Effect of supersaturation on hillock of directional Growth of KDP crystals

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KDP single crystals were grown in aqueous solution by using “point seeds” with a defined crystallographic direction of 59° to the Z axis. When hillock slopes on the (100) face of KDP crystals were measured within the supersaturation (σ) range of 0 < σ < 0.06, the slope of hillocks with hollow cores depended nonlinearly on supersaturation. Below σ = 0.02, the hillock slope depended on supersaturation, but when σ was ≥ 0.02, the hillock slope increased more gradually and was less dependent on supersaturation. Hollow funnel-shaped growth dislocation on the (100) face of KDP crystals was observed at σ = 0.04, characterized by large holes with micro-steps and step bunching inside, the formation of which were analyzed. The result verified that the reversed growth appears to occur within hollow channels found on growth hillocks.

Results

Structure of growth hillocks. Previous research has shown that the growth rate of the surface of a crystal is closely related to the hillocks on its surface. Land and De Yoreo5 demonstrated that under certain conditions, dislocation
Sources form due to the incorporation of micro-crystals, which subsequently act as growth sources by stacking onto the hillocks. In our experiments, when the supersaturation level reached 0.02, hillocks with hollow cores on the (100) face of KDP were observed. As shown in Figure 2, the hillocks possessed two-fold rotational symmetry, corresponding to the space group \( I \bar{4} 2d \) of the KDP crystal. The hillocks were oriented along the four step directions on the (100) face and the rounded sections at the top of hillock, apparent in ex situ AFM morphology results, resulted from post-growth annealing. Depending on the ex situ image, incorporation of steps emerging in the hollow cores were verified.

Figure 3 and Table 1 show the dependence of hillock slope on supersaturation values for \( \sigma \) between 0 and 0.06. The data shows that the hillock slope rises abruptly until \( \sigma = 0.02 \), beyond which it increases more slowly and levels off.

Hollow dislocation-growth source. As shown in Figure 4, a special spiral dislocation on the (100) face of the KDP crystal grown at \( \sigma = 0.04 \) was observed with AFM. Its morphology, which appeared to be a funnel-shaped hole, does not resemble hillocks reported previously. The hollow core was a rounded parallelogram, which exhibited two-fold rotational symmetry, namely the symmetry in the crystallization direction of [100] or [010], given that the space group of KDP crystal is \( I \bar{4} 2d \). The depth of this hole was about 420 nm, and contained numerous micro-steps with heights ranging from 6.3 to 50 nm, which grew and were incorporated inside it. This reverse crystal growth occurred on the (100) face of the KDP crystal.

**Formation of the hillocks with hollow core.** Classical nucleation theory allows us to know that a critically spontaneous nucleation radius \( r_c \) decreases with increasing supersaturation:

\[
r_c = \frac{\alpha \sigma}{kT \sigma}
\]

where \( \alpha \) is the inverse of the number density of molecules in the solid, \( \sigma \) is the free energy of the step edge per unit step length per unit step height, and the value of them shows in Table 2, \( k \) is the Boltzmann constant, \( T \) is the Kelvin temperature of crystal growth, and \( \sigma \) is the supersaturation value. As shown in Figure 5, the breadth of the metastable region becomes narrow with decreasing growth temperature. As previously reported, if the supersaturation of the KDP growth solution was large enough to exceed demand for solute by the metastable boundaries of growth, micro-crystals will appear in solution. These micro-crystals will land on either the (100) or (101) face of the KDP crystal and begin their growth. De Yoreo et al. postulated that particles floating in solution are more likely to land on the upward-facing surfaces (pyramidal faces) because of their proximity to that surface, resulting in the bias toward inclusion formation in the pyramidal sectors of the crystals.

In our experiments, the (100) face of KDP crystals grown with point seeds, whose crystallographic direction is 59° with respect to the Z axis, are upward-facing and more available to bind to most of the micro-crystals floating randomly in solution. Once a particle randomly lands on a (100) face, an inhomogeneous surface supersaturation field is created due to the difference of the velocity of solute diffusion to the upward-facing (100) face, and subsequent macro-steps propagate the instability, resulting in lattice defects. Each defect would then become an origin of a dislocation with a large strain field. Several research teams have postulated that the resulting strain field associated with a dislocation would produce a hollow core. In short, crystal growth under these conditions will produce hillocks with hollow cores on crystal faces that are not parallel to the vertical direction of the crystallizer.

**The effect of a hollow core on the slope of hillocks.** Burton, Cabrera, and Frank proposed the classically basic relationship between the structure of a dislocation source and the vicinity of the resultant growth hillock during the growth of single crystals. Within this sample model (BCF model), hillock slope value can be derived when the supersaturation, the temperature, the free energy of the step edge and the height of an elementary step are available; the hillock slope, \( P \), for an isotropic screw dislocation can be derived by:

\[
p = \frac{mh}{19r_c + 2L}
\]

where \( m \) is the number of unit steps in Burgers vector, \( h \) is the height of a single step, whose value shows in the Table 2, and \( 2L \) is the length of the perimeter at the surface surrounding the group of dislocations which create the hillock. When \( L = 0 \), \( P \) is proportional to supersaturation. However, \( L \) is not equal to zero in reality, so the dependence of hillock slope on supersaturation predicted by the BCF model does not correlate linearly with supersaturation.

When a dislocation source on the (100) face generates a hollow core on the top of a hillock, the steps must spiral around the hollow core. Thus, we expect that 2L is equal to 2r_c rather than zero. A model of a hillock with a hollow core is shown in Figure 6; \( L_1 \) and \( L_2 \) are roughly equal to the lengths of the chords of the hollow core. A parallelogram spiral makes one full rotation about a core of radius \( r_c \).
Because of its two-fold rotational symmetry, the model can be described by the following equations:

\[
\begin{align*}
\tau &= 2 \left( \frac{L_1 + l_{sc}}{v_i \sin \theta} + \frac{L_2 + l_{fc}}{v_f \sin \theta} \right) \\
l_{sc} &= \frac{2r_{sc}}{\sin \theta} \\
l_{fc} &= \frac{2r_{fc}}{\sin \theta} \\
v_i &= \omega \beta_i (c - c_e) \\
\beta_i &= \beta_{vi} \exp \left( \frac{-E_{as}}{kT} \right)
\end{align*}
\]

where time of one full rotation about a core of radius \(r_0\) is given by \(\tau\), \(\theta\) is the acute angle of hollow parallelogram core, \(v_i\) and \(v_f\) are the step movement velocity of the slow side and fast side respectively, \(r_{sc}\) and \(r_{fc}\) are the critical radii of the slow and fast sides, respectively, \(l_{sc}\) and \(l_{fc}\) are the critical length of the slow and fast sides, respectively, \(\beta_i\) is a kinetic factor, \(E_{as}\) is energy barrier, the value of \(\beta_{vi}\) and \(E_{as}\) shows in Table 2, and \(c_e\) and \(c\) are the equilibrium and actual concentrations of KDP salt, respectively. The hillock slope of the \(i\)th sector is given by

\[
P_i = \frac{mh}{v_i^2} = \frac{\frac{mh}{2} \left( \frac{L_1 + l_{sc}}{v_i \sin \theta} + \frac{L_2 + l_{fc}}{v_f \sin \theta} \right)}{v_f \sin \theta}
\]

The hillock slope versus supersaturation along with curves predicted by equation (7) is shown in Figure 7, which agrees well with the experimental data when \(m\) is equal to 10 at a supersaturation range between 0 and 0.06. The \(l_{sc}\) or \(l_{fc}\) decreased while supersaturation increased, \(l_{sc}\) and \(l_{fc}\) are about 20 nm when \(\sigma = 0.06\), and the value of them will decrease largely with increases in supersaturation. However, \(L_1\) and \(L_2\) are on the order of hundred nanometers and the values of \(L_1\) and \(L_2\) are much larger than \(l_{sc}\) and \(l_{fc}\), thus \(L_1 + l_{sc} \approx L_1, L_2 + l_{fc} \approx L_2\), equation (7) can be changed to:

\[
P_i = \frac{mh}{v_i^2} = \frac{\frac{mh}{2} \left( \frac{L_1}{\sin \theta} + \frac{L_2}{j \sin \theta} \right)}{j \sin \theta}
\]

Table 1 | Average value of hillock slopes in different supersaturations

| \(\sigma\) | \(P_0\) | \(P_1\) | \(P_2\) | \(P_3\) | \(P_4\) | \(P_5\) | \(P_6\) | \(P_7\) |
|---|---|---|---|---|---|---|---|---|
| 0.007 | 0.0181 | 0.0302 | 0.0315 | 0.018 | 0.018 | 0.02 | 0.04 | 0.055 |
| 0.00181 | 0.00302 | 0.00369 | 0.00439 | 0.00472 | 0.00501 | 0.00518 | 0.00537 |

Table 2 | Values of parameters\(^6\) used in all evaluating equations

| \(\alpha\) (erg cm\(^{-2}\)) | \(\omega\) (cm\(^2\) molecule\(^{-1}\)) | \(h\) (cm) | \(E_{as}\) (ev molecule\(^{-1}\)) | \(E_{af}\) (ev molecule\(^{-1}\)) | \(\beta_{as}\) (cm s\(^{-1}\)) | \(\beta_{af}\) (cm s\(^{-1}\)) |
|---|---|---|---|---|---|---|
| 24 | \(9.68 \times 10^{-23}\) | \(3.7 \times 10^{-8}\) | 0.26 | 0.21 | \(2 \times 10^3\) | 6.54 \(\times 10^2\) |

Figure 3 | Average value of hillock slope vs. supersaturation.

Figure 4 | AFM topology of a growth dislocation hole on (100) face of KDP grown at \(\sigma = 0.04\), (65 \(\times\) 32.4 \(\mu m\)).
From equations (8) and (9), the hillock slope, \( P \), becomes constant gradually with the increase in supersaturation, as verified by the experimental data shown in Figure 3.

De Yoreo et al. analyzed the effect of supersaturation on the slope of growth hillocks with holes on the (101) face of a KDP crystal and found that the slope of hillocks with a hollow core tend to be independent of supersaturation. From our experiments, we have also reached a similar conclusion, that the slope of hillocks with a hollow core on the (100) face correlates with the size of the hollow core rather than the supersaturation value.

The analysis of the formation of reversed growth. Hollow dislocation-growth in our experiment can be regarded as a kind of reversed crystal growth. As we know, reversed crystal growth in nanocrystals has been described in detail, which basically follows a sequence of steps: 1) amorphous aggregates get together to form a disordered cluster; 2) the surface of the disordered cluster crystallizes first; 3) finally, the interior of cluster crystallizes from surface to core. The growth of the (100) face of KDP crystals had been investigated in previous work, but no such reversed growth had been reported. However, in our growth study, when supersaturation is 0.04, the reversed growth occurred on the (100) face of the KDP crystal. From the experimental data and conclusion above, we deduce that the formation of the reversed growth in a single crystal occurs if the following conditions are met: 1) there is a big funnel-shaped hole on growth face which favors entry of growth-supplying solutes and 2) the supersaturation of the growth solution is moderate.

Discussion

Using AFM scanning, hollow cores have been found in hillocks on the (100) face of KDP crystals which were grown using point seeds with a defined crystallographic direction of 59° with respect to the Z axis. With increasing supersaturation, the hillock slopes rise slowly and approach a constant when \( \sigma \) is \( \geq 0.02 \); above this value, the slopes depend on the geometry and size of hillocks with holes, rather than on supersaturation. Taken together, the conclusion reached by other groups when pooled with our observations, indicate that hillocks with hollow cores form easily on the faces that are not

![Figure 5](https://www.nature.com/scientificreports)  
**Figure 5** | Stability of supersaturated KDP solutions: (1) solubility curve (2) meta-stable boundaries of solutions with (■) a growing crystal and (Λ) experiments with the empty platform.

![Figure 6](https://www.nature.com/scientificreports)  
**Figure 6** | Model of a hillock with a core.

![Figure 7](https://www.nature.com/scientificreports)  
**Figure 7** | Hillock slope versus supersaturation along with curves those predicted by equation (7) for \( L_1 = 100 \) nm, \( L_2 = 86 \) nm at \( m = 1, m = 5, \) and \( m = 10 \).
parallel to the vertical direction of crystallizer. Reversed crystal growth in large holes occurs readily, demonstrating that the solution in the holes not only forms inclusions, but also supplies growth units. The present results reveal a new phenomenon of single crystal growth, which warrants further investigation.

**Methods**

**Material preparation.** The growth solutions of KDP were prepared by dissolving KDP salt (≥99.9% purity) in 18 MΩ de-ionized water. The solutions were filtered by using a polysulfone filter with a pore diameter of 0.1 μm. Crystallization was performed in a 5000 ml glass container. Holden-type crystallizers with temperature control accuracy of ±0.1°C were used throughout the experiments. All KDP crystallization solutions had initial growth temperatures of 56°C. The supersaturation was controlled by reducing the temperature of the growth solution, which could be calculated as:

$$\sigma = \frac{c-c_c}{c} \quad (10)$$

The KDP point seeds with a defined crystallographic direction of 59° with respect to the Z axis, which is shown in Figure 1, were used in our experiments. The crystal was rotated in a ‘forward-stop-backward’ mode with a speed of 77 rpm.

**Imaging experiments.** Ex situ AFM measurements were performed using a Bruker Dimension Icon Scanning Probe Microscope (SPM) system in ScanAsyst mode with standard SiN cantilevers. KDP crystal samples used for AFM characterization were grown from solutions with varying supersaturation values.

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**Author contributions**

X.S. put forward this research direction. F.L., I.Z. and H.Z. contributed to crystal growth. G.Y. carried out the AFM experiments. F.L., L.Z. and H.Z. contributed to crystal growth. F.L., L.Z. and H.Z. contributed to crystal growth. F.L., L.Z. and H.Z. contributed to crystal growth.

**Additional information**

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