A kinetically driven growth mechanism: AlF$_3$ over Cu(0 0 1)

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Abstract

A new diffusion model based on kinematic properties and supported by Metropolis Monte Carlo free energy minimization and density functional theory calculations is proposed in this work. This new mechanism breaks the isotropic features of random adatom diffusion over a single crystal surface, not only about the main directions but also about the sense of movement. The present model allows us to understand all of the anomalous growing features characterizing the behaviour of an insulator film, such as aluminum fluoride, over a metallic Cu(1 0 0) single crystal surface. The growth process of this system is characterized by several non-fully understood features, including a large diffusion coefficient, sticking at both sides of steps, and island atomistic arrangement along special directions. Although we focus our analysis on the AlF$_3$/Cu(1 0 0) system, our conclusions may be extended to the diffusion of other complex molecules over different surfaces.

Keywords: diffusion, solid surfaces and interfaces, Monte Carlo methods, electronic structure

AQ1 (Some figures may appear in colour only in the online journal)

1. Introduction

Our comprehension of the atomistic mechanisms related with the thin film growth has impressively evolved over the last few years [1, 2]. The way that an adatom diffuses over a surface reaching either defects, steps, or another diffusing adatom to nucleate, determines the basic paths of growth. Although this diffusing mechanism can be as simple as one atom jumping from one equilibrium site to the nearest one, it can also involve more complicated processes, such as atomistic exchange [3, 4], subsurface diffusion [5, 6], and long jumps [7], including even memory effects [8], to mention some of the most relevant discoveries. In addition, the design of new methods to obtain flatter surfaces and sharper interfaces leads to the fabrication of elaborated artificial structures, such as magnetic superlattices [9], involving the growth of flat and structurally almost perfect layers. However, layer by layer (LbL) growth, where no atomic level starts to growth before the preceding atomic monolayer (ML) is completely filled, is the exception

rather than the rule. Intermixing, even between bulk immiscible materials, and defect generation, to mention a couple of facts, may lead to the development of roughness from the very beginning of the growth [10].

The diffusion of an adatom on a flat surface is by far the most important kinetic process in film growth. Smooth, uniform films could not be formed without enough surface mobility. In the extreme case of zero mobility parallel to the surface, an adatom stays where it lands and the resulting growth front is very rough. Island nucleation is the only possible growth mechanism over a perfectly plane surface. However, a real surface is composed of flat terraces limited by steps. While ascending steps constitute nucleating sites, descending ones usually act as atom mirrors, since the Ehrlich Schwoebel barrier [11] (i.e. the energy needed for the adatoms to overcome the steps, falling down to the lower terrace) is too high compared to the energy needed to return to the inner terrace. Although the decoration of steps at the upper side is disfavoured in metals [12] and insulators [13]
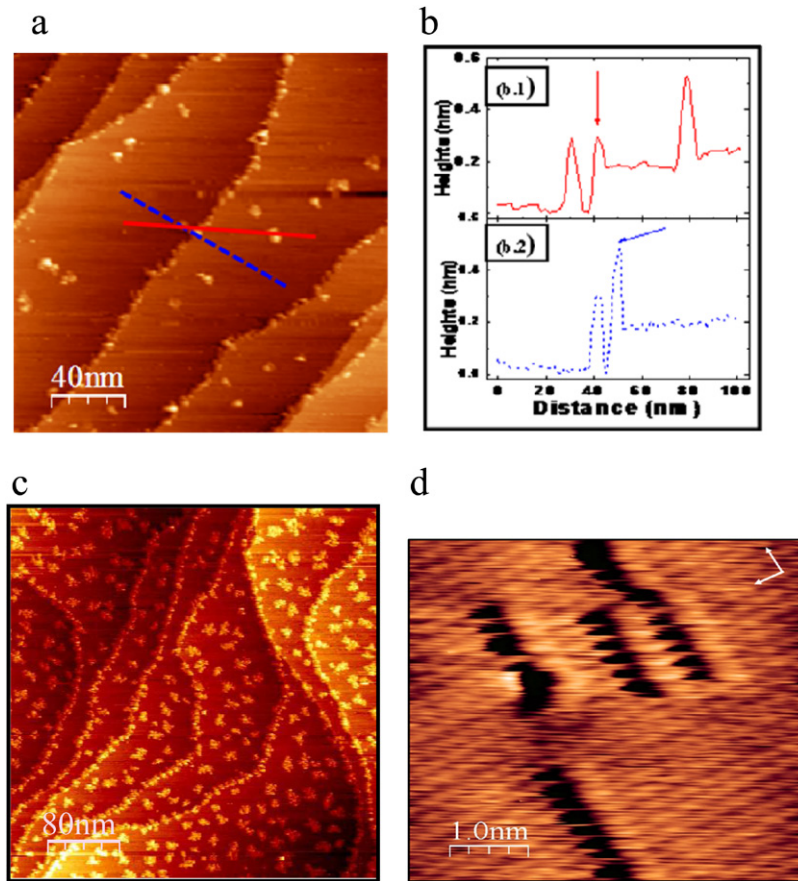
Figure 1. Snapshot of STM images of AlF$_3$ on Cu(1 0 0) for different coverages and resolutions: (*a*) 0.05 ML, (*b*) STM profiles corresponding to figure 1(*a*), (*c*) 0.25 ML, (*d*) over-terrace nucleation depicted with atomic resolution. The arrows in (*d*) show the close-packed directions directions (1 1 0) and (1 −1 0) of the Cu(1 0 0) substrate.

due to this mechanism, it has been experimentally observed. To explain this behaviour, a model based on the modification of the nature of the step by the adatoms has been proposed [12, 14]. Thus, a competition between on terrace and at (ascending) steps nucleation is established. For large atomic/molecular diffusion lengths, as compared to terrace size, adatoms have enough time to reach the steps sticking there, otherwise they may nucleate over the terrace. Thus, assuming that the adatoms either stick at the steps or give place to a nucleating island over the terrace, we can determine the diffusion length by measuring either the island density or the size of the denuded zone.

The growth of insulator films is a physical phenomenon that is even more important than metallic growth due to technological requirements, and it is certainly more complicated from the basic physics point of view. In this work we introduce the theoretical results related to the growth of AlF$_3$ on Cu(1 0 0) [15, 16]. This system presents a clear technological interest from several aspects, ranging from solar cell technology [17] to molecular biology [18], but our main interest here is focussed on the description and understanding of its unusual experimental behaviour from the very beginning of the deposition process.

Figure 1 shows three scanning tunnelling microscopy micrographs of the Cu(1 0 0) surface taken in ultra high

vacuum at room temperature [16]. The coverage of 0.05 and 0.25 ML AlF$_3$ are shown in figures 1(*a*) and (*c*), respectively. Some features deserving to be mentioned are

(a) The STM profiles shown in figure 1 reveal that AlF$_3$ molecules nucleate at both step sides, which is a quite unusual experimental behaviour. This conclusion can be easily reached by measuring the height of island in three situations, that is: (a) isolated in middle terrace, (b) at the ascendant step (arrow in figure (*b*)1) and descendant step (arrow in figure (*b*)2). AQ2

(b) A diffusion path length (DPL) of around 20 nm is obtained from the island density measurements in figures 1(*a*) and (*c*). The same result is obtained from the measurement of the maximum size of the terraces that do not allow island nucleation on them (lower left corner at figure 1(*c*)). By taking the deposition rate of ~2 × 10^{-2} ML s^{-1} into account, we obtained a value for the diffusion coefficient at room temperature of ~10^{-10} cm^2 s^{-1}; that is, roughly one order of magnitude larger than for Cu on the same substrate [2, 8].

(c) The unusual AlF$_3$ nucleation only along the high symmetry [1 1 0] axis of the fcc Cu lattice. The first stage of the over-terrace nucleation is depicted with atomic resolution in figure 1(*d*), where the small island nucleation along

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[1 1 0] axis is clearly shown. The nearby AlF_3 chains are separated by at least one Cu row, which is understandable considering the size of the molecule.

(d) The growth of AlF_3 on the Cu(1 0 0) surface is characterized by dendritic island formation. At around coverages of 0.05 ML, the terrace islands display a shape evolution from a compact to a fractal-like form. These fractal-like islands cover the substrate with a single ML film, up to depositions of 0.80 MLs, while for larger coverages the growth results in the formation of 3D islands [16].

Kinetic Monte Carlo (KMC) simulations have allowed us to understand some of the issues related to the growth mechanism in an AlF_3/Cu(1 0 0) system, such as the shape transition from compact to fractal, the growth of smaller islands close to and around the steps, and the dendritic 2D island formation [16]. Although the KMC method can enable the study of diffusion processes, including time, it is not able to identify the new mechanisms that are responsible for any process on a surface. Within KMC it is necessary to include all of the possible mechanisms with their respective barriers to obtain a realistic description of the system; that is, one needs to fully know the processes before starting the simulation. No hidden mechanism can be found using only KMC. Additionally, the morphology of the basic blocks on which the islands are built has not been revealed in these studies. The purpose of this work is simply to identify the structure of these blocks based on *ab initio* and Monte Carlo (MC) calculations. In so doing, it is possible to find an explanation for several non-fully understood features in the AlF_3/Cu(1 0 0) system, including a large diffusion coefficient, nucleation on both sides of the steps, and the island atomistic arrangement along special directions for small coverage.

2. Theoretical methods and details of calculations

Our theoretical modelling effort is based on Metropolis MC free energy minimization simulations using N-body interatomic potentials and density functional theory (DFT) calculations.

2.1. MC method

We use an MC method [20] that employs realistic potentials, including a density-dependent term, to account for many-body interaction. The interaction potentials employed to describe the Al–Al, Cu–Cu, and Al–Cu interactions have been obtained using the second-moment approximation of the tight-binding scheme (TB-SMA). The model also includes a short-range repulsive pair potential plus a long-range many-body contribution that are based on a tight-binding description of the electronic structure [21, 22]. The Born–Mayer pair potential and the classic 6–12 Lennard-Jones potential are used to describe the F–F and Al–F interaction. In addition, the ionic pairs (Al–Al, F–F and Al–F) are augmented with Coulomb interactions [23].

The methodology uses a standard Metropolis MC method with periodic boundary conditions. The simulation slab was built from seven layers, each of which had 144 atoms of Cu. The last three Cu layers were frozen to simulate the bulk, while all of the remaining atoms of the sample were allowed to move. At a given temperature T, in each step of our MC simulation, every atom in the sample is randomly displaced a fraction of a lattice constant and the energy of the resulting configuration is calculated based on a set of interatomic potentials. The configurations are then accepted or rejected in the usual way: those with an energy lower than the former one are automatically adopted; if the final energy is higher, then the decision is taken after comparing the Boltzmann factor ($p_i = \exp(-E_i / kT)$) of the energy increment with a random number.

Here, it is important to remark that the purpose of using this kind of computational modelling is not to reproduce exactly every detail of the real process but rather to create an idealized, simplified system where one would be able to identify the main features and driving mechanisms of the observed behaviours. The same methodology has been used previously with high success to discover a new diffusion collective mechanism explaining the instabilities of Co film grown over Cu(1 1 1) [12], the ordered structure and melting behaviour of Pb overlayers on Cu(1 0 0) [24], and to understand the effect of surfactants on Cu(1 1 1) surfaces [6].

2.2. Ab initio method

The Quantum Espresso code [25] is applied to study the effects of the Cu(1 0 0) surface on the AlF_3 molecule's geometry. The ultrasoft pseudo-potential of Vanderbilt type, scalar relativistic with the generalized gradient approximation of Perdew, Burke, and Ernzerhof, was selected for the three elements from the QE database. A Cu slab with five layers of 3×3 fcc unit cells (90 atoms) is used for this purpose. The electron states are expanded in plane waves with kinetic energy cutoffs of 25 and 400 Ry for the wave function and the charge density, respectively. Brillouin-zone (BZ) integrations are performed with the Marzari–Vanderbilt smearing special-point technique, using a smearing parameter of 0.02 Ry and a 441 k-point mesh. The AlF_3 molecule (four atoms) and bi-molecule (eight atoms) are located at a distance 1.8 Å over the surface. A convergence threshold of 5×10^{-6} Ry for the self-consistency and 2×10^{-3} Ry Å^{-1} for the minimization of forces is used in the optimization structure procedure. We use damped dynamics (quick-min Verlet) for structural relaxation following the procedure implemented in the code. The theoretical lattice parameter $a_{Cu} = 3.651$ Å obtained with this method agrees very well with the experimental value $a_{Cu} = 3.615$ Å.

3. Results

3.1. Structure of the basic block

The first step to understand the basic mechanism behind the unusual experimental results observed in the AlF_3/Cu(1 0 0) system is to find the competing structures formed by the AlF_3 molecules on the Cu(1 0 0) surface at the initial stage of the deposition process. Before searching for the basic block with
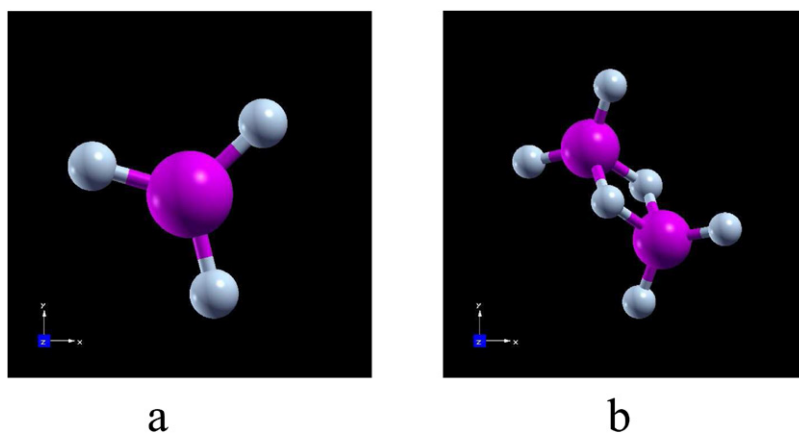
Figure 2. Geometrical structure of: (*a*) isolated AlF$_3$ molecule. (*b*) isolated bi-molecule.
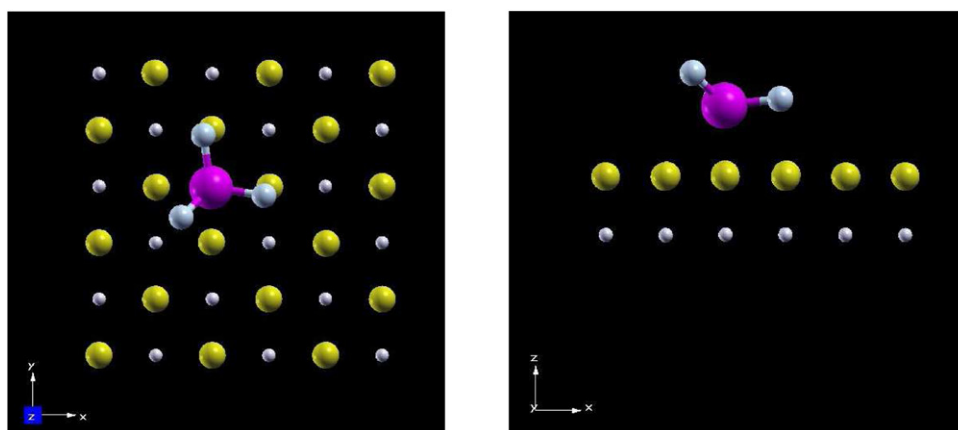

Figure 3. One molecule bonded to Cu(1 0 0) surface. Left: Upper view. Right: Side view. Grey circles: F atoms. Yellow circles: Surface Cu atoms. Small grey circles: Cu atoms below the surface. Red circle: Al atom. The F in the bridge position is located higher than the F bonded to the Cu atoms.

which the islands are built, the behaviours of the isolated AlF$_3$ molecules and bi-molecule were studied using the Quantum Espresso code.

The *ab initio* results show that the free-molecule is characterized by a triangular planar shape with the Al atom in the centre, as shown in figure 2(*a*). The distance between Al and F atoms is $d_{Al-F} = 1.642$Å, which is in close agreement with the experimental results of $d_{Al-F} = 1.654$Å [26]. The free bi-molecule shows a compact geometry that is characterized by two interconnected tetrahedrons, each of which has an Al atom located in the centre, as shown in figure 2(*b*). There is no information available in the literature regarding the shape of an isolated bi-molecule. The bi-molecule is energetically more stable than two isolated AlF$_3$ molecule by 230 meV/atom.

The geometry of the single molecule in contact with the surface is shown in figure 3. The AlF$_3$ molecule adsorbs on Cu(1 0 0) surface with the Al atom located in the four fold hollow site at a distance of 2.13 Å. Two atoms of F are located at a distance of 2.34 Å and one at 3.13 Å over the surface. At the same time, the Cu surface is slightly corrugated near the Al atom.

While the geometry of the single molecule remains almost unchanged in contact with the surface, the situation changes completely as soon as another molecule is added. Indeed, a major restructuring is observed between the two molecules and the surface in the *ab initio* calculations. To understand this behaviour, several configurations were studied by changing the way that both molecules are joined along the [1 0 0] and [1 1 0] directions of the fcc lattice. The minimum energy state for the bi-. While the geometry of the single molecule remains almost unchanged in contact with the surface, the situation changes completely as soon as another molecule is added. Indeed, a major restructuring is observed between the two molecules and the surface in the *ab initio* calculations. To understand this behaviour, several configurations were studied by changing the way that both molecules are joined along the [1 0 0] and [1 1 0] directions of the fcc lattice. The minimum energy state for the bi-molecule is reached when it almost recovers the near isolated shape along the [1 1 0] direction of the fcc lattice. While the tetrahedron formed by the F atoms and the Al atom at a distance of 3.16 Å remains almost unchanged, the F atoms bonded to the other Al atom at a distance of 2.04 Å resembles the shape of one AlF$_3$ molecule over the surface. Both parts of the bi-molecule are connected by one F atom at a height of 3.13 Å. The final geometry, once the forces are minimized, is shown in figure 4. The energy

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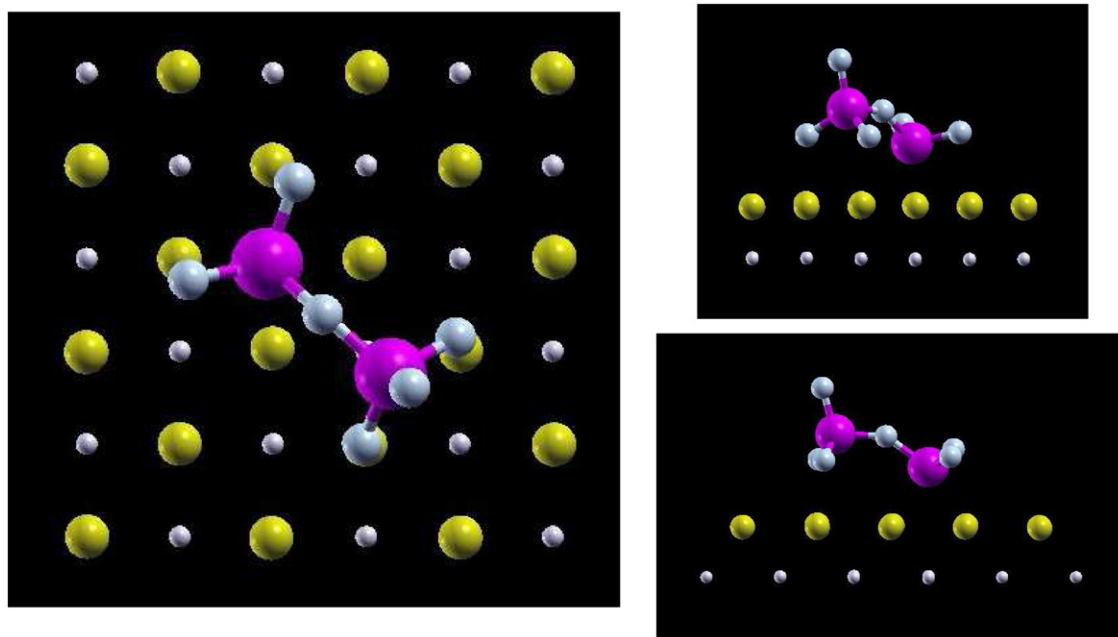J. Phys. D: Appl. Phys. **00** (2014) 000000

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Figure 4. Final configuration of the bi-molecule on the Cu(100) surface obtained from DFT. Left: Upper view; Right up: Side view along the channel [100]; Down: rotated 45º respect to the upper figure.

difference between the unrelaxed (planar Al_2F_6 bi-molecule) and the relaxed (figure 4) configurations is 75 meV/atom (7.5 eV in a cell of 100 atoms), showing the high stability of the last structure.

In contrast to the isolated molecule's behaviour, the binding energies to the surface of the AlF_3 molecules and the bi-molecule are 877 meV and 367 meV, respectively, showing that one molecule is energetically more stable than the bi-molecule over the surface. The DFT calculations only allow us to identify the shape of the basic structures formed by the AlF_3 molecules on the Cu(100) surface at the beginning of the deposition process; that is, random AlF_3 molecules or a bi-molecule with lower binding energy. The relation of these structures with the huge diffusion length, the shape of the island, and the deposition on both sides of the steps cannot be deduced with these DFT results. Additional information from another method is needed in order to understand the overall behaviour of the AlF_3/Cu(100) system. We used MC calculations with phenomenological potentials for this purpose. It is important to remark that the shape of the bi-molecule obtained with this method is the same as that obtained from DFT calculations, giving support to the potential that is used in our simulations.

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3.2. Diffusion mechanism

The second step in our research is to understand the behaviour of each basic structure formed on the Cu(100) surface by studying the diffusion mechanisms. In principle, the best approach to study surface diffusion is by means of molecular dynamics (MD). By proposing an interacting potential, one can calculate the force exerted on each atom and, by resolving the Newton equations, we can determine the movement of the adsorbed atoms over the surface. The problem in surface diffusion is that the time step needed in MD is in the order of femtoseconds, while the time for reasonable simulations of the experimental results may be in the order of microseconds. On the other hand, KMC may appear as a good alternative. In KMC we propose all of the mechanisms through their activation barriers, and so the computational time is largely improved. Knowing the barrier, we can study the different processes (such as nucleation, segregation, diffusion and so on, including the temperature dependence for instance) with a reasonable CPU time consumption. However, KMC is limited to the mechanisms that we are able to introduce into the simulation. In other words: the mechanism we already know. Thus, there is no chance of discovering a new mechanism based on KMC simulations.

Our proposal is based on the application of a Metropolis MC methodology. We have used it with great success in the
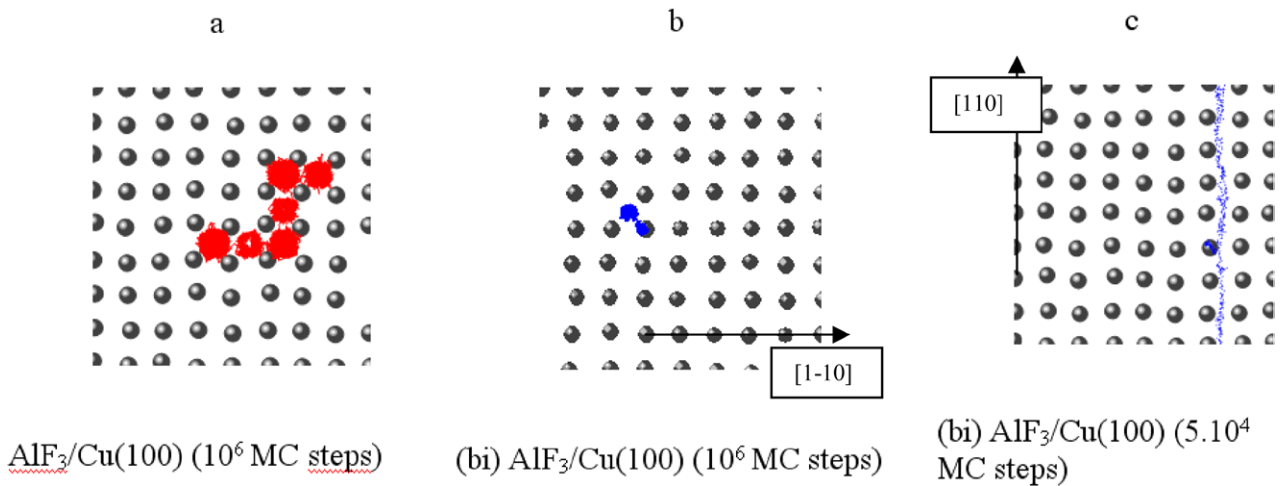
Figure 5. Different paths given by the MC simulations for aluminum fluoride on Cu(0 0 1). (*a*) The red circles represent the position of the Al atom. (*b*) and (*c*): the blue circles represent the position of the Al's centre of mass.

past, discovering, for instance, the subsurface diffusion in Pb/Cu(1 1 1) system [6] and the explosive formation of vacancy island in Co/Cu(1 1 1). As is widely known, MC simulation loses the time variable, which is present in both MD and KMC. How then are the trajectories interpreted in Metropolis MC method? In the Appendix we show how the number of steps can be, in a limited way, correlated with evolving time. It is clear that while no absolute values of diffusion coefficients can be obtained, the energy barrier and diffusion path can be undoubtedly determined.

Once we have shown the power of the Metropolis MC simulation, we can apply it to our problem. Thus, in figure 5 we depict the corresponding results for a molecule (AlF$_3$) and a bi-molecule (Al$_2$F$_6$) of Aluminum Fluoride, with the structure suggested by DFT and MC calculations, as discussed above. The results depicted in the left column (*a*) show the sites visited by a single AlF$_3$ molecule over a Cu(0 0 1) surface at room temperature. The middle column (*b*) shows the results for a planar bi-molecule (Al$_2$F$_6$) and the right column (*c*) depicts those corresponding to a stand up molecule, like that described in figure 4.

The sites visited by the single molecule, coming from MC simulations, show an agreement with the equilibrium state predicted by DFT calculations. The adsorption site is actually the four fold hollow (FFH) site. The diffusion path is found by hopping. On the other hand, the nucleation of a couple of AlF$_3$ molecules with a planar geometry gives place to an almost immobile entity (central column). This situation shows that the planar bi-molecule may be the smallest island that turns immobile. However, the immobilization occurs only if the bi-molecule remains in the planar form. The diffusion of the standing bi-molecule is completely different. One direction over the surface and one sense of movement are favoured for the bi-molecule diffusion. We then have that a double molecule could move along the [1 1 0] surface channels with a preferred sense in an easier way than the most bonded structure formed by a random (planar) AlF$_3$ molecule. It is important to point out here that the transition from planar bi molecule to the standing up configuration occurs spontaneously within

the MC approach and at room temperature. In fact, the discovery of this mechanism started from this study. The broken symmetry shown by the DFT calculation, with the almost free shape of the bi-molecule over the surface, gives us the explanation of this behaviour. The axis of the bi-molecule clearly transforms one of the [1 1 0] directions into a preferential direction. On the other hand, the tilted axis privileges not only the direction but also one of the senses of movement. These facts dramatically change the diffusion scenario. In the first place, the area covered by the diffusing bi-molecule is largely increased, enhancing the diffusivity of the system. Note the different 'time' scales for both kinds of molecules: while we have 10^6 steps for the isolated and for the planar bi molecule, we have only 5×10^4 steps for the stand up molecule.

4. Discussion

The results obtained with the MC and DFT methods show that the bi-molecule stands up, breaking the square symmetry of the Cu(0 0 1) surface. In this way, not only is a direction privileged but so is a sense of movement. Knowing from DFT that the structure of such a molecule has a preferred axis along both aluminum atoms, the preferred diffusion along the $(\pm 1 \pm 10)$ channels is not shocking at all. As regards the question: Why has this bi-molecule a preferred sense of movement? The answer is related to the tilted axis. In fact, to alter the sense of movement, the bi-molecule must change its orientation, surmounting an energetic barrier. This is done by changing the particular Al atom bond to the surface, which is a mechanism that needs an important triggering energy, as was computed by DFT calculations. It is proven then that changing the orientation of the tilted axis is energetically disfavoured, but is it clear why the movement is favoured along one sense? The results obtained from DFT and MC simulation have a common feature: a tail formed by non-equivalent Al atoms, with one of them located closer to the surface (figure 4). The bi-molecule diffuses in the sense determined by the Al atom located closer to the surface. This fact is understood by taking into account the capability of
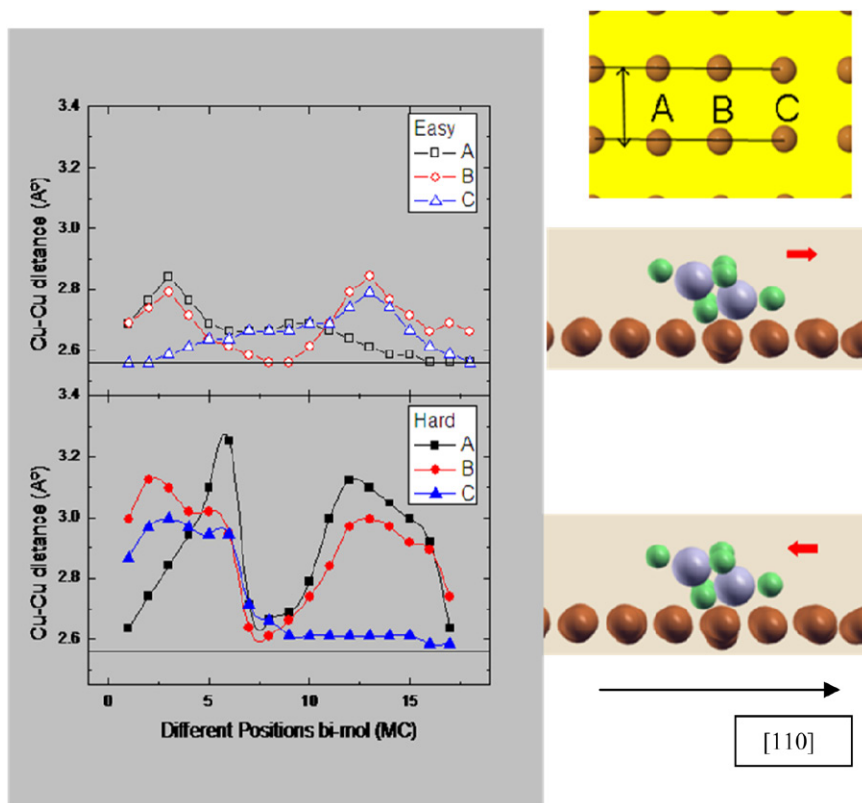
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Figure 6. The displacement of the surface Cu atoms due to the bi-molecule movement along hard and easy senses is depicted in the left column. The atoms labelled A, B and C and the sense of movement are shown in the right column. An important atomic rearrangement is observed in the Hard sense compared to the Easy movement.

rearranging the Cu atoms belonging to the surface. In figure 6 we show the rearrangement of atoms belonging to the surface and to the bi-molecule. We have labelled the distances among surface Cu atoms, located immediately below the bi-molecule along the path, as A, B, and C. While the Cu atoms located in front of the Al nearest to the surface have no movement restrictions, those below the bi-molecule tail are strongly affected by the F–Cu attractive potential. Any movement, of those Cu atoms, perpendicular to the surface must surmount the additional barrier imposed by Al and F atoms moving over them. Thus, Cu atoms forming the surface diffusion barrier behave in a different way, depending on the movement sense. This is observed in the different Cu–Cu distances in each of the characteristic points of the barrier shown in figure 6. The system is clearly softer in the movement with the tail backward because of less movement restrictions of Al and Cu atoms related to the barrier. Moving the tail forward indeed requires harder work.

How does this mechanism explain all of our experimental results? To answer this question, let us start with the simplest result: the enhanced mobility. Although the atom aggregation is a fact that usually lowers the resulting cluster mobility, until the island ceases any movement at all, the opposite fact has also been reported. Thus, oscillatory behaviour, depending on the compactness of the island shape, has been measured through field ion microscopy on Rh [27]. The idea behind this mechanism is the sequential displacement of atoms belonging to the edge of the island. On the other hand, a theoretical work on large island diffusion has suggested the existence of magic sizes for the increase of Ag mobility on Cu(001) [28, 29]. This work

invokes vacancy formation and collective movement to explain this behaviour, but this result still waits for experimental support. In the current case, we are suggesting that it is the structural rearrangement of the less bonded bi-molecule that has made the movement easier. This rearrangement is frequently observed in organic molecules but not for small inorganic molecules, like AlF_3. One can reasonably expect that a combination of the surface symmetry and the molecular shape will have an influence on the diffusion direction [30]. However, the direction, as well as the sense of movement, and the mobility, are modified in our case by a self-restructuration, influencing the growth direction.

We still have to explain the preferential alignment of the small islands. When one molecule moves randomly over the surface (figure 1(*a*)), it can either reach a step or another free molecule. If it finds a step, then it will be captured only if the step is an ascendant one, otherwise it will return to the terrace. If it finds another free molecule, they together could form a growing block. Once the bi-molecule is formed, it can stand up and the DPL will be enhanced, as described in the preceding paragraph. But, this is not the only effect; that is, the movement will be only along [1 1 0] and [1 $\bar{1}$ 0] directions of the fcc lattice. These preferred directions explain the alignment of the small islands that are observed in figure 1(*d*). In fact, and irrespective of energetic calculations, molecules will collide only along these two directions. Then, the island may either only be along the [1 1 0] direction or it may form a 90° angle. At most, collisions along contiguous parallel surface channels could occur, introducing a sort of kink, as is observed in figure 1(*d*) (upper right coalescence).

Finally, how can this diffusion mechanism explain the nucleation at both step sides? As we have stated above, nucleation on the upper side of a step rarely occurs because the atoms and molecules stay at these locations only a few times, which is not enough to allow the encounter with another atom/molecule. The preferential nucleation for an atom reaching the lower step side is due to the energy gained by the increase of neighbour atoms occurring in this site. This is not the case for the upper side, and it is easier for the adatoms to come back to the terrace since, as we already stated, the jump to the lower terrace is limited by the Ehrlich Schwoebel barrier. However, for the stand up bi-molecules, the inversion of movement sense is not an easy fact since it involves a restructuration of the molecule–surface structure. If one stand up bi-molecule reaches the lower side of a step, it will normally be bound to it. However, if it arrives to the step by the upper side, it will rest at this position for a long time since it cannot easily change the sense of movement; as we mentioned previously, this mechanism needs an important trigger. Thus, the rest time will largely be increased, which is enough to favour the encounter with another bi-molecule, allowing at this point the upper side step nucleation.

5. Conclusions

We present a new diffusion mechanism that is capable of explaining a series of unusual experimental results of the growth of aluminum fluoride films over a (0 0 1) copper surface. One of the main results of this work is that the diffusion entity in this system is the bi-molecule and not the most energetically stable AlF_3 single molecule. In addition, it was found that the diffusion mechanism is based on a change of the movement regime over the surface, which is characterized by the competition among the inner molecule electron interactions and the molecule–surface interactions. The interaction among two molecules and the substrate modifies the absorption geometry, breaking all of the symmetries of the system. After which, the formed bi-molecule is able to move only along the compact directions and, most the time, in the same sense. Any change, either in direction or in sense of movement, requires an important additional energy. The kinetics of this movement regime alone are able to explain all of the experimental features; that is, the large diffusion path, the lower and upper step nucleation and the initial island nucleation along preferred directions.

Acknowledgments

Appendix The power of MC to study surface diffusion mechanisms

Surface diffusion is associated with the ability of the system (characterized mainly by the adsorbate position) to go through a position of higher energy, known as the bridge point or barrier energy. Since the probability of accepting a new position with higher energy depends on the Boltzmann law ($\sim \exp(-\Delta E/kT)$) with ΔE, k and T, the increase in energy, Boltzmann constant and temperature respectively, it is clear that as larger the diffusion energy barrier (E_b), the lower the probability of surmounting the barrier will be. In this way, the 'time', measured as the number of MC steps needed for the adatom to change of adsorbing site will be related to E_b and T. Studying this 'time' as a function of T will allow us to determine E_b. On the other hand, the adatom will not evolve in position in a random way. It will follow the paths with lower barrier energies, and the frequency of choice of paths with different barriers will depend on the energetic differences and temperature. In this way, by using Metropolis MC simulations we are able to determine the possible paths and the frequency of choice. Indeed, we are not able to calculate the diffusion coefficients because time is not involved, but we are certainly able to calculate the energy barriers, which is a not an allowed fact in KMC. Additionally, we are also able to calculate the relative diffusion coefficients, that is, the ordinate axis in an Arrhenius graph may be in arbitrary units, but the relative values are valid and the slopes are valid in an absolute way. By using this kind of simulation, we have already described the diffusion of Cu on Cu(1 1 1) under the effect of Pb as surfactant through the atomic exchange mechanism [6]. It is important to remark here that this mechanism was accepted at that time only for open surfaces, like the (1 0 0) ones. The other experimental results we explained using this model were the nucleation at upper steps and the mechanism of vacancy island formation in Co/Cu(1 1 1) system [12].

In the figure, as an example of the power of this method to study surface diffusion, we show the evolution of a Cu adatom for two of the most common Cu faces. In the right column, we depict a sort of Arrhenius graph corresponding to both these cases. As discussed above, the inverse of the number of MC steps (the adatom remains in one position) may be taken as proportional to the frequency jump. The value of 350 meV and 32 meV for Cu(1 0 0) and Cu(1 1 1), respectively, are very encouraging. From the data compiled by Antczak and Ehrlich [2], we can see that the experimental values range from 280 to 480 meV for Cu(1 0 0) and from 30 to 64 meV for Cu(1 1 1), which are in an excellent agreement with the values we obtained from our simulations. But, the interesting results do not end with the quantitative agreement (figure 7).For instance, for the Cu(1 0 0) face, there is no　AQ4 direct experiment to define if surface diffusion is conducted by means of either jumping or exchange mechanisms. This is due to the fact that noble metals are not suitable for field ion microscopy measurements, which is the ideal experimental setup for this kind of determination. The usual way is to calculate the energy barriers for both mechanisms and compare the results to the macroscopic experimental values. However, following Antczak and Ehrlich's compilation, and depending on the methods and potentials used, the values obtained for these barriers range from 250 to 1250 meV for jumping and from 180 to 1020 meV for exchange, preventing us from reaching any conclusion.

The results coming from MC simulations give us a clear clue about this problem. With any previous assumption, results for
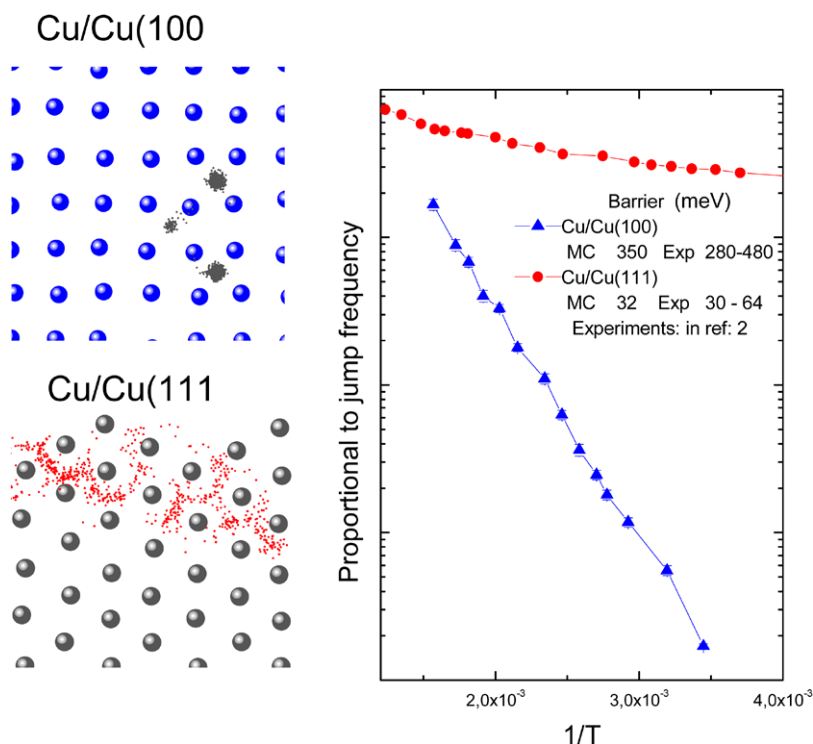
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Figure 7. Left column: different paths given by the MC simulations for Cu on Cu(1 0 0) (*a*), and on Cu(1 1 1) (*b*) for 460 K 10^5 MC steps. Right column: Arrhenius graphs corresponding to both Cu faces.

Cu(1 0 0) and Cu(1 1 1) depicted on the left column of figure 5 strongly suggest that for the (1 0 0) face the main diffusion mechanism is exchange and jumping for the (1 1 1) face. In fact, for (1 1 1) the adatom jumps through bridges along triangular directions and for (1 0 0) the diffusing adatoms change and the visited sites are those located along [1 1 0] directions, as expected in exchange diffusion.

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