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Monte-Carlo Modeling of Crystallization of Thin Films

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Three-dimensional kinetic modeling of crystallization of microareas of melt has been carried out in view of interaction of atoms with the substrate, spontaneous formation of crystal clusters with the diamond-type lattice (parameters of silicon) or a simple cubic lattice. For the cubic lattice interaction of atoms with the neighbors from the first second and third coordination spheres was taken into account. Some characteristics of epitaxial films obtained in result of calculations are discussed.

Keywords: thin films, Monte-Carlo modeling, crystal clusters, spontaneous crystallization, epitaxy.

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I. Introduction

The thermodynamic theory of homogeneous and heterogeneous formation of the centers of crystallization becomes incorrect for the case of very high driving forces of phase transition, when nuclei become so small that for them the basic concepts of thermodynamics lose sense. That limits also applicability of phenomenological theories of mass crystallization. Statistico-mechanical theories advanced for this case, for example Walton's and Rodin's theory, are not without certain weak sides [1,2].

In spite of significant progress in the question of application of dynamic modeling for studying growth of crystals [3,4], there are still no works in which formation of three-dimensional nuclei of a new phase is obviously. Modeling of such processes by the Monte Carlo method is undoubtedly useful. At Monte Carlo modeling of crystallization process in [5] analytical expression for speed of formation of crystallization centers was used, and that has made modeling indirect. In the work [6] dedicated to the three-dimensional Monte Carlo method of modeling of process of epitaxy, the stage of formation of crystallization centers was not considered. Results of kinetic modeling, at which with some slice of time all atoms are necessarily tested for the possibility of their transition from one phase in another, are reflected below and the possibility of formation of crystal is taken into account.

II. Method of modeling

The variant of Monte Carlo method [7-9] for

modeling of the structure of a crystal face was modified to simulate heterogeneous spontaneous crystallization. The structure of the melt was supposed to be the same, as the structure of crystal (diamond-type lattice or a simple cubic lattice). The possibilities to attach atoms to the crystal nucleus and to detach them have been calculated for the average lifetime τ_+ of an atom with one ss-bond (type "solid-solid") at the surface of a crystal cluster.

The probability to detach an examined atom in time τ_+ is determined by the exponential factor from energy modification U at replacement of its bonds of the type "solid-solid" (s-s) on bonds of a type "liquid-solid" (l-s):

$$p^- = \nu_0 \tau_+ \exp[-U/kT]. \quad (1)$$

In case of the account of interaction only with the nearest neighbors $U = 2n\phi$, ϕ is the change of energy per one bond of one atom, and n is the number of the nearest solid atoms. In approximation, that the energy of a bond V_{sl} ("solid-liquid") is equal to the energy of a bond V_{ll} ("liquid-liquid"), $\phi = \Delta H/z_1$, ΔH – melting heat counting upon one atom, z_1 is the total number of the nearest neighbors for the given structure. In case of the account of interaction with the next atoms from first second and third coordination spheres $U = 2(n_1\phi_1 + n_2\phi_2 + n_3\phi_3)$, n_1 , n_2 and n_3 are corresponding numbers of the neighbor "solid" atoms, and ϕ_1 , ϕ_2 , and ϕ_3 are corresponding energies. The account of interaction with the neighbor atoms from different coordination spheres is carried out for the case of a simple cubic lattice. The case of weak dependence of energy of interaction on distances was examined, so that $\phi_1/\phi_2/\phi_3 = (1/r_1^3)/(1/r_2^3)/(1/r_3^3)$, where r_1 , r_2 and r_3 are the radii of coordination spheres. Here it was taken into account, that to detach an atom from position at the break of step it is necessary to spend work $\Delta H = 2(z_1\phi_1 + z_2\phi_2 + z_3\phi_3)$, where z_1 , z_2 and z_3 are

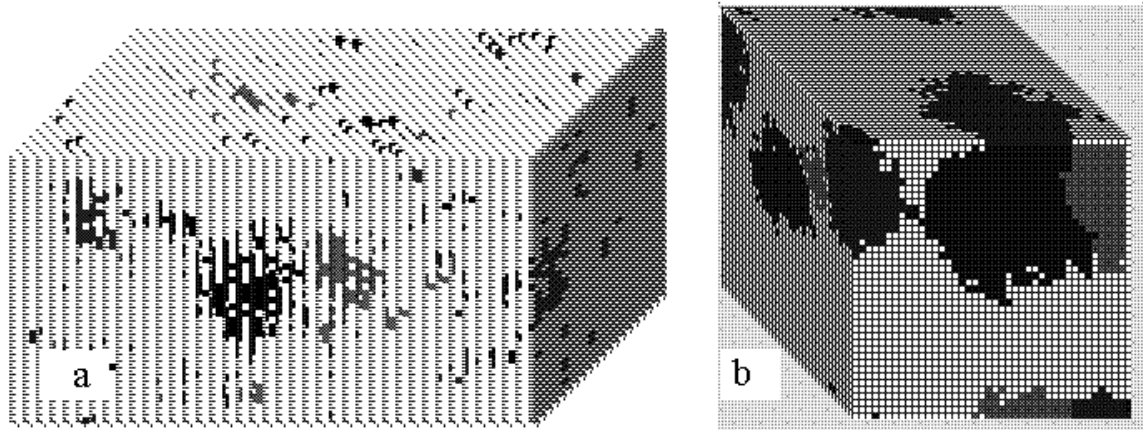


Fig. 1. External borders of examined domains in the time of growth of crystallization centers.

corresponding coordination numbers [10].

The probability for an atom to be attached to a nucleus is bound up with a difference of chemical potentials $\Delta\mu$ of two phases

$$p^+ = v_0 \tau_- \exp[(\Delta\mu - \Delta H)/kT]. \quad (2)$$

The probability of formation of a crystal cluster from three or four atoms during time τ_- was determined as exponential factor from work, which is necessary for this (in units of kT):

$$pp^+ = v_0 \tau_- \exp[(\Delta\mu n_k - b_1\phi_1 - b_2\phi_2 - b_3\phi_3)/kT], \quad (3)$$

where b_1 , b_2 and b_3 are corresponding numbers of the bonds with liquid atoms from the first, second and third coordination spheres (because of the small size of clusters). Just as in [4], we supposed an opportunity of formation of crystal clusters with conditionally different orientations (6 variants). The examined area was usually chosen $80 \times 80 \times 40$ in atomic units. Various boundary conditions were applied: periodical, or additional boundary planes of "liquid" atoms. The existence of single "solid" and single "liquid" atoms was forbidden.

To simulate epitaxial growth certain interaction of atoms with a substrate was considered – "melting" of the atom placed near substrate was assumed to be connected with change of energy of its bonds, $u_s = f n_s \phi$, where n_s is the number of bonds with atoms of the substrate; f is the multiplier of slacking interaction energy on a comparison with interaction of atoms in the volume (for one of six conditionally different orientations of clusters this interaction was set stronger two times). There were used parameters, that are typical for silicon, and also larger value of entropy of fusion $\Delta H/kT = 7.2$ which, according to [11], allows to receive results at Monte Carlo modeling concerning to structure of a surface and kinetic growth of silicon, that does not conflict with experimental data.

Procedure with operation of recursion was used for the analysis of size distribution of clusters. Corresponding results were checked also by display and analyzing of the received structure of consecutive planes. On fig. 1 the image of external shape of examined volume is shown for the case when centers of crystallization reached external borders (for a diamond-type lattice and for a simple cubic lattice).

III. Results and their discussion

First we studied the dependencies on supercooling of the waiting time of appearance of the first crystallization center. As it was obtained, results are weakly sensitive to the initial size of crystal clusters (3 or 4 atoms) and to character of boundary conditions on lateral and top borders of area. The last obviously means that the examined volume is already big enough so that occurrence of symmetric clusters on borders does not essentially influence probabilities of formation of nuclei of the critical size. Received results are reflected in fig. 2 and 3. Values of the logarithm of the average time of waiting (in relative units, t_w/τ_0 , τ_0 is the period of oscillations of an atom) for appearance of the first center of crystallization are pointed along the ordinate axis. On fig. 2 the data are given, received for a diamond-type lattice – for the case without interaction (periodic boundary conditions on the axis z) and in view of interaction of atoms with a substrate.

Clusters also appear often in superheated for hundreds degrees melts. However they disappear then so to fix clusters with size larger than minimal for their formation it is not possible.

On fig. 3 the results of studying of appearance of the centers of crystallization for crystals with simple cubic lattice are shown. There are results for the case, when interactions of atoms with only the nearest neighbors were taken into account and also for the case, when interactions with neighbors from the first, second and third coordination spheres were considered; rather weak dependence of energy of interaction from distance has been considered: $\sim r^{-3}$.

Apparently from figures, in all cases crystallization begins when supercooling is higher than certain threshold value character – it is practically impossible to obtain the centers of crystallization below certain values of supercooling. Waiting times grow with the decrease of supercooling very quickly. Rate of formation of the centers of crystallization is an inverse dependence to the value of waiting time, $I = 1/(\tau_w V)$ where V is the size of the examined volume.

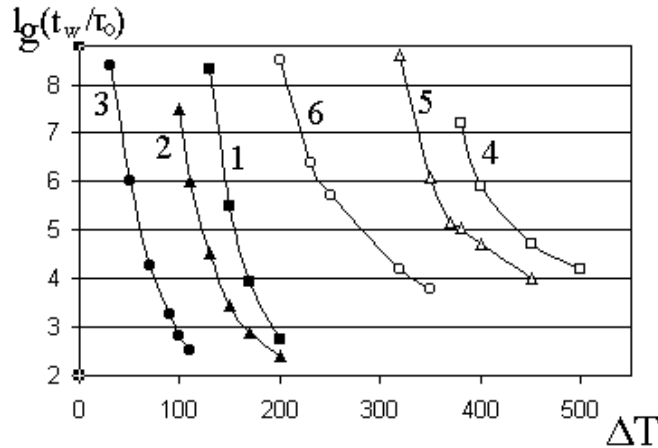


Fig. 2. Dependencies on the supercooling of the time of waiting of the first crystallization centers (diamond-type lattice), for 1-3 $\Delta H/kT_f = 3.5$; for 4-6 $\Delta H/kT_f = 7.2$; 1,4 – without interaction with a substrate; 2,5 – weak interaction with a substrate: $u_s = 0.8\phi$ for the basic orientation of clusters, 3,6 – 1.6ϕ .

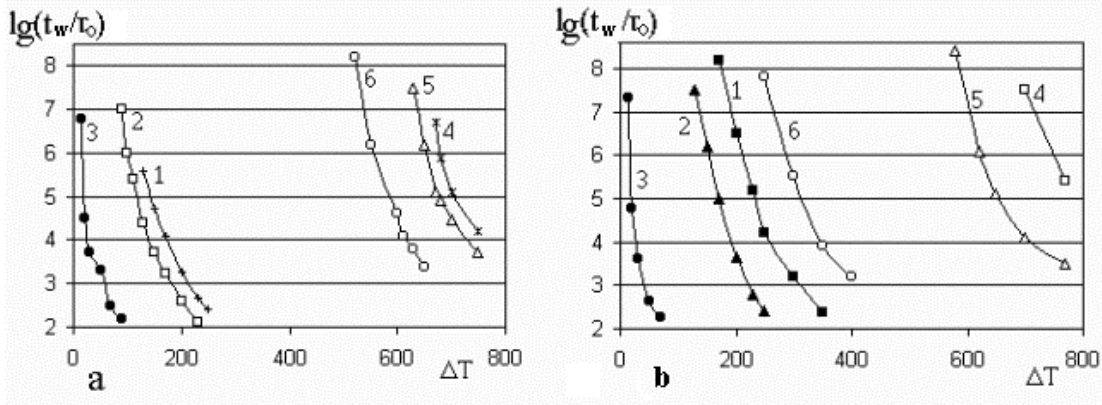


Fig. 3. Dependencies on the supercooling of the waiting time of the first crystallization centers, a – interaction only with the nearest neighbor atoms, b – interaction with atoms from the first, second and third coordination spheres, b – for 1-3 $\Delta H/kT_f = 3.5$; for 4-6 $\Delta H/kT_f = 7.2$; 1,4 – without interaction with a substrate; 2,5 – weak interaction with a substrate: $u_s = 0.8\phi$ for the basic orientation of clusters, 3,6 – $u_s = 1.6\phi$.

Values of nucleation rate correlate with theoretical estimations because of high values of coefficient staying before the exponent in analytical formulas [12]. Results obtained for parameters of silicon exclude however forming of pure amorphous state without crystallization centers. When using in calculations of very high rate of cooling – 10^8 degrees/s by introduction of time dependence on temperature, crystallization always took place even for value of entropy of melting $\Delta H/kT_f = 12$. Apparently it is concerned with weak points of the method of modeling. Simulation scheme developed in [6,7] is fully applicable only for the case of crystallization of the lattice gas. It could not be excluded also, that such states with very small crystals, which were obtained at high supercoolings in our simulation, are usually accepted as amorphous. Accounting of interaction with the neighbor atoms from the second and third coordination spheres (fig. 2b) causes increase in times of waiting. The reason of this is that full energy of

bonds of surface atoms for small clusters becomes essentially less than for big ones because there are few second neighbors and there are no third neighbors, and increase in their size becomes less probable. For entropy of fusion $\Delta H/kT = 7.2$ the times of waiting become large enough (threshold supercoolings for the given size of volume ~ 600 K). However accounting of interaction with second and third neighbors in the substrate increases its influence and facilitates nucleation (compare curves 6 on fig. 3a and fig. 3b). When temperature decreasing, time slice τ_- (lifetime of adsorbed atom) is increasing.

Essential facilitation to nucleation caused by interaction of atoms with the substrate is quite predicted. Probabilities of attaching and detaching of an atom in the near-surface layer change essentially as well. That causes epitaxy. On fig. 4 we show dissections of a part of the examined volume. Besides on fig. 4a only the first layer is shown, and on fig. 4 – 20 layers in which "liquid" atoms were not filled by color, so in the picture all crystal clusters are visible, including the center of

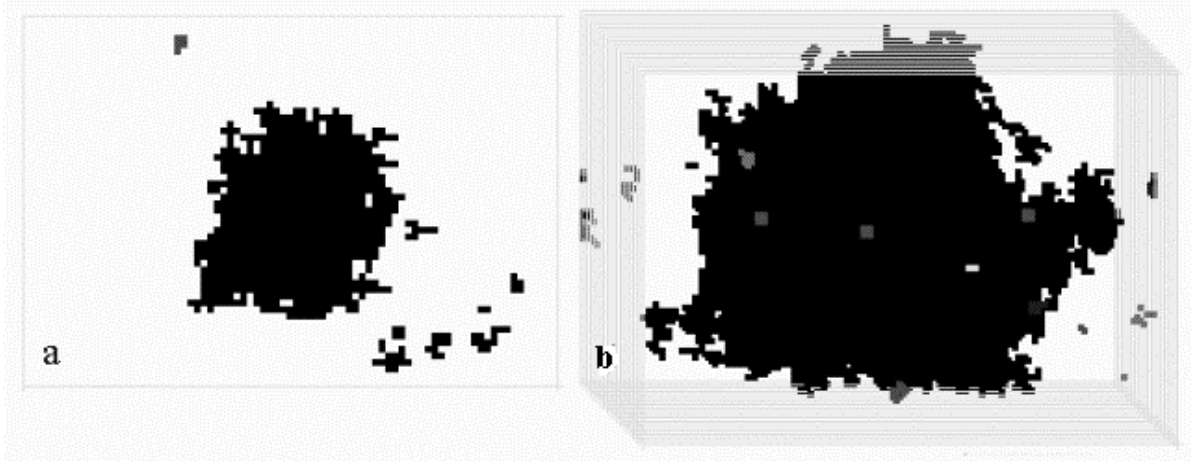


Fig. 4. Epitaxial crystallization of the film, $\Delta H/kT_f = 3.5$, supercooling $\Delta T = 70$ K, interaction with the substrate: a – $u_s = 0.8\phi$ for the nuclei marked by black color, b – $u_s = 0.4\phi$ for the others.

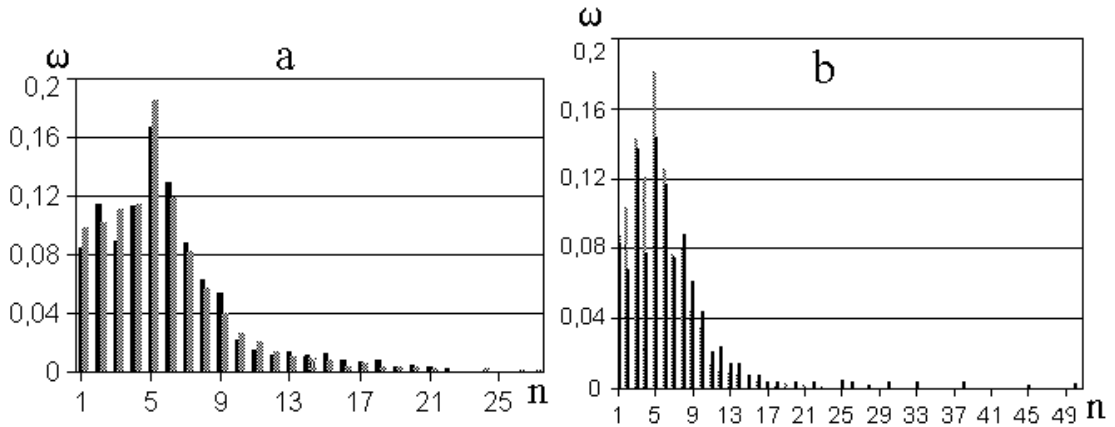


Fig. 5. Distribution of clusters in sizes, a – interaction with the substrate is absent; b – with interaction, $u_s = 0.8\phi$ for black columns (simple cubic lattice, $\Delta H/kT_f = 3.5$, supercooling $\Delta T = 70$ K).

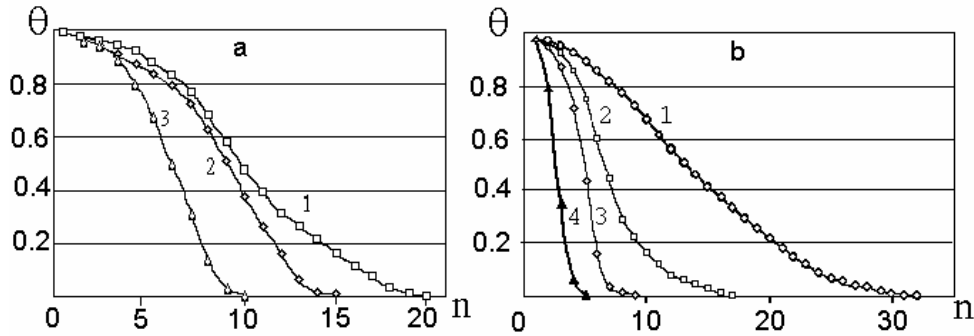


Fig. 6. Filling of consecutive layers by "solid" atoms, $\Delta H/kT_f = 7.2$, a – simple cubic lattice (with accounting of distant interaction), for 1-3 $\Delta T = 350, 400$ and 450 K; b – diamond-type lattice, for 1-3 $\Delta T = 100, 200$ and 250 K, 4-autoepitaxy, $\Delta T = 250$ K.

Clusters of the basic orientation are black here. They are two-dimensional at the appearance. Growing centers of crystallization become three-dimensional. Anisotropy of growth rate is big enough.

Fig. 5 shows distributions of clusters in sizes. Appearing of clusters with 3 or 4 atoms was supposed in programs. It causes the position of maximum of distribution, but practically does not influence distribution at big sizes. Single "solid" atoms were

forbidden. Fig. 5 a corresponds to absence of interaction of atoms with the substrate. When accounting the interaction, epitaxy takes place (fig. 5b) – the part of clusters with the correct orientation (relative to the substrate) is increasing and their average size is increasing as well. That facilitates formation of centers of crystallization centers. Distributions obtained for the correct orientation of the clusters are shown by black columns.

For application of epitaxial films they must be qualitative enough. As process of crystallization consists from casual events, their imperfections are possible. It is reasonable to determine, as it was done in [5], degree of filling by «solid» atoms of consecutive layers at the certain filling (sufficiently close to 1) of the first layer. Examples of such dependencies are reflected on fig. 6 for the case of rather strong interaction with the substrate ($u_s = 1.6\phi$ – the change of energy of one bond at melting equals 2ϕ).

As it follows from the graphs, the high degree of filling of the first layer (0.98) is achieved at the beginning of filling from the 7th to the 30th layers, depending on the magnitude of the energy of interaction with the substrate (there are only 7 partially filled layers at autoepitaxy) and on the value of supercooling. At high supercooling the continuous films are being formed at their smaller thickness. This result is in good coordination to the data of the calculations obtained analytically in [13,14]. As very thin films are not continuous, the stage Ostwald's maturing (see, for example, in [15]) for them is necessary.

IV. Conclusions

The developed method for kinetic Monte Carlo modeling of three-dimensional crystallization in view of spontaneous formation of the centers of crystallization in volume of the initial phase and on a substrate is applicable for investigation of the thin films formation, including epitaxy, and visualization of such processes at atomic scale.

At the weak interaction of atoms with a substrate

partial epitaxy takes place, when probability of formation of crystal clusters with non basic orientation is large enough. At the significant interaction almost full epitaxy takes place.

Unhomogenities of epitaxial films on thickness are determined by value of supercooling, energy of connection with a substrate and by anisotropy of growth rate of crystallization centers which depends on entropy of fusion. For the used parameters it is found, that practically full filling with "solid" atoms of the layer nearest to the substrate ($\theta = 0.98$) is achieved at the maximal sizes of the crystallization centers in the perpendicular direction to the surface about 10-30 nuclear layers. This size causes relief of surface films.

Accounting of interaction of atoms with the neighbor atoms from the second and third coordination sphere (and also from the first) results in essential increase of threshold supercoolings for beginning of spontaneous crystallization in the volume of liquids. This effect becomes insignificant, when interaction with a substrate is taken into account. The overestimated value of entropy used in calculation influences more essentially nucleation and shapes of nanocrystals. In this case more real values of supercoolings, which are necessary for formation of crystallization centers have been obtained. However monotonous increase with supercooling of the rate of formation of crystallization centers that is obtained in our solutions contradicts experimental data. Therefore the model for simulation should be modified to take into account more really interaction in a liquid phase and activation processes at the moments of transition through the interface.

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Монте-карло моделювання кристалізації тонких плівок

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Проведено тривимірне моделювання кристалізації мікрообластей розплаву з урахуванням взаємодії атомів з підкладкою, спонтанного утворення кристалічних кластерів із ґраткою алмазу (параметри кремнію) чи простою кубічною ґраткою. Для кубічної ґратки врахована взаємодія атомів із сусідніми атомами з першої другої і третьої координаційних сфер. Обговорюються деякі характеристики епітаксціальних плівок, що отримані внаслідок розрахунків.