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Interactions of hydrogen and methyl radicals with diamond C(111) studied by sum-frequency vibrational spectroscopy

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Methyl-radical and atomic hydrogen adsorption on C(111) have been studied by infrared-visible sum-frequency vibrational spectroscopy. Methyl iodide, di-tert-butyl-peroxide, and methane passing through a hot filament are used to produce methyl radicals (CH_3). Low-energy CH_3 from pyrolytic dissociation at ~800 °C adsorb intact on the surface, but with surface annealing above 350 °C, convert to tetrahedrally bonded CH. High-energy CH_3 produced at ~1800 °C convert readily to CH upon adsorption. Co-dosing a high-temperature (~800 °C) C(111) substrate with hydrogen and methane via a hot filament at ~1800 °C yields only the stable tetrahedrally-bonded CH-species on the surface. They appear to stabilize the diamond surface structure. The coverage is not full, leaving sites open for CH_3 to adsorb and convert to CH as is necessary for chemical vapor deposition diamond growth. [S0163-1829(96)00136-1]

I. INTRODUCTION

For chemical vapor deposition (CVD) diamond-thin-film growth[1] using thermal or plasma activation of gas phase species, the conditions leading to good diamond growth are generally known but the detailed mechanisms are not yet clear. Although a great deal of work has been done in the studies of gas composition and gas phase reactions under CVD conditions, very little is known about the surface species existing and surface reactions occurring during the diamond growth. In an attempt to determine the growth mechanism, various techniques, such as resonance-enhanced multiphoton ionization[2] and substrate microprobes,[3] have been used to identify gas phase species near the surface. However, the data do not provide direct information on which surface species are present, causing ambiguity in the interpretation of the results. Clearly, for a better study of the growth process, an *in situ* probe involving surface-vibrational spectroscopy that allows identification of surface species is desirable. Indeed, electron-energy-loss spectroscopy[4–6] and Fourier-transform infrared spectroscopy[7] have been employed for such studies. More recently, infrared-visible sum-frequency generation (SFG) as a surface vibrational spectroscopic probe has been developed.[8] Its high-sensitivity, high-resolution, and high-surface specificity makes it ideal for *in situ* probing of CVD growth processes.

Hydrogen has been found to be a key ingredient for consistently high-quality diamond growth.[1] The study of hydrides on diamond surfaces is important and has been carried out by several researchers. Waclawski *et al.*[4] first used high-resolution electron-energy-loss spectroscopy (HREELS) to obtain the vibrational spectrum of an as-polished C(111) surface and concluded that the surface was terminated by CH_3. Lee and Apai[5] studied hydrogen adsorption on C(111). From their HREELS spectra, they identified the presence of surface-phonons on the bare reconstructed C(111) surface, and suggested a plethora of different hydrogen terminations for hydrogen adsorption on C(111). Aizawa *et al.*[6] used HREELS to study the C(111) surface of diamond homoepitaxially grown by CVD under microwave plasma-assisted deposition conditions. They also interpreted the spectrum as due to the presence of CH_3 termination on the surface.

In our earlier work using nonlinear optical spectroscopy,[9,10] the interaction of atomic hydrogen with the diamond C(111) surface was also investigated. The SFG probe proved to be extremely powerful at studying the nature of the hydride termination. Atomic hydrogen (dosed or as-polished) was shown to terminate the C(111)-(1×1) bulk-terminated surface at top sites as a monohydride species. Upon hydrogen desorption at high-temperatures (>1150 °C), the surface undergoes a reconstruction to the (2×1) geometry.

Although the study of hydrides on a diamond surface is important, we have not addressed the issues associated with the diamond growth. Typically, CVD diamond growth involves a hydrocarbon gas such as methane, which is often heavily diluted by hydrogen ($<1\%$ CH_4 in H_2). The gas mixture is passed through a hot filament or plasma-decomposed before impinging onto the high-temperature substrate (~850 °C).[11] The successful use of methane suggests that CH_x ($x=1,2,3$) radicals may play an important role in the growth process. There is the question whether any of the CH_x radicals appear on the surface during the process. *In situ* vibrational spectroscopic studies are clearly in order. If a methyl species is able to sit at top sites, the characteristic vibrational signature should be distinctly different from that of the monohydride.[9,10] In this paper, we will address the problem of methyl adsorption and conversion on the diamond C(111) surface.

We first describe briefly, in Secs. II and III, respectively, the relevant aspects of SFG spectroscopy and the experimental arrangement. We then present the experimental results in Sec. IV and give a qualitative discussion in Sec. V.

II. SUM-FREQUENCY VIBRATIONAL SPECTROSCOPY

Infrared-visible SFG as a surface-vibrational spectroscopic technique has been described in earlier publications.[8] The process is forbidden under the electric-dipole approximation in a medium with inversion symmetry, but is necessarily allowed at a surface or interface. It has therefore been used as a surface-specific analytical tool. The SF output from a surface, usually taken in the reflected direction, is proportional to the absolute square of the surface-nonlinear susceptibility $\chi^{(2)}$. If the infrared-input is tuned over a surface-vibrational transition, $\chi^{(2)}$ is expected to be resonantly enhanced, thus providing the spectroscopic information.

Generally, $\chi^{(2)}$ has a resonant and a nonresonant part and the resonant contribution can come from several resonances. We can write

$$\mathcal{S} \propto |\chi^{(2)}|^2 \propto \left| \chi^{(2)}_{\mathrm{NR}} + \sum_q \chi^{(2)}_{R,q} \right|^2, \tag{1}$$

where $\mathcal{S}$ is the SFG signal, $\chi^{(2)}_{\mathrm{NR}}$ is the nonresonant contribution and

$$\chi^{(2)}_{R,q} = A_q / (\omega - \omega_q + i\Gamma_q) \tag{2}$$

is the resonant contribution from the qth-resonant mode characterized by the strength A_q, resonant frequency ω_q, and damping constant Γ_q. Interference between various terms in Eq. (1) can distort the spectral line shape. Parametric fitting of an experimental spectrum by Eqs. (1) and (2), however, allows the determination of all the parameters characterizing the resonances.

The independent nonvanishing elements of $\chi^{(2)}$ can be determined by SFG measurements using various polarization combinations. For example, $\chi^{(2)}_{yyz}(\omega_{\mathrm{SFG}} = \omega_{vis} + \omega_{\mathrm{IR}})$ ($\hat{z}$ being along the surface normal and $\hat{x}$ along the surface in the plane of incidence) for a surface with inversion symmetry in the plane can be obtained with s-polarized output, s-polarized visible input, and p-polarized infrared input (denoted as ssp). This is the element that provides the most spectroscopic information about H and $\mathrm{CH_x}$ adsorbates on diamond.

With the assumption that adsorbate-adsorbate interaction can be neglected, $\chi^{(2)}_R$ of adsorbates can be related to the resonant polarizability α_R of a bond or group of atoms in the adsorbate.

$$\chi^{(2)}_{R,ijk} = N_S \sum_{lmn} \langle (\hat{i} \cdot \hat{l})(\hat{j} \cdot \hat{m})(\hat{k} \cdot \hat{n}) \rangle \alpha^{(2)}_{R,lmn}. \tag{3}$$

Here, N_S is the surface density of adsorbates, $\hat{l}$, $\hat{m}$, $\hat{n}$ describe the molecular coordinate axes, and the angular brackets denote an average over the orientational distribution of the bond or atomic group. Consider, for example, a monolayer of methyl ($\mathrm{CH_3}$) radicals adsorbed on a surface. Let $\alpha^{(2)}$ be the polarizability of the $\mathrm{CH_3}$ group. We find for an azimuthally-symmetric orientational distribution,[12]

$$\begin{aligned}
\chi^{(2)}_{R,YYZ}(v_s) &= N_s \alpha^{(2)}_{\zeta\zeta\zeta}[(\gamma+1)\langle\cos\theta\rangle + (\gamma-1)\langle\cos^3\theta\rangle],\\
\chi^{(2)}_{R,YYZ}(v_d) &= -\frac{N_S}{2}\,\alpha^{(2)}_{\zeta\eta\eta}\langle\cos\theta\,\sin^2\theta\rangle,\\
\chi^{(2)}_{R,YZY}(v_s) &= N_S \alpha^{(2)}_{\zeta\zeta\zeta}(1-\gamma)\langle\cos\theta\,\sin^2\theta\rangle,\\
\chi^{(2)}_{R,YZY}(v_d) &= \tfrac{1}{2} N_S \alpha^{(2)}_{\zeta\eta\eta}\langle\cos^3\theta\rangle,
\end{aligned} \tag{4}$$

where v_s and v_d refer to the symmetric and antisymmetric $\mathrm{CH_3}$ stretch modes, respectively, $\hat{\zeta}$ and $\hat{\eta}$ are unit vectors parallel and perpendicular to the $\mathrm{CH_3}$ symmetric axis, respectively, $\gamma = \alpha^{(2)}_{R,\zeta\zeta\zeta}/\alpha^{(2)}_{\eta\eta\zeta}$ is estimated to be 1.66 based upon Raman-depolarization measurements of the $\mathrm{CH_3}$ symmetric stretch of methanol,[13] and θ is the polar angle of the $\mathrm{CH_3}$ symmetric axis with respect to the surface normal.

III. EXPERIMENTAL ARRANGEMENT AND SAMPLE PREPARATION

The experimental setup was similar to that described earlier in the SFG study of hydrogen adsorption on diamond C(111).[9,10] In the present experiment, measurements were made on C(111) with different dopants under a variety of substrate temperatures, dosing conditions, and subsequent processing.

The diamond substrate was polished and cleaned in the usual way. A well-ordered hydrogen-terminated C(111)-(1×1) surface could be obtained consistently by atomic-hydrogen dosing (through a hot filament[14] at temperature ∼1800 °C) on the diamond substrate at ∼850 °C. It was characterized by a single, narrow CH stretch peak at ∼2835 $\mathrm{cm^{-1}}$ in the SFG spectrum. The (1×1) surface structure remained upon hydrogen desorption until a coverage of less than 0.05 ML at which the surface reconstructs to (2×1).[9] Most of our dosing experiments used the nearly bare C(111)-(1×1) surface as the starting substrate.

For the study of methyl-radical adsorption on C(111), methyl radicals were produced by thermal dissociation of a number of parent molecules using a hot filament. The production of $\mathrm{CH_3}$ from methane ($\mathrm{CH_4}$) (dissociation energy $E_{\text{C-H}} = 435$ kJ/mol) required a hot filament temperature (∼1800 °C) similar to that for production of H from $\mathrm{H_2}$ ($E_{\text{H-H}} = 436$ kJ/mol). Two other methyl-radical production processes allow lower hot filament temperatures (∼800 °C). Methyl iodide ($\mathrm{CH_3I}$) ($E_{\text{C-I}} = 234$ kJ/mol) dissociates into a methyl-radical and a reactive iodine atom. Both will adsorb onto the diamond surface. Di-tert-butyl peroxide $[\mathrm{(CH_3)_3COOC(CH_3)_3}]$ (DTBP) experiences a breaking of the peroxide bond[15] producing an unstable intermediate that results in decomposition into stable acetone molecules and methyl radicals. Acetone does not seem to adsorb on C(111) and has little effect on radical adsorption on C(111). Dosing with acetone (10^{-5} torr) with the same hot filament was found not to cause any changes to the covered or bare diamond surface. Only if the hot filament temperature was increased to ∼950 °C did the SHG or SFG show any changes indicating a modification of the surface, presumably from the activated acetone molecule. Considering that the concentration of the acetone from the DTBP pyrolysis is much lower, the presence of acetone during the DTBP dosing should be negligible. Total dosing pressures of the gases were typically 10^{-5} torr. For the methyl iodide, DTBP, and acetone dosing discussed above, gas was obtained from vaporization of liquid. A freeze-pump-thaw method was performed to remove dissolved volatiles. We also ensured that the filament of the ion pressure gauge had no effect on the excitation or decomposition of CH_3I, DTBP, or CH_4. The substrate temperature could be affected by the hot filament, but the effect was hardly detectable with the filament at ~800 °C and had a rise of ~150 °C with the filament at ~1800 °C.

Unless noted otherwise, the SFG spectra presented in this paper were taken with the *ssp*-polarization combination as this gave the strongest signal.[9]

IV. EXPERIMENTAL RESULTS

A. Establishment of C(111)-(1×1) structure

In our studies of radical adsorption on C(111), the majority of the experiments started with a nearly-bare surface with the (1×1) structure because this is presumably the surface effective for diamond CVD growth. As mentioned earlier, the (1×1) surface can be achieved with ~5% ML of hydrogen coverage. Dosing the bare C(111) surface with methane could also convert the surface structure from (2×1) to (1×1). This was observed with activated methane adsorption using low-energy electron diffraction (LEED), temperature-programmed desorption, and second-harmonic generation, but it took ~0.3 ML coverage for the (1×1) unreconstructed phase to appear clearly in the LEED pattern.[16] The SFG spectra of the methane-dosed (through a hot filament) C(111) surface starting with the bare reconstructed (2×1) structure, however, did not show any discernible features. The same was true for CH_3I and DTBP dosing. Only after annealing at sufficiently high-temperature would the CH_x peaks emerge from the spectra. This could be due to adsorption-induced surface disordering leading to broadening, and hence a weak-spectrum.

In the following, we will not discuss more results of dosing on C(111)-(2×1) as the starting surface, but focus our attention on experiment with C(111)-(1×1) as the starting surface. In our earlier work,[14] it was found that a ~5% ML hydrogen coverage was sufficient to maintain the C(111)-(1×1) surface structure. In the present work, we consider a surface "nearly bare" as a (1×1) surface with 5–10 % hydrogen coverage. This nearly-bare surface was reliably achieved in the following way. It was first exposed at ~800–850 °C to atomic hydrogen for 10–15 min at a molecular hydrogen pressure of 10^{-5} torr to achieve a well-ordered (1×1) surface with monohydride termination. Subsequently, thermal desorption was employed to produce a well-ordered surface with partial monohydride coverage. SFG was used to monitor the reduction of H coverage to 5–10 %. Absence of the C-C stretch modes (in the 1300–1550-cm^{-1} region) in the SFG spectrum was taken as evidence of the existence of the (1×1) surface structure.

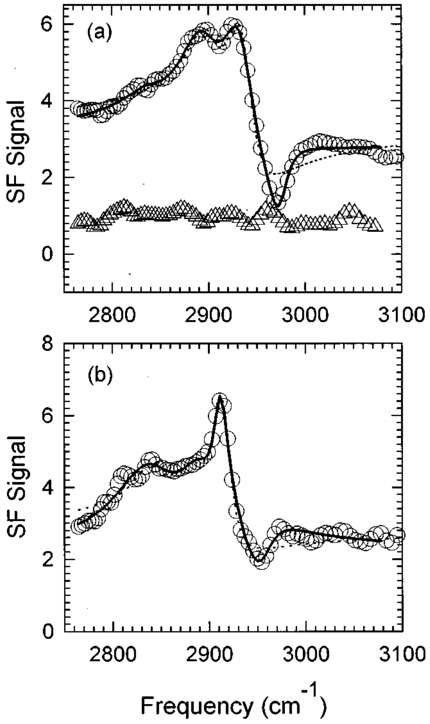

FIG. 1. SFG spectra of the room-temperature diamond C(111) surface dosed by (a) DTBP and (b) CH_3I through a hot filament at ~800 °C. Polarization combinations *ssp* (open circles) and *sps* (open triangles) were used. Solid curves are theoretical fits using Eq. (1) with fitting parameters listed in Table I. The dotted curves are fits neglecting contribution from the asymmetric CH_3 stretch mode. The SF signal is in arbitrary units.

B. Dosing of DTBP and CH_3I

As we mentioned in Sec. III, $(CH_3)_3COOC(CH_3)_3$ (DTBP) and CH_3I at ~800 °C decompose as follows:

$$(CH_3)_3COOC(CH_3)_3 \rightarrow 2CH_3 + 2(CH_3)_2CO,$$

$$CH_3I \rightarrow CH_3 + I.$$

Dosing of DTBP or CH_3I on a nearly-bare C(111)-(1×1) surface through a hot filament at ~800 °C would result in CH_3 adsorption on the diamond surface. In the case of DTBP, coadsorption of acetone appears negligible, but in the case of CH_3I, coadsorption of I is energetically favorable. Figure 1(a) shows the SFG in the CH stretch region of C(111)-(1×1) dosed by activated DTBP to the saturation level. The spectrum obtained with the *sps*-polarization combination (*s*, *p*, and *s* referring to the polarizations of the SF-output, visible input, and infrared input beams, respectively) is weak and does not exhibit any discernible features. The *ssp*-polarization combination yields a clear spectrum, although it does not have the profile of an absorption spectrum because of the interference between resonant and nonresonant contributions to the SFG. We can use Eqs. (1) and (2) to fit the observed spectrum and find the resonant modes and their characters. In Fig. 1(a), the solid line corresponds to a four-mode fit with the fitting parameters listed in Table I. The four modes at 2840, 2896, 2935, and 2975 cm^{-1} can be attributed to the CH stretch, $CH_3(s)$ (symmetric stretch), CH_3(FR) (Fermi-resonance between symmetric stretch and bending), and $CH_3(d)$ (asymmetric stretch), respectively. In comparison, it is known that H on C(111)-(1×1), in stable equilibrium, has a stretch-frequency of 2835 cm^{-1} (corre-

TABLE I. Fitting parameters for SFG (ssp) spectra of nearly-bare C(111) surfaces dosed by activated DTBP and CH_3I, shown in Figs. 2(a) and 2(b), respectively.

($\omega,\Gamma = cm^{-1}$)	CH ($\omega,\Gamma,A/\Gamma$)	$CH_3(s)$ ($\omega,\Gamma,A/\Gamma$)	CH_3(FR) ($\omega,\Gamma,A/\Gamma$)	$CH_3(d)$ ($\omega,\Gamma,A/\Gamma$)	$\chi_{NR}^{(2)}$ ($\lvert\chi_{NR}^{(2)}\rvert,\phi$)
DTBP	2840,25,1.1	2896,25,4.9	2935,21,8.7	2975,15,−5.8	17,230°
CH_3I	2839,42,6.3	2889,27,6.6	2910,10,8.9	2955,19,−30	15,240°

sponding to H adsorbed on a top site with an sp^3-bond). The $CH_3(s)$, CH_3(FR), and $CH_3(d)$-modes of alcohols or alkane chains have frequencies at 2875–2880, 2935–2940, and 2960–2975 cm^{-1}, respectively. We note that in our fitting of the spectrum, it was necessary to include the $CH_3(d)$-mode. Its contribution to $\chi^{(2)}$ is opposite in phase to that of $CH_3(s)$ and CH_3(FR) and makes the dip at 2970 cm^{-1} more pronounced.[17] Exclusion of the $CH_3(d)$-mode leads to a poorer fit in the 2970 cm^{-1} region as depicted by the dotted curve.

The spectra of Fig. 1(a) yield the following information. The CH species (or H) adsorbed on the surface is small (~10% ML estimated by comparison with the signal from a saturation coverage of H). The CH_2 species may also be present on the surface, but their amount is also not very significant. From the geometric consideration, it is unlikely that the C(111)-(1×1) surface could support the bridge sites needed for CH_2 adsorption. The CH_3 species appears to be the dominant adsorbates on the surface. The polarization dependence and the appearance of the $CH_3(d)$-mode in the ssp-spectrum suggest that the CH_3 radicals are oriented on average with the symmetric axis along the surface normal, but the orientational distribution has a large angular spread.

Similar results were found when the nearly-bare C(111)-(1×1) surface was dosed with CH_3I through a hot filament at ~800 °C. The ssp-SFG-spectrum is displayed in Fig. 1(b); the sps-spectrum is again weak and offers little information. Possibly because of coadsorption of I on the surface, the surface density of CH_3 is smaller than that in the DTBP case, resulting in a weaker spectrum. However, the spectrum can still be fit with four resonant modes using Eqs. (1) and (2). The fitting parameters are listed in Table I. As in the case of DTBP-dosing, the four modes at 2939, 2889, 2910, and 2955 cm^{-1} are assigned to CH-stretch, $CH_3(s)$, CH_3(FR), and $CH_3(d)$, respectively. The frequencies of the CH_3 modes appear redshifted from the usual ones, perhaps because of influence from I as coadsorbed-neighbors. The observed spectrum again suggests that the C(111)-(1×1) surface is mainly covered by CH_3 (together with I) with only a small amount of H or CH.

If either of the above CH_3-covered diamond surface were heated, conversion of CH_3 to CH could result. Figure 2 describes a set of ssp-SFG-spectrum for a DTBP-dosed surface heated to different temperatures. (All spectra were taken with the sample heated to the stated temperature for 10 min and then cooled down to room temperature for the SFG measurement.) It is seen that with increasing temperature the CH_3 modes reduce in strength, but the CH peak grows. In the intermediate temperature range, a new peak at ~2865 cm^{-1} is clearly visible. This appears to be the same mode that has been observed in the spectra taken when a bare-reconstructed C(111)-(2×1) surface was dosed and partially covered by atomic hydrogen.[10] It was believed to be a CH-stretch mode associated with H adsorbed at unrelaxed surface sites. (It could be that H adsorbed on C in a metastable geometry with a strained sp^3-bond.) At sufficiently high temperatures (>650 °C), only the ~2835 cm^{-1} CH-peak dominates. The spectra in Fig. 2 clearly indicate that CH_3 adsorbed on C(111)-(1×1) can be converted into CH when the substrate temperature is sufficiently high.

Figure 3 shows a similar set of spectra for the CH_3I-dosed C(111)-(1×1) surface. They exhibit the same behavior suggesting the conversion of CH_3 to CH at sufficiently high substrate temperatures. We note that in both cases, conversion of the CH_3 species is already significant at ~350 °C. This was found to be true even if the substrate was kept at that temperature for only ~1 min. The process is apparently surface-mediated since in the gas phase a much higher temperature would be required to break the CH covalent bonds.

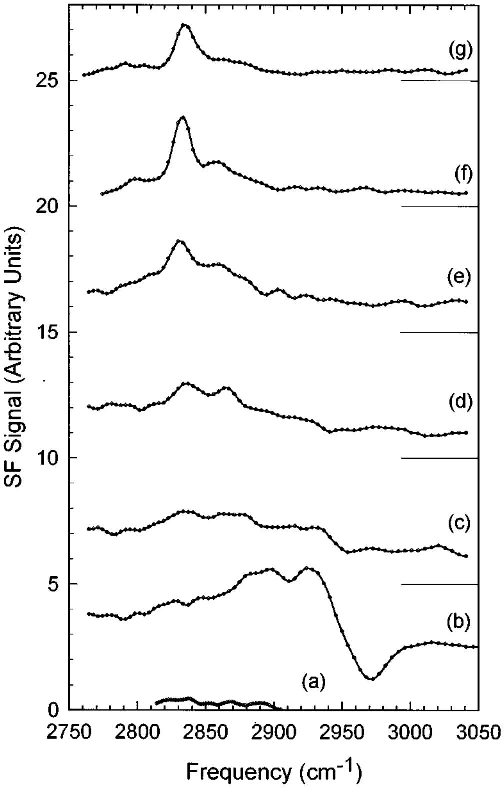

FIG. 2. SFG spectra exhibiting the effects of surface annealing after dosing of DTBP (through an ~800 °C hot filament) on C(111) at room temperature. (a) Nearly-bare surface, (b) as-dosed surface, (c)–(g) dosed surface annealed at 350 °C, 500 °C, 620 °C, 740 °C, and 800 °C, respectively. Spectra (c)–(g) have been incrementally shifted upwards by five units for clarity.

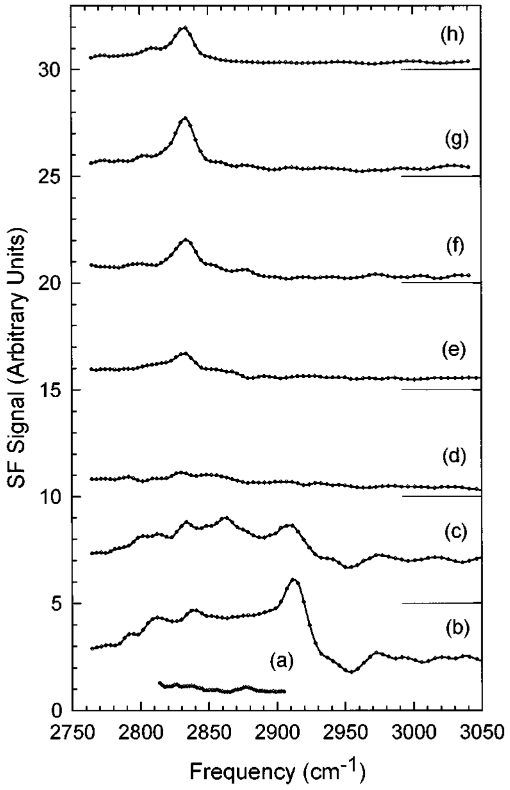

FIG. 3. SFG spectra showing the effects of surface annealing after dosing of CH_3I (through an ~800 °C hot filament) on C(111) at room temperature. (a) Nearly-bare surface, (b) as-dosed surface, (c)–(h) surface annealed at 350 °C, 450 °C, 550 °C, 660 °C, 740 °C, and 800 °C, respectively. Spectra (c)–(h) have been incrementally shifted upwards by five units for clarity.

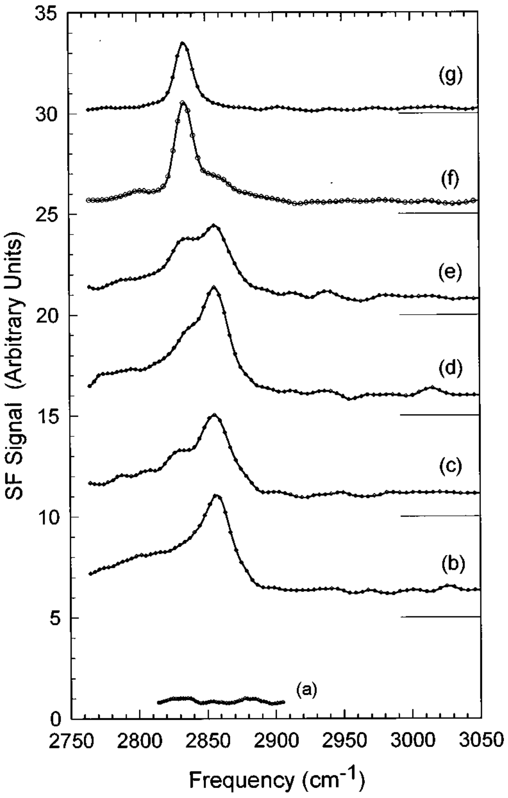

FIG. 4. SFG spectra showing the effects of surface annealing after dosing of CH_4 (through an ~1800 °C hot filament) on C(111) at room temperature. (a) Nearly-bare surface, (b) as-dosed surface, (c)–(g) surface annealed at 350 °C, 450 °C, 555 °C, 660 °C, and 775 °C, respectively. Spectra (b)–(g) have been incrementally shifted upwards by five units for clarity.

The conversion of the methyl species on the C(111) surface seems to have begun at temperature around 250 °C.

C. Dosing of CH_4

CH_4 decomposes into CH_3 and H at ~1800 °C. Therefore, dosing of CH_4 on C(111)-(1×1) through a hot filament at 1800 °C could lead to adsorption of CH_3 and H on the diamond surface. One would then expect to observe CH and CH_3 modes in the SFG spectrum. The spectra in Fig. 4, taken from an as-dosed C(111)-(1×1) surface and a dosed surface that has been annealed for 10 min at various temperatures, however, show little evidence of the presence of the CH_3 species. Only two peaks are prominent in the spectra, one at 2835 cm^{-1} and the other at 2865 cm^{-1}. As we discussed earlier, they can be identified as the CH-stretch modes associated with H adsorbed at top sites of C(111)-(1×1) and at local unrelaxed sites, respectively. At low temperatures ($\leq$150 °C), the 2865-cm^{-1} mode appears to dominate. With increasing annealing temperatures, the 2865 cm^{-1} mode is converted increasingly to the 2835 cm^{-1} mode. At the annealing temperature of 775 °C, part of the H has been desorbed, leading to a lower peak at 2835 cm^{-1}.

There are three possibilities why the CH_3 signal in the spectra of Fig. 4 is weak. First, CH_3 might not readily adsorb on the surface. This is not likely considering that CH_3 does appear on the surface when dosed with CH_3I. Second, the surface with CH_3 adsorbates might be disordered and the orientational distribution of CH_3 might have a wide angular spread. Disordering could be caused by high-energy H and CH_3, which were generated by the very hot (~1800 °C) filament, impinging on the surface. We have found that dosing of H on a room-temperature diamond surface does lead to gradual disordering of the room-temperature surface. Third, the adsorbed CH_3 might have been converted to CH upon adsorption. The conversion process could be more efficient than in the cases of CH_3I and DTBP-dosing because of the higher energy possessed by the impinging species. The last two possibilities may be both operative.

To see whether the energy carried by CH_3 has any effects on the CH_3 adsorption and conversion, we have studied CH_3I-dosing with the hot filament set at ~1800 °C instead of ~800 °C. The spectra in Fig. 5 appear quite different from those in Fig. 3. With the hot filament at ~1800 °C, the CH_3 spectral features are very much weaker and both CH stretch modes, at 2835 and 2865 cm^{-1}, are now prominent even though the substrate is never annealed. Clearly, a significant portion of CH_3 adsorbed on the surface must have converted to CH upon adsorption. The presence of the two CH modes indicates that part of the CH-species is in the unrelaxed position. With the substrate heated to and annealed at increasingly high temperatures, the CH-mode at 2835 cm^{-1} associated with H adsorbed at the top site of the well-ordered C(111)-(1×1) structure becomes more and more pronounced

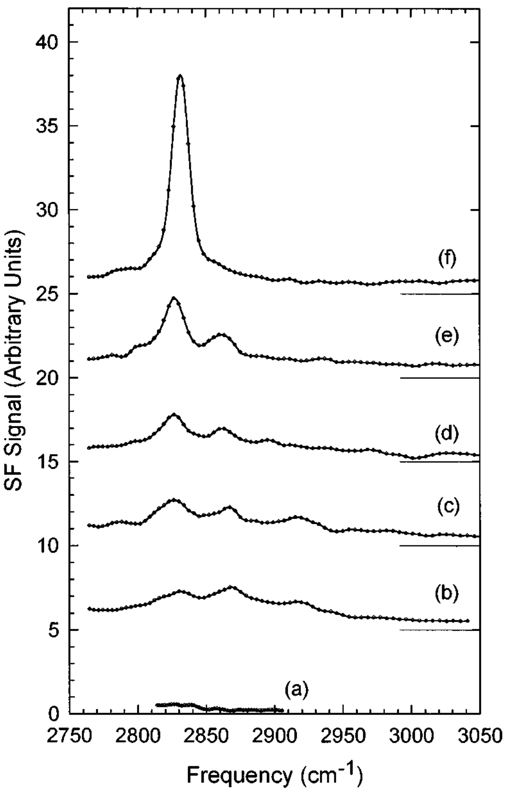

FIG. 5. SFG spectra showing the effects of thermal treatments after dosing of CH_3I (through an ~1800 °C hot filament) on C(111) at room temperature. (a) Nearly-bare surface, (b) as-dosed surface, (c)–(f) surface annealed at 350 °C, 450 °C, 550 °C, and 660 °C, respectively. Spectra (b)–(f) have been incrementally shifted upwards by five units for clarity.

as more adsorbed species are converted into this most stable adsorbed species. The result of this experiment indicates that the more energetic CH_3 impinging on the C(111) does tend to make the surface disordered and enhances the conversion of CH_3 to CH on the surface.

With CH_4-dosing, direct adsorption of H on the C(111) surface must also occur. This makes the CH spectral feature much more prominent in comparison with the CH_3I dosing case [Fig. 4(b) versus Fig. 5(b)].

D. Dosing on high-temperature substrates by activated hydrogen and methane

The usual CVD growth of diamond occurs with the substrate kept at high temperatures (~800 °C).[1] To simulate the CVD condition, we have studied dosing of CH_4 on C(111)-(1×1) kept at ~820 °C. The SFG-spectrum was taken after the heated nearly-bare surface had been exposed to 10^{-5} torr of CH_4 for 5–10 min and cooled down to room-temperature. It was found to be very weak with a hardly visible feature at 2835 cm^{-1}, indicating the presence of less than 5% of H adsorbed on the surface. This spectrum is very different from the one taken with the substrate kept at room-temperature all the time [Fig. 4(b)]. A possible explanation is that CH_3 radicals react with the high-temperature surface in many different ways resulting in many different CH_x adsorbed species and a very much disordered surface that limit the hydrogen adsorption or formation of the stable CH species with C saturated by tetrahedrally-ordered sp^3-bonds.

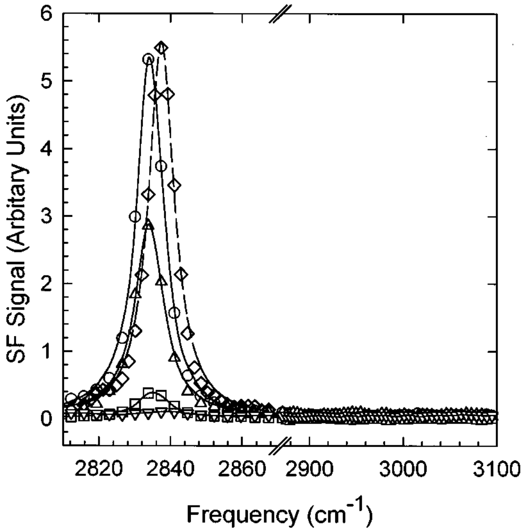

FIG. 6. SFG spectra of C(111) at 820 °C dosed by activated CH_4/H_2 mixtures. (a) 100% H_2 (diamonds), (b) 0.5% CH_4/99.5% H_2 (circles), (c) 10% CH_4/90% H_2 (up triangles), (d) 50% CH_4/50% H_2 (squares), and (e) 100% CH_4 (down triangles). The lines represent fits to the data using Eq. (1) with a single resonance.

Dosing with a mixture of H_2 and CH_4 improves the chance of forming stable CH species. Figure 6 shows that as the H_2/CH_4 composition changes from 0/100 to 50/50, 90/10, and 100/0, the 2835-cm^{-1}-mode increases in strength from 5% to 10%, 50%, and 100%. The gas pressure used was 5×10^{-6} torr and the spectra appeared independent of the dosing time after 15 min of dosing. The single, narrow peak at 2835 cm^{-1} in the spectra is an indication that H is always associated with the stable CH species on the surface. It can come from direct adsorption of H as well as conversion of the adsorbed CH_x species.

It has been found that dosing of atomic hydrogen on a high-temperature C(111)-surface stabilizes the surface in the (1×1) structure.[10,18] In the present experiment, we have studied a C(111)-surface dosed by activated CH_4 [Fig. 4(b)] and subsequently exposed to atomic hydrogen with the substrate heated to ~820 °C. A single, narrow peak at 2835 cm^{-1} was observed in the spectrum indicating the appearance of a well-ordered C(111)-(1×1) hydrogen-terminated structure. We note that for effective CVD diamond growth, the typical gas mixture often used contains an excessively large amount of H_2,[1] e.g., H_2/CH_4 of 100/1. Presumably, the role of H_2 is to supply H to keep the surface in the well-ordered C(111)-(1×1) structure and to abstract unwanted CH_x-adsorbed species, leaving only CH and CH_3 species that are adsorbed to the substrate by sp^3-bonding.[10,18]

Dosing of activated CH_4 on a well-ordered hydrogen-terminated C(111) surface was found to reduce significantly the 2835 cm^{-1} CH-peak, but this was presumably due to surface-disordering incurred by high-energy bombardment of H and CH_3 as the full strength of the peak could be fully recovered by subsequent annealing of the substrate. The same was true with activated CH_3I-dosing. The results suggest that either CH_3 cannot easily replace the adsorbed H, or CH_3 would replace H, convert into CH, and form a new relaxed tetrahedrally-bonded surface CH layer. The latter appears energetically less favorable.

V. DISCUSSION

The experiment described above shows that SFG vibrational spectroscopy can be used to monitor *in situ* radical adsorptions and reactions on a surface. This is just what we need to understand the mechanism of a CVD process. Methyl radical (CH_3) adsorption on diamond C(111) is likely the first step of CVD-homoepitaxial growth of diamond from the (111) surface. However, in usual CVD diamond growth, high-temperature hot filaments (~1 800 °C) are often used to thermally dissociate methane or methyl derivatives to produce methyl radicals. It is then possible that other CH_x ($x=1,2$) radicals may also be produced in the process. In order to study CH_3 adsorption on C(111) without the complication of coadsorption of CH_x, we must choose methyl derivatives that can decompose and produce CH_3 at a sufficiently low-temperature such that the probability of thermal-dissociation into CH_x ($x=1,2$) is negligible. DTBP and CH_3I satisfy the condition; they yield CH_3 in passing through a hot filament at ~800 °C. The SFG vibrational spectra of the DTBP and CH_3I-dosed C(111) surfaces at room temperature are indeed dominated by the CH_3 stretch resonances. The resonant features in the spectra appear to be significantly broader than those of CH_3 in the spectra of well-ordered alkane chains. The nonresonant background also appears to have increased after dosing. Both probably arise from surface-inhomogenity and disordering caused by radical bombardment of the surface and adsorption on nonequilibrium sites. Interactions of CH_3 with neighboring coadsorbed species (such as I in the case of CH_3I) could also shift the frequencies of the CH_3 modes. We have observed that if the hot filament was adjusted to higher-temperatures, and/or DTBP or CH_3I-dosing lasted over a longer period, the SFG-spectra of CH_3 on C(111) were significantly poorer.

The SFG-spectra of DTBP and CH_3I-dosed C(111) surface at room-temperature show no discernible features due to CH_x ($x=1,2$). This indicates that the surface coverage of CH_x must be relatively insignificant. From energy consideration, the appearance of CH_2 species is believed to be unlikely. Not only the production of CH_2 by our hot filament should have been negligible, but conversion of CH_3 to CH_2 on the surface should have been impeded by the lack of appropriate adsorption sites on the C(111) surface.

One would expect that the SFG-spectra could allow a quantitative evaluation of the CH_3 orientations and coverages on the C(111) surface. Unfortunately, this would be possible only if the orientational distribution of the adsorbed CH_3 were known and a reference spectrum for a C(111) surface fully covered by CH_3 were available. Neither is true in the present case. In particular, we do not yet know how to prepare a diamond surface with a well-ordered full monolayer of CH_3-adsorbates. We are therefore forced to discuss our results in relative, qualitative terms. The study of H-adsorbates on C(111) is different. The 2835 cm^{-1}-peak in the SFG vibrational spectrum is well understood as the CH stretch mode for H adsorbed on top sites of a C(111)-(1×1) structure with an sp^3-bond. The reference spectrum of a fully H-terminated C(111) surface is available. Thus the strength of the 2835-cm^{-1}-peak can be used as a direct measure of the H coverage on the surface.

The SFG spectra indicate that if the C(111) surface is dosed by DTBP or CH_3I through a hot filament at 800 °C, CH_3 (and I)-species seem to have a dominant coverage on the surface. Only after the surface is annealed at high-temperature for a sufficient amount of time will CH_3 be converted to CH. However, if the dosing is through a hot filament at 1800 °C, then CH_3 impinging on the surface can be readily converted to CH. The latter situation is also what happens with CH_4-dosing although in this case both CH_3 and H from dissociation of CH_4 will impinge and adsorb on the surface. Conversion of CH_3 to CH on the surface is obviously surface-mediated because the surface annealing temperature required for the conversion is only several hundred degrees, which is an order of magnitude less than what is needed for decomposition of CH_3 to CH in the gas phase.

We also note that from the observation of two CH stretch peaks (at 2835 and 2865 cm^{-1}) in the spectra, there appears to be two general configurations of CH on the C(111)-surface, irrespective of whether the CH species comes from CH_3-conversion or directly from H-adsorption on C(111). One is the stable configuration in which the C atom of CH connects with three neighboring C by tetrahedral-sp^3-bonding into a well-ordered local diamond structure. The other is a metastable configuration in which C of CH is bonded to the neighboring C in an energetically less favorable position. Recently, Busmann *et al.*[19] used scanning tunneling microscopy to probe the surface of vapor-grown polycrystalline diamond films. They observed in the (111) surface domains a $\sqrt{3}\times\sqrt{3}\ R\ 30°$ superstructure. This superstructure was attributed to the formation of carbon trimers on the surface. Molecular dynamics calculation has shown that such a structure could be stable and the trimers could support monohydride termination with one hydrogen atom bonded to each carbon atom at a near-top site. More recently, Zhigilei, Srivastava, and Garrison[20] in their molecular dynamics simulation have found that at relatively low-surface coverages of H on C(111), part of the hydrogen atoms could be adsorbed on carbon atoms at localized highly strained configurations intermediate between (1×1) and (2×1) structures. These adsorbed hydrogen atoms actually lead to a CH stretch-vibrational peak at a higher frequency than the one arising from the bulk-terminated hydrogen atoms. Thermal annealing or higher hydrogen coverages could relax the strained configuration and convert the higher-frequency peak to the lower one.

The formation of the stable CH species on the C(111) surface at low-temperatures may take two steps. First, adsorption of H on C or conversion of CH_3 to CH yields the metastable CH species. Then, surface-annealing converts the metastable CH to stable CH. Annealing also appears to be effective in removing the surface disorder incurred by bombardment of radicals during adsorption. We have found that the stable CH peak in the spectrum of a fully-annealed, initially CH_3-saturated, C(111) surface never has a strength half as strong as that of a fully H-terminated C(111) surface. This indicates that the saturation coverage of CH_3 can never reach a full monolayer (referred to the surface carbon monolayer).

Dosing of C(111) at high-temperatures (~820 °C) by H_2 and CH_4 gas mixtures through a hot filament (~1800 °C) yields spectra with only a single discernible peak at 2835 cm^{-1} representing the stable CH species. The strength of the peak increases very gradually with the hydrogen composition in the mixture. This indicates that H only appears on the surface with the stable sp^3-bonding. Its surface coverage is determined by dynamic equilibrium between adsorption and desorption and only approaches a full monolayer at a H partial pressure of $\sim 5\times 10^{-6}$ torr. The equilibrium surface coverage of CH_3 is even much lower at the same partial pressure. Any adsorbed CH_3 may have been rapidly converted to stable CH, but the amount must be small.

Our spectroscopic results suggest the following picture. H and CH_3 radicals can adsorb on the C(111) surface. The former adsorbs with a higher probability and bonds to the surface carbon atoms in two possible configurations, one stable and one metastable as mentioned earlier. At sufficiently high surface temperatures, the adsorbed CH_3 can be converted to CH through surface-mediated reactions, first into the metastable configuration and then to the stable one. Increasing the temperature speeds up the conversion. At normal CVD operating temperatures, only the stable CH species has a detectable amount on the surface. Higher hydrogen-dosing pressures lead to higher coverages of the surface by the stable CH species and a better ordered C(111)-(1×1) surface. We realize from the surface geometric consideration, conversion of CH_3 into a stable or metastable CH on the surface would require reactions with several neighboring adsorbed CH_3 radicals to establish a local tetrahedral diamondlike structure.

How can the above picture be consistent with what we know about CVD homoepitaxial diamond growth? In the CVD process, it is important to have a large H_2/CH_4 ratio ($\sim$100) in the gas mixture for healthy growth. The role of the excessive amount of atomic hydrogen is believed to be promotion of sp^3-bonding of adsorbed hydrocarbons and removal of graphitic carbons with non-sp^3-bonding.[18] Our spectroscopic study here indicates that under normal CVD conditions, the C(111) surface is mostly covered by H at top sites with a well-ordered (1×1) structure. Because of thermal activation, there always exists a significant number of open sites on the surface, and H and CH_3 can compete to occupy these sites. If CH_3 is adsorbed on an open site with a diamondlike sp^3-bonding, then it is not likely to be removed by incoming H. If the bonding is graphitic, then it would be preferentially cleaned off by incoming H. Conversion of CH_3 to CH would have to wait until other CH_3 adsorbates appear by adsorption or diffusion at the neighboring sites so that reactions can occur to link the C atoms into the tetrahedral structure. This CVD process results from a delicate dynamic balance of absorption, desorption, and abstraction of H and CH_3 and conversion of CH_3 to CH. One would therefore expect that the diamond growth-rate must be slow and can be appreciable only if high-pressure gas mixtures are used. These are of course well-known facts in CVD diamond growth.

We should remark, in closing, that there is always the possibility that our low-gas-pressure study could yield results very different from those of a practical CVD process with much higher gas pressure. Although the experiment reported here was conducted with the sample in an ultrahigh vacuum chamber, our SFG spectroscopic technique should be applicable to samples in real CVD atmosphere. Such an experiment is being planned.

VI. CONCLUSION

SFG vibrational spectroscopy provides a powerful means to probe *in situ* adsorption and conversion of H and CH_x on diamond surfaces. Low-energy methyl radicals (CH_3) can be produced by passing CH_3I and DTBP through a hot filament at ~800 °C. The methyl radicals can then adsorb on the diamond (111) surface intact. Surface annealing even at relatively low-temperatures (>350 °C), however, can convert CH_3 to CH. The conversion leads first to a CH bonded in a metastable configuration and then to a CH bonded in a diamondlike stable configuration. The amount of CH_2 species on the surface, if any, is small. This conversion process could be important in CVD diamond growth. With the hot filament set at ~1800 °C, high-energy CH_3 are produced from pyrolytic dissociation of CH_3I and CH_4. Upon adsorption on the C(111) surface, most of the methyl radicals seem to convert immediately to CH. Thus, energy input is clearly required for the conversion of CH_3 to CH, either in the form of energy carried by CH_3 or in the form of thermal energy existing on the surface. To partially simulate the conditions of normal CVD growth, dosing of H_2 and CH_4 through an ~1800 °C hot filament onto a C(111) substrate at ~800 °C, has been studied. Hardly any species appears detectable on the surface if the proportion of H_2 in the mixture of $\sim 10^{-5}$ torr is not significant. With increasing proportion of H_2, the surface is seen to be covered more and more with the stably bonded CH species. The high proportion of H_2 in the gas mixture for CVD homoepitaxial diamond growth seems to serve the important function of maintaining the well-ordered C(111)-(1×1) surface structure (mostly H-terminated), uncontaminated by graphitic-carbon species, that is required for the epitaxial growth through CH_3 adsorption and conversion. *In situ* SFG spectroscopic studies of real CVD diamond growth may also be possible.

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