

Energy barriers for diffusion on stepped Rh(111) surfaces

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Abstract

Energy barriers for different moves of a single Rh adatom in the vicinity of steps on the Rh(111) surface are studied with molecular statics. Interatomic interactions are modeled by the semi-empirical many-body Rosato–Guillope–Legrand potential. We systematically calculated the barriers for the descent at straight steps, steps with a kink and small islands, as well as barriers for diffusion along the step edges. The descent is more probable on steps with a {111} microfacet and near kinks. Diffusion along a step with a {100} microfacet is faster than along a step with a {111} microfacet. We also calculate barriers for diffusion on several surfaces vicinal to Rh(111). © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Surface diffusion is a very important process in many phenomena, in particular in crystal growth. That is why the diffusion of single adatoms on stepped metal surfaces has been recently widely investigated both experimentally and theoretically. Energy barriers for the moves of an adatom on a surface with steps or islands are not easily accessible by experiment, but for many elementary processes they can be calculated on microscopic level by molecular dynamics. A knowledge of the barriers can then be utilized in the construction of kinetic Monte Carlo models to study growth processes.

The diffusion energy barriers have already been calculated for various metals and different surface orientations. For example, in the case of an fcc

(111) surface there are calculations for Al [1–3], Ag [4], Au [4], Cu [5], Ni [6], Pt [7,8], and Ir [9]. In most of these studies the semi-empirical potentials were used owing to their simplicity, allowing a systematic study of numerous possible processes. Comparable *ab initio* calculations demand much more computer power; therefore, the number of investigated processes must be considerably reduced. Although the recent first principles calculations [7] indicate that in the case of Pt(111) the semi-empirical potentials may be insufficient, in many other studies they lead to reasonable results and their application has helped, at least qualitatively, in understanding diffusion energetics and revealed new processes (e.g. see Ref. [10]).

In this paper we study diffusion on a stepped Rh(111) surface. The research was motivated by a recent scanning tunneling microscope (STM) experiment on unstable growth of Rh(111) [11], where a coarsening due to a step-edge barrier was

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observed over three orders of magnitude of deposited amount. A more recent observation on Pt(111) [12] indicates almost no coarsening over a similar interval of deposited material. Whereas the step-edge barriers on Pt(111) surfaces were extensively studied (see references cited in Refs. [7,8]), results for Rh(111) are not available. We present here a systematic study of energy barriers for inter-layer transport as well as for diffusion along the step edges.

2. Method

Our simulations were done for finite atomic slabs with a free surface on the top, two atomic layers fixed on the bottom, and periodic boundary conditions in the two directions parallel to the surface. The slab representing the substrate of the (111) surface was 11 layers thick with 448 atoms per layer. We used systems of approximately 5000 atoms consisting of 19 to 44 layers, with 110 to 240 atoms per layer for diffusion along channels on the vicinal surfaces (311), (211), (331), (221) and (322). The semi-empirical many-body Rosato–Guillope–Legrand (RGL) potential [13] including interactions up to the fifth-nearest neighbors [14] was used. For computational details see Refs. [8,9].

The energy barrier for a particular diffusion process was obtained by testing systematically various possible paths of an adatom. The path with the lowest diffusion barrier was chosen to be the optimum one, and the diffusion barrier E_d was calculated as $E_d = E_{\text{sad}} - E_{\text{min}}$ where E_{sad} and E_{min} are the total energies of the system with the adatom at the saddle point and at the equilibrium adsorption site respectively. We considered both the jump and exchange processes. The minimum energy path for jump diffusion was determined by moving an adatom in small steps between two equilibrium positions and by allowing the adatom to relax in a plane perpendicular to the line connecting two equilibrium positions. The remainder of the atoms in the system were allowed to relax in all directions.

The energy barrier for the exchange process was determined by moving the edge atom, which should be replaced, in small steps toward its final

position. This final position was one of neighboring equilibrium sites. The moving atom was allowed to relax in the plane perpendicular to the exchange direction at each step, whereas the other atoms, including the adatom, relaxed freely in all directions.

3. Results

3.1. Flat surface

In our simulation we obtained an energy barrier of 0.15 eV for self-diffusion on the flat Rh(111) surface, which is in good agreement with experiments. In a field-ion-microscope (FIM) experiment [15] a barrier of 0.15 ± 0.02 eV was found, and recently a value of 0.18 ± 0.06 eV was obtained in an STM experiment [11] from the temperature dependence of island density. The results of molecular statics calculations and experimental values are summarized in Table 1. We also calculated the binding energy for the supported dimer. The value $E_B = 0.57$ eV is in good agreement with the 0.6 ± 0.4 eV obtained in the STM experiment [11].

3.2. Descent to the lower terrace

We studied the descent of an adatom to the lower terrace from both types of step on the (111) surface, i.e. step A with a {100} microfacet and step B with a {111} microfacet (see Fig. 1). We performed calculations for several geometries: straight steps, steps with a kink, and also for a small island of 3×3 atoms. For all geometries considered we systematically investigated all possible adatom jumps and pair exchange processes.

Table 1

Self-diffusion barriers E_s on a flat Rh(111) surface; SCh: Sutton–Chen potential; LJ: modified Lennard–Jones potential

	Method	Ref.	E_s (eV)
Experiment	FIM	[15]	0.15 ± 0.02
	STM	[11]	0.18 ± 0.06
Theory	LJ	[16]	0.234
	SCh	[17]	0.106
	RGL	present study	0.15

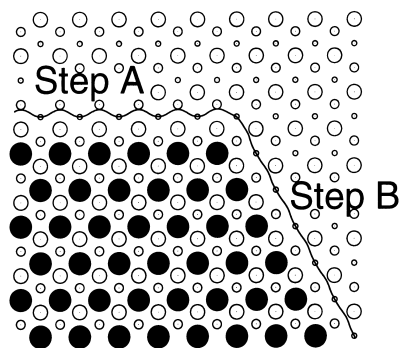


Fig. 1. Two types of step edge, A and B, for a large island. Solid line shows the diffusion path along the island edge. The atoms of different layers from the surface to the bulk are shown as large filled circles, large open circles, small open circles, and tiny open circles.

Our results for straight steps and steps with a kink are summarized in Table 2.

The energy barrier for a direct jump from the upper to the lower terrace is 0.73 eV for straight step A and 0.74 eV for straight step B. The presence of a kink decreases the barrier for the jump to 0.57 eV on both steps. We can see that the energy barriers for the jumps are always larger than for the exchange, which are 0.47 eV and 0.39 eV for steps A and B respectively.

In more complex geometries the number of competing processes to be energetically compared increases, e.g. in the case of step B with a kink we

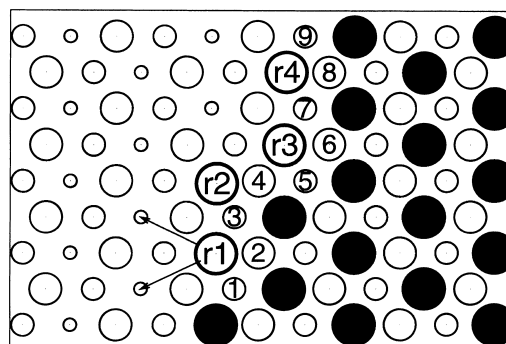


Fig. 2. Different exchange processes near a kink site on step B on an Rh(111) surface. The edge atoms undergoing exchange diffusion (r1–r4) and starting positions of an adatom (1–9) are shown. The four topmost atomic layers from the surface to the bulk are distinguished by different circle radii (cf. Fig. 1).

consider four types of process according to which step-edge-atom (denoted by r1, r2, r3, or r4) is pushed out (see Fig. 2). We call them exchange next to corner, exchange over kink I, exchange over kink II, and exchange next to kink respectively. We consider all possible combinations of initial and final positions. For example, in the case of the exchange next to the corner there are three possible processes: 1→r1, 2→r1, 3→r1. In the process 3→r1, for example, the adatom starts in the fcc site labeled by 3 and pushes out the edge atom r1. Two possible directions of moving for pushed atom r1 are shown schematically in Fig. 2.

The lowest barrier for the inter-layer transport is the barrier for two exchange processes near the kink on the step B (0.24 eV), i.e. the Ehrlich–Schwoebel barrier is only 90 meV. The barriers for exchange processes on the step A are significantly higher. For a 3×3 island, the minimal values were obtained for the exchange of the atom in the middle of the edge (0.43 eV for A-type edge and 0.24 eV for B-type edge). We found that for Rh(111), similar to Pt(111) [8], the barriers for the descent at a small island are significantly lower than for the descent at straight long steps.

3.3. Diffusion along the step edges

Fig. 3 shows the energy profile for the diffusion along two edges of a large island. The structure in the middle corresponds to a diffusion around the

Table 2
Energy barriers E_d for descent at steps on Rh (111)

Step	Process	E_d (eV)
A	Jump over step	0.73
	Jump over kink	0.57
	Exchange over step	0.47
	Exchange next to corner (3→r1)	0.81
	Exchange over kink I (3→r2)	0.47
	Exchange over kink II (4→r3)	1.0
	Exchange next to kink (9→r4)	0.80
B	Jump over step	0.74
	Jump over kink	0.57
	Exchange over step	0.39
	Exchange next to corner (3→r1)	0.24
	Exchange over kink I (3→r2)	0.48
	Exchange over kink II (7→r3)	0.63
	Exchange next to kink (9→r4)	0.24

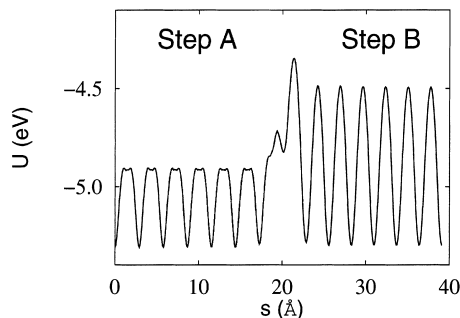


Fig. 3. Dependence of the adatom energy for the path along the edge of a large island. The path is composed from three sections: along edge A, around the corner and along edge B.

corner formed by two edges. The angle contained by the edges is 120° . There is a small minimum just at the corner positions. The transport between two edges is asymmetric.

We found that the diffusion along the straight step of type A is faster (the barrier is 0.40 eV) than along the step of type B (the barrier is 0.81 eV). This could be attributed to a purely geometrical effect due to different local geometries along the steps. The adatom diffusing along the step B has to pass closer to the topmost atoms of the lower terrace than when it is diffusing along the step A (see Fig. 1).

There are no available experimental data for diffusion along the steps on an Rh(111) surface. Only one measurement on the (311) and (331) surfaces has been published [15]. In order to have some comparison, we calculated the energy barriers for the diffusion along steps on vicinal surfaces with terraces: (211), (311)-surfaces with step edges of type A, and (332), (221) and (331)-step edges of type B. The results are summarized in Table 3.

Table 3
Calculated activation energy barriers E_d for diffusion along steps on different surfaces

Step A		Step B	
Surface	E_d (eV)	Surface	E_d (eV)
111	0.40	111	0.81
211	0.41	332	0.80
311	0.45	221	0.78
–	–	331	0.78

The vicinal surfaces are ordered according to the distance between terraces.

We can see that there is a clear tendency with the decreasing distance between steps. In the case of the A-step the barrier along the step is increasing with increasing step distance, whereas for the B-step it is decreasing. We obtained barriers of 0.45 eV and 0.78 eV for the diffusion along steps on the (311) and (331) surfaces respectively. Experimental results of FIM measurements are the energy barriers $E_{311}=0.52$ eV and $E_{331}=0.62$ eV [15]. There is qualitative agreement between experimental and calculated data: $E_{311} < E_{331}$.

4. Conclusion

Using the RGL potential we calculated the energy barrier for self-diffusion on a flat Rh(111) surface and the binding energy of a supported dimer; the results are in good agreement with the experimental data. With the same potential, we systematically studied energy barriers for the descent at straight as well as rough steps on Rh(111). We found that the lowest energy barrier for descent to the lower terrace is for the exchange process near a kink on step B. We also calculated barriers for the diffusion along step edges on an Rh(111) surface and along step edges on several vicinal surfaces. We found that the diffusion along step A is faster than along step B, which is in qualitative agreement with the FIM experiment. We observed that these barriers are slightly affected by the step–step interaction.

We expect that, owing to rather large barriers for the diffusion along steps, both steps will be rough during the growth at lower temperatures and the interlayer transport will prefer step B. At a higher temperature the diffusion along step A starts to be active and the descent on both steps will be possible. However, step B will remain rough and the descent on this step will be easier. In island growth this would imply that B-edges of an island will grow faster than A-edges; therefore, B-edges will become shorter. However, the number of kinks for the easy descent on a shorter B-edge will be lower. Hence we expect that for a certain interval of temperatures the shape of the growing island

will be asymmetric with longer A steps. This picture seems to be in agreement with the morphologies presented in [11].

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