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Atomic-scale self-propagation of a molecular reaction on a semiconductor surface: O_2/β-SiC(100)-3×2

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The atomic-scale propagation of the reaction between molecules (O_2) and a semiconductor surface (silicon carbide) has been investigated by scanning tunneling microscopy. The results reveal a self-propagation reaction mechanism that gradually turns the initially inactive sites ($>$96% on the clean surface) into sites active to oxygen. This produces a patchwork of oxidized islands spreading over the surface. Numerical simulation of their growth (shape and dimension) as a function of further oxygen deposition supports such a self-propagation mechanism versus conventional nucleation-growth schemes. [S0163-1829(98)51524-X]

Reactions between molecules and a surface play a crucial role in many important areas of science and technology such as microelectronics, catalysis, or corrosion. In recent years, scanning tunneling microscopy (STM) has opened up unique opportunities for investigating such reactions at the atomic scale both on metallic[1–4] and semiconductor[5,6] surfaces. Metallic surfaces have very different reactive properties compared to semiconductors.[5] Indeed, on metallic surfaces, the so-called ''nucleation-growth'' and other related models have been quite successful in explaining a number of molecular adsorption reactions.[1–4] The key features of the classical ''nucleation-growth'' model are (i) the relatively high sticking probabilities of molecules on the surface, (ii) diffusion of adsorbates and/or of substrate atoms on the surface, and (iii) clustering by attractive interactions of adsorbates and/or formation of reactive substrate islands. Unfortunately, this classical ''nucleation-growth'' model often fails to explain molecular reactions on semiconductors. In fact, sticking coefficients of molecules on semiconductor surfaces are often very weak, especially so for oxygen.[6,7] It follows that the adsorption of molecules tends to be preferentially activated at atomic defect sites[6,7] and to decrease once the defect sites have all reacted.[7] Second, surface diffusion (of adsorbates and substrate atoms), which is an essential feature of the classical nucleation-growth model, is not likely to exist or to be important on semiconductors (at least at room temperature). This is related to the existence of localized surface states on semiconductors, which reduce the surface mobility as compared to metals. As a consequence one generally does not know for semiconductors how the molecular reaction starting at defect sites can further expand over the surface leading to complete surface reaction.

In this paper, we investigate, by scanning tunneling microscopy, how an oxidation reaction can propagate at the atomic scale on a cubic silicon carbide (100) surface [β-SiC(100)] exposed to successive doses of oxygen. We show evidence for a self-propagation reaction mechanism that gradually turns the initially inactive sites ($>$96% on the clean surface) into active sites. This results in the formation of a patchwork of oxidized islands on the surface. The numerical simulation of the oxidation growth further supports the validity of this self-propagating model that appears to be very different from conventional nucleation-growth mechanisms.

A β-SiC(100) surface has been chosen because silicon carbide is a very promising advanced material, especially as a refractory semiconductor for high-temperature, high-power, high-voltage, and high-frequency electronic devices and/or sensors.[8,9] In addition, it was recently shown that the Si-rich (3×2) surface is especially active to oxygen with SiO_2 formation starting already at low temperature (unlike silicon).[10] Growing layers of oxides, which is an important step in the chemistry of electronic devices, has been primarily studied by photoemission spectroscopy.[10] Furthermore, contrary to previous beliefs, it has been recently demonstrated[11,12] that very flat and well-ordered surfaces of clean β-SiC(100) can be produced. This progress has opened up the possibility of performing atom-resolved STM investigations of the initial oxidation.

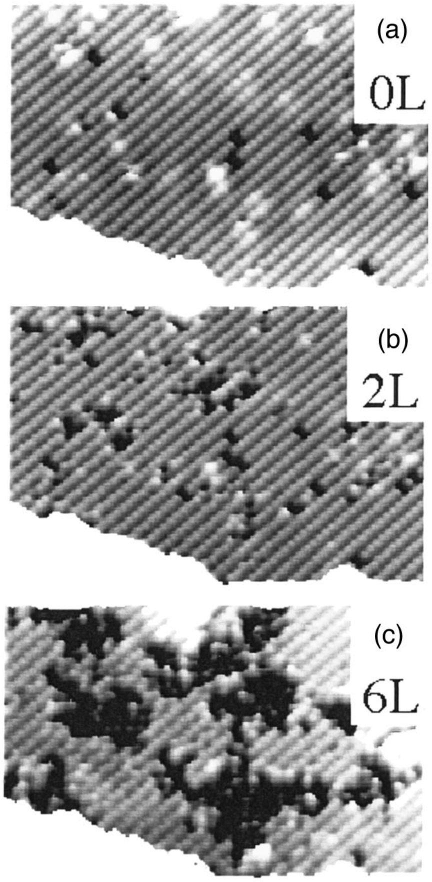

FIG. 1. 255×190 Å^2 STM topographs ($I = 0.2$ nA, $V_{\mathrm{sample}} = -2.5$ V) of the same area of a β-SiC(100)-3×2 surface; (a) clean, (b) after a 2-L O_2 exposure, and (c) 6-L O_2 exposure (cumulative).

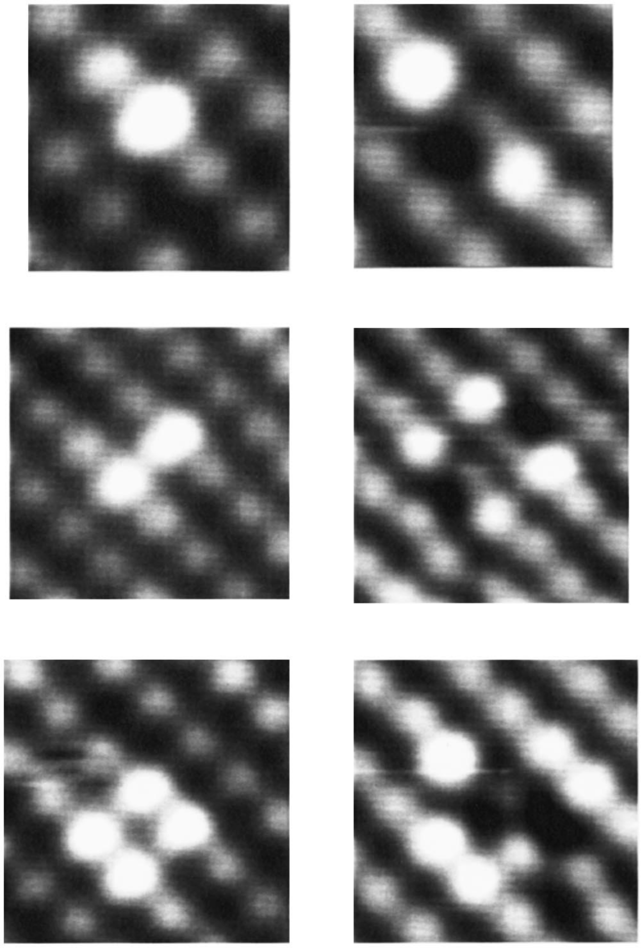

FIG. 2. STM topographs ($I = 0.2$ nA, $V_{\mathrm{sample}} = -3.5$ V) of three selected areas of the clean β-SiC(100)-3×2 surface (left side) and the same, after exposure to 0.5-L O_2 (right side).

A clean β-SiC(100) 3×2 surface is prepared in UHV (ultra high vacuum) according to the procedure described previously[11] and exposed at room temperature to successive doses of molecular oxygen. Figure 1 shows STM topographs of the same area of a clean and oxygen exposed β-SiC(100) 3×2 surface. The clean β-SiC(100) 3×2 surface is composed of dimer rows (seen in Fig. 1 as oval spots) that are ~8.5 Å apart while dimers within a row are separated by ~6 Å.[11] Several types of defects appear on the clean surface [Fig. 1(a)] including missing dimers.[11] One should also notice the existence of several brighter oval spots, which are of special interest, and which will be shown to play a central role in the reaction between oxygen and the surface. These brighter features indicate a local change in the electronic density of states of the Si dimers, probably induced either by an underlying impurity or by a local sublayer dislocation. This latter case can possibly occur by replacing C with Si in the carbon layer.

We now look at the effect of oxygen deposition on the silicon carbide surface, which can be followed in Fig. 1. The reaction is clearly nonuniform since it gives rise to several patches appearing darker in the STM topographs. One of the most striking aspects of this reaction is that upon additional O_2 exposures, the oxidized patches grow by clustering new oxidized sites around the existing oxidized sites while large areas of the surface remain unaffected. A detailed comparison of the clean and oxygen covered surfaces for the same area indicates that the oxidized patches start to grow selectively at the brighter defect sites. Figure 2 provides deeper insights into oxygen-surface interaction. The left side of Fig. 2 displays three selected areas of the clean surface exhibiting one, two, and four brighter spots, respectively. The right side of Fig. 2 shows the same areas exposed to 0.5 L of oxygen. Amazingly, some of the bright active sites of the clean surface have turned dark (or half dark), while the reaction leads to new bright sites appearing at the nearest-neighbor positions. This feature emphasizes that new bright sites can be induced along the same dimer row (Fig. 2 top, middle, and bottom) as well as along an adjacent dimer row (Fig. 2 bottom), although this latter case is less frequently observed. A closer inspection of dark oxidized sites in the occupied electronic state topographs indicates that the corresponding dimers are asymmetric since only one half of the oval spots appears dark. In the unoccupied electronic state topographs (not shown here), the whole corresponding oval is much brighter and slightly displaced (by ~0.5 Å) towards the dark half observed in occupied states. The oxidation of the Si dimer may proceed by O_2 attaching to one of the silicons followed by insertion of one or both oxygens into the Si backbonds. This is similar to the oxidation of silicon surfaces.[13] The effect of O insertion is to remove electron

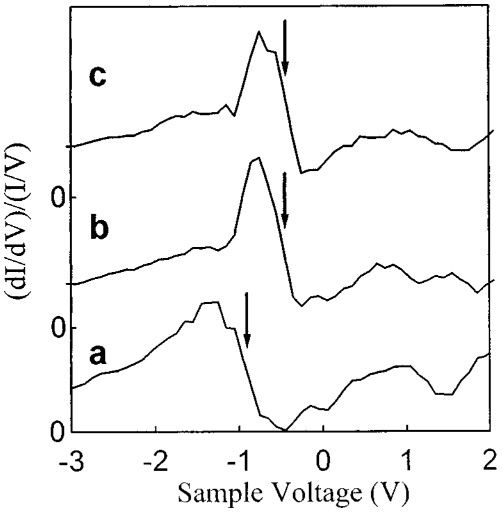

FIG. 3. $(dI/dV)/(I/V)$ curves recorded at different sites of a 0.5-L O_2 exposed β-SiC(100)-3×2 surface; (a) normal nonreacted dimer site, (b) initial nonreacted active bright site, (c) bright site induced by O_2 absorption.

density from one of the silicons giving the half dark-half bright appearance of the oxidized dimer that we observe.

These results (Fig. 2) illustrate an atomic-scale model of a self-propagating mechanism that explains the clustering of oxygen influenced sites (Fig. 1). In this model, the oxygen molecule adsorbs preferentially on the brighter active sites of the clean β-SiC(100) surface, which turn dark upon adsorption of oxygen. Each reacted site (dark sites in Fig. 2) induces one or several new bright active sites on neighboring silicon dimers. These new sites are now active towards further O_2 molecule adsorption and therefore contribute to the step-by-step growth of the oxidized islands.

In order to gain insight into the electronic nature of these defects that seem to play a central role in the oxidation process, we perform scanning tunneling spectroscopy[14] (STS) at various sites of the clean and oxygen modified areas. STS is known to be a very powerful probe of the local electronic structure.[14] $I(V)$ characteristics, especially the $(dI/dV)/(I/V)$ curves, reflect the local electronic density of states. In Fig. 3, one can easily deduce, by a simple visual inspection, that the initially brighter sites of the clean surface and the oxygen-induced bright sites have exactly the same spectroscopic signatures. This very interesting feature evidently suggests that both sites have similar electronic properties, and play the same role in the reaction between oxygen and the surface.

It is now interesting to compare the respective ''electronic'' signatures of active (bright) and nonactive (normal) sites. One can deduce from Fig. 3 that the active brighter sites have occupied valence states closer by 0.5 eV to the Fermi level than other normal sites on the β-SiC(100) surface. Molecular chemisorption on a surface requires electron transfer from the substrate to unoccupied molecular orbitals.[15–17] Such a charge transfer is favored by occupied valence states of the substrate lying close to the Fermi level,[15] which correlates with the present observation (Fig. 3). This neatly explains why these β-SiC(100) brighter surface sites, which have valence states closer to the Fermi level, preferentially react with oxygen.

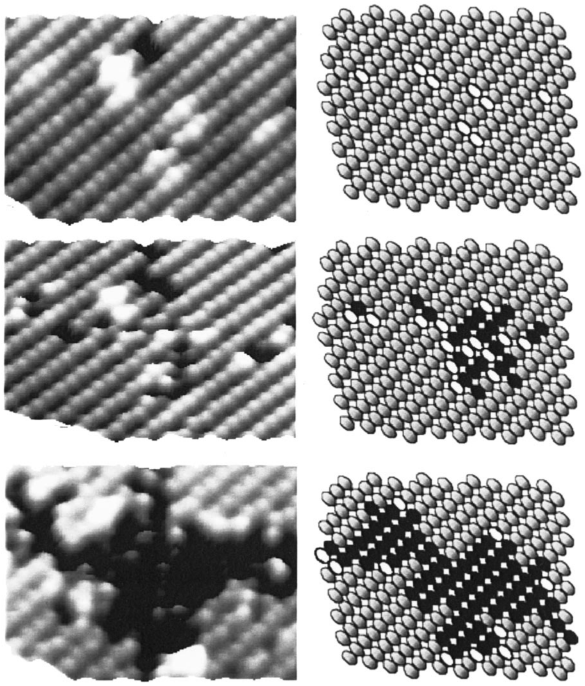

FIG. 4. Left side: 105×77 Å^2 STM topographs ($I=0.2$ nA, $V_{\text{sample}}=-2.5$ V) of the same area of a β-SiC(100)-3×2 surface; clean (top), after exposure to 2-L O_2 (middle) and a cumulative 6-L O_2 exposure (bottom). The 2-L topograph has 22 reacted dark sites and the 6-L topograph has 79 reacted dark sites. Right side: corresponding simulation of the growth of the reacted area. White ovals represent active bright sites, gray ovals represent nonreacted normal silicon dimer ovals, and black ovals represent oxidized sites. The 2-L simulation (middle) shows 22 reacted oxidized sites, and the 6-L simulation (bottom) shows 75 oxidized sites.

In order to substantiate quantitatively this self-propagating reaction model, we perform statistical simulations of oxidized patch surface growth and correlate the results with the experimental data. For a given oxidized patch recorded with the STM as a function of the O_2 exposure (Fig. 4), we first locate the initial bright active site positions on the clean surface. We then simulate the oxygen adsorption by selecting at random which active site is going to adsorb an oxygen molecule. The experimental O_2 exposure is simulated by steps of 0.1 L. At each step, the adsorbing probability of an O_2 molecule is $0.1Sn_a$, S being the sticking coefficient and n_a the total number of active sites. Once an active site has adsorbed a molecule, we again select at random which neighbor site(s) is going to become active, with a mean number $n_\parallel$ and $n_\perp$ for unoxidized neighboring sites along and perpendicular to the same silicon dimer row, respectively. We then repeat the simulation until we reach the experimental O_2 exposure, $S=1$, $n_\parallel=1.13$, and $n_\perp=0.37$ parameter values are directly deduced from the comparison between STM topographs of elementary active sites recorded before and after low O_2 exposure (0.5 L) (Fig. 2). Note that there is no adjustable parameter in the simulation. It is therefore quite remarkable that the simulated and experimental oxidized patches fit very well (Fig. 4). Within statistical deviations, the overall shapes are well reproduced by the simulation. As shown in Table I, the agreement is not only qualitative but moreover quantitative if we consider the total

TABLE I. Comparison between the observed number of oxidized sites for four selected patches and the simulated growth using the same number and distribution of initial bright sites (clean). The first three patches are on a large flat terrace and the fourth is on a small island having only 68 dimers; here the experimental boundaries are imposed on the simulation. The simulations are averaged over at least ten runs.

		Clean	2 L	6 L
Patch 1	Experiment	8	22	79
	Simulation	8	21±2	74±2
Patch 2	Experiment	3	6	48
	Simulation	3	8±1	50±5
Patch 3	Experiment	5	13	44
	Simulation	5	13±2	48±3
Patch 4	Experiment	7	18	47
	Simulation	7	17±3	49±3

number of oxidized sites at each O_2 exposure. Although a limited number of oxidation patches are presented here, we have investigated the growth of many other patches, not only on wide flat terraces (patches 1–3) but also near step edges and on small islands of the SiC surface (patch 4). We emphasize that within our model, gas phase O_2 molecules directly react with bright surface sites. This implicitly rules out the existence of a mobile molecular precursor on the surface having a non-negligible mean free path ($>$1–2 interatomic distances). This assumption is justified for several reasons. First, we found no evidence on STM images of any mobile precursor. Second, if the mobile precursor existed, the oxidation growth near step edges and on very small islands ($<$50 silicon dimers) would be much reduced as compared to flat terraces. On the contrary, in all cases the propagation of the oxidation reaction has been found to fit well with our self-propagation model.

In conclusion, we have investigated the atomic-scale interaction of molecules (O_2) with a silicon carbide surface. We have discovered an interesting self-propagation phenomenon: an oxygen molecule initially reacts to an active defect site and induces one or several new neighboring active sites that will themselves react with further O_2 molecules contributing to the spreading of the surface oxidation. As a result of this self-propagating effect, the reaction of oxygen molecules with the surface is found to develop as a patchwork of oxidized islands. This self-propagation nature is further supported by the simulation of oxide patch growth as a function of oxygen exposure, which is in excellent agreement with the experiments. We emphasize that the self-propagation mechanism is markedly different from the classical nucleation-growth models that have been developed to explain molecular reactions on metals. Note also that this self-propagation effect is probably not limited to silicon carbide oxidation only, although the detailed mechanisms may be different for other molecule-semiconductor systems.

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