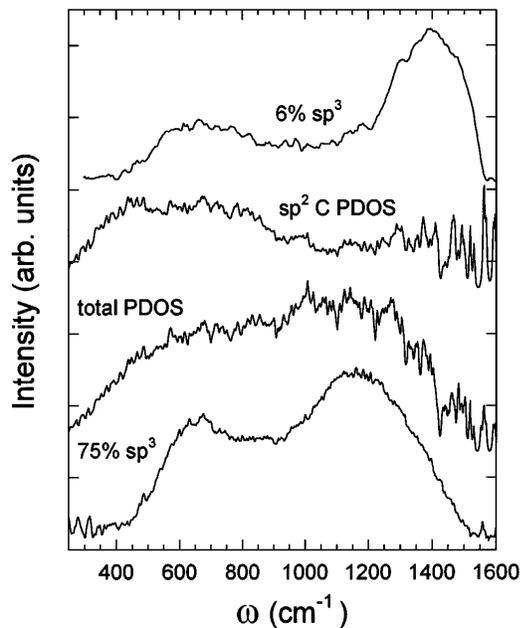


FIG. 3. The deconvoluted lower frequency uv Raman spectra of DLC with 75 at. % sp^3 C atoms and of sputtered a -C with 6 at. % sp^3 C atoms shown for comparison with the theoretical total and sp^2 C PDOS for an a -C network containing 74 at. % sp^3 -bonded C atoms.

networks, it is useful to decompose these spectra into two contributions. Such decompositions for DLC films with 20, 30, and 75 at. % sp^3 C content are shown in Fig. 4. The Raman spectrum of sputtered a -C shown as the dotted lines in Fig. 4, was used to estimate the contribution from sp^2 -bonded C atoms. Of course, it should be realized that this procedure is limited in that it eliminates only those sp^2 C atoms whose nearest neighbors consist mostly of sp^2 C atoms. The resulting sp^3 C contributions in Fig. 4 have a striking resemblance to the theoretically calculated PDOS of the sp^3 C network [18] within a -C having 74 at. % sp^3 C atoms. This supports the validity of the spectral decomposition and once again shows the agreement between the experimental sp^3 PDOS and theoretical predictions. It is interesting to try to estimate the sp^3 fraction from Raman spectra and compare it to that obtained by EELS. In order to do that, it seems reasonable to calculate the intensity of the peak at ~ 1150 cm^{-1} , built up mostly by sp^3 C sites, relative to that of a peak at ~ 1600 cm^{-1} , which is attributed to the sp^2 C, and compare it to that of a sample with a known sp^3 C percentage. This procedure yields relative intensities of ~ 0.28 and ~ 0.38 for the films with 20 and 30 at. % sp^3 C bonding, respectively. The ratio of the relative intensities is $R \approx 0.38/0.28 = 1.36$.

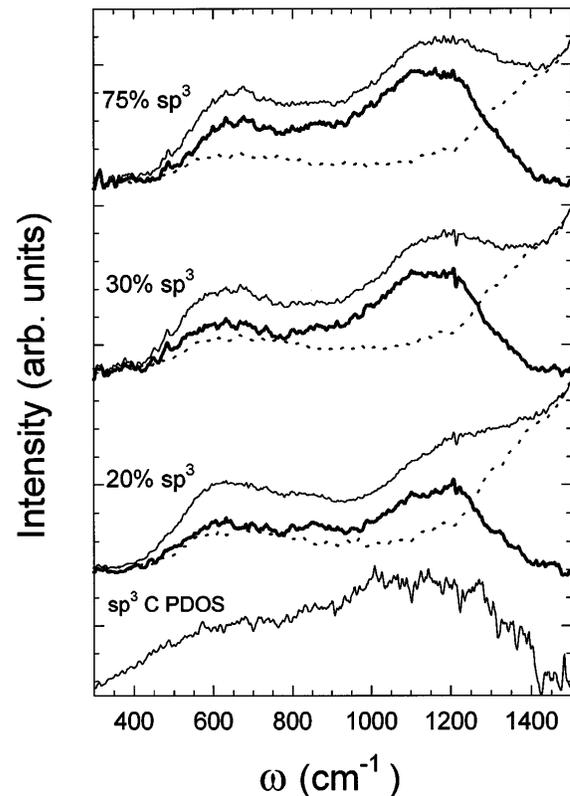


FIG. 4. Decomposition of uv Raman spectra of DLC (thin solid) with 20, 30, and 75 at. % sp^3 C atoms into sp^2 (dotted) and sp^3 C (thick solid) contributions, and comparison of the latter with the theoretical sp^3 C PDOS calculated for a network having 74 at. % sp^3 C atoms.

Using sp^2 and sp^3 percentages obtained by EELS, the ratio is calculated to be $r \approx 0.43/0.25 = 1.71$, which is $\sim 20\%$ higher than the value obtained from the Raman spectra analysis. The discrepancy between the Raman and EELS ratios becomes substantially larger for the film with 75 at.% sp^3 C, where calculations yield $R \approx 0.42/0.28 \approx 1.5$ and $r = 12$, respectively. This discrepancy may be explained by the following. The intensity at 1150 cm^{-1} arises mostly from sp^3 C atoms whose nearest neighbors contain either zero or one sp^2 C atom [19]. This suggests a model in which the sp^3 C atoms grow mostly in clusters as their concentration does not exceed $\sim 25\text{--}30\%$. However, when the sp^3 content increases from ~ 25 to 75 at.%, most of the additional sp^3 C atoms do not gather into clusters but rather are dispersed within the sp^2 C. The significant shift and broadening of the high frequency peak support this model as well. Furthermore, it is also possible that EELS substantially overestimates the amount of sp^3 C atoms when they are randomly distributed among sp^2 C atoms. Consequently, this leads to a high discrepancy between the sp^3/sp^2 ratios obtained by Raman spectroscopy and EELS.

To summarize, uv Raman scattering appears to be a successful technique for the characterization of bonding in DLC. uv Raman scattering measurements clearly reveal the presence of the sp^3 -bonded C network within the DLC structure. Obtained from Raman spectra, experimental PDOS of DLC are in excellent agreement with theoretical calculations. We believe that utilizing uv photons with an even shorter wavelength may provide additional information about the structure and dynamics of DLC.

We thank R.W. Collins for useful discussions. We also thank C.Z. Wang and K.M. Ho for providing us with their unpublished results. This work was supported by DOE Grant No. DE-FG02-84ER45095, NSF Grant No. DMR-9623315, and AFOSR Grant No. F49620-95-1-0167.

*Corresponding author.

- [1] J. Robertson, *Prog. Solid State Chem.* **21**, 199 (1991).
- [2] S.D. Berger, D.R. McKenzie, and P.J. Martin, *Philos. Mag. Lett.* **57**, 285 (1988).
- [3] D. Muller, D.R. McKenzie, and B.H. Pailthorpe, *Phys. Rev. Lett.* **67**, 773 (1991).
- [4] J.J. Cuomo, D.L. Pappas, J. Bruley, J.P. Doyle, and K.L. Saenger, *J. App. Phys.* **70**, 1706 (1991).
- [5] K.W.R. Gilkes, P.H. Gaskell, and J. Robertson, *Phys. Rev. B* **51**, 12303 (1995).
- [6] P.J. Fallon and L.M. Brown, *Diam. Relat. Mater.* **2**, 1004 (1993).
- [7] K.C. Bastillo, M.A. Petrich, and J.A. Reimer, *Chem. Materials* **2**, 202 (1990).
- [8] H. Pan, M. Pruski, B.C. Gerstain, F. Li, and J.S. Lannin, *Phys. Rev. B* **44**, 6741 (1991).
- [9] R. Shuker and R. Gammon, *Phys. Rev. Lett.* **25**, 222 (1970).
- [10] J.S. Lannin, in *Semiconductors and Semimetals*, edited by J.I. Pankove (Academic Press, New York, 1984), Vol. 21, p. 159.
- [11] J. Wagner, M. Ramsteiner, Ch. Wild, and P. Koidl, *Phys. Rev. B* **40**, 1817 (1989).
- [12] R.J. Nemanich, J.T. Glass, G. Lucovsky, and R.E. Shroder, *J. Vac. Sci. Technol. A* **6**, 1783 (1988).
- [13] V.I. Merkulov and J.S. Lannin, in *Proceedings of the 22nd International Conference on Physics of Semiconductors*, edited by D.J. Lockwood (World Scientific, Singapore, 1995), p. 2681.
- [14] G.P. Lopinski, V.I. Merkulov, and J.S. Lannin, *Appl. Phys. Lett.* **69**, 3348 (1996).
- [15] P.J. Fallon, V.S. Veerasamy, C.A. Davis, J. Robertson, G.A.J. Amaratunga, W.I. Milne, and J. Koskinen, *Phys. Rev. B* **48**, 4777 (1993).
- [16] V. Pajcini, C.H. Munro, R.W. Bormett, R.E. Witkowski, and S.A. Asher, *Appl. Spectrosc.* **51**, 81 (1997).
- [17] C.H. Munro, V. Pajcini, and S.A. Asher (to be published).
- [18] C.Z. Wang and K.M. Ho, *Phys. Rev. Lett.* **71**, 1184 (1993).
- [19] C.Z. Wang and K.M. Ho (private communications).