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Normally unoccupied states on C(111) (diamond) (2×1): Support for a relaxed π-bonded chain model

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A normally unoccupied electronic state on the reconstructed (2×1) surface of C(111) (diamond) is characterized with angle-resolved two-photon photoelectron spectroscopy. The state is seen in the bulk band gap, lying 4.8 eV above the valence-band maximum. Comparison between the measured dispersion of this band and published theoretical band-structure calculations supports a relaxed Pandey π-bonded chain model of the surface reconstruction.

The (111) surface of the diamond allotrope of carbon is unstable with respect to reconstruction,[1,2] a property shared by the other tetrahedral group-IV semiconductors, Si and Ge. Common to these elemental solids is the creation of singly occupied surface dangling bonds upon truncation of the solid to form the (111) face; an energetically unfavorable situation. One of the reconstructed phases exhibited by all of these surfaces is the so-called (2×1) surface,[3] involving a structure which exhibits a real-space period doubling along one mesh vector and retains the truncated-bulk period along the other mesh vector. The electronic and geometric structure of the C(111) (diamond) (2×1) surface is not only of fundamental interest, but is of growing technological relevance as well. For example, the formation of the (2×1) phase may play an important role in determining the morphology[4] of diamond films grown by deposition from the gas phase.

We have applied angle-resolved two-photon photoelectron spectroscopy in this work to the study of normally unoccupied (empty) electronic states on the (2×1) surface of C(111) (diamond), since it is known that the energy and dispersion of these states depend sensitively upon the structural details of the reconstruction. As in recent two-photon photoemission work on the Si(111)-(2×1) surface,[5] empty surface states are populated via intense pulsed photoexcitation and are subsequently ionized by a second photon which can be made spatially and temporally coincident with the first. Angle-resolved empty-state binding energies yield $E(k_\parallel)$ dispersion relations which are compared with recent theoretical calculations.

Both air-cleaved and mechanically polished C(111) (diamond) surfaces are known to be terminated with hydrogen (predominantly bound as a monohydride[6]) and exhibit helium and low-energy electron diffraction (LEED) patterns having (1×1) symmetry.[6,4] Heating this surface to temperatures of 1225–1275 K causes the desorption of hydrogen and the formation of an apparent (2×2) LEED pattern,[1,2,4] comprised of three nearly equivalent domains of (2×1) symmetry.[7] Structural and electronic aspects of this reconstruction have received considerable experimental and theoretical attention. Models based upon surface π-bonded chains, first proposed by Pandey,[8] are currently favored, but questions regarding multilayer relaxations and intrachain dimerization remain. Ion scattering,[7] comparison between calculations[8–10] and photoemission from occupied states,[11,12] electron-energy-loss spectroscopy (EELS),[13] and x-ray absorption[14] all support a π-bonded chain model. In addition, recent evidence suggests antiferromagnetic spin ordering within the proposed π-chains.[15]

The experimental approach, the associated apparatus, and sample preparation have been described in detail elsewhere.[16,17] Both a synthetic, semiconducting crystal[18] and a natural type-IIa sample were investigated. Data will be presented only for the former; no significant differences could be discerned between the (2×1) empty surface state spectra obtained from these samples. Sharp (1×1) LEED patterns were recorded for both samples upon flashing to 800 K. Annealing the samples repeatedly at temperatures > 1275 K desorbed hydrogen from the (1×1) surface,[19,4] resulting in the appearance of sharp, high-contrast LEED images of three nearly equivalent domains of (2×1) symmetry. Angle-resolved photoemission data were collected when the energy-averaged $\frac{1}{2}$-order spot intensities had grown to at least 50% of the averaged first-order spot intensities. After experiments were completed on a given sample, Auger electron spectroscopy confirmed surface cleanliness.

Two-photon photoemission data were acquired for both the (1×1) and (2×1) surfaces using photon energies ($h\nu$) of $3.4 < h\nu < 5.6$ eV. Laser-pulse energy densities were kept below 3 mJ cm^{-2} to prevent space-charge spectral broadening. Polarization of the light could be varied continuously between pure *s*-polarized and *p*-polarized. Stimulated Raman scattering in a cell pressurized with 6.3 atm H_2 was employed to generate light at 6.4 eV for one-photon measurements. Using one-photon photoemission at $h\nu = 6.4$ eV, the energy of the valence-band maximum (VBM) was found to be -1.6 ± 0.2 eV with respect to the Fermi energy (E_F); the sample work function was found to be 4.4 ± 0.2 eV (vacuum level, E_V, 6.0 eV above E_{VBM}). The $E_F - E_{\mathrm{VBM}}$ splitting agrees well with previous measurements, but the work function is ~ 0.5 eV less than values reported previously.[11,20] The value of $E_V - E_{\mathrm{VBM}}$ was determined before acquiring two-photon photoemission data to ensure that the energy of the empty state referenced to the VBM is accurate for each run.

Figure 1 compares the two-photon photoemission spectra from the (1×1) and (2×1) surfaces, as well as the po-

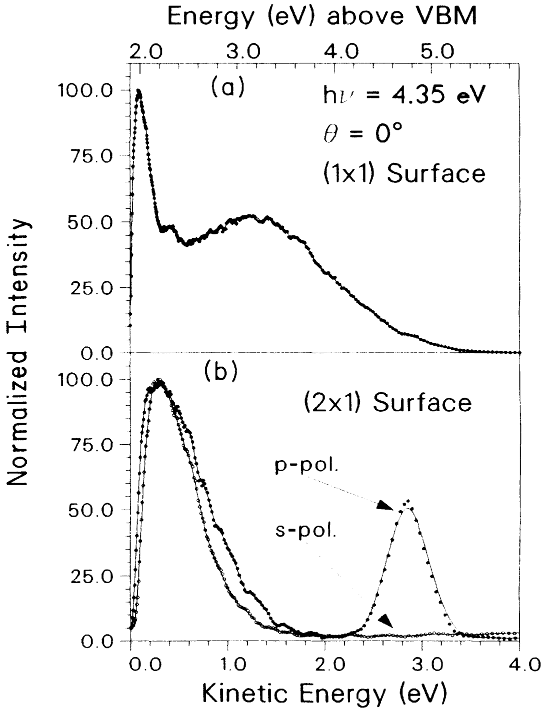

FIG. 1. Normal emission ($\theta=0°$) two-photon photoelectron kinetic energy spectra of the C(111) (diamond) (1×1) (top panel) and (2×1) (lower panel) surfaces. The lower panel also shows the polarization dependence of the (2×1) empty-state two-photon photoemission intensity.

larization dependence of the emission intensity from the (2×1) surface. The (1×1) surface yields a spectrum with a sharp, low-energy spike characteristic of a negative electron affinity,[21] and a broad, structureless feature we associate with secondary electrons. We find no evidence for an empty surface state on this surface. In contrast, upon formation of the (2×1) surface we find intense two-photon photoemission from an empty state lying in the band gap 4.8 eV above the VBM at $\bar{\Gamma}$. In normal emission the state is detectable only when p-polarized excitation is used, demonstrating that the empty states are of even symmetry. The surface-state assignment of this feature is determined by the following observations: (1) The state lies in the absolute bulk band gap; (2) the binding energy of the state is invariant (±0.1 eV) in normal emission with respect to $h\nu$ between 3.75 and 4.9 eV (i.e., the state exhibits no dispersion as a function of the wavevector projected along the surface normal); (3) the state depends sensitively upon the chemical and structural state of the surface [e.g., reformation of the (1×1) surface, ion bombardment, and annealing to ~1575 K each cause the (2×1) empty state to disappear]. The observations listed in (3) discount the possibility that the observed state originates from surface graphitization. Ion bombardment and very high-temperature annealing are known to graphitize diamond surfaces[22,23] and yet these treatments cause the disappearance of the two-photon feature we observe.

Since the apparent (2×2) symmetry of the reconstructed surface consists of three nearly equivalent (2×1) domains, a polar angular scan along a given laboratory azimuth may contain photoemission contributions from the azimuth ϕ of one domain plus azimuths rotated by $\phi\pm120°$ for the other two domains. We have chosen the high-symmetry azimuths $\bar{\Gamma}-\bar{J}$ and $\bar{\Gamma}-\bar{K}$ of the (2×1) surface Brillouin zone (SBZ) for one domain (see inset, Fig. 3) to determine the $E(k_{\|})$ dispersion relations of the (2×1) state. The $\bar{\Gamma}-\bar{J}$ direction of the chosen domain is parallel to the chain axis of one domain in the π-bonded chain model and lies 30° off the $\bar{\Gamma}-\bar{J}'$ direction for the other two domains. Figure 2(a) shows the variation in measured (2×1)-state kinetic energy versus θ for this

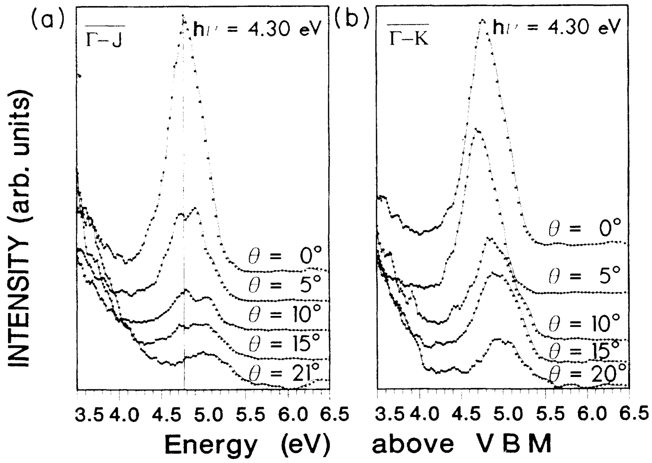

FIG. 2. Plots of the measured kinetic energy of the (2×1) empty state versus θ along (a) the $\bar{\Gamma}-\bar{J}$ laboratory-frame azimuth, and (b) the $\bar{\Gamma}-\bar{K}$ laboratory-frame azimuth. For clarity, only data for one side of the zone are plotted.

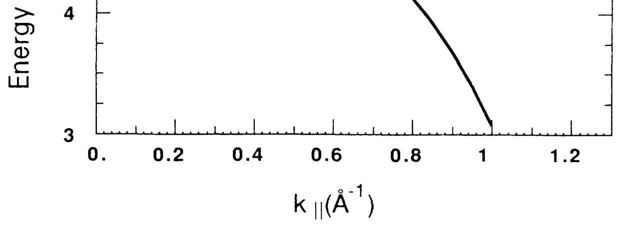

FIG. 3. Experimental (2×1) empty surface-state $E(k_{\|})$ dispersion (triangles) plotted for the $\bar{\Gamma}-\bar{J}$ direction of the SBZ (see inset). Solid and open symbols correspond to positive and negative polar angles, respectively. Plotted for comparison is the calculated empty state $E(k_{\|})$ dispersion curve of Vanderbilt and Louie, Ref. 9(b), for an undimerized π-bonded chain with $+8.1\%$ double-layer relaxation.

laboratory azimuth. The contributions of two classes of (2×1) domain are apparent; one feature disperses upward in energy with increasing θ, another weaker feature has nearly constant energy over the sampled region of θ. We assume that the dispersive feature in Fig. 2(a) is derived from the domain oriented along $\bar{\Gamma}-\bar{J}$, while the nondispersive feature is associated with the two domains oriented 30° off $\bar{\Gamma}-\bar{J}\,'$. This assignment is consistent with bands calculated for π-bonded chain geometries, which show far less dispersion along $\bar{\Gamma}-\bar{J}\,'$ than along $\bar{\Gamma}-\bar{J}$.[8,9] For the laboratory direction $\bar{\Gamma}-\bar{K}$, two domains share the $\bar{\Gamma}-\bar{K}$ azimuth and should contribute equally to the photoemission intensity while the third domain will be oriented along $\bar{\Gamma}-\bar{J}\,'$ (i.e., normal to the π-bonded chains). Figure 2(b) shows the measured variation in kinetic energy versus θ for this azimuth and, as can be seen, only one spectral maximum is apparent, dispersing upward with increasing $k_{\parallel}$.

Figure 3 plots the experimental $E(k_{\parallel})$ dependence for the direction $\bar{\Gamma}-\bar{J}$ of the (2×1) SBZ, determined from the centroid energy of the dispersive feature of Fig. 2(a). Due to insufficient photon energies in attempted *two-color* experiments ($h\nu_1\leq4.4$ eV, $h\nu_2\leq6.5$ eV), we were unable to measure the empty state dispersion beyond $0.3\bar{J}$. Also shown in Fig. 3 is the (2×1) band structure calculated by Vanderbilt and Louie[9(b)] for a fully relaxed π-bonded chain model with no dimerization. The energy position and slight upward dispersion (0.3 eV) of the state from $\bar{\Gamma}$ to $0.3\bar{J}$ are in good agreement with the calculated band dispersion. Moreover, this state is observed only in p-polarized excitation, confirming the even symmetry and, hence, the p_z character of the orbitals which form the surface state. Agreement between experiment and theory is achieved only if the bonds between the surface double layer and the second double layer are allowed to lengthen: $+8.1\%$ with respect to the bulk spacing for the structure used to calculate the bands shown in Fig. 3.[9(b)] In contrast, band calculations for a π-bonded chain geometry with no relaxation between the surface double layer and the bulk place the empty state above the gap at ~6 eV near $\bar{\Gamma}$.[9(a)]

Empty states have been seen previously on the (111) (2×1) diamond surface by Pepper[13] and Morar *et al.*,[14] who used EELS and soft x-ray absorption spectroscopy, respectively. The EELS measurement integrates over the SBZ and is subject to uncertainties in the spectral subtraction procedure employed, making detailed comparison to the current results difficult. It is nonetheless interesting to note that the loss feature would be expected to extend to ~6 eV based on the energy difference at $\bar{\Gamma}$ between the empty state seen here and the filled state seen earlier.[11,12] Indeed, x-ray absorption *does* exhibit a weak feature ~6 eV above the filled (2×1) surface state (4.8 eV above VBM), assigned as excitation to an empty state at the zone center,[14] in excellent agreement with the current results.

Inequivalence of the π-bond lengths between atoms constituting the π-chain (dimerization) causes a gap to open between filled and empty states at the $\bar{J}$ point of the SBZ. The dispersion of the surface state along $\bar{\Gamma}-\bar{J}$ near $\bar{J}$ and the magnitude of the empty-filled band gap near $\bar{J}$ (~1 eV from Pepper's EELS investigation[13]) can therefore provide sensitive tests of the extent of dimerization within the π-bonded chains. An undimerized π-chain geometry is favored by the calculations of Vanderbilt and Louie,[9] in contrast to the dimerized π-chain geometry favored by both Pandey[8] and Dovesi *et al.*,[10] who find a calculated minimum energy structure with ±0.09-Å dimerization.[24] The results shown in Fig. 3 agree *best* with bands calculated for an undimerized geometry, but in the region of the SBZ we have been able to map, *all three* calculations yield $E(k_{\parallel})$ dispersions having shapes which agree generally with these results (although the band calculated by Dovesi *et al.* appears to be shifted rigidly by $+2.5$ eV compared to our data). Thus, we are unable to conclude if dimerization is present in the π-chain geometry. Ion scattering data[7] suggest a strongly dimerized π-chain, but recent LEED *I-V* analysis[25] of the (2×1) surface supports dimerization of less than 8%. A quantitative determination of the dimerization must await more extensive two-color experiments and LEED *I-V* analysis, currently underway in our laboratory.

In summary, we have characterized a normally unoccupied surface state on the reconstructed C(111) (diamond) (2×1) surface. The energy and dispersion of this state are consistent with a relaxed Pandey π-bonded chain model. In addition, we find that this state has even symmetry, reflecting its p_z parentage. The issue of dimerization within the π-chains cannot be resolved from the present measurements alone.

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