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Resonant Raman scattering of amorphous carbon and polycrystalline diamond films

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Resonant Raman scattering has been used to study amorphous carbon and polycrystalline diamond films. The incident photon energies were varied over the range 2.2–4.8 eV. In hydrogenated amorphous carbon films containing both sp^3- and sp^2-bonded carbon, a high-frequency shift is observed for the main Raman peak with increasing photon energies up to 3.5 eV. This shift is interpreted in terms of scattering from π-bonded carbon clusters which is resonantly enhanced for photon energies approaching the π-π^* resonance of sp^2-bonded carbon. In polycrystalline diamond films excitation with photon energies ≥ 3.0 eV enhances the Raman signal from the sp^3-bonded diamond phase relative to the scattering by sp^2-bonded carbon and with respect to the underlying broadband luminescence. The Raman band arising from scattering by sp^2-bonded carbon shows a high-frequency shift with increasing photon energy for energies ≥ 3.0 eV. Possible models for the structure of this sp^2-bonded carbon phase are discussed on the basis of the present Raman data.

I. INTRODUCTION

Amorphous carbon films have been investigated intensively in the past.[1] Depending on the deposition techniques and conditions used for the preparation these films are either graphitelike consisting entirely of sp^2-bonded carbon or contain both sp^2- and sp^3-hybridized carbon and hydrogen to passivate dangling bonds. The latter amorphous carbon films may be mechanically soft with a relatively large optical band gap of $\sim 2-3$ eV, so-called "polymerlike" films, or hard and dense with an optical band-gap energy of $\sim 1-1.5$ eV. We will focus on these hard and dense films, which have also been called "diamondlike",[1] in the following.

Detailed insight was gained into the chemical composition, e.g. hydrogen content, and into the local bonding arrangement, e.g., sp^2- to sp^3-bonding ratio, in the hard and dense carbon films.[1] However, only little is known about the medium-range order in this material. Based on the relatively low optical band-gap energy (1.0–1.5 eV) of these films, Robertson and O'Reilly suggested the following model to account for this property: sp^2-bonded carbon is localized in graphitic clusters which consist of four or more fused sixfold rings.[2,3] These clusters are connected by sp^3-bonded carbon. The energy states close to the valence- and conduction-band edges are derived from π states of the sp^2 carbon clusters which therefore also determine the optical band-gap energy.[2,3] The above model is able to explain the low optical band-gap energy found in hard hydrogenated amorphous carbon films (*a*-C:H). It is further consistent with photoluminescence data on hard *a*-C:H, which indicate localized energy states for energies $\sim 0.5-1$ eV above the optical band gap.[4] However, further experimental verification of this model seems to be desirable.

Recently also polycrystalline diamond films have received considerable interest.[5] In these films sp^3-bonded carbon is present as small diamond crystals.[5,6] This has been proven by a variety of experimental techniques such as secondary electron microscopy, electron and x-ray diffraction, and Raman spectroscopy.[5] In the latter technique crystalline diamond shows up as a sharp Raman line at 1332 cm^{-1}. Raman scattering reveals further a broad band at higher frequencies (~ 1550 cm^{-1}). This band has tentatively been associated with amorphous sp^2-bonded carbon or amorphous SiC.[7] The actual structure and the size of the regions consisting of sp^2-bonded carbon, however, is still unclear.

Raman scattering has been extensively used to study both amorphous carbon[8–10] and polycrystalline diamond films.[5,7,11] Surprisingly almost all the Raman studies so far were performed using the same incident photon energy of 2.41 eV (514.5 nm). Only recently the concept of resonance Raman scattering, which is widely used to study crystalline materials,[12] has been applied to *a*-C:H.[13] A pronounced change in the shape and the peak position of the Raman bands was observed for photon energies approaching the π-π^* transition energy.[13] These results were confirmed later by Yoshikawa *et al.*[14,15]

The purpose of the present study was to extend the resonance Raman study of *a*-C:H to higher photon energies—up to 4.8 eV—which is close to the onset of the σ-σ^* transition in both sp^2- and sp^3-bonded carbon.[16] The results obtained give additional strong support to the model suggested in Ref. 10. Resonant Raman scattering was used further to study the incorporation of sp^2-bonded carbon in polycrystalline diamond films. The organization of this paper is as follows. In Sec. II details of the sample preparation and of the Raman experiment are described. Sections III A and III B cover the experimental results and their discussion on *a*-C:H and polycrystalline diamond, respectively. The conclusions are given in Sec. IV.

II. EXPERIMENT

The *a*-C:H films used in the present study were prepared by 13.56 MHz rf plasma deposition from hydrocarbon gases.[17,18] The films obtained are hard and dense (density 1.8 g/cm^3) and consist of $\sim\frac{2}{3}$ sp^3-bonded and $\sim\frac{1}{3}$ sp^2-bonded carbon.[16,19] They contain typically 35 at.% hydrogen.[20] The thickness of the films was 1 μm. Films containing only sp^2-bonded carbon were produced by thermal annealing of plasma-deposited *a*-C:H at 600 °C for 4 h in vacuum, which leads to graphitic microcrystalline sp^2 carbon.[19,21]

Polycrystalline diamond films were prepared either by microwave-plasma-assisted chemical-vapor deposition (samples 1 and 3)[22] or by hot-filament-assisted chemical-vapor deposition[23] (sample 2). In both cases single-crystal Si was used as a substrate. Samples 1 and 3 are relatively thick films of 10 μm thickness. The approximate size of the diamond crystals in sample 1 is ~ 5 μm. Sample 2 shows incomplete coverage of the substrate and a size of the diamond crystals of ≤ 1 μm. Sample 3 was of poor structural quality. No individual grains could be resolved by secondary electron microscopy.

The Raman spectra were recorded at room temperature in backscattering geometry. They were excited with several lines of a Kr-ion and an Ar-ion laser covering photon energies in the range 2.18–3.54 eV. In addition the frequency doubled output of an Ar-ion laser operating at 514.5 nm (2.41 eV) was used extending the range of excitation energies available up to 4.82 eV. The scattered light was filtered and dispersed in a triple monochromator and detected with an intensified silicon diode array. The spectral resolution varied between 6 cm^{-1} for the lowest and 30 cm^{-1} for the highest incident photon energy used. Typical data acquisition times were in the range 30 sec to 5 min for a Raman spectrum.

III. RESULTS AND DISCUSSION

A. Amorphous carbon

Figure 1 shows a series of Raman spectra of *a*-C:H prepared by plasma deposition. The incident photon energies range from 2.18 to 4.82 eV. For photon energies increasing up to 3.54 eV a pronounced high-frequency shift is observed for the main Raman peak. Its position shifts from 1500 cm^{-1} (excitation at 2.18 eV) to 1600 cm^{-1} (excitation at 3.54 eV). The intensity of the main peak measured relative to the shoulder at ~ 1300 cm^{-1} increases simultaneously. Increasing the incident photon energy further to 4.82 eV the position of the main peak remains fixed at 1600 cm^{-1}. The low-frequency shoulder at ~ 1300 cm^{-1}, however, regains intensity relative to the main peak. These findings are independent of the thickness of the *a*-C:H film or of the technique used for film depositions, i.e., plasma or ion beam deposition.[13] It has been shown previously that this high-frequency shift of the main Raman peak goes along with a resonant enhancement of the efficiency of the scattering at ~ 1600 cm^{-1} for photon energies up to 3.5 eV.[13]

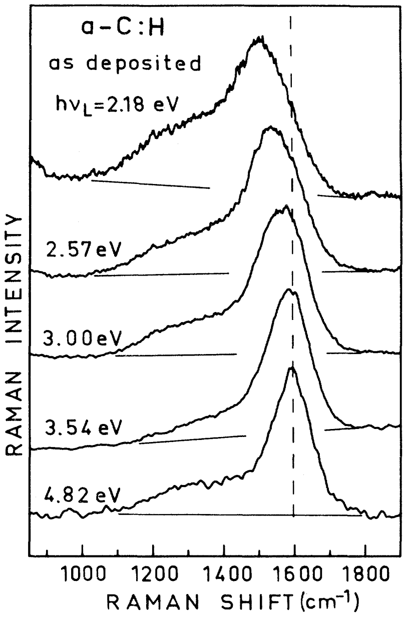

FIG. 1. Raman spectra of plasma-deposited hard *a*-C:H excited at different photon energies given in the figure. The drawn lines indicate the underlying luminescence background, the dashed line marks the peak frequency found for excitation at 4.82 eV.

Raman spectra of *a*-C:H annealed at 600 °C, which contains only sp^2-bonding carbon,[9,21] are displayed in Fig. 2. The spectra excited with photon energies ranging from 2.18 to 4.82 eV show a relatively sharp peak at 1600 cm^{-1} (*G* peak) and a somewhat broader peak at ~ 1350–1400 cm^{-1} (*D* peak). The *G* peak has been assigned to scattering by optical zone-center phonons (E_{2g} mode) in graphite. The *D* peak has been interpreted by scattering of disorder activated optical zone-edge phonons.[21] Independent of the incident photon energy the frequency of the *G* peak remains at 1600 cm^{-1}. This is in

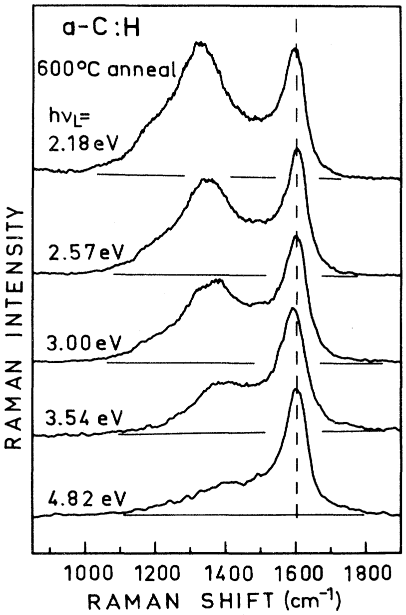

FIG. 2. Same as Fig. 1 but for microcrystalline graphite prepared by thermal annealing of *a*-C:H at 600 °C.

contrast to the frequency shift observed for the main Raman peak in as-deposited *a*-C:H (see Fig. 1). The *D* peak shows a high-frequency shift and a reduction in relative intensity with increasing photon energy up to the highest energies used. A similar shift of the *D* peak to higher frequencies has been observed in a variety of graphitic materials such as pyrolytic carbon, glassy carbon, compression annealed pyrolytic carbon (CAPC), and Ar-ion bombarded CAPC.[24] At present both the frequency shift of the Raman *D* peak[24] as well as the change in the *D*/*G* intensity ratio found in the present annealed *a*-C:H sample[13] are not understood.

With the above experimental results in mind, we have to note that extreme care should be taken when analyzing the shape of Raman spectra of *a*-C:H. Such an analysis has been performed by Beeman *et al.*[25] to extract information on the sp^2- to sp^3-bonding ratio and on bond angle fluctuations from Raman data. We feel that this kind of analysis should be revisited in the light of the present resonance Raman data on *a*-C:H.

Summing up the experimental results we can state that the Raman spectra of *a*-C:H films containing both sp^3- and sp^2-bonded carbon exhibit a well-defined high-frequency shift of the main Raman peak when increasing the incident photon energy up to 3.5 eV. This frequency shift was found to be caused by a resonant enhancement of the Raman efficiency of the high-frequency vibronic excitation ($\sim 1600\ \mathrm{cm}^{-1}$).[13] Increasing the incident photon energy to 4.8 eV no further shift of the main Raman peak is observed. The relative intensity of the low-frequency shoulder at $\sim 1300\ \mathrm{cm}^{-1}$ decreases for photon energies up to 3.5 eV but increases again when going to an incident photon energy of 4.8 eV. In graphitelike microcrystalline carbon films containing only sp^2-bonded carbon the position of the microcrystalline main Raman peak (*G*) at $\sim 1600\ \mathrm{cm}^{-1}$ is independent of the incident photon energy over the whole energy range investigated. The low-frequency *D* peak shows a high-frequency shift and its relative intensity decreases monotonously over the whole range of photon energies. Therefore we conclude that the frequency shift of the main Raman peak observed in as-deposited *a*-C:H containing both sp^3- and sp^2-bonded carbon is dissimilar to the photon-energy-dependent effects found in the Raman spectrum of graphitic materials containing only sp^2-bonded carbon.[13,24]

The changes in the Raman spectra of as-deposited *a*-C:H upon variation of the excitation energy are difficult to understand within a homogeneous structural model.[1] Thus we assume in the following a heterogeneous structure, involving two phases. They differ in their electronic and vibronic properties with the individual vibrational modes essentially localized within the corresponding phase.[13] Consequently the experimentally observed Raman spectrum is a superposition of the two distinct vibronic Raman spectra as indicated schematically in Fig. 3(a). As a consequence of the different electronic properties the dispersion curves of the individual Raman scattering efficiencies are expected to be different. This implies that for a change in the photon energy used to excite the Raman spectrum also the relative intensities of the contributions from the two phases change. Such a change in the relative intensities, in turn, may cause an apparent peak shift in the measured Raman spectrum as indicated in Fig. 3(b). Here we want to point out that the line shapes assumed for the two individual contributions from phase 1 and phase 2 are only schematic. Figure 3 should not be understood as an attempt to perform a line-shape fitting to the experimental spectra. To account for the observed photon-energy-dependent peak shift in the Raman spectra of as-deposited *a*-C:H we have to assume that the scattering efficiency of phase 2 contributing to the high-frequency portion of the total spectrum is strongly resonant for photon energies in the range 2.2–3.5 eV. The Raman scattering efficiency of phase 1, in contrast, which contributes to the low-frequency portion has to be assumed to be much less resonant in the above range of photon energies.

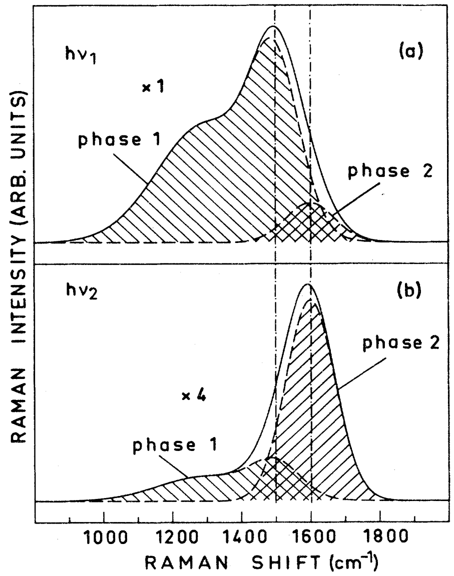

FIG. 3. Schematic presentation of a Raman spectrum composed of two different underlying spectra. Note the apparent change in peak frequency from (a) to (b) when the relative intensities of the two components are changed.

Comparing the Raman spectra of as-deposited *a*-C:H (Fig. 1) containing both sp^3- and sp^2-bonded carbon and the spectra of purely sp^2-bonded graphitic carbon (Fig. 2) it is straightforward to assign the high-frequency portion (phase 2) in the Raman spectrum of as-deposited *a*-C:H to an E_{2g}-like mode (*G* peak) in a graphitelike sp^2-bonded carbon phase. Consequently the low-frequency portion (phase 1) has to be interpreted in terms of scattering by sp^3-bonded carbon plus possible contributions of the graphitelike *D* peak. In as-deposited *a*-C:H sp^2-bonded carbon shows electronic π-π^* transitions in the energy range 3.5–6.5 eV.[16] These transitions are specific to sp^2-bonded carbon. σ-σ^* transitions occurring in both sp^3- and sp^2-bonded carbon lie at higher energies ≥ 6 eV.[16] The Raman scattering efficiency, in turn, is proportional to $|\partial\epsilon(\omega)/\partial\omega|^2$ where $\epsilon(\omega)$ denotes the dielectric function.[12] Thus one expects a resonant enhancement of the scattering by the graphitelike E_{2g} mode in phase 2 for incident photon energies in the range from 2 to 3.5 eV approaching the π-π^* transition energy, where $|\partial\epsilon(\omega)/\partial\omega|^2$ shows a maximum. This is consistent with the model discussed above to explain the high-frequency shift of the main *a*-C:H Raman peak. There we had to postulate a bigger resonance effect in the Raman efficiency for scattering by phase 2 than for scattering by phase 1 up to incident photon energies of 3.5 eV. The above assignment of phase 1 and phase 2 to sp^3- and sp^2-bonded carbon, respectively, is further consistent with the observed increase of the relative intensity of the 1300-cm^{-1} shoulder in the Raman spectrum excited at 4.8 eV. For this incident photon energy we are closest to the σ-σ^* transition energy for which we expect also a resonance enhancement of scattering by sp^3-bonded carbon (phase 1).[16] For scattering by sp^2-bonded carbon in contrast, no further enhancement is expected for excitation at 4.8 eV, relative to 3.5-eV excitation, because also the latter photon energy is already near resonance with the π-π^* transition.[16] This is consistent with the experimental finding that the main Raman peak is fixed in frequency upon increase of the photon energy above 3.5 eV.

The above concept of two phases consisting of sp^3- and of sp^2-bonded carbon, respectively, is consistent with the model introduced by Robertson and O'Reilly.[2,3] In order to explain the relatively small optical band gap of hard and dense *a*-C:H these authors presented theoretical evidence that sp^2-bonded carbon must be concentrated in graphitelike clusters consisting of four or more fused sixfold rings. These clusters have to be interconnected by sp^2-bonded carbon to account for the total sp^3:sp^2 carbon ratio of 2:1.[16,19] In the present concept phase 2 is identified with sp^2 carbon clusters of fused sixfold rings and phase 1 with interconnecting sp^3 carbon.

In analogy to the interpretation of resonant Raman data reported for transpolyacetylene,[26–28] also the following model, which is alternative in some aspects, has been discussed to explain the present Raman data on *a*-C:H:[13] Based on the assumption that different sizes of the sp^2 carbon clusters are associated with different values for the π-π^* transition energy[2,3] it was discussed that with changing incident photon energies clusters of varying sizes are probed. With the vibronic frequencies depending on the cluster size this would also lead to a frequency shift in the Raman spectrum when changing the incident photon energy. However, as stated earlier,[13] the main result of the present experiments, that clusters of sixfold sp^2-bonded carbon rings are necessary to explain the resonance Raman data, is not affected by the details of the above model.

The present resonance Raman data on as-deposited *a*-C:H, a preliminary report of which has been published already in Ref. 10, were confirmed recently by Yoshikawa *et al.*[14,15] These authors studied resonance Raman scattering of various types of amorphous carbon films and came essentially to the same conclusion as presented in Ref. 13 and in the present paper. However, the range of photon energies used was much more limited (1.9–2.7 eV) than in the present work. Yoshikawa *et al.* question the contribution of sp^3-bonded carbon to the Raman spectrum of *a*-C:H. The present resonance Raman data, however, which show an enhancement in the scattering intensity at ~1300 cm^{-1} for excitation at 4.82 eV relative to 3.54-eV excitation, indicate the presence of scattering by sp^3-bonded carbon at least for that highest photon energy used (see Fig. 1). This is consistent with the expected Raman spectrum of amorphous diamond which should exhibit its main peak at ~1200–1300 cm^{-1}.[7]

B. Polycrystalline diamond

Raman spectra of three different polycrystalline diamond films investigated in this study are displayed in Fig. 4. The spectra were excited at an incident photon energy of 3.00 eV. In the spectrum of sample 1 [Fig. 4(c)] the 1332-cm^{-1} Raman line indicative for the presence of crystalline diamond[5–7,11] is the dominant feature. At 520 cm^{-1} the optical zone-center (O_Γ) phonon line of the crystalline silicon substrate is seen. The presence of this line indicates that the 10-μm-thick polycrystalline diamond film is transparent for 3.00-eV light. Sample 2 [Fig. 4(b)] shows besides the 1332-cm^{-1} diamond line a broader peak at ~1550 cm^{-1} which has been assigned to scattering by sp^2-bonded carbon.[5–7] The spectrum of the silicon substrate with the O_Γ phonon line at 520 cm^{-1} and a peak at ~900 cm^{-1} due to scattering by two transverse-optical (TO) phonons has a much higher intensity than in Fig. 4(c) because in sample 2 the substrate is not fully covered by the diamond film. Figure 4(a) shows the Raman spectrum of sample 3. Here the 1332-cm^{-1} line of crystalline diamond and the 1550-cm^{-1} peak have almost equal intensity. No scattering is observed from the substrate. From the spectra displayed in Fig. 4 it is

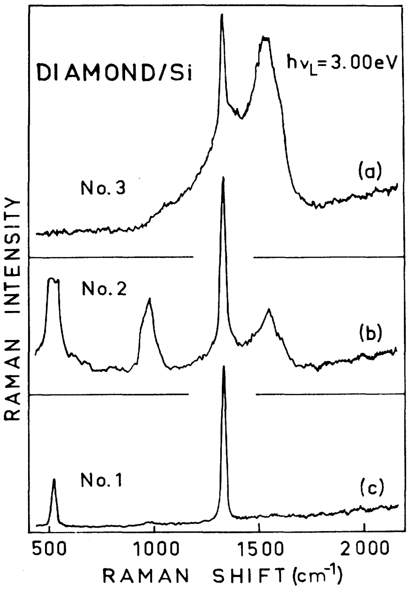

FIG. 4. Raman spectra of three different polycrystalline diamond films. The spectra were excited at 3.00 eV.

clearly seen that the relative intensity of the 1550-cm^{-1} peak increases when going from sample 1 to 3. It is further seen that sample 1 exhibits the highest quality as judged from the relative intensity of the 1332-cm^{-1} Raman line.

Figure 5 displays a sequence of Raman spectra from sample 1 excited with different photon energies as indicated in the figure. For the lowest photon energy of 2.41 eV [Fig. 5(a)] the Raman spectrum is superimposed on a broad photoluminescence background of about equal intensity.[7] The Raman spectrum shows the 1332-cm^{-1} diamond line and some weak indications of the 1550-cm^{-1} peak. The apparent increase in linewidth for the 1332-cm^{-1} line with increasing photon energy is an artifact due to the change in spectral resolution. It varies from 7 cm^{-1} for excitation at 2.41 eV [Fig. 5(a)] to 30 cm^{-1} for 4.82-eV excitation [Fig. 5(d)]. Going up in photon energy from 2.41 to 3.00 eV the photoluminescence background is strongly reduced and the 1550-cm^{-1} peak disappears completely. Increasing the photon energy further also the luminescence background vanishes. From this we can conclude that excitation with photon energies > 3 eV is a convenient way to suppress the interfering luminescence background.

Excitation at high photon energies thus allows the observation of the much weaker second-order Raman spectrum[7,29] from such diamond films. It is displayed in Fig. 6(a) for sample 1. For comparison Fig. 6(b) shows the second-order Raman spectrum of single-crystalline natural diamond. Both spectra excited at 4.82 eV are identical within the noise limits. Therefore we can exclude any effects of finite grain size in the second-oder spectrum of the polycrystalline diamond film. Such effects have been observed, e.g., for various types of microcrystalline graphite.[30]

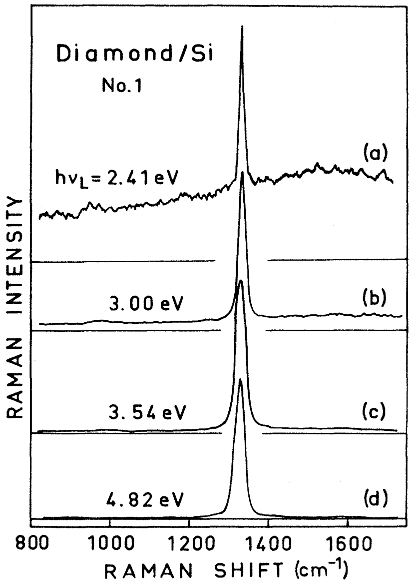

FIG. 5. Raman spectra of polycrystalline diamond film No. 1 excited at different incident photon energies indicated in the figure.

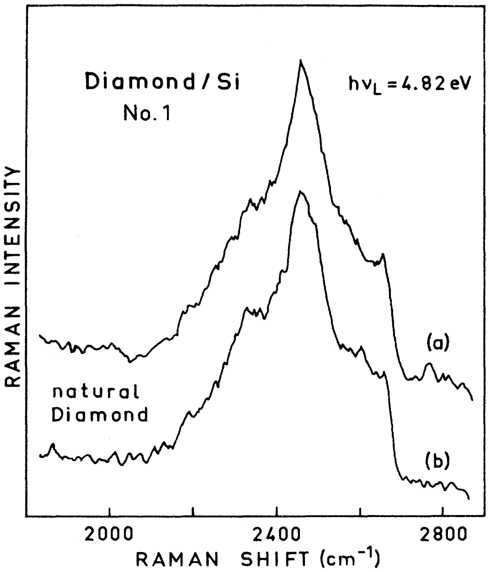

FIG. 6. Second-order Raman spectra of (a) polycrystalline diamond film No. 1 and of (b) natural diamond. The spectra were excited at 4.82 eV.

Raman spectra excited with different photon energies in the range 2.41–4.82 eV are displayed in Figs. 7 and 8 for samples 2 and 3, respectively. Both samples show besides the 1332-cm^{-1} diamond line the $\sim$1550-cm^{-1} Raman peak for all incident photon energies. The relative intensity of the latter peak decreases monotonously with increasing photon energy. Furthermore its peak position shifts by $\sim$50 cm^{-1} to higher frequencies when the photon energy is increased from 3.0 to 4.8 eV [Figs. 7(b)–7(d) and 8(b)–8(d)]. For excitation at 2.41 eV [Figs. 7(a) and 8(a)] its position is also at somewhat higher frequency than for 3.00-eV excitation [Figs. 7(b) and 8(b)]. For 2.41-eV excitation, however, the Raman spectrum is superimposed on a strong luminescence background which complicates the precise determination of the peak position.

The 1332-cm^{-1} Raman line, in contrast, remains fixed in frequency as it is expected from data reported for natural diamond.[29] The apparent increase of the spectral width with increasing photon energy is again due to the change in spectral resolution (see above). The 2TO Raman signal from the silicon substrate observed in the spectra of the sample with incomplete coverage of the substrate (Fig. 7) decreases with increasing photon energy due to the decrease in scattering volume.[31] Summarizing the above results on resonant Raman scattering by polycrystalline diamond films, we note that the relative intensity of the 1550-cm^{-1} Raman peak decreases with increasing incident photon energy. Its peak frequency shifts upon variation of the photon energy.

There are two possibilities to explain the change in relative intensity. First we can assume a resonance enhancement of the 1332-cm^{-1} diamond line for photon energies approaching the energy of the fundamental gap

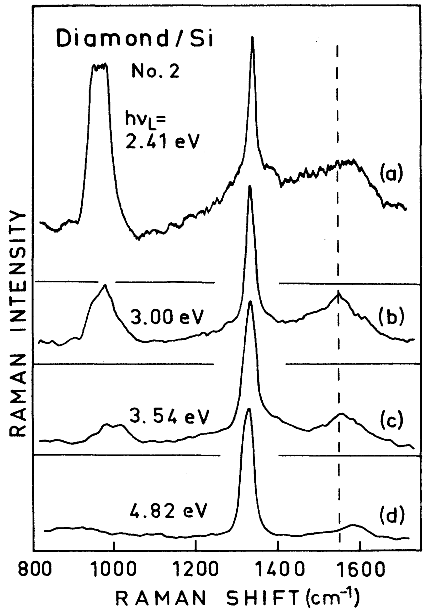

FIG. 7. Raman spectra of polycrystalline diamond film No. 2 excited at different incident photon energies indicated in the figure. The dashed line marks the position of the high-frequency Raman peak for excitation at 3.00 eV.

of diamond (~5.5 eV). However, from resonant Raman scattering on natural diamond crystals it is known that the 1332-cm^{-1} first-order Raman line shows no resonance enhancement for photon energies up to 4.8 eV.[29] Therefore we are left with the second possibility that the Raman signal from the sp^2-bonded carbon decreases with increasing photon energy. This can be due to a decrease in scattering volume with increasing photon energy, which is not completely offset by resonance effects in the scattering efficiency. Thereby we have to assume that the size of the regions consisting of sp^2-bonded carbon is larger than the optical probing depth of the Raman experiment $1/(2\times\alpha)$. Here α denotes the absorption coefficient. Taking the optical properties of microcrystaline graphite[4] as representative for the sp^2-bonded carbon in the present diamond films, the probing depth amounts to ~40 nm for excitation at 2 eV and ~15 nm for excitation at 4.5 eV.[4] Assuming the structure of the sp^2 carbon phase is more like that of amorphous carbon (a-C) the corresponding probing depths amount to ~100 and ~20 nm, respectively.[17] Therefore, taking the variation in probing depth as the mechanism responsible for the changes in relative intensity of the 1550-cm^{-1} peak, we have to postulate that the size of the regions in which the sp^2-bonded carbon is localized must exceed ~50–100 nm.

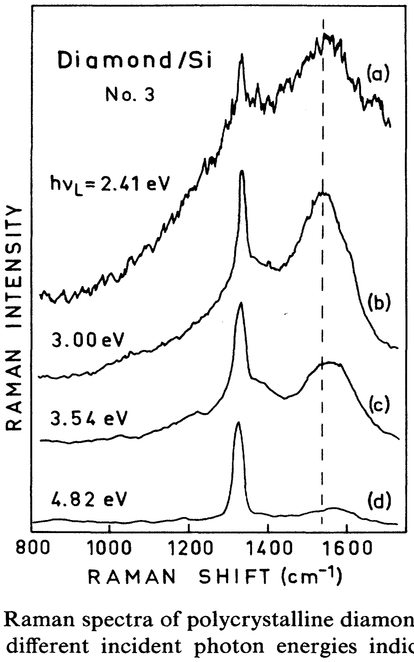

FIG. 8. Raman spectra of polycrystalline diamond film No. 3 excited at different incident photon energies indicated in the figure. The dashed line marks the position of the high-frequency Raman peak for excitation at 3.00 eV.

Similar arguments have been discussed by Shroder *et al.*[32] in an attempt to model the relative intensities of the Raman lines from sp^3-bonded carbon (diamond) and from sp^2-bonded carbon. It was concluded that the intensity of the 1332-cm^{-1} Raman line relative to the 1550-cm^{-1} peak observed in the spectrum of polycrystalline diamond films is only an indirect measure for the relative concentrations of sp^3- and sp^2-bonding carbon. This is on one hand due to the large difference in scattering efficiency of diamond and graphite with the efficiency of graphite being ~50 times larger than of diamond.[8] On the other hand also the size of the regions formed by sp^2-bonded carbon was found to have a significant influence on the relative intensities in the Raman spectrum.[32]

Now we have to discuss the structure of the regions consisting of sp^2-bonded carbon. Microcrystalline graphite can almost be ruled out because for this kind of structure the corresponding Raman peak is expected to occur at 1580–1600 cm^{-1} (Ref. 7) (see Sec. III A). However, the Raman peak assigned to sp^2 carbon in the spectrum of polycrystalline diamond films is centered at ~1550 cm^{-1}. The remaining two possibilities are (1) an amorphous network of sp^2- and possibly sp^3-bonded carbon or (2) an amorphous carbon-silicon alloy.[7] Concerning possibility (1) the structure could be very similar to the one discussed in Sec. III A for a a-C:H with the exception that in the present case the amorphous network should contain only very little hydrogen due to the high substrate temperature during film deposition.[5] Following the arguments discussed in Sec. III A also the observed shift of the 1550-cm^{-1} Raman peak upon variation of the incident photon energy is consistent with the view of a mixed sp^2- and sp^3-bonded carbon network.

From the present experiments we cannot rule out possibility (2) that an amorphous carbon-silicon network is formed. Carbon-rich a-Si$_{1-x}$C$_x$:H films prepared by plasma deposition are known to show a C-C vibrational band in the Raman spectrum the frequency of which varies between ~1470 and ~1560 cm^{-1} for $x=0.5$ and $x=1$, respectively.[33] The above frequencies are valid for excitation at 3.0 eV.[33] It is further known that this C-C vibrational band shifts in frequency upon variation of the exciting photon energy[33] in a way similar to *a*-C:H (see Sec. III A). Therefore the present resonance Raman data are also consistent with the assumption of an amorphous carbon-silicon network containing both sp^2- and sp^3-bonded carbon. The fact that different peak frequencies have been reported in the literature for the high-frequency Raman peak, e.g., ~ 1500 cm^{-1} in Ref. 7 compared to ~ 1550 cm^{-1} in the present study, could be understood in terms of different silicon contents in the amorphous carbon phase. Then, however, the question arises which might be the source for the Si contamination. The Si substrate can almost be excluded because the intensity of the 1550-cm^{-1} Raman band shows no dependence on the film thickness and it is also observed for substrates other than Si. Another possible source might be the walls of the deposition reactor made from silica. However, despite the fact that these walls become coated with carbon after several growth runs, the 1550-cm^{-1} band is also present in films deposited under such wall conditions. Considering these facts it seems unlikely that Si is incorporated in the amorphous network containing sp^2-bonded carbon.

IV. CONCLUSIONS

We have used resonant Raman scattering to study hard and dense hydrogenated amorphous carbon (*a*-C:H) and polycrystalline diamond films. The incident photon energy was varied over a wide range from 2.18 to 4.82 eV. From this experiment information is gained on the microstructure of hard and dense *a*-C:H. These films which contain both sp^2- and sp^3-bonded carbon show a high-frequency shift of the main Raman peak upon increase of the incident photon energy up to 3.5 eV. This shift is explained by scattering from π-bonded sp^2 carbon clusters which is resonantly enhanced for incident photon energies close to the π-π^* transition energy. The present finding supports the view that hard *a*-C:H consists of sp^2 carbon clusters formed by four or more fused sixfold carbon rings which are interconnected by sp^3-bonded carbon.[2,3]

In polycrystalline diamond films the luminescence background interfering with the Raman spectrum for excitation in the visible range could be suppressed by excitation with photon energies >3 eV. This allows one to observe besides the first-order also the much weaker second-order Raman spectrum of crystalline diamond. The relative intensity of the broad Raman peak at ~ 1550 cm^{-1}, which arises from amorphous carbon,[7] was found to decrease with increasing photon energy. This is understood in terms of a decreasing probing depth of the Raman experiment with increasing photon energy. It implies that the size of the regions which give rise to the 1550-cm^{-1} Raman peak must be larger than the probing depth of the Raman experiment in these regions, i.e., $\gtrsim 50-100$ nm. The observed frequency shift of the 1550-cm^{-1} peak upon variation of the incident photon energy is consistent with the view that this peak arises from scattering in an amorphous network of sp^2- and sp^3-bonded carbon.[7]

ACKNOWLEDGMENTS

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