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Site-selective reactivity of ethylene on clean and hydrogen precovered Si(001)

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ABSTRACT

Site-selective adsorption of ethylene on Si(001) has been investigated by means of scanning tunneling microscopy (STM). Two different adsorption pathways are identified with ethylene adsorbed on one and two dimers, respectively. Preadsorption of atomic hydrogen is found to increase the reactivity of the two-dimer pathway, which is the minority channel on the clean surface, by a factor of 45. The results are interpreted in the framework of a precursor mediated adsorption process with a conversion barrier between precursor and final adsorption state that can be efficiently controlled by changing the local electronic structure of the surface.

1. Introduction

The fundamentals and applications of molecular electronics have been the subject of intense research over the recent past [1]. One topic of special interest were the electronic [2] and structural [3–5] properties of organic molecules adsorbed on silicon surfaces, as silicon represents the most important basis of conventional semiconductor microelectronics up to now and seems to be the most promising candidate for designing molecular electronic devices [6]. In contrast to metal surfaces, the electronic states on semiconductor surfaces are generally much more localized. Accordingly, since there is no extensive charge redistribution, the local electronic properties depend essentially on the details of the surface configurations. As a consequence, surface reactivity is expected to correlate not only with the concentration of dangling bonds, i.e., number of reactive sites, but with the local electronic properties of the dangling bond states as well. Such a correlation of the surface's local electronic structure and its chemical reactivity is then of great importance for the understanding and the control of functionalization of semiconductor substrates by organic molecules. A very strong correlation between local electronic structure and reactivity was indeed observed for hydrogen dissociation on Si(001), a prototype reaction for activated adsorption on semiconductor surfaces [7]. Experimentally, site-specific reactivity at locally distorted configurations like steps or dangling bonds in the neighborhood of preadsorbed atomic hydrogen were shown to exceed the reactivity on the undisturbed dimer row structure by many orders of magnitude [8–13]. DFT calculations correlated this site-selective reactivity to the local electronic structure of the single configurations [14].

In this study, we expand the concept of site-selective reactivity at locally distorted configurations to more complex, organic molecules. As an adsorbate, we chose ethylene (C_2H_4) which serves as a model system for barrierless, non-dissociative adsorption of organic molecules on semiconductor surfaces. The C_2H_4/Si(001) system has been studied extensively both by experimental and theoretical methods [15–27]. It is now commonly accepted that ethylene adsorbs non-dissociatively on one Si-dimer through stable di-σ Si–C bonds via a so-called [2 + 2] cycloaddition reaction. This kind of adsorption geometry upon a single Si-dimer without breaking the Si–Si dimer bond was supported by a variety of experimental techniques including electron energy loss spectroscopy and low energy electron diffraction [15], near edge X-ray absorption fine structure (NEXAFS) [20], angle resolved photoelectron spectroscopy [21], photoelectron diffraction [22], and STM investigations [17,23,27], and is also in agreement with theoretical results [18,19,21,24,26].

Here we use hydrogen preadsorption on Si(001) in combination with scanning tunneling microscopy to investigate the effect of the surface's local electronic properties on the reactivity of C_2H_4. We show that by hydrogen precoverage the order of the site-specific reactivity of major and minor reaction channel for C_2H_4 adsorption on Si(001) can be reversed.

2. Experiment

The experiments were performed using a commercial STM (OMICRON VT-STM) in an ultrahigh vacuum chamber with base pressure below 1×10^{-10} mbar. All experiments were carried out using n-doped silicon samples oriented within 0.25° along the (001) direction. The Si(001) samples were prepared by degassing the sample at 700 K and repeatedly flashing to temperatures above 1450 K by means of direct current heating. Slow cooling down to

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room temperature with rates of about 1 K/s then results in a clean and well ordered Si(001) 2 × 1 reconstruction with a minimum of defects [28]. Hydrogen precovered surfaces were prepared by dosing highly purified H_2 gas (99.9999% purity) via a gas inlet system which was equipped with a liquid nitrogen trap to freeze out residual impurities. Molecular hydrogen was dissociated at a hot tungsten filament (approx. 2000 K) which was positioned 5 cm from the sample. Typical exposures were 5×10^{-7} mbar H_2 gas for 40 s. Ethylene with 99.95% purity was dosed via a second gas inlet system with typical exposures of 0.01 L to 1 L of C_2H_4 gas. For some of the experiments tip and sample were kept in tunneling contact during C_2H_4 dosing. To reduce shadowing effects, the tip was then moved 100 nm away from the area of interest. Except for a reduced C_2H_4 coverage, no influence of the tip on the adsorption behavior was found when performing control experiments with the tip retracted from the surface. All experiments were performed at room temperature, ion gauge readings were corrected for relative ionization probabilities.

3. Experimental results

As a first step, the adsorption of ethylene on a clean Si(001) surface was investigated. Fig. 1 shows STM images of Si(001) covered by approximately 0.06 ML C_2H_4 (1 ML $\hat{=}$ 1C_2H_4 molecule per Si-dimer). In the filled-state image displayed in Fig. 1a, black features parallel and perpendicular to the dimer rows are observed. Furthermore, in the empty-state image in Fig. 1b, the black features

Fig. 1. STM images (7 × 7 nm²) of Si(001) covered with ≈0.06 ML ethylene. (a) Negative sample bias (−1.4 V), (b) positive sample bias (+1.0 V); tunneling current was I = 0.2 nA for both images. Two different adsorption geometries are observed: ethylene adsorption on top of a single dimer (one-dimer configuration) appears as black features perpendicular to the dimer rows both in empty- and filled-state images. An example is labeled red in (a) and (b) and sketched in (c). Adsorption of ethylene on two Si-atoms of adjacent Si-dimers (two-dimer configuration) appears as black features parallel to the dimer rows (labeled blue). This adsorption pathway results in two single dangling bonds on the opposite dimer atoms appearing as bright features in the empty-state image (b) and is sketched in (d).

parallel to the dimer rows go along with bright dangling bond states on their opposite dimer atoms. The observed features are correlated to two adsorption configurations of ethylene on a clean Si(001) surface: The black features which cover one dimer both in filled- and empty-state image are associated with ethylene molecules adsorbed on top of a single-dimer ('di-σ' or 'one-dimer' configuration, sketched in Fig. 1c) as reported in former STM studies [17,23,27]. Additionally, the bright elliptical spots in the empty-state STM images are interpreted as a second adsorption geometry with the ethylene molecule being adsorbed on top of two adjacent Si-atoms of neighboring dimers ('end-bridge' or 'two-dimer' configuration, sketched in Fig. 1d). The latter geometry results in two single dangling bonds opposite to the adsorbed ethylene molecules thus leading to the observed bright, elliptical protrusion in Fig 1b. Please note that for simplicity the Si-dimers are plotted symmetrically, although it is well known that the Si-dimers are alternatingly buckled along the dimer rows with one upper and one lower Si-atom. This buckling is observed with the STM only at temperatures below 200 K due to fast dynamic flipping of the dimers from one tilt direction to the other at higher temperatures [29,30].

On a clean Si(001) surface with ≈17000 clean Si-dimers we found 1721 C_2H_4 molecules adsorbed in one-dimer configuration while only 107 adsorbed in two-dimer configuration. Thus, the relative reactivity of the two-dimer configuration with respect to the one-dimer configuration was calculated to be 6.2% by comparing the numbers of ethylene molecules adsorbed in both configurations. Whereas the two observed adsorption geometries were also found for the adsorption of acetylene (C_2H_2) on Si(001) [31–34], the two-dimer (end-bridge) configuration was not reported for the C_2H_4/Si(001) system so far. Due to the very rare occurrence of this configuration, it is not expected to show up as a prominent feature when using techniques which average over the whole surface, e.g. NEXAFS or photoelectron spectroscopy. However, it was not observed in former STM studies of the C_2H_4/Si(001) system either [17,23,27]. One might therefore speculate on some influence of the scanning tip on the adsorbed molecules, e.g. tip-induced change of adsorption sites from one-dimer to two-dimer configuration. Such an influence can be excluded for our experimental conditions since no change was observed during several successive scans across the same surface area. Adsorption of water, which leads to a similar signature in the STM images, was also excluded by carefully checking the purity of the ethylene gas during exposure.

The adsorption behavior of C_2H_4 changes when atomic hydrogen was preadsorbed. An example of such a H-precovered surface before and after C_2H_4 exposure is shown in the empty-state STM images in Fig. 2a and b, respectively. Without C_2H_4 exposure, three different features induced by H-precoverage can be distinguished in Fig. 2a: (i) Bright elliptical protrusions which represent two hydrogen atoms adsorbed on two adjacent Si-dimers leaving two single dangling bonds at the opposite sites of the dimers. In previous studies, this reaction site was called 'H4 configuration' since hydrogen precoverage and in total four dangling bonds are involved [11]. (ii) Grey circular protrusions that are originated from single adsorbed hydrogen atoms leaving a single dangling bond on the opposite dimer atom. (iii) A few elliptical black features perpendicular to the dimer rows are observed which can be related to either the adsorption of two hydrogen atoms on the same Si-dimer or to some missing-Si-dimer defects. Such a hydrogen precovered Si(001) surface represents the initial state for the following adsorption experiments.

Fig. 2b shows the same surface area as in (a) but after ethylene exposure. Three types of obvious changes are identified: at first, similar to the experiments on the clean Si(001) surface, black features perpendicular to the dimer rows as well as bright elliptical spots parallel to the dimer rows appear on clean silicon dimers.
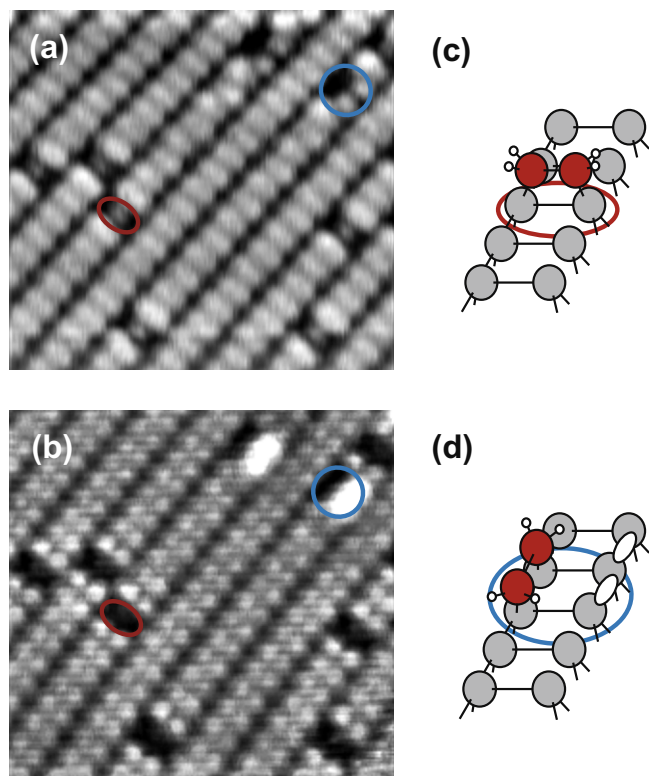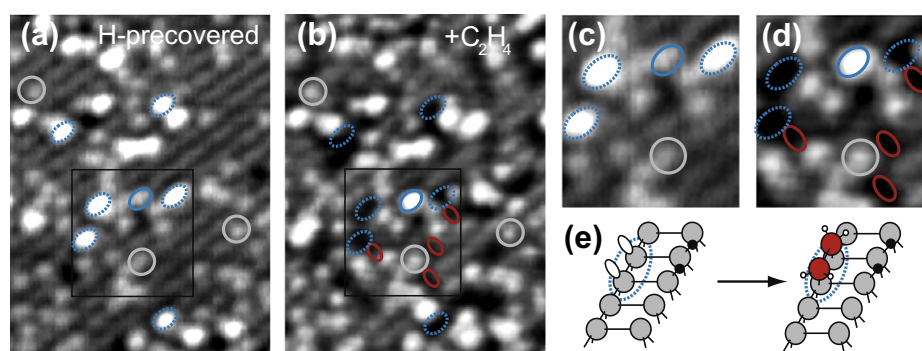
Fig. 2. STM images (16×11 nm^2 in (a) and (b), positive sample bias $U = +0.8$ V; tunneling current $I = 0.2$ nA) of Si(001). (a) after precoverage with atomic hydrogen and (b) after additional ethylene exposure. (c) and (d) show detailed images of (a) and (b), respectively. After hydrogen precoverage, grey circular features (some labeled by grey circles) and bright elliptical features (some labeled by blue dashed ellipses) are observed. The former ones are identified as single adsorbed hydrogen atoms while the latter ones are caused by the adsorption of two hydrogen atoms on two adjacent Si-dimers (H4 configurations). After ethylene exposure, black elliptical features perpendicular to the dimer rows (labeled red) and additional bright elliptical spots parallel to the dimer rows (labeled blue) are observed in (b) due to C_2H_4 adsorption on clean dimers. In addition, some of the bright H4 configurations vanish (labeled by blue dashed ellipses) indicating the passivation of their dangling bonds by adsorbed ethylene molecules. (e) Sketch of the H4 configuration before and after ethylene adsorption.

They are again identified as ethylene molecules in the one-dimer and two-dimer configuration, respectively. In addition, some of the bright H4 configurations vanish and appear as dark spots after ethylene exposure. This is interpreted in terms of adsorption of an ethylene molecule at these special reaction sites leading to the passivation of the two remaining dangling bonds of the H4 configuration. The vanishing H4 configurations are labeled by blue dashed ellipses before and after the ethylene adsorption in Fig. 2a and b, and in the magnifications (c) and (d). The sketch in Fig. 2e shows the H4 configuration before and after the adsorption of ethylene. Dangling bond configurations correlated to single adsorbed hydrogen atoms show no reactivity.

For quantitative evaluation of the adsorption probabilities on the H-precovered Si surface, the relevant configurations before and after ethylene adsorption were counted. The results are summarized in Table 1 including the absolute numbers of initial and final configurations of the different adsorption geometries as well as the relative occurrences of the final configurations with respect to the initial configurations. In our experiments, a total number of 33×10^3 Si-dimers were evaluated. The concentrations of the H4 configurations and single H-atoms were approximately 0.02 ML and 0.11 ML, respectively, leaving 28×10^3 clean Si-dimers. On these clean and undistorted parts of the H-precovered surface we found 1291 and 100 C_2H_4 molecules adsorbed in one-dimer and two-dimer configuration, respectively. From the ratio of these numbers, we obtain a relative reactivity of the two-dimer configuration of 7.7%, in good agreement with the value of 6.2% found on the clean surface. The effective enhancement of the site-selective reactivity induced by hydrogen precoverage is determined by comparison of the adsorption probability at the H4 site with the occurrence of the two adsorption geometries on clean silicon dimers. With respect to the very rare occurrence of the two-dimer configuration on the clean parts of the surface, the number of H4 configurations saturated with C_2H_4 implies a strong enhancement in reactivity at the H4 sites relative to the two-dimer adsorption on the clean Si-dimers. Quantitatively, dividing the relative occurrence of 0.163 for the C_2H_4-saturated H4 configuration by 0.004 for the clean two-dimer configuration, one calculates an enhancement in site-specific reactivity at the H4 configuration by a factor of 45 when compared to the two-dimer configuration on the clean surface. Even when compared to the relative occurrence of the one-dimer configuration of 0.047 the reactivity at the H4 sites is a factor of 3.5 higher. Thus, at the distorted H4 configurations the adsorption of C_2H_4 on two adjacent Si-dimer atoms becomes even more reactive than the one-dimer adsorption pathway. In other words, at the H4 sites the minority reaction channel (two-dimer configuration) exceeds the majority reaction channel (one-dimer configuration) with respect to site-specific reactivity. Depending on the hydrogen coverage it thus allows for the control of how the majority of the ethylene molecules adsorb on the Si(001) surface. For the determination of absolute sticking probabilities s_0 on the clean surface, we compared the reactivity of ethylene and water on Si(001), the latter being well investigated with s_0 reported to be unity [35,36]. With comparable gas exposures of ethylene and water we found nearly the same adsorbate coverage thus pointing towards $s_0(C_2H_4) \approx 1$, in good agreement with previous studies [16].

4. Discussion

In this investigation, two adsorption configurations are found for C_2H_4 on the clean Si(001) surface: the one-dimer (di-σ)

Table 1
Number of configurations before and after ethylene adsorption on clean and hydrogen precovered Si(001). N_0 represents the number of initial configurations of the respective reaction pathway, i.e. clean Si-dimers and H4 configurations. N_i represents the number of finally adsorbed ethylene molecules in the different configurations with N_i/N_0 being the ratio of the numbers of final to initial configurations, i.e. the relative occurrence. The ratio N_2/N_1 shows the preference of the one-dimer pathway compared to the two-dimer pathway on the clean dimers. The comparison of N_i/N_0 of the different configurations reveals the enhancement in reactivity of the H4 configuration relative to the adsorption on clean Si(001).

Configurations	Initial sites	C_2H_4 one-dimer		C_2H_4 two-dimer		Ratio
	N_0	N_1	N_1/N_0	N_2	N_2/N_0	N_2/N_1
Clean surface						
Clean dimers	17000	1721	0.101	107	0.006	0.062
H-precovered						
Clean dimers	27762	1291	**0.047**	100	**0.004**	0.077
H4	731	–	–	119	**0.163**	–

configuration which accounts for over 90% of the total ethylene coverage and the much less frequent two-dimer (end-bridge) configuration. In the case of a hydrogen precovered Si(001) surface, one observes a considerable enhancement of reactivity for adsorption in the two-dimer configuration at H4 sites when compared to the clean surface.

At a first view, this increase in reactivity by hydrogen precoverage causes some surprise since the initial sticking coefficient of the one-dimer configuration is close to unity [16]. As a consequence, our findings imply an apparent sticking probability which is a factor of 3.5 larger than unity for ethylene at the H4 configuration. This seeming discrepancy can be solved if one takes into account that C_2H_4 adsorption proceeds via a precursor state [16,24–26] and that this precursor is mobile and possesses a finite lifetime as strongly supported by recent low-temperature STM measurements [27]. Accordingly, one might envision the following scenario: the probability of the complete adsorption process is subdivided into a 'precursor adsorption probability' and a 'conversion probability'. The precursor adsorption probability determines the probability that a ethylene molecule in the gas phase attains the precursor state. This probability should be close to unity and is not influenced by the different final adsorption configurations. In contrast, the conversion probability stands for the probability to attain the final chemisorbed state while the molecule is located at a single adsorption site. According to our findings, this conversion probability should be considerably lower than unity for one- and two-dimer configurations, especially lower than the conversion probability at the H4 site. Thus, after adsorption in the precursor state, the ethylene molecule diffuses in average over the distance of several surface lattice constants and probes several adsorption sites. On the clean surface, it finally adsorbs in either the one- or two-dimer configuration. On the hydrogen precovered surface, however, there is a high probability that the precursor state is converted into a final adsorption state as soon as the ethylene molecule reaches an H4 configuration, leading to preferential adsorption at these sites. Hence, this qualitative approach can explain the enhancement in reactivity of the H4 configuration relative to the clean surface configurations also in the case of an overall initial sticking coefficient of unity.

For the clean surface, the observed lower conversion probability from the precursor to the final chemisorbed state in case of the two-dimer pathway is backed by first-principle density-functional investigations [24]. In this study, Cho et al. identify a precursor state for C_2H_4 adsorption both for the one-dimer and two-dimer pathway. In this precursor state, the C_2H_4 molecule is chemically attached to the lower atom of the buckled Si-dimer on which, in the case of the clean surface, the more p-like, energetically unfavorable thus unfilled dangling bond is localized. An energy barrier between that precursor and the final adsorption state of 0.02 eV and 0.12 eV was calculated for the one-dimer and the two-dimer configuration on the clean surface, respectively [24]. As a consequence, lower but finite adsorption probability through the two-dimer pathway is expected in good agreement with our observation of a 15 times higher sticking probability for the one-dimer configuration.

In the case of the hydrogen precovered surface, we again interpret the observed enhancement of sticking probability in the framework of a precursor mediated process: the adsorbed hydrogen atoms induce a locally distorted electronic configuration at the H4 site which is likely to change the energy barrier between the precursor and final state. According to our findings, this barrier is indeed reduced by the preadsorbed hydrogen atoms, very similar to the case of activated hydrogen dissociation on Si(001) [11]. Especially with respect to the two-dimer reaction channel for ethylene adsorption on the clean surface, this reduction of the energy barrier seems very plausible: during the transition from the precursor to the final state a second π-like bond between the dangling bonds of one dimer has to be broken in case of the clean dimers which costs extra energy compared to the one-dimer pathway. At the H4 site, no such bond breaking is necessary, leading to the proposed reduction of the energy barrier. Furthermore, the electronic states of the single dangling bonds of the H4 sites are both close to the Fermi level and filled with one electron. Thus no extensive charge redistribution is necessary when establishing the two Si–C σ-bonds of the final adsorption state in contrast to the one-dimer configuration; for the latter one an electron has to be transferred from the energetically more favorable, doubly occupied sp^3-like dangling bond of the upper atom of the buckled Si-dimer into the Si–C bond. As a consequence, an even higher reaction probability for the H4 channel when compared to the one-dimer channel on the clean surface is expected, in agreement with our experimental observation. The interpretation is further backed by experiments on Si(114), where C_2H_4 adsorption at the rebonded, non-dimerized step atoms was shown to exhibit the highest reactivity [37].

5. Conclusion

In summary, we found two ethylene adsorption geometries on clean Si(001) with ethylene adsorbed on one and two dimers, respectively. In particular, the less reactive two-dimer adsorption site has not been observed experimentally so far. Furthermore, distortion of the electronic configuration by preadsorption of atomic hydrogen is found to increase the reactivity of the two-dimer adsorption site by a factor of 45. Even when compared with the one-dimer adsorption on the clean surface, i.e. the major reaction channel, the reactivity of the hydrogen precovered two-dimer adsorption site is 3.5 times higher. This is interpreted in terms of locally distorted dangling bond configurations which lead to site-selective reactivity in the case of the barrierless, non-dissociative adsorption of ethylene on Si(001), similar to the case of the strongly activated H_2 dissociation on Si(001). It is furthermore related to a precursor mediated chemisorption process and the control of the energy barrier between precursor and final state by the H-induced distortions. Thus, we were able to control the site-selective reactivity of the C_2H_4/Si(001) system, which serves as a model system for adsorption of organic molecules on semiconductor surfaces. The results are therefore expected to be also applicable to more complex systems thus leading to a better understanding of functionalization of Si(001) by means of organic molecules.

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