

An interrelation between the adsorption-desorption and surface diffusion mechanisms under concentration decomposition of an open submonoatomic overlayer

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Thermodynamic and kinetic formation of a sub-monoatomic adsorbed film under its precipitation from the atmosphere of vapor phase upon atomically smooth single-crystal surface in and subjected to rapid quenching is studied. Early and late time asymptotics for the coverage dispersion as well as the scaling behavior of the average domain size is founded. In considered case average size of inhomogeneity on the late stage increase of root law, but thickness of transition region between enriched and depleted parts of film decrease of inverse root law by time.

Рассмотрена термодинамика и кинетика формирования субмоноатомной адсорбированной пленки при осаждении ее из паровой фазы путем быстрой закалки на атомарно-гладкую монокристаллическую поверхность. Определены ранние и поздние временные асимптотики для дисперсии покрытия, а также скейлинговое поведение среднего доменного размера. Показано, что в рассмотренном случае средний размер неоднородностей на больших временах растет по корневому закону, а толщина переходной области между обогащенными и обедненными участками пленки убывает со временем по закону обратного корня.

1. Introduction

The main attention to studying adsorption processes on a solid surface, first of all, is conditioned by practical significance of the obtained results for technological applications. At the same time, the studying of adsorption state allows us to obtain fundamental information about physico-chemical processes of submonoatomic layer formation. The studying of ultrathin (submonolayer) films both on metallic and semiconductor substrates is of special interest, in particular, for application in microelectronics (see, e.g. [1-4]).

The main difficulty of generalization and adequate description of experimental results is connected with a complex character of growth process of such films, with their morphology and properties depending on many factors, in particular, growth conditions.

It is not evident that adsorption film growing upon atomically smooth single-crystal surface in the atmosphere of rare gas makes uniform submonolayer coverage.

The properties of the overlayer formed in such a way depend not only on sorption capability of a substrate, but they are determined substantially by the character of intralayer (lateral) interaction [5], too.

If this interaction is of repulsive character, two-dimensional phase transition of order-disorder type [6-9] will be observed in the film. Otherwise, under attractive lateral interaction, the coverage tends to separate upon the regions enriched and depleted by the adatoms [10-12].

As is known, the surface diffusion plays an important role [13-16] in this process. However the role of absorption/desorption processes in the kinetics of submonolayer film formation up to the present remains unclear [17].

There is essential distinction between two mechanisms of coverage spatial inhomogeneity formation. It may proceed either by surface uphill diffusion with continuous decrease of thermodynamic potential down to certain intermediate (so-called spinodal) coverage rates or by the formation of two-dimensional nucleus inside those a coverage has a true equilibrium value. However in this case, certain energetic barrier must be overcome.

Our goal is to study in detail the deposition process onto a single-crystal substrate from a vapour phase under low temperature. We consider the situation, when the adsorption is fast, and uphill diffusion plays no essential role in the processes of concentration separation. Since the adsorbed overlayer is an open system, the adsorption/desorption process of atoms from a vapour phase onto cold substrate plays a limiting role in formation of adlayer morphology, as will be indicated below.

2. Basic thermodynamic relations

Let us consider the situation when a massive single-crystalline substrate possesses an atomically smooth surface and is placed in a gaseous atmosphere under a pressure P . The atom deposition onto the substrate surface may proceed from this vapour phase.

Appreciable adsorption will take place in the case when the interaction energy of adatoms with the substrate u_0 (or rather a difference between the energy of atom on the substrate surface and in a gaseous phase) is a negative one, i.e. $u_0 < 0$.

In a manner like [18], we shall consider the process of the submonoatomic adlayer formation by atom condensation onto substrate surface.

Since in practice such type of experiments assumes high vacuum conditions, the vapour can be considered as an ideal gas. Next, due to the infinitely small mass ratio of the submonolayer and the substrate, we can assume that the substrate temperature T during the deposition process will be a constant. So their temperatures should in fact be always coincident.

The study of the overlayer decomposition kinetics must rely on a prior thermodynamic analysis, whose purpose is to elucidate the equilibrium states, which the adsorbate film is must be reached at the end of relaxation.

Since we intend to construct a phenomenological theory it is necessary to introduce certain order parameter(s) defining possible macroscopic states of the adsorbed film. For the purposes of the present problem, it suffices to introduce a single macroscopic parameter, namely the coverage ϑ ($0 < \vartheta < 1$) defined as the ratio of the number of adsorbed atoms N_{ad} to the total number of available interstitial sites N .

Lateral attraction between adatoms is included into the model by introducing the negative energy of pair-wise nearest-neighbor interaction $u_L < 0$

Under the specified assumptions, the mean-field nonequilibrium free energy of the atomic submonolayer has the form

$$f(T, \vartheta) = -Nu_0\vartheta - 2Nu_L\vartheta^2 + NT[\vartheta\ln\vartheta + (1 - \vartheta)\ln(1 - \vartheta)], \quad (1)$$

where the last term is with an accuracy of temperature factor the overlayer configurational entropy, $\vartheta = N_{ad}/N$ is the coverage, as for the configuration number Z , here it is equal to 4. In Eq. (1) and later on, we shall use for absolute temperature the energetic unity, i.e. we shall assume that Boltzmann

constant is equal to the unity ($k_B = 1$). Besides, for convenience we shall assume that $u_0 = |u_0|$ and $u_L = |u_L|$. The problem as we have posed it deals with an open system (submonolayer), whose peculiarity lies in the fact that it is in a simultaneous contact with two different reservoirs – the substrate and the gaseous phase. Interaction with the former is a thermal one such that imposes on overlayer the substrate temperature. As for the vapour phase its interaction with the adsorption film is essentially of different nature, namely it is a material contact so far as these two systems can exchange particles via adsorption and desorption. Under these circumstances the correct thermodynamic potential to be minimized in order to determine the equilibrium coverage is the thermodynamic potential

$$\omega(P, T; \vartheta) = f(T; \vartheta) - \mu_g(P, T)\vartheta, \quad (2)$$

where $f = F/N$ is the free energy per one adsorption site and μ_g is the gaseous phase chemical potential. Once we know the potential (2) as a function of P , T and ϑ the equilibrium value of ϑ is determined as such that minimizes ω under the given values of P and T :

$$\left(\frac{\partial\omega}{\partial\vartheta}\right)_{P,T}\bigg|_{\vartheta=\vartheta_{eq}} = \left(\frac{\partial f}{\partial\vartheta}\right)_{P,T}\bigg|_{\vartheta=\vartheta_{eq}} - \mu_g. \quad (3)$$

Derivative $\partial f/\partial\vartheta = \partial F/\partial N_{ad}$ is by definition the overlayer chemical potential $\mu(\vartheta, T)$, so Eq. (3) basically says that the chemical potentials of the adsorbed film and the gaseous phase are equal at equilibrium:

$$\mu(\vartheta_{eq}, T) = \mu_g(P, T). \quad (4)$$

Since the gas can be considered as an ideal one and chemical potential of it can be written in the form [19]

$$\mu_g(P, T) = T \ln(P/P_T), \quad (5)$$

where P_T gives the order of magnitude of liquefaction pressure and for a single-atomic gas is expressed by the relation

$$P_T = T \left(\frac{mT}{2\pi\hbar^2}\right)^{3/2}; \quad (6)$$

here m is the mass of adatom.

Differentiating the free energy (1) with respect to the number of adsorbed atoms $N_{ad} = \vartheta N$ yields an explicit expression for the overlayer chemical potential

$$\mu(\vartheta; T) = -u_0 - 4u_L\vartheta + T \ln \frac{\vartheta}{1-\vartheta}. \quad (7)$$

Simple analysis shows that Eq. (7) defines a monotonic function of ϑ for $T > T_c \equiv u_L/k_B$ and a non-monotonic function for $T < T_c \equiv u_L/k_B$. In the latter case it is represented by a distinctive van der Waals type loop curve with three intersection points with the chemical potential of deposited gaseous phase. The mean intersection point corresponds to an absolutely unstable state of adsorbed layer. And two extremes intersection points of chemical potential correspond to thermodynamically equilibrium rates of coverage, i.e. the stable states of adsorbate.

If one takes into account spatial inhomogeneity of adsorbate overlayer, then its thermodynamic potential of grand canonical ensemble may be presented in the form of functional

$$\Omega(P, T, \vartheta) = \int_S \left[\omega(P, T, \vartheta) + \frac{1}{2} \gamma (\nabla\vartheta)^2 \right] \sigma dS, \quad (8)$$

where σ is the surface density of a number of particles; γ is a constant evaluated as $\gamma \approx r_0^2 u_L$, r_0 is the characteristic radius of lateral interaction; $\omega(P, T, \vartheta)$ is the specific thermodynamic potential of adsorbed overlayer which is described by expression (2).

3. Derivation of kinetic equation

Suppose that we are quenched suddenly the substrate or rapidly changed a pressure of external gas. As a result of it, circumstances of thermodynamic equilibrium (4) are disturbed. Since the adsorbed overlayer is an open system, then either adsorption of atoms on substrate or its desorption occurs in depending on relationship between chemical potentials of gas and adsorbed overlayer. The driving force is a difference of atomic chemical potential in gaseous phase and in adsorbed overlayer. In other hand, the diffusion process takes place in the course of which rearrangement of adatoms proceeds.

Thus the rearrangement process of atoms upon the substrate subjected to adsorption and/or desorption of atoms may be described by equation of continuity with a source.

$$\frac{\partial \vartheta}{\partial t} + \text{div } \mathbf{J} = \left(\frac{\partial \vartheta}{\partial t} \right)_{ext}, \quad (9)$$

where the source, responsible for adsorption/desorption of gas atoms onto substrate, may be presented of the form

$$\left(\frac{\partial \vartheta}{\partial t} \right)_{ext} = -\beta (\mu - \mu_g) = -\beta \frac{\delta \Omega}{\delta \vartheta}, \quad (10)$$

therewith β is the sticking coefficient of adatoms to substrate, which may be evaluated as $\beta \sim (t_a u_L)^{-1}$, where t_a is the characteristic time of adsorption process. An expression for the flow of adatoms may be presented in the form

$$\mathbf{J} = -M \nabla \frac{\delta \Omega}{\delta \vartheta}. \quad (11)$$

Here M is a generalized mobility of adatoms, which has a form

$$M = b \vartheta (1 - \vartheta), \quad (12)$$

where b is a constant depending on temperature. Substituting Eqs. (10), (11), (12) into Eq. (9) we get the following evolution equation:

$$\begin{aligned} \frac{\partial \vartheta}{\partial t} + 4b u_L (1 - 2\vartheta) (\nabla \vartheta)^2 + b [4 u_L \vartheta (1 - \vartheta) - T] \Delta \vartheta + b \gamma (1 - 2\vartheta) (\nabla \vartheta, \nabla (\Delta \vartheta)) + \\ + b \gamma \vartheta (1 - \vartheta) \Delta (\Delta \vartheta) = \beta [\mu_g + u_0 + 4 u_L \vartheta - T \{\ln \vartheta - \ln (1 - \vartheta)\} + \gamma \Delta \vartheta]. \end{aligned} \quad (13)$$

In order to simplify Eq. (13), let us assume that the coverage rate in adsorption layer changes in the vicinity of 1/2, i.e.

$$\vartheta = 1/2 + v(x, t), \quad (14)$$

where $v(x, t)$ is a variation of coverage rate providing $v(x, t) \ll 1$. After substituting (14) to Eq. (13) and regrouping of terms, we get

$$\begin{aligned} \frac{\partial v}{\partial t} = \beta \left[\mu_g + u_0 + 2 u_L + 4 u_L v \left(1 - \frac{T}{u_L} \right) - \frac{16}{3} u_L v^3 \right] + \left[-D_0 \left(1 - \frac{T}{u_L} \right) + \beta \gamma \right] \Delta v + \\ + \frac{4}{3} D_0 \Delta v^3 + 2b \gamma (\nabla v^2, \nabla (\Delta v)) - \frac{1}{4} b \gamma \Delta (\Delta v). \end{aligned} \quad (15)$$

In Eq. (15) an expression, standing before the second derivative with respect to x of coverage rate is the effective surface diffusion coefficient which on condition that $T < T_c$ turns out a negative one ($D_{eff} < 0$) as a rule at the low temperature, i.e. rearrangement of atoms along substrate may led to uphill diffusion or spinodal decomposition. The distinctive feature of spinodal decomposition is formation of inhomogeneous submonolayer film having the places with different coverage rate. The summand $\beta \gamma$ in effective diffusion coefficient, caused by adsorption of atoms onto substrate, plays a role of a small positive addition, which makes the spatial inhomogeneities to smooth. It is only an impair condition for surface spinodal decomposition.

Some attention should be paid to two last summands in Eq. (15). One can see that the last by one summand is smaller than the last one, therefore we should not take it into account later on.

Next we introduce dimensionless time and spatial coordinate in Eq. (15), using the following relations:

$$\tilde{\tau} = t/t_{sd}, \quad \xi = x/r_0, \quad t_{sd} = r_0^2/\tilde{D}_0, \quad \tilde{D}_0 = b u_L, \quad (16)$$

where t_{sd} is a spinodal decomposition time, \tilde{D}_0 is the part of surface diffusion coefficient, which is not dependent on the coverage rate.

Then having regard to expressions (16), we get the dynamical equation of the form

$$\frac{\partial v}{\partial \tilde{\tau}} = \varepsilon \left[\delta + 4\alpha v - \frac{16}{3}v^3 \right] + [\varepsilon - \alpha]\Delta v + \frac{4}{3}\Delta v^3 - \frac{1}{4}\Delta(\Delta v), \quad (17)$$

where the following notations are introduced:

$$\delta = \frac{\mu_g + u_0 + 2u_L}{u_L}, \quad \alpha = 1 - \frac{T}{T_c}. \quad (18)$$

However it should be noted because of its nonlinear character the Eq. (17) is a complex one for studying generally. However this problem can be simplified, if we notice that the key parameter determining the character of the adlayer evolution process is the ratio of adsorption/desorption and surface diffusion times such as $\varepsilon = t_{sd}/t_a$. And therefore, depending on ε in adlayer different scenarios can be realized. If $\varepsilon \ll 1$ ($t_{sd} \ll t_a$), the spinodal decomposition takes place in submonolayer film, whereas processes of adsorption/desorption will be go on slowly. And conversely, if $\varepsilon \gg 1$ ($t_{sd} \gg t_a$), the main processes influencing the film formation will be of adsorption/desorption ones, and spinodal decomposition in this case can not be taken into account.

4. Correlation analysis of evolution equation

Using the physical parameters characterizing adsorption [9] and surface diffusion [12] in the case of metal atom deposition at a metal surface, we get the estimation $\varepsilon \sim 10^5 \div 10^6$. On condition that $\varepsilon \gg 1$, uphill diffusion process responsible for two-dimensional spinodal decomposition occurs quite slowly. Therefore, in this situation, the adsorption/desorption process of atoms onto substrate from gaseous phase will play an essential role in Eq. (17). Besides, we suppose, that the chemical potentials of gas and adsorbed layer are close one to another, i.e. the parameter $\delta \ll 1$. Subjected to the assumptions pointed above, the Eq. (17) takes the form

$$\frac{\partial v}{\partial \tau} = \left[4\alpha v - \frac{16}{3}v^3 \right] + \Delta v, \quad (19)$$

where Δ is two-dimensional Laplacian, τ is a dimensionless time, with $\tau = t/t_a$. Here t_a is the time characterizing the absorption process. The initial condition should be attached to this equation

$$v(\rho, \tau)|_{\tau=0} = v_0(\rho), \quad (20)$$

where ρ is a two-dimensional radius-vector placed in the plane of formed adsorbed film. Since in the process of rapid cooling of substrate, the coverage fluctuations on its surfaces have a random character, the function $v_0(\rho)$ appearing at the initial condition takes a random character as a function of coordinates. It follows that the solution of evolution Eq.(19) will be a random functions of coordinates as well. So, a necessity appears to carry out statistical analysis of Eq. (19) with random initial condition (20). After multiplying the both parts of Eq. (19) by $v(\rho', \tau)$ and averaging over ensemble of random field realization, we obtain the equation of the form

$$\frac{\partial K(\mathbf{s}, \tau)}{\partial \tau} = 8 \left[\alpha - \frac{4}{3}K(0, \tau) \right] K(\mathbf{s}, \tau) + 2\Delta K(\mathbf{s}, \tau), \quad (21)$$

$$K(\mathbf{s}, \tau) = \langle v(\rho', \tau)v(\rho, \tau) \rangle \quad (22)$$

is the two-point correlation function, with $\mathbf{s} = \rho' - \rho$. In order to obtain the closed equation for correlation function of the second order (22) we decoupled correlator of the fourth order for random function $v(\rho, \tau)$ on the product of two correlators of the second order assuming that the considered random field has the overall non-Gaussian character. As for the initial correlation function, it would be reasonable to select the correlation function of a Gaussian form

$$K(\mathbf{s}, 0) = K(0, 0) \exp(-s^2/R_0^2) = D_0 \exp(-s^2/R_0^2). \quad (23)$$

If we carry out the Fourier transformation on the coordinate \mathbf{s} in Eq. (21), it takes the following form

$$\frac{dK(\mathbf{q}, \tau)}{d\tau} = 8 \left[\alpha - \frac{4}{3}K(0, \tau) \right] K(\mathbf{q}, \tau) - 2q^2 K(\mathbf{q}, \tau). \quad (24)$$

Since Eq. (24) is an ordinary differential equation with separating variables, then under the assumption that the function $K(0, \tau)$ is known the solution can be written formally in the form

$$K(\mathbf{q}, \tau) = K(\mathbf{q}, 0) \exp \left(\int_0^\tau [8(\alpha - (4/3)K(0, \tau')) - 2q^2] d\tau' \right). \quad (25)$$

In order to find correlation function $K(0, \tau)$ we realize inverse Fourier-transform

$$K(0, \tau) = (2\pi)^{-2} \int \int K(\mathbf{q}, \tau) dq_x dq_y. \quad (26)$$

Substituting the expression (25) into integral (26), we obtain

$$K(0, \tau) = (2\pi)^{-2} \int \int dq_x dq_y K(\mathbf{q}, 0) \exp(-2q^2\tau) \exp \left(8 \int_0^\tau (\alpha - (4/3)K(0, \tau')) d\tau' \right). \quad (27)$$

We find Fourier-transform of $K(\mathbf{q}, 0)$, in (27), applying to initial correlation function (23) transformation of Fourier on the \mathbf{s} variable

$$K(\mathbf{q}, 0) = \pi R_0^2 D_0 \exp(-q^2 R_0^2/4). \quad (28)$$

And, finally, substitution of the expression (28) into (27) yields

$$K(0, \tau) = \frac{D_0 R_0^2}{R_0^2 + 8\tau} \exp \left(8 \int_0^\tau (\alpha - (4/3)K(0, \tau')) d\tau' \right). \quad (29)$$

Since $K(0, \tau) \equiv D(\tau)$, where $D(\tau)$ is a dispersion of coverage as a function of time, the integral Eq. (29) is nothing but the condition of the self-consistency for this function. Substituting $K(\mathbf{q}, 0)$ from (28) into Eq. (25), we obtain Fourier-transform of the correlation function $K(\mathbf{q}, \tau)$:

$$K(\mathbf{q}, \tau) = \pi R_0^2 D_0 \exp \left(-\frac{q^2}{4} (R_0^2 + 8\tau) \right) \exp \left(8 \int_0^\tau (\alpha - (4/3)K(0, \tau')) d\tau' \right). \quad (30)$$

In order to find the correlation function, i.e. $K(\mathbf{s}, \tau)$, it is necessary to apply the reverse Fourier transformation on variable \mathbf{q} to the expression (30). Then we obtain

$$K(\mathbf{s}, \tau) = \frac{D_0 R_0^2}{R^2(\tau)} F(\tau) \exp \left(-\frac{s^2}{R^2(\tau)} \right), \quad (31)$$

where

$$R(\tau) = \sqrt{R_0^2 + 8\tau} = R_0 \sqrt{1 + 8\tau/R_0^2} \quad (32)$$

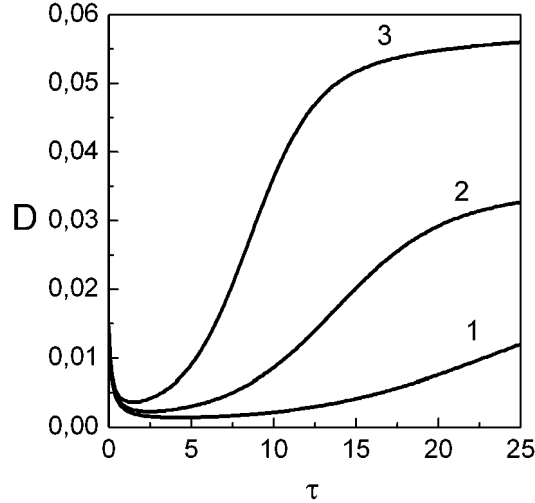


Fig. 1. The evolution of coverage dispersion (time is measured in units of t_a). Curves 1–3 correspond to substrate temperatures $T_1 = 97$ K, $T_2 = 95$ K, $T_3 = 93$ K ($T_c = 100$ K), respectively.

is time dependence of the correlation radius,

$$F(\tau) = \exp \left(8 \int_0^\tau (\alpha - (4/3) K(0, \tau')) d\tau' \right) \quad (33)$$

is a function, depending only on time.

Using integral Eq. (29), we try to investigate the evolution behavior of the dispersion of coverage in adlayer, $D(\tau)$, for the early ($\tau \ll 1$) and late ($\tau \rightarrow \infty$) times.

Let $\tau \ll 1$, then $K(0, \tau) \ll 1$ and Eq. (29) can be rewritten in the form

$$D(\tau) = \frac{D_0 R_0^2}{R_0^2 + 8\tau} \exp(8\alpha\tau) \approx D_0(1 + 8\alpha\tau) (1 - 8\tau/R_0^2) \approx D_0 [1 + 8(\alpha - 1/R_0^2)\tau]. \quad (34)$$

At the initial moment of time the correlation radius is small ($R_0 \approx 1$). Besides, at the low temperatures ($T < T_c$), i.e. when the condition $\alpha < 1$ is satisfied, the expression (34) is conveniently presented in the form

$$D(\tau) \approx D_0 [1 - 8(1/R_0^2 - \alpha)\tau], \quad (35)$$

i.e. for $\tau \ll 1$, the dispersion $D(\tau)$ decreases by the linear law (35).

At the late time (i.e. for $\tau \rightarrow \infty$) $K(0, \tau) \rightarrow 3\alpha/4$ like

$$(\alpha - 4K(0, \tau)/3) \sim 1/(R_0^2 + 8\tau), \quad (36)$$

Therefore it follows from Eq. (29) that $D(\tau) \rightarrow const > D_0$.

Computational solutions of integral Eq. (29) for the different substrate temperatures T (with $T < T_c$), presented in Fig.1, confirm the results of asymptotical analysis, too.

Further we estimate qualitatively the transient layer thickness between enriched and depleted regions of overlayer to establish the time evolution way. We assume that the region enriched of adsorbate has a form of a disk of radius $R(\tau)$, and the transient layer has a form of a ring. The profile of a spatial distribution of v^2 as a function of the distance r of disk center is shown in Fig.2. The area of the enriched region can be evaluated as $S \sim R^2(\tau)$, and the area of the transient region (transient layer) will be $\Delta S \sim R(\tau)\delta(\tau)$. Then we evaluate the variation of v^2 moving from an enriched region to a depleted one with using $R(\tau)$ dependence defined by (32)

$$\Delta(v^2) \sim \alpha - \alpha \frac{S}{S + \Delta S} \sim \frac{2\alpha\delta}{\sqrt{R_0^2 + 8\tau}}. \quad (37)$$

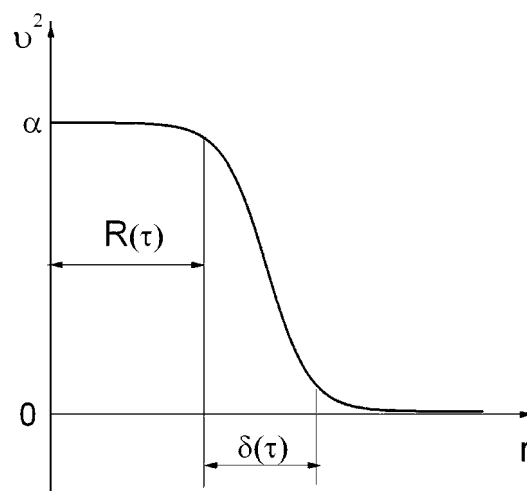


Fig. 2. Profile of spatial distribution value v^2 as a function of the distance from domain center $r : R(\tau)$ and $\delta(\tau)$ are the domain size and the thickness of a transient region, respectively.

In other words, in accordance with (36), the variation of v^2 obeys the law

$$\Delta(v^2) \sim 1/(R_0^2 + 8\tau). \quad (38)$$

The comparison of the relations (37) and (38), finally, gives us the qualitative temperature and time dependence of the thickness of the transient layer

$$\delta(T, \tau) \sim \frac{1}{\alpha(T)\sqrt{R_0^2 + 8\tau}}. \quad (39)$$

As is seen from (39), the thickness of the transient layer in a submonolayer film is inversely proportional to the closeness of the film temperature to the critical one. The decrease of the thickness of the transient region with time obeys the inverse square root law ($\delta \sim 1/\sqrt{\tau}$).

5. Conclusions

In this paper, we have considered formation of a submonolayer film as a result of atom deposition from gaseous phase on the cold substrate, when the lateral interaction is attractive. In addition we have taken into account clearly that adlayer is an open system related to reservoir of particles in gaseous phase.

We have analyzed thoroughly the case, when the characteristic time of surface diffusion considerably exceeds the adsorption one. It is found that in this situation the separation process of overlayer is limited only by the adsorption processes, not by the surface diffusion ones, despite the quenching of the adsorbed film proceeds below the spinodal.

To describe the kinetics of submonolayer film formation, we used a statistical approach, since the fluctuations of the coverage rate are of random character at the initial moment of time. So we have not only a possibility to study the thermodynamic equilibrium states of a submonolayer film at the late times, but also to describe the evolution character of the coverage rate depending on the initial prehistory of its preparation.

In particular, the asymptotical analysis of evolution of v^2 value at the early and late times is performed. The numerical solution of integral equation for dispersion function confirmed these results. The non-monotonic character of its behavior indicated to the existence of the incubation period of developing the spatial inhomogeneities of the adsorbed overlayer.

It is established that inhomogeneity characteristic size grows by square root law, whereas the thickness of the transient region decreases as inverse square root of time.

In other words, it is shown that depending on technological prehistory of the system adsorbate-substrate, either homogeneous submonolayer film may be formed on a surface of the latter of one or other density, or heterogeneous structure, consisting of regions depleted and enriched of adatoms. It should be pointed out that the result obtained here for submonolayer films may be generalized easily into multilayer films.

References

1. A.Zangwill, E.Kaxiras, *Surf. Sci.*, **326**, L483 (1995).
2. I.Doudevski, W.A.Hayes, and D. K. Schwartz, *Phys. Rev. Lett.*, **81**, 4927 (1998).
3. I.T.Koponen, M.O.Jahma, M.Rusanen, and T.Ala-Nissila, *Phys. Rev. Lett.*, **92**, 086103-1 (2004).
4. R.Vardavas, C.Ratsch, R.E.Caffisch, *Surf. Sci.*, **569**, 185 (2004).
5. O.M.Braun, V.K.Medvedev, *Usp. Fiz.*, **32**, 328 (1989).
6. E.P.Feldman, K.V.Gumennyk, L.I.Stefanovich, *Surf. Sci.*, **604**, 1854 (2010).
7. O.M.Braun, M.V.Paliy, M.Peyrard, *Phys. Rev.B.*, **55**, 4797 (1997-I).
8. A.Fedorus, V.Koval, A.Naumovets, *Low Temp. Phys.*, **27**, 850 (2001).
9. A. Fedorus, G. Godzik, A. Naumovets, H. Pfnur, *Surf. Sci.*, **565**, 180 (2004).
10. A.G. Fedorus, A.A. Mitryaev, M.A.Mukhtarov et al., *Surf. Sci.*, **600**, 1566 (2006).
11. L.Proville, *Phys. Rev.B.*, **64**, 165406, (2001).
12. L.Proville, *Phys. Rev. Lett.*, **88**, 046102-I (2002).
13. K.S.Schneider, W.Lu, T.M.Owens et al., *Phys. Rev.Lett.*, **93**, 166104-1 (2004).
14. A.V.Myshlyvtsev, A.A.Stepanov, C.Uebing, V.P.Zhdanov, *Phys. Rev.B.*, **52**, 5977 (1995-II).
15. A.T.Loburets, N.B.Senenko, Yu.S.Vedula, A.G.Naumovets, *Ukr. Fiz. Zh.*, **50**, 805 (2005).
16. R.Panat, K.J.Hsia, D.G.Cahill, *J. Appl. Phys.*, **97**, 013521 (2005).
17. Hongting Shi and Jun Ni, *Phys. Rev.B.*, **65**, 115422 (2002).
18. S.A.Kukushkin, A.V.Osipov, *Usp. Fiz.*, **41**, 983 (1998).
19. L.D.Landau, E.M.Lifshitz. *Theoretical Physics. Statistical Physics*, Pergamon, Oxford, (1980).

Взаємозв'язок між процесами адсорбції/десорбції та механізмом поверхневої дифузії при концентраційному розшаруванні відкритої субмоношарової плівки

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Розглянуто термодинаміку та кінетику формування субмоноатомної адсорбованої плівки при осаджуванні її з парової фази шляхом швидкого загартування на атомарно-гладку монокристалічну поверхню. Визначено як ранні, так і пізні часові асимптотики щодо дисперсії покриття, а також скейлінгову поведінку середнього доменного розміру. Показано, що у розглянутому випадку середній розмір неоднорідностей на пізніх стадіях зростає за кореневим законом, а товщина перехідної області між збагаченими та збідненими ділянками плівки зменшується з часом за законом оберненого кореня.