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Stochastic formalism for nucleation under unsteady conditions

Miguel A. Durán Olivencia, Fermín Otálora Muñoz, *Laboratorio de Estudios Cristalográficos IACT-CSIC-UGr, Granada (Spain).* E-mail: maduran@lec.csic.es

Kinetics of nucleation are relatively well understood under steady-state conditions, the main problem still unsolved being the large uncertainties introduced by the stochastic nature of nucleation. To tackle this problem, a probabilistic formulation for nucleation kinetics is required instead of the deterministic formulations currently available. Some approaches in this direction have been presented mainly related to the derivation of kinetic information from experimental data [1], but a general formalism for stochastic nucleation is still incomplete at best.

A Langevin-type stochastic differential equation (LT-SDE) is proposed to mode the fluctuating behaviour of the cluster radius in the spherical shape approximation. Indeed, an analytical solution for the probability density function of induction time is obtained not only for stead but also unsteady work of cluster formation. The latter condition allows for the study of time-dependent (supersaturation, pressure, temperature, etc.) nucleation processes from a stochastic point of view.

Crystallization under unsteady conditions are getting very important in mainstream fields like protein crystal growth, where the small volumes involved and the wide metastable area in the phase diagram imposes the use of large supersaturation values induced by diffusion of the precipitant. In such conditions, the stochastic effects in nucleation are largely controlled by unsteady kinetics and can be responsible for the selection of the supersaturation at which nucleation happen (which is central for the quality of the crystals obtained) and, more importantly, the kinetic selection of polymorph.

[1] A. F. Izmailov, A. S. Myerson, S. Arnold, *Journal of Crystal Growth* **1999**, *196*, 234-242.

Keywords: stochastic, nucleation, crystallization

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Nucleation and growth of crystals within the frames of the quataron concept

Askhab M. Askhabov, *Institute of Geology, Komi Science Centre, Ural Branch, Russian Academy of Sciences, Syktyvkar (Russia).* E-mail: xmin@geo.komisc.ru

The problem of crystals nucleation has come into scientific use in XIX century as a problem of the origin of a new phase in the course of phase transition. More or less finished theory has been formed by the beginning of XX century. According to the classical molecular-kinetic theory of phase-formation, the nucleus of a new phase is formed as a result of consecutive joining of atoms to each other. With that, that grouping of atoms or molecules which has reached such sizes that can exist in equilibrium in the environment is called a critical nucleus. We alternatively suggest another two-step mechanism of crystals nucleation. According to this mechanism nucleation is preceded by the stage of clusterization of substance which results in the formation of special nano-size clusters in crystal-forming media (clusters of "hidden" phase or quatarons). Formation of clusters of hidden phase occurs on the mechanism of self-organization and is conditioned by specific behaviour of substance at nano-level. The top radius boundary of spontaneously formed clusters of "hidden" phase is limited by size

4δ where δ – approximately corresponds to diameter of cluster-forming atoms, molecules or other structural units. Namely clusters with radius $r \geq 4\delta$ are potential centers of crystallization. They, at observance of some not severe conditions, are transformed to crystal nuclei.

As to crystals growth, corresponding theoretical concepts in general were developed by mid of last century on the basis of solution of the problem on the nature of building units. The key competitive ideas for concepts development were:

1. Crystals grow by joining of separate atoms (ions) or molecules (Kossel-Stransky concept).

2. Building units at crystals growth are separate crystal blocks (Fedorov-Balarev concept).

In principle, realization of these two extreme variants does not contradict the general laws of physics and chemistry. The majority of modern models of crystals growth are built within the frames of these concepts. However every year collects more and more experimental data obtained, first of all, on the basis of direct researches of the structure of crystal-forming media by spectroscopic methods and observations over growth of crystals by means of atomic-force microscopy, testifying to more difficult character of crystal-forming and to existence of differently organized atom-molecular groupings in crystal-forming media. In this connection the idea on building units as particles of larger, than separate atoms or molecules, but not crystal particles is discussed and finds more and more proofs. The ideas on the multi-route and combined character of growth of crystals become dominating. As to our quataron concept, the mechanism of crystals growth lying in its basis is trivial and simple. Quatarons, appearing on a growing surface of a crystal, either break up to separate atoms (further - atomic growth) or form two-dimensional nuclei (layer-by-layer growth). In rare cases they can form fractal structures on the surface (fractal growth) or inhibit growth. On their fundamental properties quatarons appeared to be ideal structures as building units. Among the advantages of the quataron concept is that only it operates with nonequilibrium structural units at description of crystals growth, which, in turn, also takes place only in nonequilibrium conditions. The basic laws of formation and growth of crystals find explanation within the frames of the quataron concept.

Keywords: crystallization, nucleation, cluster.

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Direct AFM-observations of Dissolution Processes on Dioxydine Crystal Defects

Natalya N. Piskunova, *Institute of Geology, Komi Science Center, Ural Branch of RAS, Syktyvkar (Russia).* E-mail: piskunova@geo.komisc.ru

Presented here are the results of *in-situ* AFM (atomic-force microscopy) investigations of the crystallization in solution. It is shown that dissolution of the crystal surface of the organic compound of dioxydine ($C_{10}H_{10}N_2O_4$) simultaneously follows two fundamentally different mechanisms: 1) the mechanism of formation of hollow nucleus on the crystalline defects; 2) the layer-by-layer mechanism activated by screw dislocation. It is the first time when we have received successive images of dioxydine surface dissolution on dislocational spirals of different type. We have studied the differences in sculpture and behaviour of multifilar spirals formed by screw dislocations located at distance more and less then $2\pi rc$ (r_c – the radius of the critical nucleus). We show how the form of complex dislocation canal depends on position of canals of single dislocations. It has been established that growth and dissolution on the screw dislocations on the face (100) of dioxydine

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crystal occurs mainly due to the expansion of elementary layers of growth. They are 8.8 Å units high, which is equivalent to parameter *a* of a unit cell, and given the peculiarities of the specific structure, is also equivalent to one of the sizes of $C_{10}H_{10}N_2O_4$ molecule.

The statistical data processing reveals considerable differences in tangential dissolution rate on the two spirals, consisting of nine and four screw dislocations correspondingly. Right-screwing growth layers of the left spiral join, at some distance, the left-screwing steps of the right spiral, forming an even more complex source – a growth analogy of dislocational Frank-Read source. To calculate the tangential rates for such source, each image was overlaid by a special grid affixed to defined points – canals of dislocations. Then the position data of intersection points of grid meridian and the step contour were taken. Each two images required more than a thousand of coordinate readings. Then we schemed the step rate distribution for every image pair. The distribution came out to be bimodal, which required segregation of the results for the left and the right spirals. Each distribution was then approximated to the lognormal distribution, average tangential rates were determined as expectation value, and rate fluctuations were calculated as a mean-square deviation. The results show that for the left source steps the average tangential rate is two times greater than that for the right source ones throughout the whole experiment. On the whole, the tangential rate decreases towards the end of the experiment. The rate fluctuations for the steps of both groups also reveal an almost monotonous decrease. This means that the system is working towards equilibrium. The amount of substance in the solution is increasing and dissolution is going to give place to equilibrium. This brings forward an important inference: the left and the right part of the same growth source, located at a less than a micrometer distance from each other, have a different effect on the boundary layer of the solution. We have shown that the interface needs to have the horizontal concentration gradient of the substance which would provide a faster tangential rate of the left spiral at growth and a more active decrease at dissolution. The same assumption has been verified for bigger (100 mkm) hillocks.

Keywords: AFM, crystal, growth.

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In situ observation of stress and strain evolution during surfactant-mediated growth of Ge on Si

Hidehito Asaoka,[a]   Tatsuya Yamazaki,[a,b]   Shin-ichi Shamoto,[a]
[a]Quantum Beam Science Directorate, (Japan) Atomic Energy Agency, Tokai, Ibaraki 319-1195, (Japan). [b]Eiko Engineering Co., Ltd., Hitachinaka, Ibaraki 312-0024, (Japan). E-mail: asaoka.hidehito@ jaea.go.jp

Interplay of surface stress and surface free energy determines the growth mode of heteroepitaxial layers. Therefore, surface morphology is sensitive to the presence of a third species on the surface, so-called surfactant. For instance, it is well known that the Stranski-Krastanow (SK) growth mode of Ge on Si can be suppressed with the surfactant. In such a surfactant-mediated epitaxy (SME), a flat Ge layer grows on Si while the surfactant floats up to the growth front and always covers the Ge surface. The stress in the Ge layer is relaxed by injection of dislocations into the Ge/Si interface.

Recently, Bi has attracted a lot of attention as a surfactant in Ge/ Si(111) heteroepitaxy due to its ability to suppress Ge-Si intermixing and provide a chemical contrast between Ge and Si in a Scanning Tunneling Microscope (STM), allowing fabrication of self-organized Ge/ Si(111) nanostructures on the Si surface during STM measurement. In addition, low incorporation of Bi in the Ge layer allows to remove it from the flat Ge surface even after Bi-mediated growth.

We have focused on the stress and strain evolution during the initial stages of Bi adsorption on Si(111) 7x7 and Bi-mediated growth of Ge on Si(111). The stress and strain behavior and surface morphology were observed simultaneously by using real-time measurements of the substrate curvature and Reflection High Energy Electron Diffraction (RHEED). We find a clear difference in the surface stress between the clean Si(111) 7x7 surface and the Si(111) √3x√3 surface covered with one monolayer of Bi (1 ML = 7.8×10^{14} atoms/cm^2). Subsequent Ge deposition on Bi-adsorbed Si surface provides an increase in compress surface stress accompanied by simultaneous stress and strain oscillations. The compress stress is followed by clear stress relaxation at the critical coverage of 2 bilayers (1 BL = 2 ML) due to a variety of strain relief mechanism including injected misfit dislocation and increasing surface roughness on the Ge surface.

Keywords: epitaxy, heterostructure, stress

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Hydrothermal Synthesis of New Er$_x$Ni$_x$Zn$_{1-2x}$O Nanomaterials and Their Physical Properties

Abdolali Alemi, Saeideh Jannesar Ahmadi, Aliakbar Khandar
Department of Inorganic Chemistry, Faculty of Chemistry, University of Tabriz, (Iran). E-mail: Alemi.aa@gmail.com

Zinc oxide (ZnO) is a wide-gap semiconductor, which is transparent from the visible to infrared regions and is resistant to reductive ambient. Because of these properties, it is expected to be applicable as a material for transparent electrode and window layers of solar cells. Among the different methods of synthesis of ZnO nanostructures, the hydrothermal method is attractive for its simplicity and environment friendly conditions. In this research, New Er$_x$Ni$_x$Zn$_{1-2x}$O based nanomaterials were prepared by hydrothermal method. Zn (NO$_3$)$_2$.6H$_2$O (x≪ 1 mmol) and NaOH (0.6 g) were added to distilled water (60 mL), and stirred well for 20 min at room temperature. Afterwards, Ni (NO$_3$)$_2$.6H$_2$O and Er$_2$O$_3$ with various stoichiometric ratio were added, and the mixture was transferred to a 100 mL Teflonlined autoclave. The autoclave was sealed, maintained at 180 °C for 48 h, and then cooled to room temperature. The white precipitate obtained was filtered and washed with ethanol and water. Powder XRD patterns indicate that the Er$_x$Ni$_x$Zn$_{1-2x}$O crystals (x = 0.00-0.04) are isostructural with ZnO. SEM images show that co-doping of Er^{3+} and Ni^{2+} ions in the lattice of ZnO results in different nanorods and nanoparticle morphology. UV-Vis absorption and emission spectroscopy reveals mainly d-d electronic transitions of the Ni^{2+} ions in case of nanomaterials.

[1] R.E.I. Schrop, A. Madan, *Journal of Applied physics* **1989**, *66* ,2027-2031
[2] X. Chao, C. Lixin, S. Ge,L.Wie, Q. Xiaofei ,Y. Yaqin, *Journal of alloys and compounds,* **2010**, *497* , 373-376.

Keywords: hydrothermal, semiconductor , solar cells

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A Novel Three Dimensional Framework Induced by π⋯π Stacking of 2,2'-(alkylene-1,6-diyl)diisoquinolinium from Q[6]-based Pseudorotaxane

Gang Wei,[a]   Zhi-Fang Fan,[b,c] Xin Xiao,[b] Yun-Qian Zhang,[b] Sai-