Adsorption dynamics of ethylene on Si(001)

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The dynamics of ethylene adsorption on the Si(001) surface was investigated by means of molecular beam techniques. A constant decrease of initial sticking probability $s_0$ was observed with increasing kinetic energy indicating a non-activated adsorption channel. With increasing surface temperature, $s_0$ decreases as well, pointing towards adsorption via a precursor state. Quantitative evaluation of the temperature dependence of $s_0$ via the Kisliuk model was possible for surface temperatures above 250 K; below that value, the temperature dependence is dominated by the adsorption dynamics into the precursor state. Maximum surface coverage was found to be reduced with increasing surface temperature, which is discussed on the basis of a long lifetime of the precursor state at low temperatures. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.3700180]

I. INTRODUCTION

Adsorption of organic molecules on semiconductor surfaces is envisioned as a possibility to combine conventional semiconductor and molecular electronics.¹,² This led to extensive studies of the adsorption of smaller organic molecules such as ethylene, acetylene, benzene, and others, on Si(001),³−⁵ which is the technologically most relevant semiconductor surface. Detailed information on the adsorption sites, adsorption geometries, and degree of ordering at higher coverage are now available for these systems. Especially for the C₂H₄/Si(001) system, the adsorption geometry has been controversially discussed for many years.⁶−¹⁰ Recently, adsorption in a di-sigma-configuration on one dimer as the majority adsorption species and a di-sigma-configuration on two neighbored dimers as a minority adsorption configuration was established in literature.¹⁷,¹⁸ In both cases, the double bond of the C₂H₄ molecule is broken and two Si–C sigma bonds are formed.

Despite the detailed experimental and theoretical investigations on adsorption geometry and related phenomena, only little or no information is available on the reaction dynamics of such systems. However, detailed knowledge of the adsorption dynamics could lead to a better control of the adsorption process and in consequence to the formation of better interfaces between the semiconductor surface and the organic molecules. In the case of ethylene on Si(001), a very early study reports on the temperature dependence of the initial sticking probability.¹⁹ Since the experiments were performed with thermal C₂H₄ gas, no information on the influence of kinetic energy was obtained. More recently, a scanning tunneling microscopy (STM) investigation at low temperatures revealed a very long-lived, mobile precursor state for ethylene on Si(001) with conversion rates as low as 10⁻⁶ s⁻¹ between precursor and final state at 80 K.²⁰ Interplay between this long-lived precursor state and a changed local electronic configuration as obtained by means of H-precoverage was shown to strongly influence the ratio of the two adsorption geometries.¹⁷ Furthermore, the system shows a pronounced difference in the adsorption behavior below and above half a monolayer coverage. For $\Theta \leq 0.5$, i. e., with one carbon atom per two silicon surface atoms, the sticking probability is high and domains of 2 × 2 and 2 × 4 superstructures are observed for those C₂H₄ molecules which are absorbed in the one-dimer configuration.¹³ For higher surface coverage, the sticking probability drops significantly, presumably due to strong interaction of two ethylene molecules in the one-dimer configuration on two directly neighbored silicon dimers; such an adsorbate-adsorbate interaction has been directly observed at $\Theta = 1$ by means of angle-resolved photoemission experiments.²¹ Thus, even for ethylene on Si(001), one of the most simple systems for adsorption of organic molecules on semiconductor surfaces, the dynamics are expected to be more complex and worth a more detailed investigation.

In this study, we made use of molecular beam techniques to investigate the adsorption dynamics of the C₂H₄/Si(001) system. Initial sticking probabilities $s_0$ were measured as a function of kinetic energy $E_{kin}$ of the impinging C₂H₄ molecules and as a function of surface temperature $T_s$. $s_0$ was found to decrease monotonically with increasing kinetic energy, indicating a non-activated reaction pathway. Increasing surface temperature also leads to a reduced initial sticking probability, typically interpreted as indication for adsorption via a precursor state. The functional form of the dependence on kinetic energy does not change with surface temperature indicating that the dynamics are mainly determined by adsorption into the precursor state. Quantitative description of the temperature dependence via the well established Kisliuk model²²,²³ which is based on the interplay between conversion of the precursor state into the final state and desorption from the precursor state into the gas phase was possible for $T_s \geq 250$ K. At lower temperatures, the dynamics of the adsorption into the precursor state has to be taken into account. Furthermore, the maximum surface coverage was found to decrease with increasing surface temperature by more than a factor of two. The latter observation is discussed on the basis.
of a long lifetime of the precursor state, which at lower surface temperatures is comparable to or longer than the relevant time scale of the molecular beam experiment.

II. METHODS

The experiments were performed in a four-stage molecular beam apparatus, with a base pressure in the sample chamber below $3 \times 10^{-11}$ mbar. The molecular beam was created via supersonic expansion from a heated molybdenum nozzle (backing pressures $\leq$ 2 bar, orifice diameter 100 $\mu$m) located 30 cm upstream from the sample. Ethylene and helium gas with a purity of 99.999% were additionally passed through a dry ice cooling trap close to the nozzle. Translational energy of the molecules was controlled either by heating the nozzle, seeding the C$_2$H$_4$ in helium, or a combination of both. Time-of-flight measurements were used to evaluate the resulting velocity distribution, speed ratio $S$ was determined to be $S = 7$ for the pure C$_2$H$_4$ beam at room temperature. With the C$_2$H$_4$ beam on, the typical background pressure measured in the sample chamber was $\leq 1 \times 10^{-9}$ mbar. Using seeded beam techniques, a further pressure increase was caused by the helium gas up to $2 \times 10^{-8}$ mbar.

Sample preparation was described in detail elsewhere. In short, the natural oxide of the rectangular Si(001) sample ($11 \times 60$ mm$^2$) was removed by repetitive resistive heating up to 1300 K. Both, during surface preparation and during the experiments, the sample holder was kept at liquid nitrogen temperature. Surface temperature was measured by means of a thermocouple glued to the center of the sample’s rear side. Cooling rates of about 1 K/s result in a well ordered Si(001)2$\times$1 reconstruction as observed by means of a sharp low energy electron diffraction pattern. Between subsequent adsorption experiments, the surface was cleaned by heating the sample to 1100 K.

The method of King and Wells was applied to determine absolute sticking coefficients as a function of exposure to the molecular beam. In order to do so, the clean Si sample was positioned in the molecular beam in front of a quadrupole mass spectrometer (QMS). The latter one was used to record the C$_2$H$_4$ pressure in the sample chamber as a function of time. By means of an additional, pneumatically driven shutter in front of the Si sample, the molecular beam was blocked and unblocked in less than 0.1 s. Upon retraction of the shutter at time $t_0$, the clean surface is exposed to the molecular beam and the background pressure drops due to adsorption on the reactive surface (compare Fig. 1). Since we ensured that the Si sample was larger than the molecular beam at the sample position, this pressure drop is proportional to the initial sticking coefficient $s_0$. Pressure changes with increasing exposure then reflect changes of the sticking probability with surface coverage $\Theta$. Taking into account the constant flux of the molecular beam,

$$\Theta \propto \int_{t_0}^{t} s(i)dt = \Theta^*$$

applies. As a consequence, the sticking probability $s$ as a function of relative surface coverage $\Theta^*$ is readily calculated from the measured adsorption curves; in our experiment, the detectable sticking probabilities are limited to $s \geq 0.02$.

III. RESULTS

Examples of the adsorption curves as obtained by means of the King and Wells method are shown in Fig. 1. For all three curves, one observes a pronounced initial drop of the QMS signal, thus a high initial sticking probability. For higher surface temperatures, the initial pressure drop and thus $s_0$ is lower than for low surface temperatures; the highest value of $s_0$ was found to be 0.7 at low surface temperature and low kinetic beam energy. For $T_s = 80$ K, the signal stays constant with increasing exposure time, i.e., the sticking probability does not change with increasing surface coverage until a given saturation coverage is reached and the signal rises to the initial value. On the other hand, for $T_s = 317$ K, the signal rises immediately after the initial drop, i.e., the sticking probability continuously decreases with increasing surface coverage. This difference in the dependence of $s$ on surface coverage will be discussed in more detail below.

The initial sticking coefficients $s_0$ are plotted in Fig. 2 as a function of kinetic energy $E_{\text{kin}}$ of the molecular beam.
at three different surface temperatures. For all three surface temperatures, \( s_0 \) decreases with increasing kinetic energy of the molecular beam. For constant kinetic energy, \( s_0 \) decreases with increasing surface temperature. Whereas full symbols represent data points recorded with the nozzle at room temperature and varied ethylene/helium ratio in the beam, the empty symbols reflect data points recorded with a heated nozzle \( (T_N = 400–700 \text{ K}) \). In the former case, the fraction and distribution of internally excited molecules in the beam is constant and only the kinetic energy is varied. In the latter case, both kinetic energy and the degree of internal excitation is increased with increasing nozzle temperature \( T_N \). No pronounced difference between the data measured by the two different methods is observed; as a consequence, we conclude on a minor influence of molecular excitations on the adsorption of ethylene in the parameter range covered by our experiment.

The dependence of the initial sticking coefficient on surface temperature is illustrated in more detail in Fig. 3 for two different beam energies. We find for all beam energies a continuous drop of the initial sticking probability with surface temperature.

In Fig. 4, sticking probabilities as a function of surface coverage are shown for a constant beam energy and different surface temperatures. The depicted relative surface coverage has been extracted from the uptake experiments as described in Eq. (1). In addition to the decrease of \( s_0 \) with increasing surface temperature, the maximum surface coverage as well as the functional form of \( s(\Theta) \) changes with increasing surface temperature: at low \( T_s \), \( s \) stays constant over a wide coverage range until saturation is reached, whereas at higher temperature \( s \) decreases continuously with increasing coverage. At this point, one has to keep in mind that our experiment is limited to \( s \geq 0.02 \), thus the apparent saturation coverage in our experiment might underestimate the real saturation coverage at given experimental parameters as will be discussed in more detail below.

IV. DISCUSSION

For the discussion of our data, we start with the dependence of the initial sticking probability on kinetic energy (Fig. 2). The observed decrease of \( s_0 \) with \( E_{\text{kin}} \) is typically correlated to a non-activated adsorption pathway for which it is important that the impinging molecules dissipate their kinetic energy during the adsorption process.\(^{28}\) The more energy the molecules carry, the less likely it is that they can dissipate enough energy to be trapped in the adsorption well and not to be reflected from the surface. We fit the dependence of \( s_0 \) on \( E_{\text{kin}} \) with the simple functional form

\[
s_0 = A \times \exp(-kE_{\text{kin}}).
\]

Good agreement between data and fit functions is obtained for a constant \( k \) thus varying only \( A \) with surface temperature.

The observed decrease of \( s_0 \) with increasing surface temperature is typically interpreted as a sign of a less strongly bound precursor adsorption state.\(^{29}\) Once the molecule is adsorbed in this precursor state, there is still a finite probability that desorption from the precursor state occurs rather than conversion into the final state. In case of an overall non-activated adsorption pathway, the energy required for conversion into the final state is lower than the energy required for desorption out of the precursor state into the vacuum. With increasing surface temperature, the relative importance of the latter process thus increases and the sticking probability decreases as observed. We interpret the fact that \( A \) and \( k \) of our simple parametrization are decoupled from each other in the following way: the adsorption probability into the precursor state is governed by the kinetic energy whereas for the conversion probability into the final state the surface temperature is the predominant parameter.

A quantitative description of the dependence on surface temperature is derived when the two competing processes, i.e., conversion into the final state and desorption into the vacuum, are described via the reaction rates \( k_s \) and \( k_d \), respectively,

\[
k_i = \Theta_p \cdot v_i \cdot \exp\left(-\frac{\epsilon_i}{k_B T_s}\right),
\]

with \( \epsilon_i \) being the respective energy barrier and \( \Theta_p \) the surface coverage of molecules in the precursor state. The sticking
probability is then derived from
\[ s_0 = s_p \cdot \frac{k_s}{k_a + k_d}, \tag{4} \]
with \( s_p \) being the probability for an impinging molecule to get adsorbed in the precursor state. Equations (3) and (4) can be combined to
\[ s_0 = s_p \cdot \left[ 1 + \frac{v_d}{v_a} \cdot \exp \left( -\frac{\varepsilon_d - \varepsilon_a}{k_B T_s} \right) \right]^{-1}, \tag{5} \]
which shows the explicit temperature dependence of \( s_0 \). This functional form is part of the well-known Kisliuk model.23 Reorganization of Eq. (5) leads to
\[ \ln \left( \frac{1}{s_0/s_p} - 1 \right) = \ln \left( \frac{v_d}{v_a} \right) - \left( \frac{\varepsilon_d - \varepsilon_a}{k_B T_s} \right). \tag{6} \]

In Fig. 5, the two data sets from Fig. 3 are plotted in the form of Eq. (6) assuming \( s_p \) to be close to the highest value of \( s_0 \) measured for the respective beam energy. Apparently, both data sets do not follow a straight line indicating some deviation from the simple Kisliuk behavior. If we fit the Kisliuk model to the high temperature results only (dashed lines), the difference between the barriers, \( \varepsilon_d - \varepsilon_a \), is deduced to be 0.15 eV and 0.2 eV for \( E_{\text{kin}} = 316 \text{ meV} \) and for \( E_{\text{kin}} = 77 \text{ meV} \), respectively. The corresponding functional forms are also plotted in Fig. 3, the deviation between the low temperature data and the Kisliuk fit is clearly observed. Obviously, there is a slight temperature dependence of \( s_0 \) in a temperature regime for which the Kisliuk model predicts that almost all molecules adsorbed in the precursor state convert into the final state, i. e., that \( s_0 \) does not change with surface temperature. We therefore attribute this additional temperature dependence to the dynamics of the adsorption into the precursor state itself, i. e., that the adsorption probability \( s_p \) into the precursor is reduced at increased surface temperature. In Fig. 5, we extended the Kisliuk model by such an additional temperature dependence of \( s_p \) in the low temperature regime (solid curve). A good qualitative agreement between the data and the model is then achieved.

When we compare our results for \( \varepsilon_d - \varepsilon_a \) with the results of an earlier experiment with a molecular doser (0.13 eV, Ref. 19), we find reasonable agreement. This is especially true if we take into account that we compare results for thermal gas with a molecular beam experiment. Furthermore, in the former experiment the accessible temperature range for the Kisliuk evaluation was limited and the deviation from Kisliuk behavior at lower temperatures could not be detected.

Here we would like to point out that, at low surface temperature, the lifetime of the precursor state was observed to be much longer than the typical timescale of our experiment. Quantitatively, STM measurements of ethylene adsorption in the temperature range between 80 and 100 K found conversion rates \( k_a \) between \( 10^{-6} \) and \( 10^{-4} \text{s}^{-1} \). From an extrapolation of these data, we expect lifetimes of the precursor state comparable to or shorter than the timescale of our experiment (1–10 s) only for surface temperatures above 250 K. The above discussion of the initial sticking probabilities \( s_0 \) is unaffected by these long precursor lifetimes as they should rather lead to an underestimation of \( s_0 \) by the Kisliuk model and not higher values as observed in Fig. 3. On the other hand, a long lifetime of the precursor state has a pronounced influence on the adsorption behavior at higher coverage.

First, the constant sticking probability over a wide coverage regime as observed at low temperatures (Fig. 4) implies either the existence of an extrinsic precursor, or, more likely, only weak repulsion if an impinging \( \text{C}_2\text{H}_4 \) molecule hits the surface on a site which is already covered by an \( \text{C}_2\text{H}_4 \) molecule.23 For example, if the precursor is mobile and long-lived, it may give way to the incoming molecule even at higher surface coverage. To higher surface temperatures, the higher fraction of molecules adsorbed in the final state in combination with the coverage dependence for the transition from the precursor into the final state and the reduced lifetime of the precursor state leads then to a faster drop of sticking probability with increasing surface coverage.23

Second, the observed reduction of maximum surface coverage with increasing surface temperature is uncommon for a first order reaction as the transition from the precursor into the final state is expected to be. However, for the \( \text{C}_2\text{H}_4/\text{Si}(001) \) system, it has been shown by means of room temperature STM measurements that the sticking probability significantly drops at 0.5 ML coverage, i. e., when every second dimer is reacted by a \( \text{C}_2\text{H}_4 \) molecule. Locally ordered (2 × 2) and (2 × 4) structures are then observed.13 Only towards much higher ethylene dosage, a full monolayer coverage with every Si dimer covered by one ethylene molecule is achieved.21 With the limitation of our King and Wells experiment to rather high sticking probabilities (\( s \geq 0.02 \)), the maximum surface coverage at \( T_s \approx 300 \text{ K} \) is therefore correlated to \( \approx 0.5 \text{ ML} \). Accordingly, at lower surface temperatures, a surface coverage of \( \approx 1 \text{ ML} \) is achieved. This observation might be explained taking into account the low conversion rates \( k_a \) from precursor to final state at low temperatures,20 leading to much

\[ \text{FIG. 5.} \quad \text{Kisliuk plot of } s_0 \text{ using Eq. (6). Two data sets for two different beam energies are shown. Linear fits to the data (dashed lines) are applied for } T_s > 250 \text{ K to deduce } \varepsilon_a - \varepsilon_d; \text{ for } E_{\text{kin}} = 316 \text{ meV, the influence of an additional temperature dependence for adsorption into the precursor state is illustrated by the solid curve. The straight solid line indicates the results of Clemen et al.}^{19} \]
longer lifetimes of the precursor state when compared to the relevant timescale of our experiment. As a consequence, during the adsorption measurement only little or no adsorption into the final state takes place at lower temperatures and the whole surface is covered with ethylene in the precursor state. The latter one was calculated to be localized on one silicon atom; a higher maximum surface coverage thus seems to be plausible in this case even at low ethylene dose. Only at temperatures for which the inverse conversion rate is lower than the relevant time scale of our experiment, i. e., above 250 K, significant conversion from the precursor into the final state takes place, thus leading to the observed decrease of the apparent maximum surface coverage to about half the value when compared to the experiments at lowest temperatures. A further decrease of the apparent maximum coverage is observed in our experiment at 400 K. It can be explained by the increase of the desorption rate out of the precursor, which leads to the observed drop of the initial sticking probability. Towards higher surface coverage, the sticking probability drops further and will be too low to be detected in our King and Wells experiment.

Although there is no unambiguous spectroscopic evidence for such a very long-lived, mobile precursor state, differently bound species have been observed by means of high resolution electron energy loss spectroscopy and near-edge X-ray absorption fine structure measurements at low temperatures. Furthermore, the experiments on ethylene adsorption on a H-precovered Si(001) surface are difficult to be explained without the existence of such a mobile precursor: Mette et al. observed by means of STM that the reactivity of C$_2$H$_4$ in the two-dimer configuration is strongly enhanced in the presence of two hydrogen atoms pre-adsorbed on two neighboring Si dimers; the site specific reactivity of this configuration was found to exceed unity. That means that the reactive area is larger than the adsorption site itself, a fact which was explained by a mobile precursor which can probe several adsorption sites before its conversion into the final adsorption state.

Finally, we note that a similar mobile precursor state of C$_2$H$_4$ has been proposed for Ge(001) based on STM adsorption experiments. In contrast to C$_2$H$_4$/Si(001), a change from overall non-activated to activated adsorption at increased surface coverage was suggested for C$_2$H$_4$/Ge(001). Thus, a comparative study of the dynamics of C$_2$H$_4$ on Ge(001) and Si(001) could reveal some interesting aspects of the adsorption dynamics of organic molecules on semiconductor surfaces.

V. CONCLUSIONS

In conclusion, we found the adsorption dynamics of ethylene on Si(001) to proceed via a non-activated reaction channel which includes a long-lived precursor state. Whereas the energy dependence of the sticking probability is governed by adsorption into this precursor state, conversion of the precursor into the final state mainly determines the dependence of $s_0$ on surface temperature. Only at low surface temperature, the adsorption dynamics into the precursor state is observed to influence the temperature dependence of the sticking probability as well. At surface temperatures $\geq$ 250 K, quantitative description of the temperature dependence via the Kisliuk model was possible. The long lifetime of the precursor state allows furthermore for a higher saturation coverage at low temperatures indicating that the ethylene molecules can be more densely packed in this configuration.