Diffusion mechanisms for trimers on Ag(111) surfaces and across facet-facet edges

Boris Aguilar
Facultad de Ingeniería Mecánica, Universidad Nacional de Ingeniería.
E-mail: boaguilar@gmail.com

Alberto Coronado
Department of Mechanical, Aerospace and Nuclear Engineering, Rensselaer Polytechinc Institute.
E-mail: am.coronado@gmail.com

Recibido el 07 de Julio del 2006; aceptado el 14 de julio del 2006

Energy barriers for the diffusion of atoms across multilayer facets is a key factor on surface processing and nanostructure fabrication. This work presents molecular statics calculations of diffusing Ag trimers near and across Ag{111} facet-facet edges. We calculate activation energies using Effective Medium Theory, as total energy calculator, and Nudged Elastic Band method to obtain the minimum energy path. The simulation results show that near the edge and before diffusing down, the trimer prefers a configuration of closed triangle (HCP-T). The facet-facet barrier increases gradually with the number of facet layers. After the second layer the barriers reache a constant value of 0.35, 0.45 and 0.53 eV for adatoms, dimers and trimers respectively.

Keyword: Facet-facet barriers, activation energies, Nudged Elastic Band method.

Las barreras energéticas de activación para la difusión de átomos entre facetas multicapas es una factor clave en la fabricación de nanoestructuras y en el procesamiento de superficies. Este trabajo presenta cálculos de estática molecular de trímeros de átomos de Ag que se difunden entre facetas Ag{111}. La energía de activación se calcula usando el método "Effective Medium Theory", como calculador de la energía total del sistema, y el método "Nudged Elastic Band" para obtener la trayectoria de mínima energía. Los resultados de la simulación muestran que cerca del borde entre facetas y justo antes de la difusión, los trímeros prefieren una configuración triangular (HCP-T). La barrera faceta-faceta se incrementa gradualmente con el numero de capas de la faceta. Después de la segunda capa, la barrera alcanza un valor constante de 0.35, 0.45 y 0.53 para átomos simples dímeros de átomos y trímeros de átomos respectivamente.

Palabras claves: Barreras faceta-faceta, energías de activación, Método Nudged Elastic Band.

1. Introduction

Nanostructures such as nanowires on surfaces will play a very significant economic role at the heart of the next generation of electronic devices. Thin films can present steps and facets that could provide a good template for the self-assembly of nanostructures. Consequently, controllable growth of plain or patterned surfaces is one of the most active research areas nowadays [1].

Diffusion barriers control mass transport during surface deposition and determine the formation and stability of well defined patterns, necessary for nanostructures fabrication. Adatom diffusion on flat surfaces has been exhaustively studied for many years using diverse computational and experimental methods.

Ag adatom diffusion barriers for hopping and exchange processes on Ag{111} and Ag{100} flat surfaces has been intensely studied. Zhang et al. summarized the results calculated by different methods of the energy barrier for the diffusion of adatoms on Ag{100} surfaces [2]. The energy barriers reported are in the range of 0.37 to 0.48 eV for hopping process. Diffusion of small clusters on Ag{111} flat surfaces have also been studied. The energy barriers increase gradually when we consider adatoms, dimers and trimers, but stay almost constant for tetramers [3].

An adatom coming to the edge of a step feels a barrier that prevents it from going over the edge, the Ehrlich-Schwoebel (ES) barrier. Dimers and trimers present bigger ES barriers than adatoms [4]. On the other hand, Ag{111} deposited surfaces are very rough with mountains as high as 30-40 atomics layers (multilayer growth)[5]. This can be explained by the relatively high difference between the hopping activation energy on a flat surface and the energy barrier to descend a step. In this context a three-dimensional (3D) Ehrlich-Schwoebel (facet-facet) barrier is defined [6] as a generalization of conventional ES barriers.

In this work, we calculate facet-facet diffusion barriers on Ag{111} surfaces for Ag adatoms, dimers, and trimers. Particular attention was focused on trimers. Some aspects of the diffusion near the facet border is also studied. Effective Medium Theory (EMT) as interatomic potential and Nudged Elastic Band (NEB) method as minimum energy path calculator is employed. The paper is organized as follow: in section 2 we describe the simulation methods, in section 3 the simulation results are discussed and finally in section 4 we present the conclusions.

2. Simulation Methods

In order to find the minimum energy path (MEP) and the activation barrier between two states, the system total energy must be evaluated. For this purpose there are many methods available, one of most precise and general is Density Functional Theory (DFT). Unfortunately this method is not feasible when working with systems that have more than few hundred of atoms.

In this work the Effective Medium Theory (EMT) potential was used to calculate the total energy for the system [7]. The EMT potential, based on DFT concepts,

gives a realistic description of the metallic bonding, particularly in FCC elements like Ag [8]. Computationally, EMT is not much more demanding than pair potentials, but due to its many body nature it gives a far more realistic description of material properties. Additionally, the EMT method can be successfully employed in systems with up to millions of atoms. The total energy minimization was carried out by using the conjugate gradient method, taking the maximum force between atoms as parameter of convergence.

Currently there is a variety of methods to calculate activation energies of rare events. In this work we used the Nudged Elastic Band (NEB) method [9,10,11]. The NEB method is numerically more efficient than the molecular dynamics simulation in determining activation energies. In this work we used between 5 to 30 images to calculate the MEP and the results were always very consistent. The minimization of the band was carried out by using the steepest-descent algorithm, until the maximum force between atoms is lower than 0.005 eV/A.

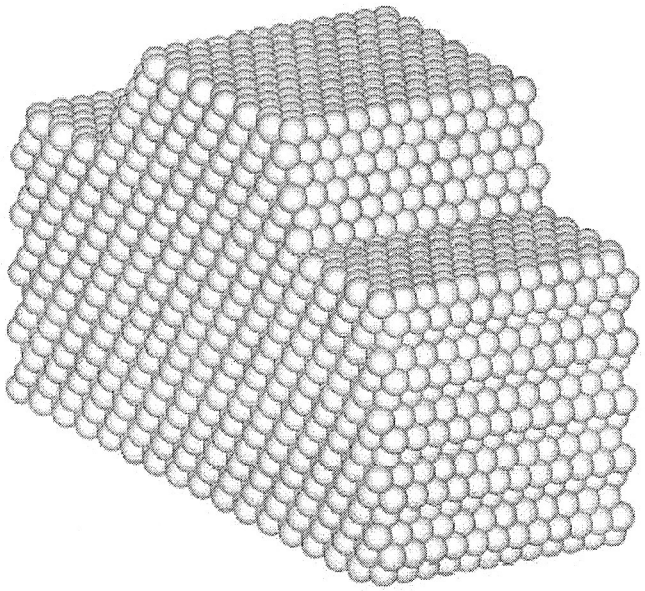

Figure 1. *Configuration used in the calculations.*

3. Simulation Results

In order to compare the magnitude of the diffusion barriers obtained in this work and to validate our procedures, first we begin considering results of widely available diffusion barriers of Ag atoms on Ag surfaces.

Our calculations yield an energy barrier of 0.38 eV for adatom hopping process and 0.68 eV for the exchange process on an Ag{001} flat surface, this values are very similar to those summarized by Zhang et al. [2].

On a flat Ag{111} surface, an atom may occupy either FCC or HCP sites, which energetically are very similar being the FCCs slightly more favorable. The activation energies we obtained are 0.07, 0.11 and 0.17 eV for Ag adatoms, dimers and trimers on an Ag{111} flat surface, respectively. Chang et al. obtained similar results by using the Embedded Atom Method (EAM) interatomic potential [3].

Adatom diffusion across steps (one layer facets) has also received great attention. It was found experimentally that the energy barrier of an adatom descending a step is 0.15 eV higher than diffusion on flat Ag{111} surfaces [12]. We obtained an energy barrier of 0.22 eV for adatoms descending steps. When the number of layers (N) is bigger than two, the energy barrier remains at 0.35 eV, see Table 2. This is in accordance with the results reported by Wang et al. for Cu [13].

In the case of dimers we consider only the diffusion of one of the dimer atoms because it was shown that this process has smaller energy barrier [14]. Energy barriers for stepping down of Ag dimers increases from 0.26 eV (N=1) to 0.45 eV (N>2), see Table 2.

Trimers on an Ag{111} surface can have many configurations, but it was found that the most stable is the compact triangular form [3]. Trimers can occupy four possible places: FCC-H, FCC-T, HCP-H, and HCP-T, see figure 2. FCC and HCP means that the three atoms are sitting on FCC or HCP sites. H means that the center of the triangle is on a hollow site and T on a top site. The four cases present small energy differences. However, near the edge HCP-T is the most stable configuration, see table 1.

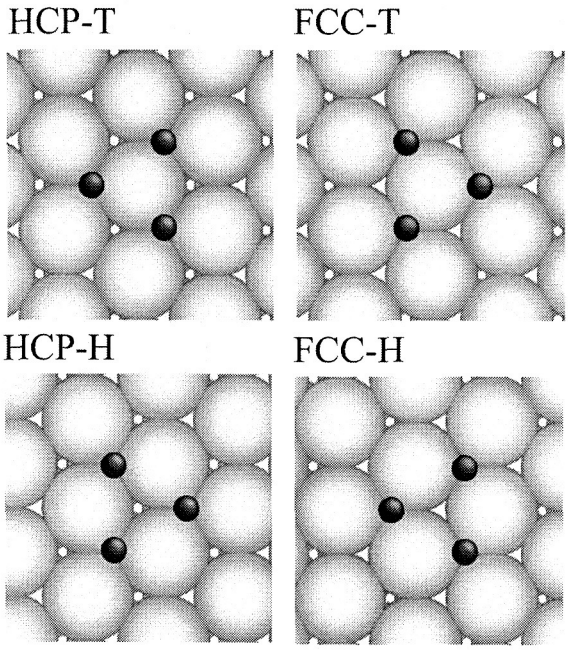

Figure 2. *Compact triangle configurations of trimers next the edge.*

Tabel 1. *Energy realtive to HCP-T configuration.*

Configuration	Energy (eV)
HCP-T	0
FCC-H	0.01
FCC-T	0.01
HCP-H	0.02

We have examined many mechanism for stepping down of trimers. The mechanisms that presented the smallest activation energies occupy HCP-T positions before diffusing down Ag{111} facets. This position corresponds to two of the trimer atoms aligned in front of the edge. HCP-T positions can be reached by translation from FCC-H (0.14 eV) or by a rotation from FCC-T (0.15 eV).

Figure 3(a) shows the translation of a trimer diffusing from FCC-T to HCP-H to FCC-T and Figure 3(b) shows the rotation from FCC-T to HCP-T positions. Black spheres represent the HCP and FCC locations and the white spheres represent the saddle points configurations. The maximum activation energy is 0.17 eV, which corresponds to translation from HCP-H to FCC-T positions (image 10).

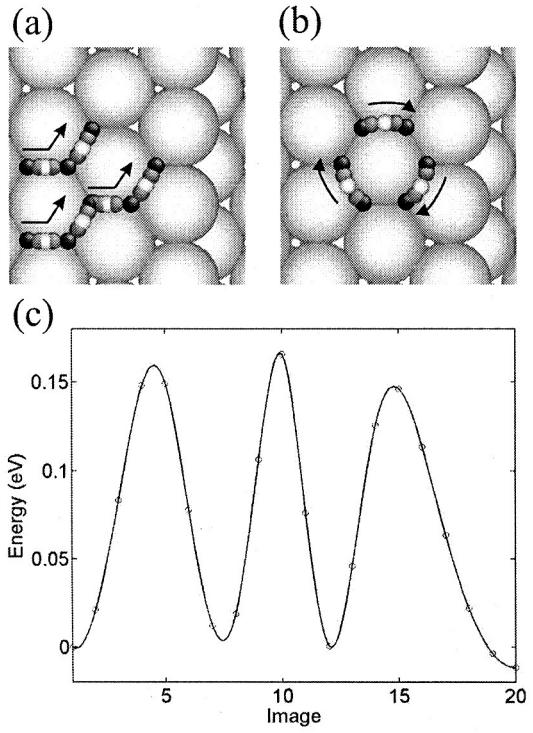

Figure 3. *Diffusion of Ag trimers on an Ag{111} surface. (a) Translation from FCC-T to HCP-H to FCC-T positions, (b) rotation from FCC-T to HCP-T and (c) minimum energy path for the diffusion.*

The trimer steps down the facet after reaching the HCP-T position at the edge. In principle the atoms of the trimer can diffuse through hopping or exchange processes, but in general hopping requires a greater amount of energy making it a less frequent process. In this work we concentrate in exchange processes only. The two atoms closest to the edge (HCP-T) can diffuse simultaneously or one-by-one. In the case of a step (N=1), our calculation yields an energy barrier of 0.73 eV for the simultaneous diffusion of two atoms of the trimer and 0.33 eV for the diffusion of one atom. For this reason we only concentrate in the diffusion of one atom of the trimer atoms.

Fgure 4 shows the stepping down process of one of the trimer atoms. Black spheres represent the initial and final states, on the other hand white spheres represent the saddle point configuration (maximum energy of the MEP).

During the stepping down the trimer tries to stay in the compact triangle configuration. The maximum energy of the MEP is 0.33 eV and corresponds to the breaking down of the triangle configuration (image 8). The energy barrier of trimers exceeds by 0.11 and 0.07 eV the energies of adatoms and dimers, respectively. These results show that it is more difficult for trimers to diffuse down because of the great stability of the compact triangle configuration.

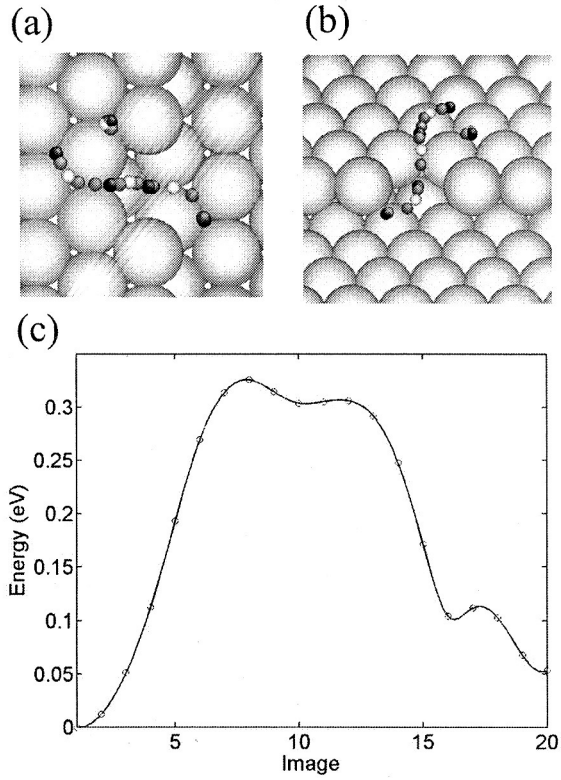

Figure 4. *Trimer diffusion process from {111} to {111} facets in the case of N=1 (step). (a) Top view, (b) projection view and (c) minimum energy path of the process. Black spheres are initial and final states, white spheres correspond to the saddle-point configurations.*

For multilayer facets we only concentrate on one-by-one diffusion mechanisms because they are energetically more favorable. Table 2 shows the energy barriers of trimers diffusing down multilayer facets. The values for trimers show similar trends for adatoms and dimers. For facet-facet barriers (N>2) it was obtained 0.53 eV.

Table 2. *Energy barrier between Ag{111} facet versus number of layers.*

	N=1	*N=2*	*N=3*	*N=4*	*N=5*
Adatoms	0.22	0.34	0.35	0.35	0.35
Dimers	0.26	0.44	0.45	0.45	0.45
Trimers	0.33	0.52	0.53	0.53	0.53

4. Conclusions

We have reported the results of facet-facet barriers to the diffusion of adatoms, dimers and trimers on Ag{111} surfaces. Our calculations show that the most stable configuration for trimers next to the edge of Ag{111} facets is HCP-T. The mechanisms with lower activation energies occupy this position before crossing the edge. One-by-one atom diffusion mechanisms is preferred by dimers and trimers. Saddle point configurations for trimers correspond to the breaking down of the compact triangle arrangement. In the case of monolayer steps (N=1), trimers require 0.35 eV to diffuse down. For facets (N>2) the diffusion barrier, 0.53 eV, becomes independent of the number of layers, so following the same trend of adatoms and dimers.

1. J.J. de Miguel,and R. Miranda, J. Phys.: Condens. Matter **14** (2002)R1063.
2. C.M. Zhang, M.C. Bartelt, J. Wen, C.J. Jenks, J.W. Evans, and P. Thiel, Surf. Sci. **406** (1998) 178.
3. C.M. Chang, C.M. Wei, and S.P. Chen, Phys. Rev. Lett. **85** (2000)1044.
4. M. Bockstedte, S. Liu, O. Pankratov, C. Woo, and H. Huang, Comput. Mater. Sci. **23** (2002)85.
5. K. Bromann, H. Brune, and K. Kern, Phys. Rev. Lett. **75** (1995)677.
6. S.J. Liu, H. Huang, and C.H. Woo, Appl. Phys. Lett. **80(18)** (2002)3295.
7. K.W. Jacobsen, J.K. Norskov, and M.J. Puska, Phys. Rev. B **35** (1987)7423.
8. K.W. Jacobsen, P. Stoltze, and J.K. Norskov, Surf. Sci. **366** (1996)394.
9. B.J. Berne, G. Cicotti, D.F. Coker, *Classical and Quantum Dynamics in Condensed Phase Simulations.* (World Scientific, 1997).
10. G. Henkelman, and H. Jónsson, Phys. Rev. Lett **90** (2003)116101.
11. G. Henkelman, B.P. Uberuaga, and H. Jónsson, J. Chem. Phy. **113** (2000)9901.
12. J. Vrijmoeth, H.A. van der Vegt, J.A. Meyer, E. Vlieg, and R.J. Bhem, Phys. Rev. Lett. **72** (1994)3843.
13. J. Wang, H. Huang, and T.S. Cale, Modelling Simul. Mater. Sci. Eng **12** (2004)1209.
14. A.M. Coronado, and H. Huang, CEMS-Comp. Model. Eng. Sci. **10(1)** (2005)39.