PHYSICAL REVIEW B VOLUME 55, NUMBER 16 15 APRIL 1997-II

Dispersions of surface states on diamond (100) and (111)

R. Graupner, M. Hollering, A. Ziegler, J. Ristein, and L. Ley
Institut für Technische Physik, Universität Erlangen-Nürnberg, Erwin-Rommel-Straße 1, D-91058 Erlangen, Germany

A. Stampfl
School of Physics, La Trobe University, Victoria 3083, Australia

(Received 5 September 1996)

We present angle-resolved photoelectron spectra and surface state dispersions for the clean, 2×1 reconstructed (111) and (100) surfaces of diamond. For the (100) surface a surface state is found in the gap of the projected bulk band structure around Y, which has a binding energy of 2.7 eV at Y (relative to the Fermi level) and a dispersion in the Γ-Y direction of 0.5 eV, consistent with theory. At Γ a surface resonance is observed at 1.4 eV binding energy. No surface states were observed above the valence-band maximum. Our results on the (111) surface show a strongly dispersing surface state that reaches its maximum 0.5 eV below the Fermi level at K. This result implies a gap of at least 0.5 eV in the surface electronic structure, which has consequences for the surface reconstruction in terms of a π-bonded chain model. [S0163-1829(97)03416-4]

I. INTRODUCTION

When systematic studies of diamond surfaces began in the late 1960s the similarities between diamond and silicon surfaces were emphasized and research concentrated mainly on silicon. Recent developments, however, have rekindled the interest in diamond as a semiconductor material that might offer novel applications due to its energy gap of 5.5 eV, exceedingly high heat conductivity, and a hole mobility that is higher than in silicon. The key development is without doubt the possibility to deposit large areas of thin-film diamond from the gas phase by a variety of chemical vapor deposition (CVD) processes. This might also open the way to utilize one of the unique surface properties of diamond, namely, its negative electron affinity in the form of cold cathode emitters.[1] These potential applications have led us to study the electronic properties of diamond surfaces. In this paper we report the electronic structure of clean, reconstructed diamond (100) and (111) surfaces. Diamond surfaces are conventionally prepared by polishing with cast iron wheels using a suspension of diamond powder in olive oil. After transfer into UHV and annealing at about 500 °C a 1×1 low-energy electron diffraction (LEED) pattern is observed for the (111) (Refs. 2 and 3) and (100) (Refs. 4 and 5) surfaces. It is generally believed that these surfaces are terminated by hydrogen. Upon annealing above 900 °C the hydrogen desorbs and the LEED pattern changes on both surfaces corresponding to a 2×1 reconstruction.

The accepted model for the 2×1 reconstructed diamond (100) surface is that of π-bonded dimers as shown schematically in Fig. 1. This structural model is similar to that of the 2×1 Si (100) surface[6] except that most calculations favor symmetric, nonbuckled dimers for diamond,[7–12] whereas in silicon tilted dimers are established.[13] Despite this consensus about the atomic structure of the (100) surface, remarkable differences exist as far as its electronic structure is concerned. Theoretical results range from an almost dispersionless surface state band in the middle of the bulk band gap[14] to a wide splitting of occupied and empty surface states such that the former lie below the valence-band maximum throughout the surface Brillouin zone (SBZ).[12] The only experimental information available so far stems from angle-resolved photoemission spectra (ARPES) performed by Wu *et al.*[15] on diamond (100) 2×1 surfaces. They identify two surface related features that disperse with emission angle.

The surface structure that evolves upon terminating each surface atom by one hydrogen atom without destroying the dimer rows (monohydride dimer row reconstruction) is believed to be the stable (100) surface during CVD growth.[7] Indeed, a 2×1 reconstruction is observed on diamond surfaces that are prepared using a hydrogen plasma in a microwave reactor at temperatures that are characteristic for CVD growth[16,17] or grown homoepitaxially on single-crystal diamond.[18] The termination by hydrogen atoms was confirmed by high-resolution electron-energy-loss spectroscopy (HREELS).[19] Most theoretical papers agree that there are no occupied surface states in the projected band gap for the

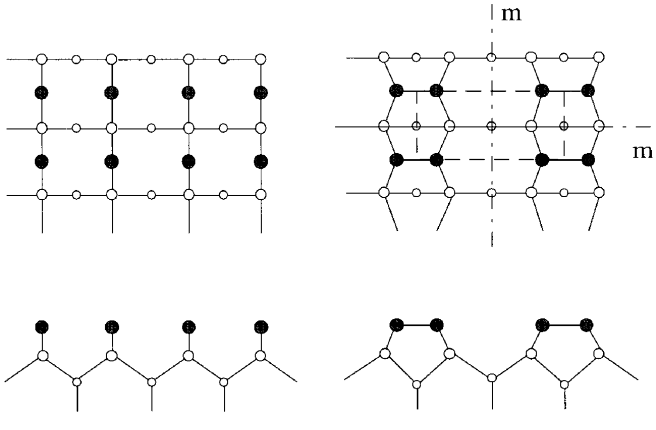

FIG. 1. Atomic structure of the ideal (left) and the 2×1, π-bonded dimer row reconstructed diamond (100) surface. The surface atoms are filled and the surface unit cell of the reconstructed surface is shown by the dashed line. Mirror planes are indicated by m.

0163-1829/97/55(16)/10841(7)/$10.00

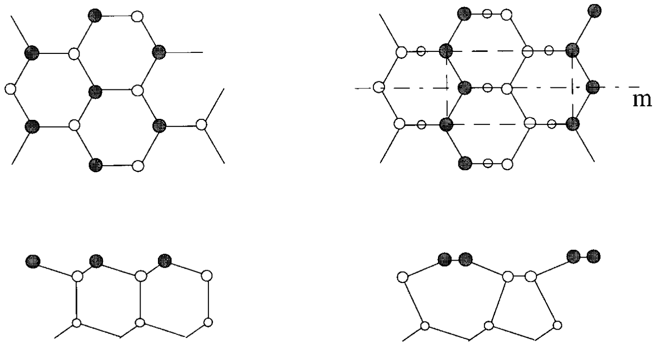

FIG. 2. Atomic structure of the ideal (left) and the 2×1 reconstructed diamond (111) surface according to the model of π-bonded chains. The surface atoms are filled and a surface unit cell of the reconstructed surface is shown by the dashed line. If a dimerization in the chains occurs, the mirror symmetry m is lost.

monoatomically terminated dimer row reconstruction.[20,12]

The question whether higher hydrogen terminations of the (100) surface do exist is still under debate. A termination of both dangling bonds by hydrogen, which would result in a 1×1 structure, would be accompanied by a strong repulsion between the hydrogen atoms on adjacent surface atoms due to the small interatomic distances of the diamond lattice (1.54 Å as compared to 2.35 Å in silicon). Therefore, the dihydride surface is found to be unstable in some of the theoretical investigations.[7,9] The experimentally observed 1×1 structure[4,5,15] might therefore just reflect the periodicity of the bulk material under a disordered surface.[19] An intermediate surface termination with hydrogen atoms that would show alternate rows of dihydride and monohydride termination is predicted theoretically,[21] but not confirmed experimentally.

On the ideal, bulk terminated (111) surface of diamond every surface atom exhibits one or three dangling bonds per surface atom. Of these alternatives the one with one dangling bond per surface atom is usually considered exclusively for energetic reasons (Fig. 2). Initial LEED measurements on diamond (111) were carried out by Marsh and Farnsworth[2] and Lander and Morrison.[3] A 1×1 LEED pattern was observed on the as-polished surface. Both observed half order spots after annealing, but could not distinguish between a 2×2 reconstruction or three, 120° rotated domains of a 2×1 reconstruction. Later Derry *et al.*[22] were able to observe a LEED pattern on a sample that showed a clear one-domain 2×1 reconstruction. Hamza *et al.*[23] performed electron stimulated desorption in combination with LEED on (111) surfaces. The desorption of H^+ ions took place at considerably lower temperatures (830 °C) compared to the occurrence of the half order LEED spots (1000 °C). They concluded that the desorption of hydrogen is a necessary but not sufficient condition for the reconstruction of the (111) surface. Pioneering work in photoelectron spectroscopy of diamond (111) surfaces was published by Pate *et al.*[24] They observed occupied states extending up to the Fermi level in the fundamental band gap. These surface states evolved upon formation of the 2×1 LEED pattern. Upon exposure to atomic hydrogen the LEED pattern reverted to 1×1 and the surface states in the bulk band gap vanished. Angle-resolved photoelectron spectroscopy was carried out by Himpsel *et al.*[25] for the 2×1 surface over a limited range of angles. They observed a surface state at an energy of 1 eV below the valence-band maximum, which showed an upward dispersion of about 1 eV from the center of the SBZ with $k_\parallel$ increasing in the [011] direction. However, they did not trace this surface state throughout the whole surface Brillouin zone.

The large bandwidth of the surface states seen in the photoemission experiments leads to the π-bonded chain model of Pandey[26] as the structural model for the hydrogen-free diamond (111) surface, again similar to the reconstruction of the silicon (111) surface. The surface atoms, which are second nearest neighbors for the bulk terminated surface, become nearest-neighbor atoms and form chains in the [101] direction (Fig. 2, right). The resulting π interaction along the chains leads to a dispersion of the occupied and empty surface bands of several eV. However, as long as the distance between adjacent surface atoms in the chains is equal, i.e., as long as no dimerization in the chains occurs, the surface is predicted to be semimetallic with a vanishing gap at the K point of the SBZ.[26] A dimerization has no effect on the size of the surface unit cell, i.e., the LEED pattern would remain 2×1, but is expected to open a gap between occupied and empty surface states.[26] An indication for such a gap in the surface band structure was found by Pepper.[27] He carried out electron-energy-loss spectroscopy (EELS) on diamond (111) surfaces and reported an energy gap of 2 eV, which could be observed in the characteristic loss region of annnealed sufaces. Namba *et al.*[28] combined ultraviolet excited photoemission spectroscopy and EELS and compared their results to the calculation of Pandey.[26] They also postulated a gap of about 2 eV in the surface band structure that supported the model of dimerized chains. The occupied states, however, did extend up to the Fermi level. Strong experimental support for the model of dimerized chains came from ion scattering experiments by Derry *et al.*[22] They were not able to explain their data without assuming a strong dimerization between adjacent surface atoms along the chains. An analysis of LEED intensities, on the other hand, supports the model of undimerized chains.[29] A study of the unoccupied surface states seen in two-photon photoemission[30] was unable to determine whether a a gap is present in the surface band structure. Theoretical papers differ with respect to dimerization depending on whether they base their calculations on experimental data or perform total-energy calculations to obtain the minimal-energy structure. A fit to the experimentally determined surface state energies of Himpsel *et al.*[25] by Vanderbilt and Louie[31] results in dimerized chains. Dimerized chains are also obtained if a band gap in the surface band structure is assumed *a priori*.[32] Only one total-energy calculation obtains dimerized chains with an energy gap of 0.3 eV,[33] while most authors postulate undimerized chains[34,35] and a semimetallic surface.

To summarize, there appears to be agreement on the general structure of the hydrogen-free, reconstructed diamond (100) and (111) surface. However, considerable controversy exists concerning the electronic structure of both surfaces. Moreover, on the (111) surface an additional dimerization may be present that is connected very sensitively with changes in electronic structure.

In this paper we present angle-resolved photoemission data for the hydrogen-free, 2×1 reconstructed (111) and (100) diamond surfaces with the aim to derive the dispersion relations of the occupied states. Our approach differs from that of previous work in that we do not start from mechanically polished surfaces. Instead, we employ a chemical polishing process involving a hydrogen plasma that yields a superior surface finish.

II. EXPERIMENTAL DETAILS

The samples we investigated were natural type-IIb (i.e., boron-doped) single crystal diamonds with polished (100) and (111) surfaces. For the (111) surface we also used a cleaved sample that gave results identical to those of the polished surface. As it turned out that the polished surfaces did not exhibit dispersing features in ARPES experiments they were subjected to an additional *ex situ* dry chemical polishing process by exposing them at a temperature of 800 °C for 15 min to a microwave hydrogen plasma.[17,16] After this treatment the (111) surface showed a sharp 1×1 LEED pattern indicating a bulklike termination of the surface covered with hydrogen atoms. After annealing at 1200 °C a three-domain 2×1 reconstruction occurred, which is characteristic for the hydrogen-free surface. The (100) surface exhibited a two-domain 2×1 reconstruction immediately after the same plasma preparation as performed on the (111) surface. Diamond (100) prepared that way is terminated monoatomically by hydrogen, as was confirmed by HREELS recently.[19] Annealing at 1200 °C has no effect on the symmetry of the LEED pattern of the (100) surface. However, the annealing temperature is well above the temperature necessary for a complete desorption of hydrogen (1050 °C).[19] Surfaces so prepared were free of any contamination as monitored by x-ray excited core level spectroscopy. All temperature measurements were carried out using an optical pyrometer. As diamond is transparent to the wavelength used by the pyrometer, all temperatures are given for the tantalum sample holder on the backside of the diamond sample. The actual temperature of the sample surface might have been considerably lower.

Angle-resolved photoelectron spectroscopy was carried out at the TGM 4 monochromator at BESSY, Berlin. As an electron analyzer we used the Toroidal Energy Analyser of Leckey and Riley,[36] which has an angle resolution of about 2° and the combined energy resolution of monochromator and analyzer was typically 200 meV. All measurements were performed in *p* polarization, i.e., with the **E** vector of the light in the azimuthal plane of the energy analyzer. The measured binding energies refer to the Fermi level E_F, which was determined on a clean polycrystalline gold sample and spectra were taken before and after annealing at 1200 °C, i.e., on the hydrogen terminated as well as on the clean diamond surfaces.

III. RESULTS AND DISCUSSION

A. The (100) surface

A set of photoelectron spectra ($\hbar\omega = 35$ eV, azimuth along [011]), taken on a hydrogen-covered diamond (100) 2×1 surface, is shown in Fig. 3, left-hand side. The relative orientation of the SBZ of the two 2×1 domains with respect to the [011] direction is explained in Fig. 4. The spectra are dominated by a sharp peak (*A*) at near-normal emission and a broad structure between 4 eV and 8 eV binding energy for emission angles larger than 20°. Figure 3, right-hand side, shows a set of spectra under the same experimental conditions after annealing at 1200 °C. Two new features appear between 1 eV and 3 eV (*B*,*C*), one of which (*B*) exhibits a clear dispersion as a function of emission angle. We ascribe these new structures that evolve upon annealing to the intrinsic surface states of the clean, 2×1 reconstructed surface (π-bonded dimer row reconstruction).

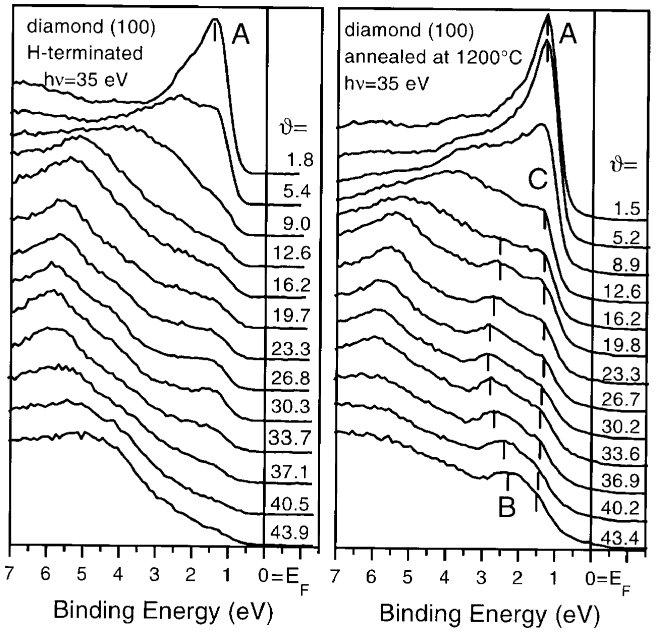

FIG. 3. Angle-resolved photoelectron spectra ($\hbar\omega = 35$ eV, azimuth [011]) of a diamond (100) surface, prepared in a microwave hydrogen plasma at 850 °C (left) and after annealing at 1200 °C (right).

If one attempts to trace the energies for structures *B* and *C* as a function of emission angle or, equivalently, of $k_{\parallel}$, the parallel component of the **k** vector, one faces the problem that both structures seem to join peak *A* at normal emission. Peak *A*, however, is unambigously related to the bulk as it appears in the spectra of the annealed as well as on the hydrogen terminated surface. If this structure originated from a direct transition between bulk states, the corresponding ini-

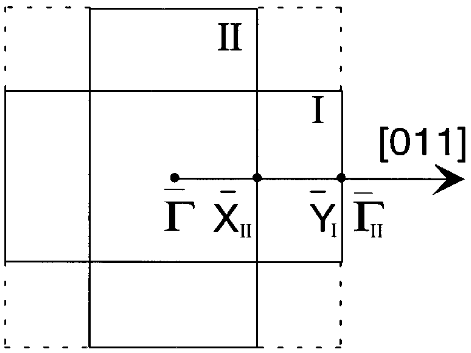

FIG. 4. Surface Brillouin zone of a two-domain, 2×1 reconstructed diamond (100) surface.

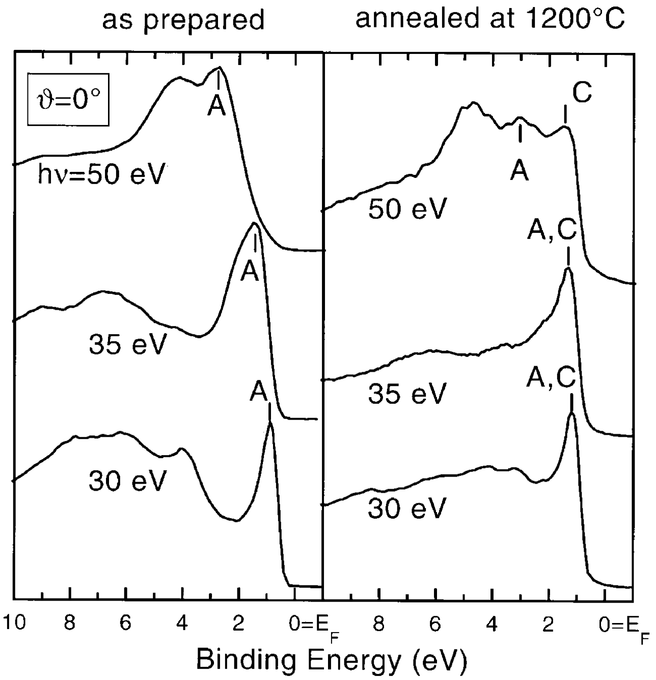

FIG. 5. Normal emission spectra for the as-prepared (left) and the annealed (right) diamond (100) surface. *A* denotes a direct transition between volume states and *C* the surface state.

tial state is expected to show a dispersion in $k_\perp$ and the peak position should change as the photon energy is varied. This is demonstrated in Fig. 5 for the normal emission spectra $(k_\| = 0)$. Peak *A* moves in both sets of spectra by 1.6 eV when going from 30 eV to 50 eV photon energy, a movement that corresponds to the dispersion of the topmost valence band (Δ_5) along the Γ-X direction of the bulk Brillouin zone. In the $\hbar\omega = 50$ eV spectrum of the annealed sample bulk (*A*) and surface state emission (*C*) are clearly seperated. From the spectra taken with $\hbar\omega = 30$ eV it is evident that the surface state is degenerate with bulk states at $k_\| = 0$ and thus forms a surface resonance at the $\bar{\Gamma}$ point, the center of the SBZ. A closer look at the sharp maximum in the $\hbar\omega = 30$ eV spectrum of the as-prepared as well as of the annealed surface reveals that it is shifted by 0.3 eV towards higher binding energies after annealing. This shift is induced by a change in surface band bending, which is a well-known effect of annealing of hydrogen passivated (100) (Refs. 15 and 37) and (111) surfaces[38–40] of *p*-type diamond.

In Fig. 6 the $E(k_\|)$ dispersion relations of structures *A*, *B*, and *C* are plotted as they were obtained from the spectra taken at $\hbar\omega = 50$ eV. The dispersion of structure *B* is symmetric around $k_\| = 1.25$ Å^{-1} with a maximum dispersion of about 0.5 eV between $k_\| = 0.7$ Å^{-1} and 1.9 Å^{-1}. Structure *C* shows a weak dispersion of about 0.25 eV with a shallow minimum at $k_\| = 0.6$ Å^{-1}. On account of the symmetry of their dispersion relations we identify these two structures as surface states belonging to either one of the two rotated domains of the 2×1 reconstructed surface. Peak *B* is symmetric with respect to the boundary of the surface Brillouin zone of domain I $(\bar{Y}_I$, see Fig. 4), whereas structure *C*, having double periodicity, would be consistent with a surface state on domain II.

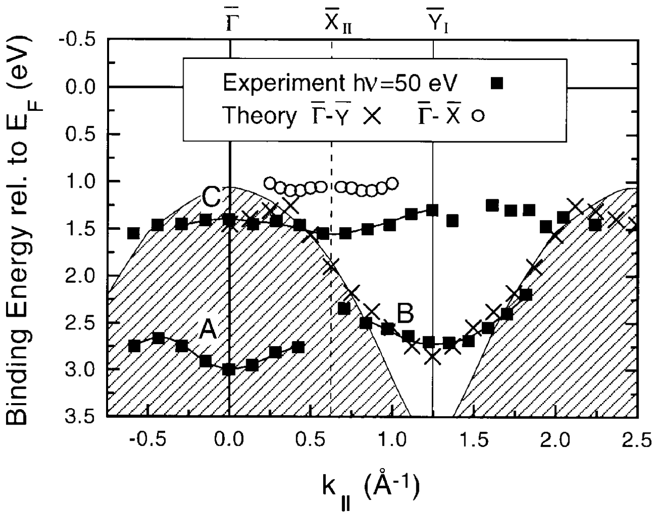

FIG. 6. $E(k_\|)$ relation for the topmost surface state on the diamond (100) surface as obtained by using $\hbar\omega = 50$ eV (black squares), compared to a calculation of the band structure of the intrinsic surface states (crosses, the Γ-Y direction; circles, the Γ-X direction). The shaded area is the projected bulk band structure.

Moreover, as the direction $\bar{\Gamma}$-$\bar{Y}$ is the direction along the chains in real space, a larger dispersion compared to the Γ-X direction is expected. This is confirmed by the experimentally observed dispersion relation.

In Fig. 6 we also compare our experimental results with the surface state dispersion as calculated by Furthmüller *et al.*[12] To do so we adjust theory and experiment using the strongly dispersing feature *B*, which agrees to within ±0.2 eV with the calculated surface state dispersion over the range in $k_\|$ where *B* is observed. This incidentally places the calculated valence-band maximum 1.0 eV below E_F. Experimentally, an upper limit for $E_F - E_{\mathrm{VBM}}$ can be given by inspection of the normal emission spectra of the annealed surface in Fig. 5. The minimum binding energy of 1.2 eV for a bulk derived feature is seen at $\hbar\omega = 30$ eV. Therefore, $E_F - E_{\mathrm{VBM}}$ has to be less than 1.2 eV. Our alignment of theoretical and experimental data to a common energy scale is thus compatible with this limit. The surface state *B* is related to the formation of π-bonding orbitals.[12]

We suspect that the surface state feature reported by Wu *et al.*[15] at normal emission and Francz *et al.*[37] (named S_1 in their papers) is indeed due to a combination of the surface resonance (*C*) and the direct transition from the bulk valence band (*A*). Both groups used a photon energy of about 40 eV, which results in spectra similar to the one recorded with $\hbar\omega = 35$ eV in Fig. 5 where no clear distinction between surface and bulk related features is possible. The binding energies of 1.5 eV and 1.4 eV reported in Refs. 15 and 37, respectively, are in accordance with the binding energy of 1.3 eV measured at $\hbar\omega = 35$ eV for peak *A* on the annealed surface if one takes the dispersion of bulk related features as demonstrated in Fig. 5 into account. At the boundary of the surface Brillouin zone (*Y* in our notation) Wu *et al.*[15] measured a binding energy of 2.4 eV for the surface state, which is slightly lower than the 2.7 eV determined here for structure *B*. However, the general form of the dispersion relation is the same.

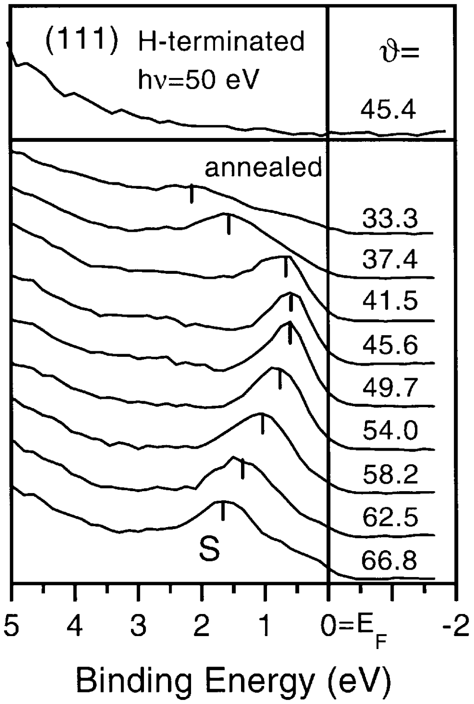

FIG. 7. Angle-resolved photoelectron spectrum taken at 45.4° taken from the as-prepared diamond (111) surface compared to a set of photoelectron spectra from $\theta = 33.3°$ to 66.8° taken from the surface annealed at 1200 °C. The photon energy is 50 eV at normal incidence of the incoming light and the measured azimuthal direction is [110].

The calculated dispersion of the same surface state in the direction Γ-*X* is shown in Fig. 6 as open circles.[12] Structure *C* does indeed have a weak dispersion as predicted by theory, but the energies are considerably different. At *X* the energies differ by 0.5 eV. We note that a very similar surface state was observed on (100) surfaces of silicon. Johansson *et al.*[41] observed an additional flat surface state band (called *B* in their publication) close to the valence-band edge on a single-domain, 2×1 reconstructed and hydrogen-free surface in the Γ-*Y* direction. The definite answer as to whether structures *B* and *C* belong to the same surface band might only be possible if one is able to measure single-domain reconstructed surfaces of diamond.[18]

B. The (111) surface

Figure 7 compares an angle-resolved photoelectron spectrum of a hydrogen terminated surface at a polar angle $\vartheta = 45°$ with a set of spectra taken from the annealed, hydrogen-free 2×1 reconstructed diamond surface at emission angles from $\vartheta = 33°$ to 67°. The azimuthal direction is [110], the photon energy $\hbar\omega = 50$ eV, and the light impinges along the surface normal. The feature labeled *S* that is absent in the spectrum of the hydrogenated surface is ascribed to emission from a surface state. It disperses towards lower binding energy until it reaches a minimum of 0.5 eV below E_F at $\vartheta = 46°$ and then moves back towards higher binding energies. In Fig. 8 the dispersion relation for this structure is plotted. The dispersion is symmetric with respect to $k_\parallel = 0$ Å^{-1} and $k_\parallel = 2.5$ Å^{-1}. It is at the latter **k** point in the SBZ where according to all current calculations the uppermost occupied band of surface states reaches its highest energy (i.e., lowest binding energy), as will be discussed below. The fact that experimentally the uppermost occupied surface band approaches E_F by no more than 0.5 eV implies a surface energy gap of at least that magnitude. Moreover, no other dispersing feature was found closer to E_F at any other $k_\parallel$ point.

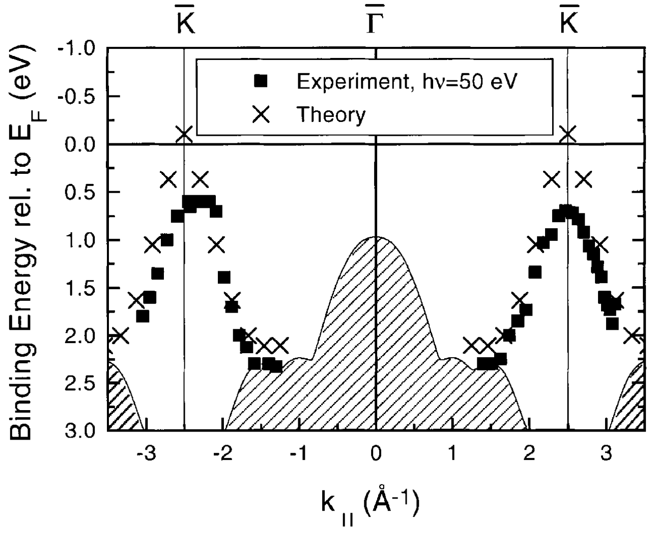

FIG. 8. $E(k_\parallel)$ relation of the structure seen in Fig. 7 for positive and negative angles. The crosses represent the results of an *ab initio* molecular-dynamics calculation of the surface states of the clean, reconstructed diamond (111) surface. The shaded area is the projected bulk band structure.

The overlapping SBZ's of three 2×1 domains are shown in Fig. 9. For domains I and II the $k_\parallel$ vector along [110] crosses the boundaries of the respective first SBZ at an angle of 60° and meets the Brillouin zone corner ($K_{\mathrm{I,II}}$) at $k_\parallel = 2.5$ Å^{-1} in the adjacent SBZ. From here it runs back until finally at $k_\parallel = 5$ Å^{-1} a Brillouin zone center (Γ) is reached again for both domains. The trajectories along [110] through the domains I and II are related to each other

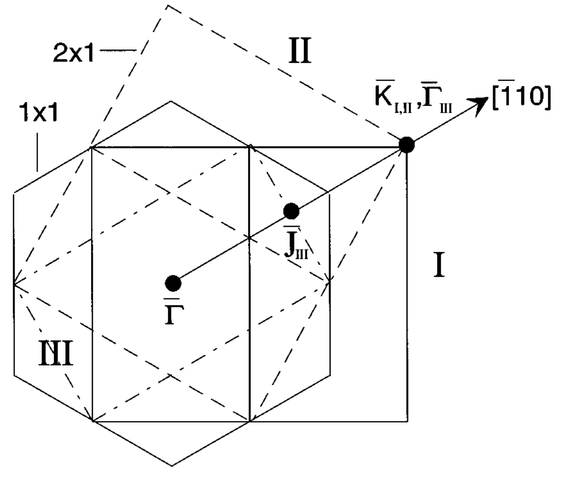

FIG. 9. Surface Brillouin zones of a three-domain, 2×1 reconstructed diamond (111) surface.

via the mirror operation *m* (Fig. 2) and time-reversal symmetry, which ensures $E(\mathbf{k}_{\parallel})=E(-\mathbf{k}_{\parallel})$ for surface states. As long as the surface reconstruction is such that *m* is conserved any $\mathbf{k}_{\parallel}$ vector along $[\bar{1}10]$ is equivalent in both domains. If the mirror symmetry is lost by dimerization, for example, a general point along $[\bar{1}10]$ is no longer equivalent in both domains except for the **k** vectors corresponding to the center $(\bar{\Gamma})$ and the corner $(\bar{K})$ of the SBZ's, respectively. These **k** points are equivalent in domains I and II even without mirror symmetry on account of the translational symmetry of the lattice alone. For domain III $\bar{J}$ lies at $k_{\parallel}=1.25$ Å^{-1} along $[\bar{1}10]$ and the next $\bar{\Gamma}$ is at $k_{\parallel}=2.5$ Å^{-1}. Taking these symmetry considerations into account, the dispersing structure in Fig. 7 is very likely a combination of the surface state dispersion for domains I and II. If no dimerization is present (i.e., the mirror symmetry of the surface unit cell is preserved) only one dispersing surface state is expected to be observed for both domains. If a dimerization takes place, two different structures might, in principle, be observed, which should, however, meet at $\bar{K}$ at $k_{\parallel}=2.5$ Å^{-1}. Moreover, at $\bar{K}$ the maximum in the surface state dispersion is expected as alluded to above.[26]

In Fig. 8 our measured and a recently calculated[42] surface state dispersion are compared. The theoretical data are taken from an *ab initio* molecular-dynamics calculation that predicts an undimerized, π-bonded chain reconstructed surface with no energy gap in the surface band structure. Therefore, the highest occupied orbital in the calculation corresponds to the Fermi energy E_F and theory and experiment can be compared without further adjustment of the energy scales. The bulk valence-band maximum is predicted to lie at 1.0 eV below E_F. The calculation reproduces the measurements remarkably well over most of the SBZ. However, whereas the calculation predicts that the surface state crosses E_F at $\bar{K}$ the experimental dispersion remains 0.5 eV below E_F. We are thus led to conclude that the surface band structure of the 2×1 reconstructed (111) surface has a gap of at least 0.5 eV. Nevertheless, in the spectra of Fig. 7 photoemission intensity is observed right up to E_F, which was reported by other authors as well.[25,43,40] This intensity is weak and nondispersing and is in our opinion not related to the well-ordered part of the diamond surface that gives rise to the dispersing surface state and the 2×1 LEED pattern. Instead, it might be due to patches on the surface where locally a graphitization as a result of the annealing step has occurred. This seems most probable for the (111) surface due to its hexagonal structure. Graphitization may take place on steps of the (111) surface as was shown theoretically.[44] Another place where graphitization may occur are twins on the (111) surface.[45] Twin formation is a common phenomenon in homoepitaxial CVD growth on (111) faces of diamond. As our preparation technique is very similar to CVD growth conditions it cannot be excluded that locally twins have formed on our surface.

Himpsel *et al.*[25] were able to observe a surface state dispersing upward in the same azimuthal direction as shown in Fig. 8 with an energy difference of 1 eV between $k_{\parallel}=0.8$ Å^{-1} and $k_{\parallel}=1.3$ Å^{-1}. This structure is not seen in our measurements. Presumably the peak they observed is the same surface state, however, for domain III near $\bar{J}$. As mentioned, the experimental surface state dispersion requires a gap in the surface state band structure of at least 0.5 eV, which is in agreement with the early EELS mesurements of Pepper.[27] An opening of a gap in the surface band structure is usually ascribed to a dimerization of the surface atoms within the π-bonded chains.[26] Most recent theoretical publications on the structure of the (111) surface of diamond, however, agree that no dimerization along the chains occurs. A recent calculation by Schmidt *et al.*,[46] for example, shows that even the slightest dimerization increases the total energy of the surface. Therefore, the question remains whether there exists an alternative mechanism that would open up a gap in the surface band structure of diamond.

IV. CONCLUSION

Angle-resolved photoemission experiments on plasma-polished, hydrogen-free 2×1 reconstructed diamond surfaces reveal strongly dispersing occupied surface states on both surfaces. The surface state dispersions determined for the (100) surface are in general agreement with those expected for a surface reconstructed in the form of π-bonded dimers according to recent band-structure calculations.

For the (111) surface the dispersion relation is in general agreement with a reconstruction in the form of π-bonded chains. However, contrary to most total-energy and band-structure calculations, which predict a semimetallic surface, our results support a semiconducting surface with a gap of at least 0.5 eV. This result is in agreement with most surface reconstructions of covalently bonded semiconductors where reconstructions lead to a semiconducting as opposed to a metallic surface state eigenvalue spectrum, a point that has been stated succinctly by Duke[47] recently. At the same time it raises the question as to whether this gap in the surface band structure is necessarily connected with a dimerization of the atoms in the π-bonded chains, a belief that is generally held up to now, but appears to be in conflict with the results presented here and total-energy calculations that exclude dimerization on energy grounds. On the experimental side similar investigations on single-domain reconstructed (100) and (111) are desirable because they would allow an unambigous sampling of the surface state dispersions along different directions in the SBZ.

ACKNOWLEDGMENTS

We would like to thank G. Kern and Professor J. Hafner for calculating dispersion relations along special directions of the diamond (111) surface and supplying these data prior to publication for comparison with our experiments, and K. Janischowsky and R. Stöckel for the hydrogen plasma preparation. The authors gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft (Project No. Le 634/5-2) carried out under the auspices of the trinational ''D-A-CH'' cooperation of Germany, Austria, and Switzerland on the ''Synthesis of Superhard Materials.'' The measurements at BESSY were supported by the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie under Contract No. 05 622 WEA 7.

[1] C. Wang, A. Garcia, D. C. Ingram, M. Lake, and M. E. Kordesch, Electron. Lett. **27**, 1459 (1991).
[2] J. B. Marsh and H. E. Farnsworth, Surf. Sci. **1**, 3 (1964).
[3] J. J. Lander and J. Morrison, Surf. Sci. **4**, 241 (1966).
[4] P. G. Lurie and J. M. Wilson, Surf. Sci. **65**, 453 (1977).
[5] A. V. Hamza, G. D. Kubiak, and R. H. Stulen, Surf. Sci. **237**, 35 (1990).
[6] R. E. Schlier and H. E. Farnsworth, J. Comput. Phys. **30**, 917 (1959).
[7] Y. L. Yang and M. P. D'Evelyn, J. Vac. Sci. Technol. A **10**, 978 (1992).
[8] Z. Zhang, M. Wensell, and J. Bernholc, Phys. Rev. B **51**, 5291 (1995).
[9] T. Frauenheim, U. Stephan, P. Blaudeck, D. Porezag, H. G. Busmann, W. Zimmermann-Edling, and S. Lauer, Phys. Rev. B **48**, 18 189 (1993).
[10] C. Kress, W. G. Schmidt, and F. Bechstedt, Phys. Rev. B **50**, 17 697 (1994).
[11] P. Krüger and J. Pollmann, Phys. Rev. Lett. **74**, 1155 (1995).
[12] J. Furthmüller, J. Hafner, and G. Kresse, Phys. Rev. B **53**, 7334 (1996).
[13] W. Mönch, in *Semiconductor Surfaces and Interfaces*, edited by G. Ertl, R. Gomer, and D. L. Mills, Springer Series in Surface Sciences Vol. 26 (Springer-Verlag, Berlin, 1995), and references therein.
[14] V. I. Gavrilenko, Phys. Rev. B **47**, 9556 (1993).
[15] J. Wu, R. Cao, X. Yang, P. Pianetta, and I. Lindau, J. Vac. Sci. Technol. A **11**, 1048 (1993).
[16] B. D. Thoms, M. S. Owens, J. E. Butler, and C. Spiro, Appl. Phys. Lett. **65**, 2957 (1994).
[17] O. M. Küttel, L. Diederich, E. Schaller, O. Carnal, and L. Schlapbach, Surf. Sci. **337**, L812 (1995).
[18] N. Lee and A. Bazian, Phys. Rev. B **53**, R1744 (1996).
[19] B. D. Thoms and J. E. Butler, Surf. Sci. **328**, 291 (1995).
[20] B. N. Davidson and W. E. Pickett, Phys. Rev. B **49**, 11 253 (1994).
[21] S. H. Yang, D. A. Drabold, and J. B. Adams, Phys. Rev. B **48**, 5261 (1993).
[22] T. E. Derry, L. Smit, and J. F. Van der Veen, Surf. Sci. **167**, 502 (1986).
[23] A. V. Hamza, G. D. Kubiak, and R. H. Stulen, Surf. Sci. **206**, L833 (1988).
[24] B. B. Pate, P. M. Stefan, C. Binns, P. J. Jupiter, M. L. Shek, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **19**, 349 (1981).
[25] F. J. Himpsel, D. E. Eastman, P. Heimann, and J. F. van der Veen, Phys. Rev. B **24**, 7270 (1981).
[26] K. C. Pandey, Phys. Rev. B **25**, 4338 (1982).
[27] S. V. Pepper, Surf. Sci. **123**, 47 (1982).
[28] H. Namba, M. Masuda, and H. Kuroda, Surf. Sci. **33/34**, 187 (1988).
[29] E. C. Sowa, G. D. Kubiak, R. H. Stulen, and M. A. V. Hove, J. Vac. Sci. Technol. A **6**, 832 (1988).
[30] G. D. Kubiak and K. W. Kolanski, Phys. Rev. B **39**, 1381 (1989).
[31] D. Vanderbilt and S. G. Louie, J. Vac. Sci. Technol. B **1**, 723 (1983).
[32] C. Kress, M. Fiedler, and F. Bechstedt, Europhys. Lett. **28**, 433 (1994).
[33] S. Iarlori, G. Galli, F. Gygi, M. Parinello, and E. Tosatti, Phys. Rev. Lett. **69**, 2947 (1992).
[34] D. Vanderbilt and S. G. Louie, Phys. Rev. B **29**, 7099 (1984).
[35] G. Kern, J. Hafner, and G. Kresse, Surf. Sci. **352-354**, 745 (1996).
[36] R. C. G. Leckey and J. D. Riley, Appl. Surf. Sci. **22/23**, 195 (1985).
[37] G. Francz, P. Kania, G. Ganther, H. Stupp, and P. Oelhafen, Phys. Status Solidi **154**, 91 (1996).
[38] B. B. Pate, M. Oshima, J. A. Silberman, G. Rossi, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. A **2**, 957 (1984).
[39] J. F. Morar, F. J. Himpsel, G. Hollinger, J. L. Jordan, G. Hughes, and F. R. McFeely, Phys. Rev. B **33**, 1340 (1986).
[40] R. Graupner, J. Ristein, and L. Ley, Surf. Sci. **320**, 201 (1994).
[41] L. S. O. Johansson, R. I. G. Uhrberg, P. Mårtensson, and G. V. Hansson, Phys. Rev. B **42**, 1305 (1990).
[42] G. Kern, J. Hafner, and G. Kresse, Surf. Sci. **366**, 445 (1996). The particular direction used here was calculated for us by the authors using the same potentials.
[43] B. B. Pate, M. H. Hecht, C. Binns, I. Lindau, and W. E. Spicer, J. Vac. Sci. Technol. **21**, 364 (1982).
[44] B. N. Davidson and W. Pickett, Phys. Rev. B **49**, 14 770 (1994).
[45] G. Jungnickel, D. Porezag, T. Frauenheim, M. I. Heggie, W. R. L. Lambrecht, B. Segall, and J. C. Angus, Phys. Status Solidi **154**, 109 (1996).
[46] W. G. Schmidt, A. Scholze, and F. Bechstedt, Surf. Sci. **351**, 183 (1996).
[47] C. B. Duke, Chem. Rev. **96**, 1237 (1996).