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RATE OF THIN FILM FORMATION ON SOLID SURFACE.

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Abstract

Numerical simulation of adatoms clusterization of solids surfaces under plasma influence is interesting for creation of thin films and covers with necessary behaviour. Release coatings, anticorrosion covers, nano-functional, resistant to pollution and ultrahydrophobic coverings are examples of coatings with defined properties. The study of nano-capsules and ions implantation into near surface layers, interstitial atoms and formed clusters migrations from solids to surface is very important for creation of self-repair materials and coves. The fluctuation stage of thin films formation is examined in this paper.

The modified by ions substrate is chosen metal. The thin film formation is examined using stochastic approach [1-4]. The surface of metal substrate has been contacted with vapour of another metal. Thin films behaviour differs from behaviour of solids consisting from same material. Cover formation includes adsorption, creation of new phase islands, increase/decrease of them sizes, motion of new phase islands on surface and others processes. The initial fluctuating stage of thin films formation is of great important, parameters of processes during this stage determine the behaviour of covers in many respects. The duration of this stage is approximately 10^{-4} sec. Increasing or decreasing of island (i.e. cluster of adatoms) depends on fluctuations during its sizes stochastic changes and jump-like fusion of clusters. Initial stage of cover formation has been considered as the geterogeneous first-order phase transformation (from vapour to liquid on the substrate), here have not be examined chemical reactions during fluctuation stage of this phase transition. Let us model the stochastic diffusion of islands on the surface as a brownian motion adapted for flat coordinate configuration. Following previous experience of computer simulation [1-4] we can use stochastic analogue approach. The sizes of islands formation and stochastic migration of islands processes have the different time of development. So, typical time for change of island size 10^{-8} sec and for migration on substrate surface 10^{-7} sec. The moving of clusters on surface is realizes under exposure of surface potential and long-range indirect potentials of interaction of clusters each with other.

The phase transition on the surface can be formulated using fundamental Leontovich equation, which is presented by the system of two kinetic equations of Kolmogorov-Feller and Smolukhovskii-Kramers kinds (which have been received after splitting procedure of problem):

$$\frac{\partial f_r(g,t)}{\partial t} = \frac{\partial \left[D_g(g,t) \dfrac{\partial f_r(g,t)}{\partial g} \right]}{\partial g} + \frac{1}{kT} \frac{\partial \left[D_g(g,t) f_r(g,t) \dfrac{\partial \{\Delta\Phi(g,\vec{r},t)\}}{\partial g} \right]}{\partial g} + S_\alpha(f_\alpha)$$

$$f_r(g,0) = f_{0g}, \quad \left. \frac{df_r(g,t)}{dg} \right|_{g \le 2} = 0, \quad f_r(g,t)|_{g<2} = 0,$$

$$\frac{\partial f_g(\vec{r},t)}{\partial t} = \frac{\partial\left[D_r(\vec{r},t)\dfrac{\partial f_g(\vec{r},t)}{\partial r}\right]}{\partial \vec{r}} - \frac{\partial\left[\dfrac{\vec{F}(\vec{r},t)}{M_g\gamma} f_g(\vec{r},t)\right]}{\partial \vec{r}}, \qquad f_g(\vec{r},t)|_{t=0} = f_{0r},$$

$$f_g(\vec{r},t)|_{x=x_{\text{left}}} = f_g(\vec{r},t)|_{x=x_{\text{right}}}, f_g(\vec{r},t)|_{y=y_{\text{left}}} = f_g(\vec{r},t)|_{y=y_{\text{right}}}$$

where S_α is source of vapour which generats ion with f_α - maxwell ion function, g is the number of atoms which is consisted in island-clusters, $D_g(g,t)$ is the diffusion coefficient in the space of cluster sizes; $f_r(g,t)$ is the bubble size distribution function – the probability to find the cluster with size g in interval of values of g [g,g+Δg], $\Delta\Phi(g,\vec{r},t)$ is the Gibbs energy, M_g is the cluster mass, γ is constant of friction, distribution function $f_g(\vec{r},t)$ is the islands space function $(\vec{r})$, $\vec{r}$ is the position of cluster mass centre in orthogonal coordinates system: x_{left} = –200, x_{right} = 200, y_{left} = –200, y_{right} = 200, $F_x = -\dfrac{\partial U(x,y)}{\partial x}$, $U(x,y)$ is the potential of long-range clusters interaction between them through phonons and oscillation of electron density. The form of potential is similar [2-4], firstly this interaction had been formulated by [5] in problem of light defect clusterization into lattice.

$$U(x,y) = \sum_{i\neq j}^{N} \frac{b_r\left[\frac{3}{5} - \frac{(x_i-x_j)^4+(y_i-y_j)^4}{(\vec{r}_i-\vec{r}_j)^4}\right] + a_r\cos(\vec{c}_r(\vec{r}_i-\vec{r}_j))}{|\vec{r}_i-\vec{r}_j|^3}. \qquad r_i = \sqrt{x_i^2+y_i^2},$$

a_r, b_r, c_r is model parameters. The non-linear functional coefficient of equation $D_x = \dfrac{D_0 e^{-E_m/kT}}{\gamma M_g}\left(1+\alpha_x\Delta x^2\right)$ is stochastic diffusion coefficient of islands on surface, D_0 is coefficient diffusion of adatom on surface, E_m is bonding energy of adatom with surface, $0 \le \alpha_x \le 1$ is parameter of model.

The Gibbs energy looks like following:

$$\Delta\Phi(g,\vec{r},t) = \begin{cases} -(a_\Phi - c)g + bg^{2/3} + \Delta\Phi_r, & \Delta\Phi(g,\vec{r},t) < \Delta_{break} \\ -(a_\Phi - c)g + bg^{2/3} + \Delta\Phi_r - \Delta\Phi_{break}, & \Delta\Phi(g,\vec{r},t) > \Delta_{break} \end{cases}$$

where $a_\Phi = \dfrac{\pi(2-3\cos\theta+\cos^3\theta)}{3V_{a\partial am}}(\chi_\beta - \chi_\alpha)$, $(\chi_\beta - \chi_\alpha)$ is difference of chemical potential of phases (vapor and liquid), $b = 2\pi(1-\cos\theta)\sigma_{\alpha\beta} + \pi\sin^2\theta(\sigma_{\beta S} - \sigma_{\alpha S})$, $\sigma_{\alpha\beta}, \sigma_{\beta S}, \sigma_{\alpha S}$ are surface tension between vapour of metal and metal liquid in island, liquid island and substrate, vapour and substrate, c is coefficient of elastic lattice reaction, Δ_{break} is the energy required for breaking of a single bond with lattice, in our case it is value from laboratory experiment, $\Delta\Phi_{break}$ is the bond energy in lattice, $\Delta\Phi_{break} = N_b\Delta_{break}$, N_b is

number of broken bonds. $\Delta\Phi_r$ shows influence of substrate lattice and the fact that influence of substrate lattice decreases when cluster size increases, when cluster locates in point (x,y) $\Delta\Phi_r = \Psi(\vec{r},g)(2-\cos(\frac{2\pi x}{a_x})-\cos(\frac{2\pi y}{a_y}))$, here a_x and a_y are lattice parameter on *x* and *y* axes. Ψ is model function which is depended on islands sizes, also the dislocation of the lattice. If cluster locates in point *(x,y)* then $\Psi(\vec{r},g)\sim \frac{1}{\sqrt{g}}$, otherwise Ψ~1, the dislocation can be simulated by Ψ decreasing in same times. All parameters are non-dimensional, it is traditional for kinetic theory. The $D_g(g,t) = D_{g0}g^{2/3}$ and $\Delta\Phi(g,\vec{r},t)$ are nonlinear functional-coefficients which dependence on clusters sizes. Gibbs energy includes difference of chemical potential of vapour and liquid phases, interface tensions on surfaces of condensate- vapour, condensate- substrate, substrate- vapour, elastic force of lattice and possibility of relcases of part of connections in lattice, non-equivalence of islands positions on surface. The heterogeneous condensation is considered on substrate and on clusters surfaces. For solve kinetic equations authors used original computational method of stochastic simulation [1-4, 6]. The main idea of this method is using the fundamental qualities of partial differential equations Fokker-Planck kind, which give us possibility to present physical problem by set Ito-Stratonovich equations with functional-coefficients. SDE are equivalent to kinetic problem formulated with Fokker-Planck formalism. We replace of kinetic equation by these stochastic analogs – stochastic differential stochastic Ito-Stratonovich equations /SDE/. The SDE (analogue of equation for $f_r(g,t)$) looks like following:

$$\frac{dg}{dt} = -\frac{1}{kT}D_g(g,t)\frac{\partial\Delta\Phi(g,t)}{\partial g} - \frac{1}{2}\frac{\partial D_g(g,t)}{\partial g} + \sqrt{2D_g(g,t)}\xi(t),$$

$$t_0 \le t \le T_k,\ \ g(t_0) = g_0 \in [g_{\min}, g_{\max}],\ g(t) > 2,$$

where T_k is duration of fluctuating stage, ξ is stochastic function related with increment of Wiener process, g_0 is initial cluster size, g_{min} and g_{max} are borders of unstable region of initial size of cluster which calculated from $\left|\Delta\Phi(g_{cr}) - \Delta\Phi(g_{\min})\right| = \left|\Delta\Phi(g_{cr}) - \Delta\Phi(g_{\max})\right| = kT$, *T* is temperature of cluster, $\partial\Delta\Phi/\partial g\big|_{g_{cr}} = 0$, g_{cr} is critical size. For solve of systems of stochastic equations authors modified Artemiev's method [7]; it is a second-order accuracy method, with infinite domain of stability. For all i=1,2,...10^6 trajectories of Wiener stochastic process we can use the following determination of the function $\xi_i = \sqrt{-2\log\alpha_1}\cos(2\pi\alpha_2)$, where α_1 и α_2 are random numbers evenly distributed in region (0,1).

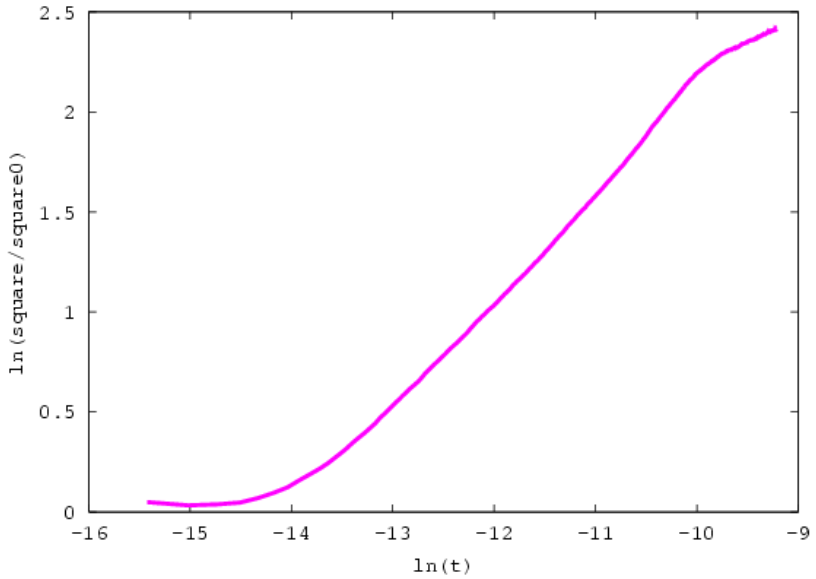

Figure 1. This figure describes change of logarithm of the ratio of total islands square from total islands square at initial time moment depend on logarithm of time. Time is supposed in second.

Conclusions

As we can see from presented pictures, radius of islands distribute uniformly from 5.31 Å to 17.7 Å at initial time moment. From 10^{-4} sec form of distribution function shows that two most probably radiuses exist. The first size (~ 16 Å) is similar to critical size and corresponds to newly form clusters, second size (~ 61 Å) corresponds to islands which grow including at the expense of fusions during calculation.

The number of islands placed near linear dislocation is more than clusters number far from it approximately at 8 times. So, the thin films formation begins on defects of surface such as dislocations.

Three stage of cover formation during fluctuation stage are discovered. The first stage lasts from 0 to $8 \cdot 10^{-7}$ sec, it is stage of slow development. The second stage continues from $8 \cdot 10^{-7}$ sec to $5 \cdot 10^{-5}$ sec and it is stage of quick growth of thin film. The third stage lasts from $5 \cdot 10^{-5}$ sec to 10^{-4} sec and it is notable for deceleration of growth velocity. At that, cover square increases at 11 times approximately with respect to cover square at initial moment of time.

The calculations confirm that influence of cover reaches on depth of 5 lattice parameters approximately. At the same time, stress on surface and near surface layers caused by thin film formation does not exceed the stress caused by blisters development. The stress on surface connected with cover growth increase at 21 times during fluctuating stage.

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