

Electronic structure of Si(111)-bound alkyl monolayers: Theory and experiment

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We elucidate the electronic structure of both filled and empty states of ordered alkyl chains bound to the Si(111) surface by combining direct and inverse photoemission spectroscopy with first principles calculations based on density functional theory. We identify both filled and empty interface-induced gap states, distinguish between those and states extending throughout the monolayer, and discuss the importance of these findings for interpreting transport experiments through such monolayers.

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I. INTRODUCTION

The electronic structure at interfaces between molecular and nonmolecular phases, a subject of considerable recent interest,¹⁻³ is very sensitive to basic aspects of the interface, e.g., molecule-substrate bonding, molecular orientation, and geometric structure. The electronic structure is also crucial for understanding charge carrier injection and transport, as it is the “arena” in which charge transport processes take place and any barrier for transport will be defined by this structure.

Long-chain alkanes, a fundamental class of organic compounds and a useful model for polyethylene—a simple polymer⁴—can form well-ordered monolayers on (semi)-noble metals, facilitating both experiment and comparison to theory.⁵⁻¹² Indeed, much work is directed at understanding metal/alkane interfaces.^{5-7,10,11} Equally interesting and important, however, are semiconductor/alkane interfaces.¹² Molecular interfaces with semiconductors are potentially richer in their behavior than those with metals because of the variety of possible band structures and of the potential for controlling their properties via doping, temperature, or optical excitation.

A specific motivation for analyzing the Si/alkane interface is provided by our recently reported electronic transport experiments for the Si/alkane/Hg heterostructure, which were interpreted with the aid of ultraviolet photoelectron spectroscopy (UPS) and inverse photoemission spectroscopy (IPES).¹² This analysis exposed rich transport phenomena that stimulated the present theoretical study, where we aim to help identify the electronic states that define the energy levels determining the interface energetics in general and the tunnel barrier in particular.

Here we elucidate the electronic structure of the Si(111)/alkane interface. This is achieved through analyzing both filled and empty states, by combining first principles calculations based on density functional theory (DFT) with the direct and inverse photoemission spectroscopic data that were used also for interpreting the transport results. Importantly, we identify both filled and empty *interface-induced* gap states and distinguish between those states and molecular states extending throughout the monolayer.

II. EXPERIMENTAL APPROACH

Alkyl chains of various lengths were deposited at the Weizmann Institute on *n*- and *p*-Si(111) (1–10 ohm cm) as a densely packed monolayer of aliphatic chains.¹²⁻¹⁴ All Si(111)/C_{*n*}H_{2*n*+1} samples were characterized by water contact angle, ellipsometry, and Fourier transform infrared spectroscopic measurements. The absence of oxide at the alkyl/Si interface was verified by x-ray photoelectron spectroscopy (XPS).

Electron spectroscopy of filled and empty states of Si(111)/C_{*n*}H_{2*n*+1} was performed at Princeton University in an ultrahigh vacuum (UHV) chamber (base pressure=6×10⁻¹¹ Torr) equipped with both UPS and IPES. The samples were sent from the Weizmann Institute under inert atmosphere and transferred to the UHV system with minimum ambient exposure time. Valence band spectra were obtained by UPS, using the He II line (40.8 eV) of a discharge lamp, with a resolution of 150 meV determined from the width of the Fermi edge measured on a clean polycrystalline Au substrate. Empty states were measured by IPES in the isochromat mode using a photon detector centered at a fixed energy of 9.2 eV, with a resolution of 450 meV.¹⁵ The C₁₈H₃₇, C₁₆H₃₃, C₁₄H₂₉, and C₁₂H₂₅ samples were measured at 80 K, while the C₁₀H₂₁, C₈H₁₇, and C₆H₁₃ samples were measured at room temperature. Experimental times were generally kept to a minimum to minimize damage to the molecular layer¹⁶ (an issue elaborated below). The photocurrent density was 2–3 nA/mm² in He II UPS, and the sample current density was ~25 nA/mm² in IPES. The UPS and IPES energy scales were aligned by measuring the position of the Fermi level on a freshly evaporated Au film. The position of the vacuum level, *E*_{vac}, was measured for each surface using the onset of photoemission.

III. COMPUTATIONAL APPROACH

Theoretical electronic structure calculations were done for alkyl chains chemisorbed on a Si(111) surface in a symmetric slab configuration¹⁷ within a three-dimensional periodic supercell, as shown in Fig. 1. All calculations were performed with at least six atomic layers of silicon and at least

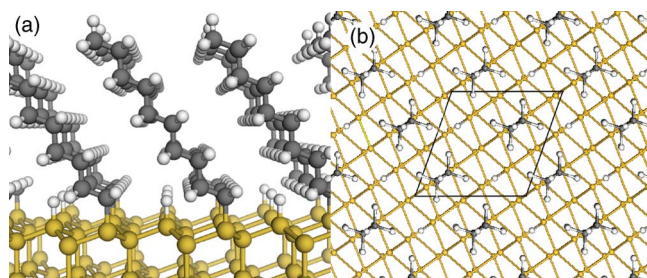


FIG. 1. (Color online) “Ball and stick” models of the slab geometry used for simulation of $C_{10}H_{21}$ alkyl chains adsorbed on Si(111) surface. (a) Side view. (b) Top view (down the molecular backbone). A single-surface unit cell with two alkyl chains and two passivating H atoms is also shown.

20 “atomic layers of vacuum,” found sufficient for mimicking a surface-terminated material. Because previous experimental^{18–20} and theoretical^{8,9} analyses suggested a molecular coverage of half the Si atoms on the surface, a 2×2 surface structure²¹ with alkyl chains attached to two of the four surface Si atoms,⁸ was used, as shown in Fig. 1(b). Dangling surface Si bonds were passivated by H atoms (also shown in Fig. 1). Additional calculations were performed on hypothetical “freestanding” arrays of alkane chains, formed by removing all Si atoms from the above-described supercells and replacing C-Si bonds with C-H bonds.

The Kohn-Sham equations of DFT were solved using the plane-wave approach as implemented in the Vienna *ab initio* simulation package (VASP).²² The local density approximation²³ (LDA) was employed for the exchange-correlation functional. Theoretical simulation of experimental spectra was performed by computing partial density of states (pDOS) curves corresponding to the contribution of the alkyl chains and the highest silicon monolayer (including all passivating hydrogens) to the total DOS. Only for the case of a H-passivated Si surface were all Si layers used.

The raw theoretical pDOS spectra were further modified so as to compensate for inherent limitations of state-of-the-art DFT computations. First, it is well known that even when LDA yields density of states spectra that are in excellent agreement with experiment, it does so only to within a rigid shift.²⁴ This shift can ultimately be traced back to an effective averaging over a discontinuity in the exchange-correlation Kohn-Sham potential at integer particle numbers, that is present in the exact exchange-correlation potential but missing in LDA.²⁵ Thus, the filled state pDOS was shifted downwards (by 2.0 eV) so as to provide best agreement with experiment for the positions of the leading UPS peak. Second, the Kohn-Sham gap is known to underestimate the true band gap even if the exact functional is used.²⁶ Therefore, the empty state pDOS curve was rigidly shifted independently (by 1.25 eV upwards) so as to provide best agreement with experiment for the positions of the leading IPES peak. Note that, partly because of these shifts and partly because of the quantum size effect associated with simulating Si with a slab of only a few monolayers, the Si band gap is too large (see below). Third, Kohn-Sham eigenvalues are *approximations* to relaxed electron excitation energies. Agreement

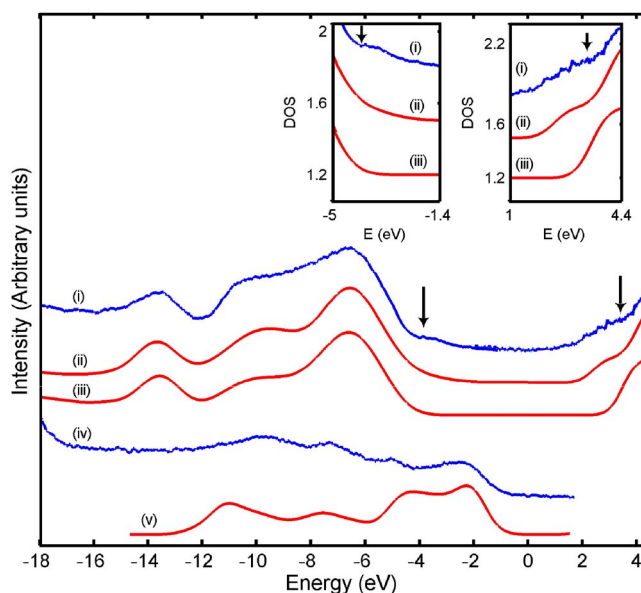


FIG. 2. (Color online) Experimentally measured (i) and theoretically simulated (ii) UPS and IPES data for a $C_{10}H_{21}$ alkyl chain adsorbed on the Si(111) surface, together with theoretically simulated UPS and IPES data for a hypothetical freestanding $C_{10}H_{22}$ alkane chain monolayer (iii). Also shown are experimentally measured (iv) and theoretically simulated (v) UPS data for a H-passivated Si(111) sample. Inset: zoom-in on the near-gap region of curves (i–iii). Arrows in both main figure and inset denote highest occupied and lowest unoccupied monolayer states (see text for details).

tends to be better for higher lying electrons (i.e., those in orbitals closer to the highest filled one) than for lower lying ones,²⁷ resulting in a somewhat “compressed” band. Therefore, the occupied pDOS curve was additionally stretched by 15%, so as to provide best agreement with the position of deeper lying UPS peaks—a frequently employed procedure for correcting for the difference between the shifted Kohn-Sham eigenvalues and the true one-particle excitation energies.²⁸ Finally, the shifted and stretched simulated UPS curves were convoluted with a 1.0 eV (0.9 eV for the H-passivated surface) wide Gaussian. The simulated IPES curves were convoluted with a 0.5 eV wide Gaussian. Unlike the previous steps, this broadening is *not* due to a limitation of DFT. Rather, it is aimed at mimicking the effective experimental resolution.

IV. RESULTS AND DISCUSSION

Figure 2 compares experimental UPS and IPES spectra of a $C_{10}H_{21}$ self-assembled alkyl chain monolayer on a Si(111) substrate with theoretical simulations for both a $C_{10}H_{21}/Si(111)$ slab and a “freestanding” $C_{10}H_{21}$ layer. For comparison, experimental and theoretical spectra of H-passivated Si(111) surface are also shown. For the purpose of focusing on electronic states relevant to transport, Fig. 3 compares experimental UPS and IPES spectra of alkyl chains of various lengths with theoretical simulations, in an

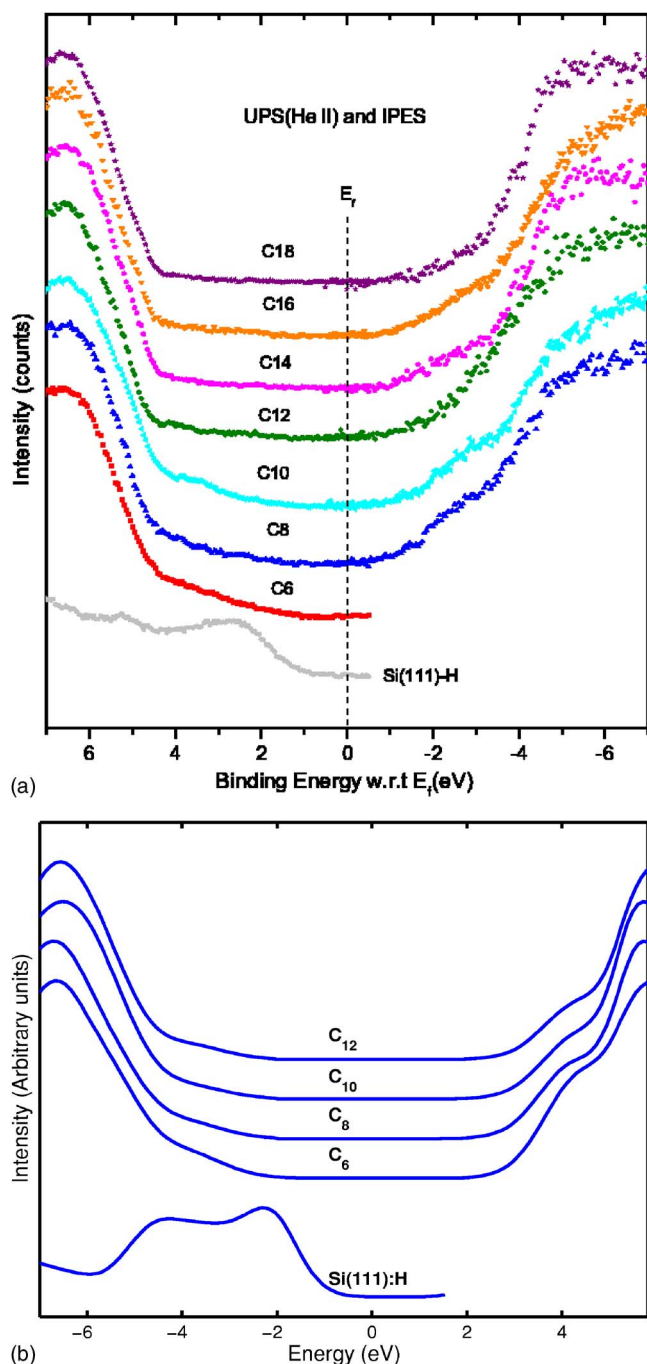


FIG. 3. (Color online) (a) Experimentally measured UPS and IPES data in an energy window around the Fermi level, for a C_nH_{2n+1} alkyl chain adsorbed on the Si(111) surface ($n=8, 10, 12, 14, 16, 18$). Also shown are UPS data for C_6H_{13} on the same surface and for a H-passivated Si(111) sample. (b) Theoretically simulated UPS and IPES data in an energy window around the Fermi level, for a C_nH_{2n+1} alkyl chain adsorbed on the Si(111) surface ($n=6, 8, 10, 12$). Also shown are the simulated UPS data for the H-passivated Si(111) surface. Both experimental and theoretical curves were normalized to leading peak intensities.

energy window around the Fermi level. To gain further insight into the origins of the electronic structure of the observed spectra, Fig. 4 provides a theoretical electronic structure map of $C_{10}H_{21}/Si$ —a contour plot of the local density of

states as a function of position perpendicular to the interface and of energy.

Figure 2 reveals that the experimental spectrum of $C_{10}H_{21}/Si$ differs dramatically from that of the H-passivated Si surface, indicating that the UPS signal from the alkyl chains dominates. Such domination is reasonable in light of the surface sensitivity of UPS and IPES and the length of the alkyl chains. It is further supported by the fact that very similar spectral features are found in UPS spectra from alkane chain crystals²⁹ and other alkane-containing systems.^{5–7,29–31} Assignment of individual spectral features to specific alkyl-related orbitals was already given in previous work of Seki, Ueno, and co-workers^{4,6,29,30} and is not repeated here.

Figure 2 also shows very good agreement between theory and experiment. All major features found experimentally by UPS and IPES for the $C_{10}H_{21}$ chain are reproduced in the simulated spectra.³² Likewise, major UPS features of the H-passivated Si surface are reproduced by the computation.

Overall agreement with the experimental spectral features is important because it allows us to rely on the computation of quantities not accessible in the present experiments, especially the spectrum of the hypothetical freestanding alkane chain monolayer (Fig. 2) and the electronic structure map (Fig. 4), for further interpretation. Such agreement is not trivial because the success or failure of DFT-based interpretation/prediction generally rests on the adequacy of the approximate functional used. This can be a problem in studies of organic/inorganic interfaces because, while LDA is known to work very well for Si,³³ it may fail on the organic side.³⁴ In our case, the above-mentioned band shifting and valence band “stretching” suffice for obtaining quantitatively meaningful results, lending credence to the rest of the analysis. LDA failures in electronic structure calculations of organic molecules can often be traced back to a spurious self-interaction (i.e., a Coulomb repulsion of an electron from itself) in highly localized orbitals.³⁴ Here, this is not a major problem.

Obtaining this level of agreement between theory and experiment requires a broadening of the theoretical data by a 1.0 eV Gaussian—clearly significantly larger than expected from instrumental resolution (0.15 eV for UPS and 0.45 eV for IPES) and thermal broadening. For the low-temperature spectra, broadening by a somewhat narrower, but still significant, Gaussian of width ~ 0.5 eV was found to be necessary. Added to the fact that UPS spectra of Si(111)- $C_{16}H_{33}$ taken with 25 meV resolution nearly overlap with the spectra taken with 150 meV resolution,¹⁶ this result suggests that the low-temperature effective experimental resolution is limited by inhomogeneous broadening resulting from residual static disorder in the alkyl monolayer. The broadening used to fit theory to experiment may therefore serve as a figure of merit for the “electronic structure quality” of the layer.

The theoretical spectra of the “Si-adsorbed” and freestanding alkane monolayers (Fig. 2) are nearly indistinguishable, again supporting the dominant alkane chain contribution. However, a subtle but significant difference is identified in the “tail” regions of the UPS and IPES spectra, ~ 2 –3 eV below and above the Fermi level, respectively (see inset of Fig. 2). These “tails” are present in the experiment and in the

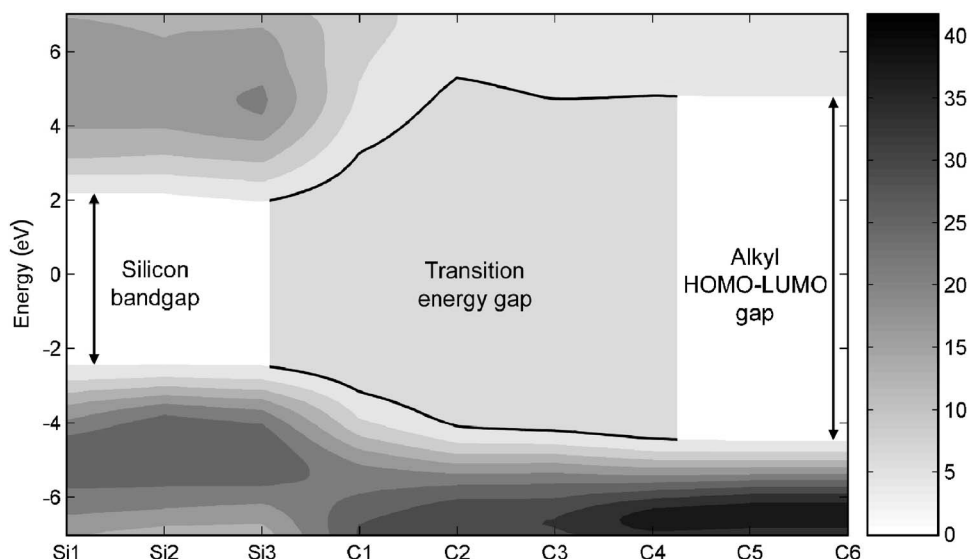


FIG. 4. Contour map of the local density of states for the $C_{10}H_{21}$ alkyl chain on Si(111), as a function of position perpendicular to the interface and of energy. The gradual evolution of the electronic structure along the alkyl chain is highlighted by indicating the band gap in the silicon (which is spuriously large due to adjustment of the alkyl gap, see text), the (correct) alkyl HOMO-LUMO gap, and the IDIS-related variable energy gap in the transition region.

Si-adsorbed calculation, but absent in the freestanding simulation. They are absent in previous measurements of alkane chain crystals²⁹ but similar tails are present in UPS measurements of methyl-terminated Si(111) surfaces.³⁵

For proper interpretation of the data, we need to consider that saturated hydrocarbons can be damaged during UPS and exposure to electron beams of certain energies³⁶ and that such damage increases the intensity of the low energy UPS and IPES tails. As shown in Fig. 3(a), even for spectra taken with minimal exposure time, as in our experiments, these tails are not eliminated. Indeed, a detailed study of damage causes and consequences for alkyl chain monolayers suggests that even a rigorous correction procedure does not eliminate the tails.¹⁶ These tails, therefore, are part of the intrinsic Si/alkyl monolayer spectrum—in agreement with our theoretical findings of Fig. 3(b). Further analysis shows that orbitals involved in the Si-C bonding are at ~ -5.8 eV and ~ -6.4 eV—well outside the tail energy (and energies of transport-relevant orbitals in general), ruling out a different simple explanation.

Figure 3 provides also further insight into the nature of the UPS and IPES tails. In both experiment [Fig. 3(a)] and theory [Fig. 3(b)], it is readily observed that the intensity of these tails relative to that of the leading peak decreases with increasing chain length.³⁷ Because both UPS and IPES are surface-sensitive, this strongly suggests that these tails are related to the underlying silicon and/or the Si-alkyl interface. However, as noted above, they do not correspond to levels of orbitals involved in the actual Si-C interfacial chemical bonding.

In experiment, the UPS and IPES tails decay because of the finite electron mean free path. The latter is expected to be longer in the IPES experiment than in the UPS experiment due to the lower kinetic energy of the electrons in the former.³⁸ Indeed, the decay of the IPES tail with increasing chain length is more gradual than that of the UPS tail. Interestingly, the exposure time of the Si(111)/ $C_{10}H_{21}$ spectrum has been longer and indeed a “bump” due to UV damage is showing in that spectrum. Nevertheless, the trend is clear. In the simulated spectra, the tails decay with chain length, even

though the electron mean free path is not included in the computation. This is because the contribution of the interface region to the overall pDOS is smaller for the long chains than for the short ones.

Figure 4 shows that the UPS and IPES “tails” are observed in the Si local DOS, decaying gradually into the alkane chain, so that from the local DOS of (roughly) the fourth CH_2 group and onwards, no significant tail state is seen. Such behavior is known in inorganic heterostructures as “induced density of interface states” [IDIS, sometimes referred to as interface-induced gap states (IFIGS)]^{39–41}—a generalization of Heine’s “metal-induced gap states” (MIGS) concept for metal/semiconductor interfaces.^{41–43} MIGS are Bloch states of the metal that tail into the semiconductor over the energy range where the conduction band of the metal overlaps the forbidden gap of the semiconductor. IDIS are similar, but both filled valence states and empty conduction states tail from the lower gap material (Si, here) to the higher gap material (alkyl chains, here). Note that the experiment presented here does not fully detect the Si substrate as such because of the thickness of the alkyl monolayer, and only very weak emission from states reaching to the top of the Si valence band can be recorded via UPS.¹⁶ The present experiment does, however, detect the IDIS tails due to their hybridization with molecular states. Thus, with these relatively long alkyl chains, agreement between theory and the combined UPS/IPES experiment (Fig. 2) is maintained despite the spuriously large adjusted Si band gap. The “deeper” IDIS (i.e., those closer to the top of the Si valence band and bottom of the Si conduction band) are missing theoretically because of this large gap. However, they are also missing experimentally because the degree of hybridization with molecular states decreases with the “depth” of the state.

For inorganic heterojunctions, MIGS and IDIS concepts were very useful for understanding localized interface states and their effect on interface band alignment.^{39–43} However, analyses of metal/organic interfaces based on these concepts are relatively few (and recent).^{11,44–47} This is even more so for organic/organic interfaces,⁴⁸ and we are not aware of any use of IDIS in the analysis of molecular/nonmolec-

ular interfaces. The recent Cu/alkane interface analysis by Kiguchi *et al.*¹¹ [via near-edge x-ray-absorption fine structure (NEXAFS) experiments] appears to be the only one to point out a direct experimental signature of MIGS. Our results are distinct in several aspects. First, IDIS, rather than MIGS, are identified. Second, they are identified for *both* filled and empty states. Third, the electronic structure signature of these states is obtained directly.

The identification of IDIS has important consequences for the assignment of what are commonly denoted as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) at an interface, using Figs. 2 and 3. Technically (but *only* technically), these should be assigned to the top and bottom of the two observed IDIS tails, respectively, because IDIS necessarily involve some hybridization with molecular orbitals. However, these levels are not the ones determining the *overall* barrier height for electrons (holes) between the Si conduction (valence) band and the alkyl conduction (valence) band, because they decay rapidly into the alkyl chain. Instead, those are determined by the lowest unoccupied and highest occupied alkyl levels *that extend throughout the chain*. The energy positions of such states are easily identified via Fig. 4 and, as an example, they are denoted as arrows in Fig. 2. They are the first “knee,” and not the “tail onset,” in both the UPS and IPES spectra. One can retain the HOMO and LUMO nomenclature for these states, but with “M” standing for “monolayer” rather than “molecular,” i.e., denoting states extending throughout the monolayer.⁴⁹

Figure 4 shows that transition from the electronic structure of silicon to that of the alkyl chain is far from abrupt, but instead increases gradually over ~ 4 CH₂ units—a non-negligible length for alkyl chains short enough to support

experimentally detectable currents through them. This suggests that a complete transport analysis, beyond, e.g., simple Simmons-type analysis,⁵⁰ should employ a more elaborate model of an energy-dependent density of states, as in Fig. 4.

V. CONCLUSIONS

We have elucidated the electronic structure of both filled and empty states of ordered alkyl chains bound to the Si(111) surface by combining direct and inverse photoemission spectroscopy with first principles calculations based on density functional theory. We identified both filled and empty interface-induced gap states and distinguished between those and molecular orbitals extending throughout the monolayer. Finally, we showed that distinguishing between these two types of states is crucial for interpreting transport experiments.

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¹D. Cahen, A. Kahn, and E. Umbach, *Mater. Today* **8**, 32 (2005).

²H. Ishii, K. Sugiyama, E. Ito, and K. Seki, *Adv. Mater. (Weinheim, Ger.)* **11**, 605 (1999).

³A. Nitzan and M. A. Ratner, *Science* **300**, 1384 (2003).

⁴K. Seki, N. Sato, and H. Inokuchi, *Chem. Phys.* **178**, 207 (1993).

⁵A.-S. Duwez, S. Di Paolo, J. Ghijsen, J. Riga, M. Deleuze, and J. Delhalle, *J. Phys. Chem. B* **101**, 884 (1997).

⁶D. Yoshimura, H. Ishii, Y. Ouchi, E. Ito, T. Miyamae, S. Hasegawa, K. K. Okudaira, N. Ueno, and K. Seki, *Phys. Rev. B* **60**, 9046 (1999).

⁷A.-S. Duwez, G. Pfister-Guillouzo, J. Delhalle, and J. Riga, *J. Phys. Chem. B* **104**, 9029 (2000).

⁸L. Zhang, K. Wesley, and S. Jiang, *Langmuir* **17**, 6275 (2001).

⁹A. B. Sieval, B. van den Hout, H. Zuilhof, and E. J. R. Sudhölter, *Langmuir* **16**, 2987 (2000); **17**, 2172 (2001).

¹⁰D. M. Alloway, M. Hoffman, D. L. Smith, N. E. Gruhn, A. L. Graham, R. Colorado Jr., V. H. Wysocki, T. R. Lee, P. A. Lee, and N. R. Armstrong, *J. Phys. Chem. B* **107**, 11690 (2003).

¹¹M. Kiguchi, R. Arita, G. Yoshikawa, Y. Tanida, S. Ikeda, S. Entani, I. Nakai, H. Kondoh, T. Ohta, K. Saiki, and H. Aoki, *Phys.*

Rev. B **72**, 075446 (2005).

¹²A. Salomon, T. Boecking, C. K. Chan, F. Amy, O. Girshevitz, D. Cahen, and A. Kahn, *Phys. Rev. Lett.* **95**, 266807 (2005).

¹³M. R. Linford, P. Fenter, P. M. Eisenberger, and C. E. D. Chidsey, *J. Am. Chem. Soc.* **117**, 3145 (1995).

¹⁴O. Seitz, T. Boecking, A. Salomon, J. J. Gooding, and D. Cahen, *Langmuir* **22**, 6915 (2006).

¹⁵C. I. Wu, Y. Hirose, H. Siringhaus, and A. Kahn, *Chem. Phys. Lett.* **272**, 43 (1997).

¹⁶F. Amy, C. K. Chan, W. Zhao, J. Hyung, M. Ono, T. Sueyoshi, S. Kera, G. Neshet, A. Salomon, L. Segev, O. Seitz, H. Shpaisman, A. Schöll, M. Haeming, T. Boecking, D. Cahen, L. Kronik, N. Ueno, E. Umbach, and A. Kahn, *J. Phys. Chem. B* (to be published).

¹⁷A. Natan, L. Kronik, and Y. Shapira, *Appl. Surf. Sci.* **252**, 7608 (2006), and references therein.

¹⁸A. B. Sieval, R. Linke, H. Zuilhof, and E. J. R. Sudhölter, *Adv. Mater. (Weinheim, Ger.)* **12**, 1457 (2000).

¹⁹S. Nihonyanagi, D. Miyamoto, S. Idojiri, and K. Uosaki, *J. Am. Chem. Soc.* **126**, 7034 (2004).

²⁰X. Wallart, C. Henry de Villeneuve, and P. Allongue, *J. Am. Chem. Soc.* **127**, 7871 (2005); P. Gorostiza, C. Henry de Ville-

- neuve, Q. Y. Sun, F. Sanz, X. Wallart, R. Boukherroub, and P. Allongue, *J. Phys. Chem. B* **110**, 5576 (2006).
- ²¹G. P. Srivastava, *Rep. Prog. Phys.* **60**, 561 (1997).
- ²²G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996). Core electrons were treated using the projector augmented wave method [G. Kresse and D. Joubert, *Phys. Rev. B* **59**, 1758 (1999)]. A k -point grid of $5 \times 5 \times 1$ and a cutoff energy of 400 eV were used and all coordinates were optimized with residual forces smaller than ~ 0.05 eV/Å.
- ²³R. M. Dreizler and E. K. U. Gross, *Density Functional Theory* (Springer, Berlin, 1990).
- ²⁴L. Kronik, R. Fromherz, E. Ko, G. Ganteför, and J. R. CheLIKowsky, *Nat. Mater.* **1**, 49 (2002); M. Moseler, B. Huber, H. Häkkinen, U. Landman, G. Wrigge, M. A. Hoffmann, and B. v. Issendorff, *Phys. Rev. B* **68**, 165413 (2003); O. Guliamov, K. A. Jackson, and L. Kronik, *J. Chem. Phys.* **123**, 204312 (2005).
- ²⁵M. J. Allen and D. J. Tozer, *Mol. Phys.* **100**, 433 (2002).
- ²⁶J. P. Perdew and M. Levy, *Phys. Rev. Lett.* **51**, 1884 (1983); L. J. Sham and M. Schlüter, *ibid.* **51**, 1888 (1983); R. W. Godby, M. Schlüter, and L. J. Sham, *ibid.* **56**, 2415 (1986).
- ²⁷D. P. Chong, O. V. Gritsenko, and E. J. Baerends, *J. Chem. Phys.* **116**, 1760 (2002).
- ²⁸M. S. Hybertsen and S. G. Louie, *Phys. Rev. B* **34**, 5390 (1986).
- ²⁹K. Seki, S. Hashimoto, N. Sato, Y. Harada, K. Ishii, H. Inokuchi, and J.-I. Kanbe, *J. Chem. Phys.* **66**, 3644 (1977).
- ³⁰K. Seki, N. Ueno, and H. Inokuchi, *Chem. Phys.* **182**, 353 (1994); N. Ueno, K. Sugita, K. Seki, and H. Inokuchi, *Phys. Rev. B* **34**, 6386 (1986).
- ³¹J. Hwang, E.-G. Kim, J.-L. Brédas, and A. Kahn (unpublished).
- ³²For the UPS data, these include the “tail” leading to a peak at ~ -6 eV, followed by a broad plateau ending at a shoulder at ~ -10 eV, a significant “dip” at ~ -12 eV, another peak at ~ -13.5 eV, and a smaller peak at ~ -15 eV [the latter for the shorter alkyl chains, but not for the longer ones (not shown)]. For the IPES, these include the “tail” at ~ 2 eV leading to a “knee” at ~ 3 eV.
- ³³M. T. Yin and M. L. Cohen, *Phys. Rev. Lett.* **45**, 1004 (1980).
- ³⁴N. Dori, M. Menon, L. Kilian, M. Sokolowski, L. Kronik, and E. Umbach, *Phys. Rev. B* **73**, 195208 (2006).
- ³⁵T. Miyadera, A. Koma, and T. Shimada, *Surf. Sci.* **526**, 177 (2005); R. Hunger, R. Fritsche, B. Jäeckel, W. Jaegermann, L. J. Webb, and N. S. Lewis, *Phys. Rev. B* **72**, 045317 (2005).
- ³⁶See, e. g., N. Ueno, K. Sugita, O. Koga, S. Suzuki, *Jpn. J. Appl. Phys., Part 1* **22**, 1613 (1983); M. Rei Villar, M. Schott, and P. Pfluger, *J. Chem. Phys.* **92**, 5722 (1990); M. Ono and E. Morikawa, *J. Phys. Chem. B* **108**, 1894 (2004).
- ³⁷The spectrum of the C₁₀H₂₁ sample in Fig. 3(a) was collected with a longer UV exposure time. The “bump” seen on the UPS tail of it is due to UV damage (see Ref. 16 for more details).
- ³⁸Kinetic energies are ~ 35 eV and $\sim 7-9$ eV for the UPS and IPES “tail electrons,” respectively.
- ³⁹C. Tejedor, F. Flores, and E. Louis, *J. Phys. C* **10**, 2163 (1977).
- ⁴⁰J. Tersoff, *Phys. Rev. Lett.* **52**, 465 (1984).
- ⁴¹W. Mönch, *Semiconductor Surfaces and Interfaces*, 3rd ed. (Springer, Berlin, 2001), chap. 6.
- ⁴²V. Heine, *Phys. Rev.* **138**, A1689 (1965).
- ⁴³S. G. Louie and M. L. Cohen, *Phys. Rev. B* **13**, 2461 (1976).
- ⁴⁴H. Vazquez, R. Oszwaldowski, P. Pou, J. Ortega, R. Perez, F. Flores, and A. Kahn, *Europhys. Lett.* **65**, 802 (2004); H. Vazquez, F. Flores, R. Oszwaldowski, J. Ortega, R. Perez, and A. Kahn, *Appl. Surf. Sci.* **234**, 107 (2004).
- ⁴⁵J. X. Tang, C. S. Lee, S. T. Lee, and Y. B. Xu, *Chem. Phys. Lett.* **396**, 92 (2004).
- ⁴⁶Q. Sun, A. Selloni, and G. Scoles, *ChemPhysChem* **6**, 1906 (2005).
- ⁴⁷A similar concept has also been invoked to explain single-molecule transport experiments. See, e. g., G. C. Liang, A. W. Ghosh, M. Paulsson, and S. Datta, *Phys. Rev. B* **69**, 115302 (2004); Y. Xue and M. A. Ratner, *ibid.* **68**, 115406 (2003); R. Gutierrez, G. Fagas, K. Richter, F. Grossmann, and R. Schmidt, *Europhys. Lett.* **62**, 90 (2003). In this article, we concentrate on the interface between two well-defined phases.
- ⁴⁸H. Vazquez, W. Gao, F. Flores, and A. Kahn, *Phys. Rev. B* **71**, 041306(R) (2005).
- ⁴⁹G. Neshet, A. Vilan, H. Cohen, D. Cahen, F. Amy, C. Chan, J. Hwang, and A. Kahn, *J. Phys. Chem. B* **110**, 14363 (2006).
- ⁵⁰J. G. Simmons, *J. Appl. Phys.* **35**, 2655 (1964); **34**, 2581 (1963).