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Electronic band structure and ensemble effect in monolayers of linear molecules investigated by photoelectron spectroscopy

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The electronic band structure of different alkyl/Si(111) self-assembled monolayers (SAMs) was investigated using photoelectron spectroscopy (PES) with variable photon energy. We observe a significant dispersion in the valence-band spectra and a large density-of-states (DOS) effect. The dispersion can be described by quantum well states, which depend only on the local properties of the alkanes with a dispersion relation similar to polyethylene and without any significant influence of the Si/molecule interface. Furthermore, the DOS effect is due to averaging over molecules with different tilt angles and thus can be considered as indicator for the degree of orientational order within the SAM. Finally we present a structural model for a description of the PES data, which takes both aspects into account.

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I. INTRODUCTION

Self-assembled monolayers (SAMs) of short alkyl chain molecules on semiconducting or metallic substrates are an important test bed for studying charge transport across organic molecules and may themselves be of interest for various applications in organic electronics.[1] Understanding the electronic structure of these materials is crucial for a proper description of their electrical, thermal, and optical properties. Recent experiments on high-quality SAMs of alkyl chains, which are covalently bound to a Si(111) substrate, revealed that these systems have surprisingly efficient charge transport along the alkyl chains[2–5] despite of the large band gap of about 8 eV of the isolated alkane molecules. Thus the electronic structure of these alkyl SAMs is of particular interest. In general *k*-resolving techniques such as x-ray emission spectroscopy (XES) or photoelectron spectroscopy (PES) can provide information about the electronic band structure. However, as the alkyl SAMs are very sensitive to irradiation by x rays, PES is the method of choice because for the light elements the photoemission cross section is significantly higher than the x-ray emission cross section.

The alkyl SAMs studied here are prepared by liquid-solid reactions under total exclusion of air and water. The resulting films are robust in that they are formed by relatively strong chemical bonds to (50% of the Si atoms[6,7] on) the oxide-free Si surface. The bonds are sufficiently strong and the films are sufficiently dense to provide protection against oxidation of the Si surface for several months.[2,3,6] The draw back of such robust films is that, because the Si-C bond is strong, in contrast to the Au-S bond, for example, the molecules that make up the SAM cannot make "corrections" to form well-ordered monolayers. Therefore these alkyl SAMs do not have a very high degree of order as it was the case for previously studied systems,[8–11] and this of course affects the electronic structure. As there is a need for understanding the electronic structure of these alkyl-Si SAMs, it is important to determine the various influences by, e.g., defects and disorder. In this context, due to their comparatively simple molecular composition, the alkyl SAMs can serve as a model for similar systems with an intermediate degree of order. Moreover, a detailed understanding of the PES data may not only provide information about the electronic structure, e.g., band structure and interface states, but indirectly even some structural information.

In a long-range ordered arrangement of atoms or molecules there is a clear relation between the energy of the valence-band (VB) or conduction-band states and their quantum number *k*, which is known as the energy dispersion $E(k)$ or the electronic band structure. If only a small number of unit cells exists, the electronic states are smeared out in momentum space, and *k* is not a good quantum number for these systems. With increasing order these states become sharper in *k*, and ultimately form an electronic band, where the binding energy can clearly be assigned to a certain *k* point in reciprocal space. This behavior can be experimentally observed, for example, in a system consisting of a few monolayers of Ag on a Au(111) substrate, where with increasing layer thickness the quantum well states in the Ag layer resemble more and more the volume band structure.[12–14] A similar behavior can be found for one-dimensional systems, such as linear molecules,[15,16] e.g., linear alkanes or alkyl chains, which have been investigated with electron momentum spectroscopy[17,18] and (angle-resolved) photoelectron spectroscopy ((AR)PES),[9,10,15,19] which is in general a suitable technique for determining the occupied electronic band structure of a solid.[20–24] It was found that linear carbon chains consisting of about 17 repeat units resemble very well the intramolecular electronic band structure of polyethylene.[9,10,19,25,26] The electronic band states (e.g., C 2*s* or C 2*p* derived) of short linear chains are still molecular orbitals but resemble quantum well states of *s* electrons of thin metal films. To stress this analogy, we thus call the considered molecular states of our SAM system quantum well states in the following. In principle this simple description is similar to the consideration of molecular-orbital states like in Ref. 9 and references therein, as well as to the consideration of band dispersion from a tight-binding approach or from calculated ARPES spectra for finite systems based on the independent-atomic-center approximation and *ab initio* molecular-orbital calculations.[8]

A. Density-of-state effect

In general, the interpretation of ARPES for the investigation of electronic band structure is based on energy and momentum conservation, and thus only those initial states which satisfy this condition contribute to the photoelectron yield at given electron emission angle and kinetic energy. Consequently, as discussed in Sec. V, for systems with long-range order, such as single crystals, k-resolved photoelectron spectra represent to first order the electronic band structure of the occupied valence-band states.[24] Of course, k-integrated spectra then reflect the occupied density of states (DOS), when the integration covers the whole three-dimensional Brillouin zone. Usually, a real system is somewhere between these two extremes: the k vector is not perfectly well defined, and the spectrum is the result of integrating over a finite range of the Brillouin zone. Besides the finite experimental resolution, several factors such as disorder or short-range order, e.g., in polycrystals, can lead to such a momentum integration. In the following, we call this finite k-space integration the "DOS effect."

B. Band structure in alkyl SAMs

The intramolecular band structure of films of well-ordered long linear carbon chains on metal substrates has been investigated by various groups utilizing PES with variable photon energy.[9,10,19] Their results are similar to the calculated band structure of polyethylene.[25–27] Neither a perturbation of the chain periodicity by a $C=O$ unit nor the molecule-metal interface of the molecular film have a significant effect on the intramolecular band structure.[9,10] However, in the case of SAMs consisting of shorter alkanes, this may be different. For these relatively short one-dimensionally confined systems, the boundary condition, in particular the alkyl/Si interface, may play an important role.

For samples with a long-range order, as in single crystals, it is well established how to extract information about the electronic band structure from the PES data but for poorly ordered systems this is more difficult. The alkyl SAMs investigated here serve as model system for an intermediate degree of order concerning the molecular orientation and the translational invariance over only six to nine repeat units. In the following we discuss a relatively simple but consistent description of the PES data, which takes both aspects, band structure and disorder, into account. This may not only be of interest for the particular alkyl SAMs investigated here but also for other systems with an intermediate degree of order.

II. EXPERIMENTAL CONDITIONS

Densely packed monolayers of alkyl molecules on n-Si (111) substrates (1–15 Ω cm) were prepared by thermally induced hydrosylation of alkanes on H-terminated Si(111) substrates at the Weizmann Institute (Israel) and at the University of New South Wales (Australia).[2,3,28,29] Various samples were produced with different alkyl chain lengths between C_{12} and C_{18}, and were characterized by water contact angle, ellipsometry measurements, and Fourier transform infrared spectroscopy. Only samples with evidence for a dense molecular layer were chosen for further experiments and shipped to BESSY and Princeton University under nitrogen atmosphere. Using PES the samples were then checked for contaminations and possible oxidation of the interface by monitoring the O 1s and Si 2p signals of Si_xO_y.

PES was carried out at room temperature and under ultrahigh-vacuum conditions. At Princeton University the UHV chamber (5×10^{-11} mbar base pressure) was equipped with a Specs/Omicron He discharge lamp, and a cylindrical mirror analyzer with 150 meV overall energy resolution and 42° acceptance angle. The detection angle of the photoelectrons relative to the surface normal was approximately 45°. At BESSY PES was carried out at beamline UE112-PGM (5×10^{-10} mbar base pressure and $E/\Delta E > 8100$ at 20 eV photon energy) with a Specs Phoibos 150 electron analyzer ($\Delta E < 5$ meV) using p-polarized light. The setup was adjusted to normal-emission geometry with 54° angle of incidence and 2° analyzer acceptance angle, which allows the determination of the k vector of the photoelectrons from their kinetic energy by assuming a free-electron final state.

As reported earlier[30] the alkyl SAMs suffer from radiation damage on exposure to UV light and soft x rays, most probably by photoelectrons, even for relatively small radiation doses. Therefore the radiation dose was minimized by recording each spectrum at a fresh spot and by reducing the photon flux so that there were no substantial differences between two scans on the same spot (while there are differences for higher flux). In the following, all SAM spectra are normalized to the intensity maximum around 6 eV binding energy and the energies are calibrated to the Fermi level of a platinum foil.

III. ALKYL SAM VALENCE-BAND STRUCTURE

Figure 1 shows a series of $C_{12}H_{25}/Si(111)$ and $C_{18}H_{37}/Si(111)$ VB spectra recorded in 5 eV steps with photon energies ($h\nu$) ranging from 30 to 150 eV and 30 to 195 eV, respectively. The general shape is similar to that of gas phase measurements of pure alkanes[31] and Langmuir-Blodgett films of Cd arachidate (which can serve as a model of polyethylene).[9] The dispersing feature between 1 and 5 eV binding energy is located in a region, which is in the electronic gap of pure alkyl molecules.[26,27,31,32] We will note in Sec. V that the corresponding DOS originates from the VB of bulk silicon with possibly some contribution from the alkyl/Si interface.[6,33]

The electronic states between 5 and 12 eV binding energy are dominated by C 2p and H 1s contributions. The DOS between 13 and 21 eV has mainly C 2s character.[26,27,31–33] In principle the alkyl/Si(111) spectra of Fig. 1 are similar to those from films of oriented linear carbon molecules on metal substrates[9,10,19] with a polyethylenelike dispersion re-

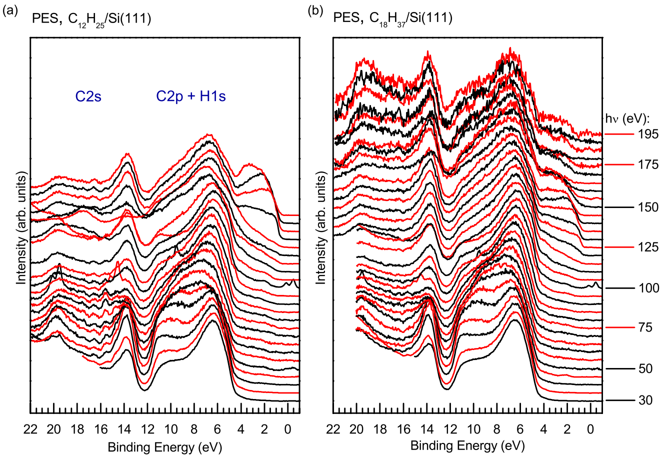

FIG. 1. (Color online) Normal-emission (2° acceptance angle) PES spectra from (a) a $C_{12}H_{25}/Si(111)$ SAM and (b) a $C_{18}H_{37}/Si(111)$ SAM recorded with p polarization of the incident light. The photon energy was scanned in 5 eV steps from 30 to 150 eV and from 30 to 195 eV, respectively. The spectra are normalized to the maximum of the C $2p$ band at about 6 eV.

lation. However, single electronic states can be resolved in the steep parts of the alkyl band structure as will be shown in the next section. Another interesting aspect, which is further discussed in Sec. V, is the fact that the VB spectrum from the comparatively short alkyl/Si SAMs changes much less with photon energy than the VB spectrum from SAMs of longer carbon chains.[9,10,19] One possible reason is that the electronic band structure is blurred by effects that will be discussed below. In the discussion of the spectra, we will neglect the contribution from Si Auger electrons as well as from second or third order excitation of Si $2p$ electrons, which appear in the spectra for some of the photon energies, especially in the C $2s$ region.

IV. ODD AND EVEN ALKYL CHAINS

In an infinite quantum well an electronic band is made up of the energy levels of $N-1$ electronic states (N is the number of unit cells), which can assumed to be equidistant in k. Because short alkyl chains consist only of a small number of repeat units, there are only a few electronic states in the energy range accessible by PES. A key question is therefore whether there is already a polyethylenelike intramolecular band structure in alkyl chains of only 12 carbon atoms.

For a better understanding of the individual features in the PES data presented in Fig. 1, it is useful to compare the electronic structure of SAMs with odd and even alkyl chain length. In Fig. 2(a) the C12, C13, and C14 alkyl molecule spectra are essentially identical. However, the center of the C $2s$ band at ~16 eV binding energy varies significantly. In the enlarged view [Fig. 2(b)] differences between the spectra from monolayers with different chain length can be identified. In the case of $C_{13}H_{27}$, for example, there is one small peak in the center of the C $2s$ band at $E_B=16.2$ eV ("O1"). For $C_{12}H_{25}$ and $C_{14}H_{29}$, in contrast, there is a dip at this energy, with two adjacent peaks ("E1" and "E2"). For the $C_{14}H_{29}$ sample the energy separation between these two peaks at $E_B=15.7$ eV (E1) and $E_B=16.7$ eV (E2) is slightly smaller than for $C_{12}H_{25}$.

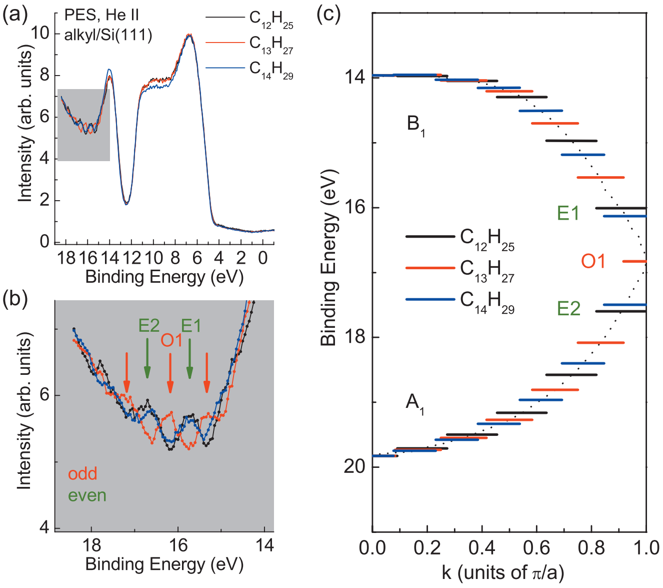

FIG. 2. (Color) (a) PES valence-band spectra of $C_{12}H_{25}$, $C_{13}H_{27}$, and $C_{14}H_{29}$ SAMs on Si(111), and (b) the respective C $2s$ signal on an expanded energy scale. (c) From the dispersion relation of long alkanes (Ref. 10) (dotted line) quantum well states are deduced for the respective molecules. Note that the electronic band structure is shifted in energy for reference to the Fermi level.

In Fig. 2(c) the C $2s$ quantum well states of the $C_{12}H_{25}$, $C_{13}H_{27}$, and $C_{14}H_{29}$ samples are deduced from the C $2s$ band of long alkyl chains.[10] For alkanes with an odd number of carbons, there is an electronic state positioned exactly at the Brillouin-zone boundary ($k=\pi/a$), which one would get for an infinite chain of carbon atoms with length of the unit cell a, in contrast to the case of even chains. This explains the PES spectra in Fig. 2(b), where the O1 electronic state of the $C_{13}H_{27}$ sample is located at the intensity minimum of the C $2s$ band. As will be discussed in Sec. V, the PES spectra have a strong contribution from the total DOS. Consequently this minimum in intensity corresponds to the steepest part of the C $2s$ band since the total DOS decreases with increasing steepness of the respective band. Thus peak O1 can be assigned to the Brillouin-zone boundary $k=\pi/a$. However in Fig. 2(b) O1 is located at about 0.6 eV lower than the electronic state at the Brillouin-zone boundary in the band structure of long carbon chains ($E_B=16.8$ eV) in Fig. 2(c), whereas the upper state at the Γ point is located at $E_B=14.0$ eV for both short and long chains. Consequently for the short alkanes the curvature of the B_1 branch is smaller than for long carbon chains and vice versa in case of the A_1 branch. This is corroborated by the difference in positions of peaks E1 and E2, respectively, when comparing the $C_{12}H_{25}$ and $C_{14}H_{29}$ samples. Peak E1 from both samples coincides while peak E2 exhibits a difference in energy of 0.1 eV.

Summarizing this analysis of the fine structure in the C $2s$ band, we find an indication for a polyethylenelike band structure in short alkanes consisting of six one-dimensional unit cells. However, this band structure is not completely developed, a point which becomes apparent in distinct deviations from long carbon chains, e.g., the larger dispersion in the C 2*s* A_1 branch and the smaller dispersion in the C 2*s* B_1 branch.

V. GEOMETRIC STRUCTURE AND DOS EFFECT

A. Photoelectron spectra and DOS effect

As described in Secs. I and I A, the experimental geometry allows probing of different points in the Brillouin zone by recording the valence band with different photon energies. At first glance, it is surprising that the SAM valence-band signature in Fig. 1 changes much less with photon energy than the corresponding data from films of long carbon chains.[9,10,19] The dispersion is blurred considerably, e.g., the electronic states in the center of the C 2*s* band contribute to the photoelectron yield over the whole photon energy range. If the respective states were well defined in momentum, they would only contribute to the photoelectron yield for certain photon energies and k values. This blurring is an indication of a significant DOS effect which is corroborated by the observation (not shown here) that a change in emission angle from 90° (normal emission) to 65° has only minor influence on the photoelectron spectra. The intensity of the C 2*p* band between $E_B=5$ and 12 eV binding energy, and the lower C 2*s* band between $E_B=15$ and 21 eV increases by ca. 25%, with the spectra being normalized to the dip at $E_B=12$ eV (not shown).

Because there is only a minor distortion of the periodic molecular alkane structure by adsorption and a low concentration of defects in the SAM,[5,34,35] it is unlikely that this DOS effect is caused by equal blurring in momentum of the electronic states over the whole Brillouin zone, as it would happen for a perfectly disordered, i.e., amorphous, system. Neither the finite length of the one-dimensional periodic chain of the alkyl molecule nor the finite experimental resolution can adequately explain this observation. Consequently, while the dispersion is determined by the local intramolecular properties, the main contribution to the DOS effect must be attributed to an angle (or k)-averaging effect due to imperfect orientation of the tilted molecules within the SAM.

B. Partial *k*-space integration by different orientations of the molecules in the monolayer

Now we consider the influence of the molecular orientation on the measured band structure. Depending on the angle of the adsorbed molecules relative to the surface normal, the tilt angle α of the molecules, and hence the normal component $k_\perp$ of the photoelectron wave vector k, has different magnitudes. This can be expressed by a change in slope of the electron final-state parabola as a function of α, as illustrated in Fig. 3. Therefore, at constant photon energy, different electronic states are probed for molecules with different tilt angles because only vertical—i.e., direct—transitions are allowed in the photoemission process. This means that, for a molecule oriented with small angle α, the probed electronic state is at larger k than for a strongly tilted one.

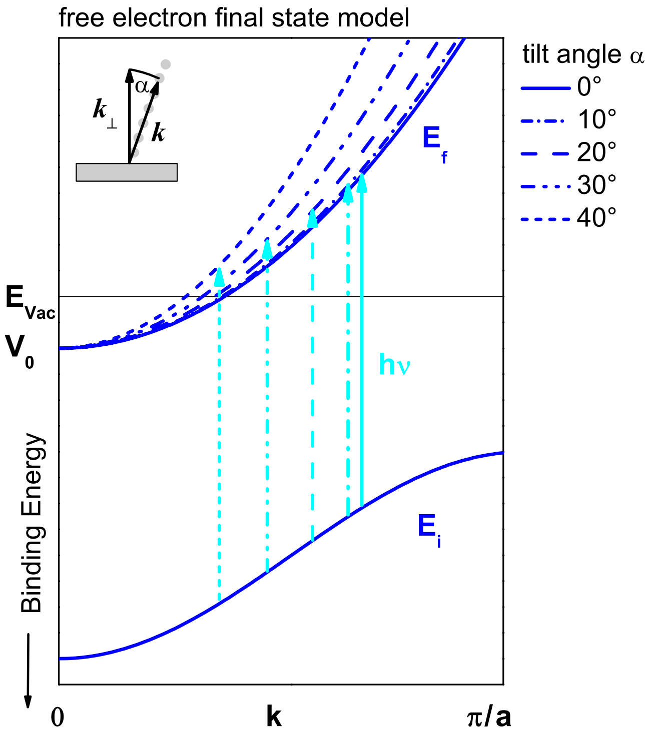

FIG. 3. (Color online) Projection of the photoelectron final state onto the one-dimensional Brillouin zone of a linear chain of atoms for different tilt angles α of the chain. For the initial state a cosine band is assumed with $E_i(k) \propto \cos(k)$, where k is the length of the reciprocal wave vector along the chain and $k_\perp = k/\cos(\alpha)$ is the momentum of the photoelectron which is emitted perpendicular to the surface, as illustrated by the inset.

Thus, for an ensemble of molecules with a distribution of tilt angles, the photoelectron spectrum is the integration over a certain range of k values, even if the acceptance angle and the photon energy are well defined. Figure 3 demonstrates that for a fixed distribution of molecules with different tilt angles, the DOS effect increases with increasing $h\nu$ (and implicitly $k_\perp$). This general behavior can be observed for all alkyl chain lengths analyzed in this work. For example, in the $C_{18}H_{37}/Si(111)$ data in Fig. 1 at $h\nu=40$ eV, there is a peak at $E_B=10$ eV, which disperses toward lower binding energy with increasing photon energy. However at high photon energies ($h\nu > 150$ eV) it returns only as a weak shoulder, which indicates a larger contribution of the total DOS to the signal than for low photon energies.

C. Modeling the ensemble effect

In order to demonstrate the validity of our model, we simulated the photoelectron spectra by estimating the probability for electronic transitions from the occupied valence states to the free-electron final state for various distributions of molecules with different tilt angles, and compared the result to the experimental data. This is based on the following simplifying approximations:

(1) The intramolecular band structure is equal to that of a perfectly ordered SAM without any defects.

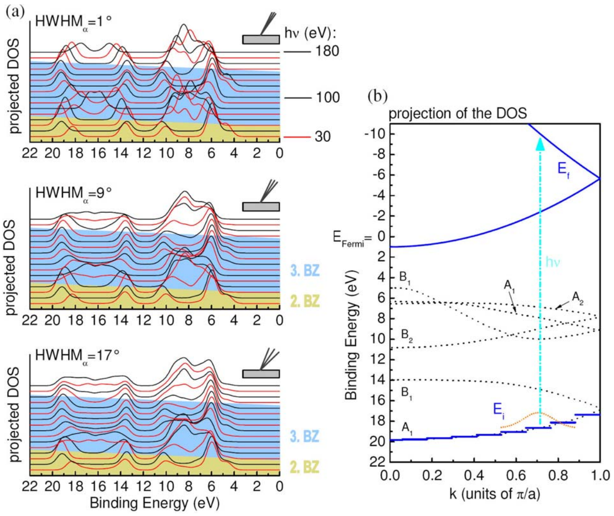

FIG. 4. (Color online) (a) Projection of the alkane quantum well states onto the free-electron final state for different ensembles of molecules with average tilt angle $\alpha_{\mathrm{av}}=25°$, and Gaussian angular distributions with $\mathrm{HWHM}_\alpha=1°$, 9°, and 17° (from top). The alkyl Brillouin-zone number is indicated on the right-hand side. (b) The quantum well states are deduced from the dispersion relation $E(k)$ of long alkanes (Ref. 10), which was shifted in energy for alignment with the experimental data, and the finite length of the alkanes is taken into account by modeling the density of each state by a Gaussian in k direction.

(2) The translation invariance is limited to one molecule (finite number of repeat units).

(3) Integration over all tilt and azimuthal angles.

(4) Free-electron final state (no final-state effects)

For the sake of simplicity and computer resources, the Si substrate and the alkyl-Si interface were neglected, and the transition probability was calculated without taking the photoemission cross section and the photoelectron mean-free path into account.

The quantum well states of a single alkane were deduced from the experimentally determined band structure of long carbon chains,[10] as indicated in Fig. 4. The contribution of the finite chain length to the DOS effect was taken into account by expanding the states in the k direction of the one-dimensional Brillouin zone. Therefore the density of the quantum well states $[\mathrm{DOQWS}_i(k)]$ is represented by a series of Gaussians with full width at half maximum $\mathrm{FWHM}=2\pi/[a(n-1)]$, which are centered at

$$k_i=\frac{2\pi i}{(n-1)a}, \tag{1}$$

where n is the number of carbon atoms in the alkyl molecule, $a=2.53$ Å (Ref. 36) is the length of the one-dimensional unit cell, and $i=0,1,2\ldots$. The probability for an electronic transition from the ith quantum well state with energy E_i to the free-electron final state with energy E_f is then proportional to the $\mathrm{DOQWS}_i(k)$, where the component k of the reciprocal wave vector along the carbon chain must satisfy the well-known relation for the energy of the free-electron final state

$$E_f=\frac{[\hbar k/\cos(\alpha)]^2}{2m_e}-V_0, \tag{2}$$

with

$$h\nu=E_f-E_i, \tag{3}$$

and the inner potential $V_0=5.5$ eV with respect to the vacuum level.[9,10,19] For comparison to the experimental data, which are referenced to the Fermi level of a Pt foil, we assume 4.5 eV for the work function of the alkyl SAM.[9,37] In the following, a Gaussian distribution of molecules with different tilt angles is assumed. Therefore the overall transition probability from the ith quantum well state is obtained by weighting the $\mathrm{DOQWS}_i(k)$ according to the number of molecules with a given tilt angle and adding up the contributions for each tilt angle from 0° to 90° in 1° steps. Because a representation of the overall electron transition probability versus binding energy E_i can be understood as total DOS, weighted by an effective $h\nu$-dependent cross section, or as a projection of the total DOS onto the free-electron final state, respectively, we refer to such a representation as projected DOS. In order to simulate the PES line shape the projected DOS was convolved by a Gaussian with half width at half maximum HWHM=500 meV.[6] This calculation was done for various photon energies $h\nu$, average tilt angles α_{av} between 18° and 35°, and different widths of angular distributions.

D. Interpretation of the projected DOS

The best agreement with the experimental data was found for $\alpha_{\mathrm{av}}=25°$, which is compatible with previous results[3,4,35] and x-ray reflectivity measurements.[38] The calculated spectra are presented in Fig. 4(a). The top panel displays the calculation for a small angular spread ($\mathrm{HWHM}_\alpha=1°$) and demonstrates that the projected DOS reflects the intramolecular alkane band structure as long as the alkane molecules are homogeneously oriented. The dispersion is thus clearly visible. However, as the orientation becomes more inhomogeneous, the dispersion is increasingly blurred. This can be observed in the middle and lower panels of Fig. 4(a), which present spectra for angular distributions of $\mathrm{HWHM}_\alpha=9°$ and $\mathrm{HWHM}_\alpha=17°$, respectively. For $\mathrm{HWHM}_\alpha=17°$ the projected DOS already looks similar to the experimental data. For example, the complete C 2s band appears in each DOS curve, and only the relative weight within the band changes.

Consequently, the general signature of the energy dependent photoelectron spectra can be reproduced by a model, which is based on the electronic band structure of a perfectly ordered alkyl SAM. In this approach the translational invariance is limited to single molecules and a distribution of tilt angles is included. Even though we neglect here the influence of the Si substrate and the alkyl-Si interface, as well as the photoemission cross section and the photoelectron mean-free path, the simulated spectra match the experimental data well. This indicates that the SAM dominates the PES data, whereas the interface and the substrate contribute only in a minor fashion.

At room temperature there are not only different tilt angles present but also conformational defects in the alkyl chains, e.g., kink and gauge defects,[34,39,40] which also contribute to the DOS effect. In our model conformational defects are not taken into account in particular but contribute to the angular distribution. Therefore the HWHM_α parameter should be considered as an effective spread in tilt angle. However, since in previous room-temperature experiments on similar alkyl systems,[9,10,19] a much smaller DOS effect was observed than for the alkyl SAMs investigated here, we assume that these defects contribute only in a minor fashion to the HWHM_α parameter.

An increase in angular spread HWHM_α beyond 17° leads to a greater DOS effect. However, no significant difference in the projected DOS curves is observed as compared to $\text{HWHM}_\alpha = 17°$. Thus we assume that this value is the lower limit of the angular spread in the investigated $C_{18}H_{37}/\text{Si}(111)$ samples. This spread could incidentally be associated with a surface roughness of about 2.6 Å, in reasonable agreement with values obtained from atomic force microscope (Ref. 41) and x-ray reflectivity measurements.[3,38,42–44] Yet, a realistic comparison would require that the roughness be evaluated for the same lateral (coherence) length scales since roughness increases with increasing coherence length.

Note, that in general the spread in tilt angle can have two explanations:

(1) the coexistence of several well-ordered domains with homogeneous but different tilt angles, or

(2) the presence of a uniform molecular layer where the tilt angle varies randomly from molecule to molecule.

The first scenario requires good lateral order within the domains whereas the second scenario does not. Since only diffuse features were observed in low-energy electron diffraction (LEED) and spot profile analysis-LEED (SPA-LEED) measurements, and also in Grazing Incidence x-ray scattering measurements rather than Bragg peaks, the second scenario appears valid. The null results from LEED give a 7 to 8 nm upper limit for the domain size. In the x-ray scattering measurements, the position of the broad scattering features would, assuming hexagonal packing, correspond to a packing density of 22 $\text{Å}^2/\text{molecule}$. This density is much less than expected for a crystalline packed layer. However the remarkable resistance of the SAM against water and air oxidation[29] may not be consistent with loosely packed molecules spread haphazardly over the surface. An explanation which is consistent with all experimental observations may be the existence of relatively small domains (2–5 nm), similar to CF_3-terminated alkylthiols on gold.[45]

VI. FITTING THE PES DATA

A. Implementing the DOS effect into the fit model

The intramolecular band structure and the tendencies observed for different alkyl SAMs can be related by applying a peak fit analysis. Given the geometry used in the present experiments, and in the absence of any DOS effect, the electronic bands should appear in the photoelectron spectrum as single peaks with their binding energies depending on k or photon energy, respectively, according to the dispersion relation $E(k)$. Counting the number of contributing bands in Fig. 4 it should be possible to apply an adequate fit to the data in Fig. 1, using six peaks with their position following the respective dispersion relation.

Because of the strong DOS effect, this procedure does not lead to reasonable results for the alkyl SAMs (and similar systems). The DOS effect can be taken into account by fitting the photoelectron spectra with a set of peaks, with each peak corresponding to a single electronic state in the band. If we keep the peak positions fixed as given by the dispersion relation and ask which molecules contribute to the signal under certain conditions, the $E(k)$ relation translates into an $I(k)$ relation which takes the partial averaging due to the DOS effect into account. According to Sec. V C, the relative intensity $I(k)$ of each peak depends on how likely an electronic transition is from the respective electronic state to the final state, which in turn depends on the angular distribution of the molecules and the photon energy $h\nu$.

However, because this approach leads to too many free parameters, it is necessary to find a minimal basis that provides a reasonable fit. We find that the data can be modeled by a set of nine Gaussians, as shown in Fig. 5(a). The energy positions of the nine peaks and their widths are constrained to be the same for all photon energies. The changes in the spectra are only reflected by the variations in peak intensities. With this approach, although very simple, it is possible to fit four PES data sets from $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, and $C_{18}H_{37}$ SAMs simultaneously, and to model the general behavior of the alkyl/Si VB spectra.

B. Interpretation of the fit result

Figure 5(b) displays the intensities of the five peaks, which represent the C 2p band, plotted against the photon energy as a result of the above-described fit. In principle we observe similar behavior for all investigated SAMs. In the C 2p band all peaks have the same intensity variation apart from the one at 3.30 eV, which originates from Si bulk with possible contributions from alkyl/Si interface states,[6,33] and is thus an indicator of the PES probing depth. Consequently, there is no significant difference between these alkanes with different lengths, a finding that has several implications.

On the one hand, this suggests that there is no significant influence of the alkyl/Si(111) interface on the intramolecular band structure. On the other hand, this is an indication that these relatively short molecules already possess an intramolecular band structure that resembles that of polyethylene. Moreover, the DOS effect is similar for the investigated samples. This suggests that the contribution of conformational defects, in our case mainly "end-gauche" and "kink" defects, is negligible because their concentration in alkane films is known to increase significantly with chain length.[34,39] The DOS effect is mainly caused by a distribution of molecular orientations, which apparently does not depend on the length of the molecules. This is in contrast to the case for alkanethiols on Ag(111) and Au(111).[46] Additionally, the variation in peak height decreases with increasing photon energy, which is due to the increase in the DOS effect with higher photon energy, as already pointed out in Sec. V B.

The antiphase variation in intensity of the peaks at $E_B = 5.9$ and 7.4 eV in Fig. 5, which is in the energy range of the

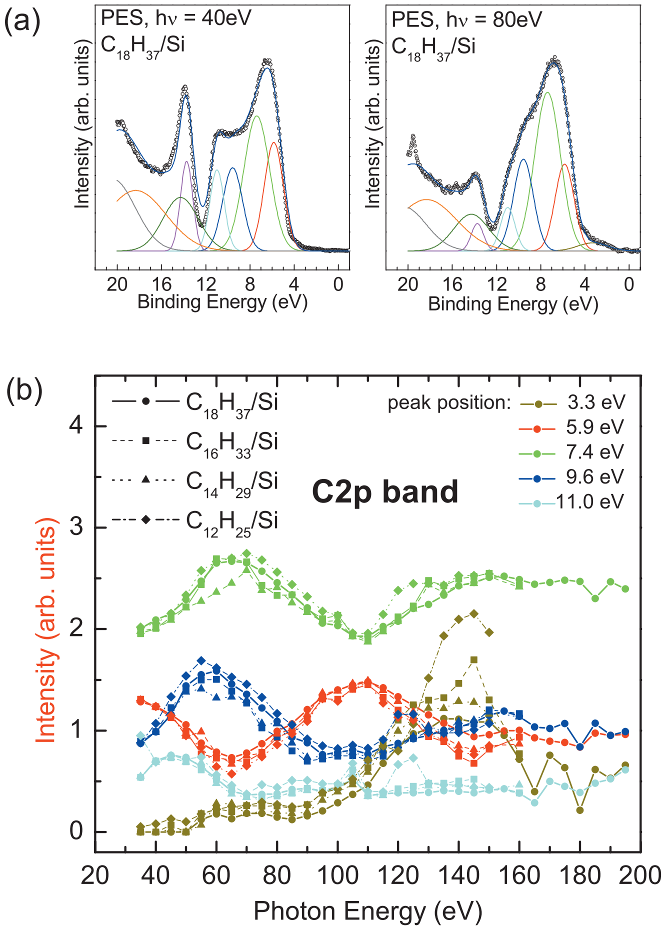

FIG. 5. (Color) (a) $C_{18}H_{37}$/Si(111) PES spectra with 40 (left) and 80 eV (right) photon energies from a simultaneous fit of all $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, and $C_{18}H_{37}$ spectra with a minimal basis set of nine Gaussian peaks for each spectrum. The position and width of the respective peaks were constrained to be the same for each spectrum and only the peak intensities were free fit parameters. (b) Intensity variation in the Gaussian peaks in the C 2*p* band over photon energy, derived from a simultaneous fit of all $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, and $C_{18}H_{37}$ spectra.

A_1 and A_2 branches of the C 2*p* band in Fig. 4(b), allows estimation of the average angular orientation of the molecules. The minimum of the 5.9 eV peak at $h\nu=65$ eV implies that the major contribution to this signal originates from the Brillouin-zone boundary while the maximum at $h\nu=110$ eV is significant for the Γ point. Thus according to Eqs. (2) and (3) we estimate the average angle α_{av} of the molecules to be 20°, which is in agreement with the literature,[47–49] and our results from Fourier transform infrared, ellipsometry, and x-ray photoemission spectroscopy (Ref. 3) as well as with the result from near-edge x-ray-absorption fine structure (Ref. 30) and theoretical tunneling distances in electronic current transport measurements.[4]

VII. SUMMARY AND CONCLUSION

Using PES with variable photon energy we investigate systematically the electronic band structure in SAMs of short alkanes covalently bound to a Si(111) substrate. We observe dispersion and a strong DOS effect due to an intermediate degree of order in the SAM which may be induced by the rigid Si–C bonds. For this system the PES data can be described consistently by taking both phenomena into account. The dispersion is modeled by quantum well states, which depend only on the local properties of the molecules with a dispersion relation similar to that found in polyethylene, even for relatively short alkyl chains. The DOS effect is not due to inhomogeneous or completely disordered alkyl SAMs but the result of ensemble averaging over molecules or molecular domains with slightly different adsorption angles. The result is nevertheless compatible with closed packed and uniformly dense monolayers of high quality.[3,49] Because the DOS effect is of the same order for all investigated SAMs, the distribution of tilt angles is similar for different alkane lengths. Furthermore, the Si substrate and the alkyl/Si interface do not affect the intramolecular band structure in a significant way, apart from the feature at $E_B=3.3$ eV, best seen at high photon energies—which is likely primarily the result of the steep rise in the cross section of Si with photon energy.

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