Evidence for Strain Induced 2D Roughening in Ag Islands on Pt(111)

P. Blandin and C. Massobrio
Institut de Physique Expérimentale, Ecole Polytechnique Fédérale de Lausanne, PHB Ecublens, CH 1015 Lausanne, Switzerland

P. Ballone
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

(Received 18 January 1994)

By static and molecular dynamics computations with embedded atom potentials we study the influence of strain and temperature on the morphology of low coverage Ag overlayers on Pt(111). Static computations show that strain reduces the contour (E_c) and kink (E_k) energies of the Ag islands. Simulations of the short time evolution (~ 10 nsec) after deposition predict that, for $T \sim 600$ K, the low E_c and E_k energies result in the roughening of the islands' boundary. This, in turn, leads to easy fragmentation of the islands, and to enhanced Ag mobility on the surface.

PACS numbers: 68.35.Rh, 61.50.Cj, 68.55.Jk, 68.60.Dv

Molecular dynamics simulations of Ag submonolayer films on Pt(111) provide direct evidence for the roughening of the Ag island boundaries at temperatures beyond 600 K. Static computations for the contour (E_c) and kink and antikink (E_k) energies, as well as a comparison with the Pt/Pt(111) surface, show that the strain due to the 4% lattice mismatch of Ag and Pt plays a crucial role in this process, since it significantly lowers the E_c and E_k energies. Our simulation shows that roughening leads to fragmentation of the Ag islands, and prevents the collapse of the adsorbate in a unique 2D aggregate. The abundant population of small islands (~ 30 atoms for coverage $\Theta = 0.25$ and $T = 800$ K) has important consequences on the long time evolution of the system. Small aggregates diffuse rapidly on the (111) surface until they reach the nearest step, where, as shown by scanning tunneling microscopy (STM) images, surface mixing takes place for T beyond 620 K [1]. In the last part of the paper, we discuss the relation of our computation with previous experimental studies of 2D roughening in adsorbates [2,3].

Deposition of thin films from the vapor is a basic process in the preparation of high quality crystals and interfaces, and has received considerable attention in recent years [4]. The thermodynamic description of the process is very simple, and can be summarized by the surface tension of the substrate, of the adsorbate, and their reciprocal interfacial free energy. A more realistic description has to take into account the kinetics of the adlayer formation, sometimes preventing the system from reaching equilibrium. More importantly, it has to include the atomistic nature of the substrate and adsorbate. At this level it is possible to distinguish different contributions to the system free energy, like the electrostatic contribution due to surface dipoles, the elastic strain due to a lattice mismatch of substrate and adsorbate, and specific chemical contributions, that, at low coverage, can manifest a strong and specific dependence on the size and shape of the clusters adsorbed on the surface.

The role of the last two contributions in the nucleation and growth of Ag and Pt on the Pt(111) surface has been the subject of a series of recent experimental papers [1,3,5,6] where TEAS (thermal energy He atom scattering) and STM techniques have been used to characterize kinetics and morphology of the deposed structures. An unexpected feature was revealed by the TEAS measurements on Ag/Pt(111), showing that diffuse He scattering, associated with small and fragmented surface structures, increases with increasing T, in contrast with established models of the adlayer formation [7]. Strain was invoked to be the driving force behind the fragmentation of large 2D islands into small clusters when heating above $T = 550$ K. More recently, a variable temperature STM study of Ag on Pt(111), has revealed the existence of a kinetic growth regime at low temperatures, featuring small cluster formation and subsequent growth of dendritic islands for temperatures up to $T = 130$ K. At higher temperatures ($350 < T < 500$ K) a thermodynamic 2D equilibrium regime establishes and large Ag islands are observed in coexistence with the 2D gas phase consisting of small Ag clusters and adatoms. As indicated by a further experimental study [1], substrate temperatures above $T = 620$ K lead to an irreversible alloy formation in which Ag clusters are dissolved in the Pt matrix and Pt clusters in the Ag layer. This process takes place over macroscopic times starting from the step edges and is confined to the topmost layer.

To elucidate the role of kinetics and of the different energy contributions in the nucleation, growth, and equilibrium properties of heterogeneous epitaxial interfaces, we resort to molecular dynamics simulations based on a realistic N body potential. On the one hand this choice confines our study to a very short time (a few nsec at most). On the other hand, it offers a microscopic description of the system, and allows a variety of computational experiments to isolate the effect of the different factors determining the system evolution.

The system is modeled by the embedded atom method

0031-9007/94/72(19)/3072(4)$06.00

[8]. The parameters for our simulation have been taken from Ref. [9]. We simulate a Pt slab of 12 layers, with an ideal (111) surface exposing 930 atoms with periodic boundary conditions in 2D. The substrate slab is relaxed, and then frozen. The resulting Hamiltonian describes an assembly of adatoms in an external potential [10]:

$$E_c = \Phi_{\mathrm{PtPt}} + \Phi_{\mathrm{AgPt}} + \Phi_{\mathrm{AgAg}} + \sum_{i\in \mathrm{Pt}} F_{\mathrm{Pt}}(\rho_i) + \sum_{i\in \mathrm{Ag}} F_{\mathrm{Ag}}(\rho_i)\,. \qquad (1)$$

The first three terms describe the short range two body repulsive potentials. The last two terms are the embedding energies of Pt and Ag, respectively. Each of the embedding densities ρ_i contains both Pt and Ag contributions. The repulsive interaction Φ_{AgPt} and the Pt contribution to the embedding densities introduce a potential corrugation for the Ag atoms commensurate with the periodicity of the Pt(111) surface. In our simulation, and in agreement with low energy electron diffraction (LEED) experimental evidence [11], the Ag islands grow epitaxially on this surface.

The frozen substrate approximation is justified by the rigid behavior of this compact surface, and by the small modulation of the potential energy, implying a moderate coupling for the in-plane movement of the substrate and adsorbate atoms. The effect of the substrate thermal movement on the adlayer is simulated by a Langevin dynamics for the adatoms. The resulting equations of motion are integrated by a velocity Verlet algorithm [12] with a time step $\Delta t = 1.4\times 10^{-15}$ sec.

At the beginning of each simulation the 930 adsorption sites continuing the fcc Pt lattice are randomly occupied by Ag atoms with coverage $\theta = 0.10$ and $\theta = 0.25$. A short time (~ 10 psec) is sufficient to reach equilibrium at the target temperature ($T = 400$, 600, 800, and 1000 K).

At all T we observe the formation of the first condensation nuclei within a few psec, indicating that the initial aggregation occurs by spinodal decomposition. At the lowest T (400 K), the growth of the nuclei is very slow, and the surface presents a large number of small aggregates. At $\theta = 0.10$, the Ag cluster size distribution displays clear peaks corresponding to compact, optimally coordinated clusters ($n = 7,10$) [6,13,14]. At $T > 400$ K the growth of the initial nuclei is rapid, and over times ranging from 2 nsec at 600 K to 0.8 nsec at 1000 K, the system reaches a stationary state. As is apparent from Fig. 1 reporting the stationary cluster size distribution at $\theta = 0.25$, $T = 1000$ K, and from Fig. 2(a) displaying a snapshot for the same system at $T = 800$ K, the stationary state does not correspond to a single, large aggregate, as suggested by elementary thermodynamics. Instead, it corresponds to a population of islands in local equilibrium with a dilute vapor, for which easy fragmentation and evaporation compensate the condensation of adatoms into islands. Visual inspection of snapshots reveals that fragmentation is triggered by an abnormal growth of fluctuations in the islands boundary, giving rise to irregular structures, with protruding parts loosely connected to the main island body. The observation of important and frequency fragmentation supports the conclusion that the configuration illustrated in Figs. 1 and 2(a) is representative of the steady state, and not the artifact of a kinetic limitation. The equilibration among islands is further enhanced by a dilute vapor of highly mobile single adatoms, that we always observe in the Ag/Pt(111) simulation.

To assess the role of strain, we average in the surface plane the contributions in Eq. (1) coming from the Pt surface structure. This has the effect of removing the strain without altering the Ag-Ag interatomic potential in a significant way. We observe two major effects. First, over a short time (few psec) the Ag-Ag distance relaxes by $\sim 4\%$, to match the bulk Ag interatomic distance. Then, over longer times, and up to 800 K, the population

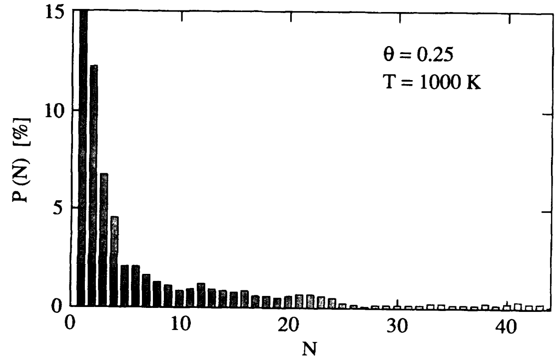

FIG. 1. Equilibrium size distribution probability for Ag islands on Pt(111).

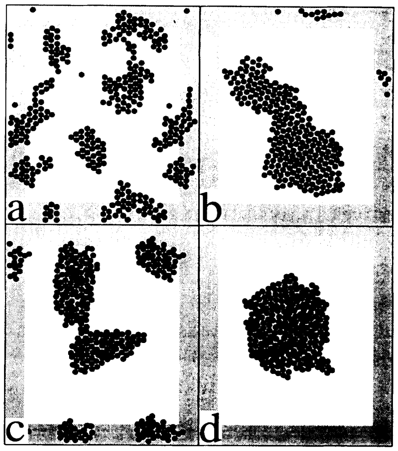

FIG. 2. Snapshots of atomic configurations during MD simulation for $\Theta = 0.25$. (a) Ag/Pt(111), $T = 800$ K; (b) Ag on the plane averaged Pt(111) potential (see text), $T = 800$ K; (c) Pt/Pt(111), $T = 1350$ K; (d) Pt on the plane averaged Pt(111) potential, $T = 1350$ K.

of the islands collapses into a unique aggregate [see Fig. 2(b)]. Only at $T=1000$ K does the thermal motion overcome the Ag cohesion, and the aggregate fragments again.

This computational experiment unambiguously demonstrates that stress plays a role in fragmenting the islands' distribution. The precise mechanism, however, requires further investigation. Clearly, strain alone does not produce fragmentation, since the elastic energy of a uniformly strained system is proportional to the number of atoms, and does not depend on its shape. This argument, however, neglects the role of the islands' contour and kinks. At the boundary strain can be released, and therefore strained islands will have relatively low contour and kink energies. This is confirmed by static computations for E_c and E_k, whose results are reported in Table I. The contour energy was computed for a rectangular adsorbed stripe limited by two parallel steps in the [100] direction, and covering one half of the surface. The kink-antikink energy was evaluated in the geometry described above by displacing one of the atoms from the edge of one step and adsorbing it on the other step. Both quantities are weakly dependent on the size and geometry of the islands. We verified that this dependence is very similar in the three systems we compare below [Ag/Pt(111), Ag/stressed Pt(111), and Pt/Pt(111)], and, therefore, it does not affect our discussion.

The role of strain is highlighted by a comparison of the results for Ag/Pt(111) with those for the strain free Pt/Pt(111) interface, whose E_c and E_k are also reported in the table. Even taking into account the different Ag and Pt cohesive energies, the E_c and E_k values for Ag appear anomalously low. As a further test, we repeated the computation for Ag with a 4% strain in the Pt substrate. As can be seen again in Table I, this artificial matching of the two lattice constants increases substantially E_c and E_k.

With increasing T, the low values of E_c and E_k for the Ag/Pt(111) interface will lead to the roughening of the islands' boundary. This expectation is confirmed by inspection of snapshots, showing that beyond 600 K the islands display irregular contours. This observation is in qualitative agreement with the STM results of Ref. [3]. A quantitative analysis is performed by subdividing the adatoms into 2D bulk, contour, and kink-antikink atoms, following simple coordination criteria. Sixfold coordinated atoms are bulk atoms, coordination 3 and 4 atoms belong to the contour, coordination 1 or 2 are kinks, while those that are fivefold coordinated are antikink atoms. The relative weight of bulk, contour, and kink-antikink atoms depends on the cluster size, and therefore we restrict our statistics to the size window $30 < N < 40$, (where N is the number of atoms in the cluster). The result of this analysis is displayed in Fig. 3. The most apparent feature is the increase of the relative number of kink-antikink atoms starting at 600 K, then saturating at 40%, probably corresponding to the stability limit of the aggregates with respect to fragmentation. Also characteristic is the behavior of the bulk component, which increases slightly from 400 to 600 K as a faster kinetics allows the rounding of the clusters, inhibited at lower T.

TABLE I. Comparison of adsorption energies (E_a), contour (E_c), and kink-antikink (E_k) energies at $T=0$ for Ag/Pt(111), Ag on Pt(111) strained to match the Ag lattice parameter, Pt/Pt(111).

	Ag/Pt(111)	Ag/Pt(111) Strained	Pt/Pt(111)
E_a (eV/atom)	3.16	3.30	5.77
E_c (eV/Å)	0.019	0.046	0.130
E_k (eV/pair)	0.23	0.30	0.78

The proliferation of kinks and antikinks has clear similarities with the roughening transition of surfaces, and for this reason we apply the same terminology, despite the obvious limits in the analogy. First of all, for short range potentials the roughening transition in 2D occurs at $T_R=0$ K [15], since the entropy contribution always overcomes the potential energy cost of kinks. However, we are concerned with finite clusters, for which the argument above does not hold, and we are not describing a true transition in the thermodynamic sense, but a gradual transformation taking place over few hundred K.

To underline again the role of stress, we repeated our computations for the Pt/Pt(111) surface. We take into account the different strength of the interatomic interaction by rescaling temperatures by the ratio of the Ag and Pt melting temperatures. As apparent in Fig. 2(c) the simulation reveals few, large adsorbed Pt aggregates. This picture is not modified by removing the surface corrugation due to the underlying Pt lattice, as can be verified in Fig. 2(d).

To summarize the simulation results, we recall that we model the Ag and Pt submonolayer deposition on the Pt(111) surface by realistic EAM potentials. The model

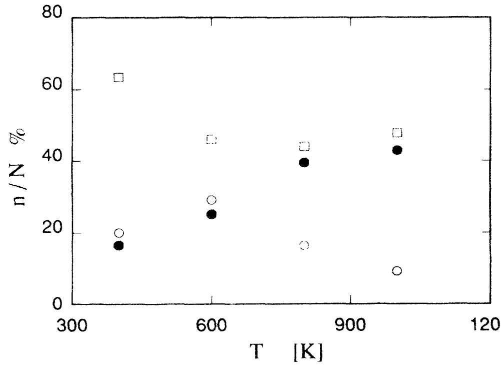

FIG. 3. Relative number of bulk (○), edge (□), and kink-antikink atoms (●) in Ag clusters with $30 \leq N \leq 40$, $\Theta=0.25$.

reproduces the main features observed in experiments, and, in particular, the 2D epitaxial growth of the film. Simulations for Ag/Pt(111) show that, starting at ~600 K, the islands' edge undergoes a roughening transition, favored by the low contour and kink energies implied by the Ag and Pt lattice mismatch. Our results are in agreement with the STM observations of Ref. [3] for the T and times for which the surface mixing discussed in Ref. [1] is not yet the dominant aspect of the system evolution.

The roughening of the adsorbate edges has been observed and discussed for other interfaces [Cu, Ag, Au, Ni, Pd/W(110) [2]] that share several features with the system we studied: They are all heterogeneous systems, with a compact substrate surface and a significant strain in the adsorbed layer. It is reasonable to expect that the microscopic description provided by our study is relevant also for these systems.

Direct comparison with recent He diffraction experiments on Ag/Pt(111) [5] at T and Θ close to those of our study is tempting, but prevented by the occurrence of the surface mixing neglected both in our model and in the discussion of Ref. [5]. However, roughening and the induced fragmentation increase the length of the adcluster edges, and could be revealed by inelastic He scattering. In the "in phase" configuration, this technique measures the total length of the islands' contour, and therefore, is particularly suitable to study the phenomena described above. We suspect that our picture has at least some relation with the observed increase of diffuse He scattering reported in Ref. [5]. More importantly, we believe that a careful choice of the temperature could allow the observation of the 2D roughening in this system before mixing takes place.

Again, both roughening and fragmentation have an important influence on the long time evolution of the Ag/Pt(111) interface. First of all, fragments of few atoms display a large mobility on the (111) surface, that, however, rapidly decreases with cluster size [11]. The abundant supply of small clusters, therefore, enhances the migration of Ag to the substrate steps, where it is permanently trapped, as shown by experiments, and in agreement with our previous computation [11]. At the steps, atoms loosely bound to Ag clusters provide favorable precursors for the inclusions of Ag into the Pt terraces. Also, the irregular and porous Ag structures in contact with the steps provide an easy path for the inverse process, by which a Pt atom or small cluster is incorporated and can rapidly migrate into the Ag aggregates.

We acknowledge H. Brune and K. Kern for several useful discussions.

[1] H. Röder, R. Schuster, H. Brune, and K. Kern, Phys. Rev. Lett. **71**, 2086 (1993).

[2] J. Kołaczkiewicz and E. Bauer, Phys. Rev. Lett. **54**, 574 (1985); Surf. Sci. **155**, 700 (1985).

[3] H. Röder, H. Brune, J-P. Bucher, and K. Kern, Surf. Sci. **298**, 121 (1993).

[4] D. W. Pashley, in *Materials Science and Technology*, edited by R. W. Cahn (VCH Publishers, New York, 1991), Vol. 15, p. 289.

[5] A. F. Becker, G. Rosenfeld, B. Poelsema, and G. Comsa, Phys. Rev. Lett. **70**, 477 (1993).

[6] G. Rosenfeld *et al.*, Phys. Rev. Lett. **69**, 917 (1992); M. Bott, T. Michely, and G. Comsa, Surf. Sci. **272**, 161 (1992); B. Poelsema *et al.*, Surf. Sci. **272**, 269 (1992).

[7] J. A. Venables, G. D. T. Spiller, and M. Hanbücken, Rep. Prog. Phys. **47**, 399 (1984).

[8] M. S. Daw and M. I. Baskes, Phys. Rev. B **29**, 6443 (1984).

[9] S. M. Foiles, M. I. Baskes, and M. S. Daw, Phys. Rev. B **33**, 7983 (1986).

[10] P. Blandin, C. Massobrio, and P. Ballone (to be published).

[11] P. W. Davies, M. A. Quinlan, and G. A. Samorjai, Surf. Sci. **121**, 290 (1982).

[12] M. P. Allen and D. J. Tildesley, *Computer Simulation of Liquids* (Clarendon, Oxford, 1989).

[13] C. Massobrio and P. Blandin, Phys. Rev. B **47**, 13687 (1993).

[14] J. W. Norskov, K. W. Jacobsen, P. Stoltze, and L. B. Hansen, Surf. Sci. **283**, 277 (1993).

[15] W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. R. Soc. London A **243**, 299 (1951).

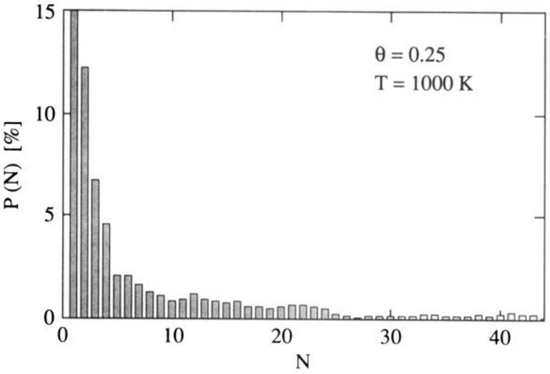

FIG. 1. Equilibrium size distribution probability for Ag islands on Pt(111).

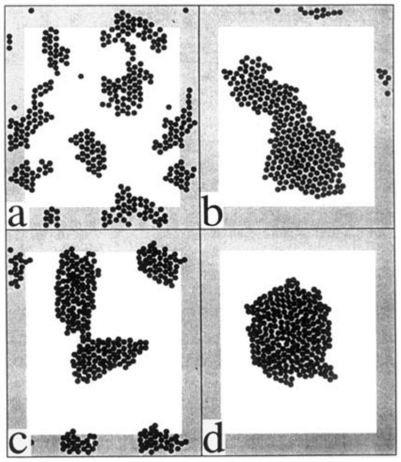

FIG. 2. Snapshots of atomic configurations during MD simulation for $\Theta = 0.25$. (a) Ag/Pt(111), $T = 800$ K; (b) Ag on the plane averaged Pt(111) potential (see text), $T = 800$ K; (c) Pt/Pt(111), $T = 1350$ K; (d) Pt on the plane averaged Pt(111) potential, $T = 1350$ K.