Cooperative effects and dipole formation at semiconductor and self-assembled-monolayer interfaces

Amir Natan,1,2 Yigal Zidon,1 Yoram Shapira,1 and Leeor Kronik1,2,*

1Department of Physical Electronics, Tel-Aviv University, Ramat Aviv 69978, Israel
2Department of Materials and Interfaces, Weizmann Institute of Science, Rehovoth 76100, Israel

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Dipole formation processes at self-assembled monolayers of benzene derivatives chemisorbed on the Si(111) surface are investigated from first principles. The surface dipole is shown to be sensitive to the molecular coverage and dominated by intramolecular charge rearrangement due to long-range, cooperative behavior. This cooperative behavior suppresses substrate contributions to dipole formation.

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A key, yet insufficiently understood, phenomenon associated with the chemisorption of self-assembled monolayers (SAMs) on metallic or semiconducting substrates is the formation (modification) of the surface dipole.1–3 Surface dipole modifications have been recently invoked as the controlling factor in arenas as diverse as charge transport,4–6 chemically sensitive field effect transistors,7 observation of novel interface magnetic phenomena,8,9 and even molecular nanopatterning.10 Dipole formation phenomena in chemisorbed systems are difficult to understand because they may involve a multitude of factors:11,12 The gas phase molecular dipole and the surface molecular density obviously affect the surface dipole, but in principle so do molecular structural relaxations, intramolecular charge rearrangement, and SAM-substrate charge transfer, with often conflicting views on the dominant mechanism(s).

Here, we present a first principles analysis of a set of molecules with a fixed binding group but different functional groups possessing a wide range of dipole moments, as is often done experimentally.2–4 We focus on a Si(111) surface with different benzene derivatives13 allowing for a systematic analysis of dipole-related phenomena in this representative system. We provide a positive identification of the primary dipole-controlling mechanism in this system and explain how this is intimately related to the ordering of the monolayer in a broad range of SAM-semiconductor interfaces.

Four benzene derivative (benzene, nitrobenzene, bromobenzene, and aniline) SAMs, adsorbed vertically on a Si(111) surface, were studied using a symmetric slab cell. All calculations were performed with at least six atomic layers of silicon and six “atomic layers of vacuum,” which were found sufficient for mimicking a surface-terminated material. Lateral periodic cell dimensions of $2 \times 1$ or $2 \times 2$ silicon atoms15 were used for studying surfaces with a full [1 monolayer (ML)] or half (0.5 ML) molecular coverage, defined as one molecule per two or per four surface silicon atoms, respectively. Dangling Si bonds were passivated by hydrogen atoms. A typical supercell is shown in Fig. 1(a).

We solved the Kohn-Sham equations using norm-conserving pseudopotentials16 constructed within the local density approximation (LDA) using a plane wave basis.17 We found a $k$-point grid of $3 \times 3 \times 1$ and a cutoff energy of 60 Ry to be sufficiently accurate. All coordinates were optimized with a maximal residual force of 0.004 Ry/a.u. For evaluating gas phase molecular dipoles, we used much larger supercells, and also Gaussian basis sets (nonperiodic configuration) for comparison. Dipole values between the two approaches varied by no more than 0.15 D. The theoretical values overestimated the experimental ones because LDA typically overestimates charge transfer in polarized systems.18

We found the adsorption energy of a 1 ML and a 0.5 ML to be very similar, with differences in adsorption energy below 0.1 eV. Importantly, we found no Si(111)/SAM interface states in the forbidden gap, leaving the interface dipole as the primary factor controlling the surface electronic structure.

Electrostatic dipoles perpendicular to the surface (z direction) were evaluated as a function of vertical position using the relation

\[ \mathbf{D}(z) = \int \rho(y) \mathbf{e}_z dS \]

where $\rho(y)$ is the charge density as a function of the y coordinate and $\mathbf{e}_z$ is the unit vector in the z direction.

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FIG. 1. (Color online) (a) “Ball and stick” picture of the $2 \times 1$ supercell used for the Si(111)-nitrobenzene SAM structure. (b) Electrostatic dipole perpendicular to the surface as a function of position inside the structure. (c) Charge density map in the yz plane, for the Si(111)-nitrobenzene SAM structure. The special planes (i), (ii), (iii), and (iv) contain the middle of the C-N bond, the C-C bond in the center of the benzene ring, the Si-C bond, and a Si-Si bond inside the bulk, respectively.
\[ p(z) = \int_{z}^{z_{cell}} z' \rho(x,y,z') dx dy dz', \]

where \( z \) is an arbitrary plane inside the structure, \( p(z) \) is the dipole between the vacuum and the plane \( z \), \( \rho(x,y,z) \) is the charge density (of both nuclei and electrons), and \( z_{cell} \) is the supercell size in the vertical direction. This way, the dipole far in the vacuum region is zero by construction and dipoles within the sample are evaluated with respect to the vacuum. Meaningful dipole values are obtained only in \( z \) planes that divide the overall structure into neutral subunits (e.g., the middle point of the various bonds). For such points, the choice of origin for \( z' \) in Eq. (1) will not affect the result and the equivalent relation

\[ p(z) = \int_{z}^{z_{cell}} (z' - z) \rho(x,y,z') dx dy dz' \]

was found to improve the numerical stability of the calculation.\(^1^9\)

The evolution of the dipole evaluated using Eq. (2) as a function of \( z \), along with the charge density map in the \( yz \) plane, are shown in Figs. 1(b) and 1(c) for the representative case of a Si(111)/nitrobenzene SAM. It can be shown that only the peaks of the dipole curve correspond to physically meaningful dipole values.\(^1^9\) Clearly, much of the dipole found in Fig. 1(b) is formed in the functional group itself, but the full value of the dipole is only reached inside the Si bulk. We therefore take the surface dipole in all discussion below as the dipole obtained at a “peak point” inside the bulk.

The surface dipole per molecule, calculated using the above method, as a function of the gas phase molecular dipole, for both 1 and 0.5 ML coverage, is given in Fig. 2. It is readily observed that there is a linear dependence of the surface dipole on the gas phase dipole over the entire wide range studied, in agreement with experiment.\(^1^1\)\(^^3\) It is also clear that the slope of this dependence is significantly different for the two coverages and is substantially smaller than 1 in either case. Surface chemisorption is thus shown to be associated with significant depolarization,\(^1^1\) which leaves 0.53 of the gas phase dipole for 1 ML coverage and 0.71 of the dipole for 0.5 ML coverage.

In order to elucidate which of the phenomenological mechanisms suggested earlier (structural relaxations, intramolecular charge rearrangement, charge transfer, image effects), if any, is responsible for the observed behavior, we calculated the dipole for the same monolayer in the absence of the substrate. This was performed by removing all silicon atoms and replacing each Si-C bond with a Si-H bond, with the molecules in either their surface-adsorbed or gas-phase optimized geometry. The results of these additional calculations are also shown in Fig. 2. Clearly, similar depolarization effects were obtained, with marginally different slopes: 0.55 (0.52) and 0.73 (0.67) for 1 ML and 0.5 ML, respectively, at the gas-phase (surface-adsorbed) geometry. These additional slope changes are much smaller than those due to coverage change (in fact, they are at the numerical noise level of our calculations—dipole changes in the range of 0.1 D). This shows that neither molecular relaxation nor charge transfer is dominant in the present case.\(^2^0\) Likewise, the lack of a substantial substrate effect also indicates a lack of a substantial image charge effect (even though our slab may not be thick enough to capture the full image effect, it would show it at least partially\(^2^1\)).

We explain this striking absence of substrate participation in the depolarization process by considering the molecular functional groups as a periodic dipolar array positioned several angstroms above the Si surface. The potential outside such a dipolar array decays exponentially, with a maximal decay length of \( L/2\pi \),\(^2^2\) where \( L \) is the larger dimension of the supercell in the \( xy \) plane, which is 6.64 Å here. Taking 4 Å as a characteristic distance from the functional group to the Si-C bond, we get a potential at the Si-C bond that is less than 2% of its value inside the dipolar layer. Thus, the potential of the dipole layer felt by the semiconductor, and ergo the response of the semiconductor to it, are far too weak to dominate the depolarization effect. We note that slowly varying perturbations in the ordered dipolar array (for example, due to local domains) may mitigate the exponential decay, causing an effective “field leakage” effect.

To test the above explanation, we attached SiH\(_3\) to a benzene derivative molecule and compared the change in the degree of charge transfer at the Si-C bond as the functional group of the benzene is changed from H to NO\(_2\) (a 4.5 D change in the LDA-computed dipole of the isolated molecule). In the closely packed monolayer (one molecule per an area of 3.8 Å \( \times \) 6.6 Å), we found that the difference in charge transfer between the H and NO\(_2\) cases was only about 0.001 e. However, with a much larger intermolecular separation (one molecule per an area of 20 Å \( \times \) 20 Å) the differ-
ence was 0.02 e. This 20-fold increase is only due to the cooperative effect of the dipolar array and not due to differences in the local chemistry. We emphasize that the degree of charge transfer across the substrate-monolayer interface is certainly chemistry-specific and can be quite different for other systems. However, the suppression of additional changes in the charge transfer, induced by modifying the functional group, is a general physical consequence of an ordered dipolar array and does not depend on the specific chemistry of the system.

To explore the role of intramolecular charge rearrangement in dipole depolarization, we compared our results to a phenomenological model where each molecule is modeled by a point dipole and the SAM is therefore modeled as a planar ordered array of vertically oriented polarizable point dipoles.23,24 The point dipole array creates a vertical electric field $E_z$ at the dipolar plane

$$E_z = -\frac{P}{a^3} \sum_{m,n=-\infty}^{\infty} \frac{1}{[n^2 + (b/a)^2]^2} = -\frac{kP}{a^3}, \quad (3)$$

where $P$ is the point dipole, $a$ and $b$ are the lateral cell dimensions, and $k$ is a purely geometric factor resulting from the infinite grid structure summation. Each point dipole $P$ is itself polarized by the electric field, i.e.,

$$P = P_0 + \alpha E_z, \quad (4)$$

where $\alpha$ is the molecular polarizability. Combining Eqs. (3) and (4) yields

$$P = \frac{P_0}{1 + ak/a^3}, \quad (5)$$

i.e., a linear relation between the surface and gas phase dipoles is found, in agreement with Fig. 2.

To examine the extent to which this picture agrees with our findings, we evaluated the sum of Eq. (3) numerically for an array of point dipoles having the same periodicity as the molecular array. Using the LDA polarizability value of the benzene ring in the $z$ direction25–25.3 a.u.3 for $\alpha$ in Eq. (5), we find a “depolarization factor,” $P/P_0$, of 0.5 and 0.76 for the 1 ML and 0.5 ML, respectively. This is remarkably close (given the crudeness of the phenomenological model) to the slopes of 0.55 and 0.73 obtained from the DFT calculations of the “SAM” without a substrate and with the gas-phase molecular geometry. This strongly supports intramolecular charge rearrangement as the dominant depolarization mechanism for the present problem.26 The remaining differences between the first principles and phenomenological theory are simply a result of the molecules not being ideal point dipoles.

The above discussion clearly shows that the dipole depolarization is a cooperative phenomenon. The computed intramolecular charge rearrangement is inherently a long-range order phenomenon and the presence of an array of molecules is essential to its existence. This is important, because first principles calculations of substrate (SAM) structures often use a model of a single molecule adsorbed on a cluster such that the local chemical environment of the molecule-substrate bonding is correct.27,28 Naturally, such calculations cannot account for cooperative molecular effects. To examine the extent to which this could be a problem in practice, we examined the extent of depolarization for a finite number of point dipoles by using Eq. (3) with a finite sum. We found, for example, that for a $2 \times 1$ and $2 \times 2$ finite array of dipoles, with 1 ML geometry, depolarization factors of 0.82 and 0.79 were obtained, compared to 0.5 of the infinite model. In other words, the finite array depolarization is substantially different from that of an infinite array. This strongly suggests that cluster model calculations involving polar molecules (or molecules that become polar upon adsorption) will paint a completely different picture of the depolarization. Lack of depolarization, in turn, may profoundly affect the electronic structure, including the presence or absence of substrate-SAM charge transfer, so that cluster models should be viewed with caution.

Studies of SAM-substrate dipole formation usually do so indirectly, by measuring surface potentials. These data are interpreted heuristically in terms of the Helmholtz equation, which relates the potential drop across the SAM, $\Delta V$, to the gas-phase dipole $P_0$,\(^1\,^3\)

$$\Delta V = 4\pi \frac{NP_0 \cos(\phi)}{AE}, \quad (6)$$

where $A$ is the surface area, $N$ is the number of molecules, $\phi$ is the molecular tilt angle, $\epsilon$ is the dielectric constant of the monolayer, and centimeter-gram-seconds (cgs) units are used. Because, in general, the potential drop across a dipolar layer is given by $\Delta V = 4\pi P/A$, for $\phi = 0^\circ$ the heuristic dielectric constant in Eq. (6) is identical to the depolarization factor, $\epsilon = P_0/P$.23 For the 1 ML coverage, we obtain a depolarization factor of $\sim 2$, in good agreement with the dielectric constant of liquid benzene—2.28.29 The experimentally estimated $\epsilon$ for such molecules in Langmuir-Blodgett films is 4–5.30 albeit for a more dense film, where the depolarization field is indeed stronger. Estimations of $\epsilon$ from $\Delta V$ measurements of SAMs on silicon based on Eq. (6) typically yield a higher value of $\sim 10$.2,3 This is usually attributed to factors such as molecular tilt (the molecules are vertical in our calculations) and/or reduced coverage, and may also result from the above-mentioned “field leakage” into the substrate for a nonideal monolayer. Our results for the ideal, vertically ordered molecular arrays should thus be viewed as a lower bound for dielectric screening effects that may be observed in practice for nonideal systems.

In conclusion, we have used first principles calculations within a periodic slab configuration, as well as phenomenological arguments, for explaining dipole formation processes at Si(111)/benzene derivative interfaces. Our results highlight the importance of long-range cooperative effects in controlling the electronic properties of SAM-substrate systems. On the one hand, the ordered monolayer results in long-range dipole-dipole interactions that drive intramolecular charge rearrangement—an effect that cannot be captured by common cluster models. At the same time, the periodic molecular array suppresses the substrate response by reducing the dipolar electric field it experiences, making molecular depolarization the dominant dipole-controlling mechanism.
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*Corresponding author. Email address: leeor.kronik@weizmann.ac.il


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20We note, however, that the remaining small effect may still be important—see V. S. L’vov, R. Naaman, V. Tiberkevich, and Z. Vager, Chem. Phys. Lett. 381, 650 (2003). The dipole change with and without the substrate in the surface-adsorbed geometry (assuming it is not a numerical artifact) would correspond to charge transfer of $-5 \times 10^{-3}$ e between molecule substrate over a distance of $\sim 5 \AA$. This would correspond to a surface charge of $\sim 10^{12}$ cm$^{-2}$, which is significant.


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26We note that a similar mechanism was recently invoked in Ref. 12 for explaining coverage-dependent dipoles in CH$_3$S and (CH$_3$)$_2$S on Au(111), even though the chemistry of this system is very different from that of the one studied here. This again emphasizes the general physical character of our conclusions.


