

Characterization of Diamond Thin Films by Core-Level Photoabsorption and UV Excitation Raman Spectroscopy

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ABSTRACT

Near-edge x-ray absorption fine structure (NEXAFS) and Raman spectroscopies have been used to characterize both nanocrystalline and faceted, microcrystalline diamond thin films grown by microwave plasma chemical vapor deposition under a variety of conditions. Raman spectroscopy is perhaps the most commonly used method of characterizing diamond film quality, whereas photoabsorption requires a synchrotron radiation source and is much less commonly used. Both methods characterize the sp^2 (graphitic) / sp^3 (diamond) electronic bonding character of the films, but Raman spectroscopy is considerably more sensitive to sp^2 than sp^3 bonded carbon. For nanocrystalline diamond, the use of a visible excitation source for Raman spectroscopy also gives rise to an intense fluorescence band which may completely mask the sp^3 Raman line, even in films with negligible (<1%) sp^2 bonding character. Near-edge x-ray absorption fine structure (NEXAFS) is a more localized measurement of the electronic bonding character, and does not have as large a variation in sensitivity between sp^2 and sp^3 phases.

Raman spectra measured using 632.8 nm light exhibit a sharp diamond phonon peak at 1332 cm^{-1} for faceted, large grain diamond films, and no obvious diamond phonon peak for the nanocrystalline diamond films. However, Raman spectra excited by 228.9 nm light exhibit a sharp diamond phonon peak for both nanocrystalline and large grain, faceted diamond films. The UV Raman results are consistent with the C(1s) NEXAFS measurements which show clear bulk diamond excitonic and sp^3 features, with little evidence of sp^2 character for all of the tested films. We conclude that the use of visible excitation Raman spectroscopy as the sole criterion for the assessment of quality in nanocrystalline diamond films is misleading, but that UV Raman spectroscopy and NEXAFS provide a consistent and reliable characterization. Nanocrystalline films grown using a fullerene precursor in an Ar microwave plasma with very low levels of hydrogen (2%) are found by both of the latter methods to consist almost entirely of sp^3 -bonded carbon with ~2% non-tetrahedral bonding.

INTRODUCTION

The remarkable properties of diamond including its extreme hardness, low coefficient of friction, chemical inertness, high thermal conductivity, transparency and semiconducting properties make it an attractive coating material for many applications. In the past 10 years, diamond deposition by chemical vapor deposition has been the subject of considerable research. Various methods for depositing diamond films have been explored and numerous techniques applied to characterize these films. The ratio of sp^2 / sp^3 bonded carbon in the film is one of the most important characteristics, as it can influence many of the film properties such as electrical and thermal conductivity.

Raman spectroscopy provides a relatively simple diagnostic which can quickly provide information on diamond films. It is commonly used as a qualitative measure of the sp^2/sp^3 carbon ratio. Single crystal diamond results in a sharp peak at 1332 cm^{-1} , while graphite produces sharp peaks at 1580 cm^{-1} and 1350 cm^{-1} . Broad features in the 1100 to 1600 cm^{-1} range have been associated with sp^2 carbon and defects in the diamond, however there is considerable discussion and a divergence of opinion concerning the exact interpretation [1]. The intensity of the various features depends on several factors, which make quantification of the sp^2 content in the film difficult. The relative intensities of the sp^2 and sp^3 carbon Raman and emission spectral features depend on the grain size [2,3], film stress [3], and excitation wavelength [2]. In the visible, the Raman spectrum is often 50-100 times more sensitive to sp^2 carbon than to sp^3 carbon [3]. As the wavelength is shifted to the blue and into the UV, the sp^2 carbon Raman intensity is expected to decrease relative to that of sp^3 carbon [2,3]. In addition, for nanocrystalline diamond, a strong fluorescence signal [3] is often seen which is sufficiently intense to mask the sharp 1332 cm^{-1} peak of diamond for visible light, but not for UV excitation.

Core-level photoabsorption has been used to characterize the empty electronic states of a wide variety of materials [4]. Specifically, the near-edge region of this photoabsorption process has been used to determine the relative quantity of sp^2 or sp^3 bonding in BN powders and thin films [5,6]. The technique is known by several acronyms -- near-edge x-ray absorption fine-structure (NEXAFS) or x-ray absorption near-edge spectroscopy (XANES). Its sensitivity to the local bond order in a material arises from the dipole-like electronic transitions from core states, which have well-defined orbital-angular momenta, into empty electronic (e.g., antibonding) states. The symmetry of the final state can be determined, and thus the difference between sp^2 (π -like) or sp^3 (σ -like) bonding can be readily observed in covalent, low-z materials. Several examples of the ability of NEXAFS to measure chemical-specific, local-bond order in thin films have been published. Although used sparingly to characterize synthetic carbon films [7-9], the potential of absorption spectroscopy for unambiguously determining the quality of CVD diamond films in lieu of Raman spectroscopy has been known since the work of Capehart et al. [10].

In this work we compare visible and UV excitation Raman spectroscopy, and NEXAFS results for small grain size diamond films grown using C_{60} in a microwave plasma chemical vapor deposition (MWPCVD) process. For these and other films grown by conventional CH_4 CVD processes, we have shown that both UV Raman spectroscopy and C (1s) photoabsorption clearly indicate the presence of nearly pure sp^3 bonding in these films, while visible wavelength Raman spectroscopy gives an ambiguous and misleading determination of the bond order in these materials.

EXPERIMENT

Diamond films were deposited in a microwave plasma-enhanced CVD reactor (ASTeX PDS-17) as described previously [11]. The films were grown on silicon (100) wafers polished with $0.1\text{ }\mu\text{m}$ diamond powder to enhance nucleation density. Film growth was monitored in situ, using laser reflectance interferometry to determine growth rate, and to indicate when the desired thickness was obtained. The first film, hereafter referred to as the C_{60} -derived film, was grown with 2 sccm H_2 , 98 sccm Ar and C_{60} vapor (at an equivalent carbon partial pressure of 600 mTorr), at a total pressure of 100 Torr, using 1500 watts of microwave power, and a substrate temperature of $850\text{ }^\circ\text{C}$ to a thickness of $4\text{ }\mu\text{m}$. A quartz transpirator was used to introduce C_{60} into the reactor [11]. A second film, hereafter referred to as the low temperature C_{60} -derived film, was

grown to a thickness of 0.25 μm , using 2 sccm H_2 , 98 sccm Ar and C_{60} vapor (at an equivalent carbon partial pressure of 600 mTorr), at a total pressure of 90 Torr, using 800 W of microwave power, at a substrate temperature of 470-500 $^\circ\text{C}$ as measured by a thermocouple embedded in the rf induction heated graphite substrate holder. A third film, hereafter referred to as the CH_4 -derived film, was grown with 2 sccm CH_4 , 98 sccm H_2 , at a pressure of 100 Torr, using 1500 W of microwave power, and a substrate temperature of 850 $^\circ\text{C}$ to a thickness of 10 μm .

The microstructure of the C_{60} -derived film was studied using transmission electron microscopy (TEM). Raman spectra of the films excited using 632.8 nm light were measured with a Renishaw Raman microscope with an output power of 25 mW focused to a spot size of about 2 μm with a 2 cm^{-1} resolution. Raman spectra of the films excited using 228.9 nm light were measured using the UV Raman spectrometer at the University of Pittsburgh, with an output power of 5 mW focused to a spot size of 30 μm with a resolution of 12 cm^{-1} [12].

The NEXAFS experiments were performed at the Lawrence Livermore National Laboratory/University of California (LLNL/UC) Beamline 8.2 at the Stanford Synchrotron Radiation Center (SSRL). The diamond reference sample was a standard Type IIA diamond. The graphite reference sample was highly oriented pyrolytic graphite (HOPG). The CVD diamond films grown at ANL were transported to SSRL in air and received no precleaning treatment prior to acquiring the NEXAFS data. The photoyield signal was acquired by monitoring the photocurrent or through collection of photoelectrons emitted from the sample via a channeltron. A Si(111) sample flashed briefly to 1250 $^\circ\text{C}$ briefly was used to normalize the light curve for each of the spectra.

RESULTS

Grain sizes of the C_{60} -derived film were determined from TEM images. Some 467 grains were measured, and the minimum and maximum grain sizes were found to be 3.2 nm and 103 nm, respectively. The average grain size is 14.9 nm, with a standard deviation of 12.9 nm [13]. For the low temperature C_{60} -derived film, no features were observed with the optical microscope, indicating a small grain size. It is presumed to also be nanocrystalline based on characterization of films grown under similar conditions. The CH_4 -derived film consisted of large, 1-3 μm faceted grains that could be observed with an optical microscope.

Raman spectra measured using 632.8 nm light excitation are shown in Fig. 1 for the three films, along with spectra from a large natural diamond and highly oriented pyrolytic graphite (HOPG) graphite. Based on the Raman data, the CH_4 -derived film clearly contains diamond, as evidenced by the sharp 1332 cm^{-1} peak in the spectrum. The nanocrystalline C_{60} -derived film shows a weak 1332 cm^{-1} peak and broad, unresolved features from 1100 to 1600 cm^{-1} that are commonly attributed to nondiamond phases and considered an indication of poor film quality. The low temperature C_{60} -derived film shows no features near the diamond band at 1332 cm^{-1} . Broad features are observed in the 1100-1600 cm^{-1} range that are commonly attributed to nondiamond phases. Raman spectra using 228.9 nm light excitation are shown in Fig. 2 for films grown under similar conditions to the C_{60} and CH_4 -derived films. The diamond peak at 1332 cm^{-1} is clearly present for both. The C_{60} -derived film shows a broad peak of comparable intensity near 1600 cm^{-1} which is associated with sp^2 carbon.

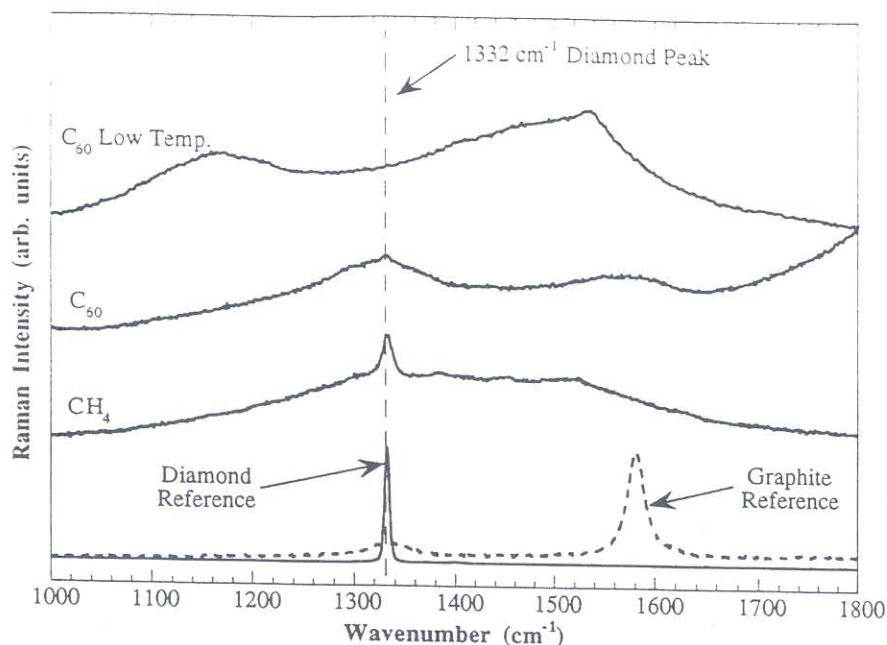


Fig. 1. The Raman spectra (633 nm excitation) from five different samples: (C_{60} Low Temp.), nanocrystalline diamond film grown using the C_{60} based deposition method and substrate temperature of 550°C ; (C_{60}), nanocrystalline diamond film grown using the C_{60} based deposition method at a temperature of 850°C ; (CH_4) diamond film with micron sized grains grown using a convention CH_4 based deposition method; (Natural Diamond), gem quality natural diamond; (HOPG), highly oriented pyrolytic graphite.

The C (1s) photoabsorption data from the diamond and graphite reference samples and from the three diamond films are shown in Fig. 3. The vertical scale is the number of counts normalized to the incident photon flux. The intensities of the diamond σ -edge and the graphite π^* peak are very similar, indicating that the relative sensitivity of NEXAFS to sp^2 and sp^3 bonding is roughly the same, in contrast to Raman spectroscopy which may be 50-100 times more sensitive to sp^2 bonding. The near-edge structure of diamond and graphite have been discussed in detail elsewhere [7-10, 14, 15]. Clearly there are significant differences in these spectra. These differences are directly related to the bonding structure of diamond (sp^3 hybridization; tetrahedral σ -bonding) and graphite (sp^2 hybridization; hexagonal σ - and π -bonding). For graphite, which is π -bonded, the most prominent feature is the π^* resonance at 285.5 eV. This feature is nearly absent in diamond and serves as one figure of merit for determination of the sp^3 to sp^2 ratio in a film. Other figures of merit are the onset of the σ -states at ~ 289 eV in diamond compared to ~ 291 eV in graphite; the presence of the diamond exciton at 289.5 eV compared with the graphite exciton at 291.63 eV; and the presence of a second dip in the density of states in diamond at ~ 303 eV.

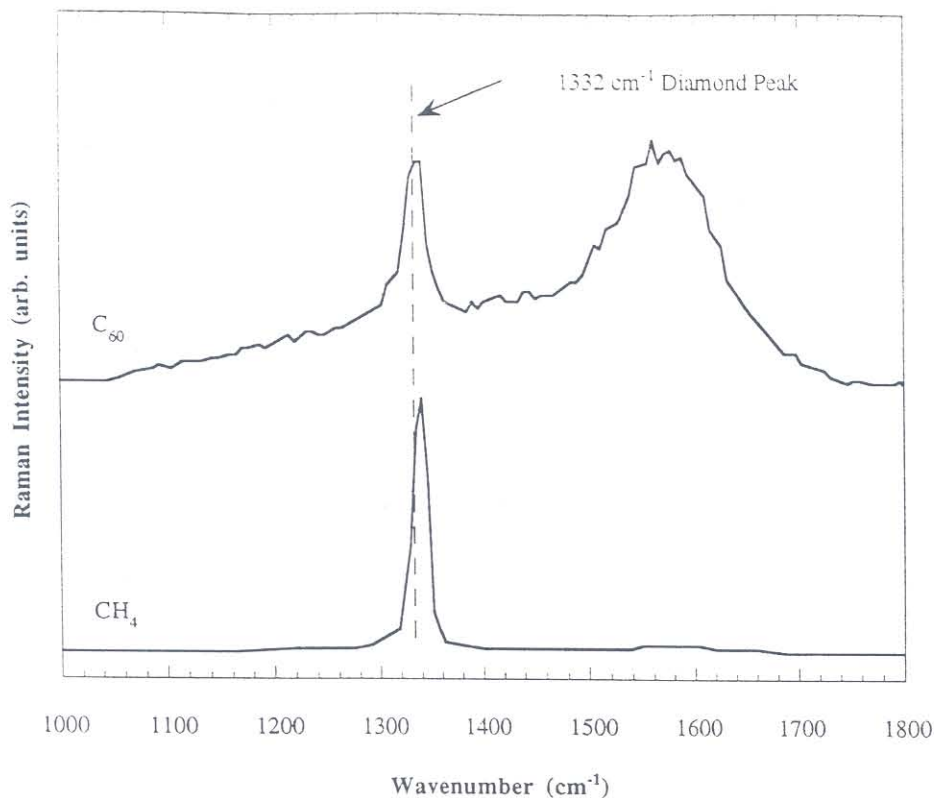


Fig. 2. The Raman spectra (228.9 nm excitation) from two different samples: (C_{60}), nanocrystalline diamond film grown using the C_{60} based deposition method at a temperature of $850^{\circ}C$; (CH_4) diamond film with micron sized grains grown using a convention CH_4 based deposition method.

The NEXAFS spectra from the C_{60} and CH_4 -derived diamond films are also shown in Fig. 3. It can be concluded that the local electronic structure of these synthetic diamond films is essentially equivalent to pure diamond since the spectra from the CVD diamond films and diamond reference are nearly indistinguishable from one another. Note that all of the qualitative markers for sp^3 bonding are clearly present in the C_{60} and CH_4 -derived diamond films. The low temperature C_{60} -derived film also appears to be diamond, although a clear diamond exciton is not evident.

The NEXAFS spectrum of the single crystal diamond shows a small sp^2 structure, roughly 1-2% of the diamond σ -edge and the graphite π^* peak. Some π -bonding is always observed [16], even in nominally pure diamond reference specimens, and is usually attributed to surface termination/reconstruction and hydrogen termination of the surface atomic layer. Since the NEXAFS measurement samples to a depth of 50-200 Å [16], the measured intensity of the sp^2 structure in the NEXAFS data is again consistent with the assumption of roughly equal sensitivities for sp^2 and sp^3 carbon-carbon bonding, with the

sp^2 phase constituting 1-2% of the carbon-carbon bonds. However, since NEXAFS is element-specific, it will not respond in the same manner to carbon-hydrogen and carbon-carbon bonds. This issue requires further exploration. Atomic Resolution TEM studies of films grown under conditions similar to the present C_{60} -derived film were unable to detect any sp^2 phase [13], suggesting that the sp^2 carbon is confined to the grain boundaries, which constitute ~2% of the carbon atoms in the nanocrystalline diamond films. Thus, we conclude that the actual percentage of sp^2 carbon-carbon bonding in these nanocrystalline films is approximately 2%. This conclusion is consistent with the UV Raman results if a sp^2/sp^3 sensitivity ratio of ~50:1 is assumed, although the UV Raman data also suggests that the carbon-hydrogen sp^2 bonding may be higher.

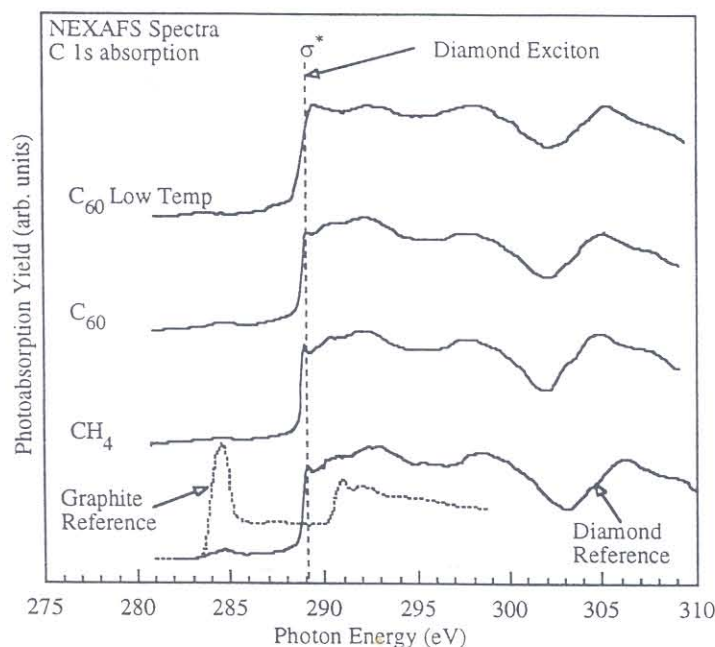


Fig. 3. The C (1s) photoabsorption data from five different samples: (C_{60} Low Temp.), nanocrystalline diamond film grown using the C_{60} based deposition method and substrate temperature of 550°C; (C_{60}), nanocrystalline diamond film grown using the C_{60} based deposition method at a temperature of 850°C; (CH_4) diamond film with micron sized grains grown using a convention CH_4 based deposition method; (Natural Diamond), gem quality natural diamond; (HOPG), highly oriented pyrolytic graphite.

CONCLUSIONS

Core-level photoabsorption and Raman spectroscopies have been used to determine the sp^2/sp^3 bonding character of both conventionally grown (H_2-CH_4) diamond thin films and nanocrystalline diamond films grown using C_{60} and CH_4 precursors in an Ar plasma with very low hydrogen concentration. Raman spectra of the conventionally grown diamond using visible light excitation exhibit both sp^3 and sp^2 peaks, although the

sensitivity for sp^2 bonded carbon is far higher than for sp^3 bonded carbon. Raman spectra of the nanocrystalline films measured with visible light excitation exhibit a strong luminescence which overwhelms the 1332 cm^{-1} peak corresponding to diamond. For UV excitation, the sp^2/sp^3 sensitivity ratio is found to be similar to that of visible Raman spectroscopy, but the luminescence is absent, and a very strong 1332 cm^{-1} peak similar in intensity to the broad sp^2 peak at $\sim 1580\text{ cm}^{-1}$ was seen in all the films. NEXAFS exhibits approximately equal sensitivity for sp^2 and sp^3 bonding character, and the measured sp^2/sp^3 intensity ratios correspond to 1-2% sp^2 character, in agreement with the UV Raman results.

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