

Computer modelling of nanoscale diffusion phenomena at epitaxial interfaces

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Abstract. The present study outlines an important area in the application of computer modelling to interface phenomena. Being relevant to the fundamental physical problem of competing atomic interactions in systems with reduced dimensionality, these phenomena attract special academic attention. On the other hand, from a technological point of view, detailed knowledge of the fine atomic structure of surfaces and interfaces correlates with a large number of practical problems in materials science. Typical examples are formation of nanoscale surface patterns, two-dimensional superlattices, atomic intermixing at an epitaxial interface, atomic transport phenomena, structure and stability of quantum wires on surfaces. We discuss here a variety of diffusion mechanisms that control surface-confined atomic exchange, formation of alloyed atomic stripes and islands, relaxation of pure and alloyed atomic terraces, diffusion of clusters and their stability in an external field. The computational model refines important details of diffusion of adatoms and clusters accounting for the energy barriers at specific atomic sites: smooth domains, terraces, steps and kinks. The diffusion kinetics, integrity and decomposition of atomic islands in an external field are considered in detail and assigned to specific energy regions depending on the cluster stability in mass transport processes. The presented ensemble of diffusion scenarios opens a way for nanoscale surface design towards regular atomic interface patterns with exotic physical features.

1. Introduction

The space- and size-dimensional effects in nanoscale surface physics are a cutting-edge problem in materials science [1-4]. This extended concern is motivated by a huge number of technological applications where detailed knowledge of the fine atomic structure of interfaces is essential. Typical examples are self-organization phenomena leading to formation of regular nanoscale objects and superlattices with exotic physical characteristics. The atomic-scale ordering of interfaces is considered as a complex superposition of ensemble of interactions in the system. In general, depending on the range they act, the interactions could be classified as two types being simultaneously in subtle competition. The first, short-range direct electronic interactions commonly relate to localized chemical bond between particles, while the second are due to long-range acting forces resulting from charge density waves, electrostatic dipole-dipole interactions, surface-state Friedel oscillations, elastic deformation of substrate lattice, etc. [3]. In the range of sub-monolayer adatom concentration, the interplay between these competing interactions generates a diversity of temperature-dependent

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two-dimensional atomic structures. The interface ordering evolves to the final equilibrium state via a complex diffusion scenario where single atoms, atomic clusters and vacancies are involved [1,5,6]. Although a large number of theoretical and experimental studies have already revealed the general features of mass transport in such low-dimensional systems, fine details of diffusion processes causing the specific ordering in the overlayers are still deficient [3,5]. A general reason is that in complex systems with reduced size, confined space dimensionality and broken symmetry as surfaces and interfaces, the simultaneously acting physical effects could not be distinguished and, therefore, their impact could not be evaluated separately. In these cases, the experimental results are strongly influenced by a number of side effects. Thus, the interpretation of advanced experiments conducted by powerful techniques as scanning tunnelling microscopy (STM), thermal energy atom scattering (TEAS) and high resolution spot profile analysis low energy electron diffraction (HR SPA LEED) is often problematic. The presence of imperfections on real surfaces, including atomic terraces, steps, kinks, vacancies, defects, grain boundaries, finite domain size, domain walls, charge density waves, surface-state Friedel oscillations, etc. makes the general scenario of atomic ordering at epitaxial interface generally not amenable to pure theoretical treatment. Overcoming these difficulties, the atomistic simulations treat successfully a number of problems of these complicated structures. Employing a reliable computational model, the computer simulations reveal important details of the interactions and the ordering resulting from them. Hence, they can be implemented to predict unexpected phenomena and to conduct and extend the physical experiment in a right direction [7]. Here we demonstrate an application of the Monte Carlo simulations pointed to two important surface diffusion problems in materials science: formation of regular surface patterns on epitaxial interface and diffusion of atomic clusters in an external field. We also discuss the equilibrium structure of the interface organized upon network of interactions and selective cluster size-dependent diffusion that could initiate formation of atomic surface patterns.

2. Computational and physical models

The computational model in the present study implies classical canonical Monte Carlo (MC) sampling with tight binding second moment approximation of electron density of states (TB SMA) many-body potential between interacting atoms. This semi-empirical TB SMA potential has been extensively applied in contemporary atomistic simulations of transition metals and intermetallic alloys [7-10]. Its advantage relates to the ability of reproducing real physical properties of surfaces and interfaces including point defects, dislocations, vacancies, grain boundaries [8,9]. Depending on the specific diffusion problem, we also apply an external field to direct the cluster migration in a specific direction and to evaluate the cluster stability. The physical model is a three-dimensional continuum space Pb/Cu(111) interface with system size of $L_x = 76$, $L_y = 44$ and $L_z = 5$ lattice units. The simulations were performed on a crystal surface with large atomic terraces. The model enables one to gain insight into the diffusion of adsorbed atoms both directly into the outermost surface layer and through the surface steps with different anisotropy and, therefore, different free energy and relaxation ability. Full lattice dynamics for all atoms is applied to allow a complete spatial relaxation of the system. The system equilibrium is realized after an average Monte Carlo time of 10^6 steps per atom. All simulation details are described elsewhere [3,10,11].

3. Diffusion barriers and nanoscale surface patterns on fcc(111) interface

The atomic-scale surface morphology provides a variety of energy barriers for surface diffusion [3, 9]. For volume-immiscible systems, the migration of a single atom on the surface evolves in two diffusion scenarios. The first relates to a simple random Einstein walk on top of the interface resulting in aggregation of atoms in large clusters and decoration of steps of substrate atomic terraces. The second scenario is more complex and involves diffusion inside the first atomic layer of the substrate. This process is governed by the subtle competition between the elastic strain energy of the substrate and the energy gained by mixing. On an atomically smooth interface, this scenario leads to formation of a stable two-dimensional (2D) surface alloy and can be realized if the energy of migrating atoms is

higher than the energy barrier for incorporation inside the substrate [4]. Refining the classical diffusion model, we showed that on vicinal surfaces, the intermixing could take place even in the case when the adatom energy is lower than that for direct incorporation inside the first atomic layer [3,9]. This effect, known as incomplete alloying, is realized exclusively via surface diffusion through the steps of atomic terraces. The simulation results reveal a 30-% lower activation energy for diffusion via step-terrace mechanism compared to that of direct incorporation. The temperature evolution of the surface-confined intermixing is demonstrated in figure 1. At a low temperature T , figure 1a, the adatoms only attach to atomic steps and decorate the terrace without interatomic exchange. More interesting is the diffusion at high temperatures. Apparently, on large terraces or flat substrate areas, the direct atomic exchange between adsorbed and substrate atoms is hampered because of energy reasons. In contrast, near the step edges, a very distinct diffusion of Pb atoms within the Cu matrix is realized, figure 1b. This atomic exchange is limited inside the terrace plane to a specific length and generates alloyed stripes in the vicinity of steps. The stripes, having a temperature-dependent characteristic width, are followed by a pure non-alloyed interface (middle part of the terrace).

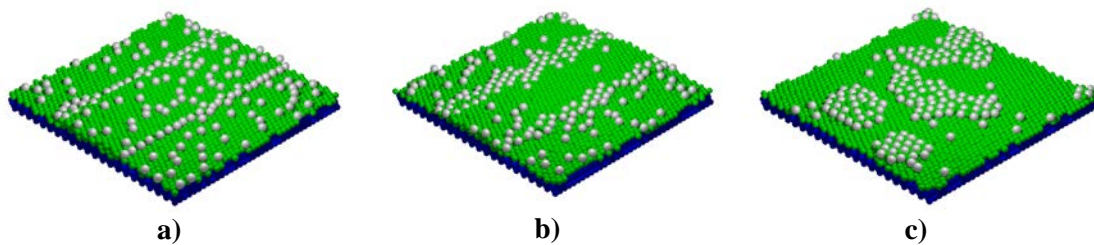


Figure 1. Snapshot of random, close-to-equilibrium atomic configuration of 0.1 monolayers Pb (light gray balls) on Cu(111) stepped surface (green balls) with initial Cu terrace of 16 atomic rows. **a)** $T = 200$ K, low-temperature step decoration. **b)** $T = 300$ K, formation of 2D stripes due to Pb diffusion across the atomic steps. No surface alloying takes place on a smooth, step-free surface area. **c)** $T = 300$ K, interface configuration for initial Cu terrace of 6 atomic rows. Completely alloyed Pb-Cu islands are formed on top of the pure non-alloyed substrate [9].

The observed dramatic diffusion slowing down towards the terrace center is a result of the interplay between elastic strain and energy gain of mixing. Two time-scale diffusion mechanisms of direct atomic exchange and vacancy-mediated diffusion take place in this complex scenario [12]. A difference is also seen in the stripe width L_S^A and L_S^B on upper “A” and lower “B” terrace step, figure 2. It originates from a step anisotropy on (111) interface orientation and a different step free energy. Our simulation data show $L_S^A \approx 1.4L_S^B$ at 300 K which is in line with the extended relaxation ability of “A” step on the terrace. The decrease of terrace width to $L_T < 3L_S$ makes the terrace unstable and completely transparent for adsorbed atoms. The instability initiates terrace rupture and formation of 2D alloyed islands, as it is shown in figure 1c. In this case, note that the surface intermixing takes place exclusively at the terrace level so that entirely alloyed islands patch the pure non-alloyed substrate. Hence, in a specific temperature gap, fine tuning of the energy of the adsorbed atoms via temperature variation can be applied to atomic-scale surface design. It is essential to point out that the final configuration seen in figure 1b represents a close-to-equilibrium state and does not change during the subsequent time evolution of the interface. The results presented reveal a classification order of surface-confined intermixing (blocked, incomplete and complete, see figure 3) and open a way for the formation of a variety of nanoscale surface patterns via fine tuning of the system temperature [9].

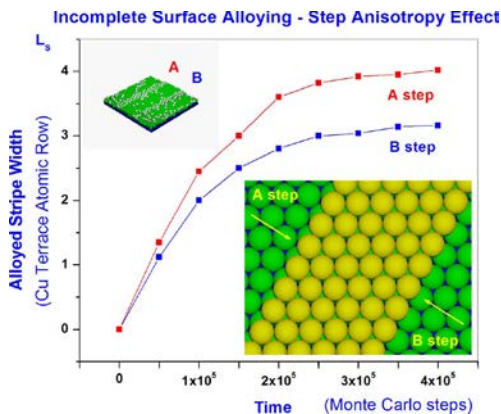


Figure 2. Step anisotropy effect at incomplete surface alloying. Snapshot of a random MC atomic configuration of 0.1 ML Pb/Cu(111) at 300 K and initial substrate terrace width of 16 atomic rows. The larger alloyed stripe width at step A is a result of the eased atomic relaxation of the terrace in that direction. (from [9] Copyright © 2009 The American Physical Society).

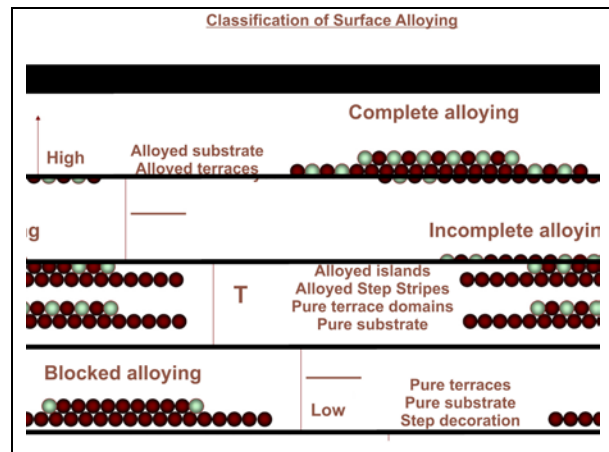


Figure 3. Classification of surface alloying with corresponding atomic configurations at the epitaxial interface (light balls indicate adsorbed atoms and dark balls indicate substrate atoms). The presented order opens up a way for fine modification of the atomic surface structure and formation of regular patterns. (from [9] Copyright © 2009 The American Physical Society).

4. Diffusion of atomic clusters in external field

In contrast to diffusion of single atoms, the migration of atomic clusters on an epitaxial interface is a tricky problem [1,2,6]. The complexity originates from a variety of diffusion mechanisms which control the island migration. For a single atom, the diffusion coefficient follows an exponential decay

as $D \approx \exp\left(-\frac{E_d}{k_B T}\right)$ where E_d is the energy barrier for migration to a randomly chosen site on the

surface. In the case of clusters, $E_d = \sum_i E_{d_i}$ and E_d corresponds to an effective energy barrier which

originates from the barriers E_{d_i} of competing specific diffusion mechanisms. For instance, the diffusion of 2D cluster is tightly dependent on the specific mass transport mechanism and scales with its size as $D_{2D} \approx N^{-\alpha}$ where $\alpha = 3/2$ for periphery diffusion, $\alpha = 1$ for terrace diffusion and $\alpha = 1/2$ for evaporation-condensation diffusion [5]. In the case of compact islands, shape effects of open or closed crystallographic forms, soliton propagation, misfit dislocation and commensurability with the substrate lattice also have a substantial impact on the island migration. All these effects have been studied in detail both experimentally and theoretically [1,2,13]. An essential problem in cluster diffusion phenomena is the atomic islands integrity throughout the surface migration. Loss of integrity leads to a variety of size, shape and lattice-misfit effects and, therefore, can dramatically influence the mass transport process. Here we discuss the impact of an external field on the stability and migration of homoepitaxial atomic islands on an epitaxial interface.

The stability of an island depends on ensemble of competitively acting forces due to lateral, normal and external field interactions. Evidently, stronger lateral and normal interactions hamper the island decomposition into small clusters. The simulation results reveal critical values of the imposed external field that cause disintegration of the islands into morphologically different atomic complexes. This effect is demonstrated in figure 4 a, b, c. Three energy regions with respect to the cluster stability can

be specified. At a weak external field along the (111) direction (1.5 % of the cluster interactions), only single atoms are detached from the cluster periphery, while the total cluster integrity is preserved, figure 4a. Increasing the external force to 2 % of normal and lateral bonding, the island disintegrates into several atomic clusters, all being compact and smaller in size, figure 4b. This effect of decomposition changes the surface diffusion mechanisms and assists dramatically the mass transport process on the interface. Let us point out that the small clusters are more stable than the large ones with respect to the same external force. They are less strongly bonded to the substrate and, therefore, they move more easily and quickly on the interface. In this case, the diffusion behavior of entire cluster gliding takes place in contrast to a periphery diffusion mechanism. Finally, attaining the specific critical value of 5 %, the external field destroys totally the atomic cluster to an ensemble of single atoms, which is seen in figure 4c. An important conclusion following from the simulation results is that the transition between the regions with a specific cluster morphology (single atoms, small compact clusters and total disintegration) is not smooth. Hence, the impact of the external field on the cluster stability and related cluster disintegration demonstrates a staircase-like behavior. This effect can be applied to a selective cluster size-dependent mass transport in nanoscale pattern formation on epitaxial interfaces.

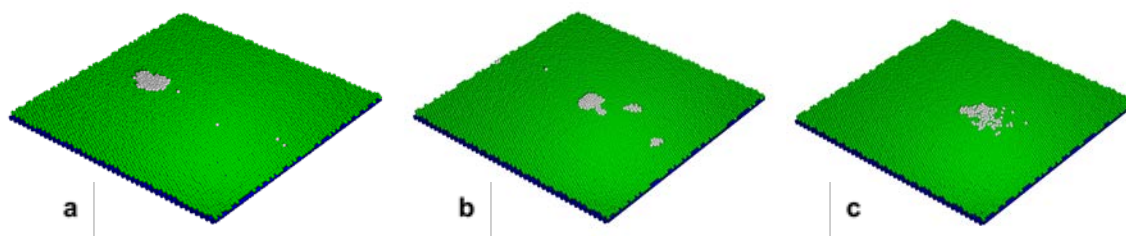


Figure 4. Diffusion of anatomic cluster in an external field. Depending on the field intensity E_{ext} related to the cluster atom interactions, three modes of disintegration are observed: **a)** $E_{\text{ext}} = 1.5\%$ – detachment of single peripheral atoms only, **b)** $E_{\text{ext}} = 2\%$ – fragmentation into small compact clusters, **c)** $E_{\text{ext}} = 5\%$ – total atomic disintegration.

5. Conclusions

The present study reveals important details of atomic diffusion mechanisms on stepped surfaces in bulk immiscible systems. On epitaxial interface with atomic terraces, the computational model reveals an energy region of formation of 2D-alloyed stripes or 2D-alloyed atomic islands. The stripes formed at the terrace edges are followed by a flat, non-alloyed, area, thus forming regular patterns on the surface. The stripe width is step-anisotropy dependent and correlates with the relaxation ability of the terraces in the specific direction. Atomic terraces having a width smaller than $3L_s$ are unstable and completely transparent for the adsorbed foreign atoms. This process leads to formation of 2D alloyed islands on top of a pure non-alloyed substrate. The scenarios presented demonstrate nanoscale patterning at epitaxial interfaces through a fine diffusion control of adatoms on the crystal surfaces. By a simple variation of the temperature, a terrace width distribution or a lattice overlayer/substrate misfit, the interface generates a variety of regular nanoscale ensembles, including alloyed stripes, alloyed islands or entirely alloyed terraces. In the presence of an external field, depending on its intensity, the atomic clusters migrating on the epitaxial interface disintegrate in three different ways: detachment of single peripheral atoms solely, fragmentation to small compact clusters and total atomic disintegration. The present report also demonstrates the extended capability of atomistic models in computer simulations to unravel simultaneously acting effects, to distinguish between them, and finally to evaluate their specific contribution to experimentally-observed complex physical phenomena.

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