

OPTIMAL CLUSTER CONFIGURATIONS AND STRAIN DEPENDENCE OF THE ACTIVATION ENERGIES ON Cu(001) SURFACES

CONFIGURACIONES ÓPTIMAS DE AGLOMERADOS Y DEPENDENCIA CON RESPECTO A LA DEFORMACIÓN DE LAS ENERGÍAS DE ACTIVACIÓN SOBRE SUPERFICIES Cu(001)

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ABSTRACT

One of the most important aspects in the epitaxial growth of thin films is the mobility of adatoms and small clusters. As this mobility is related to the activation energies, many research efforts are concentrated in the calculation and determination of the overall role of these energies. Previous studies have shown that activation energies can be easily modified, using strain fields for example, however many aspects remain still unclear. In this work we use Genetic Algorithms (GAs) to calculate optimal cluster configurations on Cu(001) surfaces modeled with the Embedded Atom Method (EAM). The optimal configurations obtained show no relationship with the strain states imposed. Additionally, we study the dependence of the hopping and exchange activation energies on the strain level of the films. It is observed that hopping shows a clear dependence on the biaxial tension or compression, in contrast to the exchange process which shows more complex dependence.

Key words.- Genetic algorithms, Activation energies, NEB method.

RESUMEN

Uno de los aspectos más importantes en el crecimiento epitaxial de películas finas es la movilidad de adatoms y pequeños aglomerados. Como esta movilidad está relacionada a las energías de activación, muchos estudios están concentrados en el cálculo y determinación del rol de estas energías. Por ejemplo, estudios previos mostraron que las energías de activación pueden ser fácilmente modificadas, usando campos de deformación. No obstante muchos aspectos aún no están muy claros. En este trabajo empleamos Algoritmos Genéticos para calcular configuraciones óptimas de agregados sobre superficies Cu(001) modeladas con el método de los átomos embebidos (EAM). Las configuraciones óptimas obtenidas no mostraron dependencia con respecto a la deformación aplicada. Adicionalmente estudiamos la dependencia de las energías de activación de salto e intercambio con respecto al nivel de deformación aplicada. Se observó que el salto muestra una dependencia clara con respecto a la tensión o compresión biaxial, en contraste al intercambio, cuya dependencia es más compleja.

Palabras clave.- Algoritmos genéticos, Energías de activación, Método NEB.

INTRODUCTION

Nanoprecision fabrication is a key aspect that has to be mastered in order to bring to us all the dreamed promises of nanotechnology. Notably,

controllable growth of plain or patterned surfaces is one of the most active research areas nowadays [1]. This process has a significant economic importance as it finds a variety of applications in the industry.

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The nucleation and assembly of nanostructures is a very complex process that is dependent 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 [2, 3].

In the last years many methods of assisted growth have been intensively studied. These methods are ion assisted deposition, surfactant mediated growth or codeposition, to name a few. In this sense one of the most promising approaches is the so called self-assembly or self-organization. One of its techniques consists in making use of buried dislocations in order to produce a long range strain field where tensile and compressive areas can be found. These specific areas are then employed to generate diverse patterned structures [1, 4]. Using tensile or compressive strain surfaces one can easily modify the activation energies [5, 6, 7]. Eventually, this could be instrumental in order to control adequately the growth of the films.

Growth of Cu surfaces has been intensively studied along many years, therefore the amount of data available is of importance [1, 8]. It was found that Cu(001) tends to grow in a more even fashion than Cu(111) [1]. This phenomenon was explained by the difference between the hopping activation energy and the Ehrlich-Schwoebel (ES) barrier. If this difference is big, like on Cu(111) surfaces, the adatoms deposited on top of the islands will tend to stay there, making the steeping down very difficult.

The resulting surfaces can be very rough, which is in general not desirable. As a result, the study of the ES barrier (and its generalizations) is of importance [9, 10, 11].

The steeping down of adatoms deposited on top of islands is an interesting phenomenon and has also received a lot of attention. Originally it was supposed that the dominant path was the hopping of the adatom.

Recent theoretical studies [12, 13, 14] showed phenomena difficult to be seen from experimental methods: the exchange could also play an important or even instrumental role on the growth of defectless surfaces.

In this paper we concentrate on Cu(001) surfaces and study diverse issues related to it. First we use Genetic Algorithms (GAs) to obtain minimum energy configurations of small clusters. Then we employ the Nudged Elastic Band (NEB) method in order to study the hopping and exchange mechanisms that would occur between optimal cluster configurations and its dependence on the strain of the film.

SIMULATION METHODS

Both searching for optimal cluster configurations and calculation of activation energies require the evaluation of the total energy, therefore the necessity of having the 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 phenomenological approximations: the Embedded Atom Method (EAM) [15], partly based on DFT concepts, has been successfully employed in systems with millions of atoms. In our calculations we have used ParaDyn [16], a parallel implementation of EAM. Moreover, for the visualization we used the AtomEye program [17].

Finding global minima is in general a difficult task. Only a few methods have demonstrated to be successful in a great range of applications, Genetic Algorithms (GAs) [18] is one of them. GAs mimic the Darwinian principle of the survival of the fittest. Even though the method has proven to be robust, it is computationally intensive, which in combination with atomistic simulation methods requires an unprecedented need of computational resources. Hence, it is a good practice to keep the size of the simulated system at manageable levels. Atomistic processes represent a great challenge for GAs and in order to maintain the ability of the method to manage hundreds of degrees-of-freedom it has been necessary to develop specific purpose implementations [19].

Nevertheless, in this work we use a general purpose implementation, the PIKAIA code [20].

Currently there is a variety of methods to calculate activation energies of rare events. We

use our own implementation of the Nudged Elastic Band (NEB) method [21] with the climbing image algorithm [22].

NEB can successfully avoid using costly Molecular Dynamics (MD) simulations to determine minimum energy paths and corresponding 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 it is related to the activation energy.

SIMULATION RESULTS

The basic configuration we employ in our calculations is a slab with six layers and 1200 Cu(001) atoms, of which the two bottom layers are fixed. The horizontal and vertical directions in the figures below coincides with vectors [100] and [010], respectively.

Additionally, periodic boundary conditions are set along the plane. In order to test our methodology we first calculate the activation energies for the hopping and exchange of adatoms on top of an unstrained surface. The values obtained are 0.50 eV for hopping and 0.75 eV for exchange, which agree with previous calculations [1, 5, 23].

The study continues with the calculation of the optimal configurations of an octamer, a cluster with eight atoms, located on top of the six layer slab. The initial arrangement is shown in Fig. 1(a), which is considered as having a potential energy of 0.00 eV.

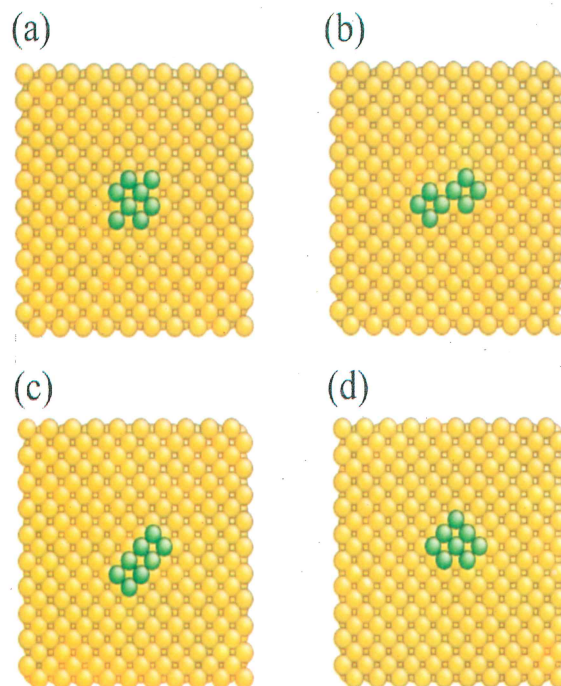


Fig. 1 Initial and optimized configurations, (a) initial configuration, 0.00 eV, (b) 0.02 eV, (c) -0.25 eV and (d) -0.29 eV (global minimum) of potential energy.

For simulation purposes the GAs parameters taken are as follows: population number 200, generations number 1000, crossover rate 0.85 and variable mutation rate 0.05-0.25. Even though the number of both population and generations employed are relatively high, in general it was not possible to optimize the positions of more than eight or eventually ten atoms. This is because the complexity of the searching space increases exponentially with each additional atom considered.

After using GAs on several runs we selected the following resultant optimal configurations. Figs. 1(b), 1(c) and 1(d) show arrangements with 0.02 eV, -0.25 eV and -0.29 eV of potential energy, respectively. The first case presents slightly more energy than the initial configuration case. Quite the opposite, the last two cases present energy levels smaller than the initial configuration, with the last case representing the global minimum. We observed that these minimum energy configurations do not depend on the strain of the film, contrary to what happens with activations energies, as will be shown below.

Furthermore, the NEB method is employed in order to study the dependence of the activation energies as a function of the strain of the film. We will center the analysis in the following two cases, the first case is shown in Fig. 2, it represents a sequence of atom jumps between the initial (Fig. 2(a)) and final (Fig. 2(d)) configurations for an unstrained surface ($\varepsilon_{xx} = \varepsilon_{yy} = 0.00$).

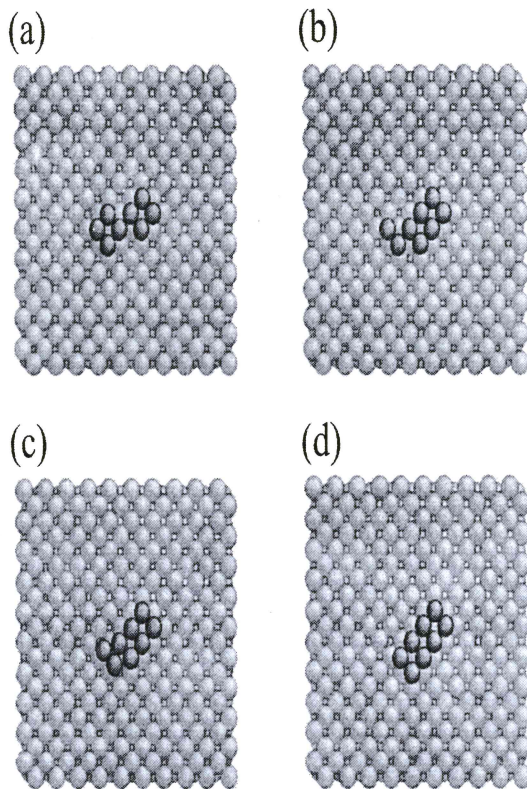


Fig. 2 (a) Initial, (b) local minimum, (c) saddle point and (d) final energy configurations.

Fig. 2(a) can be regarded as a junction of two tetramers, which in fact are the most stable configurations of four atom clusters, this arrangement has a 0.00 eV energy level.

Using the NEB method with ten images it is observed that in order to attain the final configuration one of the tetramers is initially split into two dimers resulting in the configuration shown in Fig. 2(b), which corresponds to 0.01 eV. Then the system goes to the saddle point configuration, Fig. 2(c), which corresponds to an energy level of 0.42 eV.

And finally, it is shown Fig. 2(d), the final configuration, that has -0.27 eV of energy. These results show that the process presented in Fig. 2 has more probability to happen than the hopping of a single adatom which has, as mentioned above, 0.50 eV of activation energy.

Table 1 presents the results of the activation energies obtained when the strain of the film was varied. It can be observed that biaxial tension, $\varepsilon_{xx} = \varepsilon_{yy} = 0.04$, and biaxial compression, $\varepsilon_{xx} = \varepsilon_{yy} = -0.04$, corresponds to the highest and lowest activation energies, 0.57 and 0.30 eV respectively. Besides mixed strain states present energies slightly below the unstrained case.

Table 1. Activation energies (E_a) in function of The strain.

$\varepsilon_{xx}, \varepsilon_{yy}$	0.00, 0.00	0.04, 0.04	-0.04, -0.04	0.04, -0.04	-0.04, 0.04
E_a (eV)	0.42	0.57	0.30	0.41	0.40

The results obtained show that if we want to hinder (or to favor) the process shown in Fig. 2, the step to be taken would be to apply a biaxial tension (or compression). Obviously a uniaxial tension (or compression) will be of help, but the increase (or reduction) in the activation energy will be smaller.

The second case we studied is shown in Fig. 3. This time we consider the optimal configuration of the octamer, which was previously obtained using GAs. On top of this eight atom cluster we added an adatom (the darkest atom) and we studied the dependence of the exchange mechanism in function of the strain of the film. We show the initial (Fig. 3(a)), the saddle point (Fig. 3(b)) and the final (Fig. 3(c)) configurations for an unstrained surface ($\varepsilon_{xx} = \varepsilon_{yy} = 0.00$).

Fig. 3(c) represents the most stable configuration of a nine atom cluster and we are interested in calculate the activation energy needed for the configuration shown in Fig. 3(a) to become a system with a global minimum energy. For the unstrained surface the saddle point energy obtained is 0.30 eV, which is much smaller than

the energy corresponding to exchange on a flat surface, i.e. 0.75 eV.

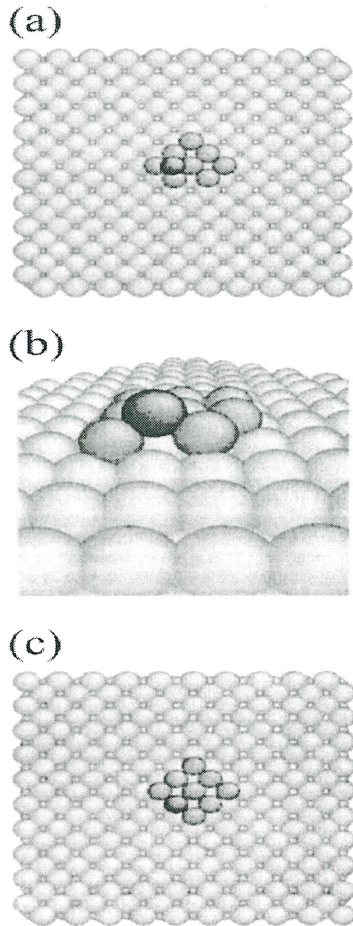


Fig. 3 (a) Initial, (b) saddle point and (c) final energy configurations.

Table 2 presents the activation energies obtained when the strain of the film is varied. In this case both biaxial tension and compression present smaller activation energies than the unstrained state. Additionally, one of the mixed strain states has 0.25 eV (smaller than the unstrained case) and the other one has 0.31 eV (slightly above than the unstrained case). In fact, these results present a smaller dependence on the surface strain

Table 2. Activation energies (E_a) in function of the strain.

$\epsilon_{xx}, \epsilon_{yy}$	0.00, 0.04,	0.04, -0.04,	-0.04, -0.04,	0.04, -0.04,	-0.04, -0.04,
	0.00	0.04	0.04	0.04	0.04
E_a (eV)	0.30	0.25	0.29	0.25	0.31

Recent calculations [5] for hopping and exchange processes of an adatom on a flat Cu(001) surface revealed that hopping has a smaller dependence on strain in comparison to exchange. In the cases studied herein we obtain an opposite tendency. Noticeably we have to consider that in essence the configuration here analyzed is different from the one presented in [5]. Considering the problem of growing flat defectless film surfaces, it is certainly of help to have activation energies to be as lowest as possible, but it is also important to consider the ability of the adatoms to step down the islands [1, 22], which in many cases occurs through an exchange process [12].

In general, purely biaxial tension or compression strain stimulates or hinders only one of either hopping or exchange processes. If our desire is to have adatoms as mobile as possible, maybe a mixed strain state will be of help. The overall effect of this supposition can only be observed using some mesoscale simulation method, like Kinetic Monte Carlo.

CONCLUSIONS

In this work we have employed the EAM potential to study some specific issues that arise in the behavior of Cu clusters. First we used Genetic Algorithms (GAs) to determine the optimal, i.e. minimum energy, configuration of an eight atom cluster. It was observed that the applicability of a general purpose implementation of GAs is limited to a small number of atoms as the complexity of the problem rises exponentially with the increase of the cluster.

Additionally we have used the Nudged Elastic Band (NEB) method to study some hopping and exchange processes. We determined the influence of the strain of the film on the activation energies and observed that for the hopping process biaxial tension or compression clearly hinders or stimulates it. On the other side, for the exchange process, biaxial or mixed strain states are not conclusive. It is necessary to consider also the cluster configuration and orientation. In this sense it would be of value to study the effects of mixed strain states in the growth of films in the long time scale, especially of time varying mixed strains.

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