Keldysh Institute • Publication search

Keldysh Institute preprints • Preprint No. 150, 2019

ISSN 2071-2898 (Print)
ISSN 2071-2901 (Online)

Zmievskaya G.I., Levchenko T.V., Maino G.

Processes of microporosity formation at initial stage phase transition

Recommended form of bibliographic references: Zmievskaya G.I., Levchenko T.V., Maino G. Processes of microporosity formation at initial stage phase transition // Keldysh Institute Preprints. 2019. No. 150. 24 p. doi:10.20948/prepr-2019-150-e
URL: http://library.keldysh.ru/preprint.asp?id=2019-150&lg=e

О р д е н а Л е н и н а
ИНСТИТУТ ПРИКЛАДНОЙ МАТЕМАТИКИ
имени М.В. КЕЛДЫША
Р о с с и й с к о й а к а д е м и и н а у к

G.I. Zmievskaya, T.V. Levchenko, G. Maino

Processes of Microporosity Formation at Initial Stage Phase Transition

Москва — 2019

[1]Змиевская Г.И., [2]Левченко Т.В., [3]Майно Дж.
e-mail: [1]zmig@mail.ru
[1]ИПМ им. М.В. Келдыша РАН, [2]ВНИГНИ, [3]Болонский Университет, Италия

Процессы формирования микропористости на начальной стадии фазового перехода

Компьютерные эксперименты по имплантации ионов могут применяться для оценки пористости объектов культурного наследия. Поры появляются под действием природных и антропогенных факторов. Их оценка осуществима по параметрам подобия и учету периодичности процессов. Обсуждается взаимодействие потока инертного газа с энергией ионов 5-10 кэВ с решеткой твердого тела. Образование пористых и напряженных структур в образце происходит для процессов длительностью 10-100 мсек. Начальная (неравновесная) стадия фазового перехода рассматривается как суперпозиция двух случайных процессов: кластеризации газовых мономеров и их Броуновского движения в кристаллической решетке многослоистого образца. Кластеризация зародышей появляется при внедрении инертного газа в решетку в форме пузырьков газа (блистеров). Кинетические уравнения для функции распределения пузырьков газа в слоях SiC и Mo заменены эквивалентными СДУ Ито-Стратоновича.

Ключевые слова: кинетическая теория, стохастическая модель, пористость, карбид кремния, кластеры пор, самоорганизация, объекты культурного наследия

[1]**Galina I. Zmievskaya,** [2]**Tatiana V. Levchenko,** [3]**Giuseppe Maino**
e-mail: [1]zmig@mail.ru
[1]Keldysh Institute of Applied Mathematics, Russia,
[2]All-Russian Research Geological Oil Institute, Russia,
[3]Bologna University, Scuola di Lettere e Beni Culturali, Italy

Processes of Microporosity Formation at Initial Stage Phase Transition

Computer experiments of ions implantation can be applied to assess the porosity in objects of cultural heritage. The pores appear under action natural and anthropogenic factors of environment, the estimation can be made thanks to existence parameters of similarity and processes periodicity accounting. The interaction of inert gas flux of 5-10 keV ions energy with lattice of solid are discussed. Formation of porous and stressed structures is about 10-100 msec. The initial (non-equilibrium) stage of the phase transition is considered as the superposition of two random processes: Clustering of gas monomers and their Brownian motion in crystal lattice of sample consisting of several layers. At phase transition the clustering of nuclei appears in result of the inert gas implantation into lattice in form of gaseous bubbles (blisters). Kinetic equations for function the distribution of gas bubbles in the layers of SiC and Mo, are replaced by equivalent SDE Ito–Stratonovich.

Keywords: kinetic theory, stochastic simulation, porosity, silicon carbide, pore clusters, self-organization, objects cultural heritage

Работа выполнена при частичной поддержке гранта РФФИ 18-01-00436

1. Introduction

Microporosity in materials is considered as the phase transition of the first kind assumed by random process of clustering in phase space of voids sizes [1, 2]. The arising gas bubbles are examined with ions of inert gas Xe^{++} with energies $5 - 10$keV and doses from 10^{15} up to 10^{17} ions/cm^2, implanted during about 100msec. In technical applications this process is called blistering. [2, 3]. Theoretical studies of an action of flows radiation on materials have fundamental meaning for clarification of nonequilibrium processes mechanisms, which are important for the forecast of silicon carbide, SiC, behaviour [4] or the prediction of set properties for new materials with disorderly distributed microporosity [5].

The plasma surface interaction during deposition of thin films as well defects formation in materials planed as thermonuclear reactors walls are the very important aspect is investigation of various physical effects, radiation- and thermal-induced processes as well as mechanical damaging accompanying the powerful impact considered. Creation on this basis of an effective computer simulation codes for evaluation, prediction and improvement of properties of construction and functional materials working at such extreme conditions is a new important application aspect of this scientific direction [2]. The turbulence theory is associated with the transition from chaos to self-organization and back, the same phenomena are observed during non-equilibrium stage of phase transition. The properties of Markov random processes are used to create mathematical models of rapidly flowing processes of the fluctuation nature in materials under conditions of radiation exposure. Turbulence as a form of motion of matter manifests itself in various environments, being a system consisting of many particles with numerous degrees of freedom and whose behavior is very difficult to control Numerous instabilities develop for the description plasma of which a mathematical apparatus has been created, including a large role fluctuations that are capable of destroying the expected modes of oscillation which in their turn can lead to new, unusual alterations of physical and mechanical properties of material [6]. For the plasma description a mathematical apparatus has been created [7]. The paper presents a model of gas bubbles formation in crystal lattice of an sample which consists of SiC and metal on metal substrate. Under the condition of «open» physical system (case of constant flux of Xe^{++}) the pores of nano-sizes are distributed on penetration depth of an inert gas. Another direction of researches connected with this type of experiments is to improve their properties by ion implantation technique. In some works attempts to investigate the gas diffusion processes taking place within the irradiated materials under different boundary conditions were undertaken. This question is of a great importance for all the above mentioned problems. Formerly in our works the damage and structure changes, produced in advanced plasma facing and constructive materials intended for inertial thermonuclear fusion reactor, have been investigated. In particular a possibility to realise combined or separate testing and treatment of materials under short pulses (10^{-7} sec)

2. Theoretical model of radiation damages in solid

The problems of damaging of materials and peculiarities of physical-chemical processes of surface melting and crystallization, thermal-mass transfer, formation and evolution of radiation defects, alteration of microstructure in conditions of impacts of extreme high pulse fluxes of inert gas will be carried out at the interface between several independent scientific directions – solid state physics, radiation chemistry, radiation material science and technology, plasma physics, physics and mechanics of destruction. Such inter-disciplinary approach to the problem under investigation will allow us to study comprehensively and in more details the nature of the phenomena as well as specific features of behavior of irradiated materials as a whole in non-equilibrium conditions created in the bulk of material by powerful ion's fluxes of short duration. Many problems of probability nature can be described using Brownian motion model and by Fokker-Planck-Kolmogorov and Einstein-Fokker equations. Molecular dynamics (MD) is the most widely used method for atomic-scale simulation. Much of our current understanding of, for example, primary damage in cascades, point defects and their clusters, crack-tip processes, comes from MD simulation. In MD, the classical equations of motion are integrated to obtain dynamical evolution of a system of atoms. The structure of the equation stochastic MD (stochastic analogue) assumes the presence of the standard Wiener process, in many cases it is related with model of Brownian motion, but these concepts can not be treated as identical ones because the first one indicates a physical process whereas the second corresponds to a mathematical object. We use stochastic analogue method for solution of kinetic equations. There arises a necessity to strictly distinguish between models (kinetic and stochastic) using stochastic differential equation Ito. In work [8] have been proven some conditions of existence and uniqueness of stochastic equations in sense of Stratonovich which introduced a new concept of solution, a so-called weak solution, assuming that it can be defined on an appropriate probability space with an appropriate Wiener processes associated with model initial stage of phase transition.

3. Model of defects interaction into lattice silicon carbide

3.1. Silicon carbide and model defects interaction into lattice. High radiation resistance of SiC in thin layer-coatings utilizing the unique properties of diamond-like materials makes them very perspective for industrial and other applications, for example, in the case when the plasma or inert gas fluxes can be harnessed to produce propulsion with high temperature of the exhaust gases. Nano-SiC materials seems will be more popular in the near future [4]. New data about the stability of physical and mechanical properties of these materials can be studied by means of computer simulation. The model of indirect elastic interaction of defects, each with other and with the boundary of layers is related with acoustic phonon's behavior, which is distorted by defects and their motion, which changes the distances between them, this

potential is long-range and self-consistent, alternating in sign character because we need to account summing up contribution from each couple interacting clusters. The model of elastic field in crystal lattice is approximated by the potential of clusters interaction into lattice derived from acoustic phonons, which is distorted by motion of defects under elastic indirect interactions of defects between themselves and with the boundary of layers. Defects are localized in potential wells of the elastic field with structures depending on distances between defects in lattice. The sizes of such structures, distribution of porosity and mechanical stress depending from density of defects were discussed. Here we pay attention on DF of defects versus its sizes in SiC layer during nonlinear stage of phase transitions. Damaging the crystalline lattice appears under the impact radiation such as laser processing surface, seasonal and diurnal changes in weather's conditions [9] as well as and other many kinds of active influence on the surface which has structure of nanosized layers. Properties of nano-modified materials, deposition thin films also as defects in materials which planned for thermonuclear technologies or semiconductor are able to be predicted by means computer simulation. The role of the fluctuational instability in the formation of porosity is studied, model was complemented by the Brownian motion of clusters with account this kind of potentials, diffusion is initiated only by potentials difference in points of lattice where gas defects stayed.

3.2. Analogues of collective processes in the lattice damage model. The specific feature of powerful radiation impact on material in this case is that the radiation dose is compressed to a very high extent – firstly in time (in the radiation source), and then (at absorption in a sample) in space. And if effective micro-volumes of the radiation impact of each individual particle inside material (for example, micro-volumes containing primary and secondary particles at absorption of fast ions) are overlapped during a certain time that is less compared with the characteristic relaxation time of the radiation-induced process (e.g. diffusion), this process acquires completely new quality. This type of interaction starts to bear evidence of a collective phenomenon. In some cases appearance of various synergy processes can be expected.

The turbulence theory is associated with the transition from chaos to self-organization and back, the same phenomena are observed during non-equilibrium stage of phase transition. The properties of Markov random processes are used to create mathematical models of rapidly flowing processes of the fluctuation nature in materials under conditions of radiation exposure. Turbulence as a form of motion of matter manifests itself in various environments, being a system consisting of many particles with numerous degrees of freedom and whose behavior is very difficult to control Plasma which consists of many particles with many degrees of freedom whose are difficult to control. Numerous instabilities develop for the description plasma of which a mathematical apparatus has been created, including a large role fluctuations that are capable of destroying the expected modes of oscillation, which in their turn

can lead to new, unusual alterations of physical and mechanical properties of material.

3.3. Porosity in objects cultural heritage. Majority objects of cultural heritage are under the influence of natural and anthropogenic factors. Frequently the qualities of multilayer structures are able to be lost under influence of dampness, of freezing, temperature change, ultraviolet radiation, the deposition of dust, of mechanical damages and others. Gaining knowledge about mechanics damaging objects of cultural heritage [9] is able to be related with study of defects nucleation due to actions radiation fluxes and stimulate study influence of other acting factors of environment. Self-organization processes widely known today: among them are the processes of streamlining the particles movement in plasma both recreated in laboratory experiments and observed in nature. It exists the fundamental problem: defects' origin in condensed matter or on the surface solid body models which can be seen as a plasma-like media The term "porous material" is related to a solid medium, either rigid or undergoing to very small deformations, and a system of voids otherwise indicated as pores. The pores allow the flow of one or more fluids, as water and/or gaseous mixture, in different phases, as liquid or gaseous phase. Porosity φ is a scalar property of porous medium which is defined by $\varphi = V_{void}/V$, where φ is porosity of the material, V_{void} is total volume of the medium which is occupied by void space, V is total volume. Note that $(1 - \varphi)$ is the volume fraction which is occupied by the solid skeleton. In particular, in this definition one takes into account only the interconnected void spaces. It is useful to distinguish between different kind of pores, potentially present in a porous material:
• open pores, which are connected one to another or with the external surface of the material;
• blind pores, which are open in only one side;
• through pores, which are communicating one to another;
• closed pores, which are isolated from the neighbors ones and they can be assumed as inactive to a transport phenomena.

The study of the deterioration of porous materials has an important application into cultural heritage field. This is true, in particular, for two reasons: first of all, because the original materials used in buildings and in monuments with historical value, e.g. stones, bricks, mortars, concretes, and so on, may have a porous structure, and then because the materials used for past restorations may be even of this type of materials. Thus, it is clear the importance of the knowledge of how these buildings' components undergo the effect of time. In parallel with the researchers working in the humanities field and art historians, a principal role is played by scientists who work in the experimental field as well as in the theoretical one, to provide the best analysis of the sample and design the most suitable restoration plan for it. Mechanisms of deterioration can be pointed out and analyzed after computer simulation of porosity structure into materials: moisture transport, heat transport and air pollution aggression.

These damage mechanisms are dangerous in general for all buildings or monuments which are exposed to the external environment, but they are obviously much more detrimental in the case of historical buildings or historical monuments because they have been exposed to the atmospheric surrounding for a long time.

The study of the deterioration of porous materials has an important application into cultural heritage field. This is true, in particular, for two reasons: first of all, because the original materials used in buildings and in monuments with historical value, e.g. stones, bricks, mortars, concretes, and so on, may have a porous structure, and then because the materials used for past restorations may be even of this type of materials. Thus, it is clear the importance of the knowledge of how these buildings' components undergo the effect of time. In parallel with the researchers working in the humanities field and art historians, a principal role is played by scientists who work in the experimental field as well as in the theoretical one, to provide the best analysis of the sample and design the most suitable restoration plan for it. Mechanisms of deterioration can be pointed out and analyzed after computer simulation of

In building materials, pores are distributed in an irregular manner and the typical pores-scale is at microscopically length.

They are constantly subjected to the terrestrial radiation that can lead to degradation effects. The radiation influence on these materials can be studied theoretically and the simulations of the damages of historical and artistic artifacts can be performed. Moreover the implantation of healing material into damages of cultural heritage for restoration and the problem of hardening of cultural objects can be studied. The typical natural terrestrial radiation is characterized by long influence of small irradiation doses, but in this work the irradiation effect is estimated equivalent to a short influence of big irradiation dose.

3.4. Thermography measurements of the porosity in walls. IR thermography is an experimental technique which allows to analyze large surfaces without damage or physical injury and allows to get information in short time: it is widely employed in the cultural heritage conservation. In this paragraph a brief description of this technique is presented. Thermography produce thermal maps of the surface area that is being analyzed. Thermal camera records temperatures of all the points on the surface and provides the thermal image, which shows the surface temperature distribution.

Thermal IR radiation recorded by the thermal camera, is composed by three components: emitted radiation, transmitted radiation and, finally, reflected radiation. Each of these radiation components is quantified by heat transported in each previous physical mechanism, and each heat flux is proportional to a specific coefficient which depends on several factors, like the kind of material, some surface properties of the building component, its temperature and so on. It can be noticed, in real building material the transmitted coefficient can be neglected and the radiation which is important in the thermographic measurement is composed by reflected and emitted

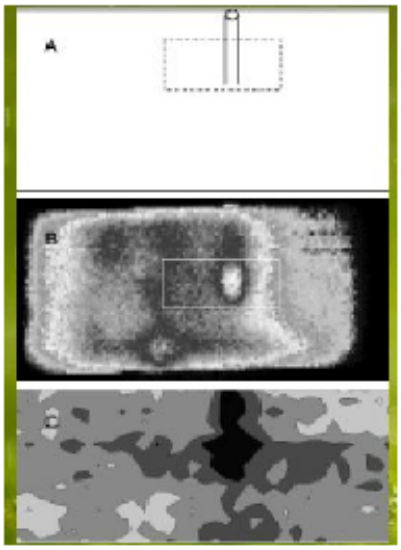

Figure 1. (A) Row figures showing the brick profile with the drill - made empty inclusion: the dashed rectangle delimits the tested area. (B) Compton spectrometry of all the mural stricture revealing the empty inclusion. (C) Image pixel density of the same tested area reconstructed by RCoSp measurements.

components only. Finally, it is worth stressing that thermography is a useful technique because of its rapidly response and its almost friendly use, but must be regarded as qualitative, in fact it can provide wrong or incomplete results. For this reason, it must be implemented with other techniques. At the end of this brief description, here some interesting applications of thermography on the historical buildings are here described. When a liquid evaporates, it become colder. In colored thermography diagnosis, moisture areas appear dark, for example blue or green, because they are colder than dry areas, which appear light, as yellow or red. This experimental analysis is used to detect a surface region with no just visible damage due to humidity, because moisture is not yet to the surface, but it still in the underlying layers. But it is less dangerous. Obviously, this kind of information is very important for the restoration planning. In the same manner, thermography analysis can be provided on a facade with visible alteration due to the capillary raises. With use of this technique, it is possible to determine, for example, he stopped of the capillary rises because zones undergo evident moisture damage results, everywhere, warmer than it should be, if there was still water. This thermal wave is due to the thermal agitation of atoms and molecules of the substance. In building physics, this is typically a surface phenomenon which interests only atoms in the most external layer of building component. In fact, in most of solids or liquids, the radiation emitted by the internal layers is self-absorbed by the material itself and in the same way, the radiation coming from the external surrounding is absorbed by the external layer of matter before this will able to achieve the inner part of matter object. In general, in building material, it can be possible to assume that the radiation emitted by an atom or molecule that is within 1 μm of distance to the

surface, is able to leave the material itself. Thermography can be employed for the study of frescoes detachment or, in general, of plaster detachment. In the first case, the measurement must be performed inside the church or other historical buildings and it is possible to exploit the external solar radiation as uniform heat source. In this situation, heat flux from the outside to the inside is stopped by a local defect which is characterized by a low heat conductibility, as air buildup which caused the detachment of the fresco plaster. For that local buildup, heat is stored on the reheated side of wall.

4. Kolmogorov equations for non equilibrium processes

A stochastic simulation model (see [2,10,11] and references therein) of initial stage of first order phase transition (or nucleation) is applied to study of blistering of Xe^{++} ions [12] in solids when vacancy-gaseous pores appear. A model of the amorphization process of silicon carbide and molibdenum layers material is represented by the Brownian motion of defects with a variable mass. The indirect elastic interaction of defects is taken into account through the crystal lattice factors (perturbation of acoustic phonons and Friedel oscillations of the electrons in the metal lattice) [2, 13]. In such an approach, the degree of porosity and a change in the strain within the layers are estimated. This nucleation model is correct under condition of the constant pressure and temperature to imitate physically meaningful thermodynamic ensembles. It is possible to estimate roughness at layer interfaces and stress using the pore DF from sizes and volume coordinates. The roughness appears because a blister comes to the layer boundary. Here we give an example of a calculation of the defect formation and the stochastic diffusion of defects in thin layers.

We use a kinetic model of the fluctuation unstable formation of Xe cluster nuclei and a model of the defect formation in metal and silicon carbide bilayers upon the boundary condition on the defect flow under the migration of blisters from a layer to a layer. In this case, the effect of boundaries on the concentration of defects in layer materials is important. Therefore, the calculation procedure [14] was modified and preliminary calculations of amorphization [15] of SiC/Mo layer materials were carried out.

Numerical analysis of helium blistering [2] in nickel has previously detected a nonlinear dependence between the average defect size and the sample temperature; porosity layers perpendicular to the incident flux; the dependence of this characteristic on the radiation dose, the temperature, and potential of the sample surface adjacent to the ion flux; and a change in the strain with bulk defect accumulation.

The following model is considered: blisters are assumed to be spherical Brownian particles (BPs), the mass of which changes because of the clusterization of gas phase nuclei in a solid lattice during the nonequilibrium fluctuation stage of the first order phase transition. Here, the coordinate of the BP center of masses changes under the effect of the total potential of the indirect elastic interaction between BPs, external and internal surfaces of the layers. Such potential has been obtained by quantum–empirical

method in [13] for weakly anisotropic lattice and point wise defects of lattice. Different characteristic time periods of blister nucleus clusterization (10^{-8} s) and Brownian motion (10^{-7} s) allowed us to divide the problem into physical processes Eqs. (1) and (2) and present each kinetic equation by its stochastic analog [16, 17]. A change in the blister size can occur as a result of inelastic collisions of gas nuclei with vacancies in their motion, in which Brownian diffusion appears in the medium. Space-time scales of fluctuational instability nucleation that observed at the initial stage of the phase transition are comparable with the sizes of a surface microstructure and of a time of their properties changes.

The Kolmogorov-Feller equation for blister size evolution (or clustering, i.e. MP in phase space of cluster sizes $\mathbf{G}$) at the point with the coordinate $\vec{r}$ is as follows:

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

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

Here $S_\alpha(p_\alpha)$ is the source of particles forming a nucleus, i.e. the source of "monomers" (vacancy or gas particles) with f_α — Maxwellian distribution function /DF/, $f_r(g,t)$ – the size of nuclei's DF at the point $\vec{r}$ of the lattice volume; T is the sample's temperature; D_g – the diffusion coefficient in the phase space $\{G\}$ defined according to nucleus sizes; $\Delta\Phi(g,\vec{r},t)$ – the thermodynamic potential of the nucleus formation, $\Delta\Phi$ is measured in kT, k is Boltzmann constant. Total potential energy of cluster formation $\Delta\Phi$ for case of vacancy-gas cluster formation may consist of a number of additive terms:

$$\Delta\Phi(g,\vec{r},t) = \Delta\Phi_\mu + \Delta\Phi_\sigma + \Delta\Phi_{el} + \Delta\Phi_b + \Delta\Phi_r + \Delta\Phi_t,$$

$\Delta\Phi_\mu = -\varphi(\xi_\beta - \xi_\alpha)g$. Here $(\xi_\beta - \xi_\alpha)$ is the difference of chemical potentials of the phases (monomers of vacancy/gas in lattice and blisters), φ is form factor. g is blister size measured in number of gas atoms. For spherical blisters $\Delta\Phi_\sigma = (36\pi)^{1/3}V_a^{2/3}\sigma_{bl}(1 - 1/3g^{-1/3})g^{2/3}$. σ_{bl} is the surface tension at the bubble–lattice interface and spherical form of blister. V_a is volume on gas atom. $\Delta\Phi_{el} = cg$ which takes into consideration elastic site bonds in the lattice (c). The rupture of relations of the atoms in the lattice around a blister is accounted by $\Delta\Phi_b$. Breaking of all ties of blisters is expected in model. $\Delta\Phi_r = \frac{\lambda_r}{\sqrt{g}}(k_x cos(2\pi(x-\psi_x)) + k_y cos(2\pi(y-\psi_y)) + k_z cos(2\pi(z-\psi_z)))$ is a part taking into account the difference between the nodes and internodes in the array. $\lambda_r, \psi_x, \psi_y, \psi_z, k_x, k_y, k_z$ are model parameters. $\Delta\Phi_t$ takes into consideration place of blister in tension fields occurring because of disparity of parameters of lattices Mo and SiC. The domain of instability of first order phase transition is determined by the equation $\Delta\Phi|_{g_{min}} = \Delta\Phi|_{g_{max}} = \Delta\Phi|_{g_{cr}} - kT$, where g_{cr} is thermodynamic critical blister size which is calculated from $\frac{d\Delta\Phi}{dg}|_{g=g_{cr}} = 0$.

D_g is the functional–coefficient of diffusion in phase space of cluster sizes $\{G\}$, $D_g = D_{g0} < g >^{2/3}$. Here D_{g0} is model coefficient which depends on the frequency of oscillations of the lattice atom, lattice parameter of material, radius of injected gas atom, modulus of rigidity of lattice material. The mathematical expectation of average size $\langle g \rangle = \int_{g_{min}} gp(g, \vec{r}, t)dg$ is expectation of blister size in lattice point $\vec{r}$. Here $g_{min} = 2$.

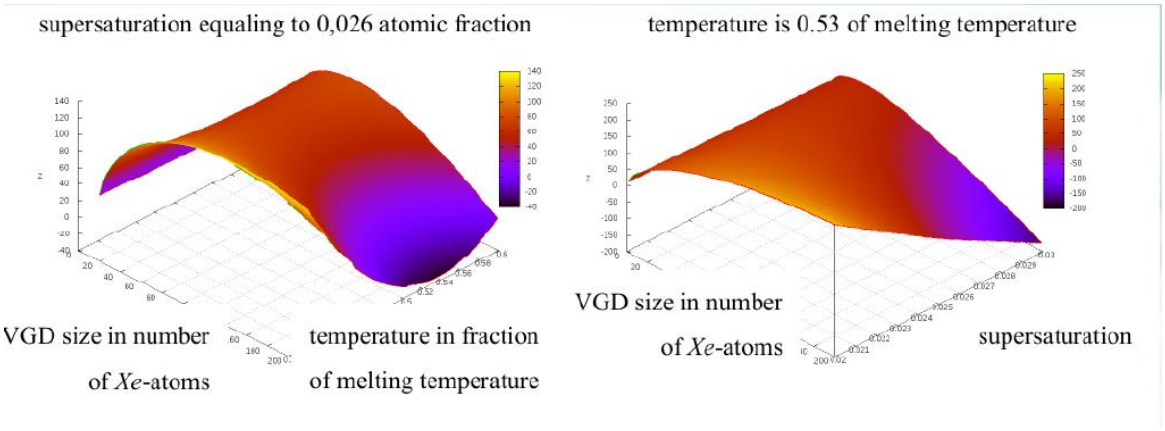

Figure 2. The Gibbs free energy (kJoul/mole) of vacancies-cluster (nuclei of the phase transition 1-st kind) versus their sizes in number of particles located in SiC lattice at $T/_{melt} = const = 0.53$ is presented.

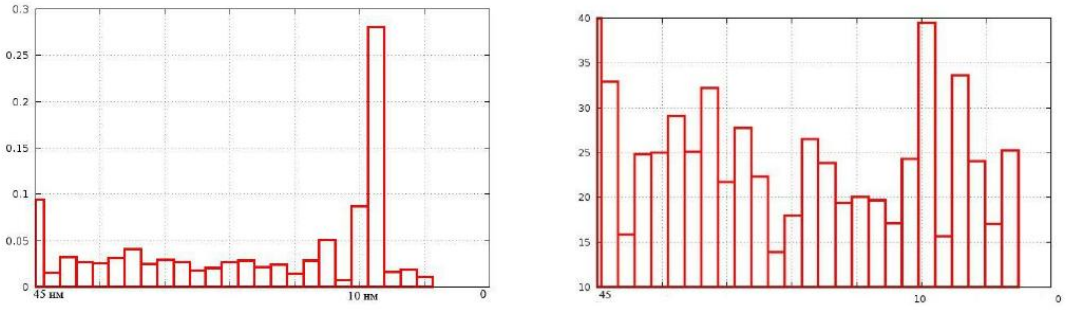

Figure 3. Left: Dependence of the total volume ratio defects consisting of embedded atoms of an inert gas, located in the layer SiC to the total volume of all defects implanted within 10^{-4} s; right: A histogram of the dependence of the mean radius of non-point defects consisting of embedded atoms Xe in the layers of the silicon carbide lattice from the depth of the layer from the surface The rate of alteration the surface area of walls pores into silicon carbide layer (which is filled xenon atoms, the X^{++} flux is equal to $10^{15} ion/cm^2$), divided on volume of layer (in $10^2 m^2/(m^3 s)$, depending on time are presented.

Einstein-Smoluchowski equation is written as

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

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

$$U(r) = U_{ij}(r) + U_{surf}(r) + U_{ph}(r) + U_{pore}(r),$$

where $f_g(r,t)$ is the DF from a Cartesian coordinates of a BP's which are counted from surface of the substrate. Masses of BP's (Mg) are measured in number of Xe atoms masses. Drains of the both monomers and BP's are designated as Q; their location depends on model. In the current model the location had been chosen on two boundaries of sample and on a boundary between layers. $F_z = -\frac{\partial U(x,y,z)}{\partial z}$ where $U(x,y,z)$ is the superposition of potentials of the indirect elastic interaction of BPs among themselves, with layer boundaries, and so on. The potential $U(x,y,z)$ is long-range and sign-variable. Interaction occurs through the perturbation of the lattice acoustic phonon's vibrations by defects of lattice and Friedel oscillations of the lattice electron density which are added to the model for metal lattice in [13]. The potential is similar to the potentials derived in [13] and potential of blister-blister interaction looks like follows:

$$U_{ij} = \sum_{i \neq j}^{N} \Big(\frac{b_r[3/5 - \frac{(x_i - x_j)^4 + (y_i - y_j)^4 + (z_i - z_j)^4}{(r_i - r_j)^4}]}{(r_i - r_j)^3} + \frac{a_r cos(c_r|\vec{r_i} - \vec{r_j}|)}{(r_i - r_j)^3} \Big)$$

where i, j are the numbers of interacting blisters if numerate them from 1 to N; b_r, a_r, c_r are model parameters of the respective layer lattice.

The dependence between concentration of VGD and the potential of elastic interaction of defects with each other and with the boundaries of the sample via acoustic phonon's and Friedel oscillations of electrons density is presented on fig. 4. Potential is normed on $(\frac{N_e V_F(2k_F)}{2\pi\epsilon^2} + W_{elast})\frac{\Omega}{kT}$, where Ω - volume of elementary cell, N_e - electron density, ϵ - permittivity, $W_{elastic}$ elastic moduli of the material, k_F is Fermi momentum of electron, $V_F(2k_F)$ is the Fourier component of the potential interaction of the electron with a point defect, k is Boltzman constant, T is temperature.

D_r is the functional-coefficient of diffusion in phase space of Cartesian coordinates of crystal lattice, $D_r = D_{r0} \cdot (1 + \alpha(\langle r^2 \rangle - \langle r \rangle^2))$. Here D_{r0} is model coefficient connected with physical parameters of problem and it depends on Gibbs free energy $\Delta\Phi(g, \vec{r}, t)$ and cluster mass, α is model parameter.

In case of $S = 0$ and $Q = 0$ kinetic equations of Einstein-Smoluchowski and Kolmogorov-Feller correspond to the following SDEs in the sense of Stratonovich:

$$dr(t) = \Big(\frac{F(r,t)}{M_g \gamma} - \frac{1}{2}\frac{\partial D_r(r,t)}{\partial r} \Big) dt + \sqrt{2D_r(r,t)} \circ dw(t) \tag{3}$$

$$dg(t) = \Big(-\frac{D_g(g,t)}{kT}\frac{\partial \Delta\Phi(g,r,t)}{\partial g} - \frac{1}{2}\frac{\partial D_g(g,t)}{\partial g} \Big) dt + \sqrt{2D_g(g,t)} \circ dw(t),\ g(0) = g_0. \tag{4}$$

The system of SDEs (3) – (4) was calculated by the numerical method [8], where

$$y = (y^{(r)}, y^{(g)})^T = (r, g)^T.$$

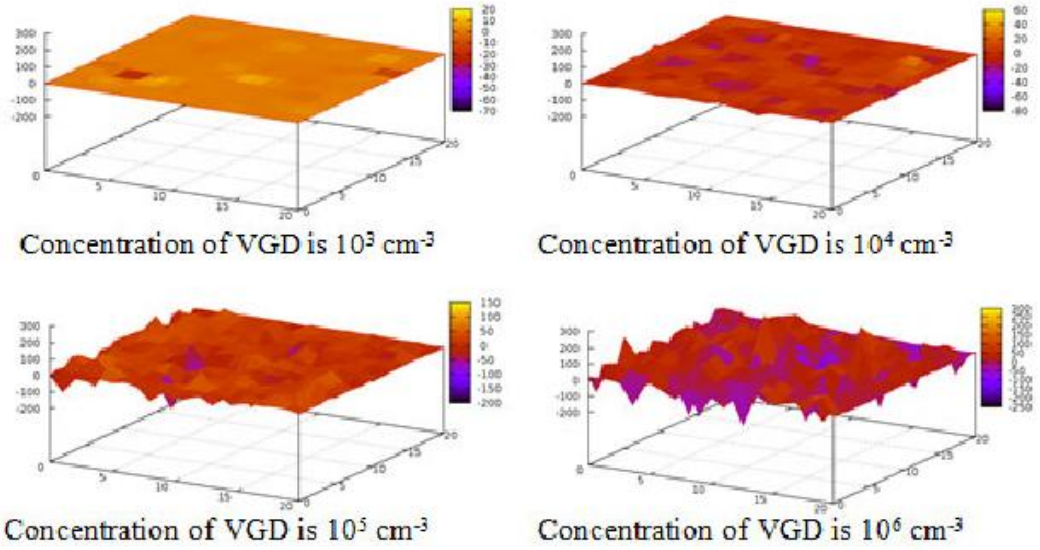

Figure 4. The projection of the potential $U(x, y, z_p)$ on the section plane of the irradiated p-th layer of silicon carbide is presented. The SiC section plane is perpendicular to the flux of ions of xenon and located in the middle layer of carbide in the initial time. The temperature is 1500 K, the radiation dose of $10^{15} cm^{-2}$, the ion energy of 5 keV. The size of the irradiated sample $3C - SiC/Mo$ is 240 nm x 240 nm x 240 nm along the axes x and y pending dimensions (one division corresponds to 12 nm, the total length on each axis is 240 nm).

The physical process of pores nucleation leads to instability of phase transition, its development simulated numerically by the algorithm which uses the Rozenbrok type methods for solving SDEs in the sense of Stratonovich. This scheme is a two-level modification of the explicit asymptotically unbiased numerical method for solving SDEs in Stratonovich sense [18], which has the second order of mean-square convergence for SDEs system with a single noise or with the additive noises. The scheme enables us to simulate of SDE's solutions which describe physical processes on different scales of characteristic times, among there : the clustering of pores in silicon carbide protective coatings and metal as well as Brownian motion of clusters in bilayer(SiC/metal). 10^6 samples of the solution were used in all numerical examples. The time mesh nodes $\{t_n\}$ include a uniform mesh with the step $\tau_g = 10^{-8}$ s and $\tau_r = 10^{-7}$, the time of finish calculation is $T_{fin} = 10^4 \cdot \tau_r$. Computer experiment of Brownian motion consists of several stages. The initiation of initial distribution of parameters (defects coordinates and forces of interaction of each with other due to indirect elastic forces in lattice through acoustic phonon's and Friedel oscillation of electron density) is first stage. Second stage is calculation of trajectories Wiener processes (SDE's solution) as model of BM into lattice under influence of collective field of phonon's vibration disturbed by lattice defects. So, DF of coordinates in phase space $\{R\}$ is determined. Macroscopic characteristics (such as porosity, value of

stress near defects and other) are examined. After then we determine new distribution of potentials values in region of model and coefficients of SDE's depended on defects DF by coordinates. The used method allows to consider collisions between vacancies and blisters during Brownian motion of defects of both types (blisters and vacancies). The recombinations of vacancies and blisters are taken into account in velocity of porosity formation calculation. The used kinetic code "Blister-Voids" consists on 7 program written in $C++$, one control module written in Python. The system RACS [19] is used for systematization and filing of calculations results.

The temperature, pressure and saturation gases (molecules-monomers and their clusters) and others needed macroscopic characteristics of multicomponent medium in form of state equation we find from the integrodifferential Boltzmann equations for kinetics of collisions which is able to be solved along with the equation for a Brownian motion clusters defects. DF's clusters on velocities and coordinates can be used similar to the methodology computer simulation [17] of gases and plasmas. As first step for representation of the initial state we derived the relation between thermodynamic parameters according assumption of equilibrium states for lattice and gases bubbles formation into solids during of phase transition at initial time period. The temperature stays invariable during short time of nonequilibrium stage of first-order phase transition (namely, the nucleation of gas) as well as we chosen the condition of "open physical system" on flux of ions Xe^{++} i.e. their values without changes. Values of local stresses which instantly changed due to the porosity in the lattice were calculated with accounting of Laplace leap of pressure on border of gas bubbles depending on their sizes. Influence of blistering on amorphous quality of lattice it possible to compare with offsets lattice nodes on the base calculations of the stationary characteristics of the elastic-plastic deformation solids [20].

5. Discussion of the results

The stochastic simulation method was applied to problem producing silicon carbide by penetration in porous thin layers of carbon- containing gas [21]. Processing of Si sample by inert gas for porosity formation is the preliminary processing before epitaxy. The DF of clusters into unit of volume SiC shown on fig. 7 as an illustration of stochastic simulation germ sizes calculated by solution of SDEs. More information about cluster formation in plasma discharge can see in [10]. This nucleation model is correct under condition of the constant pressure and temperature to imitate physically meaningful thermodynamic ensembles. The interaction potentials together with their parameters form a force field which defines how the particles in a system interact with each other. Such a potential has been obtained by quantum-empirical method in [13] for weakly anisotropic lattice and point wise defects of lattice. The implementation of this approach to indirect elastic interaction has been used to define Brownian motion of defects model. The criteria for selecting a force field takes into account the accuracy of maintaining or controlling collective character action for a bubble in

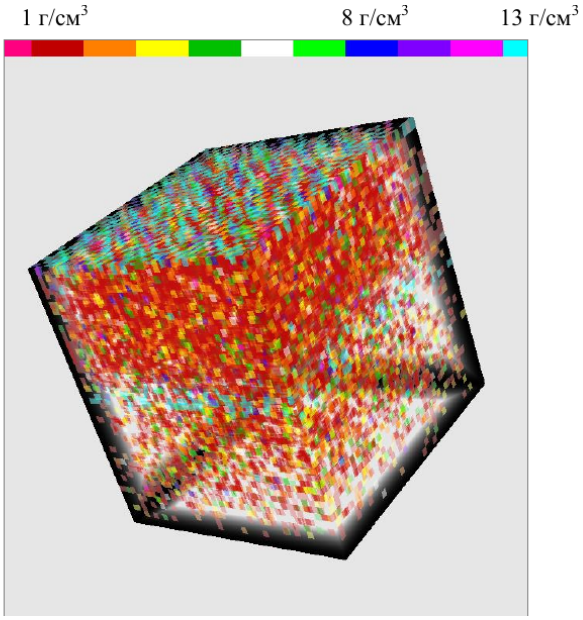

Figure 5. Dependence of density blisters in volume. The layer $3C - SiC$ has a size of 180 nm. Scale color matches shown on the top picture. The condition implantation of xenon ions with an energy of 7 keV was considered, the dose of irradiation $10^{16} ion cm^{-2}$, $T/T_{melt} = 0.53$.

lattice, transferability and computational speed. The temperature of solids was chosen in the range from $0.4T_{melt}$ up to $0.6T_{melt}$, where T_{melt} is the melting temperature of a least refractory material. This temperature was varied from 1156K to 1734K. The

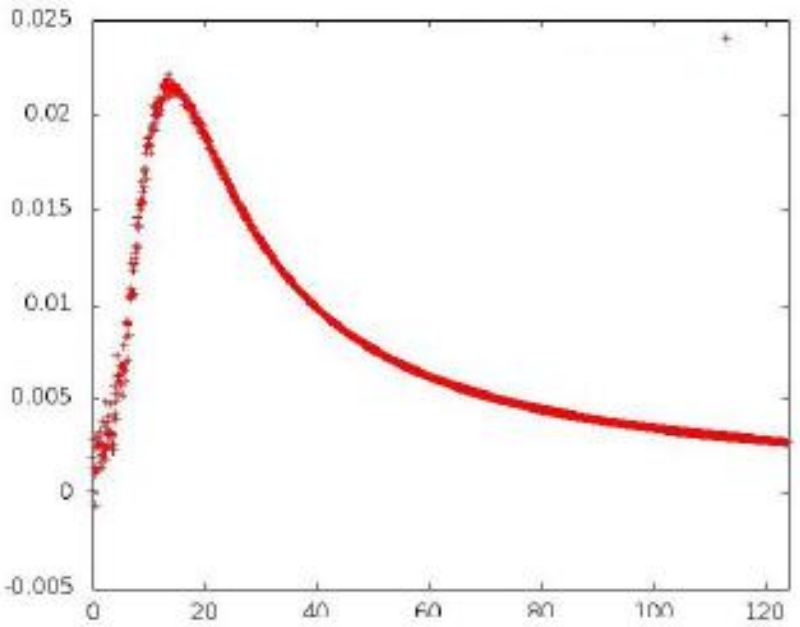

Figure 6. The rate of alteration the surface area of walls pores into silicon carbide layer, which is filled xenon atoms.

rate of alteration the surface area of walls pores into silicon carbide layer, which is filled xenon atoms, the gas flux is equal to $10^{15} ion/cm^2$, divided on volume of

layer (measured in $10^2 m^2/(m^3 s)$, depending of time are presented. There are 3 stages of nonlinear change relative growth rate of defect clusters over time: the turbulent stage growth, slowing of growth and reaching steady-state speed. Model of PT at nonequilibrium stage shows the dependence from initial size clusters: It will be various results: growth or degradation sizes during short time of nucleation. Any from clusters (of pores, of charged droplets) depends on model Gibbs free energy of germ PT formation. In points where the first derivative of thermodynamic potential in phase space of sizes is equal to zero we can see maximum of DF $p_r(g,t)$ of clusters which characterizes its behaviour during time of instability and it conform to the set of thermodynamic parameters of phase transition ($T = const, p = const$). The temperature of gaseous germ (for example, in the layer of SiC) is 0.58 of the melting temperature T_{melt} of SiC, the pressure of "$vapor$" Xe^{++} corresponds to $50Pa$, and the value of elastic stress from non coincidence of lattice parameters of SiC and Mo layers accounting in Gibbs free energy. Number of trajectories is 10^6, time step is 10^{-8} s, number of time step is 10^5. It should be noted that for the classical approach of thermodynamics to PT description it is impossible to get a nonequilibrium DF clusters (fig. 10) from clusters sizes. Time is measured in steps of algorithm.

Figure (7) illustrates changes of initial state (at the left) DF of gas-filled spherical defects depending on its radius (in angstroms) and depth from irradiated surface into two-layer sample of silicon carbide on molibdenum and final time moment (time steps of the algorithm are $5 \cdot 10^{-7}$ s), the temperature equal to 0.4 of melting temperature point the radiation dose is $10^{15} ions cm^{-2}$, 10^6 trajectories of random process were used.

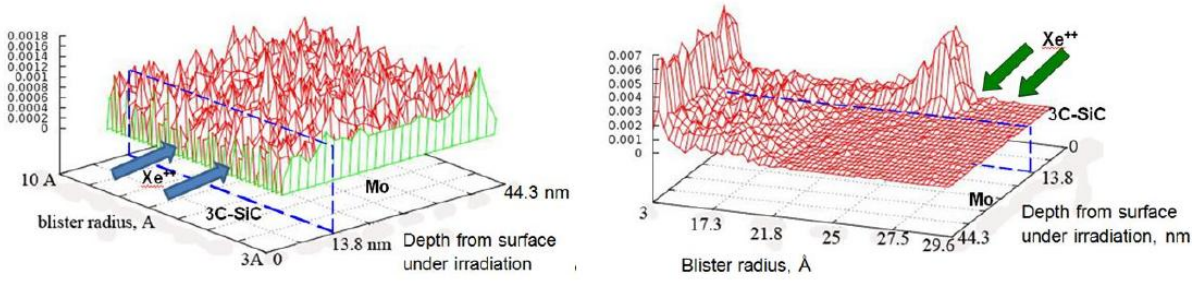

Figure 7. The surface of equal values DF VGD $f(g,z,t)$, for the initial state of the system $t = 0$ (left) and at the end of the calculation $t = t_{fin}$, the sizes of the calculated area are $438nm \times 438nm \times 44nm$. the thickness of the layer SiC is 13.8 nm. On the ordinate axis DF plotted, it normalized by the value of DF at the initial moment, on the axes x, y the sizes g of the VGD and the depth of the sample in the direction of the irradiating flow (dimensional units).

The formation of VGD in non-irradiated layer of two-layer structures consisting of layers of dielectric and metal by ion implantation with ions energies at which the average projection depths locate only the top exposed layer of dielectric is examined. The total thickness of two-layer structure is 300 nm, the thickness of dielectric irra-

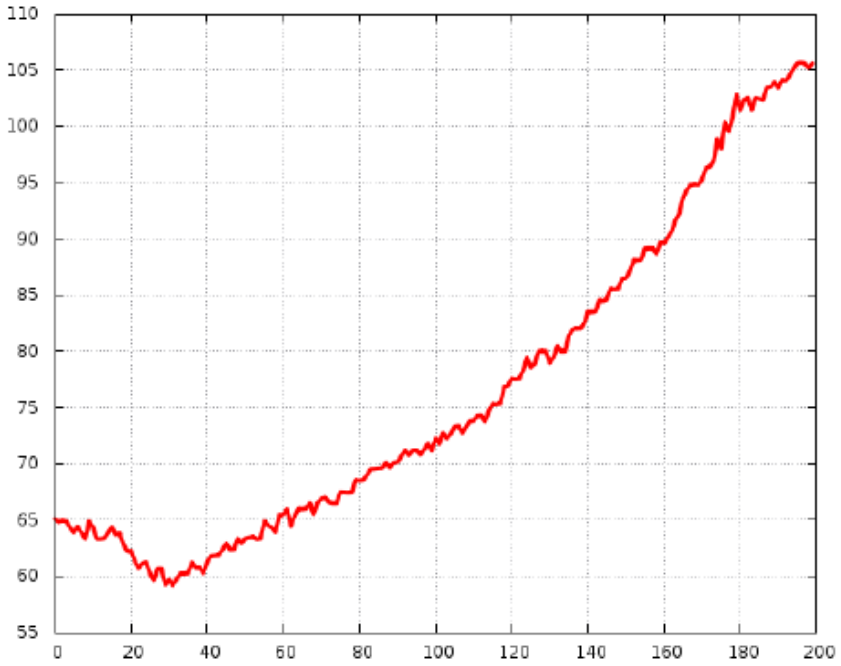

Figure 8. The expectation of the VGD size in the layer SiC established for the time $1\mu s$in the irradiation of the sample SiC/Mo with the size of the calculated area $438nm \times 438nm \times 44nm$ at $T = 1532K$, the ion energy was Xe^{++}= 4 keV, dose 10^{16} ion cm^{-2}, values $f(g,r)$ at $g(t=0)$ g_{crit}, on the ordinate axis-the average value of the size in the number of incompressible volumes of gas particles, on the abscissa axis-dimensionless calculation time.

diated layer is 150 nm. The profile density defects shows that VGDs penetrate into defended layer also, the same results confirmed by calculation of DF of VGDs and histograms of the porosity.

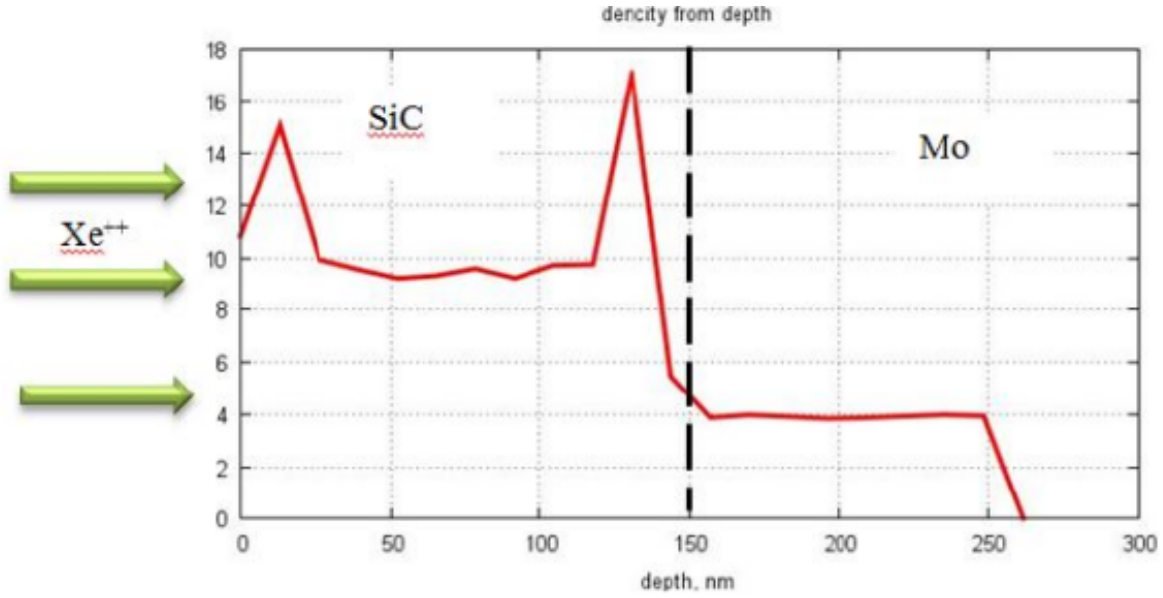

Figure 9. Distribution of porosity density calculated using non equilibrium DF

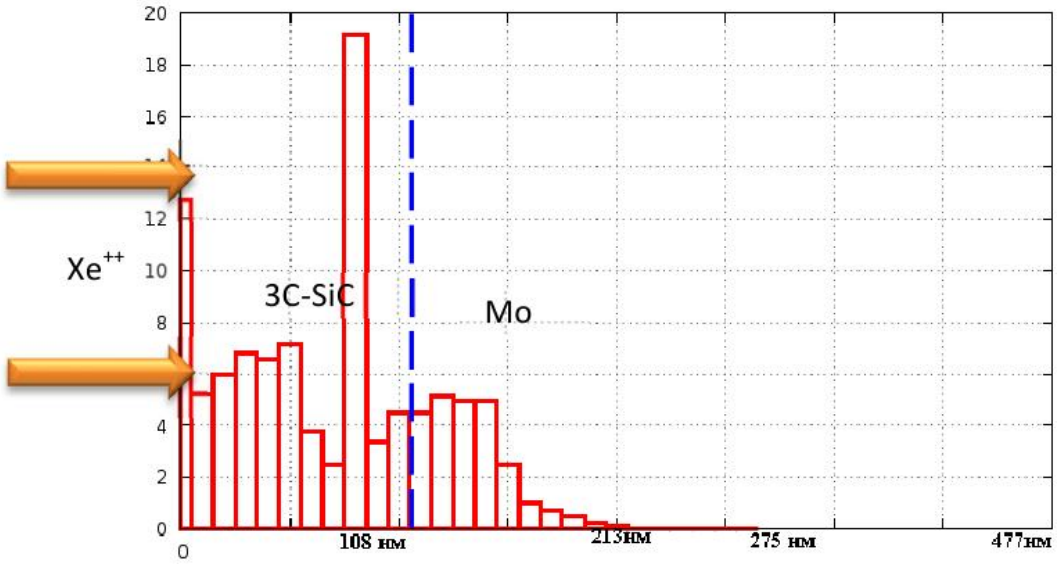

Figure 10. Histogram of porosity calculated using data: irradiation dose is $10^{15}cm^{-2}$, ions energy is 5keV.

The local stresses created by the VGDs (blisters) in the $j-$ m layer of the sample are calculated by the formula:

$$\sigma_j = \frac{0.195 r_{at}^2 \mu_{cd} b_b}{(1-\nu){a_m}^3} \int \sum_i \frac{\frac{1}{3}\ln(\langle g_i \rangle) + \ln(\frac{r_{at}}{b_b}) + \frac{4\pi\sigma_{surf}}{\mu_{cd} b_b}}{((x-x_i)^2+(y-y_i)^2+(z-z_i)^2)^{\frac{3}{2}}} (\langle g_i \rangle)^{2/3} dxdydz, \tag{5}$$

Where bubble creates at the point $\vec{r} = (x, y, z)$, located at the point $\vec{r_i} = (x_i, y_i, z_i)$ and having the size g_i, r_{at} is the radius of the implanted "monomer" of gas, the a_m is the lattice parameter of the irradiated material, μ_{cd} is the shear modulus, ν is the Poisson's ratio, b_b is the Burgers vector, σ_{surf} is surface energy. In (6) (x, y, z) - coordinates of the point where the blister is not located, but belonging to the layer j, (x_i, y_i, z_i) - coordinate of the center of mass of the $i-$ th blister with an average size $< g_i >$ calculated from $f(g_i, x, y, z_j, t)$ (DF of blisters), distance in (6) dimensionless, measured in units of a_m.

Respectively, pressure created by all bubbles at the point c radius with the vector $\vec{r} = (x, y, z)$ is defined by the Laplace expression. Increase of tension, which VGD created in the two-layer structure is nonlinear depending on time over times of the order of ms. Stress due to VGD development in model which taking into account plastic deformation, is about 2.2 times lower than stress in model taking into account only elastic deformation and lattice breaks. Maps of equal stress in cross section of two-layers $3C-SiC/Mo$ substrate is presented at initial time on fig. 11a and in finish time on fig. 11b. The cross section is parallel of Xe++ flow. Temperature is 1500K, irradiation dose is $10^{16}cm^{-2}$, ions energy is 7 keV, square under irradiation is 240 nm x 240 nm.

The porosity of two-layers structure silicon carbide/metal is calculated. The

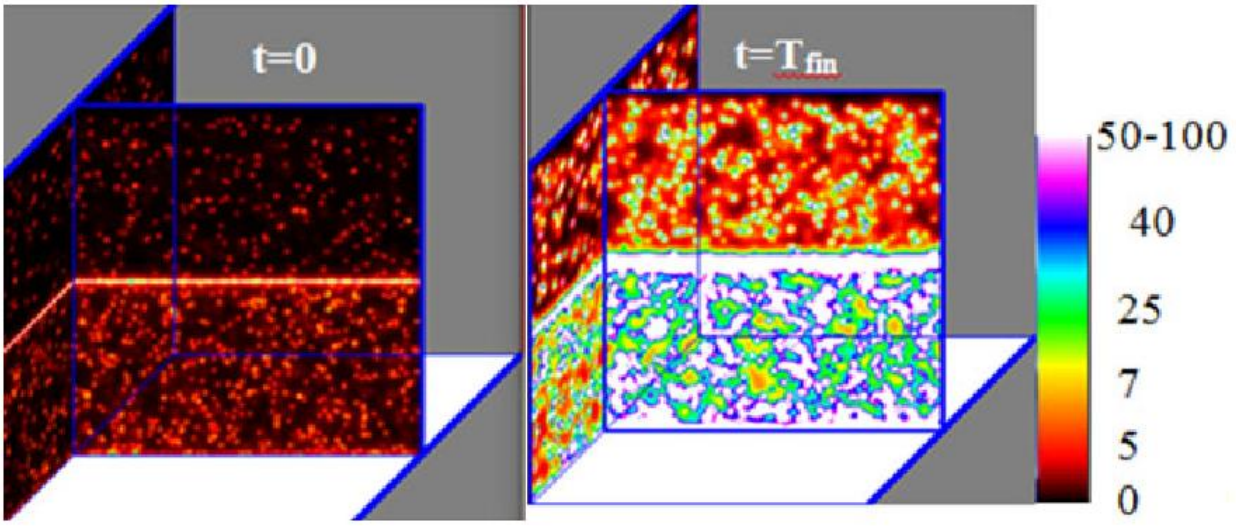

Figure 11. Color visualization of volume distribution stresses which appear due to VGDs development, influence of irradiation and the mismatch of lattice parameters of the layers is presented. Calculated values of stresses are measured in GPa. Flux of Xe^{++} penetrated and parameters of computer experiment are follows: temperature is 1500K, irradiation dose is $10^{16}cm^{-2}$, ions energy is 7 keV, square under irradiation is 240 nm x 240 nm.

maximum of porosity is equal to 48.6%. The average porosity of $fcc - SiC$ with thickness 125 nm is approximately 18%, the average porosity of Mo with thickness 110 nm is 13%, but if Mo thickness is 352 nm its porosity is 4%. The porosity of two-layers structure increases 6.31 times during fluctuation stage of VGD formation. The average porosity of silicon carbide with concentration of VGD 10^5cm^{-3} exceeds the average value of the porosity of the silicon carbide at a concentration of 10^3cm^{-3} at 8 times. The histogram of porosity distribution into thin layers of $3C - SiC/Mo$ at the end of initial stage phase transition (fluctuation stage), which is related to the average porosity of the sample at the initial moment of time, depending on the depth from surface under irradiation is presented on fig. 12. Temperature is 1530K, irradiation dose is $10^{16}cm^{-2}$, ions energy is 7 keV, square under irradiation is 240 nm x 240 nm. Crystallographic (001) plane is irradiated.

6. Conclusion

layers allow to calculate the porosity and stresses in the layers when the implementation of the gas phase in the material surface. The nuclei of silicon carbide can be modeled in the form of drops of the melt, in the form of islands of thin films, the conditions of the amorphous solidification and of nanocrystals of various politipic forms depending on the conditions of obtaining silicon carbide. Studied porosity in nano-sized layers depending on their thickness and temperature. Therefore, mathematical simulation is a numerical study 1) the possibility to use as a buffer layers of

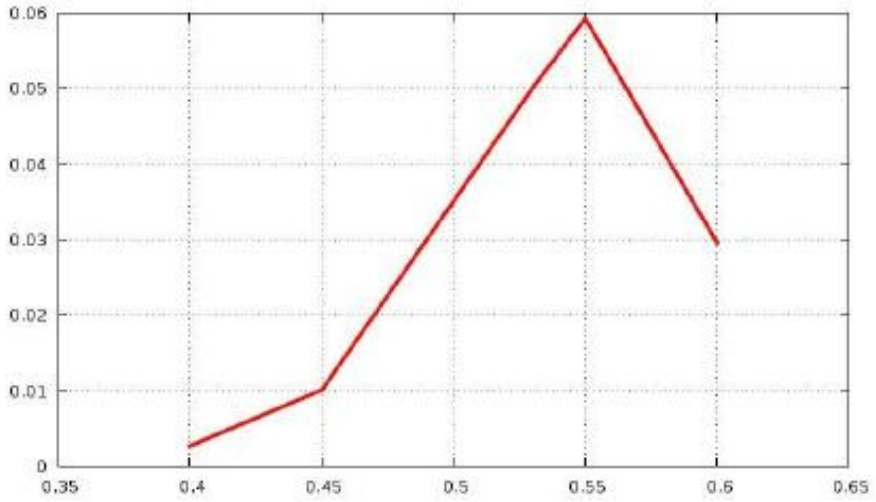

Figure 12. Dependence of averaged with volume of layer stresses arising in the silicon carbide layer under ionic implantation with Xe ions, on the layer temperature (measured at melting points material). The introduction of xenon ions with an energy of 7 keV was considered, the dose of irradiation $10^{16} ion cm^{-2}$.

nanoporous structure, which changes the voltage in buffer layer substrate, assessment of effective relaxation of mechanical stresses in the array, 2) features of the gas-phase deposition of a cubic silicon carbide in the discharge plasma and analysis of the physics of the mode of formation of crystalline powder of silicon carbide. Numerical experiments are needed for the consideration of the dependence of morphological, structural, mechanical and electrophysical properties of heterostructures SiC on the method (function) of their receipt and the applicability of instruments for electronics and Photonics. Complementary experimental methods acting on samples with various pores sizes scales (from mm up to nm) in object of architecture and paintings.

The weak nonlinear dependence of porosity and stress in unit of volume of SiC from temperature is observed in examined region of temperatures.

The stochastic simulation method [16, 17, 22, 23] is alternative method of numerical solution of quasi-linear Fokker-Plank-Kolmogorov equations using of general Rozenbrok methods for solution of SDEs in the sense of Stratonovich significantly reduce of computational complexity of problem and enhance the range of possible applications. Subjected by radiation into diamond-like materials (such asSiC) are analysed numerically. Porosity and stress in silicon carbide thin layer have been found by this method which is development of computer experiments and this approach different from traditional methods of Molecular Dynamics [24] and Monte-Carlo simulation [25].

7. Acknowledgements

Work was partially supported by RFBR grant 18-01-00436. We thank V.D. Levchenko, A.L. Bondareva and A.V. Ivanov for the visualization program and productive

discussions.

References

[1] Zel'dovich Ya.B. Eo the theory of the new phase formation, cavitation // Zh. Eksp. Teor. Fiz. — 1942. — Vol. 12, no. 11-12. — P. 525–538.

[2] A kinetic stochastic model of blistering and nanofilm islands deposition: self-organization problem / G. I. Zmievskaya, A. L. Bondareva, V. D. Levchenko, T. V. Levchenko // J. Phys. D: Appl. Phys. — 2007. — Vol. 40. — P. 4842–4849.

[3] Bondareva A. L., Zmievskaya G. I., Levchenko V. D. Stochastic model applied to plasma-surface interaction's simulation // European Physical Journal D. — 2006. — Vol. 38, no. 1. — P. 143–149.

[4] Andrievski R. A. Nano-sized silicon carbide: synthesis, structure and properties // Russian Chemical Reviews. — 2009. — Vol. 78, no. 9. — P. 821–831. — Access mode: http://stacks.iop.org/0036-021X/78/i=9/a=R02.

[5] Wiersma Diederik S. Disordered photonics // Nature Photonics. — 2013. — Vol. 7. — P. 188–196.

[6] Sigov Yu. S., Levchenko V. D. Beam-plasma interaction and correlation phenomena in open Vlasov systems // Plasma Physics and Controlled Fusion. — 1996. — Vol. 38, no. 12A. — P. A49–60.

[7] Sigov Yu.S. Computer Simulation: The link between past and future of plasma physics. Selected works. Composed by V.D. Levchenko and G.I. Zmievskaya. — Fizmatlit (Physics and Mathematics Publisher, IAPC Nauka), Moscow. (rus) 288 pp., 2001.

[8] Zmievskaya G.I., Averina T.A., Bondareva A.L. Numerical solution of stochastic differential equations in the sense of Stratonovich in an amorphization crystal lattice model // Applied Numerical Mathematics. — 2015. — Vol. International Conference «Difference Schemes and Applications» in Honor of the 90-th Birthday of Professor V.S. Ryaben'kii. — P. 15–29.

[9] Computational stochastic model of ions implantation / Zmievskaya G.I., Bondareva A.L., Levchenko T.V., Maino G. // AIP Conference Proceedings. — Vol. 1648. — 2015. — P. 230003.

[10] Zmievskaya G. I., Bondareva A. L. Crystalline islands of semiconductor films // Plasma Physics Reports. — 2011. — Vol. 37, no. 1. — P. 87–95.

[11] Zmievskaya G. I., Bondareva A. L., Levchenko T. V. Computer Simulation Model for First-Order Phase Transition Fluctuation Stage // Defect and Diffusion Forum. — 2010. — Vol. 297–301: Diffusion in Solids and Liquids V. — P. 502–507.

[12] Behrish R., Eckstein W. Physics of Plasma-Wall Interactions in Controlled Fusion // Plenum Press, New York NATO ASI Series, Series B, Physics. — 1986. — Vol. 131. — P. 413.

[13] Berzin A. A., Morosov A. I., Sigov A. S. Light-Atom Diffusion and Clustering at Crystal Surfaces // J. Phys.: Condens. Matter. — 1997. — Vol. 9.

[14] Bondareva A. L., Zmievskaya G. I. Computer Simulation Model of Nano-Islands Deposition // Nonequilibrium Phenomena. Plasma Combustion Atmosphere / Ed. by G. D. Roy, S. M. Frolov, A. M. Starik. — Torus Pres, 2009. — P. 75–81.

[15] Bondareva A. L., Zmievskaya G. I. Computer simulation of blistering in multilayer mirrors for EUV lithography // Journal of Surface Investigation. X-ray, Synchrotron and Neutron Techniques. — 2010. — Vol. 4, no. 3. — P. 480–487.

[16] Bondareva A. L., Zmievskaya G. I. Stochastic simulation of the fluctuation stage in the formation of thin films // Doklady Academii Nauk SSSR. — 2005. — Vol. 401, no. 4. — P. 471–475.

[17] Zmievskaya G. I. Stochastic analogs of nonequilibrium collisional processes // Plasma Physics Reports. — 1997. — APR. — Vol. 23, no. 4. — P. 340–353.

[18] Gardiner S.W. Handbook of Stochastic Methods for Physics, Chemistry, and the Natural Sciences (Series in Synergetics) V.13. — Berlin: Springer, 1984.

[19] Ivanov A.V. System of monitoring results and algorithms for problems of numerical simulation // Automation and modern technologies. — 2007. — Vol. 12. — P. 29–34.

[20] Kaminski M. On probabilistic fatigue models for composite materials. // Int J Fatigue. — 2002. — Vol. 22. — P. 477.

[21] Kukushkin S.A., Osipov A.V. A new method of solid-phase epitaxy of silicon carbide silicon: a model and experiment // Phys. Sol. State. — 2007. — Vol. 50. — P. 1238.

[22] Bondareva A. L., Zmievskaya G. I., Zakirov A. V. Nonequilibrium Nucleation: Silicon Carbide Clusters // Journal of Surface Investigation. X ray, Synchrotron and Neutron Techniques. — 2012. — Vol. 6, no. 6. — P. 975–978.

[23] Silicon Carbide Solid-Phase Epitaxy on a Microporous Substratum / G. I. Zmievskaya, A. L. Bondareva, Vl. V. Savchenko, T. V. Levchenko // Defect and Diffusion Forum. — 2012. — Vol. 326–328: Diffusion in Solids and Liquids VII. — P. 243–248.

[24] Norman G.Ed., Stegailov V.V. Method classical molecular dynamics: idea and reality // Nanostructures. Mathematical physics and modelling. — 2011. — Vol. 4, no. 1. — P. 31–58.

[25] Equation of State Calculations by fast Computing Machines / N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth et al. // J. Chem. Phys. — 1953. — Vol. 21. — P. 1087–1103.