Morphological and kinetic consequences of scratching of the growing crystal surface

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Abstract. Using the atomic-force microscopy (AFM) it is shown that even a minor local contact of an AFM probe with a growing crystal surface at the nanoscale leads to important crystallogenetic (morphological and kinetic) consequences. These non-linear effects are the thickening of steps, the huge fluctuations, and a loss of morphological stability of the surface even at the distance of dozens of micrometres from the contact area. Near the equilibrium state, we observed the phenomenon of simultaneous growth and dissolution at the neighbouring points of one step.

1. Introduction
Most natural crystals have traces of selective dissolution, a mineralogist sees such traces not merely as an evidence of the destruction process, but as an imprint, which allows him to reconstruct one of the historical stages of the crystal and its medium. There were attempts of experimental studies of crystals’ growth after their mechanical scratching, which led to a double increase of the growth rate. It was driven by the appearance of the more intensive growth centres [1]. Nowadays, the most informative method that enables to observe the growth and the dissolution of a crystal’s surface at nanodimensional scale is atomic force microscopy (AFM). An AFM probe can also be used as a nanoindenter patterning the growing surface. This fact was already used in a number of works studying the processes on the surface after being affected by the probe. In particular, in Ref. [2] it was shown that thin steps in a protein crystal generated from a scratch gradually aggregated in a macroscopic step with their subsequent surface smoothing. Redistribution of solute material during relaxation of a KDP crystal scratch is driven by a reduction in surface free energy, as described in well-known laws [3]. However, the possibilities of using AFM not only for observing the surface evolution, but also for studying kinetic peculiarities of crystals’ growth after the mechanical impact have not been fully investigated yet.

Therefore, in this work, using AFM, we have studied nanodimensional morphological and kinetic changes happening on the growing crystal’s surface in the area of scratching. The results are compared to crystal’s growth peculiarities without special external impacts.

2. Experimental

2.1. Model crystal
As a model, we have used dioxidine’s crystals (2,3-Bis(hydroxymethyl)quinoxaline 1,4-dioxide, C₁₀H₁₀N₂O₄). According to our X-ray structural analysis (Diffractometer Shimadzu XRD – 6000,
radiation CuKα, internal standard Si), dioxidine belongs to monoclinic system, its unit cell parameters are 8.79 Å, 15.74 Å, and 7.99 Å, beta is 102.29, and cell volume is 1081.58 Å³.

2.2. Exclusion of impurities impact
A special attention was paid to the exclusion of impurities impact on the active processes. To achieve that, the dioxidine’s solutions were thoroughly analysed using a mass-spectrometer with inductively coupled plasma Agilent 7700x. The concentrations were calculated with calibration lines set by standard solutions “High Purity Standards” with elements’ concentration of 10 mg/l. All the dioxidine solutions contained impurity traces – hundredths in mg/l.

2.3. Instrument
The investigations were carried out on an atomic-force microscope Ntegra Prima (NT-MDT, Russia) with full and intermittent contacts with a surface. We used standard silicon cantilevers (NanoProbe, Great Britain) with curvature edge radius of 5 nm. The investigations were carried out at room temperature (20 ± 2°C) in constant humidity. Snapshot “drift” from one shot to another is excluded as fixed points (dislocation channel exits) control was used.

2.4. Methods
The crystals for our in situ studies were grown directly in the fluid AFM cell. When the feedback was switched off, an AFM probe-indenter was scratching the surface.

To calculate tangential rate, each image was overlaid by a special grid (based on gnomonic projection), affixed to certain points – the channels of dislocations. Then the position data of the intersection points of the grid meridian and the step contour were taken. Each two images required more than a thousand of coordinate readings. The accuracy of coordinate measure was discretization step, which was two hundredth nm for an area of 15×15 µm². The rate formula included a time correction, which was the function of the point y-coordinate on the step. Then we schemed the step rate distribution for every image pair. Each distribution was then approximated to the lognormal distribution, average tangential rates were determined as mathematical expectation values, and rate fluctuations were calculated as mean-square deviations.

3. Results and discussion
Observation of growth and dissolution of the surface after scratching has shown that even a minor local contact of an AFM probe with a growing crystal surface at the nanoscale leads to important crystallogenetetic (morphological and kinetic) consequences. Apparently, strains appearing in the contact area are relaxed by defect formations, due to which local dissolution arises (Fig. 1). We carried out experiments with a mechanical deformation on topographically different parts of a growing and dissolving crystal. First, we scratched the place of layer-by-layer growth and then the top of the dislocation hillock.

3.1. Dissolution on the scratch
On a flat surface in the undersaturated solution, we drew the letter "O" with the probe moving it counterclockwise. Almost two hours of observations showed an intensive dissolution of the surface in the area of the scratch, which affected the surrounding surface very little (Fig. 1). In the mid of the experiment, there occurred enlargement of dissolving steps, and then they began to split into more thin ones. We have discovered anisotropy of dissolution rates, connected with one of the axes of the second order, along which the pits were eventually extended. It can be seen that the defects spread deep into the crystal.

3.2. Layer-by-layer growth area
In this area, the tangential rate of equidistant steps almost of the same height was 0.9-1.8 nm/sec. (Fig. 2, snapshot 1). Using the AFM probe, two parallel scratches were drawn on the move and against of the steps movement. The dissolution began in spite of supersaturated condition, and soon, the width of the grooves increased – on the left up to 200 nm, on the right – more than 1 µm (Fig. 2, snapshot 2). Such
The difference is caused by indenter’s different impacts: on the move and against the direction of steps movement. In case of its going against the direction of the steps movement, more defects arise because of steps’ resistance (more strain).

The steps growth rate around the scratches is 0.8 nm/sec. However, the overgrowing rate of the wide scratch is much higher: 1.2-3 nm/sec. At the same time, new growth centres do not arise. The analysis of the height distribution graphs shows that in 15 min after the surface being scratched, a lot of high steps, which were not there before, along with the original steps, arise (Fig. 2). Gradually, the original order of the steps’ movement in the part of the surface gets disordered; the surface loses its morphological stability even in the areas without direct impact.

3.3. The screw dislocation hillock

According to AFM data, the growing steps of the screw dislocation hillock were about 8 Å high, which agreed with the unit cell parameter. The tangential rate before the impact was 0.5-0.7 nm/sec. Two parallel furrows were drawn on two sides of the hillock top on the move direction and against of the steps movement (Fig. 3). This leads to the loss of morphological stability: by the 45th minute, the steps making large curves lose their original even profile and general law of collective movement. The hillock top becomes more and more flat and asymmetrical. We can observe the appearance of a certain crystallographic line, in which described processes occur more intensively. The effects of morphological instability cannot be a result of impurity damage, because there is very little amount of impurities in the solutions.

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**Figure 1.** Dissolution of the surface after the letter “O” scratched. Below is a schematic illustration of the AFM probe impact on a crystal surface in the solution.

**Figure 2.** AFM-images of the scratched layer-by-layer growth surface. Graphs show the appearance of larger growth steps after 15 minutes being scratched.
3.4. *The phenomenon of simultaneous growth and dissolution*

At the top of the hillock, we observed a phenomenon of simultaneous growth and dissolution on the one step at the distance less than 1 µm. During the second hour of the experiment, some points of the steps grew with a rate 0.9 nm/sec, and the nearest ones dissolved with a rate up to 2 nm/sec (Fig. 4). Experimental observation of the simultaneous growth and dissolution on the crystal surface is not unique. Sherwood and Ristic observed it on a millimetre scale using interferometry at the top of growth hillock in sodium chloride, which had been affected by radiation [4]. It is also worth mentioning a big number of points at the steps having zero rate at 1 h 43 min after scratching (Fig. 4). Probably, the phenomenon of simultaneous growth and dissolution at the neighbouring points of one step is also connected with approaching an equilibrium state.

3.5. *The evolution of dislocation spiral without the mechanical impact*

Experiments in the same conditions, but without any special impact have shown that the morphological structure of such hillock growth on dioxidine is quite stable. Even after five-six hours of growth steps kept the original contours, their rate was monotonically decreasing by the end of the experiment (Fig. 5).

**Figure 3.** The loss of morphological stability of the screw dislocation hillock surface even at the distance of dozens of micrometres from the scratched area.

**Figure 4.** Empirical distribution (probability) of the tangential steps’ rate before (left) and 1 h 43 min after scratching (right). Before: step – 0.1, mode – 0.7, dispersion – 0.22, average rate – 0.8 nm/sec and rate fluctuation 0.4 nm/sec. In 1 h and 43 min after scratching: step – 0.05, average rate – 1.8 nm/sec, rate fluctuation – 1.5 nm/sec. The average dissolution rate is 1.8 nm/sec, the fluctuation is 1.1 nm/sec. Picture: simultaneous growth and dissolution at the dislocation hillock. A solid line is the projection of the original step position; a dotted line is a profile of the same step after 4.5 minutes.
4. Conclusion

Thus, we believe that kinetic effects of scratching at the nanoscale account for energy factors: mechanical impact initiates formation of multiple defects spreading towards stronger bonds on the surface. These defects decrease activation barriers so much that local dissolution can occur in the area of these defects even in the supersaturated solutions. Our direct observations by AFM showed the beginning of non-linear processes: steps thickening, appearance of huge fluctuation steps rates, a loss of morphological stability of the surface even at the distance of dozens of micrometres from the contact area, and also the simultaneous growth and dissolution in the neighbouring areas.

References

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