Raman scattering characterization of carbon bonding in diamond and diamondlike thin films

R. J. Nemanich, J. T. Glass, G. Lucovsky, and R. E. Shroder
Departments of Physics and Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-8202

The atomic bonding configurations of carbon bonding in diamond and diamondlike thin films are explored using Raman scattering. The general aspects of Raman scattering from composites are presented. Effects are discussed due to crystalline or amorphous structures, large versus microcrystalline domains, and strong optical absorption and transparent regions. The Raman scattering from diamondlike films shows several features which are attributed to microcrystalline graphitelike structures which all originate from the same region in the sample. In contrast, the spectra of diamond films show features attributed to different components of a composite film. Components identified are crystalline diamond, and disordered and microcrystalline graphitic structures. The presence of precursor microcrystalline or amorphous diamond structures is also suggested.

I. INTRODUCTION

Carbon films produced by plasma enhanced chemical vapor deposition (CVD) or similar processes are hard, chemically inert, and transparent over some wavelength range. The films have been characterized as diamond[1-3] or diamondlike.[4-6] The diamondlike films are very uniform, hard, and transparent at wavelengths $> 2 \mu m$.[4-6] These films have already been applied as antireflective and/or protective coatings for infrared optics.

The plasma enhanced CVD process has also been used to produce films with optical properties very similar to diamond.[1-3] While these films could also be used for optical coatings, their potential as a high-temperature thin-film semiconductor is also being explored. One of the major limitations of these films is that they exhibit roughness due to crystalline grains of the films. To be useful as a semiconductor technology it is necessary to produce smooth films. Heteroepitaxial film growth is one of the goals of the research.

This paper discusses aspects of the characterization of the carbon bonding in diamond and diamondlike thin films.[7] We will emphasize Raman scattering, but related x-ray and electron diffraction measurements will be mentioned. These techniques are often used as structure sensitive probes. Raman scattering displays aspects of the vibrational properties of the material which can then be related to atomic bonding configurations. The films that are produced by the plasma enhanced CVD processes will exhibit varied atomic structures. In fact a particular film will exhibit variations of the structures on several scales and can be considered as a composite. We will focus on the limitations of the techniques to measuring composite films. In addition, the vibrational excitations and the atomic bonding are also dependent on the composite nature of the films and these aspects will be discussed.

The CVD process usually involves methane, hydrogen, and possibly inert gases and oxygen. Films produced by CVD deposition techniques can yield crystalline and amorphous structures. In the case of carbon films an additional question is whether the atomic bonding in the films is threefold coordinated (sp^2) as in graphite or fourfold coordinated (sp^3) as in diamond. Thus the films have the possibility of four different microstructures: amorphous or crystalline diamond, and amorphous or crystalline graphitic structures. In this terminology, we are suggesting that an amorphous network in which the local atomic configuration of the carbon is approximately tetrahedral would be called amorphous diamond, and if the nearest-neighbor configuration is approximately planar threefold carbon, then the structure would be termed as amorphous graphitic. Another very interesting possibility is an atomically mixed structure of three- and fourfold coordinated carbon. Hydrogen is also present in the films and can affect the atomic structure. While the long-term goal of the growth studies may be to produce films with a single structure, the films currently being produced are composites of the possible structures described above. The composite nature extends from the atomic scale with possible coexisting three- and fourfold carbon, up to the micron scale with crystalline and amorphous domains.

While Raman scattering and diffraction measurements are often used to characterize thin films, for the CVD films described here, the results must be interpreted in light of the composite nature of the materials. The techniques may be dominated by particular components of the structure and be insensitive to other components. For instance x-ray scattering from crystalline and amorphous regions will exhibit large differences in intensities, and the light scattering measurements are affected by the differences of the optical absorption of the different components of the film.

II. MEASUREMENT CHARACTERISTICS

The Raman scattering process involves inelastic light scattering from vibrational excitations in the sample. For crystalline samples, the spectra are due to vibrations with a wavelength determined by the scattering geometry and k-vector conservation. Because the wavelength of light is long
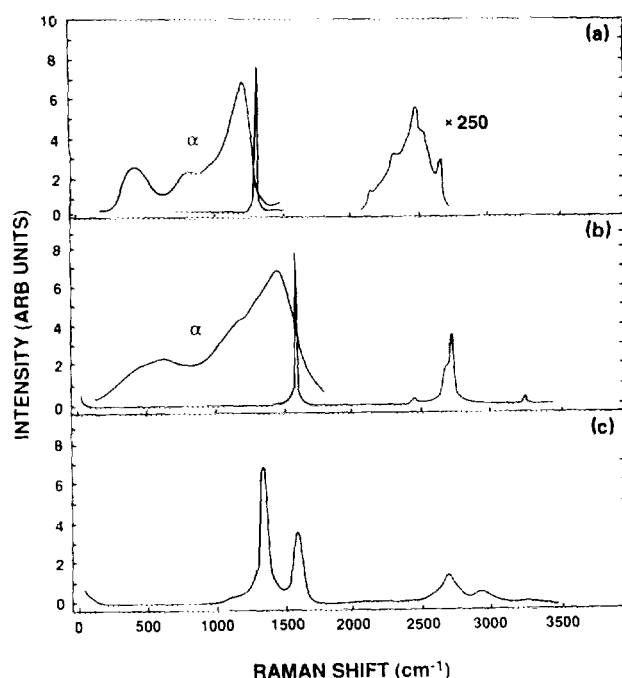
FIG. 1. The Raman spectra of (a) diamond, (b) graphite, and (c) micro-crystalline graphite. The solid lines in (a) and (b) represent the first- and second-order spectra of crystalline diamond and graphite, respectively. The line in (a) labeled α is the spectrum of a-Si scaled to the diamond frequency to represent the spectrum of amorphous diamond, while the line in (b) labeled α is that due to amorphous graphite (from Ref. 10).

on the scale of phonon wavelengths, these requirements select only wave vectors with $k \sim 0$ or Brillouin-zone-center excitations. Thus Raman spectra will display sharp peak(s) representing the zone-center mode(s). The wave-vector conditions can also be satisfied by two phonons with nearly equal and opposite crystal momentum. This scattering is termed second-order scattering. The second-order Raman component is continuous and often is similar to the vibrational density of states but on twice the frequency scale (since two phonons participate in each scattering event). The first- and second-order Raman spectra of diamond[8] and graphite[9] are compared in Fig. 1. The sharp features at 1332 and 1580 cm^{-1} are the first-order zone-center modes of diamond and graphite, respectively. These frequencies are indicative of the different bond strengths of the diamond and graphite bonding. It should be noted that the 1332 cm^{-1} mode in diamond is essentially the highest energy vibrational mode of the structure[8] while for graphite, a second-order feature is observed at 3240 cm^{-1} (or 2×1620 cm^{-1}) which is due to slightly higher energy phonons[9] than the mode at 1580 cm^{-1}. This analysis indicates that modes with energy > 1332 cm^{-1} cannot be attributed to diamond structures with long-range order.

The CVD process often leads to amorphous films, and we consider now the spectrum of amorphous carbon.[7,10] Samples considered to be amorphous graphite have been previously reported and the spectra is overlaid that of graphite in Fig. 1. The spectrum of amorphous films with diamond structure have not to our knowledge been reported. We can approximate what the spectra would look like by comparison with amorphous Si or with the density of vibrational

states of crystalline diamond. We have followed the first possibility by scaling the frequency axis of the Raman spectrum of a-Si by the ratio of the frequencies of the mode of the crystal (520/1332). This deduced spectra is also shown in Fig. 1 as an overlay to the diamond spectrum.

III. COMPOSITE PROPERTIES

Three different composite structures are considered: micron scale, microcrystalline, and atomically disordered. The following discussion outlines some aspects of the structural properties, the vibrational excitations, and the interactions with light and x rays.

For micron-scale composites, the structural properties behave as linear combinations of the properties of the constituent materials. The decay length of phonons is in general < 1 μm, therefore boundary scattering will not significantly affect the phonon lifetimes. This means that the vibrational excitations will exhibit the same spectral response as the bulk samples. Raman scattering and x-ray or electron diffraction from micron-scale composites will exhibit properties that are linear combinations of the orientation randomized (i.e., powder patterns) bulk spectra. For diamond–graphite mixtures, the diffraction efficiencies will be similar for the two components if they are both crystalline or amorphous. If, however, one component is crystalline and the other is amorphous, the x-ray scattering will be dominated by the crystalline structure. The optical properties of graphite and diamond are, of course, very different, and they will affect the Raman scattering. Because of resonance effects, Raman scattering from absorbing materials is enhanced. The absolute Raman cross sections of diamond and graphite have been measured,[11] and it is found that the 1580 cm^{-1} band of graphite is ~ 50 times stronger than the 1332 cm^{-1} band of diamond. Thus the Raman scattering will emphasize the graphitic structures.

Microcrystalline samples exhibit crystalline domains that range from 100 nm to as small as 2 nm. Because the boundary scattering of the phonons is very strong, it can be assumed that the vibrational excitations of the microcrystals will be confined to a single domain. Phonon decay lengths are often larger than these dimensions, thus the boundary scattering causes the vibrational excitations to exhibit lifetime broadened peak widths. In addition, from the Heisenberg uncertainty principle, the wave vector of the excitations is uncertain ($\Delta k \sim 1/d$, where d is the domain size), and the momentum selection rules of the Raman scattering process are relaxed.[12] These effects have been studied in graphite,[9] BN,[12] and Si.[13] The effects are pronounced on microcrystalline graphite[9] shown in Fig. 1. The microcrystalline samples show broader peaks which are shifted toward peaks in the vibrational density of states. Furthermore, a new feature in the first-order spectrum is observed at 1355 cm^{-1} which is attributed to a peak in the vibrational density of states. An additional feature is also observed at 2940 cm^{-1} in the second-order spectrum.

A composite on an atomic scale can be called either an alloy or an amorphous network. It is, of course, somewhat incorrect to label these structures as composites. In the case of carbon, an amorphous network composed of three- and

fourfold coordinated C could be possible.[7] The vibrational and electronic excitations would not be confined to a single atomic site, and thus would represent an average of the network possibilities. The optical properties would not strongly favor enhancement of the threefold (graphitic) over fourfold sites, and we would expect approximately equal scattering efficiencies. Thus we would anticipate a Raman spectrum with broad features extending from 1100 to 1600 cm^{-1}.

IV. CVD DIAMOND AND DIAMONDLIKE FILMS

Consider first the properties of diamondlike thin films produced by plasma enhanced CVD. The Raman spectra of two films produced under differing deposition conditions are shown in Fig. 2. The first thing to note is that the spectra do not compare to any of the spectra discussed as characteristic of amorphous or crystalline diamond or graphite. This implies that the samples are not characteristic of those structures. The two strongest features at 1590 and 1355 cm^{-1} are similar to the vibrational features of diamond and graphite. Thus one is tempted to consider these data as indicative of a micron-scale composite of those structures. There are two arguments against this possibility. The first is that the feature at 1355 cm^{-1} is at a higher frequency than any of the vibrations of the diamond lattice. While effects such as strain are known to shift frequencies to higher wavelengths, this large shift would indicate a compressive stress of over 10 kbar.

The second argument against the consideration of this peak as due to diamond structures is based on the interpretation of the second-order spectrum of graphite and the spectra of microcrystalline graphite samples. The strongest feature in the second-order spectrum of graphite is at 2710 cm^{-1}. This feature at twice the frequency of 1355 cm^{-1} indicates a strong peak in the vibrational density of states of graphite. The peak is also observed in the first-order spectrum of microcrystalline graphite, and its presence has been ascribed to the uncertainty of the wave vector of the vibrations due to the finite size of the domains. The next question to be addressed is whether the excitations at 1355 and 1590 cm^{-1} represent a composite nature of the film. As noted, there is a feature at 2940 cm^{-1} which also appears in the spectrum of microcrystalline graphite. This feature has been ascribed to a two-phonon excitation.[9] The energy corresponds to the sum of the 1355 and 1590 cm^{-1}. This indicates that these two modes occur in the same region of the sample. This leads to the conclusion that all of the strong features in the spectra can be accounted for by microcrystalline regions of the sample.

These results do not mean that there are no regions that exhibit diamond structure. In fact electron energy-loss experiments show features which can be attributed diamond structures. It is also difficult to account for the optical properties of the diamondlike films if they are purely graphitic
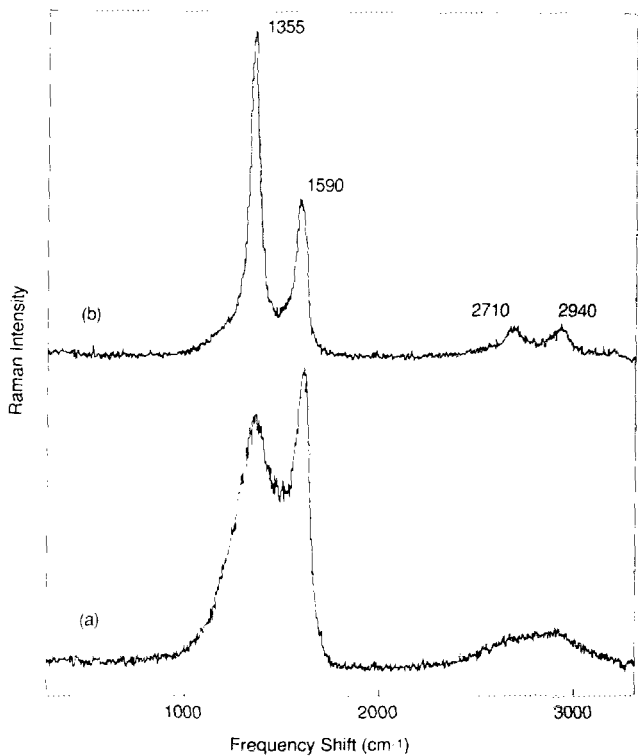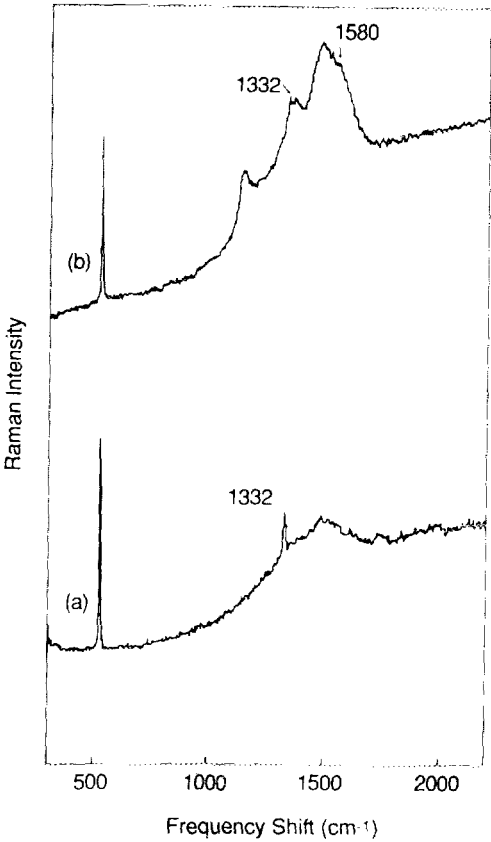
FIG. 2. The first- and second-order Raman spectra of plasma enhanced CVD films produced with different deposition conditions which are characteristic of diamondlike structures. Spectrum (b) shows distinct first-order features at 1355 and 1590 cm^{-1} and second-order features at 2710 and 2940 cm^{-1}.

FIG. 3. The Raman spectra of CVD films which exhibit the feature at 1332 cm^{-1} characteristic of crystalline diamond. The samples were prepared under different conditions using Si substrates, and the sharp feature at 520 cm^{-1} is due to the substrate. Both samples show a strong background due to luminescence. Both samples show the feature at $\sim$1330 cm^{-1} due to crystalline diamond and broad features due to other components.

structures. The Raman scattering from graphite, however, is exceptionally strong because of the high absorption. Thus it is possible that regions of microcrystalline or amorphous diamond exist in the samples, but are not detected by the Raman scattering.

Under slightly different deposition conditions, diamond thin films can be produced. The substrates are often roughened with diamond and then cleaned. The substrate roughness can act as nucleation sites for the growth of diamond films. The Raman spectra of two films prepared at different deposition conditions are shown in Fig. 3. The spectra show a sharp line at 520 cm^{-1} which is attributed to the Si substrate. The features due to the Raman scattering ride on top of a strong luminescence background. In Fig. 3(a), there is a sharp peak at 1332 cm^{-1}. This is the frequency of diamond crystals. A broad spectral component is observed which is centered at ~ 1500 cm^{-1}. This component is to be distinguished from the features similar to microcrystalline graphite at 1580 and 1355 cm^{-1}. The spectrum (b) in Fig. 3 shows a very weak spectral feature at 1332 cm^{-1} and a strong component at 1500 cm^{-1}. This spectrum also shows the double peaks at 1580 and 1355 cm^{-1} which are similar to those associated with microcrystalline graphite. Within the scope of the various possibilities described above it could be concluded that the spectral features indicate a three-component composite. The feature at 1332 cm^{-1} has the properties that it is very sharp and the intensity does not correlate with that of the other spectral components. This indicates that it is due to micron-scale or large microcrystalline regions of diamond. The other features are broad and can be ascribed to amorphous regions of the sample. These regions may exist between the diamond crystalline domains or they could be inclusions.

The broad spectral features can be separated into two components. The features at 1355 and 1580 cm^{-1} are representative of structures similar to microcrystalline graphite. The broad feature at ~ 1500 cm^{-1} does not have an obvious origin. Two possibilities for this feature are (1) an amorphous network of four- and threefold coordinated carbon or (2) an impurity-carbon amorphous network. Raman spectra of carbon-rich SiC:H alloys produced by low-temperature plasma CVD[14] show a broad Raman spectral feature centered at 1500 cm^{-1}. Secondary ion mass spectrometry (SIMS) analysis of some films has indicated the presence of Si, and other studies have reported features attributed to crystalline SiC. Thus we suggest that regions of amorphous carbon-rich SiC exist in the diamond films.

The question remains whether there is a diamondlike precursor to the formation of the diamond regions. The only unaccounted strong spectral feature in the Raman spectra is that at ~ 1140 cm^{-1}. This feature is present in films with small amounts of diamond crystalline domains indicating that it could be a precursor structure. This feature occurs in a region that might be expected for amorphous or microcrystalline diamond. The microcrystalline diamond could be traditional or a polytype in the wurtzite structure. The frequencies of wurtzite diamond have not to our knowledge been reported, but by comparison with the frequencies of SiC we would deduce a vibrational frequency of the strongest mode

to be ~ 1175 cm^{-1} with an additional weaker feature at 1330 cm^{-1}. Thus we suggest that this feature is due to regions of microcrystalline or amorphous diamond.

V. CONCLUDING REMARKS

The Raman scattering effects due to composites of carbon components are discussed. The possibilities include crystalline or amorphous diamond or graphite. The strong difference in the optical absorption of the different structures lead to large differences in the Raman sensitivity to different structures. For micron-scale and microcrystalline composites, because of the strong optical absorption, graphitelike structures will dominate the Raman spectra while x-ray or electron diffraction will be dominated by crystalline domains. For atomic-scale composites or amorphous alloys, it is proposed that the Raman scattering from diamond and graphitelike features will exhibit equal scattering strength.

The analysis of the first-order spectra of diamondlike films shows no features which can be attributed to crystalline diamond structures. Extending the analysis to the second-order spectra shows that the major features of the spectra originate from the same atomic structures. The spectra, therefore, show no evidence of composite nature, but other measurements indicate the presence of diamond structures. It is likely that these are not observed because of the weak signal from the diamond structures with respect to the graphitic structures.

The Raman spectra of diamond films show composite characteristics. Crystalline regions of diamond structure are observed along with microcrystalline or disordered graphitic structures. One feature is observed which cannot be accounted for by any of the known structures of graphite or diamond. By comparison with the spectra of amorphous and microcrystalline Si, we ascribe this feature to amorphous or microcrystalline diamond structures.

ACKNOWLEDGMENTS

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