

Diffuse Reflectance Infrared Fourier-transform Study of the Plasma Hydrogenation of Diamond Surfaces

Toshihiro Ando,* Motohiko Ishii, Mutsukazu Kamo and Yoichiro Sato

National Institute for Research in Inorganic Materials, 1-1, Namiki, Tsukuba, Ibaraki 305, Japan

Plasma hydrogenation of diamond surfaces was investigated using a diffuse reflectance infrared Fourier-transform (DRIFT) technique. Hydrogenation was carried out under microwave plasma conditions similar to those used for the chemical vapour deposition of diamond. Surface species chemisorbed on the diamond surface were characterized by DRIFT spectroscopy. The number of hydrogen-carbon bonds increased and the structure of the chemisorbed species on the diamond surfaces changed on increasing the temperature of the plasma hydrogenation.

It is very important for diamond synthesis that the chemical structure and the chemical reactivity of diamond surfaces are well characterized. The characterization of both molecules and atoms chemisorbed on the diamond surface is vital for an understanding of chemical vapour deposition processes. This information elucidates the mechanism of diamond formation from the vapour phase.

It is well known that there are three hybrid orbital states sp^3 , sp^2 and sp , of carbon that form different structures *i.e.* tetrahedral, planar and linear. Graphite is the most stable phase of carbon, whilst diamond is a thermodynamically metastable form at atmospheric pressure and room temperature. It is certain that diamond can be grown from the vapour phase under thermodynamically metastable conditions *e.g.* microwave-assisted plasma chemical vapour deposition.^{1,2} This suggests that the growing surface should be controlled and allowed to react with the species from the vapour phase in a highly selective manner. While graphite has an sp^2 hybrid orbital state, diamond has an sp^3 hybrid orbital state. We consider that the growing surface of diamond should have only an sp^3 state. It is very important that the surface chemical nature of diamond should be understood and controlled.

To date, there have been relatively few studies on chemisorption and the reactivity of diamond surfaces. Marsh and Farnsworth have reported from low-energy electron diffraction (LEED) studies that hydrogen enabled high-temperature cleaning of the diamond surface without degradation.³ Lander and Morrison have found that heating a $(2 \times 2)/(2 \times 1)$ surface in hydrogen resulted in a (1×1) LEED pattern.⁴ Pate has found that room-temperature exposure to atomic hydrogen as sufficient to remove the surface states from the reconstructed (111) surface.⁵

Matsumoto and Setaka have studied hydrogen chemisorption on diamond powders with thermal desorption spectroscopy.⁶ They have reported two states in chemisorbed with hydrogen diamond surfaces. Recently, Thomas *et al.* have studied thermal desorption from the diamond (100) surface by combined LEED analyses.⁷

Mehandru and Anderson have characterized the absorption and bonding of C-H fragments to the unreconstructed diamond surface, including the dependence on coverage and coadsorbed hydrogen.⁸ They have also calculated surface properties of clean and hydrogenated diamond.

Sappok and Boehm have detected the methylene group on the hydrogenated surface by IR spectroscopy.^{9,10} Butler and co-workers have employed *in situ* IR absorption spectroscopy to study the gaseous and surface chemical species in chemical vapour deposition processes. They have detected methyl

radical ($\cdot\text{CH}_3$), acetylene (C_2H_2) and ethene (C_2H_4) above the growing surface.^{11,12} Vibrational spectroscopy is unsurpassed in obtaining detailed information on the nature of chemisorbed molecules and atoms.¹³ In particular, vibrational spectroscopy is successful for observing hydrogen atoms bonded to carbon atoms of the diamond surface. Recently Dischler *et al.* have analysed hydrogen in polycrystalline diamond films with IR spectroscopy.¹⁴ Chin *et al.* have obtained vibrational spectra of hydrogen on diamond (111) surface by IR-visible sum-frequency generation (SFG).¹⁵ Much IR data collected for organic compounds also allows us to assign the observed spectra with high reliability. FTIR spectroscopy may be used with other sampling techniques for surface analysis including diffuse reflectance spectrometry,¹⁶ photoacoustic spectrometry (PAS),¹⁷ and multiple internal reflection spectrometry.¹⁸ We previously reported that both FTIR-PAS and DRIFT are efficient for observing the species chemisorbed on diamond surfaces.¹⁹

This paper reports an investigation on the hydrogen-plasma treatment of diamond powder by DRIFT spectroscopy. The aim is to characterize species present on the diamond surface treated under microwave-assisted plasma conditions.

Experimental

Commercially available synthesized diamond powder of 22.1 $\text{m}^2 \text{g}^{-1}$ specific surface area was used. Its BET surface area was determined with nitrogen at 77 K, using a Micrometrics Digisorb 2600 surface analyser. Before hydrogen-plasma treatment, the diamond powder was treated in a heated solution of sulfuric and nitric acids to remove impurities. The hydrogenation was performed in the microwave-plasma reactor which was also used for chemical vapour deposition of diamond.²⁰ The reaction was carried out at 20–40 Torr† in pure hydrogen (99.9999%). The temperature of the diamond surface was measured by a radiation pyrometer equipped with a silicon detector. The reaction conditions are detailed in Table 1. DRIFT spectra were recorded on an FTIR instrument (BioRad, Digilab FTS-65), equipped with a DTGS detector, in the region 4000–400 cm^{-1} with a resolution of 2 cm^{-1} . The diffuse reflectance accessory (Spectra Tech) was used for the measurement. 256 scans were accumulated for each spectrum. A KBr standard powder was used for the reference spectrum. Diffuse reflectance was converted into Kubelka-Munk units.

† 1 Torr = (101 325)/760 Pa.

Table 1 Microwave plasma-hydrogenation conditions

run	H ₂ flow /sccm ^a	temperature /°C	pressure /Torr	MW power /W	time /min
1	100	400	20	110	30
2	100	500	20	130	30
3	100	600	20	160	30
4	100	700	40	160	30
5	100	800	40	200	30
6	100	900	40	290	30

^a 1 sccm = 1 cm³ min⁻¹ under standard conditions.

Results and Discussion

The DRIFT spectra of microwave-assisted plasma hydrogenated diamond powders are shown in Fig. 1. From the spectrum of non-hydrogenated diamond, which was only washed in acid mixture [Fig. 1(a)], it appears that the diamond surface was oxidized before hydrogenation by the oxidizing acid mixture.

This spectrum shows C=O double bond stretching vibration of carbonyl at 1773 cm⁻¹ and C—O—C stretching vibration of cyclic ether at 1100–1250 cm⁻¹. The peak at 1773 cm⁻¹ corresponds to C=O vibration of carboxylic acid (COOH), carboxylic anhydride (COOCO), lactone (COO) or strained cyclic ketone (—CO—) *e.g.* cyclobutanone. The temperature-programmed desorption (TPD) mass spectrum of oxidized diamond powders shows evolution of both CO and CO₂, which suggest that both the carboxylic acid state and carbonyl state coexist. We also observed the O—H stretching vibration band over the range 3300–3700 cm⁻¹. This broad band did not distinguish clearly between the free hydroxy group bonded to the diamond surface and physically adsorbed water. As both carboxylic and carbonyl groups show polarity, water is readily physisorbed in the atmosphere. A large part of this O—H stretching band disappeared upon heating the sample *ca.* 200 °C. The C=O stretching band remained unchanged for temperatures below 400 °C under both thermal and plasma-assisted heating.

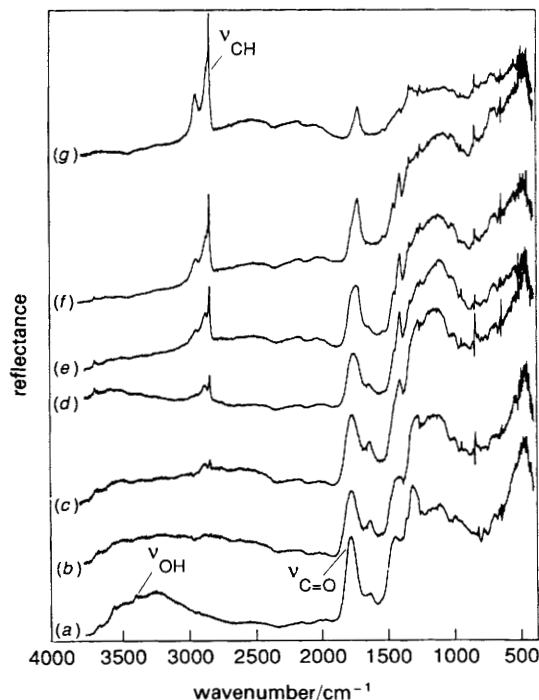


Fig. 1 DRIFT spectra of diamond powders treated under microwave H₂-plasma conditions. (a) Non-treated and treated at (b) 400, (c) 500, (d) 600, (e) 700, (f) 800 and (g) 900 °C.

Hydrogenation of diamond surfaces did proceed above 500 °C under microwave-plasma conditions. DRIFT spectra of diamond treated above 500 °C show C—H stretching vibration bands in the region from 2830 to 2960 cm⁻¹. This band was assigned to C—H stretching vibrations of the sp³ hybridized bonding. No peak due to C—H stretching vibrations of sp² hybridized bonding was observed in the region from 3000 to 3200 cm⁻¹ for all the hydrogenation experiments studied. This result indicates that hydrogenated diamond surfaces have only an sp³ hybridized state under microwave-plasma condition. This result supports the diffraction studies reported previously.^{3,4}

The peak intensity of C—H stretching vibrations increased with the hydrogenation temperature whilst the peak intensity of C=O stretching vibrations decreased. This result indicates that the extent of hydrogenation is controlled by the reaction (or substrate) temperature.

C—H Stretching Vibration

DRIFT spectra of the C—H stretching vibration region are shown in order to compare the species chemisorbed on diamond surface at different treatment temperatures (Fig. 2). It became clear that the C—H stretching vibration bands could be separated into C—H, CH₂, CH₃ groups. The symmetric stretching vibration of CH₂ and that of CH₃ appeared in the region of 2840 and 2858 cm⁻¹, respectively. The asymmetric stretching vibration band was broad in the region of 2910–2960 cm⁻¹. The assignment of C—H stretching vibration bands observed in this study is presented in Table 2. We postulate a possible correspondence between C—H and the crystallographic face with diamond structure models. As the diamond surfaces used in this study are not defined crystallographically, we cannot determine accurately what state of C—H corresponds to each crystallographic face.

In the spectrum of the hydrogenation of 600 °C, Fig. 3(d), a sharp band in the region of 2840 cm⁻¹ and a broad band in the region of 2880 cm⁻¹ were observed. The band at 2840 cm⁻¹ was assigned to the symmetric stretching vibration mode of CH₂ and the broad band at 2880 cm⁻¹ was assigned

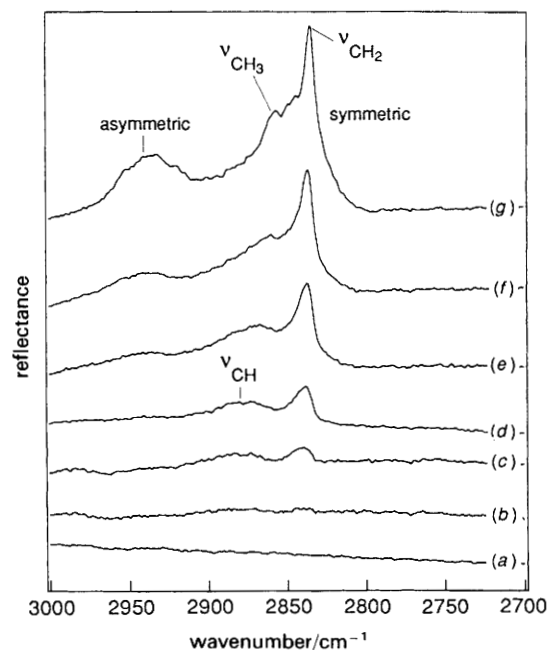


Fig. 2 DRIFT spectra of diamond powders, treated under microwave H₂-plasma conditions, in C—H stretching vibration region. (a)–(g) as Fig. 1.

Table 2 Assignment of hydrogen chemisorbed species on diamond surfaces

frequency /cm ⁻¹	mode assignment	possible correspondence to diamond surface
2830–2855	CH ₂ C–H stretching (symmetric)	(100)
2855–2870	CH ₃ C–H stretching (symmetric)	(111) + CH ₃
2875–2895	CH C–H stretching	(111), (100) – 2 × 1
2919–2935	CH ₂ C–H stretching (asymmetric)	(100)
2950–2960	CH ₃ C–H stretching (asymmetric)	(111) + CH ₃

to the stretching vibration mode of CH. In the spectrum of hydrogenation at the higher temperature, 900 °C, a new band appeared at 2858 cm⁻¹ which was assigned to the symmetric stretching vibration mode of CH₃. It is known that the absorbance of CH is considerably lower than that of CH₂ and/or CH₃ in common organic molecules. As the absorbance of CH₃ was higher than that of CH, and the CH stretching vibration band at 2880 cm⁻¹ was masked by the CH₃ stretching vibration band at 2858 cm⁻¹ in the spectrum of diamond hydrogenated at 900 °C [Fig. 3(g)]. There were three chemisorbed hydrogen species, CH, CH₂ and CH₃ in the case of hydrogenation at 900 °C.

To summarise, the diamond surface was hydrogenated in the microwave-plasma at 600 °C to give two species of hydrogen chemisorption, the CH state and the CH₂ state with vibrational bands at 2880 and 2840 cm⁻¹, respectively. The CH species corresponds to either the (111) ideal face of diamond or the (100) – (2 × 1) reconstructed face of diamond. The CH₂ species corresponds to the (100) – (1 × 1) ideal face of diamond. Diffraction studies have confirmed that the (100) – (1 × 1) surface is reconstructed at higher temperature. Hamza reported TPD of H₂ from the diamond (100) – (1 × 1) surface correlated with the surface reconstruction.²¹ In the present study, considerable amounts of CH₂ were observed in high-temperature reactions. A hydrogen plasma can maintain the (1 × 1) ideal surface up to 900 °C.

When the reaction temperature was increased to 900 °C, a new band appeared at 2858 cm⁻¹, due to CH₃ groups chemi-

sorbed on the diamond surface. This effect was noticeable at temperatures above 700 °C. Almost all the CH₃ groups were adsorbed on the (111) face, on the (100) face, steric hindrance cannot be neglected. Hydrogen molecules and/or hydrogen atoms caused dissociation of the C–C bond of the diamond crystal and combined with the carbon atoms.

Mehandru and Anderson showed from a theoretical study that a high population of adsorbed CH₃ groups was unstable due to steric repulsion.⁸ It is difficult to obtain the coverage of CH₃ groups on the surface in the present study. Chin *et al.*¹⁵ have reported two peaks due to C–H stretching vibration at 2860 and 2830 cm⁻¹ by SFG spectroscopy. They have observed that the strength of the 2860 cm⁻¹ peak could be transferred to the 2830 cm⁻¹ peak by annealing the sample at >700 °C. They also reported that the 2830 cm⁻¹ peak grew with increasing H coverage on the diamond (111) surface. In the present study, we observed a peak at 2880 cm⁻¹ by low-temperature treatment (<600 °C), and another peak at 2858 cm⁻¹ grew on heating above 700 °C. Our peak positions were different from those of Chin *et al.* Although we cannot explain the difference in peak positions, increasing treatment temperature tends to increase the intensity of the lower wavenumber peak in both studies. Formation of a surface covered with CH₃ groups is very interesting as a transient intermediate in both vaporisation and deposition of diamond. The amount of chemisorbed CH₃ increased with increase in the reaction temperature over the range 700–900 °C. This result suggests that it was easy for the carbon atom within the methyl group to migrate on the diamond surface above 700 °C. This range of temperature corresponds to that in which high quality diamond can be deposited by the microwave-assisted plasma chemical vapour deposition method.

C=O Stretching Vibration

Both the peak position and the peak intensity of C=O in the region 1600–1800 cm⁻¹ change as hydrogenation progresses (Fig. 4). The peak intensity of the band decreased with increasing reaction temperature. The concentration of C–H

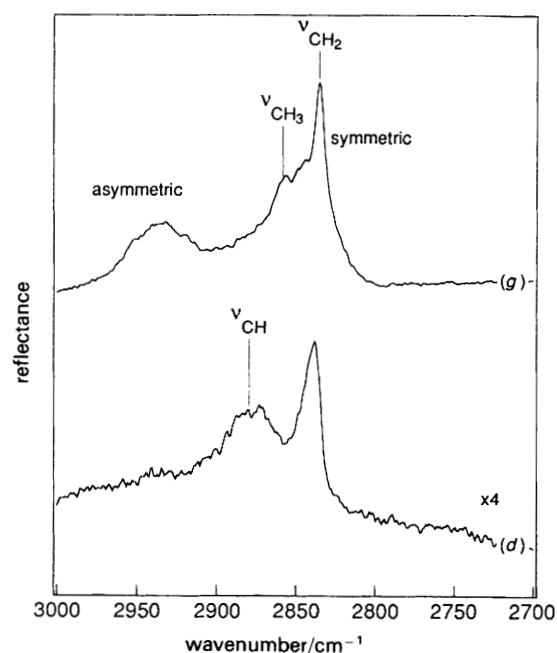


Fig. 3 DRIFT spectra 2(d), expanded by a factor of 4 for clarity, and 2(g) to show the variation in chemisorbed species with temperature

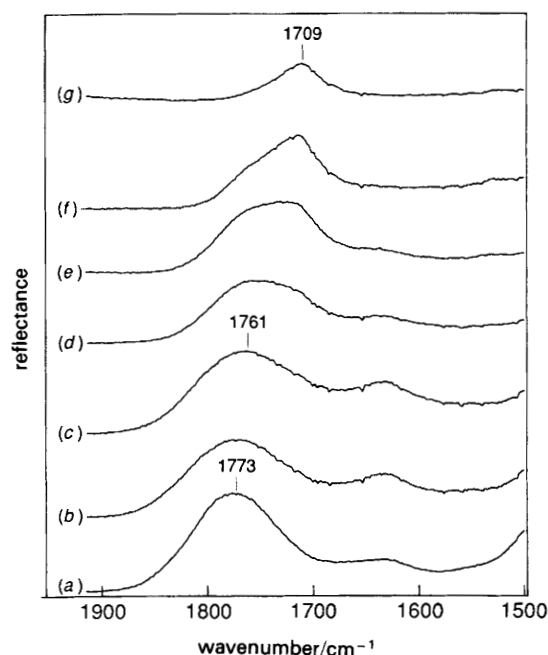


Fig. 4 DRIFT spectra of diamond powders treated under microwave H₂-plasma conditions in the C=O stretching vibration region. (a)–(g) as Fig. 1.

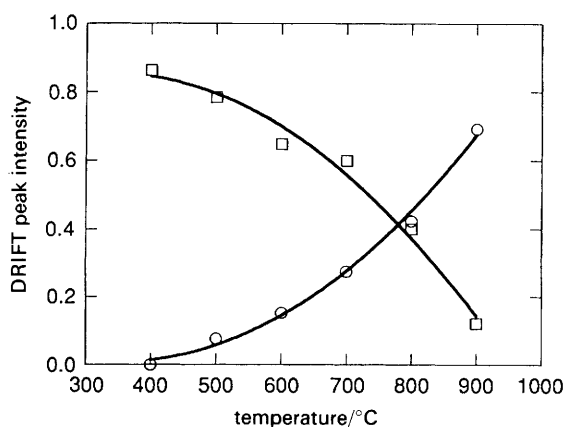


Fig. 5 Relation between the concentrations of C—H and C=O and the treatment temperature

increased while that of C=O decreased 500 to 900 °C. The increase of the peak intensity of C—H stretching vibrations paralleled the decrease of that of C=O stretching vibrations (Fig. 5), suggesting that the adsorption of hydrogen proceeded simultaneously with the elimination of oxygen on the diamond surfaces.

The peak position shifted from 1773 to 1709 cm^{-1} . The former peak is due to C=O stretching vibrations of carboxylic acid, carboxylic anhydride, lactone or strained cyclic ketone, the latter corresponds to strain-free cyclic ketones such as cyclohexanone.

Two reaction mechanisms may be proposed for the hydrogenation of C=O on the diamond surfaces. One is a stepwise reduction of carbonyl by hydrogen molecules and/or hydrogen atoms; the carbonyl group (—CO—) or carboxylic group (COO) is reduced to aldehyde group (—CHO) and further reduction produces an alcoholic OH group (—CHOH). Elimination of the OH group gives C—H. The other is thermal decomposition of the carbonyl group to give CO or of the carboxylic group to give CO_2 , subsequently hydrogen is adsorbed on the unstable surface carbon atoms.

The peak intensity of the O—H stretching vibration band in the region 3300–3700 cm^{-1} did not increase. No peak of aldehydic C—H stretching vibration was observed in the region 2700–2800 cm^{-1} . Neither alcoholic nor aldehydic species were produced on the diamond surfaces in the hydrogenation process. No hydrogenation proceeded at temperature lower than 500 °C even when the microwave supply was increased. This indicates that the desorption of C=O is the dominant process in the stepwise hydrogenation.²² Thus a thermal reaction was dominant. This result also agrees with TPD studies of diamond powders. The TPD spectra of oxidized diamond powders show that little O_2 and H_2O are desorbed from diamond surfaces.²³ The TPD spectrum of the oxidized diamond powders before hydrogen-plasma treatment indicates that oxygen may be desorbed as both CO and CO_2 . The desorption peak of CO_2 is lower than that of CO. We cannot compare the TPD spectrum exactly with this plasma hydrogenation, because two different methods were used for the measurement of reaction temperatures. We can conclude that at a relatively lower temperature, carboxylic and lactone structures are decomposed to give CO_2 , ketone structures including strained structures change into a strain-free structure and remain on the diamond surfaces. This strain-free ketone structure, is decomposed to give CO at higher temperatures above ca. 600 °C.

The control of substrate temperatures is essential for diamond synthesis by chemical vapour deposition. The importance of reaction temperature is common to this hydrogenation of surfaces.

Conclusion

DRIFT spectroscopy is an effective tool for observing the species chemisorbed on diamond surfaces. This study elucidated the changes of chemisorbed species on microwave plasma hydrogenation. Oxidation of the diamond surface with H_2SO_4 – HNO_3 produced absorption due to C=O or C—O—C, which disappeared during hydrogen-plasma treatment. CH, CH_2 and CH_3 species were clearly observed on the diamond surface by the DRIFT method. Mechanisms for hydrogen chemisorption have been discussed.

The authors thank Professor T. Suzuki for many discussions and for reading the manuscript. They are also grateful to Mr. M. Mouri for a gift of diamond powders.

References

- 1 W. A. Yarbrough and R. Messier, *Science*, 1990, **247**, 688.
- 2 J. C. Angus and C. C. Hayman, *Science*, 1988, **241**, 913.
- 3 J. B. Marsh and H. E. Farnsworth, *Surf. Sci.*, 1964, **1**, 3.
- 4 J. J. Lander and J. Morrison, *Surf. Sci.*, 1966, **4**, 241.
- 5 B. B. Pate, *Surf. Sci.*, 1986, **165**, 83.
- 6 S. Matsumoto and N. Setaka, *Carbon*, 1979, **17**, 485.
- 7 R. E. Thomas, R. A. Rudder and R. J. Markunas, *J. Vac. Sci. Technol.*, 1992, **10**, 2451.
- 8 S. P. Mehandru and A. B. Anderson, *Surf. Sci.*, 1991, **248**, 369.
- 9 R. Sappok and H. P. Boehm, *Carbon*, 1968, **6**, 283.
- 10 R. Sappok and H. P. Boehm, *Carbon*, 1968, **6**, 573.
- 11 J. E. Butler, N. Bottka, R. S. Sillmon and D. K. Gaskill, *J. Cryst. Growth*, 1986, **77**, 163.
- 12 F. G. Celii, P. E. Pehrsson, H-t. Wang and J. E. Butler, *Appl. Phys. Lett.*, 1988, **52**, 2043.
- 13 P. R. Griffiths and J. A. de Haseth, *Fourier Transform Infrared Spectrometry*, Wiley, New York, 1986, pp. 536–563.
- 14 B. Dischler, C. Wild, W. Muller-Sebert and P. Koidl, *7th Trieste Semiconductor Symposium*, June 1992.
- 15 R. P. Chin, J. Y. Huang, Y. R. Shen, T. J. Chuang, H. Seki and M. Buck, *Phys. Rev. B*, 1992, **45**, 1522.
- 16 e.g. P. Barnickel, A. Wokaum and A. Baiker, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 333; P. Persson and I. Persson, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 2779.
- 17 e.g. P. Van Der Voort, I. Gillis-D'Hamers and E. F. Vansant, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3751; I. Gillis-D'Hamers, J. Philippaerts, P. Van Der Voort and E. F. Vansant, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 3747.
- 18 e.g. K. J. Uram and U. Jansson, *Surf. Sci.*, 1991, **249**, 105; V. A. Burrows, Y. J. Chabal, G. S. Higashi, K. Raghavachari and S. B. Christman, *Appl. Phys. Lett.*, 1988, **53**, 998.
- 19 T. Ando, S. Inoue, M. Ishii, M. Kamo, Y. Sato, O. Yamada and T. Nakano, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 749.
- 20 M. Kamo, T. Ando, Y. Sato, K. Bando, J. Ishikawa, *Diamond Rel. Mater.*, 1992, **1**, 104; Y. Sato and M. Kamo, in *The Properties of Natural and Synthetic Diamond*, ed. J. E. Field, Academic Press, London, 1992, p. 424; M. Kamo, Y. Sato, S. Matsumoto and N. Setaka, *J. Cryst. Growth*, 1983, **62**, 642.
- 21 A. V. Hamza, G. D. Kubiak and R. H. Stulen, *Surf. Sci.*, 1990, **237**, 35.
- 22 T. Ando, M. Ishii, M. Kamo and Y. Sato, *J. Chem. Soc., Faraday Trans.*, in the press.
- 23 S. Matsumoto, H. Kanda, Y. Sato and N. Setaka, *Carbon*, 1977, **15**, 299.