Theory of Self-Diffusion at and Growth of Al(111)

Roland Stumpf and Matthias Scheffler
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14 195 Berlin-Dahlem, Germany
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We studied the self-diffusion at clean, flat, as well as stepped, Al(111) surfaces using density-functional theory. There are two important steps on fcc (111) surfaces, typically labeled according to their {111} and {100} microfacets. We calculated the formation energies of these steps, and analyzed the diffusion perpendicular and parallel to them. We discuss the general profile of the diffusing-atom potential-energy surface and identify the role of "normal" hopping and exchange mechanisms of diffusion at steps. From these results the equilibrium shape of islands and the temperature dependence of the island shapes under growth conditions are predicted.

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Any *realistic* surface contains steps and the understanding of adsorption, vacancy formation, surface diffusion, crystal growth, and sputter removal remains grossly incomplete as long as the influence of steps is not taken into account properly. Some effects related to self-diffusion and steps at surfaces have been modeled *phenomenologically* by continuum equations (see, for example, Ref. [1] and references therein) and some *quasiclassical, microscopic* ideas were illustrated by embedded-atom calculations [2–5]. Although many aspects can be learned from these calculations, it remains unclear when the results are physically reliable and when not. This is so in particular for a diffusing atom because different atomic arrangements may encounter a different type of chemical binding. Then quantum mechanics becomes important and it is necessary to take the quantum-mechanical kinetic-energy operator into account which, for example, actuates the shell structure of atoms and the formation of bonding and antibonding states in polyatomic aggregates. Neither the kinetic-energy operator nor a self-consistent treatment of the electronic charge density has been considered in calculations relevant to self-diffusion at stepped surfaces so far [6]. The main reason why practically no accurate calculations exist for stepped surfaces (the only exceptions are given in Refs. [6–8]) is that the computational task for such studies is significant.

In this paper we report such calculations for the self-diffusion at flat and at stepped surfaces and for step-formation energies. The calculations were performed using density-functional theory (DFT) together with the local-density approximation (LDA) for the exchange-correlation energy, modeling the surfaces by supercells. In order to ensure a negligible adatom-adatom interaction we used a coverage of 1/16. We investigated the flat Al(111) surfaces, surfaces vicinal to (111), four atom wide and infinitely long terraces (stripes and grooves), and triangular islands on Al(111). The numerical accuracy of the reported total-energy differences (with respect to the plane-wave basis set, the **k** summation, and the size of the supercell) was carefully controlled (for details see [9,10]). Our method determines the electronic ground state by minimizing the electronic free energy [10] in the iterative way suggested by Car and Parrinello [11], and simultaneously the atomic structure is optimized using damped dynamics. It may be worth mentioning that we investigated sizes of supercells equivalent to 448 atoms which compares in size to the large-supercell calculations used to study the Si(111) surface on parallel computers [12]. However, in contrast to these studies our calculations were performed on a < $15 000 workstation. The method and computer code are published in Ref. [13].

One interesting aspect of fcc (111) surfaces is that there are two important types of close packed steps. Their geometry can be recognized by the step orientation and the steepest microfacet which is indicated in Fig. 1. "Simple bond-cutting" theories [14] give that the step-formation energy of these two steps should be degenerate and (the slightly more sophisticated) theories such as the effective-medium method yield that the {111} faceted steps are slightly less favorable than the {100} faceted steps. This is in contrast to full DFT-LDA calculations (see below) which give that the {111} faceted steps have the lowest formation energy. As a consequence, the equilib-

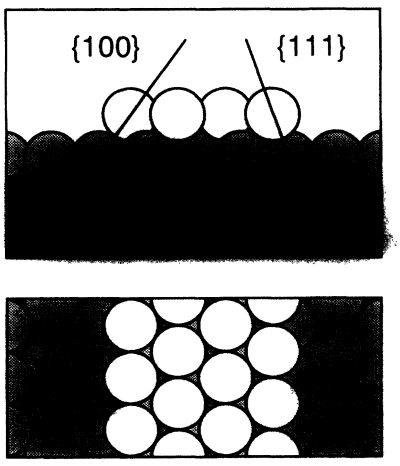

FIG. 1. Side view (upper picture) and top view (lower picture) at a four-atom wide, in ⟨110⟩ direction oriented terrace stripe on Al(111). Note the different step types at the left terrace edge (the {100} microfacet) and right terrace edge (the {111} microfacet). The two step edges are labeled as ⟨110⟩/{100} and ⟨110⟩/{111}.

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rium shape of islands is predicted to be hexagonal, where neighboring edges have a length ratio of 5:4.

We will also discuss the total-energy surface of a diffusing Al adatom at these steps. The results show that Al adatoms are attracted towards the step and that the diffusion from the upper terrace down to the lower terrace proceeds via an exchange of the adatom and a step-edge atom. This supports an earlier finding [8] that the exchange process is the rule rather than the exception. The energy barriers for diffusion parallel to step edges are found to be clearly larger than those at the flat parts of the surface or those for the diffusion from the upper terrace down. This has interesting consequences for the growth and its temperature dependence. We will estimate the different temperature regimes for three-dimensional growth, two-dimensional fractal growth, two-dimensional growth of triangular shaped islands, and two-dimensional growth of islands which have the hexagonal equilibrium shape.

Calculations of the average energy of the two step types can be performed most accurately by investigating the total energy of surfaces with terrace stripes (see Fig. 1), and comparing these results to those of the flat surface. The difference of the two step types can be obtained by investigating triangular islands adsorbed on Al(111) as these contain only one type of step. Comparing islands with 6, 10, 15, and 21 atoms we can extrapolate to the limit where the influence of the corner atoms is negligible. Table I lists the results for the total-energy differences of two triangles rotated by 60°. The data show the rapid convergence of this energy difference with island size. Dividing these energy differences into contributions from true-edge atoms and from the three corner atoms gives the energy difference of the corner atoms as 0.025 eV per atom and that of true-edge atoms as 0.017 eV per atom. From these studies we conclude that the step formation energies are $\sigma^{\langle 110\rangle/\{111\}} = 0.232$ eV per atom, and $\sigma^{\langle 110\rangle/\{100\}} = 0.248$ eV per atom. These numbers may be compared to the surface energy of the different low-index surfaces of Al which are calculated as $\sigma^{(111)} = 0.48$ eV per atom, $\sigma^{(100)} = 0.56$ eV per atom, and $\sigma^{(110)} = 0.89$ eV per atom. Thus, the energy per atom to create a step at Al(111) is about half of that to create the surface. From the step-formation energy one can directly obtain the equilibrium shape of islands by applying the Wulff construction [15]. This gives hexagonally shaped islands where the edges alternate between those with a {100} and a {111} microfacet. The calculations predict that in thermodynamic equilibrium and not too high temperatures the {111} faceted edge should be longer, and for not too small islands the edge-length ratio should be $L^{\langle 110\rangle/\{100\}} : L^{\langle 110\rangle/\{111\}} = 4 : 5$. It is interesting to note that such hexagonal islands have been observed experimentally by Michely and Comsa [16] in their STM studies of growth and sputter removal of Pt(111). These experiments show that the {111} microfacet is favored which is what we predict for Al(111). There is a quantitative difference; for Pt(111) the measured edge-length ratio is 0.66 whereas for Al our calculations give 0.81 ± 0.03. Of course, the similarity is much more than what one would have expected, as, in general, Al and Pt behave quite differently. It is interesting to notice that tips created by field evaporation and used in field-ion microscopy also frequently have the hexagonal shape with the two step types having different lengths [see, for example, Figs. 3(a) and 7(a) in Ref. [17]).

TABLE I. Total-energy difference divided by the number of edge atoms for triangular islands with only {111} and only {100} faceted steps.

No. of atoms	No. of edge atoms	ΔE (eV)
6	6	0.029
10	9	0.021
15	12	0.018
21	15	0.018

We will now analyze the total-energy surface which determines the surface diffusion and crystal growth. For example, we will study how an atom on a large island will diffuse, eventually find an edge, and possibly move down to the lower terrace. Figure 2 displays the total energy of self-diffusion at a {111} faceted step on Al(111). For any position of the generalized coordinate all the other coordinates of the diffusing atom as well as all coordinates of the other atoms of the two top substrate layers have

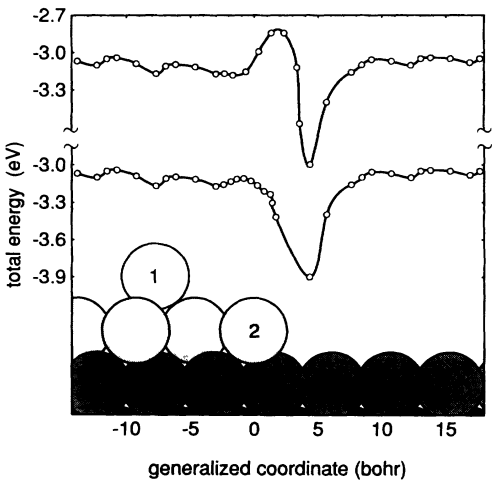

FIG. 2. Total energy along the diffusion path of an Al adatom over a {111} faceted step on Al(111). The upper curve is calculated for the "normal" hopping diffusion and the lower one for the exchange process. The generalized coordinate is $Q = X_1 + X_2$ where X_1 and X_2 are the x coordinates of the adatom labeled as No. 1 in the atomic-structure plot and X_2 is the position of a step-edge atom labeled as No. 2. The x axis is parallel to the surface and perpendicular to the step orientation. For the undistorted step $X_2 = 0$. All other coordinates of the diffusing atom and of the substrate are optimized for each position Q.

been relaxed. The upper curve in Fig. 2 displays the result obtained for the "normal" hopping diffusion, where the atom jumps over the bridge site at the ledge. The lower curve displays the results for the exchange mechanism, where atom 1 replaces atom 2, which moves to the fivefold coordinated site at the step. The energy barrier of 0.33 eV for the "hopping" diffusion is much higher than that of 0.06 eV for the exchange mechanism. It may be useful to distinguish four sections of this total-energy curve:

(1) The diffusion on the upper terrace with a weak attractive interaction towards the edge. The energy difference between a site far away and directly at the step is about 0.15 eV. This attraction is neither a result of the electrostatic interaction of the adatom and step dipoles [18], nor is it due to an elastic interaction of the adsorbate and step-induced atomic relaxations. We speculate that it is caused by an interaction of adatom- and step-induced surface states.

It is also interesting to note that the hcp hollow position is lower in energy than the fcc hollow site at low coverage. In fact, the fcc hollow and the bridge position have practically the same energy.

(2) The barrier region at the upper edge which may be preceded by a small energy minimum. In our calculations for the hopping diffusion this minimum is not more pronounced than that of the normal hcp hollow position, while for the exchange process the minimum has totally disappeared.

(3) The clear energy minimum on the lower terrace directly at the step. At this site the adatom gains an energy of 0.77 eV compared to a position on a flat part of the surface. Roughly speaking this energy gain can be understood in terms of the higher coordination of the adatom which is fivefold at the edge but threefold at a hollow site on the flat (111) surface [8].

The energy minimum for the at-step adsorption may be separated from the remaining lower terrace by a small energy barrier. In our studies for Al(111) this barrier totally disappeared.

(4) The diffusion on the lower terrace is similar to that on the upper terrace; again we find an energy gradient attracting the adatom towards the step.

The results for some important diffusion barriers for both step types are summarized in Table II. The biggest barrier of the diffusing-atom potential energy is that of an adatom adsorbed at the step edge and migrating parallel to the step. All these results have direct consequences on the temperature dependence of the growth. They could be used for a detailed Monte Carlo study but some aspects follow directly. We assume that the temperature dependence of the diffusion constant is given by $D = D_0 \exp(-E_d/k_B T)$, where E_d is the energy barrier of the considered diffusion process (see Table II). The preexponential factor D_0 is estimated from experimental and theoretical results for similar diffusion processes [5,9], which give values between 10^{-2} and 2×10^{-4} cm^2/s depending on the diffusion mechanism. Defining the temperature T_d at which a certain diffusion mechanism becomes active as that at which the adatom will jump at least once per second ($\nu_j = 1/s$) between neighboring adsorption sites a distance l apart, it follows that

$$T_d = \frac{E_d}{k_B} \ln \frac{nD_0}{\nu_j l^2}, \quad (1)$$

where for the diffusion at a step the dimensionality factor n equals 2. An error of a factor of 10 in D_0 would change the temperature T_d only by $< 10\%$. With this in mind we can use the calculated results for E_d and the estimate for D_0 [9] for a discussion of the temperature dependence of growth at a deposition rate of 10^{-2} ML/s [19].

TABLE II. Energy barriers E_d in eV for a diffusing Al adatom at perfect Al(111) and at steps.

Flat surface	hcp → hcp hopping	0.04
⊥ {111} facet	"normal" hopping	0.33
	exchange process	0.06
⊥ {100} facet	"normal" hopping	0.45
	exchange process	0.08
∥ {111} facet	"normal" hopping	0.48
	exchange process	0.39
∥ {100} facet	"normal" hopping	0.32
	exchange process	0.44

(i) At $T > 320$ K there is a lattice gas of adatoms (and also of vacancies [9]). The hexagonal equilibrium shape of islands, discussed above, should be realized, as none of the energy barriers noted in Table II implies a serious hindrance. The mass transport by the gaslike adatoms results in only two layers being uncovered.

(ii) For temperatures below 320 K the desorption of adatoms from steps is practically irrelevant (see Fig. 2). Thus, adatoms captured at a step edge will stay and the island will grow.

(iii) For 155 K$< T <$ 320 K the energy barrier for atoms on terraces to move down is still negligible and we predict layer-by-layer growth. However, the energy barriers for atoms at the step edge are becoming important with the diffusion parallel to the {100} faceted step being less hindered than that parallel to the {111} faceted step. Thus, these step edges become rough, and the island will grow faster in the direction perpendicular to the {111} faceted step edge. As a consequence the edge length of the {111} faceted steps will be reduced and the growth shape of the islands will tend towards a more triangular form with longer {100} faceted steps.

Because the energy barriers $E_d^{\parallel\{111\}}$ and $E_d^{\parallel\{100\}}$ and $E_d^{\perp\{111\}}$ and $E_d^{\perp\{100\}}$ are quite similar, the correct value of the preexponential factor D_0 may become crucial. Experiment and theory indicate that the D_0 values for exchange diffusion tend to be higher than those for hopping diffusion [5]. Therefore at low temperatures diffusion along the {100} step edge could be slower which

would favor a faster growth perpendicular to this step. Thus, some interesting changes of the growth shapes are to be expected in this temperature range.

(iv) For 25 K$< T <$ 155 K the energy barriers of diffusion parallel to both steps will prevent diffusion parallel to the steps. The diffusion at flat parts of the surface is, however, still easy and therefore the attraction of gaslike adatoms towards the steps edges is still active. As a consequence we expect that islands will be formed in a way which may be described as a "hit and stick" mechanism. Thus, the edges cannot equilibrate and fractally shaped islands with a layer-by-layer growth mode should result.

(v) At temperatures below 25 K adatoms on the upper terrace are hindered by the energy barrier to move down and may form, when they meet other adatoms, nucleation centers. We note in passing that the calculations show that an Al dimer on Al(111) is bound by 0.58 eV and is therefore stable at these temperatures. This suggests three-dimensional growth [20]. However, island edges are frayed at this temperature which may reduce the barrier, and adatoms gain energy by adsorption. We are therefore not convinced that the three-dimensional growth mode really exists for clean Al(111).

In conclusion, we presented results of accurate electronic structure and total-energy calculations which reveal several phenomena directly relevant to the description of self-diffusion at the Al(111) surface and to crystal growth. Although no experiments exist (so far) for Al(111) several similarities with other systems have been recognized. Our calculations predict that Al adatoms prefer the hcp hollow site and that they are attracted towards step edges on the Al(111) surface. The calculations show that the barrier for diffusion of Al adatoms along the {100} faceted steps is smaller than along the {111} faceted steps on Al(111). We discovered that diffusion from the upper to the lower terrace proceeds via an exchange of the on-terrace adatom with an in-the-step-edge substrate atom on Al(111). All that has been found for Ir and, in the case of the exchange, for W adatoms on Ir(111) in the field-ion microscopy studies of Wang and Ehrlich [17,21].

Furthermore, our calculations show that the energy barrier for diffusion of an Al at-step adatom parallel to the step is much bigger than that perpendicular to the step. In the temperature range where this energy barrier becomes relevant, we therefore predict fractal growth and our results suggest that fractal growth should be a common phenomenon in growth on close packed metal surfaces. In experiment fractal growth was found, e.g., for Pt on Pt(111) [22] and for Au on Ru(0001) [23]. For the growth of Pt(111) also the influence of the different mobility of adatoms at the two kinds of step on the island shape has been observed [22].

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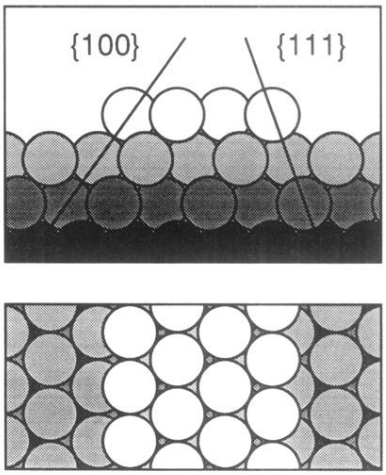

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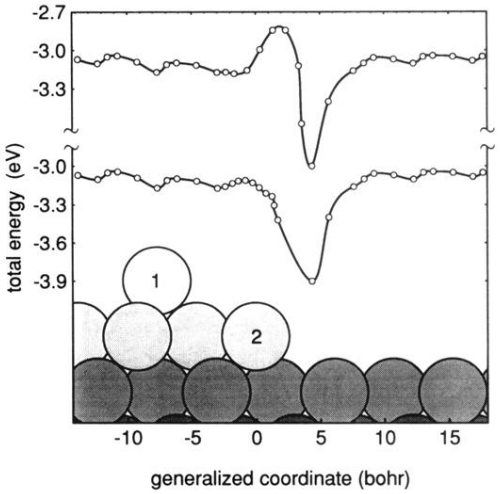

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