Surface Molecular Chain Reaction Initiated at STM-Made Individual Active Sites

Gérald Dujardin, Andrew J. Mayne, and Franck Rose
Laboratoire de Photophysique Moléculaire, Bätiment 210, Université Paris-Sud, 91405 Orsay, France

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The tip of a scanning tunneling microscope is used to manipulate individual atoms and to create, at predetermined sites on a germanium surface, single atom vacancies whose structure permits a selective reactivity towards molecular oxygen. These atomic vacancies appear to self-regenerate after reaction with oxygen, resulting in a remarkable oxygen induced chain reaction. Measured reaction parameters, such as chain breaking probabilities, are shown to provide access to detailed site dependent oxidation and diffusion rates of the atomic vacancies. [S0031-9007(99)08930-9]

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In many instances, molecular reactions at solid surfaces have been shown to be restricted to specific active sites on the surface [1]. Therefore, the control of these active sites is an important concern in surface physical chemistry, with many applications in several technological areas ranging from heterogeneous catalysis to the fabrication of nanometer-scale structures [2–4]. Despite many efforts, the control of active sites, i.e., their detailed structure and precise location on the surface, is still very crude. Recent progress has involved analyzing the role of active sites with atomic resolution using the scanning tunneling microscope (STM) [1,5]. However such studies are limited to monitoring the influence of active sites which are naturally produced in a more or less reliable way by macroscopic preparation methods. Obviously, it would be valuable to go beyond using the STM for probing only the reactivity of existing active sites and to use the STM to both fabricate at will and test active sites with atomic-scale control. Indeed, it has become conceivable to create individual active sites at predetermined places on a surface by using the STM as an atomic manipulator [6,7]. In several previous studies, the STM has been used to pattern and to probe reactive areas on passivated surfaces [2–4]. Although not performed at individual atomic sites, these studies have demonstrated that nanometer-scale structures can be built by this method.

The main issue in studying the reactivity of STM-made individual active sites is to be able to not only create active sites at will, but moreover to initiate new types of molecular reactions which would not normally occur on the surface. In particular, this would offer a unique opportunity to understand how a surface molecular reaction, starting at a specific active site, can expand over the surface. Indeed, there have been several attempts to explore how surface molecular reactions propagate by progressive structural transformations of the surface [5,8,9]. However, the understanding of such surface reactions has been limited by the unknown nature of the initial active sites and surface transformations.

We report here the first study of a surface molecular reaction initiated by controlled atomic-scale fabrication of individual active sites. The tip of a STM is used to create, at predetermined sites on a germanium surface, single atom vacancies which are shown to selectively react towards molecular oxygen. A remarkable oxygen induced chain reaction is triggered at these active sites and propagates over the surface through the self-regeneration of the atomic vacancies after reaction with oxygen. Quantitative insights into this chain mechanism are obtained by measurements of the chain breaking probabilities and provide interesting site dependent oxidation and diffusion rates of the atomic vacancies.

Studying the reaction of oxygen at individual atomic sites of the Ge(111)-$c(2 \times 8)$ surface has been chosen as the prototype experiment because the clean and regular Ge(111) surface is known to be essentially inactive to oxygen [10]. It is therefore especially challenging to create individual active sites on this surface that are reactive towards oxygen.

Room temperature STM experiments are performed in an ultrahigh-vacuum chamber where regular Ge(111)-$c(2 \times 8)$ surfaces as shown in Figs. 1(a) and 1(b) are prepared using the method described elsewhere [11]. In Fig. 1(a), the unoccupied state (positive sample bias) STM topograph shows the rows of germanium adatoms from the outermost layer of the Ge(111)-$c(2 \times 8)$ surface [12], whereas in Fig. 1(b) the rest atoms are the most prominent in the simultaneous occupied state (negative sample bias) topograph of the same area. In a preliminary experiment, we verified, by imaging the surface at both positive and negative sample bias after high oxygen exposures that the clean regular Ge(111)-$c(2 \times 8)$ surface is indeed inactive to oxygen although oxygen is known to react at some specific defect sites (not shown here) [10]. The sticking coefficient of O_2 has been estimated here to be less than 10^{-5}.

Fabricating an individual active site requires the creation, with the STM tip, of a specific local atomic arrangement capable of enhancing the sticking of molecular oxygen. The design of this atomic arrangement is facilitated by the fact that oxygen is known to preferentially react at atomic sites having a more metal-like character, that is to say, a higher local density of electronic states near the Fermi level [13]. Ideally, this metal-like character

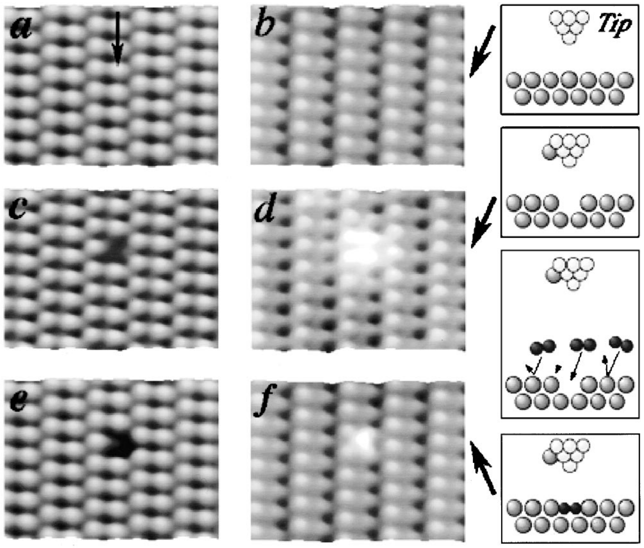

FIG. 1. 75 × 55 Å STM topographs of the Ge(111)-$c(2 \times 8)$ surface. (a), (c), and (e) are unoccupied state images taken at positive sample bias (+1 V, 1 nA tunnel current) whereas (b), (d), and (f) are occupied state images taken simultaneously at negative sample bias (−1 V, 1 nA tunnel current). (a) and (b) show the clean surface—the arrow in (a) indicates the adatom which was selectively extracted; (c) and (d) show the same area of the surface after the creation of the adatom vacancy; (e) and (f) show the same vacancy after exposure to 1 L O_2. The four diagrams on the right-hand side show schematically the STM tip above the clean surface, after the creation of the vacancy, and during and after the exposure of the surface to oxygen. The oxygen is shown in dark grey and the Ge in light grey.

might be obtained whenever the surface atoms have free dangling bonds [13]. We have realized that the extraction of a single germanium adatom from the chosen atomic site of the regular surface can produce such an atomic arrangement by releasing the dangling bonds of the three underlying Ge atoms [12]. The procedure used to extract a single Ge adatom with the STM tip is the direct STM tip-surface contact method which has been described previously [14]. An adatom vacancy created by this method is shown in Figs. 1(c) (unoccupied states) and 1(d) (occupied states).

The chemical activity of such a modified atomic site has been tested by exposing the surface to 1 L (1 L = 1 langmuir = 5×10^{-9} torr during 200 s) of gas phase oxygen. For this, the tip is withdrawn a few microns from the surface, molecular oxygen is introduced into the UHV chamber, and the same area of the surface is imaged immediately afterwards with the STM to examine the reaction products. As shown in Fig. 1, the modified atomic site is the only one on the surface which has reacted with oxygen. In the unoccupied state STM topographs [Figs. 1(c) and 1(e)] the reacted active site appears much darker. The reaction is seen more clearly in the occupied state STM topographs [Figs. 1(d) and 1(f)]. Initially, the active site appears brighter, the four spots corresponding to the rest atom sites surrounding the adatom vacancy [Fig. 1(d)]. After reaction, the active site has a markedly different appearance [Fig. 1(f)] comprising a single bright spot located at the initial missing adatom site. These differences enable us to unambiguously distinguish between unreacted and reacted active atomic sites. Another major difference is that the active atomic site slowly diffuses on the surface [15] due to thermally activated hopping of neighboring adatoms to the vacant site. Once the active site has reacted, this hopping is no longer possible and the reacted active site appears to be stable indefinitely. Indeed, further oxygen exposures do not modify this reacted site. The sticking coefficient of O_2 molecules on the active sites has been found to be close to unity (1 and 0.8 for adatom vacancies surrounded by three and four rest atoms, respectively, see later), i.e., more than 5 orders of magnitude higher than for other surface sites. This illustrates the extreme selectivity of the active site reactivity.

However, the reaction of the active atomic site is more complicated than it would at first appear. On closer examination of the surrounding area immediately after an active atomic site has adsorbed an oxygen molecule, a quite interesting oxygen induced chain reaction has been observed. This is shown in Fig. 2 which displays a sequence of STM topographs of the same area of the surface at different times. Figure 2(b) shows the initial active site, i.e., a single adatom vacancy [produced with the STM tip at the selected site in Fig. 2(a)]. After a 1 L exposure of O_2, the active site has adsorbed an O_2 molecule [the darker site in Fig. 2(c)]; however, a new single adatom vacancy has appeared nearby. We are sure that this new site is a single adatom vacancy since it slowly diffuses on the surface with time [Fig. 2(d)]. The single adatom vacancy in Fig. 2(b) looks slightly different (the surrounding adatoms are brighter) from those in Figs. 1(c), 2(c), and 2(d), most probably due to some tip change during the experiment. From many tens of such experiments there is evidence that the reacted site is located exactly where the primary active site was just before the O_2 exposure. Furthermore, the secondary vacancy is spontaneously created by the O_2 adsorption reaction itself at the closest adatom site even through it diffuses away afterwards. As a consequence, if one repeats the O_2 exposure, a chain reaction can be produced. The secondary vacancy will adsorb a molecule, become a fixed reacted site, generate a third vacancy, and so on. However this chain reaction may be broken at some point. This is illustrated in Fig. 2(e), which shows the result of a second 1 L O_2 exposure. The moving vacancy visible in Figs. 2(c) and 2(d) has now reacted with O_2 and produces two neighboring reacted sites, appearing dark in Fig. 2(e), which remained stable [Fig. 2(f)] without producing any new vacancy. In fact, it has been found that exposing a single atom vacancy to 1 L of O_2 can lead to one of the three following events: (i) no reaction at all; (ii) oxidation of the atom vacancy plus creation of a secondary atom vacancy; (iii) oxidation of two neighbor vacancies. The probabilities of each event (P_{nr}, P_{sv}, and

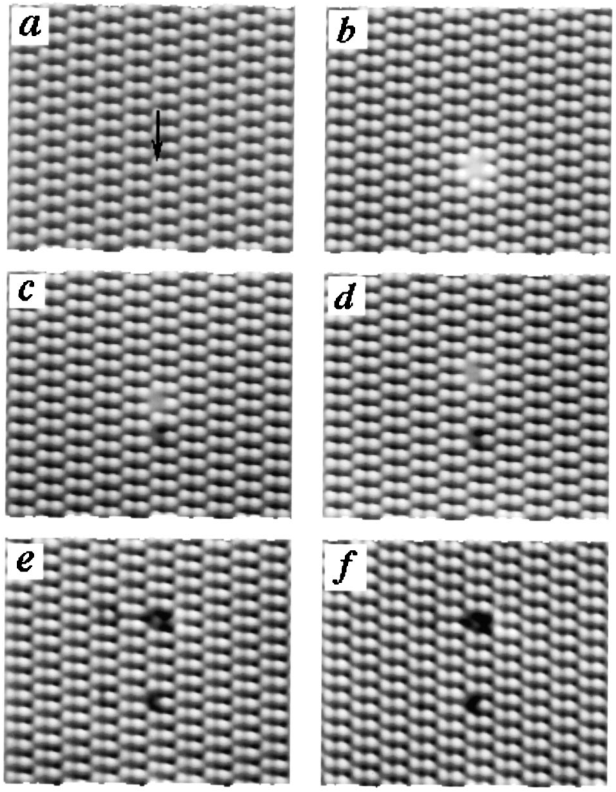

FIG. 2. A sequence of STM topographs (100 × 100 Å) of the same area of the Ge(111)-$c(2 \times 8)$ surface taken at positive sample bias (+1 V, 1 nA tunnel current) showing: (a) the clean surface (the arrow indicates the adatom which was selectively extracted); (b) the created vacancy; (c) after exposure to 1 L O_2, the oxidized vacancy (dark), and the new induced vacancy (light); (d) the induced vacancy is seen to move; (e) after a second exposure to 1 L of oxygen, the second vacancy has been oxidized as well as the neighboring site; (f) no further motion occurs. The time sequence is (a) 0, (b) 100 s, (c) 450 s, (d) 500 s, (e) 850 s, and (f) 1000 s.

P_b, respectively) are shown in Table I for initial adatom vacancies surrounded by three and four rest atoms.

The main features of the selective adsorption of an O_2 molecule on an active site and the resulting chain reaction can be understood as indicated in Fig. 3. Considering the symmetry of the reacted site in the STM topograph, we anticipate that the dissociative adsorption of the two oxygen atoms as shown in Fig. 3(c) would be appropriate. This adsorption is believed to favor the hopping of the closest Ge adatom to the primary vacant site [Fig. 3(d)]. At this point, two scenarios can happen. If another neighboring adatom hops before adsorption of a second oxygen molecule, the second vacancy will diffuse away [Fig. 3(e)] and the chain reaction will be able to develop. However, if a second O_2 molecule adsorbs before any Ge adatom can hop, the chain reaction will be broken since the structure in Fig. 3(f), consisting of two neighboring oxidized sites, appears to be stable. The key parameters of this oxygen induced chain reaction are the oxidation rates $k_{O_2}(3)$ and $k_{O_2}(4)$ and the diffusion rates $k_D(3)$ and $k_D(4)$ of adatom vacancies surrounded by three and four rest atoms, respectively. Here we assume that the oxidation rates are identical for initial adatom vacancies and for neighbor secondary adatom vacancies. The diffusion rates are those of the secondary adatom vacancies. Considering the case of a single adatom vacancy surrounded by four rest atoms and exposed to oxygen during a time t, the probability $P_{nr}(4)$ of having no reaction and the probability $P_b(4)$ of chain breaking by the creation of two neighbor oxidized sites can be calculated as follows: The probability of having no reaction during time t is the compliment of the integrated probability from 0 to t of an oxidation reaction occurring between time x and $x + dx$ where $0 < x < t$,

$$P_{nr}(4) = 1 - \int_0^t k_{O_2}(4) e^{-k_{O_2}(4)x}\, dx \,. \tag{1}$$

The breaking probability is the integrated probability over t of an oxidation reaction occurring at the initial state

TABLE I. Probabilities of events following the exposure to 1 L (5×10^{-9} torr during 200 s) of O_2 for single adatom vacancies surrounded by (a) three and (b) four rest atoms. The total number of studied oxidation events is about 100.

	P_{nr}	P_{sv}	P_b
(a)	11%	36%	53%
(b)	19%	57%	25%

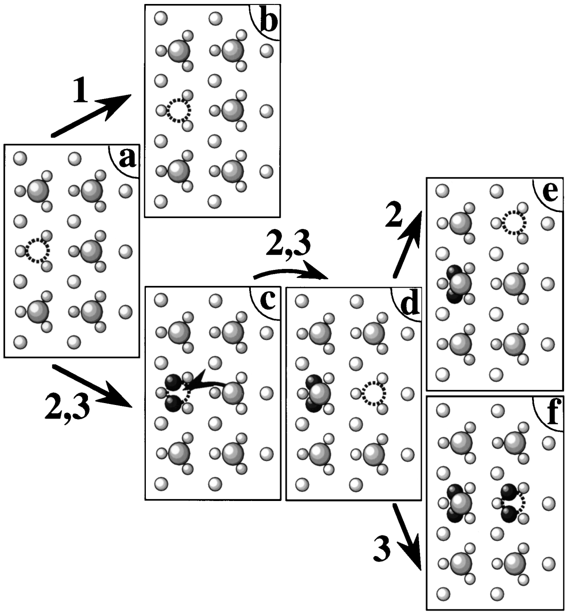

FIG. 3. A diagram indicating the possible reaction paths for (1) no reaction at all, (2) oxidation of the atom vacancy plus creation of a secondary atom vacancy, and (3) oxidation of two neighbor vacancies. Each step is labeled (a) to (f), respectively, for easier identification in the text. The oxygen is shown in dark grey, the vacancy as a broken circle, and the Ge in light grey; the sizes indicate the different layers.

between time x and $x + dx$ multiplied by the probability of a second oxidation reaction at the secondary neighbor vacancy during the time interval x to t.

$$P_b(4) = \int_0^t k_{O_2}(4) e^{-k_{O_2}(4)x} \times \int_x^t k_{O_2}(3) e^{-[k_{O_2}(3)+k_D(3)](x'-x)}\, dx'\, dx\,. \quad (2)$$

From this, $P_{nr}(4)$ and $P_b(4)$ can be calculated,

$$P_{nr}(4) = e^{-k_{O_2}(4)t}, \quad (3)$$

$$P_b(4) = \left[\frac{k_{O_2}(3)}{k_{O_2}(3) + k_D(3)}\right] \times \left[1 - e^{k_{O_2}(4)t} + \frac{k_{O_2}(4)}{k_{O_2}(3) + k_D(3) - k_{O_2}(4)} \times \left(e^{-[k_{O_2}(3)+k_D(3)]t} - e^{-k_{O_2}(4)t}\right)\right]. \quad (4)$$

Similar formulas hold in the case of a single atom vacancy surrounded by three rest atoms (by replacing 3 with 4). When deriving Eqs. (1) and (2) we have neglected the minority events, namely, for Eq. (1) the diffusion of the initial adatom vacancy followed by its oxidation and for Eq. (2) the oxidation of the initial adatom vacancy, the diffusion of the secondary vacancy, the retrodiffusion of this secondary vacancy back to its initial position and the oxidation of the secondary vacancy at its initial position. From these formulas, the results in Table I and an exposure time, t, of 200 s, we derived the following values of the rate coefficients: $k_{O_2}(3) = 1.1 \times 10^{-2}\ \mathrm{s}^{-1}$, $k_{O_2}(4) = 8.4 \times 10^{-3}\ \mathrm{s}^{-1}$, $k_D(3) = 2.2 \times 10^{-2}\ \mathrm{s}^{-1}$, and $k_D(4) = 1.2 \times 10^{-3}\ \mathrm{s}^{-1}$.

To the best of our knowledge, this is the first site dependent measurement of a diffusion rate. The $k_D(3)$ value is very close to the mean value of the hopping rate of single atom vacancies ($k_D = 2.5 \times 10^{-2}\ \mathrm{s}^{-1}$) determined from diffusion experiments [16]. However, the diffusion rate is almost a factor of 20 smaller for adatom vacancies surrounded by four rest atoms.

Equations (3) and (4) indicate that the propagation of the oxidation reaction is a complicated function of (i) the oxidation rates $k_{O_2}(3)$ and $k_{O_2}(4)$ which are linearly proportional to the oxygen pressure, (ii) the exposure via the exposure time t, and (iii) the temperature dependent diffusion rates $k_D(3)$ and $k_D(4)$. From this, it becomes possible to predict quantitatively how the oxidation reaction will expand over the surface when varying the pressure, the exposure time, and the temperature (although this is beyond the scope of this study).

These results demonstrate that one now has the ability to fabricate individual active sites having a selective reactivity and thus initiate new surface molecular reactions with an unprecedented atomic-scale control. In the prototype experiment described here, a new type of oxygen induced chain reaction has been shown to be triggered at the created individual active sites. The kinetic parameters of this chain reaction have been derived from the measurements of the chain breaking probabilities. This enables a detailed understanding of how the oxidation reaction can expand over the surface. From these results, the anticipation is to similarly prepare individual active sites with many other chemical or physical properties, hence providing new insights into surface physical chemistry and new technological capabilities for fabricating atomic-scale structures.

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