

Molecular Monolayer-Mediated Control over Semiconductor Surfaces: Evidence for Molecular Depolarization of Silane Monolayers on Si/SiO_x

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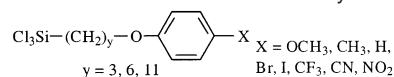
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Adsorption of molecules on surfaces of solids can change the solids' surface properties, and especially their electronic properties, in a controllable manner.¹ The most straightforward type of electronic change is that of the work function and electron affinity due to the potential drop across a layer of dipolar molecules. The expected change is given by $\Delta V = N\mu \cos \theta / \epsilon \epsilon_0$, where N is the density of dipoles, μ is the dipole moment (in Debye), θ is the average angle that the dipole makes with the surface normal, ϵ is the layer's effective dielectric constant (derivable from the molecules' polarizability²), and ϵ_0 is the permittivity of vacuum.³ Indeed, this approach has been successful by chemisorbing sets of molecules, identical except for one functional group, on a variety of semiconductors,⁴ including Si,⁵ and on metals.⁶ Here we report on a strong deviation from the expected $\Delta V - \mu$ relation. We show that it can be attributed to a decrease in the molecular dipole moment, due to changes in molecular conformation and/or order in the molecular layer.

In all cases reported until now, the $\Delta V - \mu$ relation was found to hold, within experimental error, with a close to 1 V change for n -GaAs (nearly 70% of the band gap) with benzoic acids.^{2,4-6} Such changes may, in principle, control the behavior of metal/- and semiconductor/semiconductor junctions, a matter of interest, for example, in the design and optimization of light-emitting diodes⁷ and solar cells.⁸ Our present results show that ΔV cannot be increased without limit.⁹ A limit of this type is well known for inorganic systems, especially chemisorption of Cs on semiconductors, which drastically decreases semiconductor electron affinity. As coverage increases (from 0.01 to 0.1 L), the decrease in electron affinity becomes less and less until there is actually an increase at very high (close to monolayer) coverage.¹⁰ The reason is the increasing dipole-dipole repulsion that occurs, as the Cs-Cs distance on the surface decreases. Beyond a critical Cs density, the system can decrease its free energy by electrostatic depolarization, a decrease in the surface-adsorbate dipole moment. In the case of Cs, depolarization occurs by actual charge transfer between the Cs and the surface. With molecular dipoles, the situation may be different, because of the larger number of degrees of freedom of molecules.¹¹ To test this, we used mainly σ -bonded, nonconjugated "insulating" molecules and adsorbed them on a nonmetallic surface, to decrease the possibility for charge transfer to/from the surface. Furthermore, we chose a system where the molecules are not arranged in a rigid, highly organized monolayer. Under these conditions, the dipole-dipole interaction may be decreased, for example, by reducing the distance between positive and negative poles to decrease the net dipole, that is, by a change in molecular conformation.

In Scheme 1, we show the series of molecules used.¹² The molecules are identical except for one group that, because of its varying electron-donating/withdrawing character, changes the molecule's dipole. While in the past we used mainly molecules, directly

Scheme 1. Molecules Used To Adsorb Monolayers on Si/SiO_x



bound to a semiconductor or metal surface,⁴ trichlorosilanes on oxidized Si yield a 2-D polymeric network of a monolayer of molecules, *anchored* occasionally to the SiO_x surface via Si-O bonds.¹³ This system is actually closer to an ideal dipole layer, situated above, and detached from a surface, than a monolayer composed of molecules, chemically bound to the surface. The molecules were deposited as a siloxane-*anchored* array (XPS shows full hydrolysis of the trichlorosilanes) onto oxidized (100) Si.¹³

We characterized the resulting surfaces by contact angle (CA), ellipsometry, FTIR, UV-vis, and X-ray photoelectron spectroscopies. These data suggest that the molecules form roughly one monolayer with comparable coverage for all molecules.¹⁴ However, significant structural and electronic differences are found between the NO₂ and CN derivatives and the others, with the CF₃ substituent showing somewhat intermediate behavior. Thus, hysteresis between receding and advancing contact angles more than doubles for the NO₂ and CN derivatives as compared to the others. For $y = 11$, the NO₂ and CN monolayers show a shift of the symmetric (2 cm⁻¹) and asymmetric CH₂ stretch (3 cm⁻¹), and of the tilt angle, θ , of the molecules in the monolayers ($25 \pm 1^\circ$ for OMe, Me, H, I, and Br, versus $29 \pm 1^\circ$ for CF₃, CN, NO₂) as calculated from polarized ATR-FTIR spectra.¹⁵ The UV-vis spectra of the NO₂ and CN films on the surface show a shift similar to that obtained in polar solvent.^{12,16} This suggests that, on the surface, neighboring molecules provide such a (polar) environment for each other. This is not observed with the other derivatives. These results suggest less average order¹⁴ for the NO₂ and CN monolayers than for the others.

We measured the work function of the Si/SiO_x surfaces, modified by the series of monolayers, using a Kelvin Probe setup with a Au reference, under ambient conditions. The work function is derived from the contact potential difference (CPD) between the surface and the Au reference.¹⁷ The electron affinity is then obtained by measuring the CPD under *saturating supra-band-gap illumination*, to cancel the semiconductor's band bending. The latter was found to be rather independent of the type of substituents.⁵ Results for $y = 11$ are shown in Figure 1. The most striking behavior is that of the NO₂ and CN derivatives, both of which are molecules that have large dipole moments in the free state. This behavior was found consistently for the NO₂ and CN derivatives (i.e., also with the C₃ and C₆ series) and for molecules with comparable terminal functionality on a saturated C₁₆ alkyl chain, that is, without the phenyl ether.¹⁸ The relatively high dipole moments of the CN and NO₂ derivatives suggest that, if depolarization is an issue, it will be expressed with these substituents. The dipole moments used in Figure 1 are those calculated for model free molecules, obtained from semiempirical quantum chemical calculations.¹⁹ Two dipole values for the methoxy derivative are shown, one for the syn and

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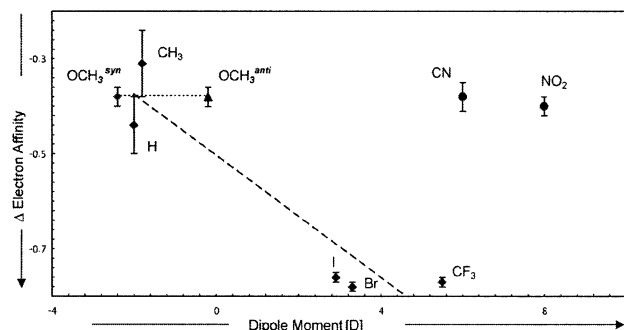


Figure 1. Plot of calculated, free molecule's dipole moments versus the CPD under saturating supra-band-gap illumination (CPD_L; 400–900 nm light) for Si/SiO_x samples onto which monolayers of the C₁₁ derivatives of Scheme 1 were adsorbed. The molecular substituents (cf. Scheme 1) are indicated next to the data points. The data are referred to the CPD_L of the bare surface, that is, $\Delta\text{CPD}_L = \text{CPD}_L(\text{with monolayer}) - \text{CPD}_L(\text{bare})$. This yields directly the difference in electron affinity (energy difference between conduction band bottom and vacuum level), due to the molecular monolayer. The dipole moments were calculated using the semiempirical PM3 method, after geometry optimization, in the energy-minimized, fully extended position of the chain.¹⁹ For this, we used model molecules (with different functional groups) of trimethoxysilane phenyl ethers to simulate the actual Si-containing end group facing the SiO_x. The dipole moments are given in Debye units, with 1 D = 3.34×10^{-30} C·m. The line gives the best linear fit ($R = 0.94$) to all except the NO₂, CN, and CF₃ data. If the CF₃ data are included (not shown), $R = 0.89$.

one for the anti conformation of the methoxy CH₃ and the first CH₂ of the alkyl chain. The anti conformer is found to be only very slightly lower in energy than the syn one. It is therefore likely that a mixture of the two is present on the surface, and, hence, the proposed fit used the average of the two calculated dipoles.

To check the depolarization idea further, we prepared monolayers of the H–C₁₁ derivative and then chemically transformed them in situ into the NO₂ derivative, as judged by IR, CA, and CPD measurements. Using various nitration conditions, we could never achieve more than 75–80% H → NO₂ conversion. Other in situ transformations (e.g., Br → H by lithiation and protonation or H → I by electrophilic iodination) were quantitative; such in situ chemistry caused no damage to the monolayer, from IR, CA, and ellipsometry. We also prepared mixed monolayers of the NO₂ and H–C₁₁ derivatives and subjected them to in situ nitration.²⁰ Here too, regardless of the initial NO₂ fraction on the surface, conversion stops when ~80% of the surface is nitrated. Up to ~75% NO₂, the electron affinity showed a regular dependence on the NO₂ fraction, as measured by CPD, consistent with depolarization becoming a factor only at high NO₂ densities.

Taken together, our results suggest that the physical phenomenon of depolarization can have chemical effects on the molecular modification of semiconductor surfaces, by decreasing the molecular dipole moment and thus the dipole–dipole interaction energy between the molecules. Whether or not this will happen depends on the balance between the energy required to place high dipole moment molecules close (molecular distance) to each other and that required to change the molecular dipole. In contrast to what has been found for atomic surface modifiers, here the primary mechanism to decrease the dipole moment (depolarization) appears to be conformational change of the molecules, with or without intramolecular charge transfer, rather than charge transfer between molecule and substrate.¹⁸ It is possible that this effect will be smaller if the molecules are either strongly chemically bound to the surface or form more rigid, highly organized monolayers (stronger van der Waals interaction between the molecules).²¹ While in such cases as well we expect a reduction in the dipole moment of neighboring molecules, other mechanisms may become dominant. Experiments

to explore these and other aspects of molecular chemical surface modifications of semiconductors are underway in our laboratories.

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Supporting Information Available: Ellipsometry, FTIR, and XPS data (RTF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (9) Results obtained up until now on metals or semiconductors (cf. data in refs 2, 4–6, 17, for example) do not suggest such a limit. We note, though, that different molecules were used (with smaller calculated dipole moments). While in several cases, for example, benzoic acid modification of CdTe (cf. Figure 3 in ref 4) or disulfide modification of CuInSe₂ (cf. Figures 6, 7 in ref 6b), the observed ΔV is significantly less than the predicted value, this is true for all substituents, not only for those with large dipole moments, and, thus, has been attributed to other factors (cf. ref 6b,c).
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- (14) Coverage was estimated from XPS, UV, and FT-IR data. The films show average order (cf. ref 4), rather than the higher order found for octadecyltrichlorosilane (OTS) on SiO₂ (cf. ref 13). Spectroscopic ellipsometry on the C₁₁ films yields a 1.9–2.2 nm thickness for the organic monolayers (on a 1.7–2.1 nm SiO_x layer), except for those with NO₂, which are slightly thicker and whose UV spectra also suggest some multilayer character; see also Supporting Information.
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- (18) Changes in interface states could be excluded as cause for the observations, because only minor differences in band bending were found within each series. This implies that the surface charge, which controls band bending, changes little between the –CN and –NO₂ derivatives, and the other ones.
- (19) Such calculations were shown to give good agreement with experimental data for benzoic acids, see (also for sign convention): Wu, D.-G.; Ghabboun, J.; Martin, J. M. L.; Cahen, D. *J. Phys. Chem. B* **2001**, *105*, 12011. Results, very similar to the ones shown here, are obtained from ab initio calculations on shorter model compounds (without the (CH₂)₁₁ chain), taking into account polarization effects.
- (20) The change in the electron affinity is greater when nitrating a mixed monolayer than when starting with pure X = H. The mixed film may provide a more homogeneous dispersion of the NO₂ groups (less dipole–dipole repulsion) than when all nitro groups are incorporated by in situ nitration, which may proceed with islands of nitration; see also Supporting Information.
- (21) The latter is unlikely at the level of organization reached here as we did not observe significant differences between molecules with $y = 3, 6, \text{ or } 11$ (to be published), but may be important for better ordered films (cf. ref 15).

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