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LETTERS

Formation of Ordered, Anisotropic Organic Monolayers on the Si(001) Surface

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It is shown that the Si=Si dimers of the reconstructed Si(001) surface can react with the π bonds of unsaturated organic molecules to produce well-defined organic films with novel physical properties. Scanning tunneling microscopy (STM) studies show that the resulting layers are ordered both translationally and rotationally, with the Si=Si dimers acting as a template for extending the translational and rotational order from the silicon substrate to the organic film. STM images and infrared spectroscopy experiments show that by using vicinal Si(001) surface having primarily double-height steps, the rotational order of the molecules can be preserved over macroscopic length scales, leading to measurable anisotropy in optical properties. It is proposed that this chemistry may provide a general method for formation of controlled organic films on Si(001) surfaces.

Introduction

The (001) surface of silicon is very important technologically as the starting point for most microelectronic devices. While microelectronics processing typically involves reactions of silicon surfaces with inorganic compounds, there is increasing interest in developing methods for coupling existing microelectronics technology with organic-based structures for applications such as nonlinear optics, thin-film displays, lithography, and molecular electronics.

The Si(001) surface is characterized by a surface reconstruction in which adjacent atoms pair together, forming dimers. Since each silicon atom of the bulk-terminated surface has two dangling bonds, the hybridization of two atoms to form a dimer can be described as formation of a strong σ bond and a weak π bond. Indeed, scanning tunneling microscope images of Si(001) reveal filled and empty electronic states having the symmetry properties expected for π -type electronic states as the highest-occupied and lowest-unoccupied electronic states.¹ The π bonding of Si(001) suggests that the reactions of this

surface should in some ways be analogous to those of double-bonded compounds of carbon and of silicon.²

Despite the great technological importance of Si(001), there has been comparatively little work attempting to fabricate well-defined organic layers. Chidsey and co-workers³ successfully formed layers of densely-packed alkyl monolayers on hydrogen-terminated Si(111) and Si(001) surfaces through a free-radical mechanism. It has been observed previously that ethylene and acetylene are capable of chemisorbing on Si(001) in a so-called "di- σ " configuration, in which the double bonds of the Si dimers and the double bonds of the adsorbed organic species are broken, forming two new Si—C σ bonds.^{4–7}

In this paper, we show that it is possible to use reactions between the oriented dimers present on the Si(001) surface and the double bonds present in unsaturated organic molecules to fabricate well-defined organic layers on Si(001) in which the molecules are ordered translationally as well as rotationally. Using cyclopentene as a prototypical example, we show specifically that (1) such reactions can be used to produce a well-defined interface between silicon and organic layers, (2) this layer contains molecules aligned along specific crystallographic direction with minimal dissociation, (3) the direc-

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tionality of molecular orientation can be maintained over macroscopic distances using miscut ("vicinal") Si(001) substrates, and (4) the resulting molecular orientation leads to measurable anisotropy in optical properties measured on centimeter length scales. We also show that addition reactions can be extended to other molecules, suggesting that the interaction of unsaturated organic molecules with Si(001) should provide a general method for fabrication of organic layers with controlled chemical functionality.

Experimental Section

All experiments were performed in an ultrahigh vacuum (UHV) system achieving a base pressure of $<1 \times 10^{-10}$ Torr. The surfaces were characterized using a number of techniques. Direct observation of adsorbed molecules and molecular layers was achieved using a home-built UHV scanning tunneling microscope (STM). All STM images shown here were obtained with a sample bias of -3 V and a tunneling current of 0.2 – 0.3 nA. Fourier-transform infrared (FTIR) absorption spectra of surface layers were obtained using a multiple internal-reflection geometry and a Mattson RS-1 FTIR spectrometer coupled to a UHV system through BaF₂ windows. X-ray photoelectron spectroscopy (XPS) experiments were performed using a Physical Electronics system with a monochromatized Al K α source. For each type of experiment, samples were prepared and characterized completely *in situ*.

Clean Si(001) samples were prepared by annealing pieces of Si(001) wafers to 1475 K while the chamber pressure was maintained at $<3 \times 10^{-10}$ Torr. This procedure produces clean well-ordered surfaces exhibiting a (2×1) reconstruction.⁸ Samples having two different levels of doping and two slightly different crystallographic orientations were used. Highly-doped (<0.15 Ω cm resistivity, Sb- and P-doped) samples were used for STM and XPS experiments, while lightly-doped (>5 Ω cm resistivity, P-doped) samples were used for infrared spectroscopy experiments to reduce free-carrier absorption in the bulk. On-axis samples were oriented to expose the (001) surface with an accuracy $\pm 0.5^\circ$. Off-axis (001) wafers were purposely miscut by $4.0 \pm 0.5^\circ$ toward the $\langle 110 \rangle$ direction.

Results and Discussion

Figure 1 depicts schematically the interaction of cyclopentene with Si(001). One mechanism for addition of an unsaturated organic molecule with the dimers of the Si(001) surface is a $(2 + 2)$ cycloaddition reaction, leading the di- σ -bonded product shown in Figure 1b.^{9,10} While this reaction is formally disallowed by symmetry considerations, it is possible that loss of symmetry (by dimer tilting, for example¹) could permit a thermal reaction by this mechanism. However, recent studies of ethylene interaction with Si(001) have shown that the σ bond of the Si=Si dimers is also broken, so that this reaction is better described as an insertion;^{11,12} for cyclopentene the analogous reaction would lead to the product shown in Figure 1c. In both cases, we note that there is no overall dissociation of the organic molecule, so that reaction by either mechanism should lead to the formation of well-defined organic layers on Si(001).

Figure 2 shows scanning tunneling microscope images of the molecular layers formed by exposure of Si(001) to 30 langmuirs (1×10^{-7} Torr for 300 s) of cyclopentene vapor at room temperature, allowing the molecules to self-assemble on the surface. While in Figure 2a,b the Si(001) surface was oriented to within 0.5° of the (001) plane, in Figure 2c the starting surface is a 4° -miscut vicinal Si(001) surface.

We focus first on the on-axis sample shown in Figure 2a,b. Here, each oval-shaped object is an individual cyclopentene

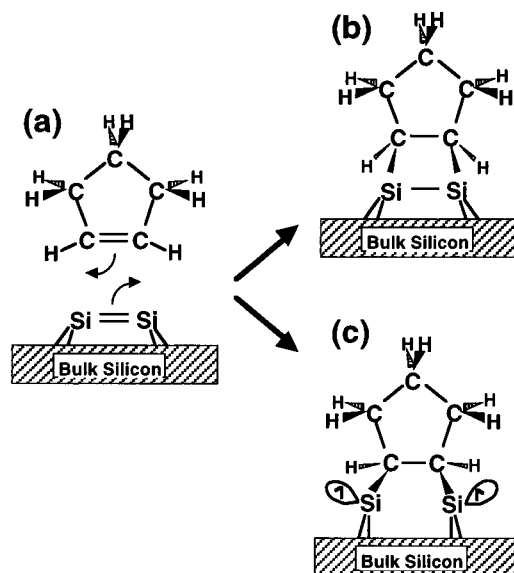


Figure 1. Schematic illustration of reactions between a Si=Si dimer and a cyclopentene molecule: (a) starting species; (b) reaction via $2 + 2$ cycloaddition reaction, leaving Si=Si dimer σ bond intact; (c) reaction involving insertion into Si=Si dimer bond, with breaking of Si=Si dimer σ and π bonds.

molecule protruding from the surface, with the direction of elongation revealing the wide direction of the ring structure. Although in Figure 2a,b the translational ordering of the molecules on the surface is not perfect, one can clearly see two important features. First, it can be seen that the molecules are aligned into rows; this demonstrates that the cyclopentene molecules spontaneously order with very specific bonding locations. Second, it can be seen that the individual molecules appear elongated and that this direction of elongation is the same for all molecules in the image; therefore, these images prove that the molecules are ordered rotationally as well as translationally. In Figure 2a,b the spacing between molecules within a given row varies but is always an integral multiple of the 3.85 Å spacing between dimers of the Si(001) surface. The presence of some vacant sites indicates that either the surface is not completely saturated or that steric interactions prevent the molecules from completely occupying all lattice sites.

On Si(001) surfaces containing monatomic steps, the bulk Si stacking sequence forces the Si=Si dimers on adjacent terraces at the surface to be rotated by 90° . These 90° rotations in bonding direction destroy the coherence of the molecular orientation on length scales greater than the average separation between steps. However, when Si(001) surfaces are cut by approximately 4° off the (001) plane (toward $\langle 110 \rangle$), the interaction energy between steps causes the surface to adopt a configuration in which there are virtually no single-height steps; instead, the surface adopts exclusively double-height (bilayer) steps.^{13,14} An important observation is that across such double-height steps the silicon dimers and the cyclopentene molecules bonded to these dimers maintain a constant rotational orientation.

Figure 2c shows an STM image obtained after exposure of a 4° -miscut vicinal Si(001) surface to 30 langmuirs of cyclopentene, with arrows indicating the positions of the double-height atomic steps. This gray scale image uses a mixture of height and curvature contrast to enhance visibility of the surface structure on multiple terraces. Figure 2c shows that on vicinal samples the molecules maintain a uniform rotational orientation across the double-height steps, effectively achieving an orientational anisotropy that is consistent over the entire sample. Additionally, we find that the the molecular ordering on films

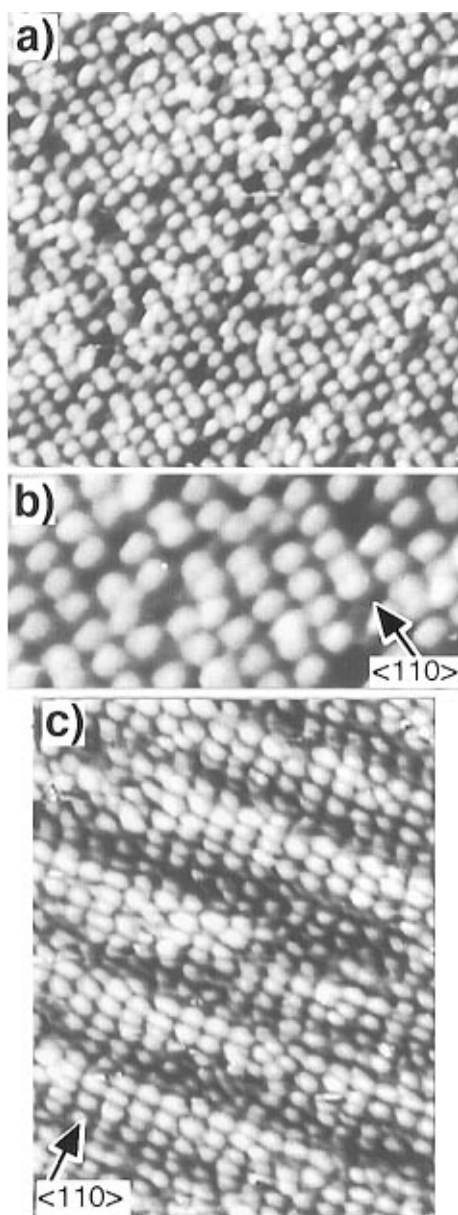


Figure 2. STM images of cyclopentene-exposed Si(001) surfaces: (a) image showing ordered molecular adsorption on a single terrace; (b) high-resolution image showing the translational ordering and consistent elongated appearance of individual molecules; (c) image obtained on 4°-miscut vicinal Si(001) substrate showing that molecular orientation of cyclopentene is retained across double-height steps. Arrows indicate positions of double-height steps.

on the vicinal sample is even slightly better than that on the extended Si(001) terraces, possibly because the presence of steps reduces steric hindrance between adjacent molecules.

Rotational anisotropy in the molecular orientation, as shown in Figure 2, is expected to lead to rotational anisotropy in optical properties such as index of refraction, reflectivity, and absorption coefficients. It is also likely that in some films this could lead to anisotropy in electronic conductivity and the formation of one-dimensional conductors.

To demonstrate that the molecular orientation shown in Figure 2 leads to measurable anisotropy in optical properties for macroscopic samples, we present infrared absorption spectra for cyclopentene-exposed vicinal Si(001) samples. Figure 3a schematically depicts the direction of the electric field relative to the silicon dimers for two different polarizations. Polarization directions A and B both correspond to *s*-polarized light, but direction A has the electric field vector **E** oriented along the

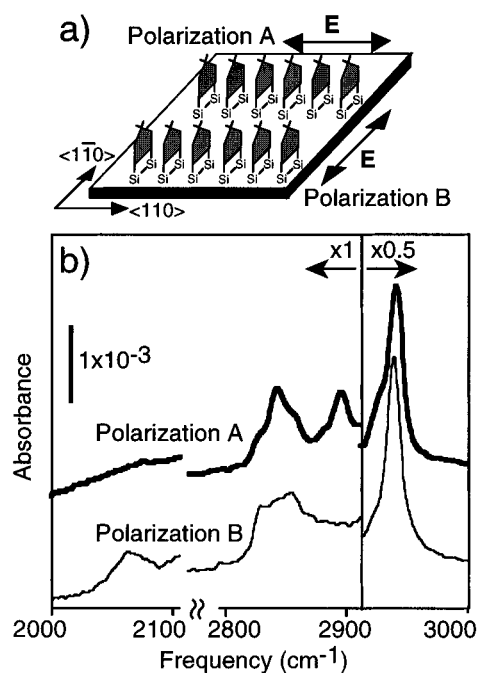


Figure 3. Anisotropy of infrared absorption of cyclopentene layer on Si(001) for *s*-polarized light: (a) definition of polarization directions; (b) *s*-polarized infrared absorption spectra for the two primary polarization directions in the Si-H and C-H spectral regions.

$\langle 110 \rangle$ direction (perpendicular to the Si-Si dimer bonds) and polarization B has **E** oriented along the $\langle 1\bar{1}0 \rangle$ direction (parallel to the Si-Si dimer bonds).

As shown in Figure 3b, the resulting spectra in the C-H stretching region (2800–3000 cm^{-1}) show significant differences between the two different polarization directions. In particular, the absorption peak at 2895 cm^{-1} is several times larger when measured using polarization direction A than with direction B, and differences are observed in the relative intensities of the overlapping peaks at 2850–2875 cm^{-1} . Although a full spectral analysis has not yet been performed, we attribute the peak at 2895 cm^{-1} to a mode involving motion of the two H atoms at the apex of the cyclopentene molecule (attached to the C atom farthest from the Si surface). As indicated in Figure 1, these C-H bonds are expected to lie in a plane perpendicular to polarization direction B but parallel to polarization direction A. Most other C-H bonds in this molecule are expected to have components of their dynamic dipole moment along both $\langle 110 \rangle$ and $\langle 1\bar{1}0 \rangle$ directions and to therefore show some absorption strength for both polarizations. The differences in absorption for *s*-polarized light along these two directions confirm that the orientation observed in the STM image (Figure 2c) is in fact maintained over centimeter distances. Although not yet measured, it is expected that the films will also exhibit anisotropy in other optical properties such as the dielectric constant, leading to optical dichroism.

The Si-H stretching region in Figure 3b shows a small peak near 2070 cm^{-1} for polarization B. This peak corresponds to the Si-H stretching mode for Si dimers with one attached hydrogen atom, suggesting that there is some dissociation on the surface.^{15,16} It is not yet clear whether this arises from impurities in the cyclopentene or if it is intrinsic to the preparation procedure. Nevertheless, the small size of this peak and the ordering observed in Figure 2 demonstrate that the extent of dissociation is small and does not significantly affect the ordering of the molecular film. Additional characterization of the bonding using X-ray photoelectron spectroscopy revealed a C1s peak with a binding energy of 284.93 eV and a smaller

peak at 284.18 eV. Since C is more electronegative than Si, the C atoms bonded directly to the Si surface are expected to be partially negatively charged and to have smaller core-level binding energies. The peak at 284.17 eV is therefore attributed to the C atoms bonded to the Si surface. The ratio of peak areas $A_{284.18}/A_{284.93}$ was approximately 2:3, consistent with the geometries illustrated in Figure 1.

The above experiments on cyclopentene can be extended to other unsaturated molecules as well. In preliminary experiments we have observed formation of similar ordered structures using other unsaturated molecules including cyclohexene and the heterocyclic molecule 3-pyrroline. While we do not know whether the σ bonds of the Si dimers are broken or are intact, these results suggest that addition reactions might be a general method for preparation of ordered, anisotropic organic films on Si(001) surfaces.

Summary and Conclusions

The addition reaction between the dimers on the Si(001) surface and the double bonds of unsaturated organic compounds can be used to produce ordered, anisotropic organic layers on Si(001). Because this reaction involves covalent bonding without dissociation, it can lead to a high degree of molecular order even at room temperature. The uniform spacing between dimers of the Si(001) surface leads to translational order of the molecular overlayer, while the inherently directional nature of the interacting π bonds translates the rotational orientation of the Si=Si dimers to the organic film. We speculate that the translational and rotational order of the first monolayer might be extended to subsequent layers by utilizing the directional nature of the surface bonding and/or steric interactions present at the surface. Additionally, such well-ordered films have

potential application as controlled bonding sites for linking various organic substituents to the Si(001) surface.

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