Surface states on reconstructed diamond (111)

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With the use of angle-resolved photoemission with synchrotron radiation, surface states on the $(2 \times 1)/(2 \times 2)$ reconstructed diamond (111) surface are characterized. These states cover an energy range of about 2 eV and exhibit maximum emission intensity at 1 eV below the valence-band maximum in normal emission (i.e., at the center $\overline{\Gamma}$ of the surface Brillouin zone). The symmetry is determined to be $\Lambda_1(s, p_z$ -like) by using polarization selection rules. For off-normal emission an upwards energy dispersion by about 1 eV is seen. This behavior is similar to the energy position, dispersion, and symmetry of surface states on the Si(111)-(2 \times 1) cleavage plane and in contrast with the momentum distribution of the π band of graphite which is peaked at the boundary of the surface Brillouin zone.

I. INTRODUCTION

As a prototype group-IV semiconductor surface, the diamond (111) surface has been the subject of several theoretical studies.¹⁻⁵ To date, only the unreconstructed diamond (111)-(1×1) surface has been considered theoretically and a strong half-filled band of surface states in the fundamental gap has been predicted.

Experimentally, a (1×1) surface has been found which is stable up to a temperature of ~900 °C, above which it irreversibly transforms into a $(2 \times 1)/(2 \times 2)$ reconstructed surface.⁶ From the symmetry of the low-energy electron diffraction (LEED) pattern it cannot be distinguished if one has a (2×2) reconstruction or three equivalent (2×1) domains.

Photoemission studies on the (1×1) surface could not find any surface states^{7,8} as predicted for an ideal (1×1) surface and several possible explanations have been given for this apparent discrepancy, e.g., hydrogen termination or graphitic reconstruction of the (1×1) surface (see Refs. 7-10). On the $(2 \times 1)/(2 \times 2)$ reconstructed surface, we have reported the existence of surface states⁹ which subsequently have been studied in more detail by Pate *et al.*¹¹ using angle-integrated photoelectron spectroscopy. Also, the existence of empty surface states has been inferred from electron energy loss data for the diamond (111) surface after annealing above 900 °C (Ref. 12).

In this work, we study the momentum distribution, energy dispersion, and symmetry of the occupied surface states of diamond $(111)-(2\times 1)/(2\times 2)$ by using angle-resolved polarization-dependent photoelectron spectroscopy. For comparison, we have done similar studies for the p_z -type π bands on the basal plane of graphite. We find that the momentum distributions of the diamond (111)- $(2 \times 1)/(2 \times 2)$ surface states are quite different from those for the graphite (0001)- $(1 \times 1) \pi$ bands and resemble closely those of the Si(111)- (2×1) cleavage plane. This suggests that the reconstructed diamond (111) surface could be a prototype for increasing our understanding of reconstructed group-IV semiconductor surfaces.

II. EXPERIMENTAL

We have studied natural and cleaved (111) surfaces of a type-II*b* semiconducting diamond¹³ with similar results. The cleaves were performed¹⁴ in a hydrogen atmosphere to saturate the surface with hydrogen which is expected to come off easily during heating. After heating these surfaces to > 900 °C in a vacuum in the low 10⁻¹⁰-Torr range, the LEED pattern changed from a clear (1×1) to a (2×1)/(2×2) pattern with second-order spot intensities being comparable with the first-order spot intensities. Special care had to be taken to avoid exposure to strong electron beams (\geq 10 µA) which trigger the formation of a disordered graphitic surface (see Ref. 15) with an extremely weak LEED pattern.

As shown in Fig. 1(a), the photoemission spectra from the diamond (111) samples already showed all features of the diamond (111)-(1 \times 1) surface^{7,15} be-

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FIG. 1. Angle-integrated photoelectron energy distribution curves (EDC's) for a photon energy hv = 80 eV from different diamond and graphite surfaces. The difference curve (c)-(b) represents the surface state emission seen for the diamond (111)-(2×1)/(2×2) surface shown in more detail in Fig. 2.

fore cleaning *in situ* with weak additional adsorbate levels at about -26 eV and below. Moderate heating (~500-900 °C) removed these features without significantly altering the structures within the dia-



FIG. 2. Difference between photoelectron spectra of reconstructed and unreconstructed diamond (111) surfaces showing extra surface state emission near the top of the valence band E_V for diamond (111)-(2×1)/ (2×2). The upper two curves (angle resolved at $h\nu = 50 \text{ eV}$) demonstrate an upwards dispersion of about 1 eV from the zone center to the zone boundary. The lowest curve (angle integrated $h\nu = 80 \text{ eV}$) gives the density of states.

mond valence band which is 22-eV wide [Fig. 1(b); compare Ref. 15 for the bulk energy bands of diamond]. The top of the valence band E_V lies 1 eV below the Fermi level E_F (see Refs. 7–9 and 16). Upon heating above 900 °C, extra states appeared near the top of the valence band [see Fig. 1(c)] which are quite pronounced in the difference spectrum [Fig. 1(c)-1(b) and Fig. 2]. Also, the Fermi level moved upwards by about 0.5 eV (see Ref. 9, between different surfaces there is a scatter of ± 0.2 eV). This can be seen by lining up the bulk feature at $E_V - 12.5$ eV (Fig. 1) and determining the Fermi edge of the tantalum sample-holder.

For comparison, we have studied various graphitic samples under similar conditions. An angleintegrated photoelectron spectrum of a heavily electron-bombarded diamond (111) surface is shown in Fig. 1(d). This surface showed no LEED pattern in the surface sensitive electron energy region around 100 eV. Figure 1(e) shows an angleintegrated spectrum of a graphite crystal¹⁷ prepared by cleaving *in situ*; this surface showed well-pronounced angular photoemission patterns. The graphite spectra have been aligned to the diamond spectra in Fig. 1 in such a way that the bulk diamond peak at $E_V - 12.5$ eV coincides with a similar but weaker structure in the graphite spectra.

III. RESULTS FOR DIAMOND $(111)-(2\times 1)/(2\times 2)$

We attribute the extra emission seen for diamond $(111)-(2 \times 1)/(2 \times 2)$ with respect to the diamond $(111)-(1 \times 1)$ surface [Fig. 1(c) - 1(b) and Fig. 2] to a band of intrinsic surface states which extends from $E_V - 1$ eV to E_V . Although these states do not lie in the band gap of diamond, they appear to interact only weakly with the bulk band states of diamond. This is inferred from the small magnitude of the energy dispersion which is observed when the photon energy hv is changed at fixed momentum parallel to the surface $\vec{k}_{||}$. For example, for $\vec{k}_{||} = 0$ (normal emission) the energy dispersion is less than 0.5 eV for 20 eV $\leq hv \leq 80$ eV (not shown). For bulk bands, an energy band dispersion of several eV is expected (see Ref. 15).

The angular behavior of the surface state emission is shown in Figs. 2 and 3. For photoelectrons escaping in the $(2\ \overline{1}\ \overline{1})$ plane [i.e., along the $\overline{\Gamma}\overline{K}$ line of the hexagonal (1×1) surface Brillouin zone in Fig. 3] we find a rather rapid upward shift by about 1 eV between $\vec{k}_{||}=0.5\overline{\Gamma}\overline{K}$ and $\vec{k}_{||}=0.8\overline{\Gamma}\overline{K}$, i.e., near the middle of the short edge of a (2×1)



FIG. 3. Angular dependence of the surface state emission on diamond $(111)-(2 \times 1)/(2 \times 2)$. Towards the Brillouin-zone boundary (see inset) an upwards energy dispersion is seen.

surface Brillouin zone $(\overline{J} \text{ corresponds to } 0.75 \overline{\Gamma} \overline{K})$. For photoelectrons escaping in the $(01\overline{1})$ plane (i.e., along the line $\overline{\Gamma} \overline{M}$ in Fig. 2) we observe no shift of the surface state peak when $k_{||}$ is increased, only an intensity decrease. This holds for most of the samples, but in some cases an upwards dispersion is observed off normal in the $(01\overline{1})$ escape plane. This may be due to a different domain distribution of a multidomain (2×1) surface.

The symmetry of the surface state band on diamond $(111)-(2\times 1)/(2\times 2)$ is obtained from the polarization dependence of the emission intensity which is shown in Fig. 4. Two normal emission spectra are shown, one with s-polarized light (with the main component of the electric field vector E in the $\begin{bmatrix} 2 & \overline{1} & \overline{1} \end{bmatrix}$ direction parallel to the surface) and a second spectrum with mixed-polarized light (with an additional component of É perpendicular to the surface). Surface state emission is mainly excited by the component of \vec{E} perpendicular to the surface, as represented by the difference curve in Fig. 3. Using dipole selection rules, this implies that the surface state is fully symmetric, i.e., $s_{,p_z}$ - type or Λ_1 symmetry if the symmetry group C_{3v} of the (1×1) or (2×2) surface is used.



FIG. 4. Polarization dependence of the diamond (111)- $(2 \times 1)/(2 \times 2)$ surface state emission showing that this state has fully symmetric Λ_1 (*s*, *p_z*-type) character. The difference curve between mixed and *s* polarization represents the part of the spectrum which is excited only by the component of \vec{E} perpendicular to the surface.

IV. COMPARISON WITH GRAPHITE

For using the diamond (111) surfaces as prototype of group-IV semiconductor surfaces it is important to know whether or not that surface undergoes a rehybridization into the thermodynamically more stable graphitic sp^2 configuration which is unstable for bulk silicon and germanium. Indeed, the angle-integrated data collected on the diamond (111)-(2×1)/(2×2) surface states so far is very similar to the behavior of the π bands of graphite which have p_z character. Our angle-resolved polarization-dependent spectra show, however, that this similarity is only superficial because the surface states on diamond (111)-(2×1)/ (2×2) have not the same momentum distribution as the π bands of graphite.

To stress the similarities between diamond (111)- $(2 \times 1)/(2 \times 2)$ and graphite, we note that the surface states seen in angle-integrated, density-of-states-type spectra of the diamond (111)- $(2 \times 1)/(2 \times 2)$ surface have binding energies similar to the graphite π bands. For the filled states this is shown in our angle-integrated photoelectron spectra (Fig. 1 and Fig. 5, dashed lines) which exhibit peaks at 2.4 and 2.9 eV below E_F for diamond (111)- $(2 \times 1)/(2 \times 2)$ and graphite, respectively. The electron energy loss spectrum which samples empty surface states of annealed diamond (111) (Ref. 12) resembles very much the loss spectrum of graphite.^{18,19} In particular, the loss



FIG. 5. Comparison of the surface state for diamond (111)- $(2 \times 1)/(2 \times 2)$ with the π band of graphite. While both states have similar binding energies in the angle-integrated spectra (dashed lines) the Λ_1 -surface state is peaked in normal emission in contrast to the graphite π band which is strongest off normal.

feature K_0 at 284 eV has been assigned¹² to transitions from the C 1s level into empty surface states on diamond (111). For graphite, a corresponding loss feature has been assigned to an excitonic transition from the C 1s level into empty π bands (Refs. 19 and 20).

In Fig. 5 we demonstrate the difference in momentum distributions between diamond (111)- $(2 \times 1)/(2 \times 2)$ and graphite (0001)-(1 \times 1). The angle-integrated spectra (dashed lines in Fig. 5) exhibit comparable strength of the diamond surface states and graphite π band but the angle-resolved spectra (full lines in Fig. 5) show that in normal emission from the graphite basal plane the π band almost vanishes at $E_F - 2.9$ eV whereas the diamond $(111)-(2\times 1)/(2\times 2)$ surface state has its intensity maximum in normal emission. The momentum distribution of the π band in graphite is peaked near the hexagonal Brillouin-zone boundary and is easily understood in terms of the calculated two-dimensional energy bands (Refs. 21 and 22) which have been confirmed experimentally (Refs. 23 and 24). The emission at $E_F - 2.9$ eV corresponds to the Q_{2u}^{-} critical point of the π_1 band. For $\vec{k}_{||}=0$, there are no states above $E_F - 4.5$ eV in graphite.

V. STRUCTURAL MODELS

One obtains structural information by comparing experimental surface state energy band dispersions with calculations for different rearrangements of surface atoms. This has been demonstrated for III-V and group-IV semiconductor surfaces. The calculations for diamond (111) (Refs. 1-5) do not take the $(2 \times 1)/(2 \times 2)$ reconstructions into account except for recent work by Pandey²⁵ which is in progress. The earlier findings¹⁻⁵ for diamond (111)- (1×1) are qualitatively similar to the results for Si(111)-(1 \times 1) calculations. They yield a halffilled band of dangling-bond-type surface states which is pinned at the Fermi level E_F . This is at variance with our data which exhibit a semiconducting surface. In a band picture, the metallic surface is a consequence of the odd number of dangling-bond electrons in the (1×1) unit cell. A similar conclusion has been reached by Pandey²⁵ for a (1×1) surface which has the first double layer of the unreconstructed diamond (111) surface compressed into a planar graphitelike structure. In this case, the broken bonds of the second double layer form a surface state band. Thus it is necessary to include the $(2 \times 1)/(2 \times 2)$ reconstruction in calculations of surface state bands.

Among the various types of reconstructions proposed in LEED work on diamond (111) surfaces^{6,26} and Si(111) surfaces, the Haneman buckling model and a new chain model proposed by Pandey²⁷ deserve special attention. A buckling reconstruction with alternate rows of atoms raised and lowered out of the surface plane has evolved into a widely accepted model for the Si(111)-(2 \times 1) cleavage surface. However, recent photoemission data²⁸ for Si(111)-(2×1) are inconsistent with band calculations for such a reconstruction. A similar situation seems to hold for diamond (111)- $(2 \times 1)/(2 \times 2)$. The experimental energy position, symmetry, and band dispersion of the surface state band on diamond $(111)-(2\times 1)/(2\times 2)$ is very similar to the observations on Si(111)-(2 \times 1) (Ref. 28) and in disagreement with a band calculation for the buckling model (Ref. 25), which yields much narrower band width and higher energy position. The only way to make the buckling model compatible with the data is to include large correlation effects²⁹ which are expected to become important for narrow bands. Pandy's chain model²⁷ appears to give energy band dispersions²⁵ which are compatible with the data for diamond $(111)-(2\times 1)/(2\times 2)$. This model has π bonding between the danglingbond orbitals within the chain similar to graphite, which yields a larger dispersion for the surface state band.

Empirically, one can reproduce essential features of the surface state band on diamond (111)- $(2 \times 1)/(2 \times 2)$ by folding the calculated π band of graphite^{21,22} into a (2×1) or (2×2) surface Brillouin zone.³⁰ In this case, the Q point of the graphite Brillouin zone would fall onto the $\overline{\Gamma}$ point of the reconstructed diamond surface Brillouin zone. Thus, the large density of states with momenta around Q_{2u}^{-} point in graphite can be transferred to the $\overline{\Gamma}$ point with $\vec{k}_{\parallel} = 0$ in diamond (111)- $(2 \times 1)/(2 \times 2)$ via the extra (2×1) - or (2×2) -lattice vector. The fact that this surface momentum transfer leads to a complete reversal in intensities between the center $\overline{\Gamma}$ and the boundary of the hexagonal (1×1) Brillouin zone indicates that there is a very strong reconstruction with respect to the

graphite lattice. This is consistent with the observation of strong second-order LEED spots.

ACKNOWLEDGMENTS

We wish to thank Dr. C. Phaal, Dr. F. A. Raal, Mr. G. C. McCallum, and the DeBeers Industrial Diamond Division, Ltd. for providing the highquality, type-II*b*, semiconducting diamond used in these experiments, and Harry Winston, Inc. for cleaving the diamond. We also wish to thank B. Reihl for help with the experiment, K. C. Pandey for providing his theoretical results prior to publication, the staff of the University of Wisconsin's Synchrotron Radiation Center, and J. J. Donelon and A. Marx for their capable help. This work was supported in part by the U. S. Air Force Office of Scientific Research (AFOSR) under Contract No. F-49620-81-C-0089.

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- ³⁰Graphite (0001) has a hexagonal-surface Brillouin zone like diamond (111)-(1×1) with 2.5% larger linear dimensions. The Q point in graphite corresponds to the \overline{M} point in diamond (111)-(1×1) (see Fig. 3).