

One-Dimensional Delocalized Adsorbate Bloch States on a Semiconductor Surface: $C_2H_4/Si(001)-(2 \times 1)$

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We report the observation of a 1D molecular adsorbate band structure caused by direct adsorbate-adsorbate interactions on a semiconductor. For ethylene chemisorbed on $Si(001)-(2 \times 1)$ two adsorbate-derived electronic states, $1b_{3u}$ and $1b_{2g}$, are found to delocalize along the Si-Si dimer rows. The corresponding bands can be followed in reciprocal space from the $\bar{\Gamma}$ point into the third surface Brillouin zone. Density functional calculations for ethylene adsorbed on a silicon slab reproduce the experimental 1D band structure and allow us to identify the origin of the lateral interactions. [S0031-9007(98)06054-2]

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It is well known that electrons (as well as other quasiparticles) in periodic lattices of atoms and molecules have to be described as delocalized states when significant interactions occur, e.g., via overlap of their wave functions. These Bloch states are characterized by their lattice quasi-momentum $\hbar k$ and their band energy $E(k)$. The amount of energy dispersion depends on the specific interunit cell interaction of the electron states. 3D solids in general exhibit dispersing Bloch states traveling in all three dimensions. However, there might be situations where the dimensionality of the electronic structure is reduced to 2D, e.g., if the mutual interaction is restricted to a plane as for layered structures such as graphite or TaS_2 [1]. Similarly 1D electronic structures have been found in special classes of materials like Krogmann salts, phthalocyanines, or conducting polymeres [2]. A different approach to electronically low-dimensional systems exploits the fact that solid surfaces intrinsically define 2D lattices. On metals, for instance, 2D band structures of surface states and adsorbate valence levels have been investigated quite extensively in the past [3–5]. Here the preparation of densely packed adlayers is a crucial prerequisite for significant lateral adsorbate-adsorbate interactions to occur and hence for the formation of a 2D dispersing band structure. On metals adlayers often rearrange and reorient themselves to achieve coverages as high as possible, e.g., by occupation of otherwise empty sites, or by a tilt or rotation of the adsorbed molecules [6]. On semiconductors such effects are less probable due to the more directional, covalentlike bonds which are expected here between adsorbate and substrate; compression effects in chemisorbed adlayers on semiconductor surfaces are rare. This and the relatively small number of adsorption systems on semiconductors investigated at all might be the reason that no studies on molecular adsorbate band structures have been reported so far. Nevertheless, direct adsorbate wave function over-

lap should also be possible on semiconductors provided the size of the surface or overlayer unit cell matches the size of the chemisorbed molecules. A further reduction of the dimensionality to electronically one-dimensional structures might be imaginable for adsorption systems which are grown on highly anisotropic surface structures. So far, even on metals truly 1D adsorbate band structures have only been reported for a weakly bound xenon layer on a missing-row reconstructed (and coadsorbate modified) $Pt(110)-(2 \times 1)$ surface [7,8]. The quite strong attractive lateral interactions within rare gas layers (as compared to the “vertical” adsorbate-substrate interaction) leads to significant wave function overlap. However, no 1D band structures of chemisorbed molecular adsorbates have been reported so far, despite the fact that geometrically 1D adsorbate structures can be prepared, e.g., by preferential adsorption at step edges on vicinal surfaces [9].

In this Letter we report the first experimental observation of a 1D molecular adsorbate band structure on a semiconductor. This is also the first demonstration of direct adsorbate-adsorbate interactions in such a system. For the unsaturated hydrocarbon molecule ethylene chemisorbed on a single-domain $Si(001)-(2 \times 1)$ surface two of the seven adsorbate-derived valence states are found to delocalize along the dimer rows (the [110] direction). Using angle-resolved photoelectron spectroscopy, the corresponding 1D-band structure has been followed in reciprocal space from the $\bar{\Gamma}$ point through two and into the third surface Brillouin zone. Detailed density functional (DF) calculations for ethylene adsorbed on a six layer silicon slab are able to reproduce the experimental 1D band structure semiquantitatively and show that the origin of the lateral interactions must be direct through-space interactions, i.e., lateral wave-function overlap.

For the angle-resolved photoemission experiments linearly polarized light from the TGM-1 beam line at the

Berlin synchrotron radiation facility in combination with a homebuilt multiangle electron energy analyzer [10] was used. To separate the photoemission signal from the two equivalent, (2×1) and (1×2) , domains of the Si(001) surface the experiments were performed on vicinal Si(001) samples (5° miscut towards [110]) which exhibit single-domain terraces 8.5 dimers wide, separated by biatomic D_B steps.

Figure 1 shows UPS data for a saturated ethylene layer chemisorbed on Si(001)- (2×1) [11]. For comparison a spectrum of the clean surface is given. Six ethylene-derived peaks can be identified at binding energies of 17.9, 14.3, 9.2, 6.7, 5.8, and 3.9 eV with respect to the Fermi level; a weak ethylene-derived shoulder at 8.2 eV is also discernible. The assignment as indicated in Fig. 1 is straightforward for the photoemission features above 6 eV, based on a comparison with gas-phase data. The two highest ethylene-derived peaks at 5.8 and 3.9 eV result from the interaction of the highest occupied and the lowest unoccupied molecular orbitals of gas-phase ethylene with the Si(001) surface, the π and π^* states, respectively. Upon adsorption they essentially evolve into the symmetric and antisymmetric linear combinations of the two newly formed Si-C bond orbitals of the di- σ bonded species. A detailed analysis of angle-resolved photoemission results, including the symmetry of the adsorbate complex and its complete electronic structure which both can be well understood on the basis of DF slab calculations, will be presented elsewhere [12,13]. In the following we focus on those purely ethylene-derived states which exhibit strong energy shifts (dispersion) with the polar photoemission angle θ : the $1b_{3u}$ and the $1b_{2g}$ bands. The symmetry labels refer to a local coordinate system of ethylene with the z axis along the C-C bond and the y axis pointing to-

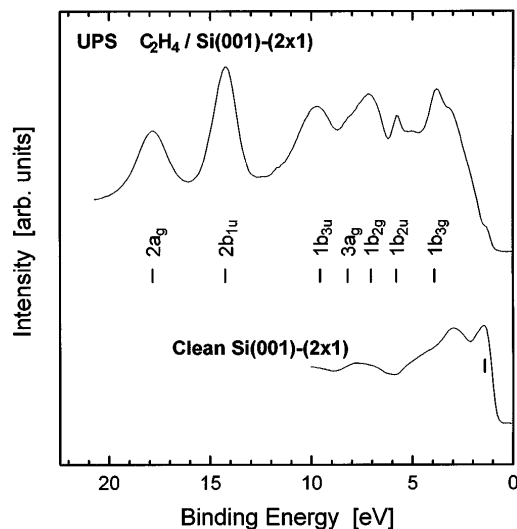


FIG. 1. UV photoemission spectra for ethylene chemisorbed on Si(001)- (2×1) . The data were measured for ethylene saturation at 90 K with 50 eV photons incident at a polar angle of 45° . For comparison a spectrum of the clean surface is also displayed (bottom).

ward the surface normal. Two sets of angle-resolved photoemission spectra for a photon energy of 50 eV are depicted in Fig. 2 for θ ranging from -6° to $+78^\circ$ in steps of 3° , from top to bottom, respectively. In Figs. 2(a) and 2(b) data are shown for photoemission within the [110] and $[1\bar{1}0]$ azimuthal planes, i.e., along and perpendicular to the Si-Si dimer rows. Light polarization and incidence angles have been chosen to optimize the signal from the $1b_{3u}$ and the $1b_{2g}$ orbitals. Clearly, the binding energies of all photoemission features, particularly for the marked $1b_{3u}$ and the $1b_{2g}$ orbitals, are independent of θ in Fig. 2(b): No dispersion of ethylene-derived states is present for photoelectron momentum k_{\parallel} along the $[1\bar{1}0]$ direction. In contrast, for photoemission in the perpendicular direction, which corresponds to a wave vector k_{\parallel} along the Si-Si dimer rows, the $1b_{3u}$ and $1b_{2g}$ ethylene molecular orbitals exhibit well-defined energy shifts [Fig. 2(a)]. Starting from binding energies of 9.2 and 6.7 eV at normal emission, both states disperse down with increasing θ as can be seen in the first eight spectra of Fig. 2(a) [14]. For the $1b_{2g}$ band, dispersion back to approximately its normal emission energy can be seen with further increasing θ , while this is barely observable for the $1b_{3u}$ band due to peak broadening at these photoemission angles. The subsequent development of both bands with emission angles can be followed easily: Both states disperse down again to 10.3 and 7.4 eV and then back to 9.2 and 6.8 eV at grazing photoelectron emission [bottom spectrum in Fig. 2(a), respectively]. If the observed energy shift with θ is due to lateral adsorbate-adsorbate interactions within an ordered adsorbate overlayer, the energy shift has to scale with the parallel momentum of the corresponding delocalized Bloch states according to $k_{\parallel} = 0.51 \text{ \AA}^{-1} \sin(\theta) \sqrt{E_{\text{kin}}/\text{eV}}$. The

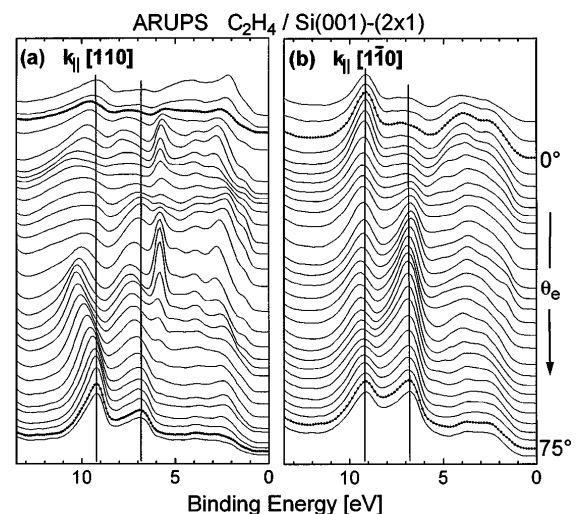


FIG. 2. Angle-resolved photoemission spectra for ethylene chemisorbed on Si(001)- (2×1) . Two sets of spectra are shown for emission angles from -6° to 78° (from top to bottom) in the [110] and $[1\bar{1}0]$ azimuthal directions, (a) and (b), respectively. The spectra were recorded at 90 K using a photon energy of 50 eV. The positions of the $1b_{3u}$ and $1b_{2g}$ states are marked by vertical lines.

positions of the photoemission peaks of both molecular states from 11 different data sets are collected in Fig. 3. In the $[110]$ direction the data show clear evidence for a strong dispersion of approximately 1.2 and 0.8 eV for the $1b_{3u}$ and the $1b_{2g}$ bands, respectively. Both bands are antibonding at the $\bar{\Gamma}$ point ($k_{\parallel} = 0$) and show a periodicity of about 1.55 \AA^{-1} . This periodicity compares reasonably well with the value expected from the real space next neighbor Si-Si dimer distance along $[110]$, as marked at the top of Fig. 3. Therefore, from the observed periodicity in k -space ethylene adsorption on every Si-Si dimer site follows. Perpendicular to the dimer rows (in $[1\bar{1}0]$ direction), none of the bands show any significant energy shifts. Especially no periodic dispersion with a periodicity of 0.82 \AA^{-1} as might be expected from the (2×1) unit cell is discernible in the data. The apparent dispersion within some of the $1b_{2g}$ data is solely due to spurious signals from 90° rotated minority (1×2) domains. Thus, the data demonstrate a low-dimensional character of the adsorbate band structure: Upon chemisorption on Si(001)- (2×1) the $1b_{3u}$ and the $1b_{2g}$ ethylene orbitals form adsorbate Bloch states which are one-dimensionally delocalized along the Si-Si dimer rows and localized in the perpendicular direction.

Two different strongly anisotropic structures exist on the vicinal Si(001) surface: the biatomic steps along $[1\bar{1}0]$ and the Si-Si dimer rows on the (001) terraces running along $[110]$. Here it is the anisotropy of the Si-Si dimer rows which causes the observed 1D adsorbate-adsorbate interaction. Delocalization occurs *perpendicular* to the steps while the electronic states stay localized along the step edges. Thus the biatomic steps are not directly involved in the localization; they have been introduced only for the preparation of a single-domain (2×1) surface. We further note that the ethylene molecules within the electronically 1D chains are oriented "side on," i.e., with their C-C axes oriented parallel to the Si-Si

dimer bond, as has been shown by symmetry analysis of the full angle-resolved photoemission data [12].

From these experimental observations two important questions emerge: (1) Why is dispersion restricted to the $1b_{3u}$ and the $1b_{2g}$ orbitals? (2) What causes the lateral interaction; is it mediated by the semiconductor substrate or related to direct adsorbate wave function overlap? To find answers, DF repeated slab calculations for ethylene adsorbed on both sides of a six layer silicon substrate slab model have been carried out by means of the full-potential linearized augmented plane wave methodology [15]. Density gradient corrected functionals have been employed for both geometry optimization (including relaxation of the surface silicon dimers) and evaluation of the one-particle energies [13]. These calculations support the assignment of the photoemission features in Fig. 1 and show a strong 1D dispersion for the $1b_{3u}$ and $1b_{2g}$ -derived Bloch states as displayed in Fig. 3. Comparison with the experimental data is excellent for the $1b_{3u}$ state. For the $1b_{2g}$ level the main features of the band structure are reproduced as well but the bandwidth is overestimated (see below for a possible explanation). The DF calculations reveal that the Kohn-Sham wave functions associated with both states are essentially restricted to the adsorbate layer (Fig. 4). The discernible substrate admixtures are far too small to give rise to any substantial substrate mediated contribution to the observed dispersion. We therefore conclude that the 1D band structure of $\text{C}_2\text{H}_4/\text{Si}(001)-(2 \times 1)$ is mainly due to direct "through-space" interaction of the adsorbed ethylene molecules. The absence of substrate-mediated interactions is corroborated by band structure calculations for an isolated adsorbate layer [13] which yield band dispersions that are very similar to those calculated for the Si(001) supported adsorption system. The vertical nodal plane of the $1b_{3u}$ and $1b_{2g}$ orbitals through their molecular axes (Fig. 4) have two effects. On the one hand, these orbitals are laterally more extended than all other ethylene orbitals which are symmetric with respect to the vertical

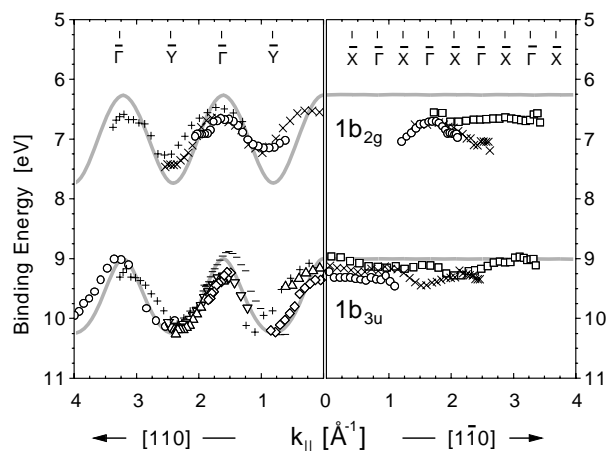


FIG. 3. Adsorbate band structure for ethylene saturation on Si(001)- (2×1) . The symbols give the experimental data derived from ARUPS spectra at 26 to 70 eV. The solid line represents the results of DF calculations for a six layer Si slab model assuming an adsorbate C_{2v} symmetry.

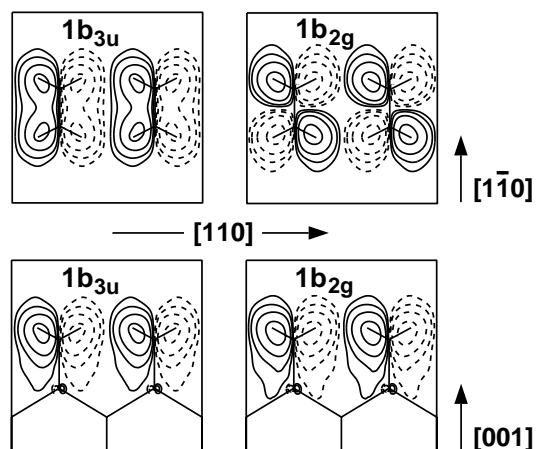


FIG. 4. Wave functions of the $1b_{3u}$ and $1b_{2g}$ derived states at the $\bar{\Gamma}$ point in top view (top) and in the $(1\bar{1}0)$ plane perpendicular to the Si-Si dimers (bottom).

molecular plane; only the former orbitals show significant dispersion, as seen experimentally. On the other hand, no σ -type overlap between the adsorbate carbon atoms and the Si-Si dimer atoms is possible which very efficiently suppresses substrate participation in $1b_{3u}$ and $1b_{2g}$ -derived states of the adsorption system. Both arguments lead to dominant direct through-space interaction.

In the past effects on the vibrational and electronic structure as well as on the adsorbate geometry due to lateral interactions have been mostly neglected in the discussion of adsorption phenomena on semiconductor surfaces. Nevertheless they might be quite important for a detailed comparison of theoretical results or properties of single adsorbates with experimental data for the interacting adlayers. For ethylene chemisorption on Si(001)-(2 × 1) the overlap of the $1b_{3u}$ and the $1b_{2g}$ wave functions leads to a Pauli repulsion along the ethylene chains. This interaction can very well influence the adsorbate energetics as well as the adsorbate geometry close to saturation coverage. Considering the specific shape of the overlapping orbitals indicated in Fig. 4, Pauli repulsion can be reduced by simultaneous rotation of all molecules around their individual y axis parallel to the surface normal and/or by a twist of the methylene groups around the individual molecular axis [13]. This necessarily influences the vibrational adsorbate properties, e.g., the frustrated rotation around the surface normal, and may even lead to a reduction of the adsorbate C_{2v} symmetry. Indeed, the calculations indicate a small energetic preference (0.025 eV) for a C_2 symmetric adsorbate structure [13]. Such a distortion driven by Pauli repulsion offers an attractive explanation for the deviation from—often assumed in previous calculations— C_{2v} symmetry derived from HREELS and ARUPS [12,16]. It also leads to a reduced width of the $1b_{2g}$ band, improving the agreement of experiment and calculation. Further properties of adsorbate systems which should be influenced by low-dimensional band structures are their photoconductivity and optical properties as well as their electronic density of states. Note that for the system presented here the 1D delocalized bands do not correspond to the highest occupied molecular orbitals. Also, 1D band formation is conceivable for the unoccupied states which are not accessible with our technique.

In summary, our photoemission data clearly demonstrate one-dimensional adsorbate band behavior for a molecular adsorbate on a semiconductor surface. After chemisorption on Si(001)-(2 × 1), the $1b_{3u}$ and $1b_{2g}$ orbitals of ethylene form Bloch states which are delocalized along the Si-Si dimer rows (with band widths of 1.2 and 0.8 eV, respectively) but are localized in the direction perpendicular to the rows. DF calculations for the C_{2v} symmetric model of the adsorption complex are in acceptable agreement with the experimental data. They clearly identify the origin of the 1D band structure as direct through-space interaction along the adsorbate rows. Most probably, Pauli repul-

sion lowers the symmetry of the minimum energy structure which in turn decreases significantly the 1D bandwidth.

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