Facet-facet barriers on Cu{111} surfaces for Cu dimers

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Abstract: Nanostructure fabrication or surface processing in general is predominantly kinetics-limited. One of the kinetics factors is surface diffusion, which involves intricate interplay between the diffusing atoms and substrate atoms. On Cu{111} surfaces, both adatoms and dimers diffuse very fast. Recent studies have shown that adatoms encounter a large facet-facet barrier, even though their conventional Ehrlich-Schwoebel barriers are small. This work examines the facet-facet diffusion barriers of dimers. Our results show that a dimer prefers diffusion through atom-by-atom mechanism, having a barrier of 0.52 eV from {111} to {111} facet and a barrier of 0.55 eV from {111} to {100} facet. When the two atoms in a dimer diffuse simultaneously, the barrier is 0.97 eV from {111} to {111} facet and 0.62 eV from {111} to {100} facet.

keyword: Facet-facet barriers, Activation energies, Nudged Elastic Band method.

1 Introduction

Nanoprecision fabrication and manipulation are key aspects that have to be mastered in order to bring to us all the dreamed promises of nanotechnology. Notably, controllable growth and mechanical testing of plain or patterned surfaces are among the most active research areas nowadays [de Miguel and Miranda (2002); Liang, Woo, Huang, Ngan, and Yu (2004)].

The nucleation and assembly of nanostructures is a very complex process that depends on parameters such as the incident flux, the film temperature, the lattice mismatch, the surface strain, etc. Furthermore, it is a problem of multiscale nature, both in the time and in the space [Wadley, Zhou, Johnson, and Neurock (2001); Ala-Nissila, Ferrando, and Ying (2002); Liu, Shi, Woo, and Huang (2002)].

When an atom lands on a surface, it diffuses along the terrace formed by that film layer trying to find the best place (energetically speaking) to settle, frequently a lower terrace. But an atom coming to the edge of a terrace feels a barrier that prevents it from going over the edge, the Ehrlich-Schwoebel (ES) barrier. This phenomenon can be explained as follows: the atom on a terrace has a certain number of nearest neighbors (its coordination number) and the bonding to these neighbors provides stability for that atom. As it reaches the edge of a terrace, it suddenly has fewer neighbors with a resulting decrease in the bonding energy manifested as a barrier for diffusion over the edge [Lagally and Zhang (2002)].

Recent calculations [Liu, Huang, and Woo (2002); Huang (2002); Huang and Wang (2003); Wang, Huang, and Cale (2004)] showed that traditional ES barriers were only a special case of a more general phenomenon. Basically, it was stated that these barriers may present 1D (one dimension), 2D or 3D forms, each of them with specific characteristics. The first case corresponds to the diffusion of an adatom across a kink, the second case to the diffusion down a step (traditional ES barrier) and the third case to the diffusion down a multistep (or facet) configuration. The last case is also known as facet-facet barrier. These concepts were summarized by Lagally and Zhang (2002). Most of these studies basically addressed the diffusion of adatoms but there has been little effort to study the diffusion of dimers and trimers down steps [Bockstedte, Liu, Pankratov, Woo, and Huang (2002)]. Therefore, the behavior of these configurations facing facets remains still as an open question.

Growth of Cu surfaces has been intensively studied for many years, therefore the amount of data available is of importance. It was found that Cu{100} tends to grow in a more even fashion than Cu{111} [de Miguel and Miranda (2002)]. This phenomenon was explained by the difference between the hopping activation energy on a flat surface and the energy barrier to descend a step. If this difference is relatively big, like on Cu{111} surfaces,

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the adatoms deposited on top of the islands will tend to stay there, making the stepping down very difficult. The resulting surfaces can be very rough, which in general is not desirable.

In this paper we concentrate on Cu{111} surfaces and study facet-facet barriers for Cu dimers. We employ the Nudged Elastic Band (NEB) method to calculate the minimum energy path (MEP) and the saddle-point configuration.

2   Simulation methods

Searching for MEPs and activation energies require the evaluation of the system total energy, therefore the necessity of having a description of interparticle interactions. In this regards, the most general and precise method is Density Functional Theory (DFT). Unfortunately this method is not feasible when working with systems that have more than a few hundred of atoms. In contrast, one of the most common phenomelogical approximations: the Embedded Atom Method (EAM) [Foiles, Baskes, and Daw (1986); Foiles and Adams (1989)], partly based on DFT concepts, has been successfully employed in systems with millions of atoms. In our calculations we have used ParaDyn (http://www.cs.sandia.gov/~sjplimp/), a parallel implementation of EAM. Moreover, for the visualization we used the AtomEye program [Li (2003)].

Currently there is a variety of methods to calculate activation energies of rare events. In this work we implemented the Nudged Elastic Band (NEB) method [Henkelman, Uberuaga, and Jónsson (2000); Henkelman and Jónsson (2000); Sbraccia (2005)]. The NEB method is numerically more efficient than the molecular dynamics simulation in determining activation energies. The method requires the initial and final states and with this information calculates a chain of "images" that initially represent some intermediate configurations between the previously defined states. This set of images is referred to as "elastic band". The energy of the elastic band is defined as the sum of the actual potential energies of all images plus the sum of fictitious elastic deformation energies of imaginary springs connecting neighboring images. This energy is minimized with respect to atomic displacements in all images. The image with the highest potential energy can be identified as the saddle point configuration and is related to the activation energy. In this work we used from 5 to 30 images to calculate the MEP and the results were always very consistent.

3   Simulation results

The basic configuration we use in our calculations is a Cu{111} slab of which the six bottom layers (approximately two times the cut-off distance) are fixed, see Fig. 1. The left facet corresponds to a {100} oriented surface and the right one to a {111} oriented surface. The maximum number of atoms used approaches 6000. Periodic boundary conditions are set along the plane. Additionally, tests to check the size independency of our results were carried with configurations of up to two times the number of atoms mentioned above.
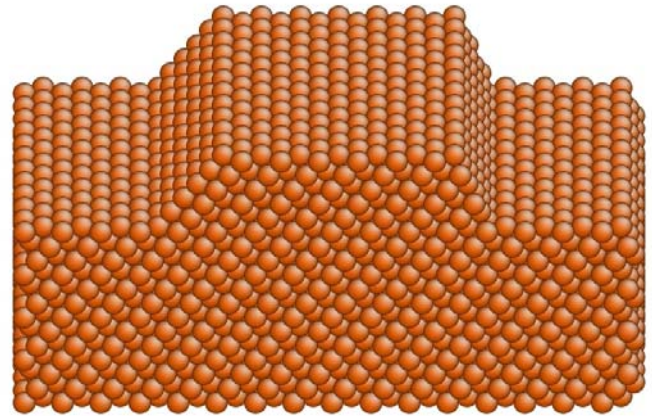

Figure 1 : Configuration used in the calculations.

In order to compare the magnitude of the diffusion barriers calculated in this work and to validate our calculations, first we begin considering results of widely available diffusion barriers.

On a flat Cu{111} surface, an adatom may occupy either FCC or HCP sites, which energetically are very similar, with the FCCs being slightly more favorable. The activation energies calculated in this work for hopping from FCC to HCP and from HCP to FCC sites have almost the same value, in the order of 0.03 eV. These results agree very well with previous calculations [Trushin, Kokko, Salo, Hergert, and Kotrla (1997); Liu, Cohen, Adams, and Voter (1991); Wang, Huang, and Cale (2004)] which determine that this value must be in the range 0.03-0.04 eV.

Diffusion down a single step ($N = 1$) has also received great attention.   In principle an adatom can diffuse

Table 1 : Activation total energies (eV) through exchange of adatoms versus the number of layers of ending step (N).

	$N = 1$	$N = 2$	$N = 3$	$N \geq 4$
{111} → <110>{100}	0.32	0.41	0.39	0.39
{111} → <110>{111}	0.09	0.27	0.28	0.28

Table 2 : Activation total energies (eV) through exchange of dimers versus the number of layers of ending step (N).

	$N = 1$		$N = 2$		$N = 3$		$N \geq 4$	
	$M1$	$M2$	$M1$	$M2$	$M1$	$M2$	$M1$	$M2$
{111} → <110>{100}	0.45	0.50	0.56	0.63	0.55	0.62	0.55	0.62
{111} → <110>{111}	0.17	0.37	0.50	0.93	0.52	0.97	0.52	0.97

through a hopping or an exchange process, but in general the hopping requires a greater amount of energy making it a less frequent process. In this work we will concentrate on exchange process only. The results obtained are shown in Tab. 1 and also have good agreement with previous calculations [Trushin, Kokko, Salo, Hergert, and Kotrla (1997); Wang, Huang, and Cale (2004)].

A step becomes a facet when its height is bigger than one atomic layer ($N > 1$). We present now the results obtained for facet-facet energy barriers through exchange processes, which are summarized on Tab. 1. In this case we use the following notation: diffusion processes from a {111} surface to a neighboring {100} (or {111}) facet, across a ridge <110>, are designated {111} → <110>{100} (or {111} → <110>{111}). In general, our results present a good agrement with those obtained by Wang, Huang, and Cale (2004).

Although it is easily observed that an adatom encounters smaller opposition to descend to a {111} facet than to a {100} facet, the increase in the activation energy from $N = 1$ to $N = 4$ in the former case is 0.19 eV and in the the later case is only 0.07 eV.

In order to calculate the activation energies shown in Tab. 1, the adatoms were placed on FCC sites, for {111} → <110>{100} processes, or HCP sites, for {111} → <110>{111} processes. If an FCC site is used for the later process, our calculations reveal a path which shows the adatom going back to an HCP site before trying to step down.

In the case of dimer diffusion, we consider two mechanisms. According to the first mechanism ($M1$), the two atoms in a dimer diffuse one-by-one. Our calculations

show that the barrier for the first atom to diffuse is always larger, and we take this value as the diffusion barrier corresponding to $M1$. According to the second mechanism ($M2$), the two atoms in a dimer diffuse simultaneously. These results are summarized in Tab. 2.

Consider first the {111} → <110>{100} processes. The

(a)

(b)

(c)

(d)
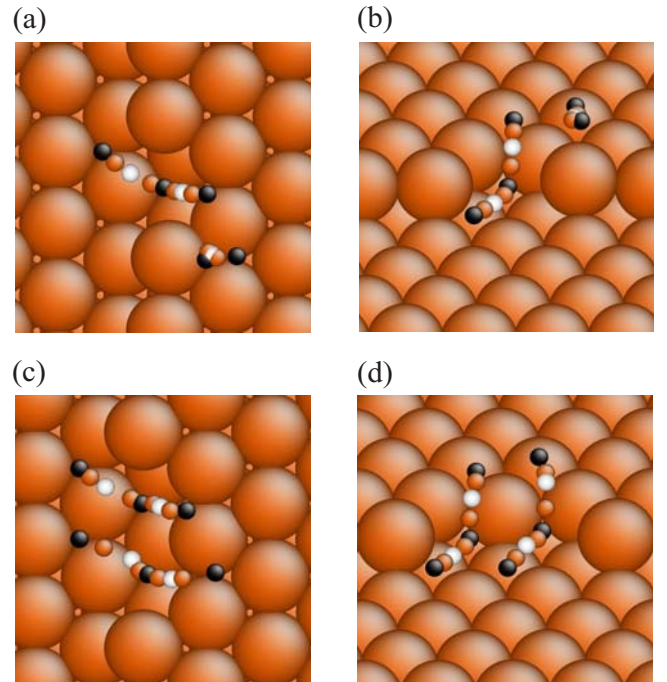
Figure 2 : Stepping down of dimers for {111} → <110>{100} processes and $N = 1$. (a) Top view and (b) projection view for $M1$. (c) Top view and (d) projection view for $M2$. Black spheres are initial and final sites, white spheres correspond to the saddle-point configurations.
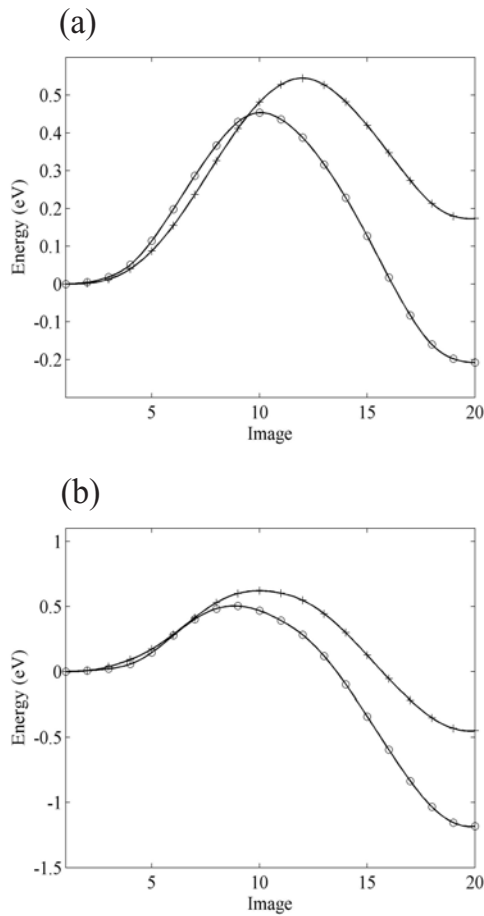
(a)

(b)

Figure 3 : MEPs for $\{111\} \to <110>\{100\}$ processes. (a) $M1$ for (o) $N = 1$ and (+) $N = 4$. (b) $M2$ for (o) $N = 1$ and (+) $N = 4$.

(a)

(b)

(c)

(d)

Figure 4 : Stepping down of dimers for $\{111\} \to <110>$ $\{111\}$ processes and $N = 1$. (a) Top view and (b) projection view for $M1$. (c) Top view and (d) projection view for $M2$. Black spheres are initial and final sites, white spheres correspond to the saddle-point configurations.

difference in the activation energies between the diffusion of adatoms, Tab. 1, and the diffusion mechanism $M1$, Tab. 2, is in the range 0.13-0.16 eV. Additionally, the difference between mechanisms $M1$ and $M2$ is in the range 0.05-0.07 eV. For both mechanisms, the diffusion barrier increases much as the number of layers N increases. See also Fig. 2 for the stepping down mechanisms for $N = 1$ and Fig. 3 for the MEPs compared for various processes.

Now consider the $\{111\} \to <110>\{111\}$ processes. As shown in Tab. 1 and 2, the difference in the activation energies for diffusion processes of adatoms and the mechanism $M1$ ranges between 0.08-0.24 eV, and the difference between mechanisms $M1$ and $M2$ is in the range 0.20-0.45 eV. See Fig. 4 for the stepping down mechanisms for $N = 1$ and Fig. 5 for the MEPs compared for various
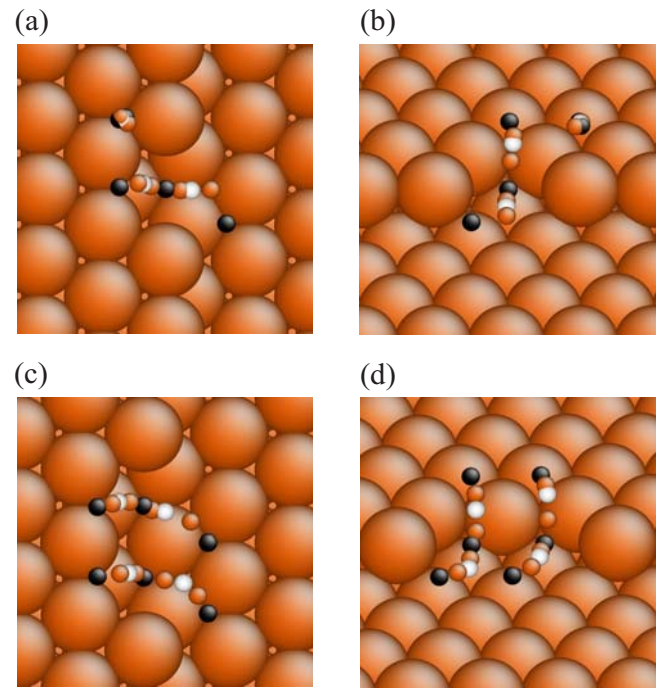
processes.

In order to put the facet-facet barriers in perspective, we will show the results obtained for the diffusion of a dimer on the flat surface depicted in Fig. 6. A pair of atoms on $\{111\}$ surfaces can diffuse one by one or simultaneously [Chang, Wei, and Chen (2000)]. In this case, we constrain the couple of atoms to move simultaneously from left to right in the figure. Black spheres represent the initial, the final and the global minimum energy configurations (images 1, 20 and 15, respectively). On the other hand, white spheres correspond to the three saddle-point configurations (images 3, 7 and 18), which correspond to activation energies of 0.02, 0.09 and 0.09 eV, respectively. Additionally, it must be noted that the final configuration is next to a $\{111\}$ step, so its energy level is substantially greater than the initial configuration. The global minimum energy configuration, which corresponds to two HCP sites were used above to calculate the energy barriers of dimers facing a step or a facet.
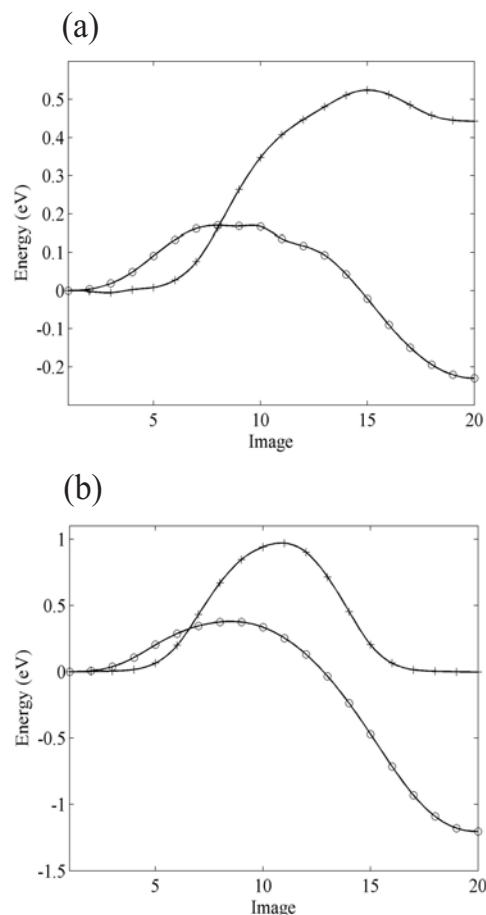
Summarizing, the activation energy for adatom hopping

(a)

(b)

Figure 5 : MEPs for {111} → <110>{111} processes. (a) $M1$ for (o) $N = 1$ and (+) $N = 4$. (b) $M2$ for (o) $N = 1$ and (+) $N = 4$.

Figure 6 : Diffusion of a dimer of Cu atoms on a Cu{111} surface.

on a Cu{111} surface is, as we mentioned, 0.03 eV, a very small barrier. For hopping of dimers we obtained two values, 0.02 and 0.09 eV. In contrast, the facet-facet barriers are substantially larger than those on the flat {111} surfaces.

sion from {111} facet to a {100} facet is 0.45 eV at $N = 1$ and 0.55 eV at $N > 2$. The large facet-facet barriers will have major impact in surface faceting, particularly facet dimensions during thin film deposition or nanostructure fabrication.

4 Conclusions

In this work, we have calculated the facet-facet barrier of Cu dimers diffusing from {111} to {111} or {100} facets. Our calculations show that the two atoms in a dimer prefer to diffuse one-by-one instead of diffusing simultaneously. Further, the diffusion barrier increases fast as a monolayer step ($N = 1$) becomes a multilayer facet ($N > 1$). The facet-facet barrier for diffusion from {111} facet to another {111} facet is 0.17 eV at $N = 1$ and 0.52 eV at $N > 2$. The corresponding value for diffu-
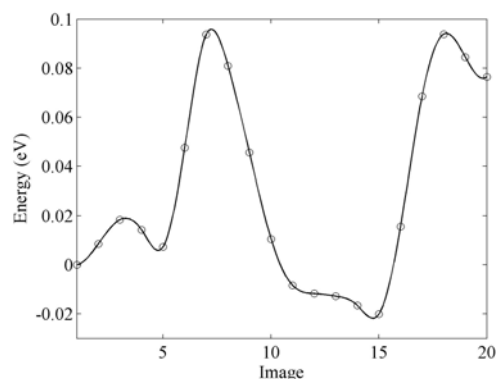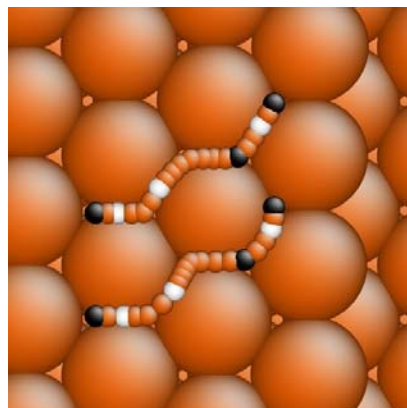
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