# Trapping-Mediated Chemisorption of Ethylene on Si(001)-$c(4 \times 2)$

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Adsorption of ethylene molecules on Si(001)-$c(4 \times 2)$ was studied using scanning tunneling microscopy at low temperatures. Ethylene molecules trapped at the surface at 50 K were imaged only after decay to chemisorption, each bonding to a Si dimer. Atomic-scale observations of temperature-dependent kinetics show that the decay exhibited Arrhenius behavior with the reaction barrier of 128 meV in clear evidence of the trapping-mediated chemisorption, however, with an anomalously small preexponential factor of 300 Hz. Such a small prefactor is attributed to the entropic bottleneck at the transition state caused by the free-molecule-like trap state.

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Adsorption of molecules on surfaces has been a subject of great interest. Many molecules go through a weakly bound trapping-mediated state before more stable chemisorption takes place. The kinetics of such trapping-mediated adsorption has long been studied theoretically and experimentally, particularly on metal surfaces [1–4]. On the other hand, on technologically important Si surfaces, similar studies of the kinetics in chemisorption are very scarce. The temperature-dependent decay of the precursor state was reported for oxygen adsorption on the Si(111)-$(7 \times 7)$ surface [5,6], but the nature of the complex oxidation process is still ambiguous [7–9].

Stimulated by recent technological advances in applications to organic thin film devices [10,11], adsorption of ethylene on Si(001) was studied as a prototype reaction of olefinic molecules on silicon surfaces [12]. This class of molecules commonly shares the chemisorption structure of a molecular adsorbate bonding to a Si dimer through stable di-$\sigma$ Si-C bonds through the so-called [2 + 2] cycloaddition reaction [7,13,14]. The chemisorption of ethylene ($C_2H_4$) molecules on Si(001) via a mobile precursor state was first suggested using a molecular uptake method [15], while its existence at the early stage of chemisorption was questioned in photoemission [16]. Recently, three-membered $\pi$-complex precursor structures were proposed by density functional calculations [14,17] similar to those of acetylene [18,19], and stable intermediate states found in electron energy loss spectroscopy at 48 K were attributed to the feature [20]. However, still lacking is firm evidence for the existence of the intrinsic mobile precursors, as well as the decay kinetic information to shed light on the gas-surface reaction dynamics on Si surfaces.

In the present Letter, we report on the investigation of trapping-mediated chemisorption of ethylene molecules on the Si(001)-$c(4 \times 2)$ surface at low temperatures using a scanning tunneling microscope (STM), an ideal tool to detect minute atomic-scale changes on the surface. By observing the decay of trapped molecules in thermal equilibrium with the surface and employing a method minimizing the tip-surface interaction, we examined the decay kinetics of the trapped molecules. The results paint quite a surprising picture of the trap state as well as its decay kinetics dominated by entropy.

Experiments were performed using a low-temperature STM (Omicron GmbH) with the base pressure below $3.0 \times 10^{-11}$ mbar, equipped with double cryoshields and a resistive heater mounted on the STM head. The preparation of a clean Si(001)-$c(4 \times 2)$ surface ($n$-type, 3 m$\Omega$ cm) with a defect density <0.1% was described elsewhere [21]. Weakly bound molecular states on the surface were prepared by introducing ethylene on a Si(001)-$c(4 \times 2)$ surface at the substrate temperatures of 50 and 80 K by backfilling the chamber at a pressure of $2 \times 10^{-8}$ mbar, monitored by a quadruple mass spectrometer. After the base pressure was restored, images were taken without an additional dose. All STM images were obtained at the tunneling current of 10 pA and the sample bias of −1.5 V.

Figure 1(c) shows a typical STM image of a Si(001) surface exposed to ethylene molecules of 5.5 L at 80 K. Upon the exposure, only a single type of features, a slight depression on a Si dimer site, was observed. As shown in Fig. 1(b), each slightly depressed feature represents a chemisorbed ethylene in a "di-$\sigma$" structure, in which the C-C bond is parallel to the Si dimer bond and two $\sigma$ bonds between C and Si atoms are formed, as represented by ball models in Fig. 1(a). This is consistent with the theoretical prediction [14] and the previous STM results at room temperature [7,13]. On the other hand, no feature attributable to trapped species was observed. Chemisorption sites were randomly distributed over the Si(001)-$c(4 \times 2)$ surface, even on neighboring dimer sites along the same dimer row, as found in Fig. 1(c). The surface was completely saturated by chemisorption sites at more than 10 L of the total ethylene dose (images not shown here).

On the other hand, a strikingly different adsorption behavior was observed at 50 K on the same amount of ethylene dose. The number of initial chemisorbed sites was drastically less than that produced by the identical dose at 80 K, as shown in Fig. 1(d). Despite the huge disparity in the chemisorption coverage, however, no difference was

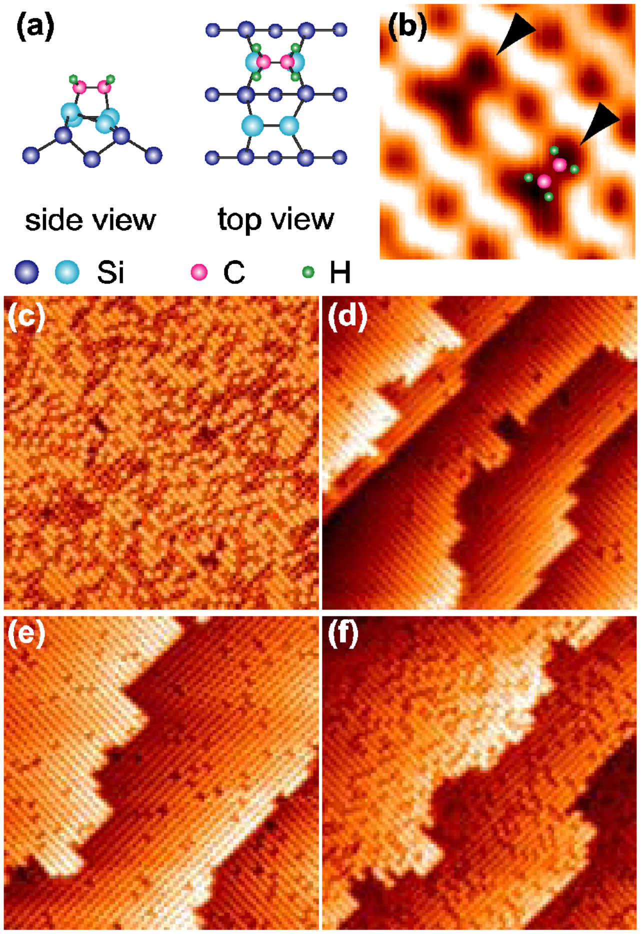

FIG. 1 (color online). (a) Schematic ball model of chemisorbed $C_2H_4$ on a Si(001)-$c(4 \times 2)$ surface. (b) An atomically resolved STM image of two chemisorbed $C_2H_4$ (black arrows) on Si(001)-$c(4 \times 2)$. The ball model of $C_2H_4$ is overlaid over one of the two reacted sites as a guide to the eyes. STM images of $30 \times 30$ nm$^2$ of a Si(001) surface exposed to (c) 5.5 L of $C_2H_4$ at 80 K and (d) the same amount at 50 K and, subsequently, annealed to (e) 80 and (f) 110 K without further dosing.

found between chemisorbed sites produced at these two temperatures, indicating that they are, in fact, identical. This was also checked by annealing the surface to 80 K and higher. As the temperature was slowly raised from 50 K, the number of reacted sites increased [Fig. 1(e)] and approached an asymptote by 110 K annealing, where there occurred no further chemisorption events [Fig. 1(f)]. This suggests that adsorbed ethylene molecules are held in a weakly bound trap state on the Si(001) surface at 50 K, although invisible to STM, and decay slowly to a more stable chemisorption state. Decay persisted over a few days at the substrate temperature of 80 K.

In order to understand the kinetics in trapping-mediated chemisorption of ethylene molecules, we investigated decay to the chemisorbed state at several substrate temperatures. We first introduced ethylene molecules of 6 L on a clean Si(001) surface at 50 K and, subsequently, raised the substrate temperature to the desired value for the decay measurement. While maintaining the temperature within ±0.5 K, we were able to obtain large-scale STM images for a few days consecutively. To avoid the tip-induced effect, special care was strenuously exercised. Not only were all images obtained at a low tunneling current of 10 pA, but also each image was acquired at a fresh new location. The possibility of tip effects on the decay rate was monitored by taking a few consecutive images over an area, followed by the inspection of an inclusive, zoomed-out large area. Any difference between the inner area scanned over repetitively and the fresh outer area would be indicative of the tip-adsorbate interactions. No such difference was found, indicating that the tip effect is negligible. In addition, our method of moving to a fresh location for each image acquisition would cause any tip effects to turn up as a constant shift in the background, which can easily be subtracted later.

Figures 2(b)–2(d) show temporal STM images taken at 0, 850, and 2840 min, respectively, after the substrate temperature was raised to 80 K as described above. It is clear that the number of chemisorbed sites increased slowly in time even at the base pressure of $3 \times 10^{-11}$ mbar [22]. Once chemisorption took place on a Si dimer, it showed neither mobility nor disappearance, indicating that the reaction is irreversible at these tempera-

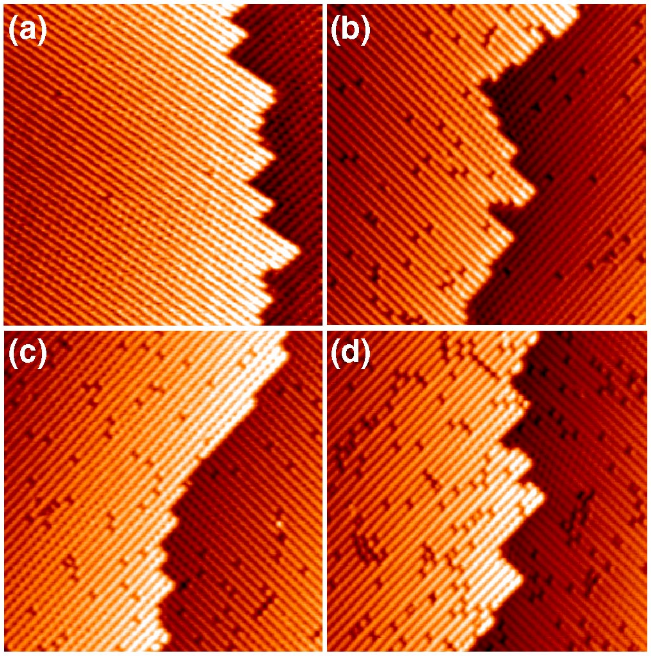

FIG. 2 (color online). (a) STM image of a clean Si(001) surface at 50 K. (b)–(d) After the surface was exposed to 6 L of $C_2H_4$ at $T_s = 50$ K, the substrate temperature was increased to 80 K and time-sequence STM images were obtained while keeping the substrate at 80 K. (b) Immediately after the substrate temperature had reached 80 K. (c),(d) Images taken at 850 and 2840 min after (a), respectively. Image size $30 \times 30$ nm$^2$.

tures. Our population analysis of chemisorbed species indicates that slight repulsion exists between the nearest neighbor sites on the same dimer row, although much weaker than that at 300 K [7].

Figure 3(a) shows thus measured chemisorption coverages as a function of time at several temperatures. Each data point was extracted from a STM image whose size is typically $80 \times 80$ nm$^2$, containing over $1.8 \times 10^4$ dimer sites. Assuming negligible interactions between adsorbates, decay and desorption of trapped molecules in time $t$ with an initial coverage $\theta_0$ may be described by the following two coupled differential equations [4]:

$$\frac{d\theta_c}{dt} = k_c \theta_p, \tag{1a}$$

$$\frac{d\theta_p}{dt} = -(k_d + k_c)\theta_p, \tag{1b}$$

where $\theta_p$ and $\theta_c$ denote the surface coverages of the trapped and the chemisorbed molecules, respectively, and $k_c$ and $k_d$ the chemisorption and the desorption rates, respectively. Figure 3(a) shows the fits to the data using the solution to Eq. (1):

$$\theta_c = \frac{k_c}{k_+}\theta_0(1 - e^{-k_+ t}), \tag{2}$$

where $k_+ = k_c + k_d$. The reaction rates are shown in solid squares in Fig. 3(b) and give an excellent fit to the Arrhenius equation $k_+(T) = k_+^0 e^{-E_+/k_B T}$, where $k_+^0$ is the preexponential factor (PEF), $E_+$ the barrier energy, and $T$ the substrate temperature. The fit, as shown in the solid line in Fig. 3(b), yields $E_+ = 128 \pm 26$ meV. On the other hand, $k_c$ can be elicited from $k_+$ using the relation $d\theta_c/dt|_{t=0} = k_c\theta_0$. A plot of $k_c\theta_0$, normalized by $\theta_0$ at 80 K, is shown in empty squares in Fig. 3(b) with the fit in the dashed line. Although the Arrhenius fit to $k_c\theta_0$ produced an activation barrier 16% lower than that for $k_+$, it is regarded as identical to $k_+$ within error bars due to the unknown $\theta_0$'s. This is consistent with a previous uptake study [15], which measured the energy difference between the desorption and the chemisorption barriers for the trapped ethylene, i.e., $E_d - E_c = 0.165$ eV, as well as the ratio of two attempt frequencies, $k_d^0/k_c^0 = 27$. Combined with our activation energy $E_c$, it produces $k_d/k_c < 10^{-5}$ and indicates that desorption may be ignored; hence, $E_c \approx E_+$ and $k_c \approx k_+$ at these temperatures. Our barrier height $E_c$ is consistent with estimates from the previous experiments [15,20] and also in line with the previous theoretical predictions [14,17] and clearly supports that the decay to chemisorption is thermally activated.

However, what is unusual about the reaction is the PEF $k_c^0$ of $3 \times 10^{2\pm2}$ s$^{-1}$. This is 10 orders of magnitude lower than the commonly used attempt frequency of $10^{12}$ at 90 K. Such an anomalously low PEF has not been reported for any adsorbates, to the best of our knowledge. Despite its large statistical uncertainty, the PEF is an integral part of kinetics; recently, anomalous lowering of the PEF indirectly elicited from metal-on-metal island growths was reported [23] and, subsequently, attributed to the artifact of missing adsorbate interactions in the mean-field type nucleation theory used for the analysis [24].

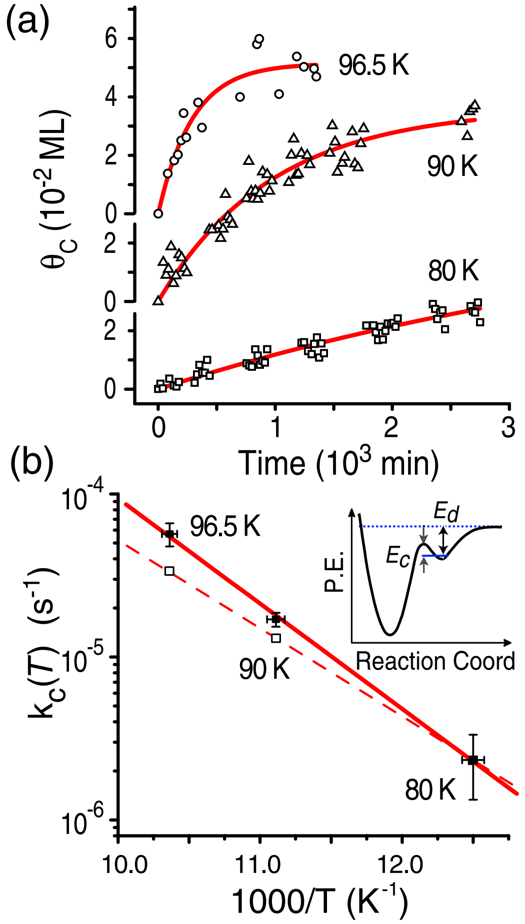

FIG. 3 (color online). (a) Temporal change of the coverage of chemisorbed ethylene on Si(001). The coverage of the first image obtained at each temperature run was used as its origin. Data are shifted vertically for clarity. Red lines represent the fits to the data. (b) An Arrhenius plot for the chemisorption rates of the trapped species, with the inset of a schematic potential energy diagram describing trapping-mediated chemisorption and desorption. See text for the explanation of solid and dashed lines.

In this work, the decay pathway to chemisorption from the trap state was *directly* measured, and the reaction barrier thus obtained is only for the single final chemisorption state, the di-$\sigma$ configuration [14,17]. If one naively assumes that the PEF represents the vibrational frequency $k_c^0$ of a precursor trapped within a harmonic potential well of depth $E_c$, then it would be placed at ~0.5 m away from the surface, which is obviously unphysical. Understanding such a low PEF would have to take into account the competition among all the possible kinetic pathways. Noting that the ethylene is a planar molecule, we considered a simple model of a free molecule trapped in an ultrathin potential well and investigated the effects of its degrees of freedom on the reaction rate, within transition state theory [25,26]:

$$k_c = \frac{k_B T}{h} \frac{Z_\ddagger}{Z_P} e^{-E_c/k_B T}, \tag{3}$$

where $h$, $Z_\ddagger$, and $Z_P$ represent the Planck constant and the partition functions of the transition and the trap states, respectively. In the model, it was assumed that the relation $Z_\ddagger = Z_\ddagger^v \approx Z_P^v$, where $v$ denotes vibrational states, justified by its large vibrational quanta [27]. The resulting estimation of the PEF indicates that each rotational and translational degree of freedom contributes 1 and 2 orders of magnitude reduction to the PEF, respectively, at 90 K. Thus, it is feasible to achieve the necessary reduction in the PEF only if all translational and rotational degrees of freedom are available to the trapped molecules. The result suggests that the trap state may be in a weakly corrugated regime on the diffusion coordinate. Despite the crudeness of the model, this picture is consistent with our observation that the trapped species remained invisible to STM even at 50 K, which gives an estimated upper limit of 0.1 eV for the diffusion barrier [28]. In comparison, noisy, speckled images of trapped species in motion were obtained below 100 K in the pioneering STM study of benzene on Si(111), aided by a large diffusion barrier of 0.4 eV [29].

Although detailed understanding will have to wait for further experimental and theoretical developments, it is concluded thus that the anomalously low PEF originates from the entropic bottleneck at the transition state reachable only at the expense of the vast phase space available to free-molecule-like trap states. Physical analogues of the present system entailing such a reduction in the PEF may be found in conventional surface-catalyzed reactions operating at high pressure and high temperature [30]. Our finding succinctly shows that the prevalent assumption of a canonical attempt frequency in reactions from a trap state is not justifiable.

In conclusion, the chemisorption of ethylene molecules on Si(001) was investigated using STM at low temperatures. Ethylene molecules first adsorbed in a trap state decay to a chemisorbed state through a thermally activated process exhibiting Arrhenius behavior with an anomalously low PEF. The origin of the suppression in the PEF is attributed to the entropic bottleneck at the transition state caused by free-molecule-like trap states. The existence of a long-lived trapped species and the simple chemisorption process makes ethylene an ideal molecule to study trapping-mediated adsorption on Si surfaces, thereby providing a fascinating view into the gas-surface reaction dynamics at low temperatures.

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