

# Inhibition of the [2+2] Cycloaddition: Maleic Anhydride on Si(100)-2×1

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The chemisorption of maleic anhydride on Si(100)-2×1 at room temperature has been studied with scanning tunneling microscopy (STM). We observe that, at low coverages below 0.12 monolayer, the unsaturated organic compound adsorbs almost exclusively on inter-dimer sites and not through a direct [2+2] cycloaddition. The STM images provide evidence that the adsorption of a second maleic anhydride molecule on an adjacent inter-dimer site results in the cleavage of the silicon dimer bond located between the two molecules. The chemisorption of the organic molecules induces a local rearrangement of unsaturated silicon dimers.

## Introduction

The potential application of hybrid silicon/organic film devices has motivated a series of investigations.<sup>1</sup> The most technically important silicon surface is Si(100), which reconstructs to a dimer row structure upon high-temperature preparation inside ultrahigh vacuum (UHV). Recently, it has been shown that, at room temperature, the five-membered cyclic hydrocarbon cyclopentene (C<sub>5</sub>H<sub>8</sub>) adsorbs on Si(100)-2×1 through a [2+2] cycloaddition, in which the translational and rotational ordering of the Si dimers is extended to the adsorbed molecule.<sup>2</sup> However, in the case of the closely related organic compound pyrroline (C<sub>4</sub>H<sub>7</sub>N) an additional reaction scheme has been observed, in which a Si–N bond is formed.<sup>3</sup>

Functionalization of the surface with anhydride groups can be achieved by the chemisorption of the five-membered, cyclic organic compound maleic anhydride on Si(100)-2×1.<sup>4</sup> A combined near edge X-ray absorption fine structure (NEXAFS) and high-resolution electron energy loss spectroscopy (HREELS) study of maleic anhydride on Si(100)-2×1 has shown that, at low dosages, molecules adsorb through a rehybridization of the carbon atoms in the olefin bond from sp<sup>2</sup> to sp<sup>3</sup>.<sup>5</sup> The observed rehybridization points to reactions I or II (Scheme 1), in which maleic anhydride adsorbs above a silicon dimer through a direct [2+2] cycloaddition or in an inter-row adsorption site between adjacent dimers in a [1+2+1] addition, respectively. At higher dosages, an additional reaction path arises, in which the unsaturated molecule bonds to one side of the silicon dimer with the olefin bond preserved and formation of an Si–H bond (reaction III), which has been attributed to the presence of surface defects.<sup>5</sup> However, the HREELS and NEXAFS studies unambiguously rule out chemisorption through cleavage of the anhydride group.<sup>4,5</sup>

In this paper, we present STM studies of the initial adsorption of maleic anhydride on Si(100)-2×1 at room temperature, to identify the adsorption site of the unsaturated molecule. In particular, we were interested in finding evidence for a weakening of silicon dimer bonds which has been suggested in the case of a direct [2+2] addition reaction.<sup>6,7</sup>

## Experimental Details

The experiments were carried out in an UHV system (base pressure < 10<sup>−10</sup> mbar) equipped with STM (Omicron). For the STM study, tungsten tips were used which were prepared by an electrochemical etching technique. The filled state STM images were taken at a tunneling current of 0.2 nA. Samples were cut from on-axis, one-sided polished, wafers (P doped) with a resistivity of 1–3 Ωcm. Clean Si(100)-2×1 was prepared by heating the silicon crystal to 1500 K while maintaining a pressure of < 2 × 10<sup>−10</sup> mbar. Prior to dosing, maleic anhydride (Aldrich, 99%) was purified by repeated sublimation and pumping cycles. Mass spectroscopy confirmed the absence of significant contaminants during the dosing at room temperature.

## Results

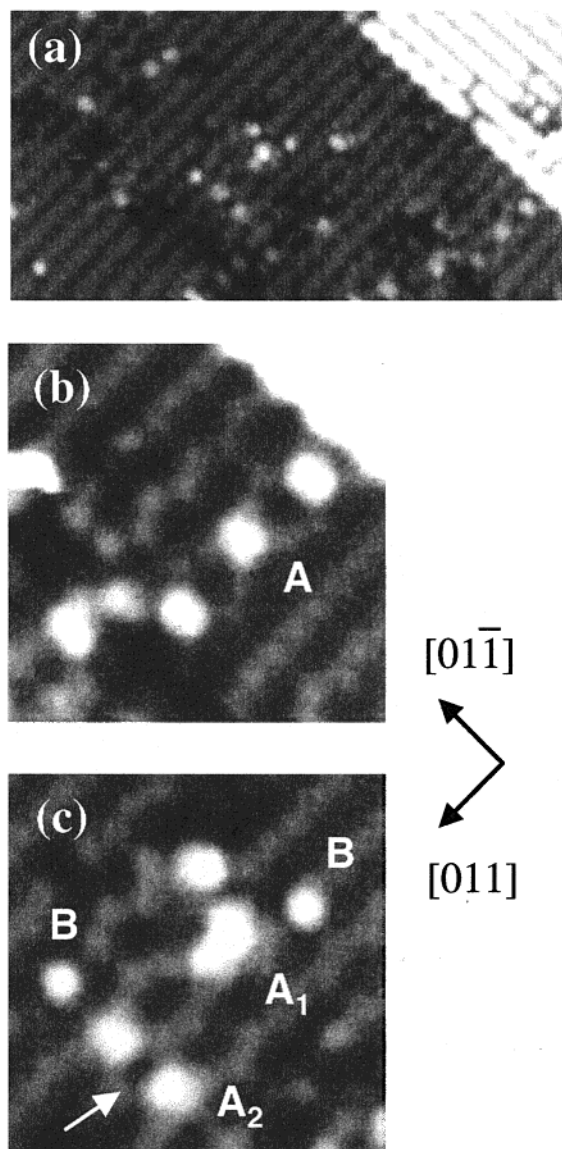
Figure 1a shows the filled state image of 0.03 ML maleic anhydride chemisorbed on Si(100)-2×1 (one monolayer (ML) corresponds to one maleic anhydride molecule for each silicon dimer). Two silicon terraces are present on the surfaces, which are separated by a single-height atomic step. On both terraces, the surface structure consists mainly of rows of symmetric dimers. However, at surface defects and at the step edge, zigzag rows of asymmetric dimers can be seen. Chemisorbed maleic anhydride molecules appear as brighter features, which are located almost exclusively *between* dimer rows.

Details of the STM image are shown in Figure 1b,c. In Figure 1b, three brighter objects (labeled with A) are located between two dimer rows. Note that the chemisorption of the three maleic anhydride molecules, which are separated by two vacant adsorption sites along [011], leads to a local rearrangement or pinning of asymmetric silicon dimers. The bright area in the top-left corner is the elevated adjacent silicon terrace.

In Figure 1c, two different adsorption geometries can be clearly distinguished. Two molecules are adsorbed on adjacent inter-row sites between the same dimer rows (A<sub>1</sub>) and two molecules on inter-row sites between neighboring dimer rows (A<sub>2</sub>). In addition, two brighter objects can be observed which are located on a dimer row (B). In the proximity of the adsorption sites, zigzag shaped asymmetric dimers are present. The arrow indicates most likely a broken silicon dimer bond between the two adsorbed maleic anhydride molecules (A<sub>2</sub>), which will be discussed later.

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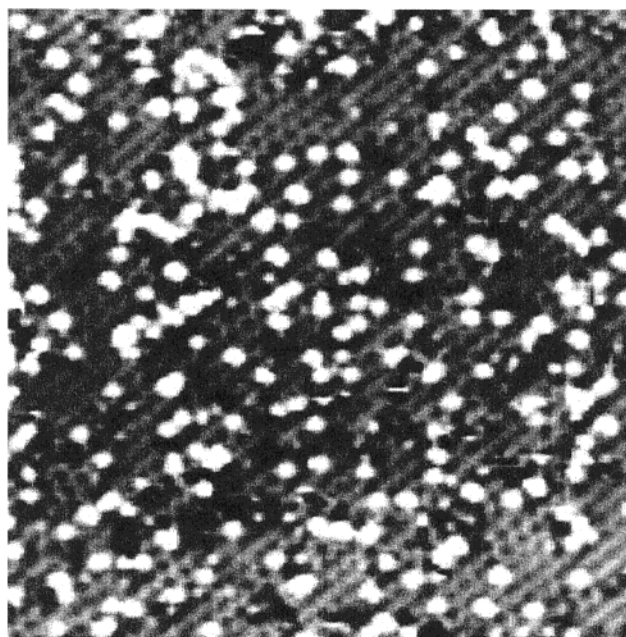


**Figure 1.** Filled state images of 0.03 ML maleic anhydride on Si(100)-2 $\times$ 1 ( $U_b = -2.3$  V). (a) In the image (200 Å  $\times$  100 Å), two silicon terraces are present which are separated by a monolayer step. Details of adsorbed molecules are shown in (b) and (c) (50 Å  $\times$  50 Å). The arrow in (c) indicates most likely a broken silicon dimer bond.

A filled states STM image of Si(100)-2 $\times$ 1 with 0.12 ML maleic anhydride is given in Figure 2. A detailed analysis of the image shows that more than 98% of maleic anhydride molecules, which can be seen as bright protrusions, adsorb on inter-row positions. In areas of otherwise clean silicon, the adsorption of maleic anhydride induces a local c(4 $\times$ 2) reconstruction of silicon dimers. The analysis also indicates the lack of a preferential adsorption of the unsaturated molecules at surface defects.

### Discussions

It is evident from the STM images that, at low coverages, maleic anhydride chemisorbs at room temperature almost exclusively on inter-row adsorption sites (reaction II in Scheme 1) which contrasts the observation made for unsaturated organic molecules previously studied.<sup>2,7</sup> In reaction II (also reaction I), the adsorption on inter-row sites involves the rehybridization of the carbon atoms in the olefin bond from sp<sup>2</sup> to sp<sup>3</sup> and the



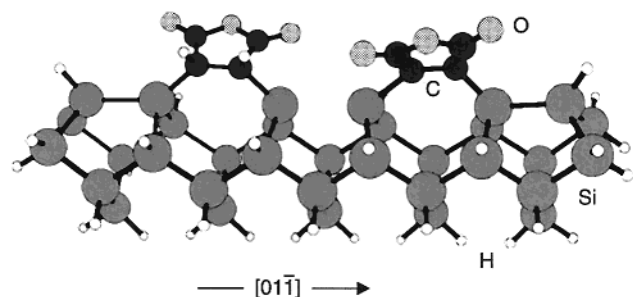
**Figure 2.** STM image (250 Å  $\times$  250 Å) of 0.12 ML maleic anhydride obtained with  $U_b = -1.8$  V. Note the honeycomb-like reconstruction of areas of unoccupied silicon dimers.

formation of two  $\sigma$ -like Si-C bonds between maleic anhydride and substrate.

Our *ab initio* Hartree-Fock calculations for the electrostatic potential, at the HF/6-31G\* level,<sup>8</sup> of free maleic anhydride indicates a substantial molecular dipole due to a charge transfer from the carbon to the oxygen atoms in the anhydride group. The charge transfer also lead to a strong electrophilic behavior of the organic compound, which is observed in many cycloaddition reactions of this molecule. In contrast, ethylene and cyclopentene, both of which prefer to adsorb on top of silicon dimers, do not possess such an electrostatic dipole.

Detailed self-consistent calculations of the electronic properties of reconstructed Si(100) surfaces by Zhu et al.<sup>9</sup> showed that the charge transfer from the "down-buckled" to the "up-buckled" silicon atom in the asymmetric dimer induces an electric dipole along the dimer axis, i.e., the upper atom is relatively electron rich. In the case of a c(4 $\times$ 2)-reconstruction, in adjacent rows "up-buckled" silicon atoms, which are negatively charged, are separated by 4.9 Å.<sup>9</sup> Thus, it is plausible to suggest that the electrophilic and polarized maleic anhydride molecule preferentially adsorbs on an inter-dimer row site between two "up-buckled" Si atoms in a [1+2+1] addition rather than on top of a single, neutral but polarized silicon dimer in a [2+2] cycloaddition. We also expect that removal of the  $\pi$ -interaction in the silicon dimer by the adsorption of maleic anhydride leads to a lengthening of the Si-Si dimer bond. It should be noted that at room temperature, asymmetric dimers are known to rapidly switch orientation due to the low activation energy involved so that dimers can appear to be symmetric in STM.<sup>10</sup> Domains of static asymmetric dimer structures are typically observed only at surface defects and step edges in room-temperature experiments.<sup>10</sup>

Figure 3 shows the result of our cluster calculation at the AM1 level of two maleic anhydride molecules on Si<sub>33</sub>H<sub>35</sub>, which models the situation in Figure 1c (A<sub>2</sub>). The maleic anhydride molecules were assumed to have adsorbed in a trans geometry relative to one other. The silicon atoms in the two lowest layers were constrained in their positions to simulate bulk silicon (Si-Si distance  $d_{\text{bulk}} = 2.35$  Å). The calculations show that

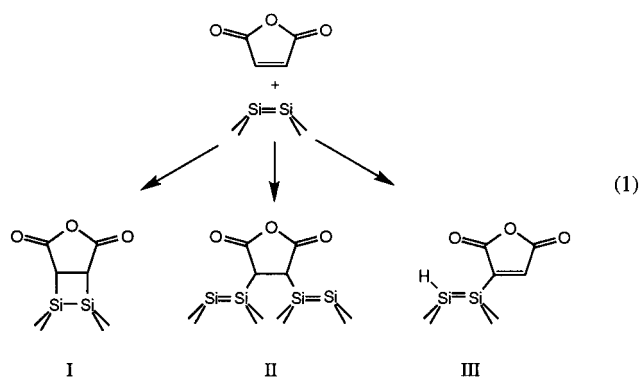


**Figure 3.** Optimized geometry of two maleic anhydride molecules in a trans conformation on  $\text{Si}_{33}\text{H}_{35}$ . The cluster calculations have been carried out at the AM1 level.

the Si–Si bonds in the outermost dimers have increased from  $2.38 \text{ \AA}^{11}$  to  $2.5 \text{ \AA}$  and the separation between silicon atoms, which are bonded to a common maleic anhydride molecule, is  $d_{\text{SiMA-SiMA}} = 4.5 \text{ \AA}$  reduced from  $5.0 \text{ \AA}^{11}$ . Note that the distance between the initially dimerized silicon atoms in the top layer between the maleic anhydride molecules is  $3.1 \text{ \AA}$ , which is substantially larger than observed in crystalline silicon. A Si–Si distance of  $3.1 \text{ \AA}$  points to a dramatic weakening of the  $\sigma$ -interaction between the silicon dimer atoms, which may lead to the breaking of the Si–Si bond. Our *ab initio* calculations at the HF/6-31G\* level for a  $\text{SiH}_3\text{-(C}_4\text{H}_2\text{O}_3\text{)-SiH}_3$  cluster suggest a Si–Si distance of  $3.58 \text{ \AA}$  for the fully relaxed structure. The *ab initio* calculations show that the total energy of the  $\text{SiH}_3\text{-(C}_4\text{H}_2\text{O}_3\text{)-SiH}_3$  cluster increases by  $0.73 \text{ eV}$  if the Si–Si distance is strained to  $4.5 \text{ \AA}$ . This relatively large strain energy suggests that the lower-level calculations on the larger cluster may misrepresent the nature of the Si–Si bonding between two adsorbates. A more accurate model might show that the Si–Si dimer bond is cleaved by adsorption of two maleic anhydride molecules to either side of the dimer, allowing  $d(\text{Si-C}_4\text{H}_2\text{O}_3\text{-Si})$  to adopt the favored distance of  $3.58 \text{ \AA}$ .

STM indicates that very few maleic anhydride molecules adsorb on top of silicon dimers (type B of Figure 1c). In the case of missing silicon atoms we would expect that maleic anhydride molecules adsorb through a C–H bond cleavage with the double C=C bond being preserved (reaction path III in Scheme 1) as found at high coverages.<sup>4</sup> This chemisorption path would involve bonding of the dissociated hydrogen to one of the neighboring unsaturated silicon atoms. Unfortunately, the STM images do not provide evidence for the presence of Si–H bonds so that a direct [2+2] cycloaddition on intact silicon dimers (reaction I) cannot be ruled out as the interpretation of type B features. We like to note that type B features may also arise from contaminant species.

## SCHEME 1



## Conclusions

In conclusion, this work shows unambiguously that the unsaturated maleic anhydride molecule adsorbs preferentially on inter-dimer sites in a [1+2+1] addition reaction. It is reasonable to suggest that the carbon atoms in the olefin bond rehybridize from  $\text{sp}^2$  to  $\text{sp}^3$  upon chemisorption in agreement with vibrational spectroscopy and NEXAFS data. After the adsorption of maleic anhydride molecules on adjacent inter-dimer sites, we observe the cleavage of the silicon dimer bond between two adsorbed molecules.

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