DISORIENTATION EFFECTS OF EPITAXY AT AQUEOUS MEDIA

A. Glikin, J. Plotkina

Department of Crystallography, St.Petersburg University, University Emb.7/9, 199034,
St.Petersburg, Russia, e-mail glikin@crystgen.geol.pu.ru

Abstract

Fixed mutual orientations of epitaxial crystals are preferably explained by the structure similarity. The process of such aggregate formation is usually discussed very schematically in terms of homogeneous or heterogeneous nucleation followed by a corrective turn to the epitaxial orientation but experimental evidences appear to be still unconvincing. The nature of a disoriented simultaneous growth of epitaxial crystals is not considered at all. Within the scope of this problem, regularities of oriented-disoriented deposition of grown or inactive crystals on a grown or dissolved seed were investigated in aqueous solutions mainly in connection with growth or dissolution kinetics. The behaviour of the epitaxial pairs KCl-NaCl, $K_2Cr_2O_7$-KBr (grown deposit, grown or dissolved seed) and $CaCO_3$ -$NaNO_3$ (inactive deposit, grown seed) was examined. The two co-existing textures featured by a kinetics were observed: “epitaxial texture” of deposited crystals grown together by the similar planes but turned variously from the fixed position; “vertical texture” characterised by arbitrary angles (up to 90°) between the similar planes of deposited and seed crystals. Additionally to the well-known crystallochemical factor of the process, evidences of the two other factors were received: kinetic one (heterogeneous nucleation on a seed in the epitaxial position followed by an arbitrary disorientation of deposited crystals by growth layers) and adhesive one (attraction of homogeneously nucleated crystals by a seed accompanied by a corrective turn to the epitaxial orientation).

1. Introduction

Epitaxy is usually interpreted by help of classic conception of a structural similarity of the crystal-partner planes grown together. This approach is used in the form suggested by L. Royer about 70 years ago and detailed later [e.g. 1-4] being kept principally in the boundless epitaxial literature during all the century [e.g. 5-8]; a number of epitaxial pairs were reviewed [9-11]. The mechanisms discussed on this basis [e.g. 1-8] can be reduced to a few fundamentals: 1) the oriented heterogeneous nucleation and growth of deposited crystals on a seed; 2) and 3) an arbitrary oriented heterogeneous nucleation followed by a corrective turn of deposited crystals to the epitaxial position or by the survive of the crystals epitaxially oriented in such an ensemble; 4) an attraction of homogeneously nucleated crystals, accompanied with the corrective turn to the epitaxial position; 5) an installation of molecular particles of deposited crystals in surface vacations and microhollows. Most of them appear to be not proved convincingly; however in fact, these ideas and well-known data on a disoriented growth together of epitaxial phases presume strong effects of growth processes; the effects seem to be not examined in detail before our work [12].

The specificity of the previous crystallogenetic experiments [12] was a combination of either growing or dissolving substrate with growing microcrystals of a deposit. The epitaxial aqua-soluble pair $K_2Cr_2O_7$-KBr was used. As displayed, the epitaxial perfection was improved with an increase of the deposited crystal growth rate and a decrease of the seed growth/dissolution rate: deposited crystals were not only disoriented in parallel of the joint plane but were also overturned; this appeared to be caused by an uneven pressure of growth layers on deposited crystals nucleated heterogeneously in the epitaxial position [12]. Similar conclusions were received for the pair
β”-$LiNH_4SO_4$-$(NH_4)_2SO_4$ [13].

The main purpose of this work is a development of the established experimental crystallogenetic approach to epitaxy on the basis of orientation-disorientation phenomena for the pairs $K_2Cr_2O_7$-KBr, KCl-NaCl and $CaCO_3$-$NaNO_3$ in aqueous solutions.

2. Experimental procedure

Similarly to [12], the pairs $K_2Cr_2O_7$-KBr and KCl-NaCl were investigated at the conditions effecting a growth of the deposited substance combined with a simultaneous growth or dissolution of the seed. All the substances acted as the deposit or substrate in different experimental series. Seeds (3-5 mm) were hung in a thermocontrolled (± 0.1°C) vessel with a solution (25-50 ml) of necessary amounts of the components. The concentrations of $K_2Cr_2O_7$ and KBr (in the ranges 1-3 and 74-76 g/100 g H_2O correspondingly) provided the process at the temperatures 31-41 °C and supercoolings/undercoolings in the range between +7 and 10 °C. The concentrations of KCl and NaCl in the solutions corresponded to the eutonic field at 40 °C (also in the presence of 0-20 mas.% $MgCl_2$); the process was carried out at the supercoolings 1.0 and 2.0 °C.

For a given solution, seeds of both the substances (one after another) were used for saturation temperature testings and crystal growth/dissolution rate measurements under microscope in situ [14]. This was followed by the exposition of a seed during 40-60 min in the solution at the conditions characterised by the growth/dissolution rates; the seed was dried after the extraction. Orientations of crystals deposited on the vertical face of the seed were examined.

Especially, inactive $CaCO_3$-microcrystals cleavaged and suspended in aqueous $NaNO_3$-solutions were deposited on grown $NaNO_3$-seeds (opposite to the classic epitaxy $NaNO_3$ on $CaCO_3$). The fourteen experiments were carried out at 35 °C and supercoolings 3 °C at an intensive stirring during 40 min; every time a seed (3-5 mm) was put to the bottom of the vessel mentioned above. Sizes of rhombohedral edges of suspended cleavages were in the range ≈ 15-500 μm, their concentration in the solutions was ≈ 0.02 g/ml. After the extraction and drying of seeds, orientations of $CaCO_3$-microcrystals deposited on the upper horizontal faces were examined.

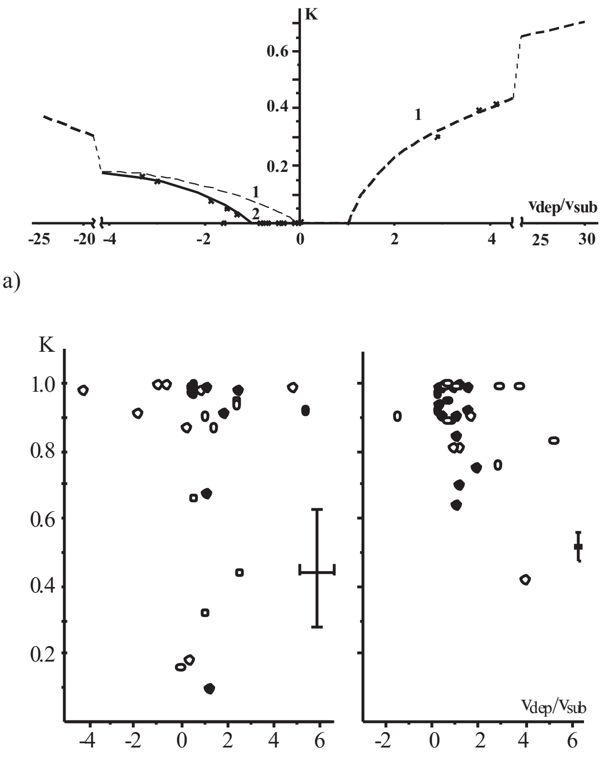
Deposited crystal deviations from the epitaxial position were measured with help of optic microscope and SEM within the minimal characteristic angle ranges 0-45° for square crystals on square substrates (the pairs $K_2Cr_2O_7$-KBr and KCl-NaCl) and 0-50° for the oblique-angled crystal pair $NaNO_3$-$CaCO_3$; distributions of crystals in orientations were plotted to histograms with the step 2° for the each experimental seed. Such a histogram is characterized in the general case by a peak presented by crystals in the epitaxial position (the maximum of the peak) and in the vicinity of it. In the particular case of the ideal epitaxy the peak is situated in the field 0-2°; on the other hand, the absence of a preferable orientation causes the uniform distribution without a peak. The epitaxy perfection was characterised by the coefficient $K = S(h-a)/nh$ where $1 \geq K \geq 0$ ($K = 1$ if all the crystals were deposited in the epitaxial position, $K = 0$ if all the crystals were disoriented uniformly), S - number of crystals forming the peak field (the area of the peak), h - number of crystals in the strict epitaxial position (the height of the peak within 0-2°), a - mean number of crystals within a 2°-step in the field out of the peak (the background height), n - the total amount of the crystals. Such an ensemble forms so called "epitaxial texture" characterised by a joint of the structure-similar surfaces of the partners; the crystals are oriented in the epitaxial position or arbitrary deviated from it.

Associating "overturned" crystals form so called "vertical textures", characterised by an discordant (angular) unconformity of structure-similar planes of the partners with an orientation of main morphological elements of deposited crystals about the normal to the substrate surface. The (010)-flattening of triclinic $K_2Cr_2O_7$ is subnormal to the cubic surface of KBr, the 2- or 3-fold axes of KBr are subnormal to the (010)-surface of $K_2Cr_2O_7$; the 2- or 3-fold axes of cubic KCl are subnormal to the cubic surface of NaCl-substrate (the same for NaCl-deposit on KCl-substrate); a solid diagonal direction (or plane) of trigonal $CaCO_3$ (e.g. 3-fold axis or plane of symmetry) are subnormal to the rhombohedral surface of $NaNO_3$-substrate. A proportion of overturned crystals and specific of their orientations were fixed.

3. Results and discussion

The both texture types of deposited crystals were observed for each the pair of the substances: either "epitaxial textures" or "vertical textures" characterised above.

The connections between a perfection of epitaxy K and growth/dissolution kinetic ratio of the substances-partners are presented at the Fig.1. One can see that the perfection of epitaxy is substantially lower for the pair $K_2Cr_2O_7$-KBr (K is not more than 0.7) than for the pair KCl-NaCl (K is not less than 0.8). Obviously, this is the consequence of the crystallochemical factor of epitaxy (i.e. of the differences of these pairs in the structure similarities of the substances): K-ions of $(100)_{KBr}$ form the square centred nets similar to the distorted K-ion net of $(100)_{K2Cr2O7}$ with the parameter difference ≈ 14 %, while the parameter difference of $(100)_{KCl}$ and $(100)_{NaCl}$ is 11 % at a perfect crystallochemical similarity of cations and the identity of anions.



a)

b)

Fig. 1. Connections of an orientation degree (K) of epitaxial crystals and a ratio between growth-dissolving rates of deposit and substrate crystals. a - the pair $K_2Cr_2O_7$-KBr (1 - data [12], 2 - our data); b, c - the pair KCl-NaCl at $\Delta T = 1.0$ °C (b) and $\Delta T = 2.0$ °C (c) (black circles - KCl-substrate, white circles - NaCl-substrate).

However the other regularities display actions of other factors.

The orientation-kinetic features of the pair $K_2Cr_2O_7$-KBr were obtained and discussed formerly [12]. In this work we have defined the position of the left branch of the plot and observed some new features of vertical textures. As a whole taking into account [12] (Fig. 1a), K does not exceed 0.7 and 0.4 on a growing and dissolving substrate relatively (independently of the combination: $K_2Cr_2O_7$ on KBr or opposite), increasing slowly in a wide range of v_{dep}/v_{sub} from $K = 0$ (slower in the case of dissolving substrates) and depending sufficiently on both absolute rates v_{dep} and $\pm v_{sub}$; $K = 0$ in the range of about $-1 < v_{dep}/v_{sub} < 1$. The discussion of these regularities [12] caused the idea of the kinetic factor which mechanism can be interpreted as a disorientation of nuclei heterogeneously deposited in the epitaxial position, by a nonuniform pressure of substrate growth layers or of their own growth layers; an increase of a nucleus growth rate strengths contacts with a substrate and a resistance to disorientation forces. In the discussed case of the pair $K_2Cr_2O_7$-KBr, the kinetic factor is substantial comparatively to the crystallochemical one.

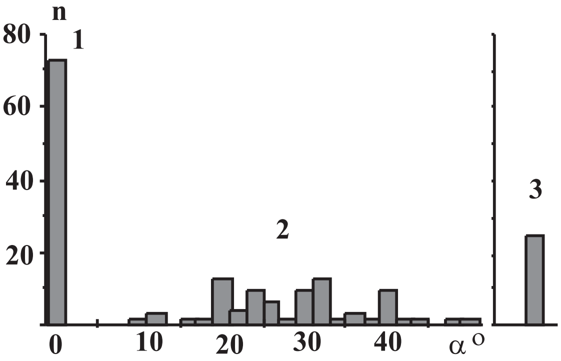


Fig. 2. The distribution of $CaCO_3$-excrescences in disorientation angles on $NaNO_3$-crystals (14 seeds): 1 - crystals in the epitaxial position (n=73; 40%); 2 - crystals in disorientation positions (n=86; 46%); 3 - crystals (n=26; 14%) joined by vertexes (12%) or edges (2%).

The vertical texture of flattened $K_2Cr_2O_7$-crystals on a KBr-substrate exists in the same range of about $-1 < v_{dep}/v_{sub} < 1$ where $K = 0$, and the share of this texture calculated at a grown substrate only, is increased with a decrease of v_{dep}/v_{sub} (up to 100 % about $v_{dep}/v_{sub} = 0$); a ratio between crystals of epitaxial and vertical textures depends on v_{sub} and is indifferent to v_{dep}. The vertical texture of $K_2Cr_2O_7$ observed in this work on a dissolved KBr substrate, cannot be explained by the idea [12] of the overturn of deposited crystals by growing substrate layers (based on the data of different effects of deposited and substrate crystal growth rates on this texture proportion). The vertical texture of cubic KBr-crystals oriented by the 3-fold axes about the perpendicular to a grown $K_2Cr_2O_7$-substrate was observed in some experiments too, from an approach to 100 % to the absence.

Deposited crystals of the pair KCl-NaCl form mainly the epitaxial textures ($[100](100)_{KCl} \parallel [100](100)_{NaCl}$) at the both combinations of deposits and substrates. The most experimental values belong to the ranges $0.9 < K \leq 1$ and $0.8 < K \leq 1$ at $\Delta T = 1.0$ and 2.0 °C correspondingly, spread within the kinetic ranges of approximately $(-4) < v_{dep}/v_{sub} < 6$ and $(-2) < v_{dep}/v_{sub} < 5$; a minor part of crystals is disoriented under to $K \approx 0.1$ ($\Delta T = 1.0$ °C) or $K \approx 0.6$ ($T = 2.0$ °C) and such values are mainly concentrated in a narrow positive range about $0 < v_{dep}/v_{sub} < 2$ (Fig. 1b, c). The differences in K appear to be connected with the growth rate variations (μm/min; supercoolings 1.0 °C and 2.0 °C correspondingly): for KCl - 0-3 and 0.2-7, for NaCl - (-3)-(+1.6) and (-1)-(+5). The kinetic effect on K for this pair appears to be similar to those of the pair $K_2Cr_2O_7$-KBr in spite of the differences in the methods (the measurements at the fixed and various parameters for the corresponding systems); the dependence of K on v_{dep}/v_{sub} is probably characterised by a coincidence with the abscissa in the positive range approximately 0-1, followed by a steep (almost vertical) part at $v_{dep}/v_{sub} \approx 1$ becoming fast to the horizontal with $K \approx 1$. This can be interpreted by the same mechanism of orientation-disorientation as above, with the predominance of the crystallochemical factor over the kinetic one in the case of the pair KCl-NaCl.

The vertical texture observed for the pair KCl-NaCl in the most experiments, does not exceed 10 %; such deposited cubic crystals are oriented by 3-fold axes about the perpendicular to a substrate.

Epitaxial texture of microcrystals $CaCO_3$ on grown $NaNO_3$-seeds is characterised by $0.1 \leq K \leq 0.7$ distributed between the experiments more or less uniformly while $NaNO_3$ growth rates varied also uniformly in the range 3.8-4.7 μm/min. In contrast to the well-known texture of $NaNO_3$ on $CaCO_3$ having $K = 1$, the discussed distribution of deposited crystals in angles has the obvious inordinary specificity (Fig. 2). The three angle areas of the epitaxial texture formed mainly by flattened (≈ 1.3:1.3:1-3:3:1) cleavages, can be divided at the plot: 1) the epitaxial position $\alpha = 0$ (≈ 40 % of crystals; thickness mainly about 15 μm, partly up to 40-50 μm); 2) the range of $0 < \alpha < 10°$ without crystals; 3) the range of $10 < \alpha < 50°$ (≈ 46 %; thickness 30-90 μm, mainly 60-70 μm) characterised by an uniform (or weak expressed normal) distribution. Taking into account the impossibility of a heterogeneous nucleation of deposited crystals in these experiments, the angle range without crystals must be interpreted as a consequence of an adhesion of $CaCO_3$-microcrystals followed by a corrective turn to the epitaxial position. Perhaps a deviation of the distribution within the third angle area (40-50°) from the uniformity to a normality is connected with a turn to the epitaxial position of a part of crystals initially oriented about the boundaries of this range.

The other crystals (≈ 14 %; sizes about 120 μm and more) of this pair belong to the vertical texture $CaCO_3$ on $NaNO_3$ with the subdivisions connected with the microcrystal size anisotropy: 1) rhombohedral isometric cleavages (≈ 1:1:1; 12 %) joined to the substrate by the vertexes at the 3-fold axes; 2) prismatic cleavages (≈ 1:1:1.3-1:1:2; 2 %) joined to the substrate by long edges.

The idea of the epitaxial orientation due to an adhesion-turn combination was already mentioned [15]. The evidence of this mechanism displayed above, causes a conclusion that nuclei or microcrystals can be adhered by a substrate in the epitaxial position due to a long-range electrostatic interaction if the fields are sufficiently anisotropic. This is confirmed additionally by our preliminary experiments displayed orientation regularities of $CaCO_3$-microcrystals on the $CaCO_3$-rhombohedron in aqueous medium to be similar to the described regularities for the pair $CaCO_3$-$NaNO_3$. Substantially, that this process appears to be indifferent to a crystallochemical correspondence at all; hence there is a competition between the adhesive and kinetic factors only when such a structure similarity is absent. The problem of epitaxy of substances with a slight or absent structure similarity [e.g. 16] as well as the artificial epitaxy [17, 7] can be probably solved in terms of this model.

The vertical texture phenomenon described first about a half a century ago for several substance pairs [18], can be also interpreted in terms of adhesion with some additional details; all the data including ours, especially the textures on amorphous substrates [18], display a non-epitaxial nature of this phenomenon. The stability of such excrescences requires a suggestion of an equilibrium of adhesive forces between a substrate and different faces of the nucleus; this is confirmed by the defined orientation of variously habited cleavages of $CaCO_3$ (isometric rhombohedral, prismatic and flattened are joined by vertexes, edges and faces correspondingly), which displays an equal attraction of the equi-square faces of a deposited crystal (when the crystals are joined by vertexes) and a stronger attraction of a larger surface (when they joined by surfaces).

On the other hand concerning a balance of adhesive forces, these pictures, and especially the stability of flattened $K_2Cr_2O_7$-crystals in quasi-vertical positions display a repulsion component of the forces. If a deposited crystal is jointed by an edge, then some difference in the sizes of the faces forming this edge must disbalance an attraction at the different sides of the edge, and cause the crystal adhesion by a face; the same must be observed due to an inclination of flattened crystals belonging to a vertical texture. Such a disbalance model appears to be avoided by repulsion forces.

4. Conclusion

The experimental results presented above motivate three factors controlling orientation-disorientation effects at epitaxial aggregate formation: crystallochemical similarity, growth-dissolution kinetics and adhesion of nucleus. Orientation features of the aggregate depend on a proportion of the factor influences. All the investigated pairs display an action of the crystallochemical factor, being more effective for KCl-NaCl and $CaCO_3$-$NaNO_3$; kinetic factor is displayed mainly for $K_2Cr_2O_7$-KBr and somehow for KCl-NaCl; adhesion is principal for $CaCO_3$-$NaNO_3$ and perhaps responsible for vertical textures in all the systems. As a whole, we consider this approach as an introduction to a crystallogenetic concept of epitaxy.

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References

1. L. Royer, *Bull. Soc. Franc. Miner.*, **51** (1928) 77.
2. G. Deicha, *Bull. Soc. Franc. Mineral. Cristallogr.*, **70** (1947) 177.
3. D.W. Pashly, *Advances Phys.*, **14** (1965) 327.
4. H. Seifert, Structure and Properties of Solid Surface (Chicago, London, 1953) 318 p.
5. H.G. Schneider and V. Ruth, Advances in Epitaxy and Endotaxy (Budapest, 1976) 344 p.
6. C.M. Pina, L. Fernández-Díaz, J. Lopes-Garsia, M. Prieto, *J. Crystal Growth*, **148** (1995) 283.
7. Handbook of Crystal Growth, Ed. D.T.J.Hurle, 3b (North-Holland, 1994).
8. M. Haag and H. Dabringhaus, *J. Crystal Growth* ,**178** (1997) 298., *J. Crystal Growth*, **179** (1997) 477.
9. O. Mügge, N. *Jb. Miner*, **16** (1903) 335 p.
10. J. Vultee, *Fortschr. d. Mineral.*, **29-30** (1952) 297.
11. M. Gebhardt, A. Neuhaus, Epitaxie-Daten anorganishe und organishe Kristalle (Heidelberg- NY, 1972) 397 p. (Landolt-Börnstein, Gr. III, Bd. 8).
12. A.E. Glikin and T.V. Kaulina, *Zapiski Vserossiiskogo Mineralogicheskogo Obshchestva* 5 (1988) 609 (in Russian).
13. C.M. Pina, L. Fernández-Díaz and M. Prieto. *J. Crystal Growth*, **177** (1997) 102.
14. T.G. Petrov, E.B. Treivus and A.P. Kasatkin, Crystal Growing from Solutions (New York, 1969) 106 p.
15. A.A. Simanovskii, in: Rost Kristallov 6, Ed. N.N.Sheftal (Moscow, 1965) 374 p.(in Russian).
16. D.W. Pashley, *Proc. Phys. Soc.A.* , **65** (1952) 33.
17. N.N. Sheftal, V.I. Klykov and R.N. Sheftal, in: Processy Realnogo Crystalloobrazovania, Ed. N.V.Belov (Moscow, 1977) p.144 (in Russian).
18. N.N. Stulov, Zapiski Vserossiiskogo Mineralogicheskogo Obshchestva 3 (1954) 241 (in Russian).