Chemical Vapor Deposition of Diamond: An in Situ Study by Vibrational Spectroscopy

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Beyond the advancements already achieved in the growth of diamond thin films by chemical vapor deposition (CVD)[1,2] there still are a number of important open issues including the further decrease of the temperature of the CVD process[1,3] without a loss in film quality. Another point into which considerable effort has been put is a comprehensive modeling.[4−7] Despite general agreement on a number of key steps and the success of models to reproduce many aspects of the CVD process,[2,8] discrepancies between simulation and experiment still exist, which indicate that essential aspects of the chemistry are not described properly by the models. This is highlighted by the comparison of a comprehensive simulation with experimental results from gas-phase spectroscopy which revealed diverging results of the gas-phase species near the substrate.[6]

Analyzing the literature reveals a striking deficit of experimental data on the surface chemistry of diamond, even though efforts based on ultrahigh vacuum (UHV) experiments have been undertaken.[9,10] In contrast to the gas-phase chemistry where a considerable experimental database exists,[6,11−15] the surface chemistry lacks the input from experiments performed under CVD conditions and, thus, is almost completely based on theoretical work.[8,16−18] The reason for this imbalance is the lack of techniques to probe surface species under the conditions of diamond CVD, that is, pressures in the tens of mbar range and temperatures of up to more than 800 °C. A technique which meets the required conditions of high surface sensitivity, specificity to chemical species, and applicability under non-UHV conditions is IR visible sum frequency generation (SFG). This interface-sensitive vibrational spectroscopy has been very successfully applied in many studies of interfaces,[19,20] including the surface of a natural C(111)-diamond in an UHV environment,[9,21−23] and the (100) surface of a homoepitaxially CVD-grown layer in an inert gas atmosphere.[24]

The experiments presented here focus on changes induced by variation of both the filament and the substrate temperature while leaving the composition of the gas mixture, the pressure, and the flow rate unchanged. Even though the substrate temperature is significantly affected by the filament temperature and, thus, could not be controlled completely independently, additional heating of the substrate allowed changing the surface temperature separately to a significant extent. A variation of about 200 °C between zero and full substrate heating could be achieved, which is sufficient to switch between conditions where the quality of the diamond deposited is high or low, respectively.[25] Therefore, variation of the filament temperature largely determines the chemistry of the gas phase, while changing the substrate temperature mainly affects the surface chemistry.

Figure 1 displays a series of SFG spectra where the filament temperature is changed. No additional substrate heating was applied, and the change in the surface temperature is solely caused by the filament. At a filament temperature of 1400 °C (not shown) no significant spectral features can be identified. This changes if the temperature is raised to 1770 °C. Besides some weak features between 2870 and 2950 $\mathrm{cm^{-1}}$ which will be discussed in more detail in a forthcoming publication,[26] two distinct peaks located at 2809 and 2855 $\mathrm{cm^{-1}}$ emerge. With further increase of the filament temperature to 1850 °C the two bands still dominate the spectrum. However, the ratio changes in favor of the band at lower frequency. Additionally, the peak of the feature at lower frequency blue-shifts significantly from 2809 to 2820 $\mathrm{cm^{-1}}$, and it seems that it is not just a blue-shift of a band but that a new band grows in, while the peak at lower wavenumbers persists as a shoulder in the spectra at higher temperatures. If the filament temperature approaches values used in diamond CVD, the low-frequency band experiences a pronounced further increase but does not shift. Even though the peak at 2855 $\mathrm{cm^{-1}}$ gets smaller relative to the band at 2820 $\mathrm{cm^{-1}}$, it is still pronounced and is not even significantly reduced compared to that at the lower filament temperature. As seen from this series the two peaks develop independently from each other, evidencing that they originate from different species.

Rather than being affected by the filament temperature, the band at 2855 $\mathrm{cm^{-1}}$ experiences a pronounced change in intensity if the substrate temperature is varied. As seen from Figure 2A as the substrate temperature increases from 660 to 750 °C, that is, a temperature where high-quality diamond films are deposited, this peak gradually disappears. Note that the intensity of the low-frequency band does not increase substantially anymore. It even seems that the intensity decreases slightly. Under conditions where good quality diamond is deposited, the SFG spectrum essentially consists of a single band centered at 2820 $\mathrm{cm^{-1}}$. This implies that the dominating species on the surface is a tertiary carbon atom with just a single C−H bond such as the structure of the

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[25] Our definition of high- and low-quality diamond is based on the characteristic peaks of diamond and graphite-type structures observed by Raman spectroscopy. Since the quality of diamond grown on diamond is difficult to assess, films grown on silicon substrates under the same conditions were measured.

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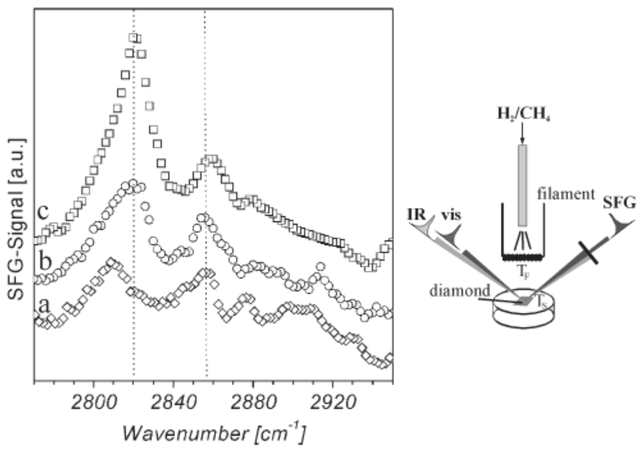

Figure 1. (Right) Scheme of the experimental setup. A gas mixture of 99.25% H_2 and 0.75% CH_4 at a total pressure of 32 mbar and a flow rate of 100 sccm was used. The filament temperature T_F was varied between 1400 and 2050 °C. The sample, a C(111) diamond type IIB ($5 \times 5 \times 0.25$ mm^3), is placed on a substrate holder. Its temperature T_S is measured by a thermocouple attached to the surface of the holder. The incoming p-polarized beams, light pulses with a duration of ~40 ps, a repetition rate of 20 Hz and pulse energies of about 80 μJ for the tuneable IR and 400 μJ for the visible at 532 nm, impinge almost collinearly onto the diamond at an angle of approximately 45°. The IR and vis beams are focused to 0.5 and 1.0 mm, respectively. (Left) Series of SFG spectra from the diamond (111) surface during the CVD process for different filament temperatures and no additional substrate heating. The substrate temperature solely results from the heating by the filament. (a) $T_F = 1770$ °C, $T_S = 570$ °C. (b) $T_F = 1850$ °C, $T_S = 600$ °C. (c) $T_F = 1950$ °C, $T_S = 650$ °C.

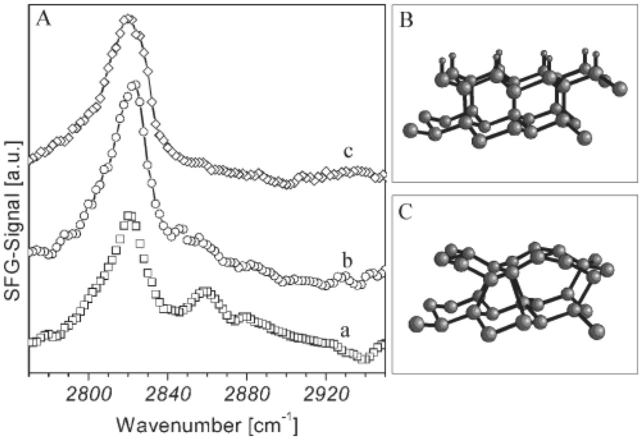

Figure 2. (A) SFG spectra from the diamond (111) surface during the CVD process as a function of the substrate temperature. The filament was kept at 1950 °C, and the substrate was heated additionally. (a) $T_S = 650$ °C (same as Figure 1c). (b) $T_S = 710$ °C. (c) $T_S = 750$ °C. (B) Illustration of the bulk terminating (1×1) structure, present if the surface is hydrogen terminated. (C) Pandey model[30] of the hydrogen-free, reconstructed (2×1) structure.

unreconstructed hydrogen-terminated surface (Figure 2B). This SFG spectrum acquired at high temperatures strikingly resembles the one measured under UHV conditions at room temperature and further supports the presence of the bulk truncated, H-terminated (1×1) surface.[21-23] However, the peak observed under CVD conditions is red-shifted by about 10 cm^{-1} compared to the UHV spectrum acquired at room temperature.[9,21,22] The difference in the temperature cannot explain the difference since switching off the methane shifts the band to the position observed in the UHV experiments.[26] Therefore, it must be a chemical effect due to reactive C−H gas phase species. Another feature we consistently observe, and which, in a similar way, was also observed in some of the UHV experiments,[9] are spectral features lower than the characteristic C−H peak, that is around 2780−2820 cm^{-1}. The clarification whether this reflects species located at steps or domain boundaries has to await systematic experiments with samples of different surface quality. An important result inferred from Figure 2A is that, under conditions of diamond CVD, no sign of CH_3 species at the surface can be identified. Only at very low filament and substrate temperatures (Figure 1a) do structures which can be associated with CH_3 appear. Recalling that CH_3 is considered an essential species in diamond growth,[7,8] this could mean either that other species such as acetylene, which would appear at much higher wavenumbers, are responsible or that the CH_3 reacts so quickly that the concentration is below detection threshold. Preliminary experiments at higher wavenumber did not yield a significant signal, and therefore, we favor the second interpretation at present.

Addressing now the origin of the second band which only appears at lower substrate temperatures and, thus, seems to be associated with low-quality diamond, we again compare the CVD with the UHV spectra. Starting from the reconstructed, hydrogen-free surface (Figure 2C) a peak at exactly the same position showed up in the UHV experiments at low hydrogen coverage.[21] Increasing the coverage resulted in the appearance of the peak at 2830 cm^{-1} indicative of the C−H species of the (1×1) hydrogen-terminated surface while the peak at 2855 cm^{-1} completely disappeared. Interestingly, this peak also showed up in CH_3-dosed surfaces, again performed in UHV.[9] This strongly suggests that the "low temperature" peak observed in our experiments is associated with a structure which is derived from the reconstructed surface and deviates substantially from the (1×1) hydrogen-terminated structure. This fits into the model that the structure of the ideally bulk-terminated diamond has to be maintained at the surface to enable the growth of a good quality diamond.

The results presented here demonstrate that SFG provides access to the surface species present on the diamond surface under CVD conditions. More generally, its suitability of studying high-temperature surface processes is evidenced. The species identified represent a first step toward the support of theoretical work by experiment and a better understanding of the surface chemistry in diamond CVD. The correlation of the vibrational bands with the structure of the surface requires the modeling of suitable structures, and the present work should encourage further theoretical work on the vibrational properties of the diamond surface.[27-29] The results strongly suggest that a key point is the identification of the species and structure associated with the peak around 2855 cm^{-1} and that modeling of the surface chemistry of diamond might require focusing on structures closer to the reconstructed surface rather than on relaxed, bulklike structures.

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