Quantification of Inert Gas Monolayer Evolution on an Atomically Rough Calcium (111) Surface Using Cellular Automata

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13. ABSTRACT (Maximum 200 words)

This report results from a contract tasking Imperial College, London as follows: The contractor will investigate the use of Cellular Automata (CA) algorithms to advance our understanding of how various transport phenomena such as surface diffusion and adsorption/desorption contribute towards the growth of surface structures.

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Executive summary

Motivation

In a previous study (EOARD contract F61708-96-W0300), we investigated inert gas monolayer formation on a flat calcium (111) surface using computer simulation. The predicted surface microstructures were examined qualitatively as a function of two adjustable parameters, temperature and flux (flux is a function of temperature and gas pressure). That report proposed several possible follow-up studies, three of which are addressed here.

Objectives

To investigate the rate of domain shrinkage as a function of domain radius.

To determine appropriate physical observables that characterize the microstructural development of the inert gas monolayer.

To incorporate the effect of surface roughness in the model. (The last study proposed placing heavy inert gas atoms like xenon on the surface to study the pinning effect it had on the domains. That proposal has been modified to use additional calcium atoms instead of xenon.)

Approach

Utilize the CA rule set that was generated from atomistic scale simulations in the last study.

Use studies of magnetic systems as models for quantification.

Incorporate surface roughness by including extra calcium atoms on the surface.

Conclusions

1. Even for multiple simulations with the same adjustable parameters, due to the random nature of the simulations there is a large variation in the physical observables from one simulation to the next. Therefore, many simulations must be performed to obtain sufficient statistics to identify the correct empirical behaviour of the total perimeter and radius of a single circular domain.

2. The rate of shrinkage of a single circular domain is independent of the incident gas atom flux for high fluxes.

3. The total perimeter between gas atom domains on the calcium surface is an appropriate physical observable, providing a good quantitative measure of the microstructure.

4. The effect of surface roughness is to increase the total perimeter between domains on the surface.

5. Empirical forms for the total perimeter as functions of time and surface roughness have been derived. Further work will allow us to determine the dependence on simulation temperature and incident gas atom flux.

Introduction

This study is an extension of a previous study[1,2] of the evolution of inert gas monolayers on a perfect calcium (111) surface. The particular system was chosen so that a microstructure of gas atoms would develop and evolve on the calcium surface, offering a simple, two-dimensional microstructure to study. That study employed cellular automata (CA) to achieve large discrete time steps in order to make long-time scales approachable, and the CA rules were based upon the results of atomistic-scale calculations. Neglecting surface relaxation and diffusion, the atomistic-scale calculations were approximate; however, the rule-oriented nature of the cellular automata procedure easily allows results of more sophisticated atomistic-scale calculations to be incorporated. Thus the previous study serves as a simple example of how to generate an appropriate rule set.

The study qualitatively demonstrated sensible behaviour, which exhibited critical dependencies on the two variables considered: temperature and flux of incident gas atoms. Furthermore, Ne and Ar behaved similarly with criticalities at different temperatures and fluxes. In this study, a third variable, the degree of surface roughness, is added. Since real surfaces are almost never atomically flat, this is an important step in making the simulation more realistic. Additionally, this study serves to develop the quantitative tools required to characterize the evolution of the surface.

The System in Detail

The general system under study is a monolayer of inert gas atoms on a calcium (111) surface. The previous study showed that Ne and Ar behaved similarly with criticalities at different temperatures and fluxes of incident gas atoms. In this study, only results for argon are presented.

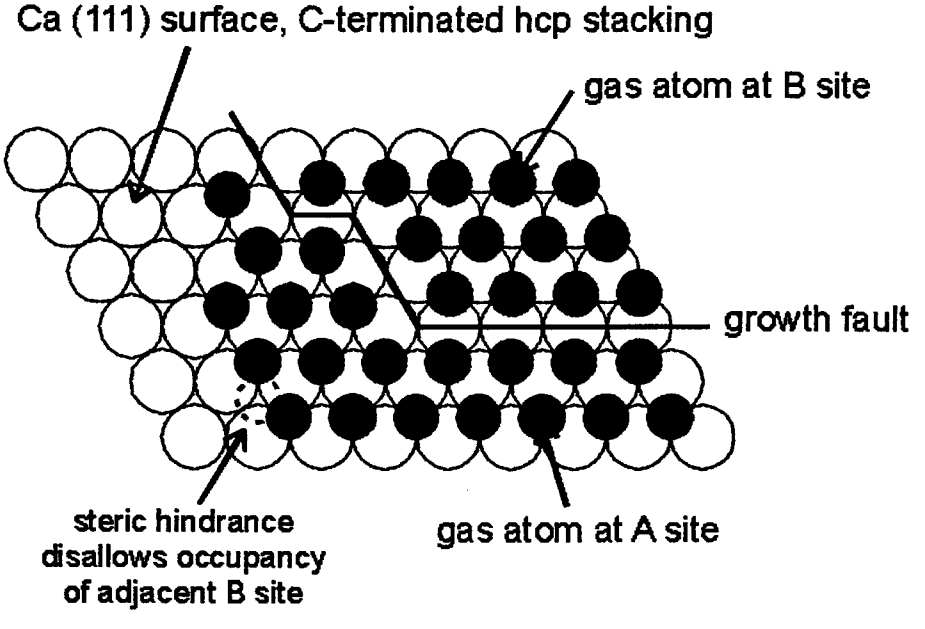


figure 1

The system was chosen because of the two-dimensional microstructure that develops as a result of the similar atomic radii of Argon and calcium. An atomically flat surface provides a good foundation for the study; thus, considering the surface to be a c-terminated abc stacking

sequence, inert gas atoms are located on the surface in either a- or b-sites. Steric hindrance prevents simultaneous occupation of adjacent a- and b-sites (figure 1). The short-range interaction between gas atoms is attractive, and under appropriate conditions domains of adsorbed gas atoms in a-sites and domains of b-site gas atoms form.

Surface roughness is incorporated by randomly placing additional calcium atoms in the a- and b-sites otherwise available for argon atoms. The interaction between these additional calcium atoms and the gas atoms is the same as the interaction between calcium atoms in the original c-terminated layer and the gas atoms. The additional calcium atoms are fixed, that is, they are not allowed to diffuse or desorb.

Methodology

Interactions in the system are approximated by considering interatomic forces only between next near neighbours, and the evolution of the system is determined by use of a stochastic model. The theoretical derivation of the stochastic model and its implementation by cellular automata are described in detail elsewhere[1,2]. This study is easily divided into three topics: (1) the evolution of a circular domain that is completely surrounded by another, (2) the quantification of surface uniformity by perimeter length, and (3) the reduction of surface uniformity by a rough surface. The initial conditions, simulation surface size, and simulation time vary depending on the topic as discussed below. In every case periodic boundary conditions are employed.

Curvature

Quantifying the time evolution of one domain completely surrounded by a second domain with a circular boundary provides a straightforward evaluation of the model. Since the energy of the surface is increased by the presence of the boundary, there is a driving force to reduce the length of the boundary. In the case of a circular boundary, the time evolution of a length parameter $l(t)$ that describes the domain size (*e.g.* radius, diameter or perimeter) evolves as:

$$l(t)=(2k\,t + l_0^2)^{1/2} \qquad (1)$$

where l_0 is the initial length parameter, and k is a rate constant proportional to $\exp(-E_b/k_BT)$. Here, E_b is the boundary energy, k_B is Boltzmann's constant and T is the temperature.

For this study, the domain radius is used as the length parameter and it is determined by a least squares fit of the perimeter to a circle. For analytical purposes, 10 runs are performed for each temperature and flux, and the radius reported at each time is the average of these runs. An initial inner domain with radius of 3 nm is used. To incorporate this domain, the simulation surface is comprised of 80x80 diamond-shaped, CA cells. The simulation time is $1\text{x}10^6$ time steps or until the interior domain disappears.

Quantification

In the contrived case of the curvature study, one could just as easily characterize the system using the area of the interior domain. The area, proportional to the radius squared, would then follow a 1/4 dependence on time. This study corresponds to the special Q=2 case of the Potts Model, known as the Ising model. In a Q-state Potts Model with large Q, the area could also be used; however, for systems with low Q, coalescence of domains occurs too rapidly, and the area is no longer a good length parameter[3]. Thus, results from studies of magnetic systems (also Q=2) are relevant.

Two characteristic lengths of a magnetic system are commonly used to quantify the domain

structure: a "persistence of spins"-like parameter[4-6] and a parameter related to the perimeter between domains[3,7]. The latter parameter is clearly more relevant to a crystallographic system. As such, both the total perimeter and average perimeter of the argon microstructure that forms on the calcium surface are considered.

A measure of surface "uniformity" is essential for evaluating film growth in manufacturing processes. Both the total perimeter and average perimeter of a monolayer offer such a measure of surface uniformity. The most uniform surface is one that has a single defect-free domain such that every gas atom has six next near neighbours. On such a surface, there are obviously no domain perimeters. When a single atom is removed, a small perimeter is created around the vacant atom. This corresponds to a small increase in the total perimeter and a small decrease in the average perimeter of the system. The total perimeter also increases as the number of domains increases. Thus, the perimeter reflects both the microstructural complexity and the atomic disorder of the surface.

Unlike the radius behaviour in the curvature study, a theoretical form for the total perimeter on a surface that contains randomly distributed domains is not well established. Several different empirical behaviours of the characteristic length l in magnetic systems have been observed[7]. Experiments have shown a $l(t) \sim t^{1/2}$ dependence[8]. Studies using the random field Ising model have demonstrated a logarithmic dependence $l(t) \sim \log(t)$ in the late stage of ordering processes in two-dimensional systems[9-13]. Monte Carlo simulations show a crossover from a $l(t) \sim t^{1/2}$ dependence to a slower, logarithmic-like growth[3,4]. Finally, $l(t) \sim (T\log(t))^4$ has also been proposed for late stage ordering processes[7,12].

The results of this study will be limited to discussing the empirical form that the data follow. The perimeter is determined by counting the number of next near neighbours to an atom that are not occupied by an atom in the same crystallographic position. In order to ensure that different sized simulation surfaces can be compared, the perimeters are scaled by dividing the perimeter by the simulation surface area. This ratio of perimeter to surface area is multiplied by the lattice constant to obtain a unitless quantity that is referred to simply as "perimeter (unitless)".

Rough Surfaces

Using total perimeter as a measure of surface uniformity, the total perimeter is determined at long simulation times after it has converged to some value. This value is the minimum total perimeter and is reported as a function of initial surface imperfection. Since lower perimeters correspond to more uniform surfaces, one expects the minimum total perimeter obtainable for a system to increase as the initial surface imperfection increases.

To achieve the study, the surface has an initial configuration of calcium atoms randomly placed in a- and b-sites. These extra calcium atoms are not allowed to move during the simulation. Surfaces comprised of 100x100 diamond cells have been used, and typical simulation times were between 200,000 and 500,000 time steps.

Results

In the diagrams of the surface, the surface is divided into diamonds -- each diamond contains one a-site and one b-site. If neither site is occupied, the diamond is black. If an a-site is occupied by argon, the diamond is red; whereas, if a b-site is occupied by argon, it is blue. For the surface roughness study, if either site is occupied by a calcium atom, the diamond is coloured yellow.

Curvature

The surface for this section of the study is 80x80 surface sites and initially has one circular domain of radius 3 nm (see figure 2a). Figures 2b through 2f show the evolution of the surface when exposed to an 8% Ar flux at a temperature of 90 K.

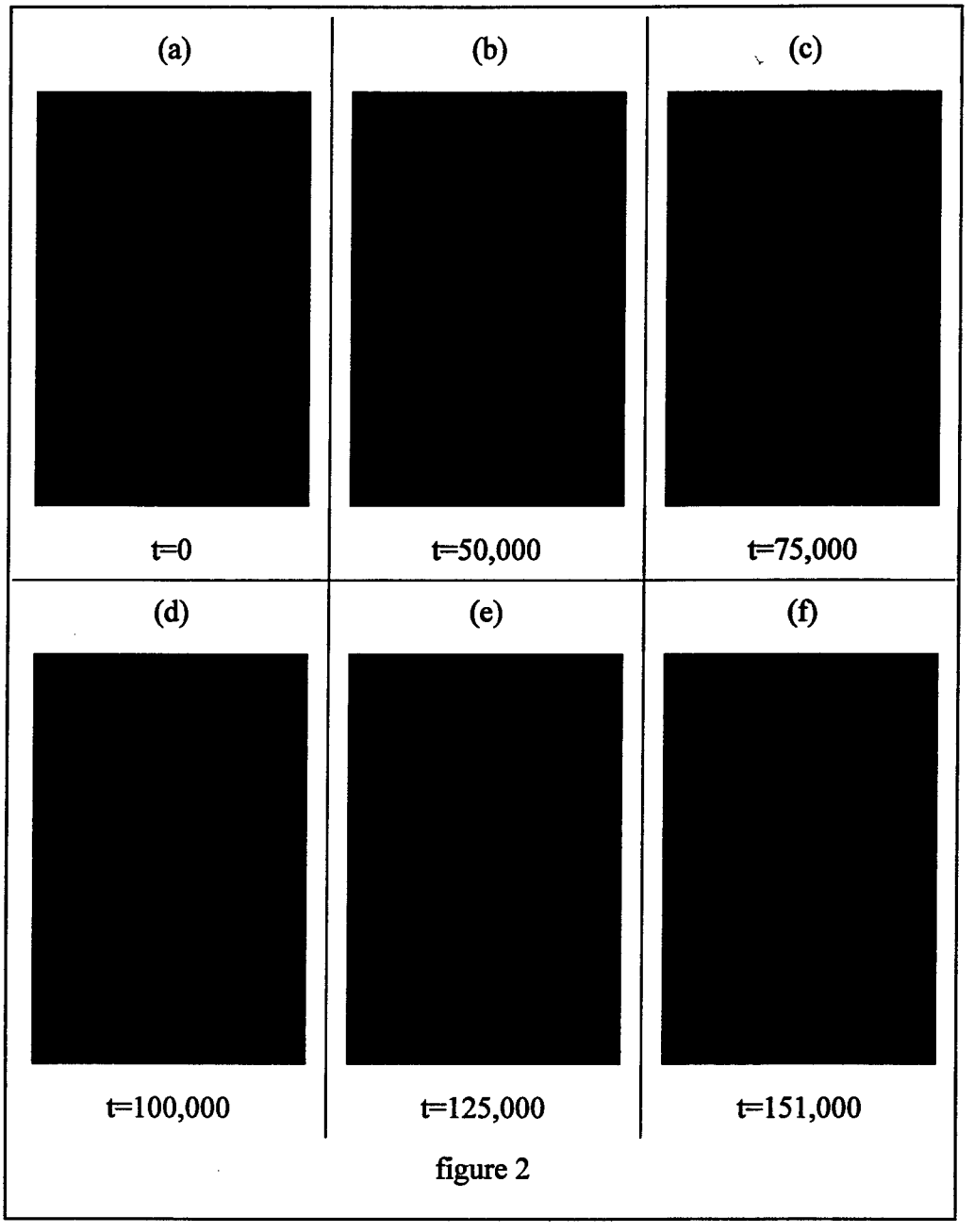


figure 2

The radius at a given time step is determined by performing a least squares fit of the perimeter to a circle. Plotting the radius versus time indicates that the system evolves according equation 1 (figure 3). For statistical accuracy, the radius as a function of time step is averaged over 10 runs for each temperature and flux. A temperature sequence corresponding to an 8% Ar flux is shown in figure 4. Figure 5 is an Arrhenius plot of the parabolic growth factor. Figure 6 shows how the Arrhenius behaviour varies as a function of flux.

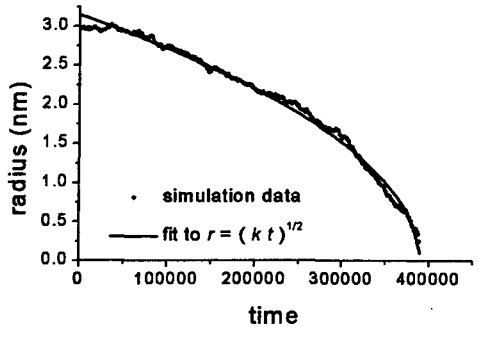


figure 3

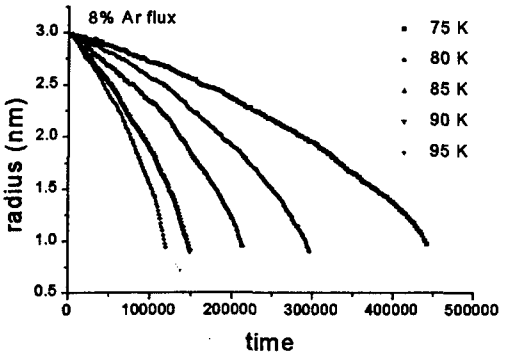


figure 4

The flux values that have been studied (i.e. 0.25% to 8%) are probably very high, and lower flux values (i.e. 0.01% to 0.1%) need to be studied in more detail. Simulations of lower flux values are much more computationally demanding because more time steps are required. For high flux values, the energy barrier and prefactor do not vary as functions of flux within the statistics of this study. This suggests that only temperature affects the rate at which the gas microstructure on the surface coarsens. The flux only plays a role in determining surface coverage at these high fluxes[2].

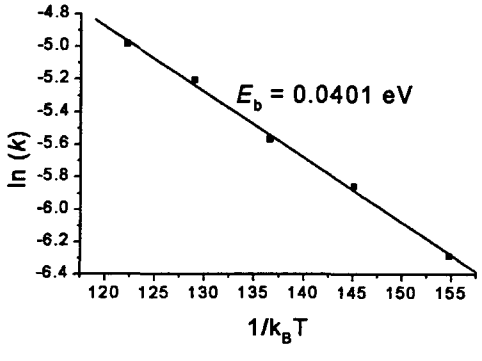


figure 5

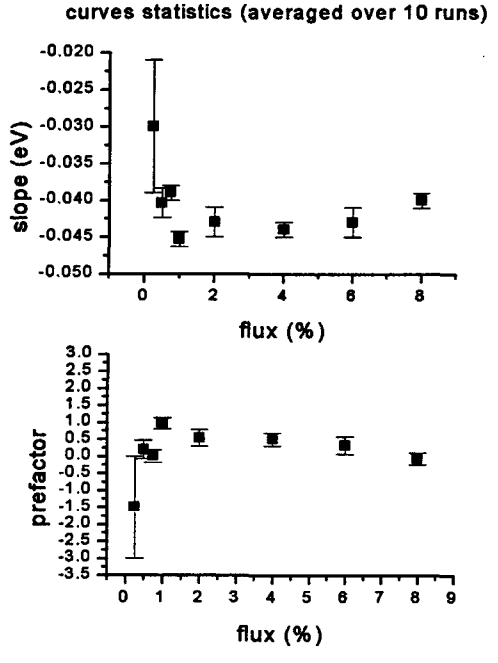


figure 6

Surface Uniformity

The length parameter of this system, which is related to similar problems in magnetism, is the total perimeter (*TP*). *TP* as a function of time is shown in figure 7 for an 8% Ar flux at 90 K after

subtracting the thermal perimeter ($TP_{thermal}$)*. The top of figure 7 shows the total perimeter (TP-$TP_{thermal}$) for a single run, and the bottom of figure 7 shows the total perimeter averaged over 10 runs. Using the averaged total perimeter, an empirical form can be deduced:

$$TP = a\, t^{1/n} + TP_{thermal}.$$

In this relation, a is a rate parameter that is probably dependent on temperature and n is a factor that is probably temperature independent but dependent on the mechanism of coarsening. At long times, but before the system reaches equilibrium, n=2, suggesting that the mechanism of equation 1 is in action. At shorter times, however, n=2.8, indicating another mechanism is at work. The single run doesn't exhibit the two mechanisms due to insufficient statistics.

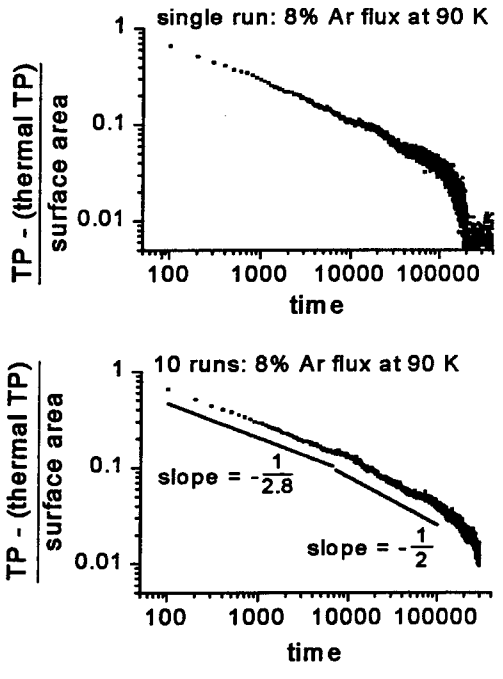


figure 7

The effect of the change in mechanism is amplified by plotting the average perimeter of each domain versus time. The average perimeter is the total perimeter divided by the number of domains; therefore, when few domains are present, the disappearance of one grain when it joins up with another results in a discontinuity in the average perimeter. Because of thermal fluctuations on the surface, two like domains that meet can come apart and rejoin frequently, resulting in a large scatter in the plot. Both the discontinuities and scatter are seen in the top of

* Starting with a surface covered entirely with gas atoms in either a-sites or b-sites but not both, a number of surface vacancies will form as desorption events occur. The number of surface vacancies in equilibrium is a function of the adsorption and desorption rates, which in turn are strong functions of the temperature. The contribution to perimeter (both the total perimeter or average perimeter) which arises from these surface vacancies is referred to as the thermal perimeter. For a given temperature and flux of incident gas atoms, the thermal perimeter is the minimum obtainable perimeter on a perfect surface.

figure 8. However, by averaging over multiple runs, the scatter and discontinuities are reduced as seen in the bottom of figure 8. Figure 9 replots the bottom of figure 8 as a log-log plot (top) and a log-normal plot (bottom).

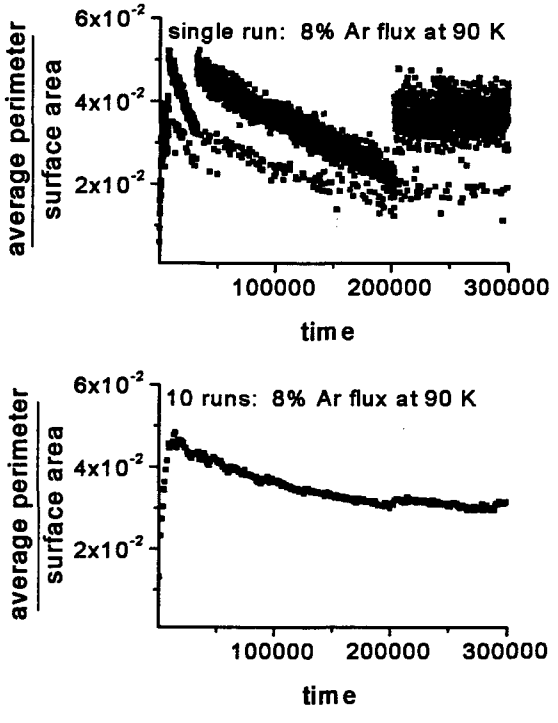


figure 8

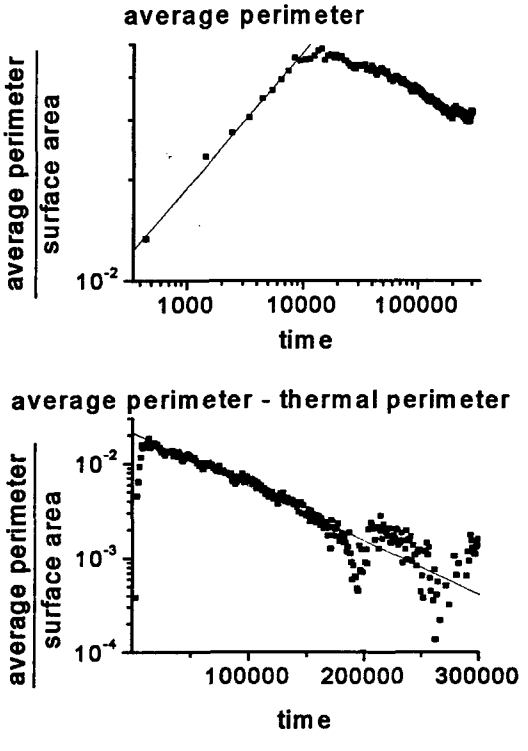


figure 9

Initially, the empty surface is randomly filled, creating many small domains that have small perimeters. As time progresses, the domains grow. Because there are only two types of domains (a-sites and b-sites), like-domains frequently meet, and this coalescence results in a rapid decrease in the number of domains and an increase in the perimeters of individual domains. Clearly, this results in an increase in the average perimeter. After this coalescence stage, some amount of perimeter exists that is greater than the perimeter caused by thermal fluctuations (the peaks in figure 9 around 10,000 time steps). This perimeter decreases as the system works to minimize the surface energy by minimizing the perimeter.

Inspection of the top plot in figure 9 suggests the following relation between the average perimeter and time:

$$\text{average perimeter} = a\, t^{1/n}.$$

In this case, n=2.5. The bottom plot in figure 9 suggests the following:

$$\text{average perimeter} = a\, e^{b\, t},$$

where a and b are constants.

Surface Imperfection

The surface for this section of the study is 100x100 surface sites and is initially free of inert gas atoms on the surface; however, the surface layer is not empty. It has additional calcium atoms at a- and b-sites. The distribution of calcium is random. An initial surface with 4% calcium coverage is shown in figure 10a. Figures 10b through 10f show the evolution of the surface when exposed to 8% Ar flux at a temperature of 90 K. Figures 11a through 11f show surfaces with different degrees of initial calcium coverage after exposure to 8% Ar flux at 90 K for 300,000 time steps.

The total perimeter is the measure of the surface uniformity, and it is plotted versus time for several degrees of initial surface imperfection in figure 12 for an 8% Ar flux at 90 K. The total perimeter does not approach zero for a perfect initial surface due to thermal fluctuation. Instead, it goes to a finite value TP_0. For each degree of initial surface imperfection, the minimum total perimeter that may be reached (TP_{min}) is determined by averaging the total perimeter at long

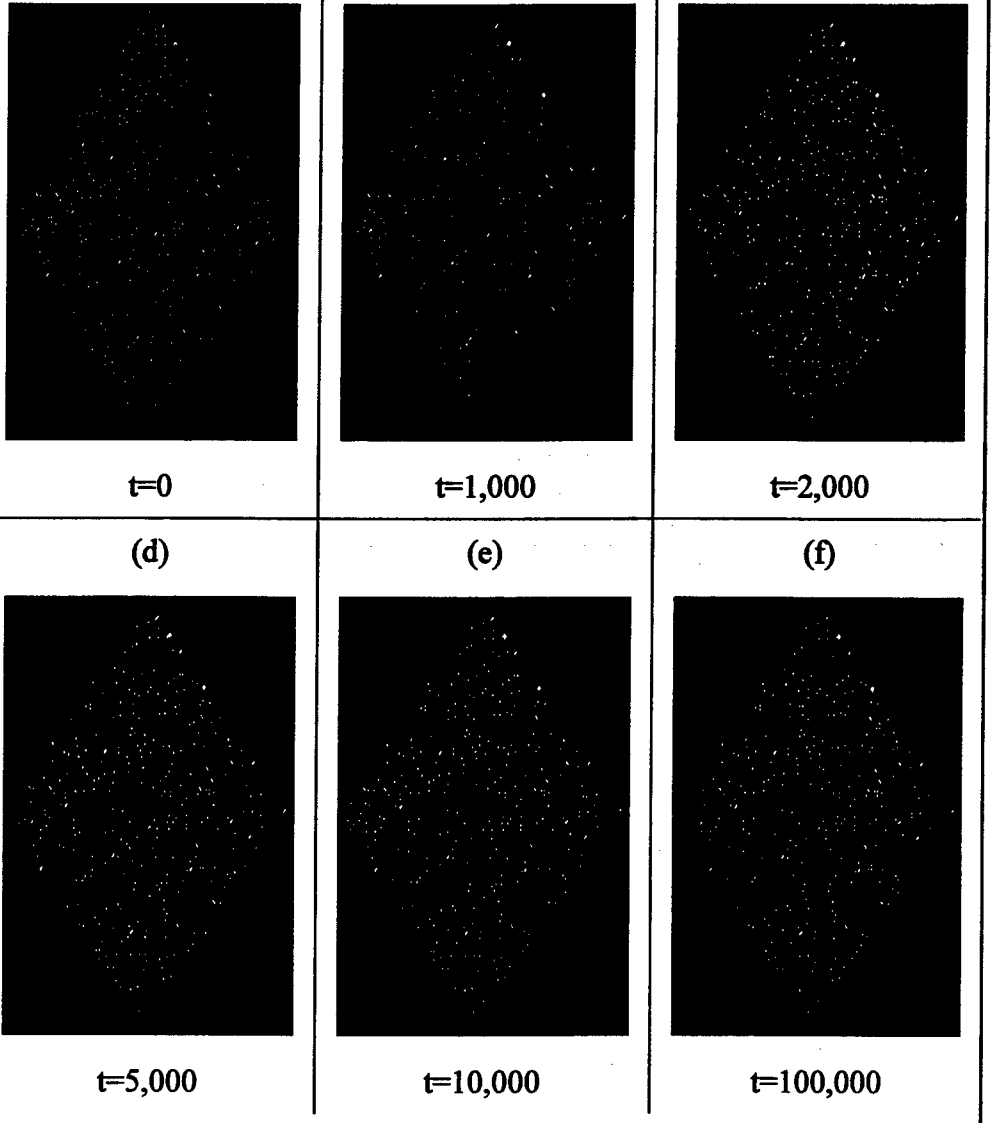


figure 10

times (after 300,000 time steps in the case of figure 12). TP_{min} is plotted as a function of initial surface imperfection in figure 13 for both an 8% Ar flux (top) and a 15% Ar flux (bottom) at 90 K. A heuristic fit that works well is

$$TP_{min}=a(\text{initial surface imperfection})^{b}+TP_{0}.$$

Within uncertainty, the fitting parameters a and b are the same for the two fluxes, but until more temperatures and fluxes are analyzed, a physical interpretation of the fitting parameters is not possible.

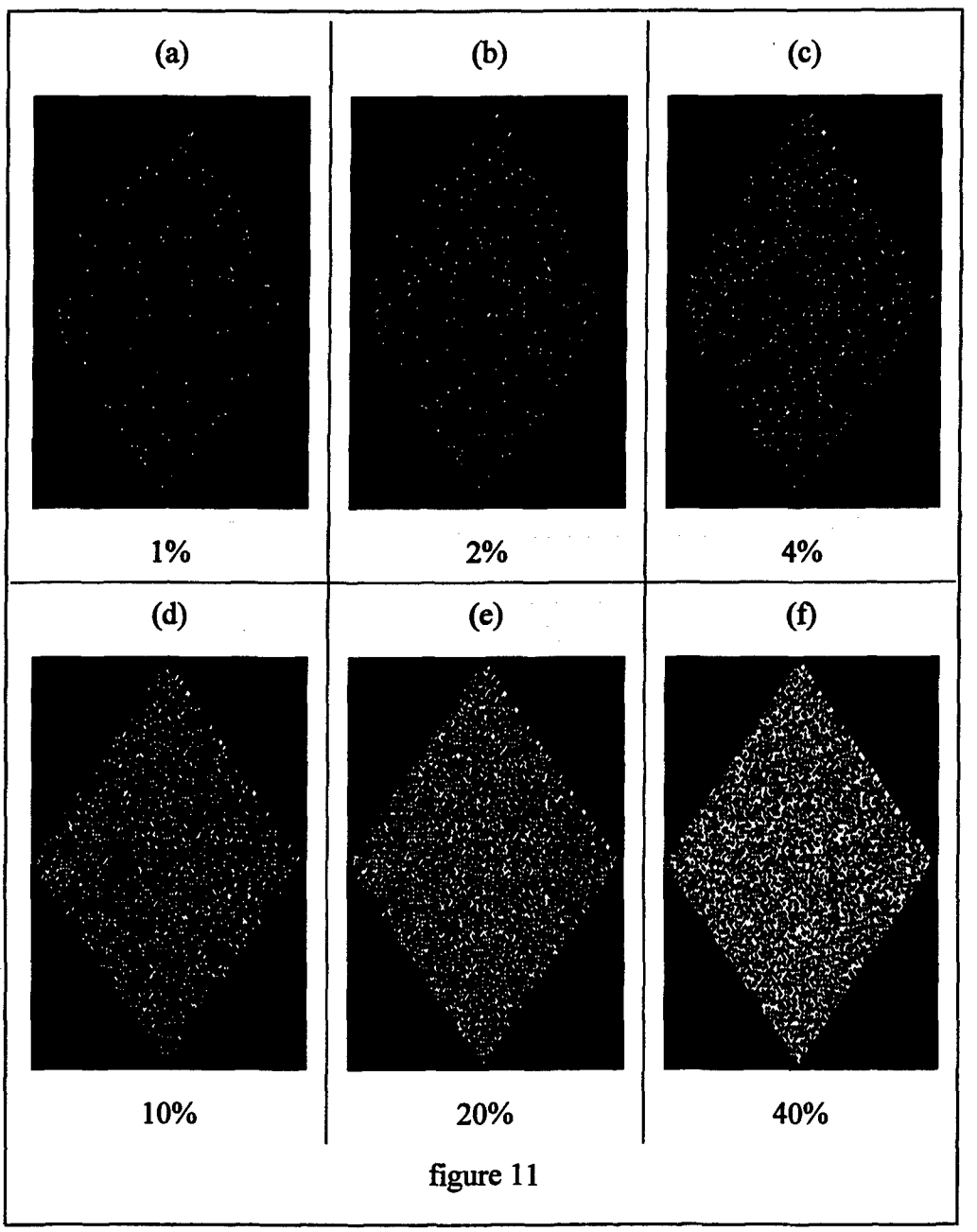


figure 11

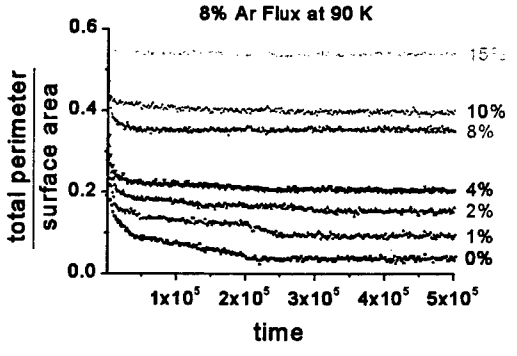
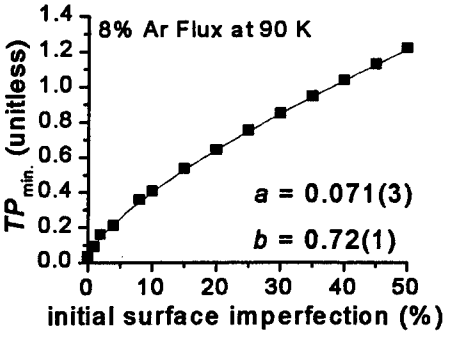


figure 12



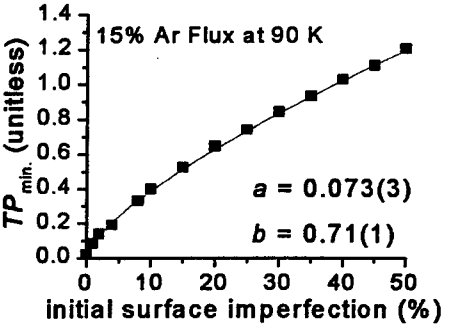


figure 13

Conclusions

- Many simulations for a single variable set (where temperature, incident gas atom flux, and surface roughness are the variables) must be performed to get good enough statistics for proper quantification.
- Within the statistics of the curvature study, domain growth rate is independent of incident gas atom flux for the high fluxes simulated.
- Two types of microstructural evolution of argon on the perfect calcium (111) surface are observed. The short-term behaviour is a coarsening of tiny, randomly placed domains that were formed in the very early stages of the simulation on the perfect surface. The long-term behaviour is a reduction of surface energy by reducing perimeter lengths.
- Empirically, the two types of behaviour can be characterized by the total perimeter *TP*. $TP \sim t^{1/2.8}$ at short times and $TP \sim t^{1/2}$ at long times. This latter behaviour has also been observed in some studies of magnetic systems (though not all studies of magnetic systems agree). More simulations must be performed to determine how constants in the empirical equations vary with temperature and flux.
- The total perimeter also offers a way to quantify the degree of surface uniformity in the presence of a rough surface. If f denotes the initial fraction of an extra monolayer of calcium on an otherwise atomically flat calcium (111) surface, the minimum obtainable *TP* is $TP_{min.} \sim f^b$ where $0<b<1$. More simulations must be performed to determine how b changes as a function of temperature and incident gas atom flux.

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