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Raman scattering of laser-deposited amorphous carbon

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Raman scattering of thin laser-deposited amorphous-carbon films reveals significant changes in lower and intermediate spectral regions with respect to rf-sputtered, predominantly threefold *a*-C. The form of the spectrum differs, however, from the expected spectrum for fourfold, diamondlike *a*-C. It is suggested that mixed bonds between threefold and fourfold sites in diamondlike materials modify the lower-frequency bond-bending modes and Raman scattering.

Considerable interest exists in both the ordered and disordered structures, bonding and physical properties of different forms of carbon. This includes films that have been termed "diamondlike." Generally, amorphous carbon (*a*-C), formed by conventional thin-film methods such as rf sputtering, is known to form a locally disordered, primarily threefold structure with sp^2 bonding and π and π^* bands.[1,2] In contrast, recent studies of laser-assisted and arc-deposited *a*-C films made from higher-energy species have suggested appreciable fourfold sp^3 bonding analogous to crystalline diamond.[3-7] However, these studies have not provided direct evidence for new bonding configurations expected if appreciable diamondlike bonding occurs. While it is implicitly assumed that new bonding will be locally like that of diamond, the presence of both threefold and fourfold structures implies, in the absence of appreciable site clustering, the formation of new bonding configurations that have a different character. Such 3-4 bonds, with neither sp^2- nor sp^3-like character, while not discussed to our knowledge in any detail, may considerably modify the structure and physical properties of *a*-C films.

Dynamical probes such as Raman scattering provide a valuable means of studying changes in local bonding in amorphous solids. However, one difficulty in *a*-C films is the strong high-frequency scattering associated with resonant enhancement of stretching modes of 3-3 bonds that modulate the π states of the system.[8] In the present study, low-frequency Raman-scattering measurements of laser-deposited *a*-C films are employed to study bonding changes. The results provide strong evidence for low-frequency bending vibrations whose spectrum differs from both that of conventional threefold *a*-C films or that expected from an amorphous fourfold diamondlike material. This implies that new bonding configurations not present in either material may play an important role both for the vibrational and electronic states of such systems.

Thin films of laser-deposited (LD) *a*-C of ~900 Å thickness were deposited at 77 K on crystalline Ge substrates under similar conditions employed for Si, sapphire, and diamond substrates. Transmission electron energy loss (TEELS) measurements for *a*-C/Si and *a*-C/sapphire have indicated ~60% fourfold bonding, while a value of ~75% has been estimated for *a*-C/diamond. The experimental details for the LD *a*-C and the rf-sputtered *a*-C are given elsewhere.[2,3] The sputtered sample contains 3 at. % H, where <1 at. % H is estimated for LD *a*-C. Raman measurements without polarization analysis were taken at low-power densities at room temperature, in vacuum, utilizing 514.5-nm photon excitation with a Spex Triplemate spectrometer (6-cm^{-1} resolution) equipped with an ITT Mepsicron multichannel detector. Backscattering geometry was used with an angle of incidence of 40° and polarization of the incident beam set parallel to the plane of incident.

Figure 1 shows the Raman spectrum of a LD *a*-C film. The sharp Ge substrate first-order and broader second-order Raman signals have been measured separately under the same conditions and subtracted. The spectrum of the total signal in the region of the Ge spectrum, which extends to 600 cm^{-1}, is also shown above for comparison. Apart from the main feature at 1550 cm^{-1}, moderate in-

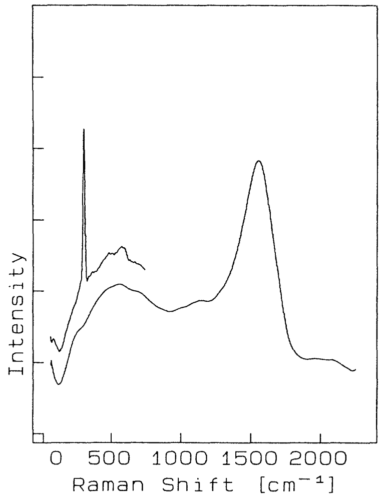

FIG. 1. The Raman spectrum of LD *a*-C after Ge background subtraction. The total signal at lower frequencies prior to subtraction is shown above.

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tensity, broad scattering is observed between 400 and 800 cm^{-1}. A weaker broad feature is also observed at ~ 1150 cm^{-1}. Figure 2 compares the Raman spectra of the laser-deposited and sputtered *a*-C.[9] The latter sample has $\sim 93\%$ of the carbon atoms threefold bonded.[2] The main peak at higher energies is narrower, shifted upward, and is more symmetric for the laser-deposited material. In contrast to rf-sputtered *a*-C, the LD *a*-C Raman spectrum also indicates a substantial intensity at both low and intermediate energies, below ~ 1100 cm^{-1}. Two broad, weaker structures at ~ 450 and 730 cm^{-1}, characteristic of the sputtered material, show no corresponding features in the laser-deposited sample. At higher energies, ~ 2000 cm^{-1}, a broad weak scattering in LD *a*-C is attributed to second-order combination scattering of the two main structures at 550 and 1550 cm^{-1}.

The more intense high-frequency peak in LD and sputtered *a*-C is associated with stretching-type modes of sp^2 bonds. The strength of the scattering from these modes is a function of the number of such bonds and substantial resonant Raman enhancement of π-π^*-type transitions.[8] As the Raman spectrum of LD *a*-C substantially differs at low and intermediate frequencies from that of sputtered *a*-C, it is useful to compare the scattering in this region to that expected for a pure fourfold, amorphous diamondlike spectrum based on *a*-Si and *a*-Ge studies. Shown in Fig. 2 is a Gaussian broadened density of states recently obtained from inelastic neutron measurements on polycrystalline diamond powder.[10] As found in *a*-Ge and *a*-Si, the broadened density of states of the crystalline form is expected to yield a first-order approximation to that found for the amorphous state.[11,12]

The comparison of the LD *a*-C Raman spectrum and the broadened diamond density of states indicates qualitatively quite different characteristics in all spectral regions. For the high-frequency region, this is attributed to the strong scattering of 3-3 stretching modes that are resonantly enhanced. At lower frequencies, the LD *a*-C spectrum peaks at ~ 550 cm^{-1}, while the diamond spectrum peaks at 750 cm^{-1}. This peak difference is quite large relative to that observed in comparisons of the *a*-Ge and *a*-Si Raman spectra and the broadened crystalline density of states at low frequencies. This suggests that these differences between the Raman spectrum of LD *a*-C and the broadened diamond density of states are structural in origin. This can be seen in more detail utilizing the form of the Raman-scattering intensity, $I(\omega)$, for an amorphous solid: $I(\omega) \sim [(n+1)\tilde{C}(\omega)/\omega]\rho(\omega)$. For a pure fourfold *a*-C, $I(\omega)$ will differ from the phonon density of states $\rho(\omega)$ due to competing weightings from the Stokes phonon population factor, $(n+1)/\omega$, and frequency-dependent coupling parameter $\tilde{C}(\omega)$. In the related *a*-Si and *a*-Ge, measurements of both the phonon density of states and Raman scattering have established the form of $\tilde{C}(\omega)$ in the low-frequency acousticlike regime.[11,12] Utilizing the empirical forms of $\tilde{C}(\omega)$ from *a*-Ge and *a*-Si that are approximately linear, and changes in $n+1 \simeq 1$ for the lower-frequency vibrations of interest, it may be seen that the peaks of the Raman intensity are expected to occur near to that of $\rho(\omega)$. This strongly suggests, for a reasonable range of choices of monatomic forms for $\tilde{C}(\omega)$, that differences between the Raman spectrum of LD *a*-C and the broadened diamond density of states have a more basic origin that is likely to be structural in character.

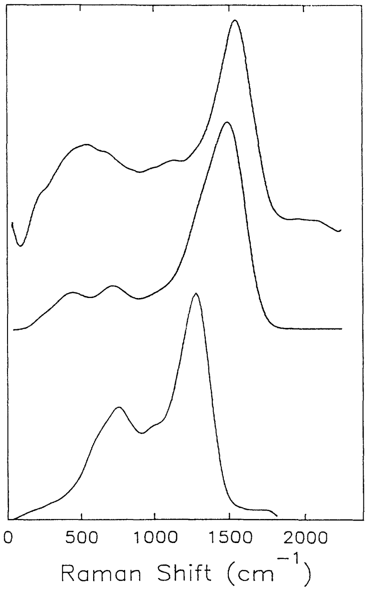

FIG. 2. A comparison of the Raman spectra of LD *a*-C (top), rf-sputtered *a*-C (center), and a Gaussian broadened density of states of crystalline diamond (bottom).

Figure 2 indicates that a linear combination of the diamond and rf-sputtered Raman spectrum for essentially threefold *a*-C will *not* yield the spectrum of LD *a*-C, as their superposition yields a peak above 750 cm^{-1}. One reasonable origin for the low-frequency scattering differences between LD and sputtered *a*-C or the diamond density of states is the presence of a substantial number of mixed 3-4 bonds. The resulting local structure of such bonds relative to pure threefold or fourfold networks will modify the vibrational modes of the system. As such, a superposition of phonon spectra of idealized threefold and fourfold systems will not yield the density of states. Lower-frequency bond-bending modes, for example, which involve pairs of 3-4 bonds with 4-4, 3-3, or other 3-4 bonds are expected to yield appreciable $\rho(\omega)$ changes. While new mixed-bond 3-4 stretching modes are also expected to contribute to that Raman spectra, resonant enhancement of 3-3 stretching modes that modulate the polarizability derivative of sp^2 orbitals may continue to dominate the high-frequency spectral range, as seen in Fig. 2.

The contribution of 3-4 bonds to the Raman scattering will be a function of the probability for different bond pairs, as well as their relative Raman cross sections. For the three distinct bond types 3-3, 4-4, and 3-4, there exists six possible bond pairs involved in $(a$-b-$c)$ bond-bending motions about b atoms. Assuming random-site occupancy, without appreciable clustering, the probability for pair formation can be readily calculated about different sites as a function of threefold and fourfold site fractions, y and $1-y$, respectively. Of these six types, four involve bonding pair configurations not present in pure threefold or fourfold systems. The assumption of limited clustering allows both a calculation of mode population changes and is consistent with the low-frequency Raman spectrum not being a superposition of threefold and fourfold contributions. Figure 3 shows the number of bending modes/atom, $N_{i-j-k}(y)$, for these types as a function of y. In addition, the total number of bending modes per atom which linearly increase from three to six between $y=1$ and 0 is shown. For the present sample, TEELS studies suggest $0.25 \leq y \leq 0.4$. If a value of $y \simeq 0.4$, which is similar to that for a Si substrate, is employed, Fig. 3 indicates 37% 3-4-4, 27% 4-4-4, and 21% for 3-4-3 plus 4-3-4 bending modes. Thus for this value of y, almost 60% of the bending modes which occur are not present in $y=0$ or 1 materials.

The range of y values here is based on an analysis of TEELS measurements on similarly deposited LD a-C on Si substrates.[5] This analysis employed a number of assumptions about limited band overlap of π^* and σ^* bands, and neglects completely the presence of new 3-4 bonds not present in either graphite or diamond. Specifically, a threefold atom bound to one or more fourfold atoms may yield a reduced contribution to the π^* band, and is likely to result in an overestimate of the actual value of the fraction of fourfold sites. However some increase in the value of y in Fig. 3 is not expected to modify the basic importance of new bond-bending modes in LD a-C that do not occur in pure fourfold or threefold systems. As such, the phrase "diamondlike films" should be used with some caution when describing these materials unless interpreted generally as systems with fourfold atoms.

While it is not yet possible to distinguish the relative importance of the different bending modes of Fig. 3 to the LD a-C Raman spectrum, a shift to lower frequencies relative to that of the broadened diamondlike spectrum is qualitatively reasonable.[13] This may be viewed as due to lower bending-mode frequencies that arise due to fewer geometrical constraints on the motion of threefold atoms. Recent theoretical calculations[14] of $\rho(\omega)$ of a model of a-C with 75% fourfold and 25% threefold bonds yield a low-frequency spectrum with qualitative similarities to the Raman spectrum shown in Fig. 2.

In addition to the changes at lower frequencies, below ~ 850 cm^{-1}, the form of the Raman spectrum of LD a-C from ~ 850 to 1300 cm^{-1} is substantially different from that of rf-sputtered a-C or the broadened diamond density of states. Scattering in the upper portion of this region may be due in part to modes with stretching character of both 3-4 and 4-4 bonds. Differences in the form of the strong high-frequency scattering between the rf and LD a-C, associated with resonantly enhanced 3-3 stretching modes, preclude, however, a precise subtraction of such contributions from the LD a-C spectrum. If the narrower, shifted high-frequency 3-3 peak in LD a-C is fitted with an approximate Gaussian, and subtracted from Fig. 2, the high-frequency difference spectrum extends to values of $\gtrsim 1400$ cm^{-1}. This is comparable to what is expected for amorphous diamond. While high-frequency diamondlike stretching modes may be present, it is not possible, with the present data, to determine if 4-4 stretching contributions are present in the LD a-C spectrum. Such scattering might be expected to be weak, with no resonant enhancement, given the large bonding-antibonding gap of sp^3 orbitals in the diamond structure. For substantial fourfold bonding fractions, the number of 3-3 stretching modes is significantly reduced. For example, for $y=0.4$ the number of stretching modes per bond is a factor of ~ 5 lower than at $y=1$. The substantial high-frequency intensity observed in Fig. 2 is thus qualitatively consistent with the considerably larger (than diamond) scattering cross section of the highest optic modes of crystalline graphite.[15] In addition to 4-4 bonds, contributions from 3-4 bonds may both increase the optical Tauc gap of rf-sputtered a-C from values of ~ 0.6 to >1.5 eV, and also yield some resonant enhancement of stretching modes for 514.5 nm (2.4-eV) excitation.

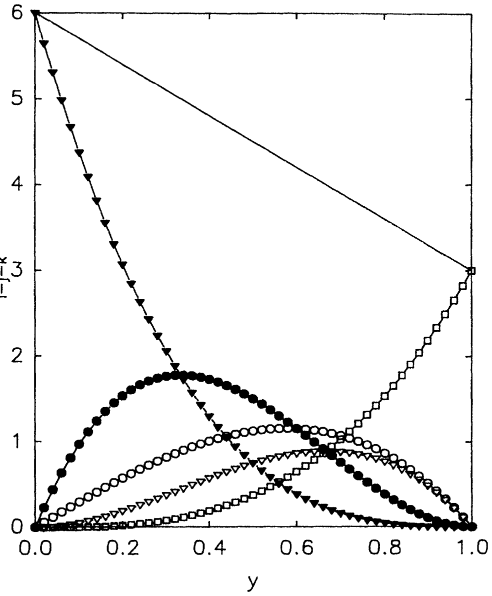

FIG. 3. The variation of the number of bonding modes per atom vs y for $N_{4\text{-}4\text{-}4}(y)$ (filled triangle), $N_{3\text{-}3\text{-}3}(y)$ (square), $N_{3\text{-}4\text{-}4}(y)$ (filled circle), $N_{4\text{-}3\text{-}4}(y)+N_{3\text{-}4\text{-}3}(y)$ (circle), $N_{4\text{-}3\text{-}3}(y)$ (triangle), and their total (solid line), where $N_{i\text{-}j\text{-}k}(y)$ denotes i-fold and k-fold atoms about a central j-fold site, $N_{3\text{-}4\text{-}3}(y)=N_{4\text{-}3\text{-}4}(y)$.

In summary, distinct differences observed in LD a-C relative to sputtered material with predominant threefold bonding have been observed in Raman scattering. The major differences are found in intermediate- and lower-frequency bands, where substantially enhanced scattering and changes in shape suggest bonding-induced changes in the phonon density of states. The results provide direct evidence for structural changes, in contrast to electronic studies which emphasize the loss of π^* band transitions of threefold networks. As the Raman spectrum at low frequency differs substantially from that expected from a pure fourfold-bonded amorphous carbon network, we suggest that mixed bonds between threefold and fourfold atoms are significant. Such bonds, with intermediate hybridization between sp^2 and sp^3, are also expected to contribute to optical absorption and may explain the much smaller effective gap of ~1.5–1.8 eV in these materials relative to the 4.5-eV indirect gap of diamond. Further theoretical studies of the role of such bonding on the vibrational and electronic states would clearly be valuable.

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[1] H. Pan, M. Pruski, B. C. Gerstein, F. Li, and J. S. Lannin, Phys. Rev. B **44**, 6741 (1991).

[2] F. Li and J. S. Lannin, Phys. Rev. Lett. **65**, 1905 (1990).

[3] J. J. Cuomo, D. L. Pappas, J. Bruley, J. P. Doyle, and K. Saenger, J. Appl. Phys. **70**, 1706 (1991).

[4] D. R. McKenzie *et al.*, Thin Solid Films **193**, 418 (1990).

[5] J. J. Cuomo, J. Bruley, J. P. Doyle, D. L. Pappas, K. L. Saenger, J. C. Liu, and P. E. Batson, in *Evolution of Thin Film and Surface Microstructure,* edited by C. V. Thompson, J. Y. Tsao, and D. J. Srolovitz, MRS Symposia Proceedings No. 202 (Materials Research Society, Pittsburgh, 1991), p. 247.

[6] S. D. Berger, D. R. McKenzie, and P. J. Martin, Philos. Mag. **57**, 285 (1988).

[7] P. H. Gaskell, A. Saeed, P. Chieux, and D. R. McKenzie, Phys. Rev. Lett. **67**, 1286 (1991).

[8] J. Wagner, M. Ramsteiner, Ch. Wild, and P. Koidl, Phys. Rev. B **40**, 1817 (1989).

[9] F. Li and J. S. Lannin, Appl. Phys. Lett. **61**, 2116 (1992).

[10] R. Cappelletti, W. Kamitakahara, F. Li, and J. S. Lannin (unpublished).

[11] N. Maley and J. S. Lannin, Phys. Rev. B **35**, 2456 (1987).

[12] F. Li and J. S. Lannin, Phys. Rev. B **39**, 6220 (1989).

[13] D. Beeman, J. Silverman, R. Lynds, and M. R. Anderson, Phys. Rev. B **30**, 870 (1984).

[14] C. Z. Wang, K. M. Ho, and C. T. Chan (unpublished).

[15] N. Wada and S. A. Solin, Physica **105B**, 353 (1981).