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Dissociative Adsorption of Oxygen on Aluminum

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Abstract—The initial steps of aluminum oxidation were studied by scanning tunnel microscopy (STM). A procedure was proposed and implemented for obtaining information on the migration of atoms formed by dissociative adsorption from the measurement of distances between adsorbed atoms visible in STM images.

INTRODUCTION

The dissociative adsorption of diatomic molecules on metal surfaces is a fundamental heterogeneous process playing an important role in catalysis. Adsorption of oxygen on the Al(111) surface is the simplest example of processes of this kind and has been considered in a great number of publications (for example, see reviews [1–3]). However, although this system is relatively simple (the absence of *d* electrons from aluminum), there is a number of unresolved problems and inconsistent data. Among these problems are the following: (a) reasons for a very low probability of dissociative adsorption ($S \sim 0.01$ at room temperature), (b) the occurrence of a precursor, (c) the nature of adsorption sites, (d) chemisorption energy redistribution pathways, etc.

In this work, we studied the initial steps of aluminum oxidation by scanning tunneling microscopy (STM). The advantage of this technique consists in the visualization of spatial distributions of adsorbed particles. This provides the means for tackling one of the fundamental questions concerning the mechanism of processes under consideration: Is the migration of "hot" oxygen atoms (atoms with considerable excess of translational energy) over long distances (approximately a few tens of angstrom units) from the site of trapping of the O_2 molecule from a gas phase possible? Different authors who used the same procedure of STM measurements in their experiments gave mutually exclusive answers to this question.

Earlier studies [4, 5] demonstrated that adsorbed oxygen atoms appeared as hollows up to 0.6 Å in depth in the topographic images of the Al(111) surface. Published data [6] on the redistribution of chemisorption energy attracted the greatest interest. Brune *et al.* [6] interpreted the results of these STM studies as follows: Oxygen atoms formed by dissociative adsorption on Al(111) "scattered" for at least 80 Å from each other. The hot-adatom mechanism was proposed in explanation of this phenomenon. According to this mechanism, the released energy of chemisorption (~5 eV/atom) was transformed into the kinetic energy of the translational motion of adsorbed atoms on the surface.

These results initiated the appearance of theoretical calculations [7], in which the mobility of hot oxygen atoms along the Al(111) surface was studied by molecular dynamics methods. The calculations demonstrated that the average distance between the atoms of a dissociated molecule is no greater than 10–15 Å even in the case of the complete conversion of chemisorption energy into the kinetic energy of atoms.

In 2001, Schmid *et al.* [8], based on the image shape analysis of several oxygen atoms adsorbed on Al(111) in topographic images, concluded that pairs of closely spaced atoms can produce merged images, which may be interpreted as the image of a single atom. In this case, they concluded that the average interatomic distance after dissociation is no greater than 5 Å.

The contradiction in the conclusions drawn by Brune *et al.* [6] and Schmid *et al.* [8] is due to the procedures used in these studies. In the former study [6], a problem appeared based on the need to distinguish between atoms generated from one molecule and those generated from different molecules. To solve this problem, Brune *et al.* [6] performed the measurements at very low surface coverages ($\Theta \sim 0.001$). In this case, scanning was performed over a large surface area (50×70 nm) in order to collect sufficient statistics and, consequently, the resolution was lost. In the latter study [8], scanning was performed over a smaller surface area; however, data were insufficient for the statistical processing of results at a low coverage.

To overcome these difficulties, it is necessary to operate under conditions when the path lengths of hot atoms are comparable to the average distance between adsorbed atoms. For this purpose, a procedure is required that furnishes information on the migration of hot atoms formed by dissociative adsorption from the measurement of interatomic distances. This procedure is proposed and implemented in this work.

EXPERIMENTAL

A commercial Omicron tunnel microscope was used. The experiments were performed in an ultrahigh-vacuum system ($P \sim 10^{-10}$ Torr) at room tempera-

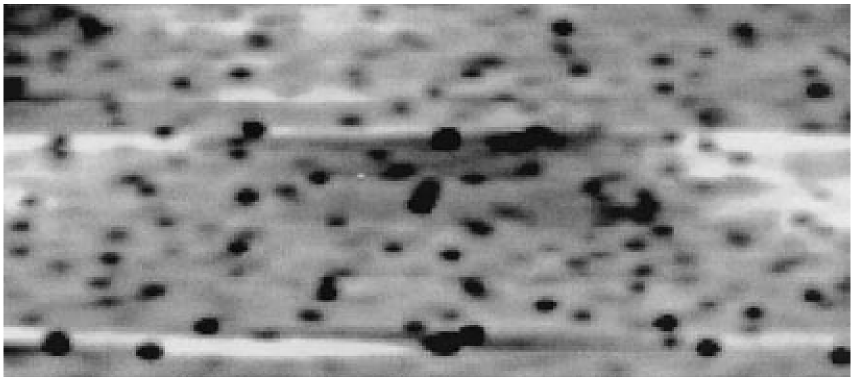

Fig. 1. Al(111) surface after exposure to oxygen (20 langmuir units). Picture size: 26 × 67 Å. Scanning parameters: $I = 5$ nA; $U = 0.8$ V.

ture. Surface preparation was performed by mechanical polishing of samples followed by electrochemical etching. Sample cleaning in an ultra-high-vacuum system was performed by 1000-eV argon-ion bombardment for many hours followed by cycles of 600-eV ion bombardment and annealing at 800 K. After sample preparation, a surface region of 3 × 7 nm was found in which the roughness was no higher than 0.2–0.3 Å [9].

RESULTS AND DISCUSSION

The atomic resolution on the test surface was reached only in very rare cases. Figure 1 shows a selected region of the surface of aluminum after a short-time exposure to oxygen (20 langmuir units). In this case, we failed to obtain the atomic resolution of the lattice; however, adsorbed atoms were clearly identified.

The results shown in Fig. 1 were used for reconstructing the distribution function of distances between the nearest adsorbed atoms of oxygen. Figure 2 (curve F_e) demonstrates the distribution function obtained from these data.

Reconstruction of Distance Distribution for the Separation of Atoms in Elementary Events of Dissociative Adsorption

We describe a method for the reconstruction, from STM data, of the distribution function for the distances between two O atoms formed by the dissociative adsorption of the O_2 molecule. This method is based on distribution functions for any nearest oxygen atoms (visible in topographical images).

An elementary event in the dissociative adsorption of a diatomic molecule is characterized by a site of collision between the molecule and the surface and by adsorption sites of the resulting atoms. The atomic coordinates and all distributions of atoms (for example, the distribution functions F_e for distances to the nearest neighbor) are directly determined in STM experiments. The challenge is to find the distribution for distances between two O atoms formed by the dissociative adsorption of a molecule from the results of F_e measurements. At low surface coverages, individual elementary events of dissociative adsorption can be considered independent. Initially, we consider this case.

Assume that the dissociative “attachment” of N_M molecules occurs at a surface (S is the surface area). Let us introduce effective radii (r_1 and r_2, respectively) to characterize surface areas per molecule and per atom: $r_1 = [S/(\pi N_M)]^{1/2}$, $r_2 = r_1 2^{-1/2}$. If the average distance between atoms (r_0) in the dissociative attachment of a molecule is

$$r_0 \ll r_2, \qquad (1)$$

and atoms are primarily arranged as isolated pairs on the surface, the function F_e can be measured directly.

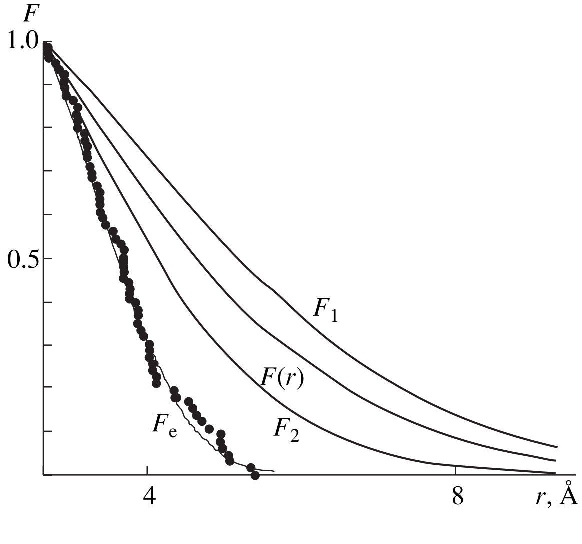

Fig. 2. Integral distribution functions for distances between nearest atoms on the surface: $F_e(r)$ is the experimental function, $F_1(r)$ is the function calculated on the assumption that $r_0 \ll r_2$, $F_2(r)$ is the function calculated on condition that $r_0 \gg r_2$, and $F(r)$ is the reconstructed integral distribution function for distances between atoms formed in an elementary event of dissociation.

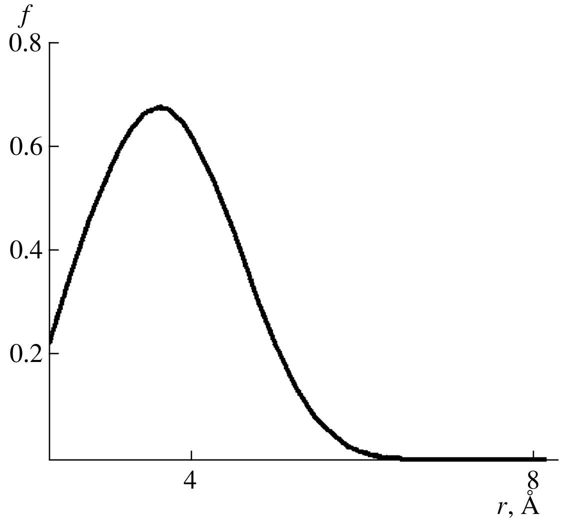

Fig. 3. Differential distribution function for distances between atoms formed in an elementary event of dissociation.

As mentioned above, this case is difficult to implement in STM experiments.

Let us consider the case of high coverages when condition (1) is violated; that is, the nearest neighbor of each adatom on the surface may be either an atom formed from the same parent molecule or an atom formed in the dissociation of another molecule. We introduce three integral distribution functions:

$$F(r) = \int_r^{\infty} f(r')\mathrm{d}r'$$

(where $f(r')$ is the distribution function sought); $F_e(r)$ is the experimentally determined integral distribution function for distances from an atom to another (nearest) atom on the surface; $F_a(r)$ is the integral distribution function for distances from an atom to the nearest of the atoms generated from other molecules. Then, $F(r)$ and, correspondingly, the sought for function $f(r) = -\mathrm{d}F/\mathrm{d}r$ can be found from the equation

$$F_e(r) = F(r)F_a(r). \quad (2)$$

Thus, the function $F_a(r)$, which depends on the sought for function $f(r)$, should be known in order to reconstruct the function $f(r)$ from experimental data. We consider that the sites of collisions between molecules and the surface are randomly distributed. It is obvious that on condition (1) the function $F_a(r)$ has the form[1] $F_a(r) = F_1(r) \equiv \exp[-(r/r_1)^2 + (r_a/r_1)^2]$ and is equal to unity in the main domain of variation of $F(r)$: $r \sim r_0$, so that, as mentioned above, $F(r) = F_e(r)$. In the other limiting case at $r_0 \gg r_2$, $F_e(r) = F_a(r)$ in the main domain of variation and, assuming a random distribution of atoms, $F_a(r) = F_2(r) \equiv \exp[-(r/r_2)^2 + (r_a/r_2)^2]$. At an arbitrary ratio between the values of r_0 and r_1, we can assume that

$$F_2(r) < F_a(r) < F_1(r). \quad (3)$$

We use Eq. (2) and formulate a procedure for adapting $F_a(r)$ and $F(r)$ distributions. We introduce the minimum distance r_a (the value of $r_a = 2$ Å was used in calculations the results of which are shown in Figs. 2 and 3).

The distribution function for the centers of segments between the positions of atoms generated from one molecule has the form

$$\mathrm{d}f_M(r) = \frac{\mathrm{d}x\mathrm{d}y}{S_M N_M} = \frac{2\pi r\mathrm{d}r}{S_M N_M}, \quad (4)$$

where N_M is the number of adsorbed molecules, and S_M is the average surface area per molecule.

Let us express the distribution function $F_a(r)$ for distances from an atom (placed at the origin of the coordinates) to the nearest atoms formed from other molecules in terms of the function $f(r)$.

For this purpose, we initially find the distribution function of atoms with consideration for only one (closer to the origin of the coordinates) of the two atoms formed from one molecule:

$$\mathrm{d}f_1(r) = \mathrm{d}f_M(r)^2\iint_{S_\rho} f'(\rho)\mathrm{d}\vec{\rho} \equiv \chi(r)\mathrm{d}f_M(r), \quad (5)$$

where S_ρ is the surface region in which the center of the system of two atoms can occur on condition that the atom closest to the origin of coordinates occurs at distance r from this origin; a factor of 2 is related to the possibility of permutation of atoms generated from one molecule. In this case, $f(r) = \frac{\pi r}{2}f'(r/2)$; that is, $f'(r)$ gives the distribution of distances between atoms and the center of the atomic system rather than between one another. This equality results from the following relationships for integral distribution functions:

$$F'(r) = \int_r^{\infty} 2\pi f'(r')r'\mathrm{d}r'; \quad F(r) = \int_r^{\infty} f(r')\mathrm{d}r'; \quad (6)$$
$$F(r) = F'(r/2).$$

From simple geometric relations, we obtain

$$\chi(r) = 2\left[1 - 2\int_{r_a}^{r} f'(\rho)\arccos(\rho/r)\rho\mathrm{d}\rho\right]. \quad (7)$$

We introduce the following functions:

$$\int_r^{R} 2r'\chi(r')\mathrm{d}r' \equiv g(r)R^2, \quad (8)$$

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[1] Here, we introduce the distance r_a of the closest approach between atoms for generality.

$$\int_{r_a}^{r} 2r'\chi(r')\mathrm{d}r' \equiv \nu(r), \tag{9}$$

where R is the entire surface radius.

The probability of atoms occurring at a distance greater than r from the origin of the coordinates is

$$F_{\mathrm{a}}(r) = \left[\frac{g(r)}{g(r_{\mathrm{a}})}\right]^{N_{\mathrm{M}}} = \left[1 - \frac{\nu(r)}{g(r_{\mathrm{a}})R^2}\right]^{N_{\mathrm{M}}}$$
$$= \left[1 - \frac{\nu(r)}{g(r_{\mathrm{a}})Nr_1^2}\right]^{N_{\mathrm{M}}} \xrightarrow[N_{\mathrm{M}} \to \infty]{} \exp\left[-\frac{\nu(r)}{g(r_{\mathrm{a}})r_1^2}\right]. \tag{10}$$

It can be seen that inequality (3) is obeyed in this case. The procedure proposed consists in the following: A function $F(r)$ that satisfies condition (3) and depends on some parameters is chosen. We vary these parameters so that the functions $F_{\mathrm{a}}(r)$ from (2) and (10) are equal to each other. As a result, we determine $F(r)$ and $f(r)$.

In this work, in the reconstruction of the distribution $f(r)$ from the results of STM measurements, which are shown in Fig. 1, the function $F(r)$ was taken in the form

$$F(r) = \exp\left[-\left(\frac{r - r_{\mathrm{a}}}{r_{\nu_4}}\right)^4 - \left(\frac{r - r_{\mathrm{a}}}{r_{\nu_2}}\right)^2\right], \tag{11}$$

where r_{ν_2} and r_{ν_4} are varied parameters.

Figure 2 shows the integral distributions $F_{\mathrm{e}}(r)$, $F_1(r)$, and $F_2(r)$. It can be seen that $F_{\mathrm{e}}(r) < F_2(r)$ over a large domain of variation; consequently, $F_{\mathrm{e}}(r)$ is noticeably different from $F_{\mathrm{a}}(r)$. This difference allows us to perform the above procedure for the self-consistent reconstruction of integral distribution function $F(r)$. Figures 2 and 3 illustrate the results.

The reconstructed function $f(r)$ exhibits a maximum at $r \sim 4$ Å. This suggests that hot oxygen atoms are separated by distances no greater than one or two lattice constants; this result is consistent with published data [8].

CONCLUSIONS

The results of this work completely resolve the contradiction that appeared after publications by Ertl and Schmid. Although cluster-size distribution [9] is similar to Ertl distribution, the average interatomic distance (the distance between oxygen adatoms formed in an elementary event) is close to the value reported by Schmid. The average value of 4 Å obtained in this work is almost equal to the surface lattice constant of Al(111); this fact excludes formation of hot atoms in the event of the heterogeneous dissociation of oxygen.

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