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AFM study of instability of growing crystal surface morphology

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Dynamics of the NaCl crystal surface growth in a supersaturated solution has been studied using atomic force microscopy and statistical image processing. The mean tangential speeds and distances between the growth steps as well as the fluctuations of those parameters during each time interval have been determined basing on the found speed and distance distributions. A trend to grouping of thin growth steps at the surface and to formation of macrosteps has been revealed. The mechanism of that grouping is discussed as a consequence of kinematical waves of step density at the crystal surface. The surface morphology stability of the crystal growing from solution is discussed. The mathematical data processing shows mutual deceleration of neighboring steps during the experiment with the kinematical density waves.

Изучено поведение поверхности кристаллов NaCl в пересыщенном растворе с помощью атомно-силовой микроскопии и применения методов статистической обработки изображений. По найденным распределениям скоростей и расстояний между ступенями роста установлены средние значения тангенциальной скорости, расстояния, а также флуктуации этих параметров за каждый промежуток времени. Обнаружена тенденция к группированию тонких ступеней роста на поверхности и формированию макроступеней. Обсуждается механизм такого группирования, как следствие формирования кинематических волн плотности ступеней роста на поверхности кристалла. Рассмотрен вопрос морфологической устойчивости поверхности кристалла в процессе его роста из раствора. Данные математической обработки демонстрируют взаимное торможение близкорасположенных ступеней в течение эксперимента с кинематическими волнами плотности.

The atomic force microscopy (AFM) is a method of high information value making it possible to study the formation of a crystal surface and to measure at a high accuracy the tangential speed of the growth steps. According to the *in situ* AFM data, the factors influencing the formation of a real structure and evolution of the crystal surface at the nanoscale level are the step speed fluctuations, the features of the step interaction, the macrostep formation and decay. Our experiments were carried out in the contact mode (the force level of 10^{-8} to 10^{-9} N) at room temperature using an ARIS 3500 atomic force microscope (Burleigh Instruments, U.S.A.). The standard silicon cantelevers from Burleigh Instruments (rounding radius of the needle tip 10–15 nm, rigidity 0.1 N/m) and from Veeco Instruments (rounding radius of the needle tip 7–10 nm, rigidity 0.1 N/m). For the investigation, we grew NaCl crystals were grown by the solvent evaporation at room temperature. The solutions were prepared using distilled water and water-soluble salt samples of analytically pure and pure grades with total impurity content varying from 0.001 to 0.05 wt. %. The crystals were selected with the (100) face oriented in the course of growing in the crystallizer downward (in the diffusion limitation mode) and upward (from here on, the first and the second experiments, respectively). The cell with the crystal was installed into a holder of the scanning AFM block and filled with the necessary amount of mother solution. Up to 100 scannings were done with 40 s intervals till the solution was depleted.

The AFM provides three-dimensional images of a surface, but does not allow to measure directly the normal growth rate that is a result of averaging over the surface area as well as over the time. Besides, the locality of AFM scan areas does not allow to judge the similarity of the phenomena over the whole face area. We have developed a fundamentally new method to process the AFM images of growing crystals that makes it possible to determine the dynamic peculiarities of crystal growth from solution [1].

On the studied areas of 7×7 μm^2 size, we have detected in both experiments similar growth steps of 1 nm height and higher that moved along the surface in the course of growth at different tangential speeds in the same direction with respect to the probe movement one (Fig. 1). We have classified the measured heights into three groups according to their behavior (the step speed depends on its height): extremely thin (up to 5 nm), thin (from 5 nm to 20 nm) and thick (from 20 nm and higher). The empiric distributions of the speeds and intervals between the steps in the two experiments were used to determine the values of mean tangential speed and mean distance as well as the fluctuations of these parameters for each time period (Fig. 2). The obtained data allow us to determine the dynamic peculiarities of crystal growth at the steady growth stage. The growing surface steady growth stage is evidenced by the constancy of normal speed R and invariability of its dispersion δR in time [2]:

$$\delta R = \overline{R} \cdot \left(\frac{\delta v_{tg}}{\overline{v}_{tg}} + \frac{\delta x}{\overline{x}} \right) \to const. \qquad (1)$$

The dispersion of normal growth speed is defined by dispersions of step tangential speeds v_{tg} and intervals between them x that are calculated from the histograms of step speed and frequency distribution approximated by the curves of logarithmically normal distribution. The data on the step speeds were distance-averaged for the steps over 50 nm interval. The average speed value was assigned to the middle of the averaging interval. In the first experiment, the average speed values vary from 3 to 6 nm/s, in the second one, from 6 to 27 nm/s.

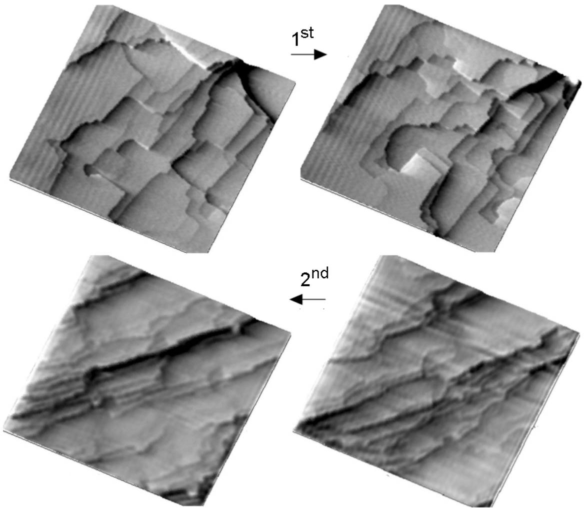

Fig. 1. Step movement on the growing surface of NaCl crystal in two experiments. The time interval between the images in 1st experiment is 1.3 min, in the 2nd experiment, 6 min. The image size is 7×7 μm^2.

Fig. 3 shows that fluctuations of normal speed δR in the first experiment remain almost constant throughout the 20 min observation, and reduce slightly towards the end. This evidences that the first system under investigation approaches the stationary growth state. In the second experiment, a considerable increase of the average tangential step speed (Fig. 2) and of the normal growth speed towards the end of the experiment (Fig. 3). For the second experiment, we distiguished three special areas marked by a sharp decrease ("drop") of fluctuation amplitude. The Fast Fourier transform shows the thrice repeated formation of kinematic density waves of growth steps at the crystal surface. Fig. 4 presents a generalizing curve that shows the ratio of maximum amplitude corresponding to the minimal frequency to the surface area under the Fourier spectrum. It is noteworthy that this occurs in the time-intervals with sharp shift of parameters fluctuations determined by statistic calculations, i.e. in the time intervals from the 4th to the 10th, from the 14th to the 17th, from the 21st to the 25th minute of the experiment (Fig. 2). As to the first experiment, no peculiar areas have been seen on the generalized plots. The second experiment has revealed considerable increase of normal speed towards the end of the observation (from 0.1 nm/s to 0.5 nm/s), whereas in the first experiment,

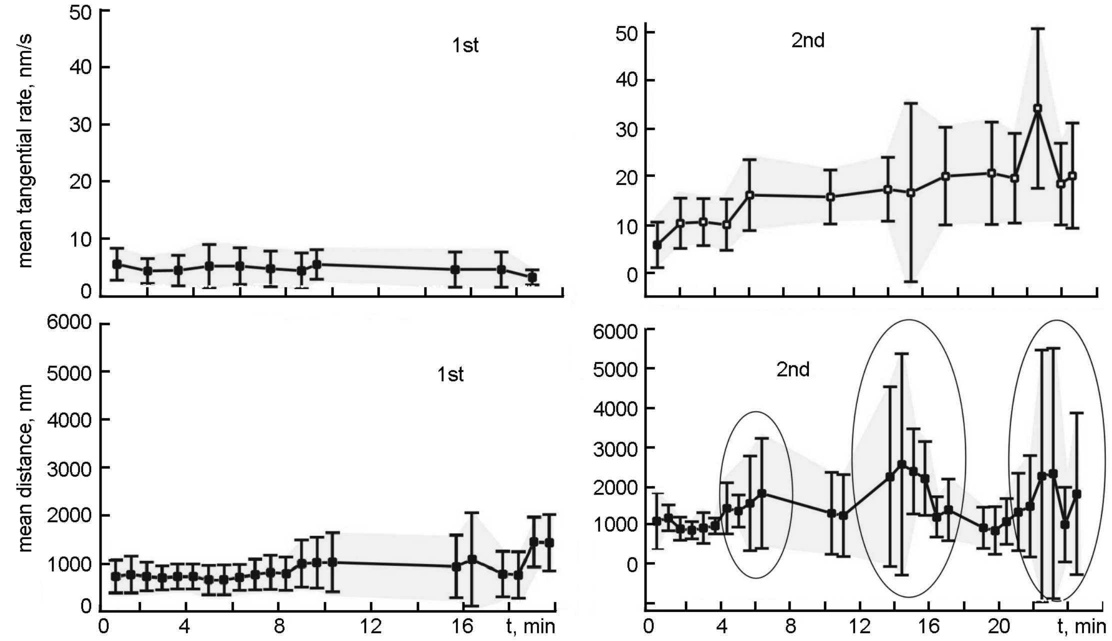

Fig. 2. Fluctuations of mean tangential step speed and the mean step spacing in two experiments. The circled areas are the time zones with formation of kinematic density waves.

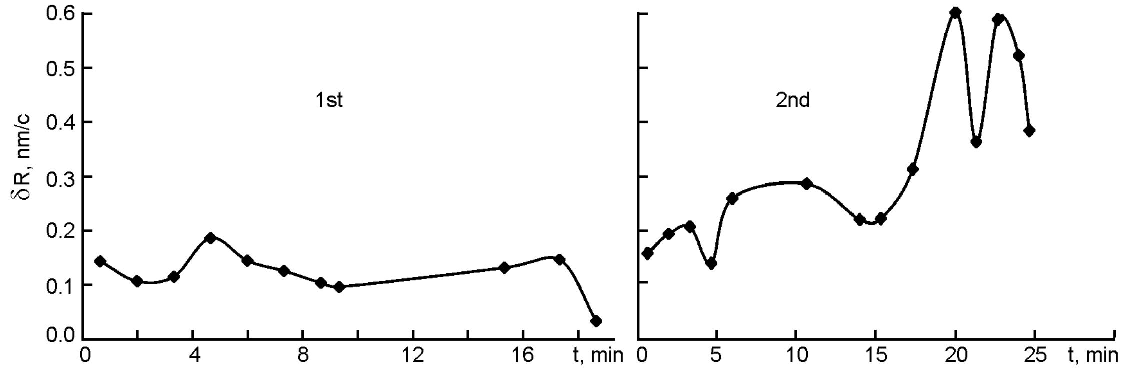

Fig. 3. Fluctuations of normal growth speed in two experiments.

the normal rate reduced from 0.16 mn/s to 0.04 mn/s towards the survey end. This happened in the conditions of no new matter inflow to the crystallizer and no vaporization of liquid from the free surface. Thus, as the supersaturation decreases at the end of experiment both the normal growth speed increase and increase of its fluctuations may occur.

The anomalous behavior of the systems under study can be explained taking into account that the three peculiar organization areas at the crystal surface being distinguished when considering statistically the AFM result from formation of certain structures in the course of growth, having a period exceeding the diagonal of the scanning area. It is possible that the grouping of the steps in this case is only a formation consequence of such structures. The self-organization in non-equilibrium systems may cause intensification of fluctuations, for example, at the generation of dissipative structures [3]. In particular, using the calculation of dissipative threshold, we have shown [4] that in two first time zones of the plot 2, the dissipative structures are formed and a macroscale work (i.e. the kinematic wave advancement) becomes possible. For the third time zone of the second experiment, the equilibrium condition of the dissipative structure is met.

In the second experiment, the growing crystal surface seems visually to be more smooth than in the first, and the growth steps do not change the direction during the

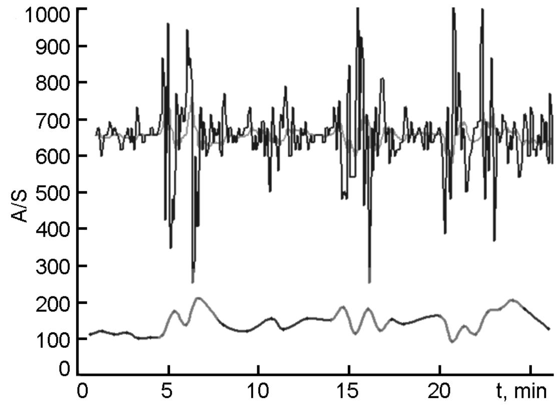

Fig. 4. Kinematic waves of the growth step density on the crystal surface (2nd experiment).

experiment (Fig. 1). However, the calculations have shown that both cases under consideration are examples of morphologically unstable surfaces. In the first case, this instability is much less apparent. Fig. 5 presents the results demonstrating the influence of step spacing on the step speed througout the both experiments. Note that the first and the second experiments were done in identical conditions, the only difference confined to the studied faces being turned upwards and downwards, respectively. It is clear from the second experiment that one and the same step spacing corresponds to a wider speed range. The parabola describing the second experiment data is more steep than that describing the first one (Fig. 5). We can suppose that the approximative dependence $\nu = a + bx + cx^2$, where $c < 0$, is universal for other substances, too. The negative coefficient c means that the reduction of the step spacing results in the decrease of the step speed and to deceleration of close neighboring steps, like in the beginning of the second experiment. The step speed also decreases if the step spacing exceeds a certain value (around 1500 nm for the second experiment), which physically denotes the lack of building material. This happens when the supply of building units to the surface occurs slower than the process of their building into the crystal, i.e. the growth rate is limited by volume diffusion.

Both faces have practically identical normal growth rate at the beginning of the survey (0.1 nm/sec and 0.16 nm/sec). The first face reduces the normal rate by the

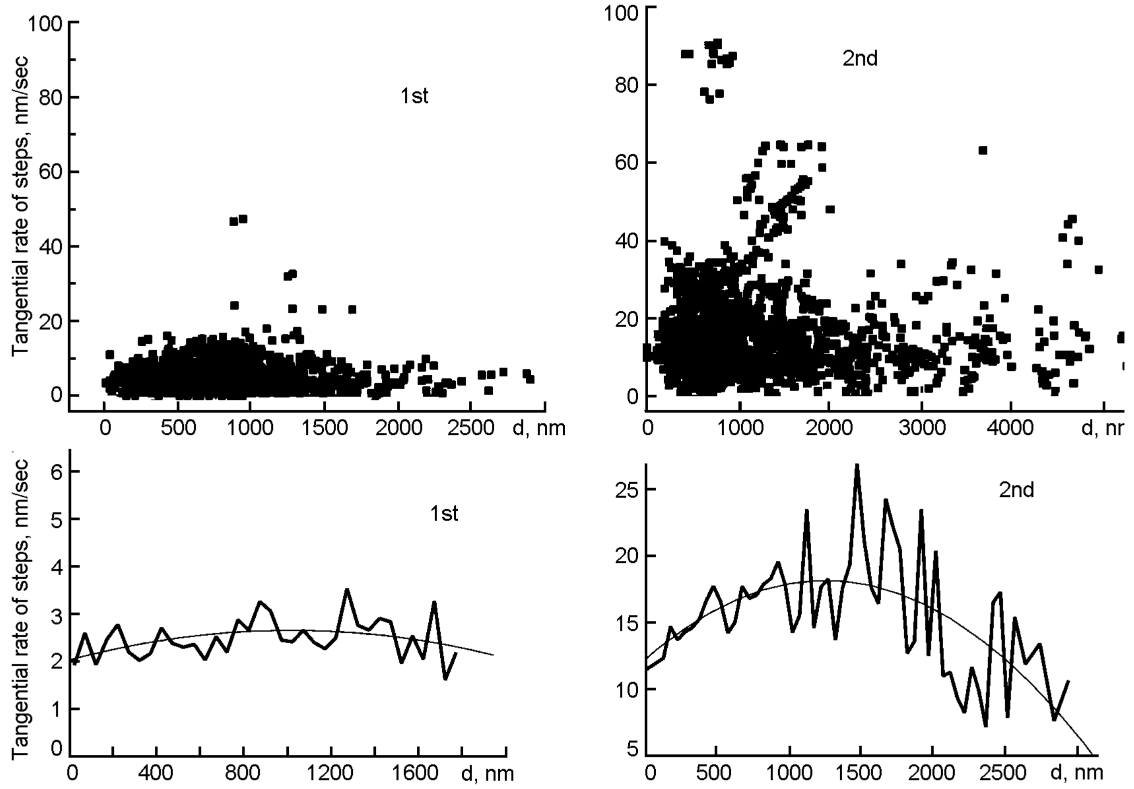

Fig. 5. Dependences of the growth on the step spacing distance between the steps during the first and the second experiment.

end of the survey to 0.04 nm/sec, whereas the face with kinematic density waves considerably increases its normal rate by the end of the survey (up to 0.5 nm/sec), despite the exhaustion of the solution.

Thus, the growth rate of crystal face can be limited by surface diffusion in one of the two identical experiments and by volume diffusion (transport processes).

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АСМ дослідження нестабільності поверхневої морфології кристалів NaCl, що ростуть

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Досліджено поведінку поверхні кристалів NaCl у пересиченому розчині за допомогою атомно-силової мікроскопії та застосування методів статистичної обробки зображень. З найдених розподілів швидкостей та відстаней між сходинками росту встановлено середні значення тангенціальної швидкості, відстані, а також флуктуації цих параметрів у кожному проміжку часу. Виявлено тенденцію до групування тонких сходинок росту на поверхні та до формування макросходинок. Обговорюється механізм такого групування, як наслідок формування кінематичних хвиль густини сходинок росту на поверхні кристала. Розглянуто питання морфологічної стабільності поверхні кристала у процесі його росту з розчину. Результати математичної обробки демонструють взаємне гальмування близько розташованих сходинок на протязі експерименту з кінематичними хвилями густини.