

Al Dimer Dynamics on Al(111)

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Al dimer dynamics on Al(111) at equilibrium and under compression is studied using first-principles density-functional theory calculations. A smooth potential energy surface provides a long-range attraction between the dimer atoms and leads to a substantial temperature window in which dissociation is frozen and exotic dimer dynamics is observed. Surface relaxations play a prominent role in the uncovering of an unexpected ground state and a new diffusion path. A way of affecting growth by compression is illustrated. The possibility of a metal quantum rotor is addressed and further examined using effective-medium theory calculations. [S0031-9007(98)06475-8]

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The wide interest in the properties of adsorbed clusters on surfaces stems primarily from a striving towards an understanding and control of epitaxial growth. Dimers often play a central role in such experiments as they may serve as nuclei for agglomeration of atoms, and hence induce two- and three-dimensional growth. The smooth potential energy surface (PES) of Al(111) ensures remarkably small diffusion barriers for kinetic processes of low coordination [1,2]. This opens up the doors to interesting surface phenomena.

An important measure in nucleation studies, and growth experiments in general, is the ratio between dissociation and diffusion rates. Key questions concern how far dimers get before they break up, and how fast they move compared to single adatoms. As we address them, we reveal how the dimer bonds crucially depend on an intricate and dynamic surface relaxation.

In homoepitaxy the main control parameters are substrate temperature and deposition flux. In pursuing the effects of strain on dimer dynamics, we discover a radical change in adsorption geometry, and observe how diffusion channels present with the unstrained substrate get blocked. This should be a valuable asset in epitaxy, as it opens up a new dimension in parameter space. For instance, layer-by-layer growth might be possible to induce at previously prohibitive temperatures and fluxes by adjusting the strain.

Homoepitaxy differs from one class of metals to another. Densely packed simple *s-p* metals belong to a class well suited for an exploratory study, aiming at concepts and trends that can be transferred to other systems. We have chosen aluminum as a prototype here, benefiting from a simple electron structure that lowers the calculational demands.

For a variety of surface phenomena, including dimer diffusion, field ion microscopy (FIM) has been successful [3,4], revealing adsorption geometries and energy barriers of elementary kinetic diffusion processes with atomic resolution. More recently, scanning-tunneling microscopy (STM) has become a competitive tool also in this area [5]. A complete understanding, however, requires several

probes of dynamics, relaxations, and electronic effects, the most accurate theoretical one being based on density-functional theory (DFT) [6,7].

We use DFT in a pseudopotential plane-wave method [8], applying both the local-density (LDA) [9] and generalized gradient approximation (GGA) [10] for the exchange-correlation functional. This approach encompasses all quantum-mechanical effects relevant for adsorption to a high level of accuracy. The LDA calculations are performed self-consistently, whereas the semilocal exchange-correlation corrections of the GGA are calculated from LDA densities, so-called post-GGA. Extensive self-consistent calculations within the GGA have shown this to be an excellent approximation due to the variational property of the total energy functional [10,11]. The numerical accuracy is carefully controlled by *k*-point summation (all values are calculated using 2, 4, 8, and sometimes 16 *k* points) at an energy cutoff of 9 Ry, using a supercell approach (82–152 atoms with >11 Å of vacuum). The sensitivity of the total energies on slab geometry, slab and vacuum thickness, dipole interactions, etc., has been tested extensively in an earlier study on low-symmetry diffusion barriers of adsorbed Al islands on Al(111) [2].

Single Al atom diffusion on Al(111) has previously been studied with STM [12] and DFT [1,2]. Even though Al is an fcc metal (atomic stacking being *ABCABC*), the hcp site (the hollow surface site corresponding to *ABCAC* stacking) is the stable binding site of the Al atom, and not until higher coverages does the fcc site become more stable [1]. The diffusion path between hcp sites goes over adjacent bridge and fcc sites which are almost degenerate in energy. The activation energy for single atom diffusion deduced from experiment, 42 ± 5 meV [12], correlates well [13] with the calculated DFT-LDA values of 40 meV [1,2], which indicates the precision in our theoretical approach. It also illustrates the smoothness of the Al(111) PES.

The gas phase Al dimer has a bond length of 2.863 Å [14], which easily changes upon adsorption. To set the

scene we consider first the case of unrelaxed $\text{Al}_2/\text{Al}(111)$. The fcc-fcc and hcp-hcp dimers are separated by 2.81 Å with the bonds pointing in a close-packed $\langle 110 \rangle$ direction. The only other short dimer resides in an fcc-hcp configuration along a $\langle 112 \rangle$ direction, with a 15% longer bond (3.25 Å). On the unrelaxed surface, this dimer has a 0.15 eV weaker bond to the surface.

When relaxations are allowed, this frozen-surface energy difference (0.15 eV) is expected to decrease. However, it surprised us that it is completely eliminated and even reversed: the *mixed* fcc-hcp dimer is energetically favored by about 0.01 eV over the hcp-hcp dimer. The hcp-hcp dimer is in turn favored by about 0.02 eV over the fcc-fcc dimer, in line with the coverage considerations above [our coverage: $2/(6 \times 5) = 7\%$]. These small numbers are of the same order as our numerical accuracy. A cautious DFT picture is that of three different dimer configurations with energies differing by a few tens meV.

A mixed dimer ground state can be understood by examining surface relaxations. The mixed dimer shortens its bond by 19% upon relaxation, whereas the same number for the *unmixed* fcc-fcc and hcp-hcp dimers is only 7%. The resulting bond lengths of the three dimers differ by $<1\%$. The main reason for this is the elasticity of the surface atom in between. In the mixed case, it is pushed down into the bulk by 0.28 Å, roughly twice as far as in the unmixed case (0.13 Å), allowing the dimer atoms to approach each other and the surface; see Table I and Fig. 1.

The dissociation energy of the adsorbed Al dimer is 0.54 ± 0.06 eV, close to the previously reported DFT-LDA value of 0.58 eV [1]. The shallow adsorption sites allow for a long-range direct attraction, and the dimer atoms have to be separated by over 5.6 Å (three lined up fcc sites in the $\langle 112 \rangle$ direction) to unbind, Fig. 2. One should therefore never observe two separate Al adatoms within any 100 Å² circle on Al(111). This is an important observation for nucleation studies [12]. The long-range attraction requires big supercells, which explains the large error bar for this particular value.

TABLE I. Bonding parameters of dimers calculated within DFT/EMT. The amount of strain is represented by the normalized lattice constant. The dimers are differentiated by their adsorption geometry: *f* stands for fcc, *h* for hcp, and *b* for bridge. The bond lengths of the dimer before and after relaxation are given by δ_0 and δ , respectively. The height of the individual dimer atoms above the surface is given by z , again within DFT/EMT. Surface relaxations are illustrated in Fig. 1. The binding energy is ≈ 0.54 eV for the three dimers.

a/a_0	ads.	δ_0 (Å)	δ (Å)	z (Å)
1	<i>ff</i>	2.814	2.610/2.770	2.05–2.05/2.09–2.09
	<i>hh</i>	2.814	2.613/2.775	2.03–2.03/2.08–2.08
	<i>fh</i>	3.250	2.643/2.788	1.99–2.00/2.06–2.06
0.95	<i>bb</i>	2.674	2.615/2.763	2.03–2.03/2.02–2.02
	<i>fh</i>	2.674	2.626/2.768	2.09–2.09/2.03–2.04

Once formed, Al dimers are thus very stable as such. Their mechanisms for migration on the Al(111) surface become a key issue. Here one has to distinguish between *intracell* and *intercell* motion [3]. In the former case, the dimer is confined to a small hexagonal cell of six sites around a given surface atom, and can carry out only localized, nondiffusive motion. The latter case signifies diffusive motion out of the cell; see Fig. 2.

Dimer diffusion takes place by concerted intercell sliding in the $\langle 112 \rangle$ direction (at an axis angle of 30°). The dimer diffuses over unmixed states with the saddle point consisting of two bridge sites in different close-packed rows. The energy barrier is 0.13 eV, leading to a substantial temperature window, about 0–50 K, in which dimer diffusion is frozen [15].

The predicted diffusion mechanism is different from the one identified in an FIM experiment on Ir dimer motion on Ir(111) by Wang and Ehrlich [3]. They find that dimers diffuse by atom-by-atom rotation out of the cell. In our case, the first step has an energy barrier of 0.50 eV, whereas the following step has no barrier at all due to the long-range attraction. Diffusion of Al dimers on Al(111) thus takes place by concerted sliding, albeit at higher temperatures dimers move less rigidly.

Confined dimer motion in the hexagonal cell proceeds in three different ways: (i) The (overall) lowest energy barrier is for a rotational type of motion around the central surface atom in the cell. Individual atom jumps over bridge sites take the dimer through fcc-fcc (highly metastable), fcc-hcp, and hcp-hcp configurations, Fig. 2. The highest energy barrier for this motion is 0.03 eV. (ii) In a concerted rotation, the dimer revolves over mixed

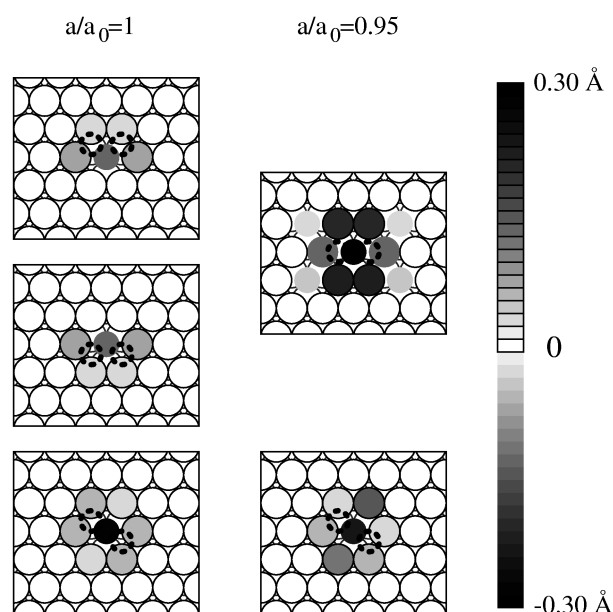


FIG. 1. Surface relaxations of stable dimers (thick dashed circles) with and without compressive strain, as calculated within DFT. The shading indicates how far out (closed circles) or in (smaller open circles) the surface atoms relax.

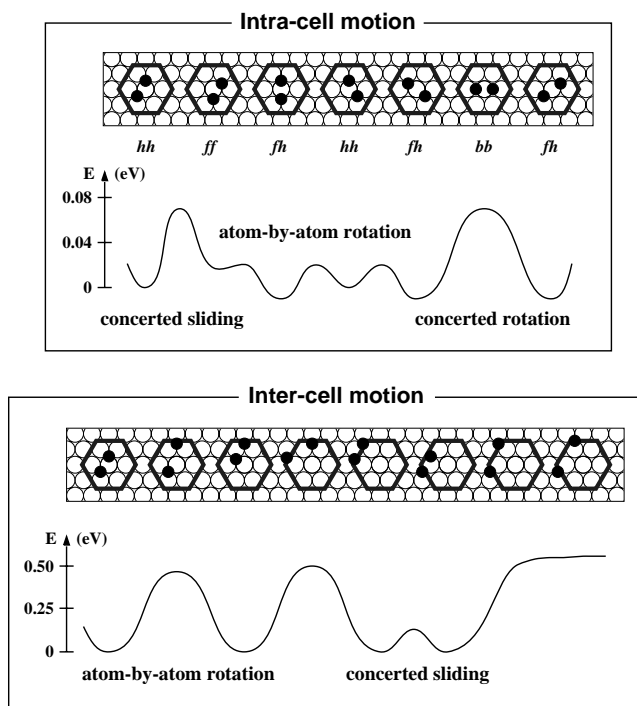


FIG. 2. Schematic illustration of confined (nondiffusive) dimer motion (upper panel) and dimer motion that leads to diffusion and dissociation (lower panel). The energy barriers are summarized in Table II (f stands for fcc and h for hcp). The hexagonal surface cell is indicated by a thick line.

states by surmounting two bridge sites (in the same close-packed row), with a barrier of 0.09 eV within GGA. (iii) In concerted sliding orthogonal to the dimer axis the dimer goes from one unmixed state to another over two bridge sites in the same close-packed row, with an activation energy of 0.08 eV within GGA. This sliding motion is equivalent to three (faster) intracell rotations, and therefore is only interesting here for its coupling to the rotation modes at high enough temperatures.

The barrier for confined atom-by-atom type rotation is low (≈ 30 meV), and we expect it to further decrease when quantum zero-point vibrations are taken into account. We examine this by considering three rotational adsorption positions: the fcc-fcc, fcc-hcp, and fcc-bri (saddle point) in between. For each position three vibrational frequencies are determined by moving one of the dimer

atoms in three orthogonal directions while keeping all other atoms fixed. The results are presented in Table III. Within the harmonic approximation of quantum transition state theory (QTST), these values yield a lowering of the largest rotation barrier (out of the mixed fcc-hcp state) by 10 meV, while the smaller one (into the mixed state) is roughly halved by the effective decrease of about 6 meV. We conclude that for temperatures below ≈ 200 K, the effective rotation barrier is only about 20 meV [16].

The small intracell barrier raises an interesting question: could there exist a type of nonactivated rotational motion, similar to the free quantum rotor observed for $\text{H}_2/\text{Cu}(510)$ [17]? To answer this question, we first note that to sustain a quantum rotor, it is not sufficient to have vanishing rotation barriers. The elastic effects have to be either negligible, or of such a nature that phonon-mediated energy dissipation during rotation is negligible. As the dimer rotates, the surface atom beneath it oscillates in and out of the surface with an amplitude of 0.15 Å, producing energetic phonons. Unless these are coupled back to the other oscillating atoms, Fig. 1, there will be a loss of energy and the rotor motion will be quenched.

Since an investigation of phonon coupling effects with first-principles techniques is infeasible, we use an approximate total-energy method, the effective-medium theory (EMT) [18]. This many-atom method has been rather successfully used in a wide range of applications [19,20]. The parameters for the potential are taken from Ref. [19]. The description of the dimer energetics within EMT is encouraging, Table II. Even though the barrier values are off by a factor of 2 on the average, all trends among the intricate barriers of rotation and sliding are accurately reproduced. The relaxation effects are also fairly well described. The dimer bonds are 6% longer and the dimers reside 0.05 Å further away from the surface in the EMT, but the variations between the different dimers (mixed, unmixed, etc.) are reproduced in detail and differ by less than 0.5% from DFT values. Only the finer relaxation details are not in agreement with DFT.

With these indications of a decent EMT interaction potential, we perform molecular dynamics simulations at various temperatures within the microcanonical ensemble. At low temperatures (around 20 K), a hindered type of off-center atom-by-atom rotation is observed, where the

TABLE II. Energy barriers of dimer motion: in separate compartments we show the energy barriers Δ of (1) concerted intracell sliding, (2) concerted intracell rotation, (3) atom-by-atom intracell rotation, and (4) concerted intercell sliding. We denote the fcc and hcp adsorption sites by f and h , respectively. The superscripts (subscripts) indicate the dimer configuration before (after) the jump. All activation energies are in meV as calculated within the LDA, GGA, and EMT.

	Δ_{hh}^{ff}	Δ_{ff}^{hh}	Δ_{fh}^{fh}	Δ_{fh}^{ff}	Δ_{hh}^{fh}	Δ_{fh}^{hh}	Δ_{ff}^{ff}	Δ_{hh}^{ff}	Δ_{ff}^{hh}
LDA	70	60	70	~ 0	30	20	30	130	130
GGA	90	80	90	20	30	30	30	130	130
EMT	16	26	31	7	16	11	21	68	78
EMT/GGA	0.2	0.3	0.3	0.4	0.5	0.4	0.7	0.5	0.6

TABLE III. Vibrational frequencies for confined dimer rotation: ω_{\perp} is the perpendicular frequency, and $\omega_{\#}$ (ω_{\parallel}) is the in-plane frequency orthogonal (parallel) to the diffusion direction.

Dimer	ω_{\perp} (meV)	$\omega_{\#}$ (meV)	ω_{\parallel} (meV)
fcc-fcc	27	27	15
fcc-bri	28	30	...
fcc-hcp	31	27	18

dimer repeatedly rotates up to half a turn before taking a rest. As the temperature is increased, the motion becomes coupled to concerted intracell (orthogonal) sliding, and at even higher temperatures the dimer leaves the cell by concerted intercell sliding. These simulations strongly indicate that the rotor is quenched by dissipative phonon processes. Based on these simulations and the large distortions of the lattice during the rotation (Fig. 1), we conclude that a free quantum rotor motion is not possible.

We now consider the effects of compressive strain on the dimer dynamics. The consequence of strain on single-atom diffusivity is well known, and in the case of Ag/Ag(111) a 5% reduction of the lattice constant roughly halves the monomer diffusion barrier [21]. All DFT calculations are repeated on slabs with a 5% reduced lattice constant. The results are striking. The fcc-fcc and hcp-hcp are no longer adsorption minima. The mixed fcc-hcp state survives, and constitutes, together with a double bridge occupancy, the new ground state. The relaxation patterns for these two strained states are shown in Fig. 1.

The unmixed states are unstable, about 0.15 eV higher in energy than the ground state. This implies a marked hampering of dimer motion that relies on access to these states. One would therefore expect the atom-by-atom rotation to be quenched by the compressive strain. More importantly, diffusion through intercell sliding should be severely impeded for the same reasons. Finding the transition state for motion on a complicated PES, especially when the initial and final states are unstable, requires special techniques (work in progress). For now, we use the EMT to estimate the blocking effect (the relative ordering of the energy barriers in the DFT calculations is once again correctly reproduced). A complicated transition path is found, and the resulting diffusion barrier is almost doubled.

The fact cannot be excluded that a free metal rotor can exist at intermediate strains and at specific temperatures, but we deem it highly unlikely due to the dissipative phonon processes. A quick calculation [$\Delta E = l(l+1)B$; $B = \hbar^2/2\mu r^2$] reveals that the rotation spectrum of such a motion would be very hard to resolve experimentally as the large mass and the long bond length of the Al dimer lead to excitation levels separated by only fractions of meV.

In summary, we present accurate total-energy calculations of Al dimer dynamics on Al(111). We predict unexpected ground states for the strained and unstrained dimer

that should be easy to verify using, e.g., STM that measures the dimer direction or the dimer height to which this tool is very sensitive. We find that Al dimers are stable up to ≈ 220 K and migrate through concerted sliding at temperatures above 50 K [15]. A rotational type of motion is activated already at about 8 K but does not lead to diffusion. By performing molecular dynamics simulations, we conclude that it is the elastic rather than electronic effects that work against a free rotor scenario. The radical compression-mediated decrease in diffusivity suggests a way of affecting epitaxial growth through strain.

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