Plasma Surface Interaction: Thin Film Formation

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Abstract. This paper deals with stochastic simulation of strongly nonequilibrium processes of thin film formation: fluctuation stage of liquid metal nano-film islands appearance and multilayers vertical film growing. Both of these problems are interesting for nanotechnology and microelectronic.

Keywords: Stochastic Models, Kolmogorov Equations, Cluster Formation, Fluctuations, Thin Films, Brownian Motion, Long-range Potentials, Islands of Liquids.
PACS: 52.40.Hf Plasma-material interactions; boundary layer effects,- 52.65.Ff Fokker-Planck and Vlasov equation

PART 1: THE STOCHASTIC SIMULATION OF FLUCTUATION STAGE OF NANO-FILM FORMATION

Introduction

The plasma surface interaction results in surface modification and plasma pollution. The plasma or metal (metal oxide) vapor influence on solid surface connects with nano-films formation. Numerical simulation of adatoms clusterization of solids surfaces under plasma influence is interesting for creation of thin films and covers with specified 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 very short duration (10^{-4} sec) as well as the strongly nonequilibrium characteristic of nano-films fluctuation stage formation are examined in this paper. In spite of the fact that fluctuation stage is non-linear its influences on process of thin film formation is very essential. Hence the study of fluctuation stage of thin film formation under plasma or metal oxide vapor is very important for thin films preparation and nanotechnology development correspondingly. The formation of liquid or glass-making thin film on nonideal surface is examined. We consider the influence of linear dislocation on nano-film formation which is arranged on the surface or into the sub-surface layer of a sample.

Self-organization and phase transformation phenomena: The fundamental problems, associated with transitions from chaos to self-organization and back are extremely difficult to solve. The self-organization into phase spaces of plasma-like media problems (such as the sizes of islands of films) have formed under follows factors: 1) constant flux of ions on the surface, 2) the long-range potentials of indirect interaction defects each with others, with surface as well as with dislocations and at the last; 3) the far from equilibrium state of media, which is presented by 4) large number of stochastic dynamical variables, the rate of variation in which are highly interrelated. The balance of energy fluxes entering and leaving an "open" system is a necessary condition for the balance of applied and friction forces in the establishing of asymptotically stable states of motion of dynamic stochastic system.

The investigation of this phenomena can be effected using the follows: quasi-linear partial kinetic equations (1) and (2) with a functional-coefficients, its stochastic analogs:$\hat{I}$to stochastic differential equations/SDE/(3) and probability distribution functions $f(t,x(t))$ /DF/ which depend on stochastic dynamical variables: $\{x_i(t), t \geq 0\}_{i=1,\ldots,N}$, here N is the number of stochastic processes $x(t)$.

Problem statement: Initial stage of cover formation has been considered as the geterogeneous first-order phase transformation (from vapour to liquid or glass-making state on the substrate), here it has not be examined chemical reactions during fluctuation stage of this phase transition. New phase islands (bits of thin film) are considered as Brownian particles with hemispheric shapes and variable masses which can migrate on surface. The kinetic theory[1], stochastic analog computer simulation method /SSM/ [2],as well method of splitting on different physical processes are used for simulation of thin film development which is based on essentially different characteristic times of

growth/degradation and migration of thin film islands. The problem of kinetic description of the phase transition at its fluctuation stage is introduced by stochastic analog method. This method is based on the strict results of the probability analysis of equations of mathematical physics; kinetic theory of plasma and rarefied gases; the theory and practice of numerical experiment in non-linear plasma simulation and SDE solution.

Let us present the model of liquid islands appearence on the surface by 2D islands brownian motion with 1D fluctuation dependent process of its mass (nucleous of new phase) formation in presence of vapor of this phase.

Kinetic equations and stochastic models

The kinetics problem (Kolmogorov-Feller (1) equation and Kramers-Smolukhovskii (2) equation) after physical processes splitting look like as following:

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

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

$$\frac{\partial f_g(r,t)}{\partial t} = \frac{\partial}{\partial r}\left[D_r(r,t)\frac{\partial f_g(r,t)}{\partial r} - \frac{F(r,t)}{M_g\gamma}f_g(r,t)\right], \tag{2}$$

$$f_g(r,t)|_{t=0} = f_{0r},$$

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

S_α is the source of metal vapor which is generated by ions with f_α — maxwell vapour function. Here $f_r(g,t)$ is the island size DF — the probability to find the cluster with size g in interval of values of $g \in [g, g+\Delta g]$, g is island's size(measured in number of particles with unit mass), $D_g(g,t)$ is diffusion coefficient in the phase space of cluster sizes **G**, $D_g = D_{g0}g^{2/3}$, D_{g0}- is coefficient which depends on T, p-temperature and metal vapour pressure. $\Delta\Phi$ is the Gibbs energy, M_g is the cluster mass, γ is a friction constant. DF $f_g(r,t)$ is the spacial island's DF, r is the position of cluster mass centre in orthogonal coordinates system: $x_{\text{left}} = -200$, $x_{\text{right}} = 200$, $y_{\text{left}} = -200$, $y_{\text{right}} = 200$, $F(r,t) = \partial U(r,t)/\partial r$, $U(r,t)$ is the potential of long-range indirect island- clusters interactions (each with other): through lattice acoustic phonons and Friedel oscillations of electron density [3].

Stochastic equations: SDE for evolution x variable (instead of three-dimensional vector $\vec{r}(x(t),y(t),z(t))$) is produced here by $\hat{I}$to equation in Stratonovich form with coefficients (4) derived from equation (2):

$$x(t) = x(t_0) + \int_{t_0}^{t} H(\tau, x(\tau))d\tau + \int_{t_0}^{t}\sigma(\tau, x(\tau))dW(\tau), \tag{3}$$

here fuctional-coefficient H and σ can be presented as follows:

$$H(x,t) = -\frac{1}{\gamma M_g}\frac{\partial U(x)}{\partial x} - \frac{1}{2}\frac{\partial D_x}{\partial x}; \quad \sigma(x,t) = \sqrt{2D_x(x,t)}, \quad D_x = \frac{D_0}{\gamma M_g}(1+\beta\Delta x^2). \tag{4}$$

Let us note, that island mass M_g is determined from (5), dW is the increment of Wiener random process on time Δt, D_x is non-linear diffusion into lattice coefficient, D_0 is parameters depends on "lattice- adatom(cluster)" binding energy.

$\hat{I}$to-Stratonovich SDE for $g(t)$ stochastic variable which is related with equation (1) can be written as:

$$\frac{\partial g}{\partial t} = -\frac{1}{kT}D_g(g,t)\frac{\partial\Delta\Phi(g,t)}{\partial g} - \frac{1}{2}\frac{\partial D_g(g,t)}{\partial g} + \sqrt{2D_g(g,t)}\xi(t), \tag{5}$$

$$t_0 \le t \le T_k \qquad g(t_0) = g_0 \qquad g(t) \ge 2, \tag{6}$$

$\xi(t)$ is a random function.

Cluster formation model: The computational 3D domain is periodic along two coordinates (x and y) while along the third coordinate (z) the boundary conditions are as follows: The top of the domain contacts with plasma, on the bottom of the domain one has the reflection from crystal lattice layers undisturbed by vacancies' with negligible

concentration. Into 3D-lattice we have to arrange the model dislocation into sub-surface volume. There are equations involving partial derivatives of islands coordinate ($\vec{r}$) on the surface of lattice(2) and its size (1) g. The Gibbs energy model of island's formation is follow: $\Delta\Phi(g,r,t) = -(a_\Phi - c)g + bg^{2/3} + \Delta\Phi_r$, here it has been accounted cluster pressure on solid surface by cg with coefficient c[5], $a_\Phi = \eta_a(\xi_\beta - \xi_\alpha)$, where $(\xi_\beta - \xi_\alpha)$ is difference of chemical potential of phases("vapour-liquid") , η_a — form factor: $\eta_a = \frac{\pi(2-3\cos\theta+\cos^3\theta)}{3V}$ where V is unit volume of evaporated atom, θ — soaking angle, index α is first metal vapour, β is cluster of liquid metal on surface, S is phase of second more refractory metal (substrate material). Coefficient b is equal to $b = 2\pi(1-\cos\theta)\sigma_{\alpha\beta} + \pi\sin^2\theta(\sigma_{\beta S} - \sigma_{\alpha S})$, where $\sigma_{\alpha\beta}, \sigma_{\alpha S}, \sigma_{\beta S}$ are surface tension between vapour of metal and metal liquid in island, liquid island and substrate, vapour and substrate. Lattice matrix potential influence is accounted by model: $\Delta\Phi_r = \Psi(2 - \cos(2\pi x/a_x) - \cos(2\pi y/a_y))/\sqrt{g}$, Ψ is simulation model parameter, which can account the decreasing of Gibbs energy on dislocation (according model assumption).

The interaction between uncharged clusters [3] in dielectric crystals is the elastic interaction through the acoustic phonons; but for metal lattice the indirect interaction has to be considered via defect-induced Friedel oscillations in the electron density (in case of weakly anisotropic lattice - for the spherical Fermi surface) and acoustic phonons [3-5]. The potential which influences on islands migration over surface($\{x,y\}$) can be presented as $U = U_{dd} + U_{ds}$, where U_{dd} is potential of indirect interaction between clusters, M_j is mass of j-th cluster:

$$U_{dd} = \sum_{i\neq j}^{N} \frac{M_j b_{rc}\left[\frac{3}{5} - \frac{(x_i-x_j)^4+(y_i-y_j)^4}{(r_i-r_j)^4}\right] + a_{rc}\cos(c_{rc}(r_i - r_j))}{|r_i - r_j|^3}, \quad |r| = \sqrt{x^2+y^2}, \tag{7}$$

U_{ds} is potential of indirect interaction between liquid cluster of less refractory metal on substrate surface of more refractory metal and dislocation or grain boundary:

$$U_{ds} = \sum_{i}^{N} \frac{M_d b_d\left[\frac{3}{5} - \frac{(x_i-x_d)^4+(y_i-y_d)^4+z_d^4}{(r_i-r_d)^4}\right] + a_d\cos(c_d(r_i - r_d))}{|r_i - r_d|^3}, \quad |r| = \sqrt{x^2+y^2+z^2}, \tag{8}$$

b_{rc}, a_{rc}, c_{rc}, b_d, a_d, c_d, M_d are model coefficients, also coordinate z_d of dislocation is equal dislocation depth if dislocation is located under surface and z_d is equal zero if dislocation is located on substrate surface. All the constants are chosen for a specific range of key physical parameters of problems.

Computer stochastic simulations: The kinetic equations(1) and (2) are replaced by set of SDEs (3) and (6), which are solved by modified [4,5] Artem'ev method SDE solution: it is a second-order accuracy method with the infinite domain of stability (according to definitions and proofs introduced in [6]). Numerical solution SDE (3), (5)is realized at the time mesh nodes t_n; $h_n = t_{n+1} - t_n$ is an integration step. Let us present example of calculation for $i-$th trajectory at time moment $(n+1/4)$ for $g(t)$ evolution solution ($g_n = g(t_n)$):

$$g^i_{n+1/4} = g_n + [\hat{I} - \frac{h_n}{2}\cdot\frac{\partial H^i_{gn}}{\partial g}]^{-1}[h_n H^i_{gn} + \sqrt{h_n}\sigma^i_{gn}\xi_{gn}], \tag{9}$$

$$H^i_{gn} = -\frac{1}{kT}D^i_{gn}\frac{\partial\Delta\Phi^i_{gn}(g^i_n,x^i_n,y^i_n,z^i_n)}{\partial g} - \frac{1}{2}\cdot\frac{\partial D^i_{gn}}{\partial g}\xi^2_{gn},$$

$$D^i_{gn} = D_{g0}(g^i_n)^{2/3}, \sigma_n = \sqrt{2D^i_{gn}(g^i_n)},$$

$$\xi_n = \sqrt{-2ln\alpha_1}cos(2\pi\alpha_2), \quad 0 \le \alpha_1, \alpha_2 \le 1. \tag{10}$$

here ξ_n are the normal random variables with zero mean and unit variance. $\hat{I}$ - unit matrix, α_1, α_2- uniformly distributed random variables in the interval $(0,1)$ are calculated with the help of a random number generator.

Results of liquid metal islands DF simulation. The numerical results give rise to the the hypothesis about self-organization in the system under study when surface defects are centres of thin film formation (fig.1, 2). The results of stochastic simulation show that dislocation influence can be neglected if dislocation depth is more than 5 lattice monolayers, while if dislocation depth is less then 5 lattice monolayers, the dislocation appears to be the centre of thin

film formation and the dislocation influence decreases nonlinearly with depth increase (fig.3). The process thin film growth on the base of new phase islands that are formed by surface potential can be described by the kinetic model of multylayer film (see Part 2)

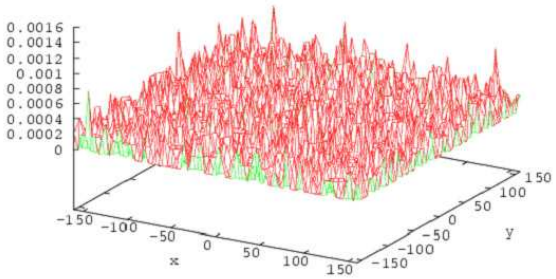

FIGURE 1. The initial island distribution function normalizes on unity as a function of *x* and *y* coordinates. The dislocation depth is 1 monolayer. All spatial coordinates are measured in substrate monolayers.

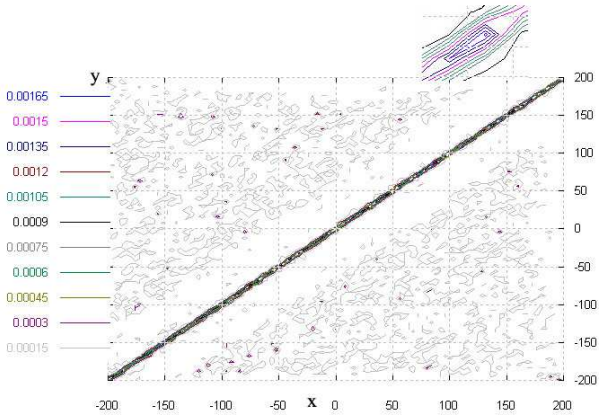

FIGURE 2. The final island distribution function as a function of *x* and *y* coordinates/

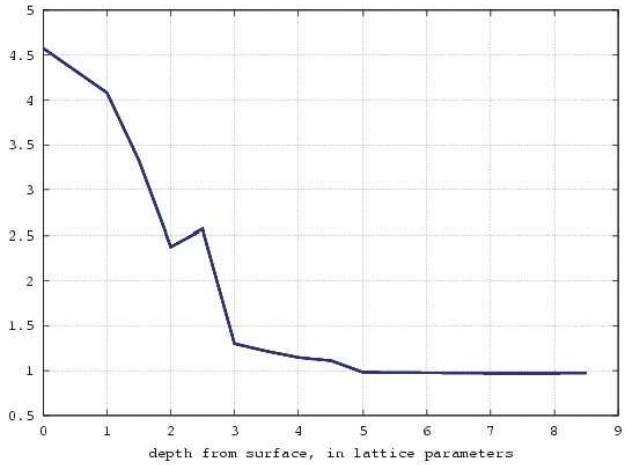

FIGURE 3. The dependence of the ration of probability of cluster location on the projection of surface dislocation line and probability of cluster location outside the projection of dislocation line as a function of dislocation depth.

PART 2:THE KINETIC SIMULATION OF MULTYLAYER THIN FILMS COVERING

Problem statment. Plasma- or gas-surface interaction results in surface modification and covers formation. Numerical simulation of adatoms clusterization on solid surfaces under plasma influence is of great interest for understanding of the process of thin films and covers creation. The 1*D*1*V* model of cover formation is examined in this paper. The deposition of several film layers that is strongly nonequilibrium process is considered. The kinetic

Fokker-Planck equation [7-9] is used for simulation of thin film formation. This equation describes evolution of the distribution function $f(x;v;t)$ that is the function of spatial coordinates and velocities versus time. The domain $x \in [0;L]$ is considered. On its left side $(x=0)$ the substrate with the potential $U_{wall}(x)$ is located while on its right side $(x=L)$ the source of adatoms with intensity I is located. Interparticle potential $u_{ij}(x)$ is cutted at $|x| \le r_{\min}$. The system is considered in the thermostat at the temperature T. To the right from the right border of this domain distribution function is considered to be constant $f(x,v,t)|_{x\in[L,\infty)} = I\delta(v-v_0)$

$$\frac{\partial f(x,v,t)}{\partial t} + v\frac{\partial f}{\partial x} - \frac{\partial}{\partial x}\Big[U_{\text{wall}}(x) + \langle U(x,t)\rangle\Big]\frac{\partial f}{\partial v} = \gamma\frac{\partial}{\partial v}\left[T\frac{\partial f}{\partial v} + vf\right] + I\delta(x-L)\delta(v-v_0);$$

$$\langle U(x,t)\rangle = \int_0^\infty u_{ij}(x-x')\,f(x',v',t)\,dx'dv'$$

$$u_{ij}(x) = \begin{cases} \text{const}, & |x| < r_{\min} \\ 4\varepsilon\left[\frac{r_0^{12}}{x^{12}} - \frac{r_0^6}{x^6}\right], & |x| > r_{\min} \end{cases}; \qquad U_{\text{wall}}(x) = 4\varepsilon\left[\frac{r_0^{12}}{x^{12}} - \frac{r_0^6}{x^6}\right],$$

where ε_{wall} and r_{wall} are wall Lennard-Jons potential parameters, ε and r_0 are interparticle Lennard-Jons potential parameters, and γ is the model parameter.

The kinetic theory, splitting on physical process, SSM method [2], leap–frog second order method as well as modified in [5] Artem'ev method [6] for solution of SDE are used for solution of this problem. The macroscopic parameters are calculated on the base of DF The self-consistent kinetic $1D1V$ model of thin film deposition is suggested. The dynamics of cover formation has been studied numerically [10]. The critical temperature is discovered, its value is $\sim 0.1\varepsilon$. If temperature is more than critical one: the thin film is unstable. The dynamics of cover formation is presented on figs 4, 5. The time step $h = 0.2$, $\gamma = 0.055$, $\varepsilon = 1.0$ for all pictures presented below, number of trajectories are $10^4 \div 10^5$, $L = 10$ for fig. 4, 5 and fig.6, 7.

Results of calculations of vertical thin film deposition. $1D1V$ kinetic model for the thin film covering dynamics is developed. Their important feature was discovered. When temperature is higher than the critical one 0.1ε (ε is depth of the Lennard-Jons potential well) the first order phase transition takes place and the deposition of more than one film layer becomes possible. It is shown that the effective cover of the fine films takes place only in the narrow range of the model parameters.

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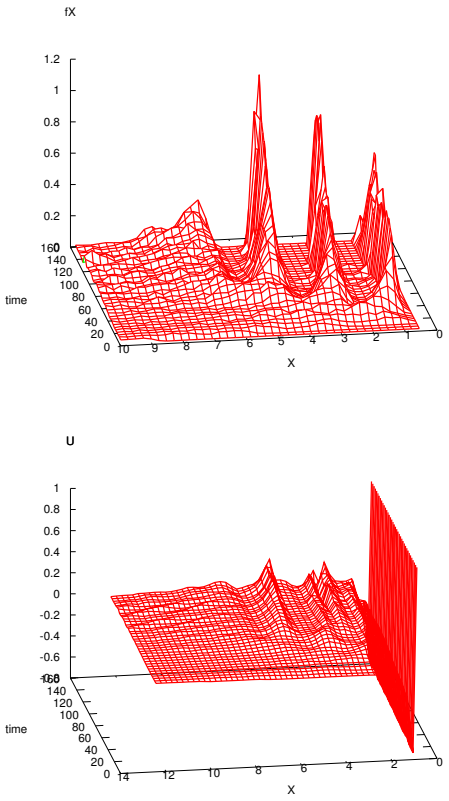

FIGURE 4. The evolution of distribution function $f(x,t)$ and self–consistent potential $\langle U(x,t)\rangle + U_{\rm wall}(x)$ for $T = 0.005\varepsilon < T_{\rm cr}$.

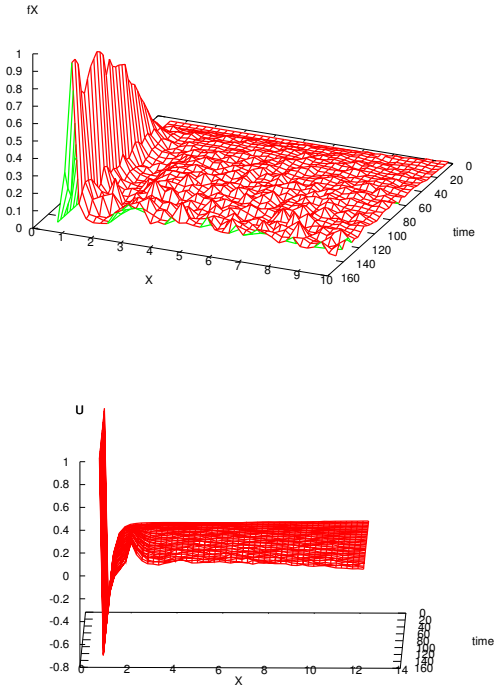

FIGURE 5. The evolution of distribution function $f(x,t)$ and self–consistent potential $\langle U(x,t)\rangle + U_{\rm wall}(x)$ for $T = 0.1\varepsilon = T_{\rm cr}$.

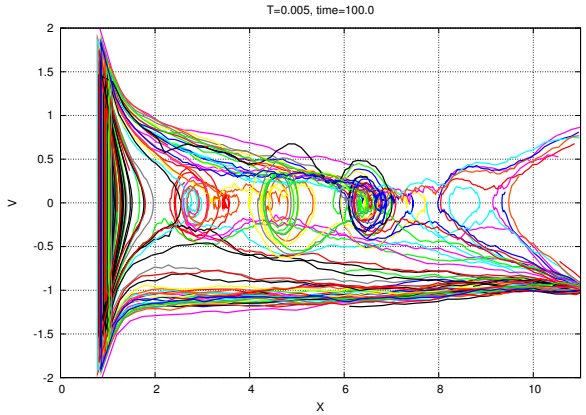

FIGURE 6. Particles tracings on phase plane $\{X,V\}$ for $T = 0.005\varepsilon < T_{\rm cr}$. The four film layers are good seen.

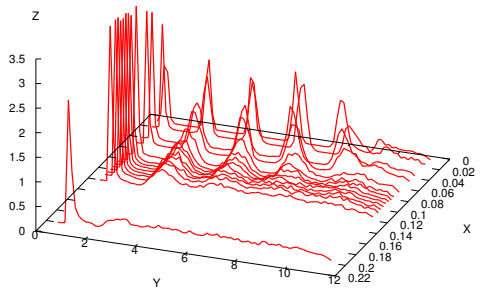

FIGURE 7. Dependence equilibrium distribution function $f_{\rm eql}(x) = f(x,t)|_{t\to\infty}$ vs temperature T. Qualitative changing of the distribution function can be seen clearly at $T \sim T_{\rm cr}$.