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C 1s excitation studies of diamond (111). II. Unoccupied surface states

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Unoccupied electronic states at the diamond (111) surface are studied by measuring both bulk- and surface-sensitive C 1s partial-yield soft-x-ray absorption spectra. Several absorption features are observed in the bulk band gap below the 289.19-eV bulk-C 1s absorption edge. They are associated with transitions from the C 1s surface core level to unoccupied surface states by their sensitivity to chemisorbed species and changes in their intensity as the electron escape depth is varied. These states have been detected previously with electron-energy-loss spectroscopy but no structure was resolved. The close proximity of the observed surface absorption (onset at $h\nu=284$ eV) with the $h\nu=285.35$ eV, C 1$s\rightarrow\pi^*$ transition in graphite indicates the existence of unoccupied π^* bands at the diamond (111) surface. An interpretation of these results in terms of the π-bonded chain model for the diamond (111) 2×1 reconstructed surface is given.

INTRODUCTION

Measurements sensitive to surface electronic structure can provide information in a variety of areas, including insight into surface geometric structure, since energy positions and bandwidths of surface states are sensitive to the surface reconstruction.[1] The electronic structure of diamond surfaces has been the subject of a considerable number of theoretical[1-4] and experimental[5-13] investigations. For the diamond (111) surface, a fair amount of information is available about occupied surface states from photoemission data,[5-11] but little is known about unoccupied surface states. So far, only the existence of unoccupied surface states has been demonstrated using electron-energy-loss spectroscopy (EELS) to observe transitions from occupied to unoccupied surface states[12(f)] and transitions from the C 1s core level to unoccupied surface states.[12(a)-(e)] In the EELS measurements no fine structure corresponding to the density of states was resolved. In the high-resolution soft-x-ray-absorption spectra reported here, considerable fine structure is observed in the C 1s to unoccupied surface-state transitions; the principal features of which can be identified with critical points of the π^* band of the chain model[2,3] for the diamond (111) 2×1 surface reconstruction.

EXPERIMENTAL

Three different preparations of the diamond (111) surface were investigated under nearly identical experimental conditions. These surfaces were also used in a companion study[13] involving C 1s core-level photoemission measurements, where a detailed description of their preparation is provided. Only a brief account is given here.

The sample used for these experiments was a naturally conductive (probably B-doped) type IIb diamond.[14] It was cleaved along a (111) plane in a hydrogen atmosphere[15] followed by transfer via load lock into ultrahigh vacuum (UHV). Once under UHV, the crystal was heated to within 100 °C of the hydrogen desorption temperature ($\simeq$900 °C), providing sharp C 1s photoemission peaks[13] indicating a homogeneous hydrogen-terminated surface. The clean surface was then produced by thermally desorbing the hydrogen, resulting in photoemission spectra with a clearly resolved surface-core-level peak indicating the probable existence of a 2×1 surface reconstruction. Finally, fluorine was deposited on the clean surface by exposing it to XeF_2 gas, which apparently chemisorbs dissociatively, releasing xenon into the ambient in analogy with its behavior on silicon.[16] Each of these surfaces was characterized with high-resolution C 1s core-level photoemission measurements which are presented elsewhere.[13]

C 1s absorption spectra were obtained by monitoring the secondary electron yield within a specified energy window as the incident photon energy was ramped across the excitation threshold. The center position of the energy window could be adjusted to either increase or decrease the surface contribution to the measured spectrum. In the surface-sensitive mode, data were taken with the electron analyzer energy window 2.5 eV wide, centered at kinetic energies (E_{kin}) between 20 and 40 eV. In this energy regime, the electron mean free path is less than 5 Å.[13] In the bulk-sensitive mode the electron analyzer energy window was 0.2 eV wide and centered at $\simeq$2.0 eV, where the mean free path is on the order of hundreds of angstroms. It has been shown[17] that the partial photoelectric yield is proportional to the absorption coefficient if the escape depth of the detected electrons is small compared with the photon-absorption length. Empirically we found this condition to be satisfied when collecting electrons with kinetic energies greater than 1 eV. For diamond, the photon-absorption length just above the bulk-C 1$s\rightarrow\sigma^*$ excitation threshold is approximately 500 Å (Ref. 18), while just below threshold where these measurements were made, it is approximately 1.3×10^4 Å.[18]

Spectra were taken at beamline U-8 of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory using a 10-m toroidal grating monochromator[19] which was calibrated against the 284.35-eV (Ref. 20) C 1$s\rightarrow\pi^*$ transition of a single-crystal graphite sample.

The incident radiation was p polarized and hit the surface at a nearly glancing ($\simeq 5°$) angle of incidence. To avoid possible problems with spectral artifacts ascribable to carbon contamination of optical components, all spectra presented here have been normalized by the spectrum from a mildly oxidized carbon-free silicon surface recorded under the same conditions. The corrected spectra, thus obtained, closely resemble the uncorrected spectra, since carbon contamination of the beamline's optical components caused intensity variations of at most 10%.

RESULTS AND DISCUSSION

In Fig. 1 the surface absorption of clean diamond is compared with the bulk absorption of diamond and graphite. The coarse bulk absorption features can be explained by transitions into unoccupied σ^* and π^* bands. Since the π-π^* splitting is smaller than the σ-σ^* splitting, one finds the π^* transitions at lower energy, e.g., the strong peak at $h\nu = 285.35$ eV in graphite. The lowest-lying states in bulk diamond are σ^* states. The sharp spike at the C $1s \rightarrow \sigma^*$ excitation threshold results from a C $1s$ bulk core exciton.[21] Even though π^* transitions are absent in bulk diamond, one observes a small amount of intensity at the π^* transition energy with the bulk diamond band gap (see inset with expanded vertical scale). Curve A in the inset was obtained in a surface-sensitive mode ($E_{\mathrm{kin}} \simeq 35$ eV) and shows considerably more intensity than curve B, which was obtained in a bulk-sensitive mode ($E_{\mathrm{kin}} \simeq 2.0$ eV), indicating that the features depicted in the inset have their origin in the surface region. For the purpose of comparison, curves A and B were normalized by scaling to a common bulk absorption value.

Figure 2 shows an expanded view of the states in the bulk band gap for the three different surface preparations studied: clean, hydrogen-terminated, and fluorine-

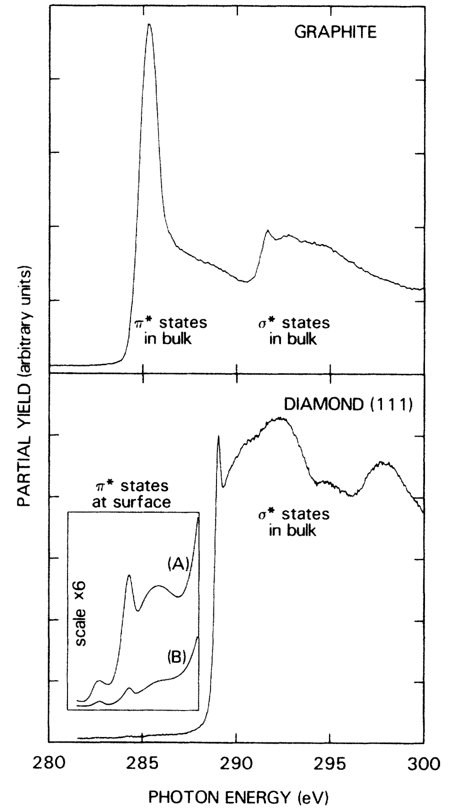

FIG. 1. Surface absorption of clean diamond is compared with the bulk absorption of diamond and graphite. The sharp spike at the diamond bulk absorption threshold indicates the existence of a bulk core exciton. The curves in the inset show the absorption in the bulk diamond band gap with an expanded vertical scale. The curve labeled A was taken in a mode more sensitive to the surface than the curve labeled B, indicating that these absorption features originate in the surface region. The close proximity of these features to the C $1s \rightarrow \pi_*$ transition energy of graphite indicates the existence of π^* states at the diamond (111) surface.

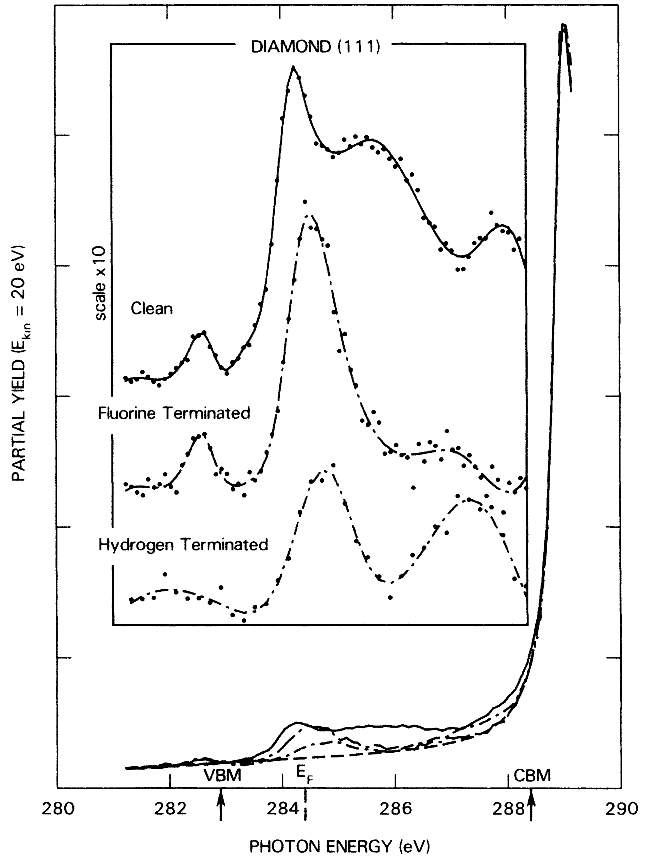

FIG. 2. Surface soft-x-ray-absorption spectra for three different preparations of the diamond (111) surface are compared. The solid curve corresponds to the clean surface, the long-dashed—dotted curve to the fluorine-terminated surface, and the short-dashed—dotted curve to the hydrogen-terminated surface. The dashed curve shows the background used to obtain the curves in the inset. The positions of the valence-band maximum, Fermi level, and the conduction-band minimum are indicated at the bottom of the figure. Notice that the chemisorbed fluorine strongly attenuates the two features lying at higher energies while leaving the two lower-lying features relatively unaffected.

covered. The band edges have been located relative to the position of the C 1*s* bulk core exciton which has been shown previously to lie 0.19 eV (Ref. 21) below the conduction-band minimum (CBM). At the surface the C 1*s* binding energy is 0.80 eV (Ref. 13) less than in the bulk; therefore, we place the surface CBM $0.80-0.19=0.61$ eV below the 289.0-eV (Ref. 21) bulk core exciton. The diamond band gap is known from optical measurements to be 5.5 eV, locating the valence-band maximum (VBM) at 282.9 eV. The Fermi level is known from photoemission measurements of the clean 2×1 surface to lie $\simeq1.5$ eV (Ref. 7) above the VBM, as shown in Fig. 2. The dashed curve represents the tail of the bulk absorption. The three spectra in the inset were obtained by subtracting the dashed background from each curve and expanding the vertical scale.

The strong influence of chemisorbed hydrogen and fluorine on the gap states indicates that the gap states are concentrated primarily at the surface and therefore do not involve significant underlayer or multilayer contributions. One possible origin for the observed states could be graphitization of the surface; however, no evidence of graphitization was found in high-resolution photoemission spectra of these surfaces.[13] Surface core excitons must play some role, since a portion of the states appear below the Fermi level. The bulk of the intensity, however, is attributable to unoccupied surface states without invoking electron-hole interactions.

It is tempting to speculate that the two lowest-lying gap states at 282.6 and 284.3 eV on the clean surface have a different origin than the two higher-lying states because of their common lack of reaction to the adsorption of fluorine. The fact that these states both extend below the Fermi level indicates they are excitonic in nature. It is found both experimentally[21] and theoretically[22] that the bulk exciton is split off from the CBM by $\simeq0.2$ eV; however, the electron-hole interaction at the surface could be more than an order of magnitude stronger as the result of reduced screening and larger effective masses. The two remaining gap states on the clean surface at 285.5 and 287.7 eV can be interpreted as unoccupied surface states, as illustrated in Fig. 3. Their greater sensitivity to fluorine adsorption can be explained by the delocalized nature of their continuum states, in contrast to the more localized nature of discrete exciton states. The dashed curve in the top panel of Fig. 3 shows the angle-integrated photoemission from the filled surface states on the diamond (111) 2×1 surface (taken from Himpsel *et al.*[8]). The solid curve shows the background-subtracted surface absorption from Fig. 2. Assuming the assignment of the two lower-lying gap states given above, the energy difference between the highest occupied π surface state and the lowest unoccupied π^* surface state would be in reasonable agreement with the 2.1-eV transition measured by Pepper[12(f)] using EELS.

For a detailed interpretation of the surface absorption features, a structural model has to be assumed. In the lower panel of Fig. 3 we give an assignment based on the chain model. In this interpretation, the 2.1-eV transition between occupied and unoccupied surface states[12(f)] (indicated by an arrow) occurs at the boundary of the surface Brillouin zone. Similar interpretations[23] have been given for Si(111) 2×1 and Ge(111) 2×1, except that band dispersions and band gaps are larger in diamond. The two continuum surface states at 285.5 and 287.7 eV can be assigned to critical points of the π^* band at the Brillouin-zone boundary ($\bar{J}\bar{K}$) at the zone center ($\bar{\Gamma}\bar{J}'$), respectively. The two surface exciton peaks are split off from these critical points by an electron-hole interaction of about 3 eV. This assignment is tentative and more accurate surface-energy-band calculations will be required to make a final decision. The energy-band dispersions shown in Fig. 3 have been taken from Vanderbilt and Louie,[1(a)] except we have rigidly shifted the π band down by $\simeq1$ eV (such that it agrees with photoemission) and the π^* band up by the same amount to obtain the observed surface band gap of $\simeq2.1$ eV.

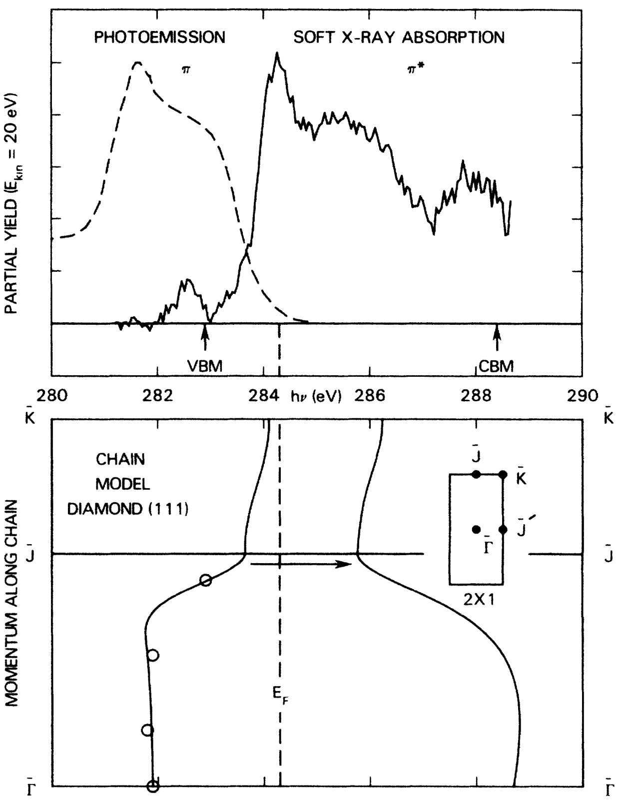

FIG. 3. Photoemission from surface states (taken from Ref. 8) and soft-x-ray-absorption spectra (from Fig. 2) of the clean diamond (111) surface are compared with a band map for the 2×1 reconstructed surface. The circles in the lower panel indicate the positions of surface bands measured with angle-resolved photoemission (from Ref. 8) and the arrow indicates the probable position of the 2.1-eV transition from occupied to unoccupied surface states. The existence of π bonding at the surface lends support to the validity of the π-bonded chain model for the diamond (111) 2×1 surface reconstruction.

CONCLUSIONS

In summary, we have made the first observation of fine structure in the density of unoccupied surface states on diamond (111). Our results can be explained qualitatively by current band calculations for the chain model for the 2×1 surface reconstruction; however, the experimentally observed energy gap between the surface π and π^* bands is not reproduced by the calculations which give a metallic surface. This discrepancy may result in part from the general tendency of local-density approximations to give gap energies too small by about a factor of 2. It is likely, however, that the current models of the electronic structure need modification. Though the details of the chain model are not in agreement with the data, the concept of π bonding at the surface is supported, suggesting that π bonding should be a significant feature of surface-band-structure models for the diamond (111) 2×1.

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