The kinetic MC modelling of reversible pattern formation in initial stages of thin metallic film growth on crystalline substrates

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Abstract

The results of kinetic MC simulations of the reversible pattern formation during the adsorption of mobile metal atoms on crystalline substrates are discussed. Pattern formation, simulated for submonolayer metal coverage, is characterized in terms of the joint correlation functions for a spatial distribution of adsorbed atoms. A wide range of situations, from the almost irreversible to strongly reversible regimes, is simulated. We demonstrate that the patterns obtained are defined by a key dimensionless parameter: the ratio of the mutual attraction energy between atoms to the substrate temperature. Our ab initio calculations for the nearest Ag–Ag adsorbate atom interaction on an MgO substrate give an attraction energy as large as 1.6 eV, close to that in a free molecule. This is in contrast to the small Ag adhesion and migration energies (0.23 and 0.05 eV, respectively) on a defect-free MgO substrate.

1. Introduction

In general, metal atom adsorption at constant dose rate on metallic or insulating substrates shows two modes of thin film growth: monolayer-by-monolayer, or 3D metal cluster formation [1–4]. The detailed understanding of this process is important for many technological applications, including catalysis and microelectronics. In particular, the model system of Ag thin film deposition on MgO has been widely studied [5–7]. For this particular system, 2D growth changes to 3D island formation at submonolayer metal coverages of 0.2–0.5 ML [1]. Electron microscopy experiments performed at low and moderate temperatures reveal two kinds of pattern formation: spherical compact clusters, and worm-like loose cluster growth [7,8]. The analysis of these structures reveals some regularities. At constant temperature, a change in adsorbate concentration increases the size of the metallic clusters, but leaves the characteristic distance between cluster centers almost unchanged. The distance is typically of order 0.1 μm, i.e. a few hundreds of lattice constants. Moreover, the variation of Ag adsorption rate and the temperature do not affect this characteristic distance strongly. However, a temperature increase from 100 up to 450 °C transforms loose clusters into compact ones [7].

There are two classes of general approach in the theoretical description of the growth mode of thin metallic

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films. The first approach assumes the system to be in a thermodynamical equilibrium, so that statistical methods can be applied [9,10]. In fact, a constant adsorbate concentration is assumed, i.e. the adsorption rate is expected to be very slow, whereas metal atom diffusion is very fast, so that the system reaches the thermodynamic equilibrium between adsorption of the two successive metal atoms. However, this is not the case when adsorbate atoms strongly interact with each other, which prevents the rapid transformation of small clusters into larger clusters (Ostwald ripening).

The alternative kinetic approach, usually based on rate equations, focuses on mobile atom diffusion and aggregation [4]. Often, a kinetic Monte Carlo (MC) or similar technique is used to model the relaxation kinetics for systems with a constant number of particles in which Ostwald ripening occurs [11,12]. We would like to mention in this respect pioneering papers by Ben-Shaul et al. [13,14] where pattern formation was studied as a result of a strong adsorbate-adsorbate interaction and diffusion.

Most of the kinetic MC simulations (see Ref. [15] and references therein) deal with the irreversible growth of aggregates, which corresponds to the limiting case of a very strong adsorbate–adsorbate interaction and/or low temperatures. This leads usually to dendritic-like adsorbate patterns (unless, e.g. periphery diffusion is incorporated). Recently, kinetic MC modelling was extended to the cases where adatoms attach to islands is a reversible process (see Refs. [16–18] and references therein). However, most of these studies are restricted to the case of a weak reversibility of particle adsorption from their aggregates.

In this paper, we perform MC simulations for a realistic process of adsorbate deposition with a given rate, taking into account both the adsorbate surface diffusion and interaction. To describe the spatial distribution of adsorbed atoms, we use the very transparent language of joint correlation functions characterizing relative spatial distribution of adsorbed atoms. Unlike many previous studies, we cover a whole range of situations, from weak to strong particle reversibility.

2. Model

We assume that adsorbate atoms arrive at the surface with a given dose rate $\zeta = ka^2$, where k is the adsorption rate per unit surface and unit time, a is the lattice constant. Typically $k = 2–8 \times 10^{13}$ Ag/cm^2 s^{-1} [5]. Adsorbed atoms are mobile on the surface. In the case of noninteracting particles, their diffusion obeys the standard equation

$$D = D_0 \exp\left(-\frac{E_a}{k_B T}\right) = \frac{a^2}{z} d, \qquad (1)$$

where E_a is the activation energy, d the hop frequency, and $z = 4$ is the number of nearest neighbors (NNs). For

the activation energy of $E_a = 0.1$ eV typical both for Ag on MgO [9,10] and on Pd [19], one finds that, in the typical experimental temperature interval of $T = 300–1000$ K, the diffusion coefficient D changes only by an order of magnitude. This clearly indicates that adsorbate diffusion is weakly activated, so that the observed temperature effects are most probably related to the interaction between adsorbed atoms. As we show below, diffusion determines the scale of structures formed, but not their type. In this sense, the incomplete information about the magnitude of D_0 has no big effect on our qualitative conclusions.

Let us translate this information to the abstract level of computer simulations. We study the adsorption of particles on sites of square discrete lattice. Each site can be either empty (state 0) or occupied by an adsorbate (state A). The adsorbate concentration C_A is the fraction of occupied sites on the lattice. Our 2D model is restricted to the growth of an adsorbate monolayer, since we are interested only in the initial stages of thin film growth. Diffusion of an adsorbed particle on the lattice is described by its hops to a free NN site.

We take into account of the short-range interaction only between particles in NN sites which is described by the parameter $E_{AA} = -\varepsilon$, with $\varepsilon > 0$ (attraction). An interaction energy is always introduced in equations in combination with the temperature, therefore the energy dependence of the model introduces the additional dimensionless parameter $\omega = \varepsilon/k_B T$. In our approach, aggregates of particles are dynamical formations; single particles can join and leave aggregates. This is in contrast to the standard phenomenological theory of nucleation and growth [4] based on the irreversible growth of aggregates exceeding some critical size. The hopping rate is determined by both the E_a value and the difference in particle energies before and after its hop. Thus it depends on the E_{AA} and the difference in the NN numbers for the initial and final states (see details in Refs. [20–22]). The typical size of the simulated surface was 256×256 sites.

It is well recognized that the formulation of the kinetic Master Equation for mobile and interacting particles is not unique [23], a fact which has led to the suggestion of many different reaction dynamics (Metropolis, Transition State Theory, etc.). Not going into details, we follow here a novel theory (the so-called standard model [20–22]) which is based on a complete axiomatic approach, free of the disadvantages of previous MC theories.

Our main interest will be focused on the pattern formed by adsorbed particles on the lattice. The structure for a given C_A is determined by the two dimensionless parameters: ω and d/ζ. The latter is typically quite large: $d/\zeta \gg 1$. We use the time increment $\zeta = 1$. The general algorithm of the kinetic MC simulations is well described in the classical Refs. [24,25], whereas the peculiarities of our modelling are discussed in Refs. [22,26].

3. Results

Let us consider the results for the large value of the dimensionless attraction energy $\omega = 3$ (weak reversibility, corresponding to a strong attraction and/or low temperatures) presented in Fig. 1(c). Four vertical windows in this figure correspond to a monotonic increase in adsorbate concentration. It is obvious that the adsorbate aggregates are very dense with only a few small holes. They are practically immobile, and no new aggregates arise. That is, all newly adsorbed particles join already existing aggregates. Small aggregates grow independently and coalesce periodically when their boundaries touch, thus forming large aggregates of irregular shape. An increase in the diffusion coefficients by a factor of $2^4 = 16$ increases the characteristic distance between aggregates by a factor of 2 (Fig. 1(d)) but preserves the similarity of patterns. This is in complete agreement with scaling arguments [26] predicting that the mean distance between aggregates is proportional to $d^{1/4}$. These aggregate structures are quantitatively analyzed below using the joint correlation functions.

The pattern formation and kinetics are governed by the ratio of the particle hopping rate to the adsorption rate. In our units, the adsorption rate is assumed to be unity. The aggregate pattern remains similar after reducing the interaction energy to $\omega = 2$, $d = 2^9 \times 10^3$. However, aggregates become here more loose than before (Fig. 1(b)). One can observe a large number of single particles which leave aggregates and walk randomly on the lattice. A further decrease in the dimensionless attraction energy down to the critical value of $\omega = 1.25$ (a strong reversibility regime) leads to the disappearance of the aggregate pattern. As one can see in Fig. 1(a), only short-range order in the distribution of particles exists (numerous very small and loose aggregates).

Now let us characterize the aggregate patterns quantitatively, using the language of the joint correlation functions $F_{\alpha\beta}(r)$ where $\alpha, \beta = 0, A$ [20]. These functions have a simple physical meaning. Assume that some site is in the state $\alpha = 0, A$. We are interested in finding a probability that a site at the distance r is in the state β. This probability, $\omega_{\beta}^{(\alpha)}(r) = F_{\alpha\beta}(r)C_{\beta}(r)$, is normalized to unity:

$$\sum_{\beta=0,A} \omega_{\beta}^{(\alpha)}(r) = 1. \tag{2}$$

Two equations follow from Eq. (2):

$$F_{0A}(r)C_A + F_{00}(r)C_0 = 1, \tag{3}$$

$$F_{AA}(r)C_A + F_{A0}(r)C_0 = 1. \tag{4}$$

Taking into account the symmetry property $F_{0A}(r) = F_{A0}(r)$, the conclusion can be drawn that of all these functions only one is independent. Therefore, hereafter we shall consider only the function $F_{AA}(r)$, which describes the correlations in distribution of adsorbate atoms.

To explain the meaning of F_{AA}, let us take some particle A. The correlation function gives the probability density of finding a particle A at a given distance r from the chosen particle placed into the origin. The random (chaotic, or Poisson) distribution corresponds to $F_{AA}(r) = 1$.

Fig. 2 shows the joint correlation functions for a dimensionless particle interaction energy of $\omega = 3$. At small relative distances, the correlation function greatly exceeds the unity thus indicating a strong adsorbate aggregation. For aggregated particles, one can define the aggregate radius R as the distance at which the correlation function approaches unity. At larger distances the correlation function becomes even less than unity: there are no other particles nearby the aggregate boundary, since all such particles are already attached. Lastly, with further increase in distance, the correlation function reaches the asymptotic value of unity once more, which corresponds to the presence of other aggregates, at these larger distances. These spacings correspond to the mean distance between aggregates, L_0, introduced above. Let us define L_0 from the minimum of the correlation function. One can see that, for the hopping rate of $d = 2^5 \times 10^3$ (curve 1), the aggregate radius R is about five lattice constants, and the scale L_0 is about 8. After the scaling d by the factor of 16 (curve 2), the shape of the correlation function remains the same, but both scales, R, L_0, double. This is in the complete agreement with scaling arguments [26].

For $\omega = 2.0$ we obtain qualitatively similar correlation functions, but with less pronounced minima due to the reduced aggregate density. The scale L_0 is still observable, and it has the same order of magnitude. However, for smaller $\omega = 1.25$, the aggregate structure completely disappears: L_0 is no longer observable, and the scale R (the mean size of the aggregate) loses its dependence on the hopping frequency (which indicates the quasi-equilibrium regime).

4. Ab initio calculations of interaction between adsorbate atoms

Let us discuss now the energetics of the interaction of the adsorbed atom with the substrate and with other adsorbed atoms. This was studied earlier by means of classical simulation methods [27,28]. It was concluded that the single Ag diffusion energy on MgO is $E_a = 0.1$ eV, the adsorption energy atop surface O^{2-} is $E_{ads} = 0.66$ eV, whereas the mutual attraction energy between NNs is about $E_{int} = 1.2$ eV. In order to check how these results are affected by neglect of the electron density redistribution, quantum mechanical calculations are necessary. Recently, we performed preliminary ab initio Hartree–Fock calculations combined with a posteriori PW-GGA electron correlation corrections to the total energy, as implemented in the CRYSTAL-95 code (see more details in Ref. [10]). We found there $E_a = 0.05$ eV, $E_{ads} = 0.26$ eV for Ag monolyer and 0.46 eV for three metal layers. In order to

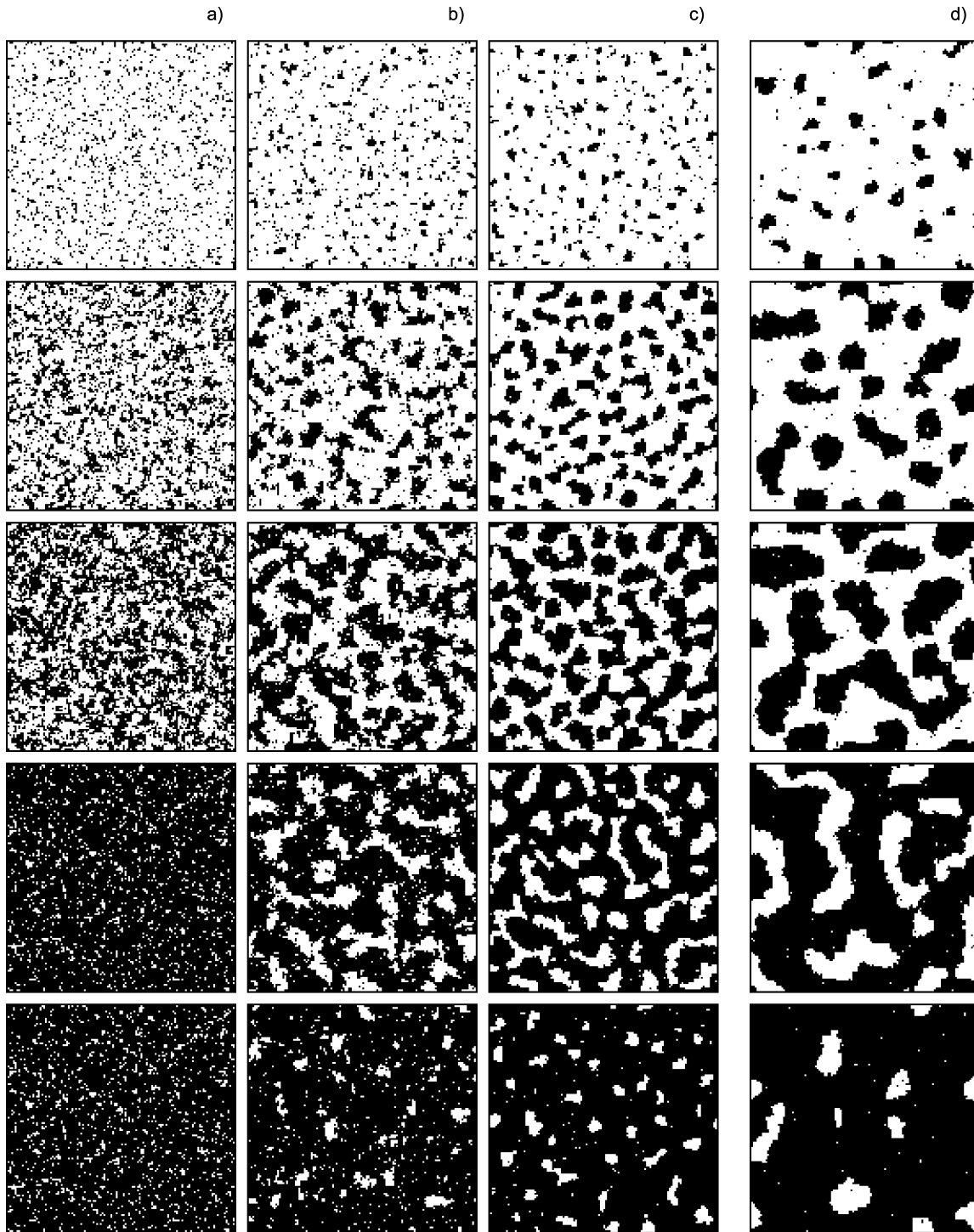a)   b)   c)   d)

Fig. 1. Snapshot of the spatial distribution of adsorbate atoms at concentrations of $C_A = 0.1, 0.3, 0.5, 0.7$ and 0.9 correspond to a series of windows, from the top to the bottom. The dimensionless attraction energy $\omega = \varepsilon/k_B T = 1.25$ (a), 2 (b), and 3 (c). (d) is the same as (c), but with the hop frequency scaled by a factor of $2^4 = 16$.
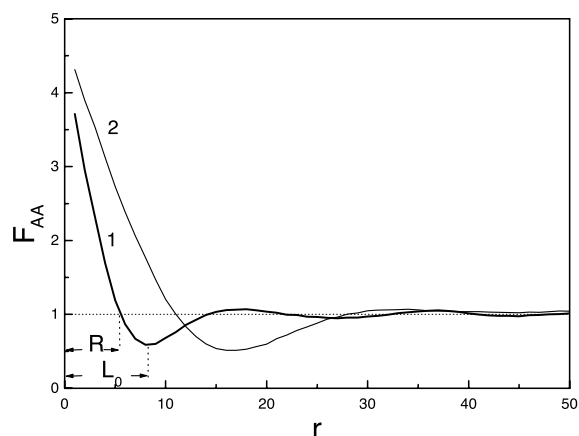
Fig. 2. The joint correlation function versus the relative distance between adsorbate atoms (in units of the lattice constant): $\omega = 3.0$, $C_A = 0.1$, hop frequency $d = 2^5 \times 10^3$ (curve 1) and $d' = 2^9 \times 10^3$ (curve 2). The units are such that the adsorption rate equals unity.

study an isolated Ag atom on MgO substrate as the reference point, we use here 3×3 extended surface supercells, and found that the attraction between two nearest Ag atoms ($R_{NN} = 2.82$ Å) on the flat MgO surface is as large as 1.6 eV. This is close to the dissociation energy of a free Ag_2 molecule (1.78 eV at $R_{eq} = 2.53$ Å). This large interaction is in contrast to the small (0.05 eV) migration energy for Ag atoms on a defectless MgO substrate.

Recent ab initio DFT calculations of the interaction between nearest Ag atoms on 1 ML Ag/Pt surface [19] give the mutual attraction energy of 0.05 eV and hopping energy of 0.06 eV. In other words, Ag adsorbate interaction energies on insulators (MgO) considerably exceed those on metals (Pt).

5. Discussion and conclusions

Our MC modelling covers a whole range of cases, from weak to strong adsorption reversibility, and demonstrates the considerable difference between simulations assuming the adsorbate concentration to be constant, and a permanent flux of adsorbates to the surface. In our submonolayer adsorbate modelling, we observe loose adsorbate aggregates in the strong reversibility regime (the dimensionless attraction energy $\omega = E_a/k_B T > 1.25$), and no pattern formation for smaller interaction energies at higher temperatures. For the particular Ag/MgO system, where there is a large attraction energy between nearest neighbor adatoms, pattern formation should occur up to very high temperatures, $T = 1000\,^\circ C$. This is confirmed experimentally [6–8]. In contrast, for Ag-1ML, Ag/Pt the critical temperature could be much lower, $T = 100\,^\circ C$.

To learn more about adsorbate growth mode, one has to go beyond 2D simulations and model a growth of several metal planes. Such calculations are now in progress.

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