Cycloaddition reaction versus dimer cleavage at the Si(001):C_5H_8 interface

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The interface formed between an ordered monolayer of cyclopentene and silicon is studied by *first-principles* density-functional calculations. Several different structural models of the interface are considered and their reflectance anisotropy spectra are calculated. The spectra turn out to be highly structure dependent and can therefore be used to monitor the interface formation. We also find that coadsorption of hydrogen, which leads to dimer cleavage, can stabilize the interface by saturating the dangling bonds and releasing the high strain energy.

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I. INTRODUCTION

The (001) surface of silicon is the starting point for the fabrication of most microelectronic devices. Therefore, Si surface reactions with metals, hydrogen, oxygen, and halogens have been intensively studied in the past.[1] However, in recent years there is an increasing interest in developing methods for coupling microelectronics with organic-based structures for applications such as nonlinear optics, thinfilm displays, lithography, and molecular electronics. For this reason, much effort has been devoted to the preparation and characterization of ultra-thin organic layers on Si(001) surfaces.[2–12] Organic overlayers may also facilitate the attachment of biomolecules, such as DNA, to the semiconductor surface.[13,14]

Chemisorption of organic molecules on Si(001) is typically accompanied by their fragmentation. Alkenes, however, can bond to the surface by breaking the π bonds of the alkene and of the Si dimers, and forming two new σ bonds. This mechanism has been exploited to prepare ordered organic overlayers of cyclopentene,[2,10] 1,5-cyclooctadiene,[4,10] 1,3,5,7-cyclooctatetraene,[5] and 1,3-dienes[6] on the Si substrate. These systems have novel and often extremely interesting properties. The chemisorption of bifunctional compounds such as 1,5-cyclooctadiene, for example, leads to the formation of an ordered array of carbon-carbon double bonds, which can then be utilized for further reactions.[10]

The adsorption of cyclopentene (C_5H_8) on Si leads to what can be considered a prototypical alkene-Si(001) interface. It is experimentally well characterized by scanning tunneling microscopy (STM) and by infrared and core-level spectroscopies.[2,4,9,10] Some adsorption geometries have also been probed by cluster[11] and density-functional calculations.[15,16] From experiment,[2] two possible scenarios have been suggested for the reaction between Si(001) and a cyclopentene molecule: a [2+2] cycloaddition reaction, leaving the Si dimer intact and an insertion reaction, where the Si dimer is broken (dimer-cleaved model). The reactions that leave the dimer intact, result in ''dimerized'' models (Figs. 1 and 2) and lead to a chemically saturated, but highly strained interface geometry.[17] On the other hand, the dimer-cleavage reaction (Fig. 3) releases the strain, but leaves unpaired electrons in the Si dangling bonds.

In this paper, we present *first-principles* calculations of the structural and optical properties of the monolayer cyclopentene covered Si(001) surface. In addition to the interface models discussed above, we consider the effects of hydrogenation on interface structure and properties. We find that the addition of hydrogen atoms stabilizes and smooths the interface, which could be beneficial for further reactions. The optical anisotropy of Si(001):C_5H_8 is found to be remarkably sensitive to details of the chemical bonding.

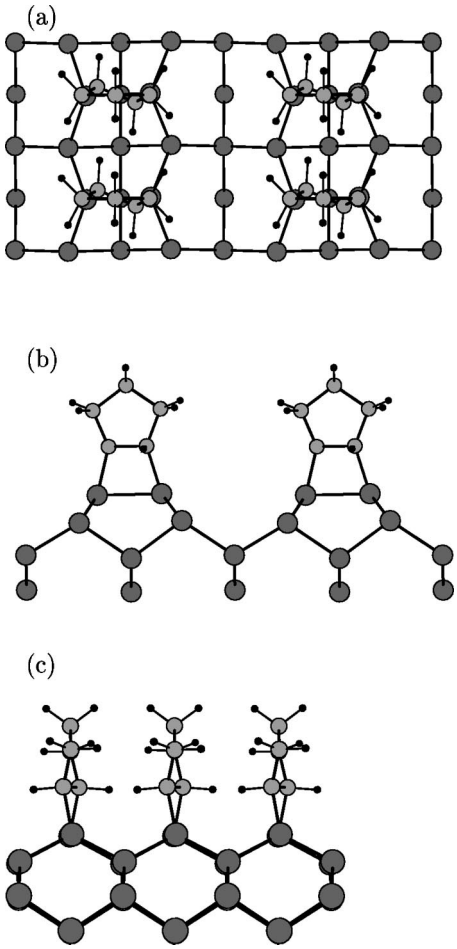

FIG. 1. Optimized geometry for the *trans*-type dimerized model of cyclopentene monolayer adsorption on Si(001): (a) top view, (b) and (c) side views. Large, medium, and small circles represent silicon, carbon, and hydrogen atoms, respectively.

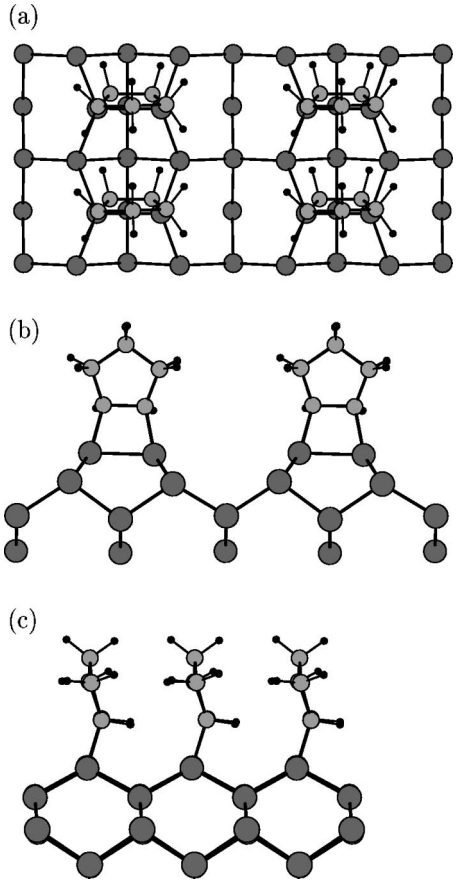

FIG. 2. Optimized geometry for the *cis*-type dimerized model of cyclopentene monolayer adsorption on Si(001): (a) top view, (b) and (c) side views. Large, medium, and small circles represent silicon, carbon, and hydrogen atoms, respectively.

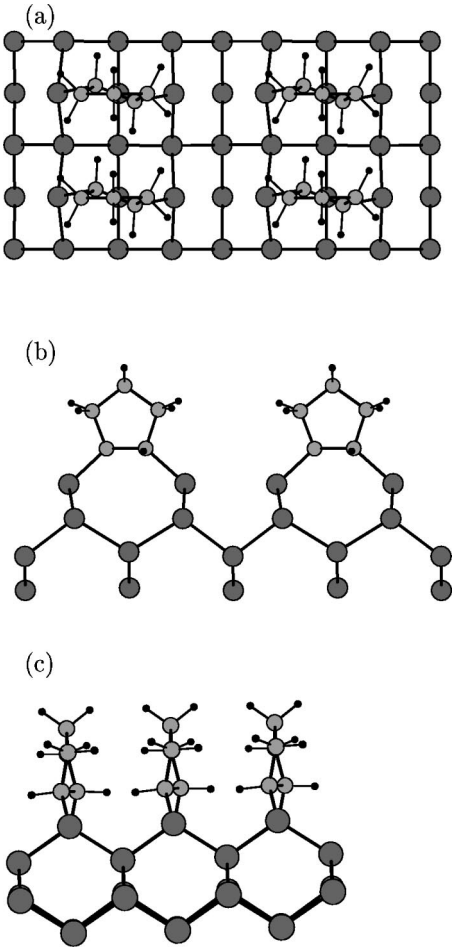

FIG. 3. Optimized geometry for the *trans*-type dimer-cleaved model of cyclopentene monolayer adsorption on Si(001): (a) top view, (b) and (c) side views. Large, medium, and small circles represent silicon, carbon, and hydrogen atoms, respectively.

II. METHODOLOGY

The calculations were performed using a massively parallel real-space multigrid implementation[18] of the density-functional theory (DFT) within the local-density approximation (LDA)[19] and within the generalized gradient approximation (GGA).[20] The electron-ion interactions were represented by nonlocal, norm-conserving pseudopotentials.[21] The spacing of the finest mesh used to map the electron wave functions and charge density was 0.16 Å for LDA and 0.12 Å for GGA, corresponding to energy cutoffs of 54 Ry (LDA) and of 98 Ry (GGA) in plane-wave calculations. We model the surface by a periodic arrangement of asymmetric slabs consisting of 12 Si layers, separated by vacuum regions of the same thickness. The dangling bonds at the bottom layer of the slab were saturated by hydrogen atoms. One monolayer (ML) of C_5H_8 was adsorbed on the Si(001) surface. A (2×2) unit cell was used in our calculations and eight special **k** points in half of the (2×2) surface Brillouin zone were employed for **k**-space integrations.

In order to assist in the experimental identification of the interface geometry, we used the ground-state electronic structure to determine the surface optical anisotropy. These calculations were performed in the independent-particle approximation following Del Sole[22] and Manghi *et al.*[23] To avoid spurious contributions from the bottom surface of the slab, a linear cutoff function was used.[24] The self-energy effects in the surface optical spectra were approximated by the scissors operator approach.[25] Our study is thus on the same level as previous *ab initio* studies of the optical properties of Si(001) surfaces.[26–28]

III. ATOMIC STRUCTURES

We first consider the adsorption of cyclopentene oriented parallel and perpendicular to the Si dimers. For acetylene on Si(001), these two adsorption geometries were found to be nearly degenerate energetically.[29] However, our results for the adsorption of cyclopentene show that the steric interactions between the larger C_5H_8 molecules strongly favor the parallel configuration, at least for 1-ML coverage. The adsorption energy for the latter case is -0.5 eV per molecule, i.e., adsorption is not favorable. This agrees with the parallel orientation of the cyclopentene molecules observed by STM.[10]

For the parallel orientation of the molecule, we consider first the dimerized model. This configuration can be further

TABLE I. Adsorption energy per molecule of C_5H_8 on Si(001) surface.

	Our LDA	Our GGA	GGA[a]	GGA[b]
Dimerized *trans*	1.6	0.8		1.05
Dimerized *cis*	1.4	0.6	1.17	0.94
Dimer cleaved *trans*	1.3	0.5		
Dimer cleaved *cis*			0.17	

[a]From Ref. 16.
[b]From Ref. 15.

classified according to the positions of the hydrogen atoms in the immediate vicinity of the Si surface. In the ''trans-type'' adsorption, the two H atoms are on alternating sides of the molecule, whereas both H atoms reside on the same side of the molecule in the ''cis-type'' configuration. The optimized *trans* and *cis* configurations of the dimerized model are shown in Figs. 1 and 2, respectively. Apart from the positions of the downmost hydrogen atoms, the main structural difference between *trans* and *cis* configuration consists in the orientation of the molecular C-C bonds near the interface. In the former case they are substantially twisted with respect to the Si dimer, as a consequence of the repulsive interactions between neighboring cyclopentene molecules. We calculate a rotation of 24° with respect to the direction of Si dimers. In addition, the Si dimers are slightly rotated with respect to the ideal direction. This is similar to the cases of C_2H_2 and C_2H_4 on the Si(001) surface,[30,31] in which the hydrogen atoms are twisted to reduce the repulsion between hydrogen charge clouds on neighboring molecules. In the present case, the twist is a consequence of repulsive interactions between the whole neighboring molecules. For the *cis*-type, there is no twist for the C-C bonds. In this case we calculate adsorption energies of 1.4 eV and 0.6 eV in LDA and GGA, respectively. Adsorption in *trans*-type configuration leads to energy gains of 1.6 and 0.8 eV, calculated within LDA and GGA, respectively. Table I lists the adsorption energies calculated by us and by other groups. Our LDA results are larger than those from literatures[15,16] and our GGA results are a little bit smaller. But the adsorption energy difference among different models are very close each other. For example, Akagi and Tsuneyuki[15] found for monolayer coverage that the *trans* configuration is favored over the *cis*-type adsorption by 0.11 eV, which is comparable with 0.2 eV in our both LDA and GGA calculations.

The cyclopentene molecules do not dissociate upon adsorption. However, the bond between the two carbon atoms attached to the surface is stretched. We calculate 1.38 and 1.51 Å for the gas phase and the adsorbed molecules, respectively. The latter value is typical for single carbon bonds and indicates that the carbon atoms at the interface are sp^3 hybridized, rather than sp^2 as in the free molecule. The Si dimer length does not change significantly upon the adsorption of cyclopentene. The dimer buckling, however, is much reduced to only 1.3°. The Si-C bond length at the interface is 1.85 Å, similar to the bulk SiC bond length.

The relaxed geometry for the dimer-cleaved model is shown in Fig. 3. Similar to the dimerized model, the cyclopentene molecules do not dissociate and the C-C bond near the interface is rotated by 24°. It is stretched to 1.56 Å and the originally dimerized Si atoms are now 4.3 Å apart. The Si-C bond length of 1.91 Å is slightly longer than the value of 1.85 Å in the dimerized model. The overall weaker interface bonding together with the partially occupied Si dangling bonds explain why the dimer-cleaved model is energetically less favored than the dimerized model, in spite of the lower interface strain. The calculated adsorption energies per molecule for the dimer-cleaved model amount to 1.3 and 0.5 eV within LDA and GGA, respectively.

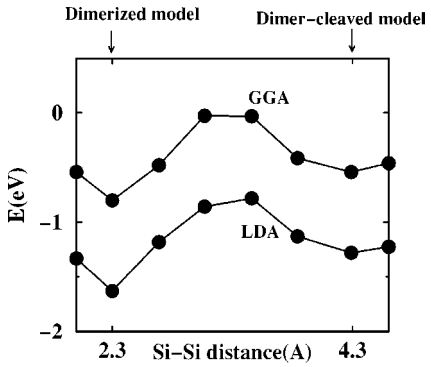

FIG. 4. Adsorption energy vs the Si-Si distance from LDA and GGA calculations. The circles represent the calculated energies and the solid lines are guides to the eye.

Compared to the adsorption of acetylene and ethylene, where the dimerized adsorption models are favored over the dimer-cleaved geometries by more than 1 eV,[32] the energy difference of 0.3 eV (both in LDA and GGA) between the two adsorption geometries of cyclopentene is relatively small. Both interface structures may thus occur at elevated temperatures. The most likely reaction pathway from the dimerized to the dimer-cleaved geometry is the breaking of the Si dimer. In Fig. 4, we show the relative adsorption energy vs the length of the Si dimer. In these calculations, we kept the coordinates of the Si surface atoms along the dimer direction fixed, while the remaining degrees of freedom and all the other atoms were allowed to relax. The energy barrier for the transition between the two structures is 0.85 eV in the LDA and 0.78 eV in the GGA. The two structures could thus coexist at the interface, with the fraction of the dimerized model being much higher.

The addition of the carbon π bond to the π bond of a symmetric surface dimer via a [2+2] cycloaddition reaction is orbital-symmetry forbidden. Indeed, the sticking probability of 0.1% for cyclopentene on the diamond (001) surface, where symmetric dimers form, is very low.[33,34] However, the symmetry of the surface dimers is broken at the Si(001) surface. They consist of a more sp^2-like ''down'' atom, which moves closer to the plane of its three nearest neighbors, and an ''up'' atom, which moves away from the plane of its neighbors and possesses an *s*-like dangling bond. The direction of the buckling alternates within each dimer row and the registry of the buckling in the neighboring dimer rows is such that the surface ground state is a reconstructed $c(2\times4)$.[1] This symmetry breakage allows for the cycloaddition reaction and is most likely responsible for the nearly

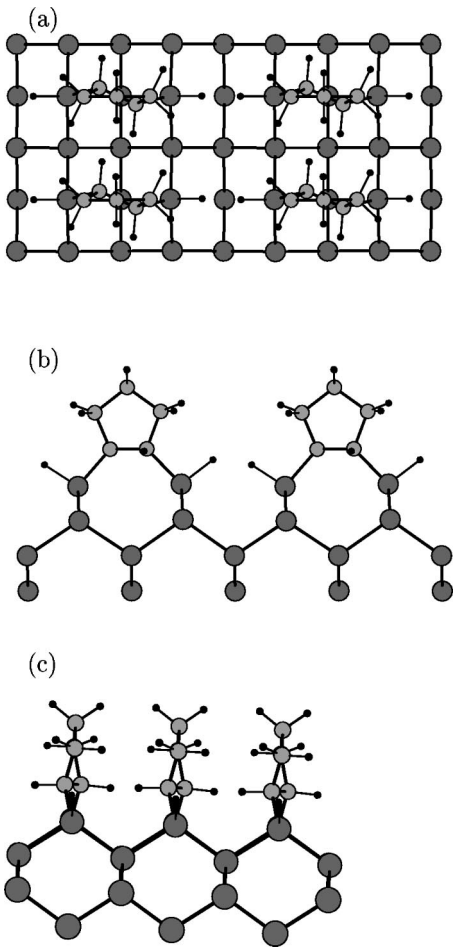

FIG. 5. Optimized geometry for the cyclopentene and hydrogen coadsorption on Si(001): (a) top view, (b) and (c) side views. Large, medium, and small circles represent silicon, carbon, and hydrogen atoms, respectively.

100% sticking probability for cyclopentene on Si(001).[33] A possible reaction pathway leading to the di-σ-bonded interface configurations discussed here has already been investigated by Cho and Kleinman.[16] They calculated an activation barrier of about 0.2 eV.

The interface geometry is very sensitive to the presence of hydrogen: if atomic hydrogen is added near the Si surface atoms, both the dimerized and the dimer-cleaved configurations relax toward the geometry shown in Fig. 5, with a Si-Si distance of 3.8 Å. The hydrogen adsorption stabilizes the interface by releasing the large strain energy in the dimerized model or by saturating the dangling bonds in the dimer-cleaved model. The adsorption energy for the coadsorption system is defined by

$$\Delta E = -[E_{\mathrm{tot}} - E(\mathrm{Si_{surf}}) - E(\mathrm{C_5H_8}) - E(\mathrm{H_2})],$$

where E_{tot} is the total energy of the total coadsorbed system, $E(\mathrm{Si_{surf}})$ is the energy of the clean Si surface, while $E(\mathrm{C_5H_8})$ and $E(\mathrm{H_2})$ are the energies of the respective gas-phase molecules. Neglecting temperature effects, our calculations for this system give adsorption energies of 2.8 eV within LDA and 2.7 eV within GGA. Due to the temperature and pressure dependence of the hydrogen chemical potential (see, e.g., Ref. 35), the relative stability of the coadsorbed system will strongly depend on the preparation conditions.

Cho and Kleinman[16] have considered the dissociation of hydrogen from the cyclopentene molecule and found that the atoms in the molecule stay in a planar geometry. In our case, where the extra hydrogen atoms are assumed to adsorb on the Si surface atoms, the molecule is twisted as in the other two models discussed above. The saturation of the Si dangling bonds leads to an efficient electronic passivation: the interface electronic states are pushed out of the region of the Si bulk band gap. Some experimental evidence supporting the suggested coadsorption of hydrogen—possibly released from fragmented molecules—is given by the observation of Si-H stretching vibrations in infrared spectroscopy.[2]

IV. SURFACE OPTICAL ANISOTROPY

The direct verification of the predicted interface geometries by techniques such as STM will be very difficult. However, one extremely structure-sensitive experimental technique, which is not restricted to ultrahigh vacuum conditions and can thus be used to monitor the interface formation *in situ*, is reflectance anisotropy spectroscopy (RAS), also termed reflectance difference spectroscopy.[36] Comparisons between the measured data and spectra computed for alternative structural models often allow for unambiguous determination of surface or interface geometries.[37,38]

In our calculations, the electronic self-energy corrections are approximately included using the scissors operator and the effects of electron-hole attraction and of local fields are omitted. However, these many-body effects usually do not qualitatively alter the spectra,[39,40] because RAS measurements obtain difference spectra, which are furthermore normalized to the bulk dielectric function. The distinct and structure-dependent RAS features predicted below should thus be reliable and well suited for monitoring of interface formation.

Figure 6 shows RAS spectra calculated for the three *trans*-type configurations studied here. In either case, the electronic transitions within the molecule do not contribute significantly to the interface optical properties in the energy range of up to 5 eV. This is expected, since each carbon atom in the cyclopentene molecule is sp^3 hybridized and chemically saturated. For the dimerized model, we only find a very weak shoulder *A*, which is due to optical anisotropies in the C_5H_8 overlayer. The peak *B* at the E_2 critical point energy of Si is related to electronic transitions between surface-modified bulk Si wave functions. This feature is typical for dimerized Si(001) surfaces.[26–28] The optical spectrum for the dimer-cleaved model is very different. Transitions involving the Si dangling bonds give rise to a strong anisotropy peak *C* at 2 eV, suppressing the weak signal from the C_5H_8 overlayer. For the hydrogenated interface, the weak signal from the C_5H_8 overlayer is again visible. For both the dimer-cleaved and the hydrogenated interface models, a negative anisotropy *D* is observed at the E_2 critical point energy of Si. The change from positive to negative optical anisotropies upon dimer cleavage at the E_2 energy calculated here (fea-

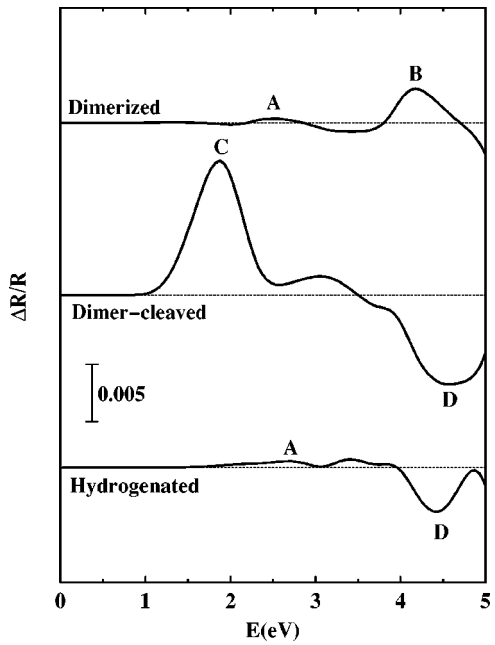

FIG. 6. RAS spectra $[(R_{[\bar{1}10]}-R_{[110]})/\langle R\rangle]$ calculated for the dimerized model, the dimer-cleaved model, and the hydrogenated interface. Zero values are indicated by dashed lines.

tures *B* and *D*) has been previously observed in experiments for hydrogenated Si surfaces.[41]

To further probe the sensitivity of RAS for the details of the interface chemical bonding, we compare in Fig. 7 the spectra calculated for both *trans* and *cis*-type dimerized models. We observe pronounced differences. For the *cis*-type, there are two dips at 1.5 eV and 3.2 eV. The positive high-energy peak splits into two. Again, we find that most of the interface optical anisotropy is not directly from the adsorbate molecules, but rather due to electronic transitions at the interface.

V. SUMMARY

We investigated the atomic structure and surface optical properties of the Si(001):C_5H_8 interface, using the real-space multigrid DFT method within both the local-density and the

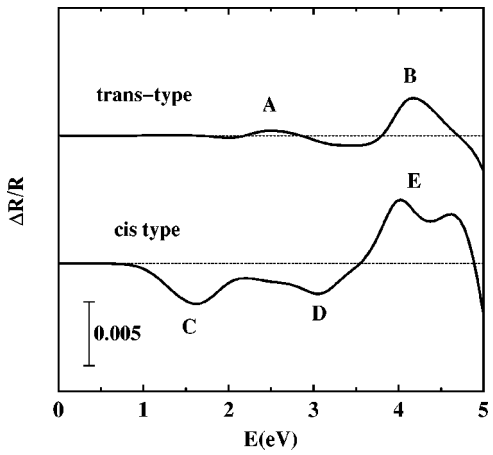

FIG. 7. RAS spectra $[(R_{[\bar{1}10]}-R_{[110]})/\langle R\rangle]$ calculated for the dimerized models of the *trans* and *cis* types. Zero values are indicated by dashed lines.

generalized gradient approximations. While the adsorption energy depends on the choice of the exchange-correlation approximation, the relative stabilities of the different models have the same trends in both LDA and GGA calculations. The formation of a dimerized structure via the $[2+2]$ cycloaddition reaction is favored over the breaking of the surface Si dimer. The adsorption of additional hydrogen atoms increases the stability of the interface by releasing the strain energy and saturating the dangling bonds. The resulting surface is electronically well passivated. We found strong and structure-dependent surface optical anisotropies, which mainly arise from electronic transitions within the substrate and between the substrate and the overlayer. Even a discrimination between *cis* and *trans*-type adsorption configurations is possible, based on measurements of the reflectance anisotropy. Surface optical spectroscopies are therefore well suited for monitoring the formation of interfaces between Si surfaces and hydrocarbon overlayers, as well as for determining the structure of the overlayer.

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