Direct verification of hydrogen termination of the semiconducting diamond(111) surface

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Low-energy, high-resolution electron energy loss spectroscopy has been used to identify the vibrational modes of hydrogen on the semiconducting diamond surface providing the first direct evidence that the (111) 1×1 surface is terminated by hydrogen. The vibrational loss spectrum from the "as-polished" surface shows two major losses near 160 meV (CH_3 deformation), a major loss at 360 meV (CH_3 stretch), and two minor losses at 520 and 720 meV (combinations and overtones). All of these losses disappear from the spectrum after heating the sample to ~1000 °C (which has been established by other experiments to be sufficient to reconstruct the surface to 2×2/2×1). The loss spectrum for the reconstructed surface is indicative of a two-dimensional metallic state of the dangling-bond surface states for clean diamond. Exposure of this reconstructed surface to atomic hydrogen results in a loss spectrum which is essentially identical to that for the as-polished surface. Further verification that the loss spectrum results from hydrogen is provided by the shift of the structure to lower loss energies when deuterium is absorbed.

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I. INTRODUCTION

Theoretically, a sharp band of occupied surface states is expected in the band gap of the ideal unreconstructed diamond(111) 1×1 surface.[1,2] For the past few years, there has been a discrepancy between this theoretical prediction of intrinsic surface states and the absence of such surface states in a series of photoemission measurements of surfaces which exhibit a 1×1 low-energy electron diffraction (LEED) pattern.[3–5] Such surfaces, which we refer to as the "as-polished surfaces," are routinely obtained[3–7] after mild (150–200 °C) bakeout from diamond crystals, which following polishing have simply been rinsed in acetone before being put into the vacuum chamber; no further sample cleaning is required. When the (1×1) surface is heated to about 1000 °C, a 2×2/2×1 reconstructed surface is obtained[8] and surface states are observed by photoemission but not in the gap as predicted for the 1×1 surface.

One of the explanations[3–6,9] which has been offered in an attempt to resolve the discrepancy, is that an absorbate such as hydrogen may yield a 1×1 LEED pattern and still be responsible for the absence of the surface states on the surfaces studied experimentally. However, a direct determination of the presence of hydrogen on the surface cannot be obtained from Auger or photoemission measurements. Pate *et al.*[5] reported photo-stimulated desorption (PSD) of hydrogen ions from the 1×1 surface of diamond, which showed that hydrogen was present. However, they were unable to determine whether the PSD H^+ yield signal originated from surface hydrogen atoms directly bonded to the surface or, rather, from those adsorbed in a complex, e.g., hydroxyl groups. Indirect evidence that hydrogen is present on the diamond(110) surface comes from investigation of the time and temperature dependence of the surface conversion at ~900 C which is consistent with the first-order desorption kinetics of a surface species; also, when the surface that has been heated is exposed to excited hydrogen,[10] the spectrum of the surface is regained.

In this paper, we present the first direct experimental observation that the diamond(111) 1×1 surface is terminated by hydrogen. We use low-energy, high-resolution electron loss spectroscopy (EELS) to observe the C–H vibrational modes of hydrogen on the semiconducting diamond surface. When the diamond is cleaned by heating to ~1000 °C, the vibrational modes of hydrogen disappear, but the loss spectrum now shows an inelastic continuum of losses which indicates that the surface state band of the diamond(111) 2×2/2×1 surface is metallic. When this reconstructed surface is exposed to atomic hydrogen, the vibrational modes characteristic of the as-polished surface reappear.

II. EXPERIMENTAL

Our measurements were performed with a UHV hemispherical electron spectrometer which was used in previously reported work.[11] A monochromatized ~5 eV electron beam was incident 60° to the sample normal and the specularly reflected electrons were energy analyzed for vibrational losses with a system resolution of ~20 meV. The intensity at the maximum of the elastic peak typically amounted to 10^5 counts/s. The spectrometer was housed in a cryopumped UHV chamber which attained a base vacuum ~1×10^{-10} Torr. The diamond sample used in this work was a semiconducting type IIb crystal polished to within 1° of the (111) direction.[12] The sample was held in a fixture using platinum foil at the rear of the crystal with small tabs bent around to the front. The foil, in turn, was spotwelded to a platinum wire at the rear which was supported in a precision sample manipulator. The sample was heated by irradiating the platinum foil at the rear of the crystal, either by thermal radiation or electron bombardment from a tungsten filament. Temperature measurements were made with a thermocouple

(W–26%Re/W–5%Re) spotwelded to a Pt tab on the side of the support fixture. For dosing the sample with atomic hydrogen or deuterium, a tungsten filament was positioned 3 cm from the front face of the crystal. Spectroscopically pure H_2 (or D_2) was leaked into the chamber to a final pressure of $\sim 10^{-6}$ Torr. At this pressure, and with the filament at 1800 °C, about 15 min were required to saturate the sample with hydrogen (or deuterium). During dosing, the sample attained an equilibrium temperature of 150 °C after about 4 min.

III. RESULTS AND DISCUSSION

The loss spectrum for the as-polished 1×1 surface is shown in the upper trace of Fig. 1. Major losses occur at 360 meV [2900 cm^{-1}] (single loss) and ~160 meV (1290 cm^{-1}) (at least two overlapping losses), with smaller losses at ~520 meV (4200 cm^{-1}) and ~720 meV (5800 cm^{-1}). For comparison, the vibrational states obtained from the ir spectrum[13] of gaseous deuterated ethane CH_3CD_3 are indicated above the trace. C–H stretch vibrations show losses at energies characteristic of the state of hybridization of the carbon atom.[14] Thus, the C–H stretch for a hydrogen atom bonded to the carbon sp^3 orbital of diamond would be expected to be near the corresponding stretch for gas-phase CH_3CD_3. As seen in Fig. 1, ν_1 and ν_7, which are the C–H stretch vibrations of $-CH_3$, coincide closely with the 360-meV loss peak; hence our assignment of the 360-meV loss to C–H stretch vibrations on diamond. The doublet structure around 160 meV is assigned to angle-changing deformations (scissorlike) ν_3 and ν_9, and the CH_3 rocking mode ν_{10}. For completeness, ν_5 shows the location of the C–C stretch. The loss around 520 meV results from the combinations of the deformation and stretch vibrations, whereas that at 720 meV is the first overtone of the stretch vibration at 360 meV. Quite good agreement of the loss spectrum with the ethane spectrum is obtained so essentially all of the structure can be accounted for with the assumption that the hydrogen atoms are bonded directly to the surface carbon atoms, and not through some intermediate species, e.g., OH. The only structure not accounted for is a very small loss ~880 meV, which conceivably may be an overtone of a small O–H stretch loss lying at an expected position ~450 meV.

In order to assure that our spectral assignment was correct, we heat cleaned the sample and then readsorbed hydrogen (or deuterium). The lower trace of Fig. 1 was obtained after the sample was heated to 1000 °C. All of the well-defined losses of Fig. 1(a) disappear, but now, the loss spectrum assumes a new character. The elastic peak broadens to ~40 meV and the loss spectrum shows an inelastic continuum with a Drude-type tail to the loss side of the elastic peak. Analogous to recent results[15] for clean Si(111) 7×7, we attribute this continuum of losses [Fig. 1(b)] to a two-dimensional metallic state of the dangling-bond surface states on diamond(111) $2\times2/2\times1$. The ideal, unreconstructed diamond(111) surface was predicted to be metallic,[1] but our results indicate that the reconstructed $2\times2/2\times1$ diamond surface also is metallic. Surface conductivity measurements[16] have indicated the possibility of a metallic surface on clean diamond. The small feature at ~170 meV is probably a carbon–carbon loss.

The loss spectra obtained after absorbing hydrogen or deuterium onto the clean diamond surface are compared in Fig. 2. All of the features previously assigned to hydrogen for the as-polished surface appear, as shown in the upper trace of Fig. 2. The lower trace shows the isotropic shift of the spec-

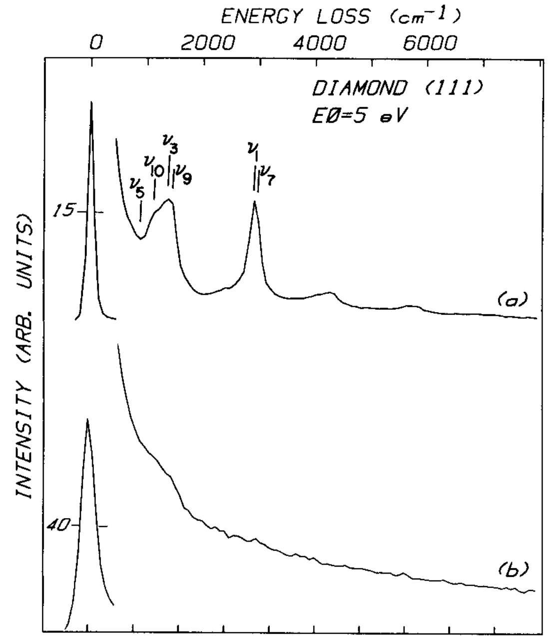

FIG. 1. High-resolution electron energy loss spectra, (a) "as-polished" diamond(111) after heating to 300 °C. (b) after heating to 1000 °C. Loss positions predicted from infrared spectrum of $-CH_3$ are indicated above the upper trace.

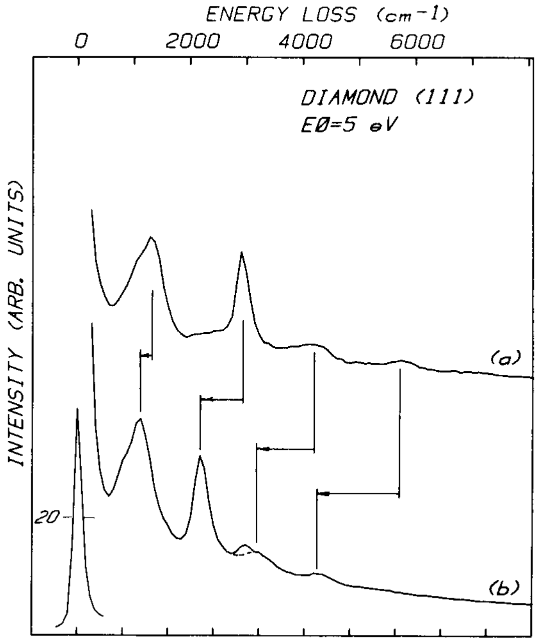

FIG. 2. Loss spectra for (a) hydrogen and (b) deuterium adsorption on diamond(111) after heating to 1000 °C. Isotropic shifts of corresponding features are indicated.

trum for the deuterated surface. The shifts of corresponding features are indicated by the connecting arrows between the two traces. On the lower trace (deuterated), some residual C–H stretch at $\sim$360 meV is indicated, probably resulting from hydrogen released by the interaction of atomic deuterium with hydrogen-containing adsorbates on metallic surfaces near the doser. All of the structure previously attributed to hydrogen for the as-polished surface (Fig. 1) is seen to shift to the positions expected for isotropic substitution.[13] Therefore, the as-polished 1×1 surface shows losses attributable only to direct hydrogen termination of the carbon dangling bonds at the diamond surface.

For the perfect, unreconstructed 1×1 diamond surface we would expect only single, carbon hybrid dangling bonds normal to the surface. Adsorption of hydrogen onto the (111) surface via these bonds should lead to a single C–H stretch loss at $\sim$360 meV, analogous to the single peak observed in the loss spectrum of hydrogen on Si(111).[17] Therefore, the observation in Fig. 1 of losses associated with angle-changing deformation modes, which involve a scissors motion of two or more H atoms, was somewhat surprising. To explain this discrepancy, we are led to conclude that the hydrogen-covered as-polished surface contains appreciable numbers of carbon atoms with multiple dangling hybrids rather than the expected single dangling bond. The good correspondence of the loss spectrum (Fig. 1) with the ethane ir spectrum implies that the adsorbed hydrogen occupies sp^3 hybrids, i.e., there is little restructuring to provide rehybridized sp^2, or sp sites. The results of our work are reminiscent of the observation[18] of a trihydride phase of hydrogen on Si(111) which was taken as supportive of the surface vacancy model for clean Si(111) 7×7. In this model $\sim\frac{1}{4}$ of the outermost surface atoms are missing which would expose second layer atoms with three dangling orbitals available for hydrogen bonding. This interpretation for Si can be applied to the diamond(111) 1×1 surface where, as for Si, a disordered distribution of such vacancies (with possible clustering) would not be apparent in the 1×1 LEED pattern. On the other hand, recent EELS spectra[19] for hydrogen and deuterium adsorption on Si(111) 7×7 show structure analogous to the results for diamond(111) presented here. This study[19] of Si also indicates that during hydrogen exposure a corrosive action takes place which removes some surface Si atoms (with SiH_4 evolution) and provides sites for SiH_3 or SiH_2 species implied by their EELS spectra. A third possibility for generation of sp^3 sites may be derived from the recently proposed[20] π-bonded chain model for the Si(111) (2×1) surface. If the chain model applies to the diamond(111) 2×2/2×1 surface, the effect of adsorbed hydrogen could be to break up the chains resulting in sp^3 hybridized carbon atoms singly backbonded to the underlying layer, with the other three hybrid orbitals occupied by hydrogen in a CH_3 species.

In conclusion, the EELS spectra reported here show directly that the diamond(111) 1×1 surface is terminated by hydrogen. The spectra also provide evidence that sp^3 dangling hybrids are present at the surface. Whether it is surface defects, the corrosive action of hydrogen, or some other mechanism that produces the sp^3 sites remain to be determined. A continuum of losses in the spectrum for the clean diamond(111) surface indicates that the reconstructed 2×2/2×1 surface is metallic.

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