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High-resolution electron-energy-loss spectroscopic study of epitaxially grown diamond (111) and (100) surfaces

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Diamond (111) and (100) surfaces have been investigated by low-energy electron diffraction and high-resolution electron-energy-loss spectroscopy (HREELS). Samples were boron-doped semiconducting diamond surfaces grown homoepitaxially on natural diamond by microwave-plasma-assisted chemical-vapor deposition. A dipole-active C-H stretching vibration was observed at 352 meV (2839 cm^{-1}) on the (111) surface and 363 meV (2928 cm^{-1}) on the (100) surface. In the off-specular EELS spectra, two C-H stretching modes (352 and 361 meV) were clearly resolved on the (111) surface, while only one C-H stretching vibration was detected on the (100) surface. The two modes on the (111) surface are assigned to symmetric and asymmetric vibrations of CH_3 species, respectively. This study clarifies hydrogen termination of the epitaxially grown diamond (111) and (100) surfaces in the forms of CH_3 (methyl) and CH (monohydride) groups, respectively.

Diamond can be synthesized by chemical-vapor deposition (CVD) including the surface reaction of methane or other organic molecules.[1,2] Although a number of studies have been done on diamond surfaces,[3–10] a basic question remains unsolved: What structure or what species exist on the surfaces as grown? It is now well established by low-energy electron diffraction (LEED) (Refs. 3 and 4) and thermal-desorption[5,6] studies that hydrogen plays an important role in the reconstruction of diamond surfaces. Scanning tunneling microscopy has shown that homoepitaxially grown diamond (100) surfaces are smooth and reconstructed to the 2×1 structure.[10]

Vibrational spectroscopy is one of the most useful methods to observe surface species,[11] and many infrared-spectroscopy studies have been done.[12–14] High-resolution electron-energy-loss spectroscopy (HREELS) allows the analysis of chemical species on a single-crystal surface even at submonolayer coverage.[15–19] Waclawski *et al.* have applied HREELS to identify the vibrational modes of hydrogen on an as-polished semiconducting diamond (111) surface.[16] They have presented direct evidence that the as-polished (111) 1×1 surface is terminated by hydrogen. They found C-H stretching and bending vibrations around 360 and 160 meV, respectively, and concluded that the surface species was CH_3 from observation of the bending mode in the specular condition. But as the substrate phonon band overlaps with this bending frequency,[20] it is still under debate whether the surface species is CH or CH_3 on the (111) surface. In fact, Lee and Apai have recently reported a substrate phonon band around 150 meV by using HREELS.[17] They concluded that the CH, CH_2, and CH_3 species coexist on the hydrogen-adsorbed surface. Because their preparation procedure contains high-temperature heating, the surface may be roughened considerably. As for the CVD-grown diamond surface, Biwu and co-workers have recently investigated polycrystalline diamond (111) facets deposited on a Si substrate by hot-filament CVD.[18,19]

In the theoretical studies, CH_3 termination has been questioned because of the high steric repulsion between adjacent hydrogen atoms.[21] But a recent slab modified intermediate neglect of differential overlap calculation revealed that CH_3 can have lower energy than CH when the large relaxation is taken into account.[22] Now it becomes more important to elucidate what species exists on the diamond surface. The CVD-grown surface is well reproducible, and therefore is suitable for studying the surface species. Here we demonstrate HREELS spectra of the epitaxially grown diamond (111) 1×1 and (100) 2×1 surfaces and offer evidence for CH_3 and CH species, respectively.

Natural diamond crystals, which were polished to within 4° of each direction of (111) and (100), were used for substrates. A boron-doped semiconducting diamond epitaxial layer was grown by microwave-assisted CVD.[23] Gaseous mixtures of methane (1.0 vol. %), diborane (2 ppm), and hydrogen were fed at the rate of 50 ml/min and the pressure was kept at 40 Torr. The supplying microwave power was about 300 W. The reaction temperature of the diamond substrate surface was kept at 770–780 °C, being measured by a radiation pyrometer equipped with a silicon detector.

HREELS measurements were performed in an ultrahigh-vacuum (UHV) chamber equipped with a high-resolution EELS spectrometer, a LEED system, and a gas introduction system.[24] The base pressure of the chamber was less than 2×10^{-8} Pa. The HREELS spectrometer consisted of a double-pass electrostatic cylindrical-deflector-type monochromator and the same type of analyzer. Ordinary cleaning methods such as Ar-ion sputtering or high-temperature annealing were not used in this study. After the CVD process, the samples were transferred to the UHV chamber through the atmosphere. Mild annealing (200–300 °C) was applied before HREELS measurements in order to remove hydrocarbon contamination.

HREELS spectra of diamond surfaces epitaxially

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grown by microwave-assisted plasma CVD are shown in Fig. 1. The electron incident and detection angles were each 72° to the surface normal. The energy resolution was 7–12 meV (56–96 cm^{-1}) in this case. We refer to this configuration as a specular reflection mode.

The specular HREELS spectrum of the (111) surface showed a sharp loss peak at 352 meV (2839 cm^{-1}), which is ascribed to C-H stretching vibrations ($\nu_{C\text{-}H}$) of sp^3-hybridized bonding, and loss bands in the region from 124 meV (1000 cm^{-1}) to 180 meV (1450 cm^{-1}), which are ascribed to mixed modes of C-H bending vibrations ($\delta_{C\text{-}H}$) and/or substrate phonon bands [Fig. 1(a)]. The loss peak of the C-H stretching mode had a small shoulder on the higher-energy side. The band of C-H bending vibrations had maxima at 134 meV (1080 cm^{-1}) and 159 meV (1280 cm^{-1}). LEED showed sharp diffraction spots with low background corresponding to a 1×1 atomic structure for the (111)-grown surface, although weak streaks indicated the steps on the surface.

The HREELS spectrum of the (100) surface showed a loss peak at 363 meV (2928 cm^{-1}) and a band in the region from 124 meV (1000 cm^{-1}) to 180 meV (1450 cm^{-1}) [Fig. 1(b)]. The band of C-H bending vibrations had a maximum at 137 meV (1105 cm^{-1}) with a shoulder at 152 meV (1225 cm^{-1}). A sharp 2×1 LEED pattern was observed for the (100)-grown surface.

The C-H stretching mode for sp^2-hybridized bonding was detected on neither the (111) nor the (100) surface in the region from 378 meV (3050 cm^{-1}) to 403 meV (3250 cm^{-1}). These spectra confirmed that the diamond surface grown by the CVD method is fully hydrogenated and carbon atoms of diamond surfaces have only an sp^3-hybridized state.

There were some differences between the spectrum of the (111) surface and that of the (100) surface. While the $\nu_{C\text{-}H}$ vibration was 363 meV for the (100) surface, it was 352 meV for the (111) surface and a small shoulder was seen around 360 meV. From their energies, the 352-meV peak on the (111) surface is assignable to the C-H symmetric stretching vibration mode of either the CH_2 or the CH_3 group, and the shoulder around 360 meV is assignable to the C-H asymmetric stretching vibration mode. The band of $\delta_{C\text{-}H}$ for the (111) surface was more clearly split into two maxima at 134 and 159 meV than for the (100) surface. As several C-H bending modes arise from a CH_2 or CH_3 group, like twisting, deformation, and scissors modes, this result is consistent with the existence of a CH_2 or CH_3 group on the diamond (111) surface. As the surface periodicity is 1×1, the CH_2 species is not probable according to the structure model. Waclawski *et al.* obtained similar HREELS spectra for the as-polished diamond (111) 1×1 surface, and concluded the presence of the CH_3 group from the C-H bending vibrations.

It is off-specular HREELS spectra (Fig. 2) that clearly evidence the presence of the CH_3 group on the (111) surface. The band of the C-H stretching vibrations was clearly split into two peaks in the off-specular spectra obtained by lower-incident-angle (θ) measurements. The peak at 352 meV (2839 cm^{-1}) was decreased in intensity and a peak appeared at 361 meV (2912 cm^{-1}) and increased in intensity with decreasing incident angle. A peak showing a large shift with incident angle in the

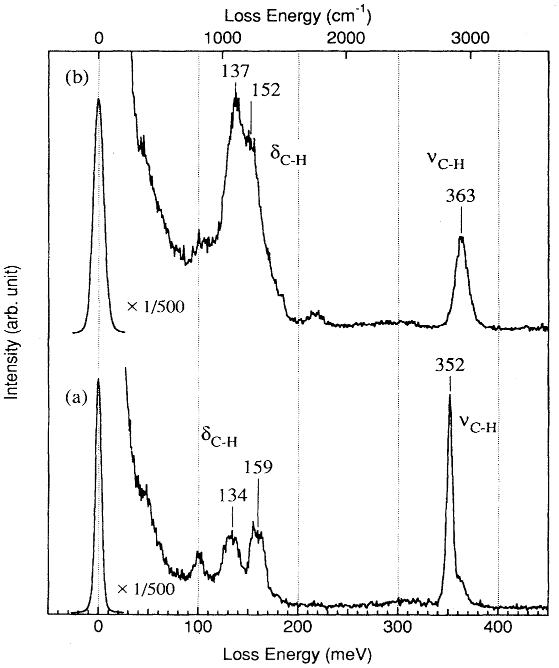

FIG. 1. Specular HREELS spectra of the epitaxially grown diamond surfaces; (a) As-grown (111) surface. Primary electron energy $E_0=4.6$ eV. (b) As-grown (100) surface. $E_0=5.0$ eV.

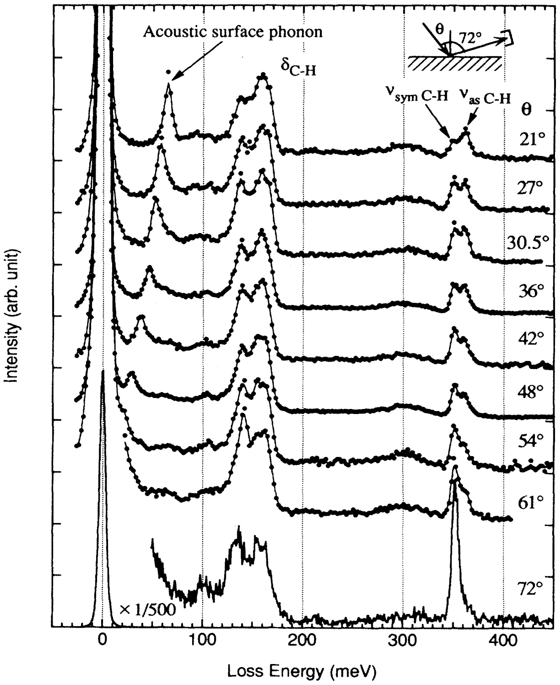

FIG. 2. Off-specular HREELS spectra of the (111) surface. Electron incident angle θ is measured from the surface normal. $E_0=15.0$ eV. Azimuth is $[1\bar{1}0]$.

lower-energy region is for an acoustic surface phonon (the Rayleigh mode), and will be discussed elsewhere.[25] The clear observation of the Rayleigh mode up to the Brillouin-zone edge indicates that the surface is fairly smooth and well ordered.

In the specular scattering condition, the dipole scattering mechanism is dominant and dipole-active modes contribute to the spectrum. In these modes the oscillating species produces a long-range dipole potential field perpendicular to the surface.[15] The 352-meV mode, which is assigned to C-H symmetric stretching vibration, can have the dipole activity, and was indeed observed in the specular spectrum. On the other hand, for C-H asymmetric modes the resulting dipole fields counteract each other, and have less intensity in the specular spectra.

In off-specular measurements, only an impact scattering mechanism dominates in the EELS spectrum. The peak intensity of symmetric vibrations should be nearly equal to that of asymmetric vibrations in the impact scattering regime. The spectra obtained showed two peaks in the C-H stretching region. If the (111) surface were terminated only by monohydride (CH) species, the off-specular spectra should show one peak in this region. The observation of the two peaks does not necessarily mean that the CH_3 and CH species coexist. Because both the CH_3 symmetric stretching mode and the CH stretching mode must be dipole-active, two peaks of comparable intensity would be observed also in the specular spectrum if CH_3 and CH coexisted. The clear contrast between the two C-H stretching modes in the specular EELS intensity proves that almost all species are CH_3 on this (111) surface. The clear appearance of the acoustic surface phonon also requires good ordering of the surface, and argues against a random distribution of CH and CH_3 species.

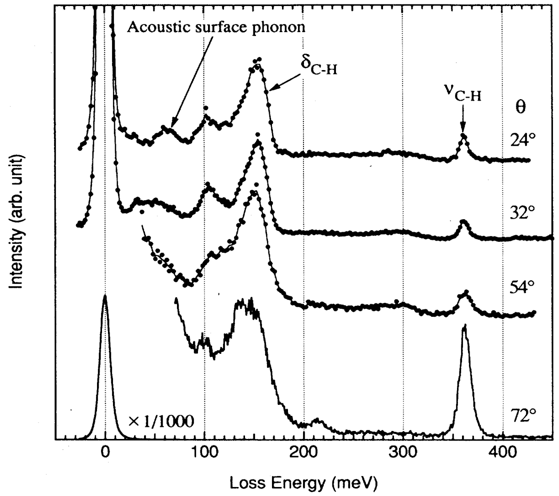

FIG. 3. Off-specular HREELS spectra of the (100) surface. $E_0 = 18.5$ eV. Azimuth is $[1\bar{1}0]$.

In the specular spectrum of the (100) surface, the peak at 363 meV is assigned to a C-H stretching vibration mode of the CH (monohydride) group. Little change in the energy of the C-H stretching vibration was observed in the off-specular spectra of the (100) surface (Fig. 3). The peak of the C-H stretching vibration cannot be divided into symmetric and asymmetric modes in the monohydride species. LEED analysis indicated the (100) surface grown had a 2×1 structure. According to the dimer model of the 2×1 reconstructed structure, it is reasonable to have the monohydride state.

In conclusion, the present study confirms that hydrogen is chemisorbed on the diamond (111) and (100) surfaces epitaxially grown by the plasma CVD method. Only sp^3-hybridized bonding exists both on the (111) and on the (100) surfaces. However, the dipole-active C-H stretching mode had different energy on each surface. In the off-specular spectra on the (111) surface, two C-H stretching modes were observed. Additionally, an acoustic surface phonon clearly appeared in the spectra up to the Brillouin-zone edge. This fact proves that the (111) 1×1 surface was well ordered and terminated by the methyl (CH_3) group. On the other hand, the (100) 2×1 surface was terminated by the monohydride (CH) group.

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