The kinetics of ordered domains in monolayer deposition

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In this work, we study the growth of ordered domains observed during deposition of a monolayer. We use mean field lattice gas model to describe the kinetics. Our results on the calculated dynamical structure factor provide insights on how the growth of ordered domains depends on the adatom/adatom interaction and the role played by the competition between the deposition and the diffusion processes. Using the dynamic scaling, we show that the growth of these ordered domains is characterized by the growth and the roughness exponents values: $2\beta = 2.64 \pm 0.05$; $2\alpha = 2.36 \pm 0.04$, satisfying the Kardar-Parisi-Zhang relation for d>1.

1. Introduction

Physical and chemical properties of adsorbed monolayers are being studied with increasing interest [1-9] because their understanding is essential for the rationalization of many phenomena and processes occurring on surfaces and interfaces, such as adsorption, catalysis, corrosion, wetting, adhesion, diffusion, etc. In particular, ordering kinetic information on the surface diffusion has been obtained using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM) [10] with quantitative information obtained from the Fourier transform of the current correlation function.
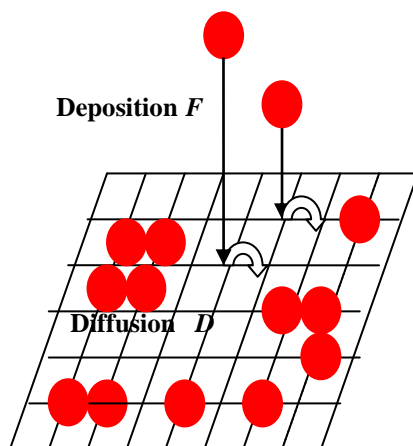

Fig.1. schematic of island formation obtained during the diffusion of the deposited atoms

Considering the deposition and diffusion of particles on a surface, one has two characteristic constants: the flux *F* and the diffusion coefficient *D*, where *1/D* is proportional to the typical time between two hops. Due to the competition between deposition and diffusion, one expects that all physical processes depend on the ratio *D/F*. If *p* denotes the coverage, then *p=F.t*, where *t* represents the time. The figure 1 schema represents the deposition and the diffusion processes during the island formation.

In this paper, we focus on the early time morphology for which the coverage is less than one monolayer; this regime is usually referred to as submonolayer epitaxy.

What is the surface ordering kinetic at a fixed value D/F in the submonolayer regime? The answer to this question depends on different parameters and can be extracted from the Fourier transform of the current correlation function which has been shown to be proportional to the square of the linear dimension « *l* » representing the ordered domain [11-14].

In this investigation, we address the questions of the kinetics of ordered domains in monolayer deposition in the framework of mean field lattice gas model. In the section II, we present the model and the formalism of the our work. In the section III, we calculate the dynamical structure factor corresponding to the diffracted intensity in LEED for several interactions and *D/F* values. Our calculations are done for repulsively interaction system. We have also determined the growth and the roughness exponents values. The obtained results are compared to the experimental ones. The section IV represents the conclusion of this paper.

2. Model and formalism

In our study, the crystalline surface is modeled by a lattice of size $L \times L$ with sites coinciding with the positions of the potential minima available for the diffusing particles. Every site of the lattice can be either occupied or empty. We introduce an occupation number n_i where i is the site label and n takes respectively the values 1 or 0, for occupied and empty site, respectively. The thermodynamic is completely determined by specifying the Hamiltonian of the system. Here, for the sake of simplicity, only the static pair interactions are taken into account. The Hamiltonian is then written as:

$$H = -\sum_{<ij>}^{N(t)} \varepsilon_{ij} n_i n_j - \mu \sum_i n_i \quad (1)$$

where the summation is over all nearest neighboring sites $<ij>$. ε_{ij} is the pair repulsive interaction energy of the particles at sites i and j. $N(t) = FL^2 t$ represents the number of the deposited atoms at time t and μ is the external chemical potential.

Let the configuration $\{n\} = (n_1, n_2, ..., n_N)$ denotes an occupation state of every site of the lattice. The diffusion process of the particles is insured by the change of the occupation numbers of the lattice sites. This can be seen as the change of the lattice configurations.

Hence, the dynamics are described by the choice of the transition rate between possible configurations. The latter is given by,

$$\omega(\{n\}, \{n'\}) = \sum_{ij} \omega_{ij}(\{n\}) n_i (1 - n_j) \delta_{n_{ji} n_i'} \delta_{n'_{jn_i}} \delta^{ij}_{\{n\}, \{n'\}} \quad (2)$$

where the last Kronecker symbol is referring to the two configurations separated by the jump of only one particle; $\delta_{n_j n_i'} \delta_{n'_j n_i}$ denotes the permutation of the occupation numbers of sites i and j; and the product $n_i(1-n_j)$ ensures the hard core exclusion condition which prohibits the double occupation at a given site.

It is clear that the transition frequency ignores the state around the arrival site in the transition rate and does not reflect the whole complexity of the diffusion process. With this choice, we define a stochastic process which is well described by the knowledge of the distribution probability of existence at time t: $P(\{n\}, t)$. The time evolution of this probability determines the dynamics of the lattice gas model. Here, we consider that the dynamics are governed by the following master equation:

$$\frac{\partial P(\{n\}, t)}{\partial t} = \sum_{\{n'\}} [\omega(\{n'\}, \{n\}) P(\{n'\}, t) - \omega(\{n\}, \{n'\}) P(\{n\}, t)] \quad (3)$$

Equation (3) which is phenomenological, favors the establishment of the desired configuration. Its stationary solution must lead to the equilibrium distribution,

$$P_{eq}(\{n\}) = \frac{1}{Z} \exp(-\beta H) \quad (4)$$

Z is the partition function given by:

$$Z = \sum_{\{n\}} \exp\left(-\frac{1}{K_b T} H(\{n\})\right) \quad (5)$$

Hence, the transition frequency has to satisfy the detailed balance condition,

$$p_{eq}(\{n\}) \omega(\{n\}, \{n'\}) = p_{eq}(\{n'\}) \omega(\{n'\}, \{n\}) \quad (6)$$

The average concentration over all possible configurations is defined by,

$$p_k = \langle n_k \rangle = \sum_{\{n\}} n_k p(\{n\}, t) \quad (7)$$

The kinetic evolution of the average concentration $p_k = \langle n_k \rangle$ at site k, is governed by the general master equation,

$$\frac{\partial p_k}{\partial t} \equiv \frac{\partial}{\partial t} \langle n_k \rangle = \sum_j \langle \omega_{jk}(\{n\}) n_j (1 - n_k) - \omega_{kj}(\{n\}) n_k (1 - n_j) \rangle \quad (8)$$

where $\omega_{jk}(\{n\})$ is the jump probability from site j to site k, depending on the local configuration. Clearly, this probability will ultimately depend on the energetic of the system. The product $n_j(1-n_k)$ imposes that site j is filled while site k is empty (resulting from the hard-core exclusion principle). We restrict the jumps to those between nearest neighbors sites k and $k+a$. At this stage, it is convenient to introduce a current operator $j_{k,k+a}(\{n\})$ along the bond $k \to k+a$. Equation (8) becomes then,

$$\frac{\partial p_k}{\partial t} = -\sum_a \langle j_{k,k+a}(\{n\}) \rangle \quad (9)$$

and the average current in the bond (i, j) is,

$$\langle j_{ij}(\{n\}) \rangle \equiv \langle \omega_{ij}(\{n\}) n_i (1 - n_j) - \omega_{ji}(\{n\}) n_j (1 - n_i) \rangle \quad (10)$$

with

$$\omega_{ij}(\{n\}) = \omega_\circ \exp\left(-\frac{\varepsilon}{K_B T} \sum_{a \neq j-i} n_{i+a}\right) \quad (11)$$

$\omega_\circ$ is the isolated (single) jump probability; $\varepsilon / K_B T = \gamma$ denotes the normalized interaction energy. The kinetic equation (9) is intractable in its present form and simplifications are necessary.

The simplest approach is the mean field approximation that consists in replacing all operators n_k for the jump probability $\omega_{ij}(\{n\})$ by their average concentration p_k at the same site k [15].
Hence, equation (9) becomes,

$$\frac{\partial p_k}{\partial t} = -\sum_a j_{k,k+a}(\{p\}) \qquad (12)$$

where the general expression of the current is written as,

$$j_{ij}(\{p\}) \equiv \omega_{ij}(\{p\})p_i(1-p_j) - \omega_{ji}(\{p\})p_j(1-p_i) \qquad (13)$$

3. Dynamical Structure Factor: Results and discussion

In the present study, we use a square lattice of size $L \times L$ sites in which the adsorbate particles diffuse according the above formalism, and we focus on a fractional area with M atoms and linear dimension $l \approx M^{1/2}$ representing the ordered domain. We calculate the dynamical structure factor $S(q,t)$ representing the diffracted intensity in LEED, expressed in the framework of the lattice gas formulation by:

$$S(q,t) = \sum_{k,m}^{L} G_{km}(t) \exp(i\,qR_{k,m}) \qquad (14)$$

where $R_{k,m}$ is the relative position between the sites k and m. q is is the deviation parameter from the Bragg condition and $G_{km}(t)$ is the density correlation function defined as:

$$G_{km}(t) = < p_k(t)p_m(t) > \qquad (15)$$

The evolution of $S(q=0,t)$ with time is therefore proportional to $< M(t) >$ representing the mean number of atoms in the ordered domains [16]:

$$S(q=0,t) \propto < M(t,T) > \propto l^2 \qquad (16)$$

For early times in the deposition process, the ordering domains linear dimension l is expected to grow with a power law of time [16],

$$l \approx t^{\beta} \qquad (17)$$

where β is the growth exponent. At a characteristic saturation time $t_c(L) \approx L^Z$ (z is the dynamic exponent), l scales as $l(L,t \rightarrow \infty) \approx L^{\alpha}$ where α is the roughness exponent.

Hence the ordered domain linear dimensions satisfy the Family-Vicsek ansatz [17]:

$$l(L,t) \approx L^{\alpha} f(t/L^Z) \qquad (18)$$

where the scaling function $f(x)$ behaves as:

$$f(x) = \begin{cases} t^{2\beta} & if \quad t << t_c \\ L^{2\alpha} & if \quad t >> t_c \end{cases} \qquad (19)$$

Taking into account equations (16), (17), and (19), $S(q=0,t)$ can be re-written as:

$$S(q=0,t) = \begin{cases} t^{2\beta} & if \quad t << t_c \\ L^{2\alpha} & t >> t_c \end{cases} \qquad (20)$$

We have calculated the dynamical structure factor $S(q,t)$ for a system with square lattice of size $L \times L$ sites and for different ratios D/F. The obtained results for different time values show that $S(q,t)$ presents a symmetric peak at $q=0$. We have only presented results for values $q > 0$, where we note that the dynamical structure factor increases with time indicating the temporal growth of ordered domains. The different peaks observed in figure 1 are best fitted by a Gaussian domain-size (length) distribution, consistent with the one observed for O/W (110) system [16].
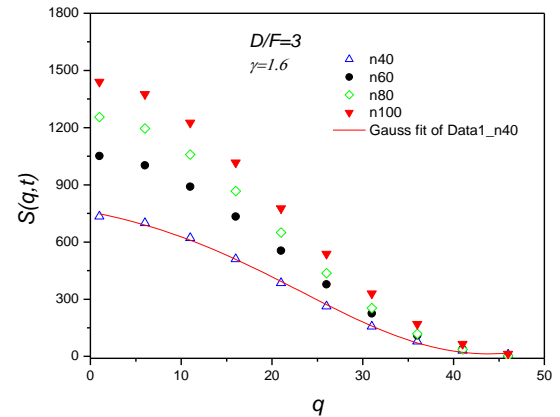

Fig. 2. A plot of the dynamical structure factor at ratio D/F=3 and for different times. The interaction energy value is fixed at $\gamma = 1.6$

In order to investigate the scaling in the growth kinetics, we have fixed the interaction value at *1.6* and we have calculated the ratio $S(q,t)/S_{max}(t)$ versus q/q_{FWHM} for different time values, with $S_{max}(t)$ representing the maximum intensity of $S(q,t)$ at time t and q_{FWHM} is the Full width at Half Maximum. The corresponding results are reported in figure *2* in which we observe that the intensity profiles collapse on a unique curve, indicating that, this ratio can be written as:

$$S(q,t)/S_{max}(t) \approx f(q/q_{FWHM}) \qquad (21)$$

where $f(x)= constant$ is a scaling function. Hence, this scaling in the ordering kinetics of monolayer

deposition is self-similar and its morphology can be determined at any times.

To check the effect of the deposition and the diffusion process on the ordered domains kinetics, we have fixed the interaction value at $\gamma = 1.6$ and we have calculated $S_{max}(t)$ as a function of the ratio D/F. The results are reported in figure 3. From this figure, we note that the maximum intensity of $S(q,t)$ increases with the diffusion coefficient, indicating that the ordered domains are reaching their equilibrium shapes.
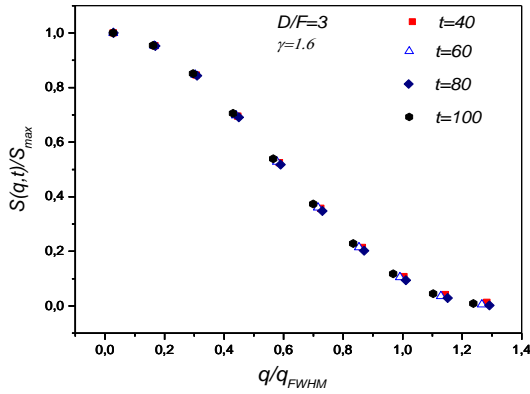

Fig 3. Ratio between the intensity profile $S(q, t)$ and its peak intensity $S_{max}(t)$ versus q/q_{FWHM} at ratio D/F=3 and for different times.

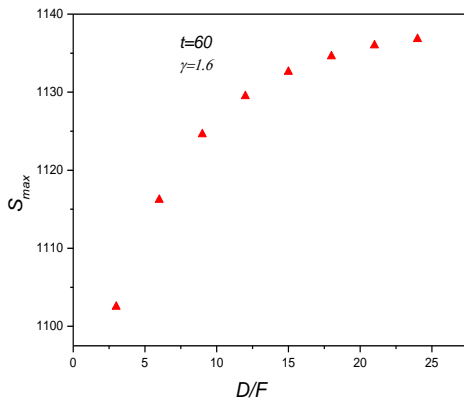The interaction energy value is fixed at $\gamma = 1.6$. The data collapse on one curve.

Fig.4. The peak intensity versus D/F at t=60. The interaction energy value is fixed at $\gamma = 1.6$

As indicated in Fig. 1, the maximum intensity $S_{max}(t)$ increases with time. In order to gain insight into this behavior, we have analyzed the time evolution of $S_{max}(t)$ by means of the dynamic scaling approach. Thus in figure 4, we report the maximum intensity $S_{max}(t)$ versus time t on log-log scales for different sample sizes. We remark that $S_{max}(t)$ presents two different regimes separated by a cross-over time. The same behavior was also found in

[18-20]. The results shows that before saturation, $S_{max}(t)$ increases with the exponent $2\beta = 2.64 \pm 0.05$, ($l \approx t^{\beta}$). The saturated value of $S_{max}(t)$ sketched as a function of the system lateral size. The calculations on log-log plot leads to a roughness exponent $2\alpha = 2.36 \pm 0.04$, in $l_{sat} \approx L^{\alpha}$. However, the obtained exponents values of α and $z = \alpha/\beta$ the dynamic exponent, leads to the relation $\alpha + z = 2.07$ more consistent with the one predicted by the Kardar-Parisi-Zhang class for systems with dimension $d > 1$ [20, 21].

In order to prove the Family-Vicsek law presented by $S_{max}(t)$, we have reported in figure 5, $S_{max}(t)/S_{max}^{sat}$ versus t/t_x where t_x is the cross-over time which separates the growth and the saturated regimes. We notice that all the curves collapse, indicating that $S_{max}(t)$ satisfies the Family-Vicsek law and thus can be written as
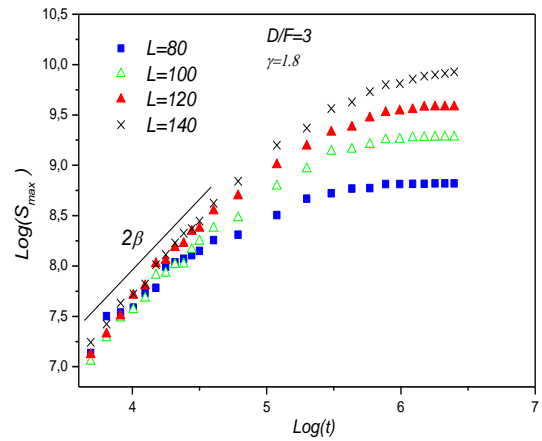
$$S_{max}(t) \approx L^{2\alpha} f(t/t_x).$$

Fig.5. The time evolution of the peak intensity on log-log scales at ratio D/F=3 and for different system sizes. The interaction energy value is fixed at $\gamma = 1.6$
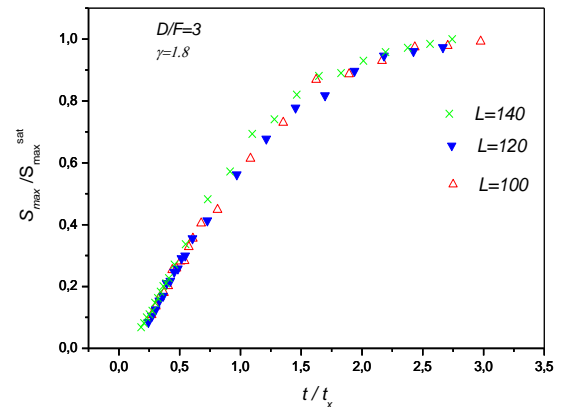

Fig. 6. Ratio between the peak intensity $S_{max}(t)$ and its saturation value S_{max}^{sat} versus t/t_x at ratio D/F=3. The interaction energy value is fixed at $\gamma = 1.6$. The data collapse on one curve.

4. Conclusion

If we wish to understand the morphology and the structure of the interfaces observed in the molecular beam epitaxial (MBE) phenomena, we must have a correct picture concerning the early time behavior. Thus the kinetic ordering of islands formation is an essential step toward a complete understanding of deposition process. In this work, we have studied the ordering kinetics established during the process of a monolayer deposition within the context of the mean field lattice gas model. We have showed how the growth of the ordered domains depends on the adatom interaction, the deposition flux and the adatom diffusion coefficient. Our results indicated that this growth is self similar. The obtained results are consistent with the one observed experimentally by using the low electron energy diffraction (LEED). However the use of the dynamical scaling shows that the growth of the ordered domains satisfies the Family-Vicsek ansatz.

Acknowledgment

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