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Tehniskā atskaite

par 2. aktivitāti:

Nanomērogu procesu modeļiem atbilstošo skaitlisko metožu izstrāde.

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Ievads

Mūsu iepriekšējos pētījumos konstatēts, ka nanomēroga procesu ietekmes uz silīcija kristāla augšanu no kausējama iekļaušanai kristāla virsmas formas aprakstam ir jāizmanto daudzmēroga pieeja, kurā nanomēroga procesi ietekmē makroskopiskus procesus caur skaitliskiem parametriem. Mūsu gadījumā tie ir augšanas ātrumi, un augšanas leņķa atkarība no kausējuma orientācijas, kuri tiek noteikti nanomērogā un to ietekme ir jāņem vērā silīcija kristāla augšanas makroskopiskam aprakstam. Zemāk ir izklāstīts skaitlisks modelis un skaitliskās metodes, kuri izmanto šos parametrus silīcija kristāla virsmas aprakstam. Modelis ļauj arī aprakstīt uz silīcija virsmas novērojamos izaugumus. Nanomēroga procesi ieiet skaitliskā modelī caur augšanas leņķu atkarību no kristalogrāfiskās orientācijas, kā arī ņemot vērā virsmas liekuma izraisīto atomu difūziju un dažādos kristāla augšanas mehānismus. Izklāsts ir angļu valodā.

1. Formation and shape of FZ silicon crystal ridges

- The goal of this study is to describe the experimental observations of the behavior of crystal surface and crystal ridges during silicon crystal growth by theoretical models including nanoscale processes

- This study must lead to the better understanding of the crystal ridge growth, and to the better understanding of the connection of the observed crystal ridge shapes and observed ridge sizes to the physical conditions (e.g. temperature gradients, crystallinity, free melt surface oscillations) at the TPL during the crystal growth.

- It is our hope that the better understanding of the crystal ridge growth will lead to a better control of the silicon crystal growth process.

1.1 2D model of crystal ridge growth and balcony formation.

We build the analysis on the study of equilibrium orientation of solid-melt, solid-vapor and melt-vapor interfaces given by Herrings equation. The equilibrium orientation of the solid-vapor interface at TPL differs from macroscopically observed orientation by Voronkov's angle χ, which arises from curvature driven diffusion of melt atoms away from the TPL, see Fig. 1.1. These findings are used to construct a numerical algorithm for the calculation of the crystal ridge height depending on the physical parameters in the vicinity of the TPL.

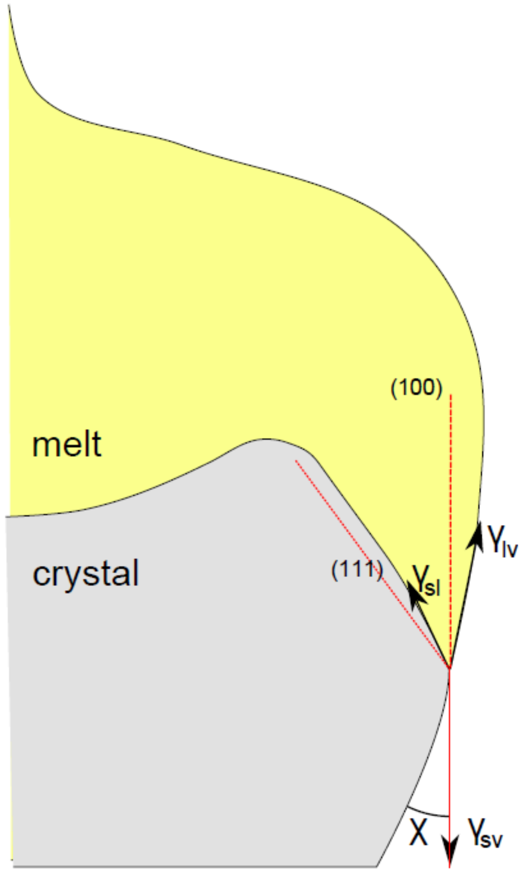

Figure 1.1: The equilibrium orientation of the interfaces at TPL is determined by corresponding interface energies and their anisotropy. Due to the Gibbs-Thomson effect at nanoscale the internal interface will curve until the orientation of the interface will coincide to the melting point temperature isotherm. During this curving the interface will necessarily have [111] orientation. Such interface will not grow unless approximately 4K undercooling is reached. Then the crystal will grow by atomic 2D nucleation. The external surface will bend moving away from the TPL and macroscopic orientation of the external surface will differ from the equilibrium orientation by angle χ introduced and analyzed by V. V. Voronkov. The value of the angle is thought to be about 20^o. If the rest of the crystal grows vertically, the crystal ridge will grow outwards.

1.2 Numerical implementation of the 2D model of ridge growth

The numerical model based on Voronkov's theory is described below:

- It is assumed that crystal shape away from crystal edges is cylindrical and crystal grows vertically. We denote the deviation of TPL line growth direction from the vertical direction by α. Then the velocity of TPL displacement in radial direction is

$$\delta\dot{r} = \sin(\alpha) v_{gr}. \quad (1.1)$$

- It is assumed that the crystal is pulled down in the vertical direction z with speed v_p, see Figure 1.2. It is further assumed the TPL line raises due to crystallization of crystal with speed $v_{gr} = v_{gr}(\Delta T)$ which depends on undercooling ΔT. Thus

$$\delta\dot{z} = \cos(\alpha) v_{gr}(\Delta T) - v_p. \tag{1.2}$$

- According to Voronkov, at ridges crystal growth angle can be different from the growth angle at rest of the TPL line due to Voronkov's angle χ and due to different meniscus orientation at TPL. The TPL line growth direction angle α depends on the angle of free melt surface and according to Voronkov also on undercooling ΔT. The undercooling is assumed to be positive for temperatures bellow melting temperature of macroscopic silicon. We can write

$$\alpha(z, r, \Delta T) = \phi_m - \varepsilon + \chi. \tag{1.3}$$

We have assumed isotropy of the growth angle ε. The exact value of the growth angle is not important for our numerical model. It is known from literature that $\varepsilon=11^o$. More precise descriptions of growth angle can be built using Voronkov's diagrams. In our calculation we use $\chi=-20^o$ whenever internal facet is present. $\chi=0^o$ otherwise.

- The orientation of free surface depends on the height of TPL δz, on radial displacement in radial direction δr. The expression for the change of melt angle $\Delta\phi_m$ is linearized in δz and δr as

$$\Delta\phi_m(z, r) = \frac{\partial\phi_m}{\partial z}\delta z + \frac{\partial\phi_m}{\partial r}\delta r \tag{1.4}$$

- The crystallization velocity depends on local undercooling. The further distinction can be made for growth having a {111} facet at crystal-melt interface and growth without internal facets. In the latter case the crystal grows by rough growth mechanism and the growth speed is approximated by

$$v_{gr} = \beta \Delta T, \tag{1.5}$$

where β=0.122 (m/sK) is used in calculations. In the former case the crystal growth by 2D nucleation.

$$v_{gr} = 0.22 e^{-\frac{140}{3\Delta T}} \Delta T^{\frac{2}{3}} \tag{1.6}$$

given by Kenneth A. Jackson in "Response to: Some remarks on the undercooling of the Si(1 1 1) facet and the "Monte Carlo modeling of silicon crystal growth" by Kirk M. Beatty; Kenneth A. Jackson, J. Crystal Growth 211 (2000), 13 by W. Miller, Journal of Crystal Growth **325** 104 (2011)". Near crystal ridges the switching between two growth regimes is made the orientation of the free melt angle at the TPL. The exact value of the critical switching angle is not known and it is treated as an empirical parameter.

- The undercooling depends on the temperature gradient along the crystal-melt interface and is assumed linearly dependent on displacement in vertical and radial directions *z* and *r*.

$$\Delta T = \frac{\partial \Delta T}{\partial z}\delta z + \frac{\partial \Delta T}{\partial r}\delta r, \quad (1.7)$$

- We allow for periodic oscillations of angle of free surface, which are observed for industrial crystal growth when using crystal rotation. Oscillations are represented by following equation

$$\Delta\phi_m = \frac{\partial \phi_m}{\partial z}\delta z + \frac{\partial \phi_m}{\partial r}\delta r + \phi(t), \quad (1.8)$$

where φ(*t*) describes time dependent meniscus oscillations due to external factors, e.g. inductor.

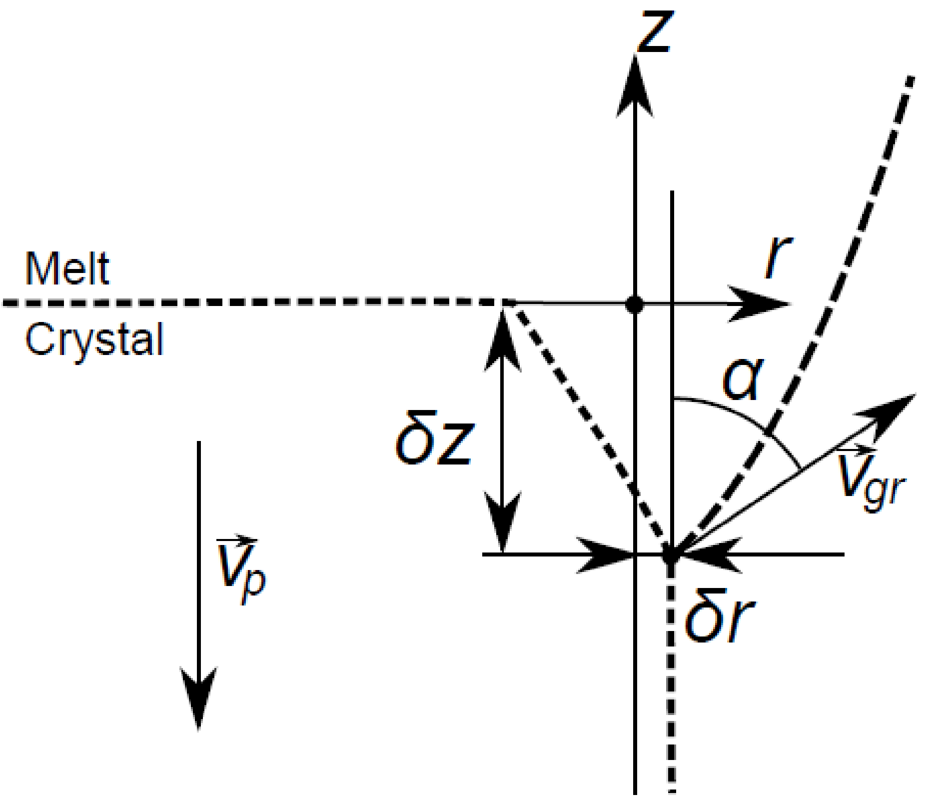

Figure 1.2: Coordinate system chosen for the description of crystal growth ridges. A crystal is shown in cross-section. Without the perturbation of the TPL by internal {111} facet at crystal ridge, the coordinates of the TPL are δ*z*=0, δ*r*=0. Due to the internal facet the TPL descends lower than the rest of the TPL.

Averaged components of temperature gradients in *r* and *z* directions are calculated as

$$\bar{G}_z \equiv \Delta T_z / \Delta z = \frac{k_s G_{s,z} + k_m G_{m,z}}{k_s + k_m}, \quad (1.9)$$

and

$$\bar{G}_r \equiv \Delta T_r / \Delta r = \frac{k_s G_{s,r} + k_m G_{m,r}}{k_s + k_m}, \quad (1.10)$$

where k is thermal conductivity and G_s and G_m are temperature gradients in solid and melt phases in the corresponding directions.

1.3 Shortcomings of 2D model of FZ crystal ridge growth.

Numerically analyzing the growth of crystal ridges in a 2D model, the TPL at crystal growth ridges is characterized by the difference in height, δz_v, with respect to the rest of the TPL and by the difference in the distance to the center of the crystal δr_v, Fig. 1.2. The solution is stable and perturbations to the values of δz and δr die out and the ridge growth in the same direction as rest of the crystal.

One of the shortcomings of our numerical description of crystal ridge growth is its 2D nature that does not allow reliable predict the width of the crystal ridges and to take into account effect of the width of the crystal ridge on the formation of the crystal ridge. This, probably, results into considerably higher calculated crystal ridges than observed in industrial crystal growth of FZ crystals.

Taking into account that our model for calculations of the ridges is still mainly qualitative, it is preferable to work with simpler and more transparent 2D model than with numerically challenging 3D model. In the next sections we will refine the 2D model in order to be able to predict the width of the crystal ridges and we will analyze consequences of this refinement, which results in a quasi 3D model of the growth of crystal ridges.

1.4 Analytical expressions for meniscus angle perturbation

In this part we will make two refinements to the crystal ridge model.

- We will make an estimate of the crystal ridge from the geometrical analysis of cross-section of {111} internal facet with the crystal-melt interface at the TPL.
- We will analyze the effect of the ridge width on the deviation of the meniscus angle at the ridge apex.

1.3.1 Analytical estimates for crystal ridge width

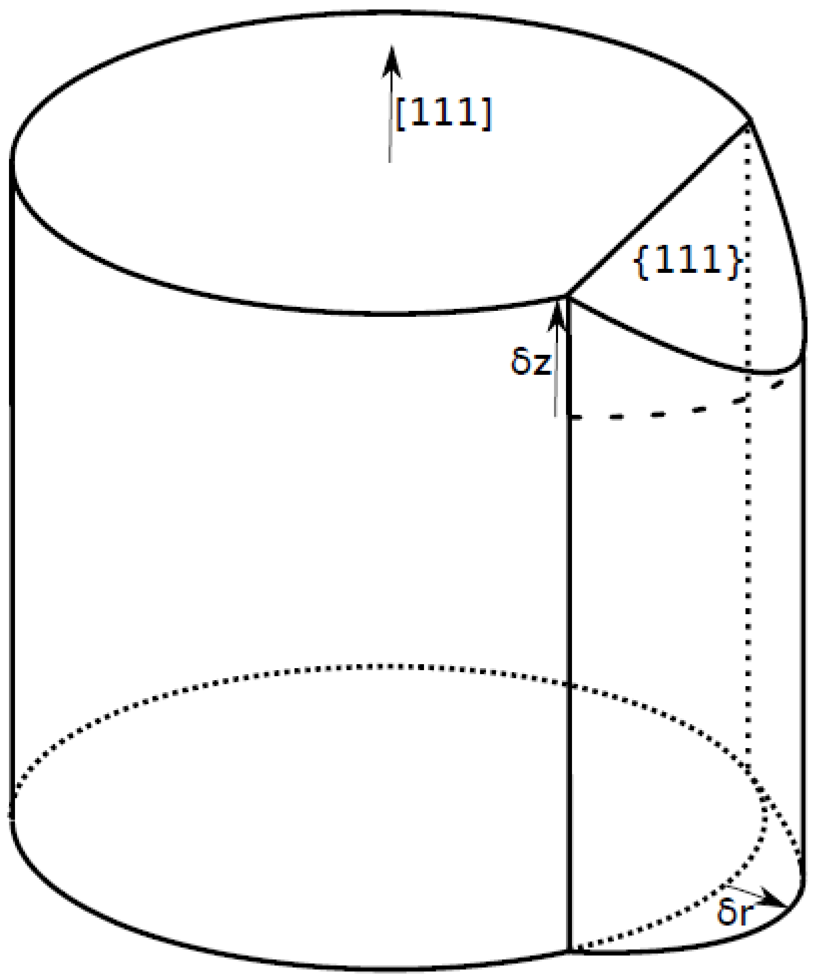

Figure 1.3: Schematic picture showing the model used to find the width of a crystal ridge from cross-section of internal {111} facet and the cylinder formed by crystal external surface.

Let's assume that at a ridge the crystal-melt interface is formed entirely by {111} internal facet as shown on Fig. 1.3. This will be approximately true for 2D nucleation growth. The curved part of the interface will be limited due to the considerable undercooling and Gibbs-Thomson effect. If the lowest point of the ridge is $z=\delta z$, $r=\delta r$, then the {111} internal facet crosses $z=0$ line at

$$r_f = -\delta z \tan(35.2^\circ) - \delta r, \tag{1.11}$$

see Fig. 1.4. Thus the maximal width of such facet, Fig. 1.5 will be

$$w_{max} = 2\sqrt{R^2 - (R - r_f)^2} = 2\sqrt{R^2 - (R + \delta z \tan(35.2^\circ) + \delta r)^2}. \tag{1.12}$$

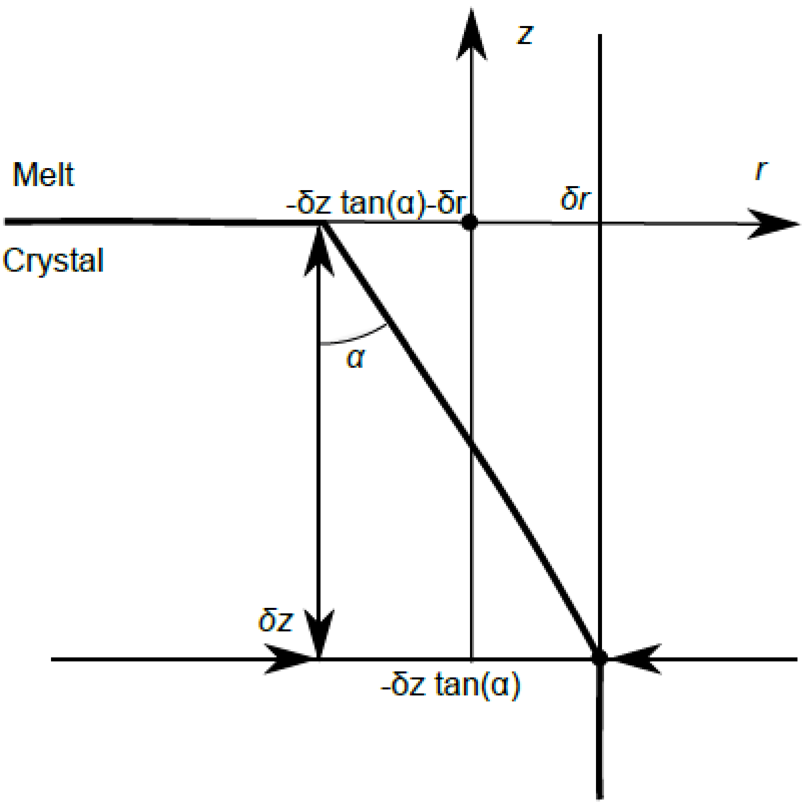

Figure 1.4: Geometrical construction for the penetration of the internal {111} facet into the crystal cylinder.

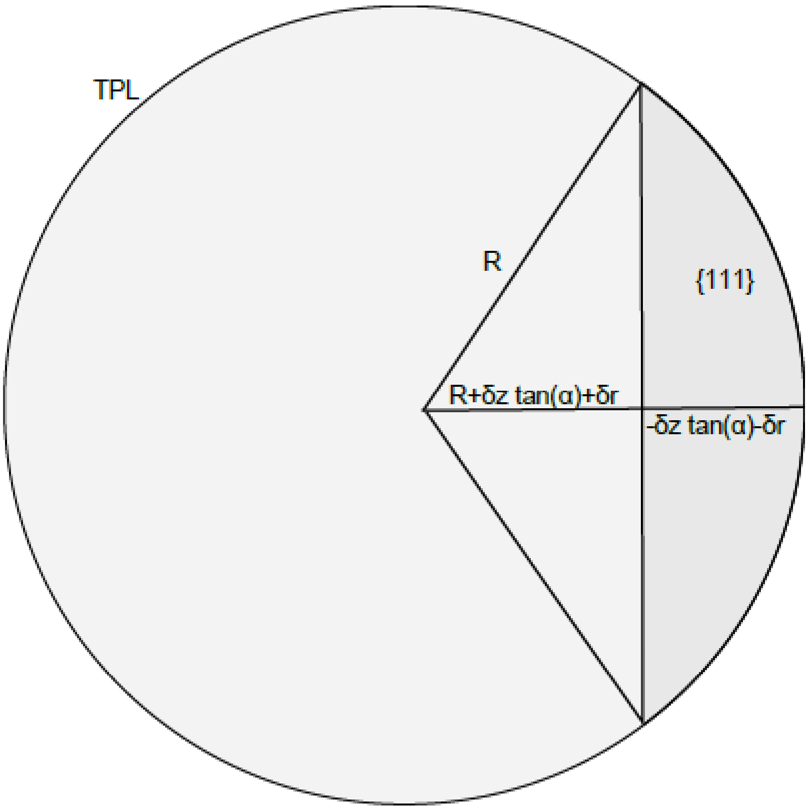

Figure 1.5: Geometrical construction for the calculation of the facet width.

If the TPL at the crystal growth ridges starts at $\delta z=\delta r=0$, the equilibrium shape of a ridge is reached by the following steps.

- If internal {111} facet is present in the relevant direction, the undercooling of the melt has to reach approximately 4 K undercooling in order for the interface to grow sufficiently fast.
- The TPL has to descend until necessary undercooling is reached.
- Descending the meniscus overhangs the TPL.
- To compensate the overhanging of the meniscus, the ridge growth outwards and the crystal ridge becomes narrower, according to Eq. 1.12.

In the real crystal growth, where the TPL can be at different initial coordinates, the steps above are not separated and happen simultaneously.

1.5 Analytical estimates for meniscus angle perturbation the crystal ridge

For the estimate of the perturbation of the meniscus angle near the crystal ridge, we will rely on perturbation treatment suggested by Voronkov in Reference: The effect of the faceting of the crystallization front on the external shape of crystals, Akademiia Nauk SSSR, Izvestiia, Seriia Fizicheskaia (ISSN 0367-6755), **49** pp. 2467-2472 (1985), in Russian. According to Voronkov the meniscus can be described by the function

$$r(z,w) = r_0(z,w) + \tilde{r}(z,w), \qquad (1.13)$$

where $r_0(z,w)$ describes the shape of the meniscus in absence of the growth ridge.

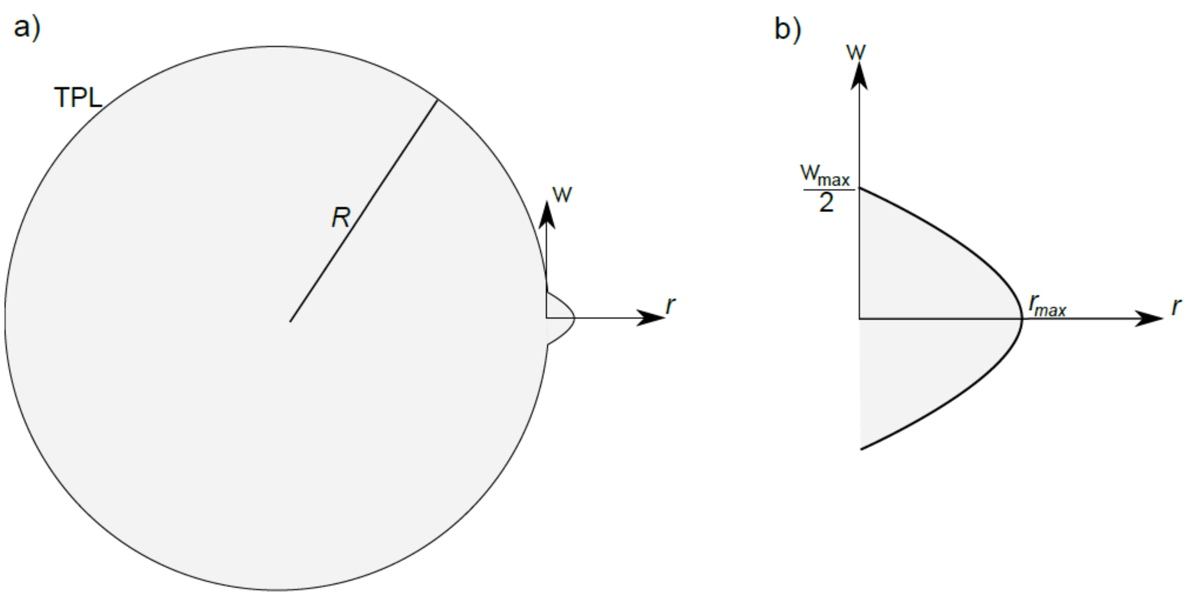

Figure 1.6: a) coordinate system chosen to describe the geometry of a ridge on a crystal surface. b) magnified view of the ridge showing the ridge height r_{max} and the ridge width w_{max}.

If meniscus is oriented close to the vertical direction and crystal ridge is small comparing to the capillary length, perturbation of meniscus satisfies the Laplace equation

$$\frac{\partial^2 \tilde{r}(z,w)}{\partial z^2} + \frac{\partial^2 \tilde{r}(z,w)}{\partial w^2} = 0. \tag{1.14}$$

Using this model suggested by V. V. Voronkov, we will find analytical solution describing the perturbation of the melt.

For boundary condition we request that the perturbation vanishes at the ridge boundaries

$$\tilde{r}(z, w = w_{max}/2) = \tilde{r}(z, w = -w_{max}/2) = 0 \tag{1.15}$$

and the meniscus slope perturbation also vanishes at the ridge boundaries

$$\tilde{\Phi}(w \pm w_{max}/2) \approx \frac{\partial \tilde{r}(z, w = w_{max}/2)}{\partial z} = \frac{\partial \tilde{r}(z, w = w_{max}/2)}{\partial z} = 0. \tag{1.16}$$

Then from the analysis of Laplace equation 1.14 the following solution satisfying the boundary condition, Eq. 1.15 and 1.16 can be found

$$\tilde{r}(z,w) = r_{max} e^{-n\pi z/w_{max}} \cos(n\pi w/w_{max}), \tag{1.17}$$

where n is positive integer. The validity of the solution can be found by substitution in Eq. 1.14 and boundary conditions. The solution for n=1 is plotted in Fig. 1.7.

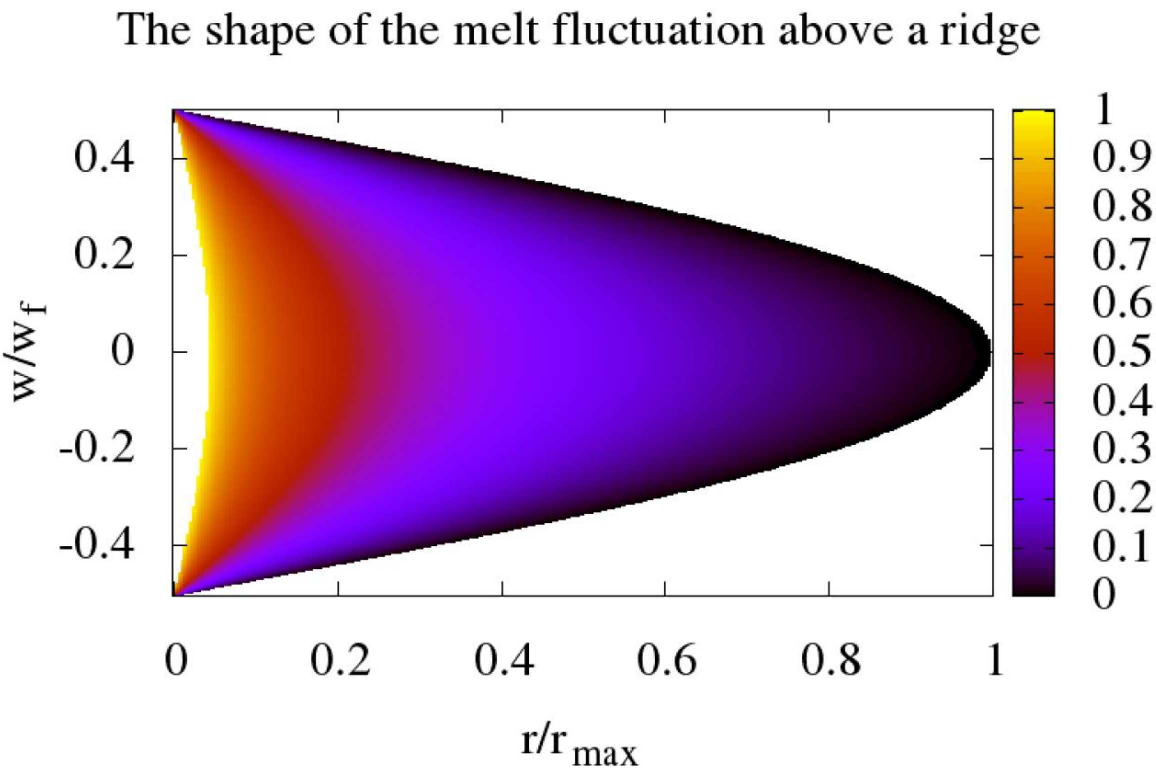

Figure 1.7: The calculated meniscus shape deviations. Different colors correspond to different height of the meniscus cross-section relatively to the ridge width, i.e. z/w_{max}.

According to solution, Eq. 1.17, the maximal deviation of the melt angle is at the apex point w=0 and is equal to

$$\tilde{\Phi}_{max} \approx -n\pi\frac{r_{max}}{w_{max}}. \tag{1.18}$$

This decrease in the melt angle has to compensate Voronkov's angle χ and increase of melt angle due to the lower positioning of the TPL at the ridge for FZ grown crystals. For FZ crystals these two effects lead to the outgrowth of the crystal ridge. Therefore at this level of description the FZ crystal ridges always grow as protrusions.

Combining this result with the result obtained in Section 1.3.1, we can observe that if a ridge growth outwards, then according to Eq. 1.12 the width of the ridge, which is equal to w_{max}, becomes smaller. If the ratio r_{max}/w_{max} increases, then according to Eq. 1.18 the meniscus bends inwards at the TPL and the outward growth stops.

Thus, the narrowing of the crystal ridge by growing outwards restricts the height of the crystal ridge and in this model the crystal ridge typically does not get higher than 1-2 mm above the rest of the crystal, depending on the temperature gradients. That is considerably lower than the crystal ridge height calculated without taking into account the crystal ridge height.

2. Voronkov's angle value for FZ crystal growth.

In our model of the ridge growth we have used the ideas presented in the articles of V. V. Voronkov. In those articles he suggested that different growth mechanisms in comparison to the rest of the crystal describe the the crystal ridge growth. In the paper V.V. Voronkov, Processes at the crystallization front, Kristaliografiya **19** 922 (1974), in Russian, he suggests that in front of {111} facets the growth angle decreases by 15° if the undercooling changes from 3.7^{o} to 0^{o} K . The change of the growth angle Voronkov explains by wetting of crystal surface by a thin film of the melt. The thickness of the film is estimated to be equal to 10 atomic layers of silicon.

Different hypothesis is present in V.V. Voronkov, Mass transfer at the surface of a crystal near to its boundary with the melt and its influence on the shape of the growing crystal, Sov. Phys. Crystallogr. 23, 137 (1978) in English. This article describes the curvature driven surface diffusion of silicon atoms and derives expression that connects the undercooling at TPL and growth angle. The Voronkov states that the change of the growth angle in front of internal facet is assumed to be $\chi = 20°$. This theory has not been disproved disapproved and it has been, for example, presented in recent books:

- Comprehensive Semiconductor Science and Technology, Editors-in-Chief: Pallab Bhattacharya and Roberto Fornari and and Hiroshi Kamimura, Elsevier, Amsterdam (2011),
- Thierry Duffar, Crystal Growth Processes Based on Capillarity: Czochralski, Floating Zone, Shaping and Crucible Techniques, John Wiley & Sons (2010).

However, an experimental or other prove of the theory of Voronkov also is missing. There has not been any development of the Voronkov's model since its publication.

It seems that Voronkov's angle has been suggested to explain the outwards growing of the CZ crystal ridges, that otherwise should always grow inwards. The physical explanation to confirm the different growth angle at ridges hypothesis has been suggested later. Here we have an opposite problem. According to available physical models of crystal growth, the FZ crystal ridges should always grow outwards. However industrially grown FZ crystals often exhibit constrictions on their surfaces at the place of the crystal ridges. Taking that into account it is natural to suggest that for FZ crystal the Voronkov's angle χ has different sign than the angle of χ for CZ growth. That would allow the formation of constrictions on the external surface of FZ crystals and might show the correct growth behaviour of the ridges depending on the temperature gradients in the melt-crystal system:

- For small temperature gradients the internal {111} facets should be relatively long to reach the 4 K undercooling necessary for 2D nucleation growth. That would mean that the TPL at the ridge lowers considerably, melt overhangs it the ridge growth outwards. The χ angle increases the value of growth angle ε and the result the ridge growth smaller than without the effect of χ angle, see Fig 2.1.
- For large temperature gradients the internal {111} facets are short, the TPL at ridges lags behind the rest of the TPL only little and the ridge has only small tendency to

outwards growth. It might not be able to compensate the increase of the growth angle $\varepsilon+\chi$ and the ridge will grow inwards.

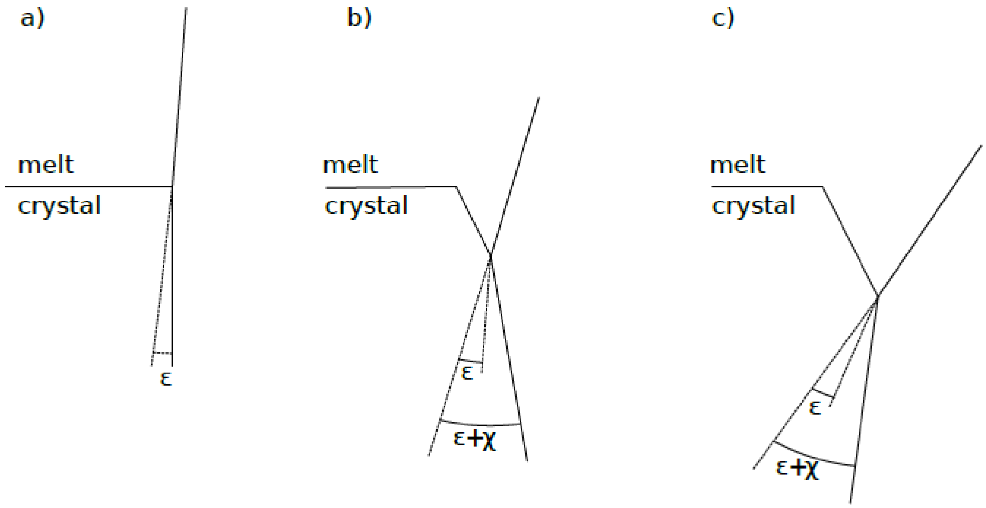

Figure 2.1: Effect of positive χ angle on the external crystal surface. a) shows crystal growth without internal facet. If the melt forms 11^o angle with the vertical, then the crystal growth cylindrical. b) un c) internal {111} results in the overhanging of the melt. Depending on the size of the internal facet the external surface will grow inwards b) or outwards c).

If we compare the FZ and CZ crystal growth, then the most obvious difference is in the orientation of the gravitational field with respect to the crystal-melt interface. In general, the mutual orientation of crystal-melt, crystal-vapor and melt-vapor interface at the TPL is described by equilibrium orientation of the interfaces. The equilibrium orientation corresponds to a minimum value of the free energy of the system. The corresponding equations without effect of gravity are derived requesting

$$\sum_{i=1}^{3} \int \gamma_i dA_i = \min, \tag{2.1}$$

where the sum runs over all three interfaces, g_i are corresponding surface energies and dA_i are they areas. The equations governing the orientation of the interfaces are found requesting that small displacements of the TPL do not change the free energy. The solution is known as Herring's equations have been used in our previous reports,

$$\sum_{1}^{3} \left(\gamma_i \vec{e}_i + \frac{\partial \gamma_i}{\partial \theta} \vec{e}_i^{\dagger} \right) = 0, \tag{2.2}$$

where e_i are unit vectors normal to the interfaces and $\vec{e}^{+}$ are unit vectors tangent to the interfaces. We do not know any theoretical study that would predict how the mutual orientation of the interfaces will change due to the effect of gravitational field. The closest systems analyzed in scientific literature are drops on inclined surfaces. There the energy contribution $U=mgh$ is included in Eq. 2.1. The Eq. 2.1 then becomes

$$\sum_{i=1}^{3} \int \gamma_i dA_i + \sum_{i=1}^{3} \int \rho g z dV_i = \min, \tag{2.3}$$

Consistent theoretical description for the three phase equilibrium orientation at the TPL in the presence of gravitational field using Eq. **Error! Reference source not found.** has not been found yet. If the corresponding boundary conditions do not allow for analytical solutions, the energy functional has to be minimized numerically.

2.1 Test calculations for the FZ crystal ridge growth including the Voronkov's angle dependence on the growth orientation.

In order to test whether the positive Voronkov's χ angle hypothesis leads to a better agreement between the calculations and the experimental results, we have performed calculations of the crystal ridge height and width for FZ crystals. It is known from the comparison to the experimental observations that our calculated positive ridge height does not agree with the observation of constriction at crystal ridges. Also calculated ridge width appears smaller in the theoretical model. We see from the Figs. 2.2 and 2.3 that introduction of positive χ angle for a model with temperature gradients components equal to 5000 K/m lead to formation of wide constrictions on the external surface of silicon crystals, in agreement to experimental observations.

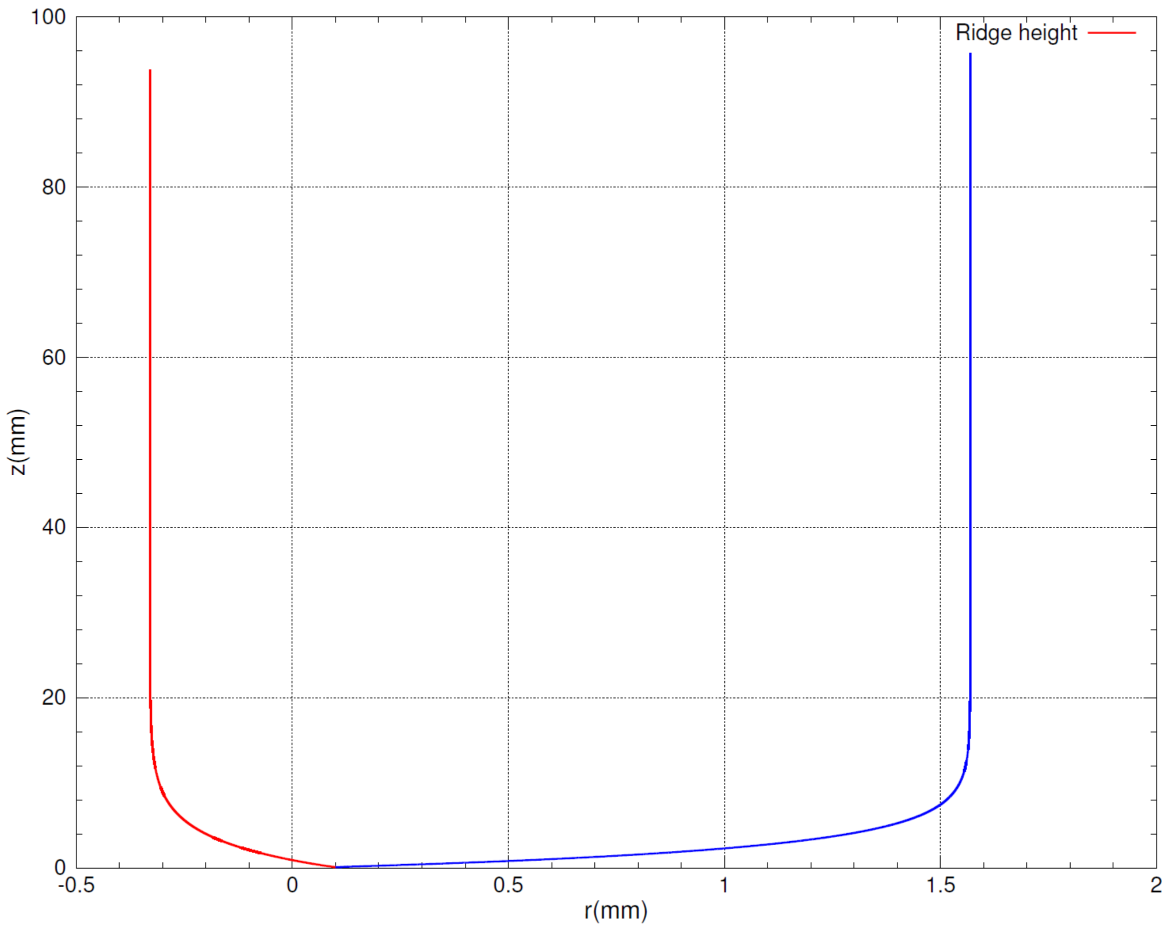

Figure 2.2: The calculated ridge height using negative value of $\chi = -20°$ angle (blue) and positive value of $\chi = 20°$ angle (red).

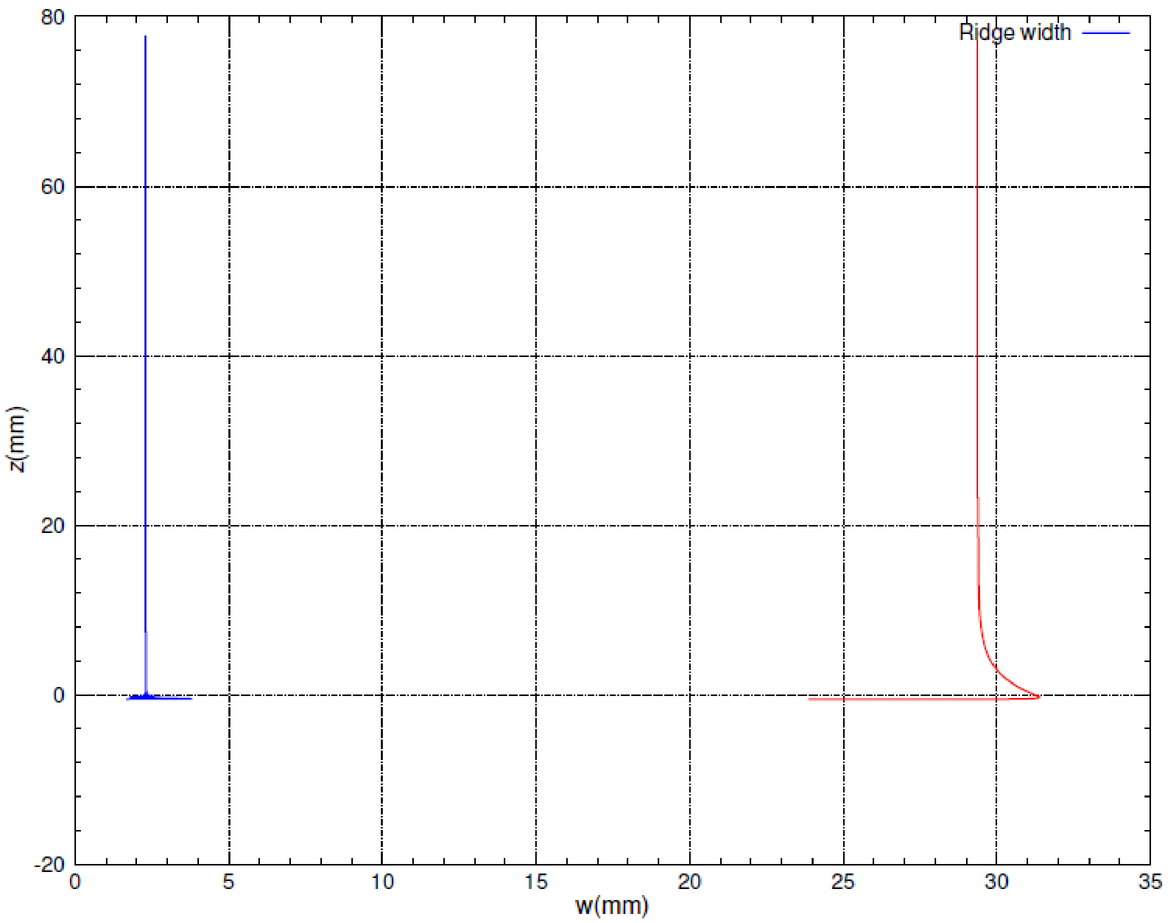

Figure 2.3: The calculated ridge width using negative value of $\chi = -20°$ angle (blue) and positive value of $\chi = 20°$ angle (red).

3 Conclusions

- The theoretical model was developed to take into account nanoscale effects on the ridge width in the 2D numerical model. The refined model is in closer agreement to the observed ridge heights and can predict the ridge width.
- The theoretical model can not predict the formation of the constrictions on the FZ crystal surfaces. It was speculated that refinement of the Voronkov's model is needed. The results of test calculations using modified value of the χ show improved agreement to the experimental observations.

Projekta zinātniskais vadītājs Dr.Phys. Jānis Virbulis