Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

Possible burst-like facet growth mode at high temperatures

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ARTICLE INFO

Article history: Received 3 March 2008 Received in revised form 11 April 2008 Accepted 19 April 2008 Communicated by Y. Furukawa Available online 3 May 2008

PACS: 81.10.-h 81.10.Aj

Keywords: A1. Diffusion A1. Growth models A1. Nucleation A1. Supersaturation A2. Single-crystal growth B2. Superionic conductors

1. Introduction

Helium crystals have been established as model systems for studying crystal surfaces [2]. In contact with superfluid helium, ⁴He crystals equilibrate their surface very rapidly, due to high thermal conductivity of both liquid and solid ⁴He and low latent heat of crystallisation. Moreover, because of the dissipation-free flow in superfluid He phase, through which all mass transport takes place, these crystals evolve very quickly [2,3]. In fact, the processes of growing and melting of ⁴He crystals on temperatures below 0.5 K develop so easily that the crystallisation waves may propagate on their surface [2]. The equilibrated macroscopic size of these crystals enables the classical optical methods to be used for study of their global growth and shape. The existence of such low temperature and quantum systems for studying crystal surfaces calls for some classical complement, that is, hightemperature system. The small group of materials which acquire their equilibrium form at macroscopic (up to 1 cm) size on an experimentally practical time scale of up to several days [4,5] also include ice single crystals [6], some organic crystals [7] and metal chalcogenides [8].

ABSTRACT

A decade ago, a burst-like growth mode of c-facets of ⁴He crystals growing at mK temperatures, characterized by the alternation of time intervals during which the facet does not advance with the intervals of its fast advancement, was found [J.P. Ruutu, P.J. Hakonen, A.V. Babkin, A.Y. Parshin, J.S. Penttilä, J.P. Saramäki, G. Tvalashvili, Phys. Rev. Lett. 76 (1996) 4187]. We investigate the possibility that a similar facet growth mode exists for facets at high growth temperatures. We have applied the digital laser interferometry for monitoring facet kinetics of spherical copper selenide single crystals during their growth at constant volume growth rate around 800 K. Our analysis of directly measured (111) facet advancement curves has revealed that they consist of time intervals during which the facet does not advance vertically alternating with the time intervals of enhanced growth, resembling the burst-like facet growth mode. The results are discussed in terms of the enhancement of the local supersaturation induced by the existence of nucleation barrier.

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Below the (0001) facet roughening temperature the surface of equilibrated ⁴He single crystals exhibits smooth $\{0001\}$ facets coexisting with the surrounding rough, rounded areas [2,3]. For ⁴He crystal facets, either without dislocations or having a very low density of them, a new growth mode of the c-facet, termed burst-like growth mode, has been detected [1,9]. The intervals of facet advancement (up to a few thousand layers per second, depending on the growth rate) alternate with intervals during which the facet does not grow, or grows very slowly. The facet growth event has been recorded by a sudden drop of overpressure (for growth rates higher than 50 nm/s), or by analysing the interference pattern for lower values of growth rate. For this burst-like facet growth mode of ⁴He crystals, the interpretation based on quantum tunnelling has been suggested [2,9,10].

Among the materials whose equilibrium shape has been investigated at higher temperatures are small metal particles (Pb, Au, Sn, In) growing on various substrates (graphite, Ru) [10,11]. However, due to the long time duration needed for shape relaxation [4], their equilibrium size has been restricted to less than $10\,\mu$ m, excluding the use of optical methods for quantitative monitoring of kinetics of their growth. Only recently, the step dynamics on small Pb crystallites grown on ruthenium substrate has been investigated in detail, using STM, at temperatures around 400 K [11].



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^{0022-0248/\$ -} see front matter @ 2008 Elsevier B.V. All rights reserved. doi:10.1016/j.jcrysgro.2008.04.030

The only materials which acquire their equilibrium shape at macroscopic size, and do so at high temperatures, well below melting temperatures, appear to be metal (silver, copper) chalcogenides (selenium, sulphur) [8]. Because of high temperature, these materials represent possible complement class of materials to ⁴He crystals. Copper and silver chalcogenides belong to the class of mixed superionic conductors, materials with high ambipolar (electronic and ionic) conductivity ($\sigma_{el} \approx 10^3 \sigma_i$ [12]), and thus with very high metal atom diffusivity. Their structural and transport properties have been widely investigated. Particularly, these properties have been investigated as functions of stoichiometry in quite some detail [13,14]. Their bulk diffusivity depends on temperature and stoichiometry, and at 800 K the diffusivity of copper selenide acquires the value $D = 6.2 \times$ $10^{-7} \text{ m}^2 \text{ s}^{-1}$ [15]. It produces fast material transport, enabling shape relaxation of these crystals to be apparently slower, but not much slower than the shape relaxation of ⁴He crystals [16]. Moreover, this value is approximately four orders of magnitude higher than the surface diffusivity of lead, which governs the relaxation processes of metal crystallites grown on different substrates [11,17]. Therefore, the growth of copper selenide proceeds via fast bulk diffusion of metal atoms through the crystal to its surface, which is embedded in the atmosphere containing the chalcogenic component, whose vapour pressure is the equilibrium vapour pressure, and thus defines the stoichiometry of the growing crystal [18]. The centimeter size is reached within several days in the metal atoms flux (solid state) controlled mode of growth, $J_{Cu} \ll J_{Se}$ [14]. We note that for one of our crystals, which has grown at higher constant volume growth rate $(0.191 \text{ mm}^3/\text{h})$, approximately 4×10^{15} copper atoms reach crystal surface per cm² per second from inside (for crystal sizes of $r \approx 2$ mm), which should be compared to approximately 5×10^{20} selenium atoms per cm² per second reaching the surface from the outside [14]. This means that the influx of copper atoms is slow enough to enable sufficient time for each copper selenide molecule to relax at the surface.

The high bulk diffusivity of copper atoms yields fast macroscopic size crystal shape relaxation. Such macroscopic size enables the implementation of optical methods, and *in situ* monitoring of crystals during growth. Both the crystal as an entity and some of its surface details (facet height) may be investigated with relatively high accuracy.

Owing to the fact that the equilibration of our copper and silver chalcogenides crystal surfaces is very fast (based on diffusivity only, $\tau = (2r)^2/(\pi^2 D) < 1$ s for crystals smaller than 2r = 2 mm), and by making use of the optical tracing of advancing crystal surface within the narrow cylindrical tube, we have been able to correlate the volume growth rate with ionic conductivity. This has enabled us to affirm a new method for measuring the ionic conductivity of mixed superionic conductors in the so far unreachable temperature range at which the electron blockade materials do not work, i.e. between 300 and 1100 °C [15].

Copper selenide crystals exhibit, during their growth under the conditions of constant volume growth rate, spherical-like growth shape with flat surfaces — facets for high-symmetry crystal orientations, separated by rounded areas [19]. In these experiments, crystal and facet (111) radii ($T_R \approx 830$ K, for (111) facets) have been recorded by CCD camera, while the facet height (distance from the sphere centre) has been deduced from these quantities. During the relatively long time of growth (measured in days), a specific, shorter time scale (up to 70 min) oscillatory behaviour of the facet size, superimposed on the global growth, has been observed. Moreover, it has been shown, at least for the limited time interval, that the facet size (radius) increases, while the facet height stays nearly the same (cf. Fig. 7 in Ref. [19]). This indication of the noncontinuous facet growth mode of copper

selenide crystals at around 800 K, resembling the burst-like growth mode of the c-facet of ⁴He crystals growing at mK temperatures, has motivated us to study the facet vertical motion in a more direct and precise way.

In order to investigate the facet height behaviour during the growth, we have applied the digital laser interferometry (DLI) method [20] for monitoring the relative facet height during the growth of spherical $Cu_{2-\delta}$ Se crystals. This method had been introduced for studying the roughening transition of hcp surface of ⁴He [21,22], with a μ m resolution, and had also been used for the investigations of the above-mentioned burst-like growth mode of c-facet of ⁴He crystals, with the resolution of a few nm [9], which enabled monitoring of facet growth for growth rates up to 50 nm/s.

The organisation of the rest of the paper is as follows. We first briefly describe the experimental setup for interferometric monitoring of the growth of spherical nonstoichiometric $Cu_{2-\delta}Se$ crystals. After that we describe the method of extracting the results by analysing the interferograms. We then present and discuss our results. We conclude the paper with our conclusions.

2. Experimental setup

Since the details of our experimental setup for growth of nonstoichiometric spherical $Cu_{2-\delta}Se$ single crystals have been described in detail elsewhere [14], we will review it here only briefly and will pay more attention to the implementation of the digital interferometry. Our crystals have grown (cf. Fig. 1 in Ref. [14]) in free space, on the small capillary tip, at a fixed temperature of around 800 K. The copper atoms influx has been streamed from a piece of pure copper, diffusing to the site of crystal growth by bulk diffusion through the polycrystalline $Cu_{2-\delta}Se$ specimen, driven by the constant chemical potential established between the pure copper and the surface of growing crystal embedded in Se vapour at constant pressure. All temperatures crucial for growth have been kept stable within 1 K.

In order to measure the vertical advancement of the developed facets, ((111) facets of cuboctahedral symmetry) we have applied the DLI method, which makes use of the sensitivity of interference and of computer processing of data supplied by the CCD camera to detect very small facet displacements with very high resolution. The schematic drawing of our Michelson interferometer set-up may be found elsewhere (cf. Fig. 1 in Ref. [23]). A laser beam (with wavelength of 632.8 nm, from a Spectra-Physics 20 mW He–Ne laser) has been illuminating the growing facet, and the sequence of interference patterns has been recorded by CCD camera [20,23].

3. The method

The vertical motion of the facet has been deduced from the phase differences between each of the two consecutive interferograms, by means of the formula

$$\Delta z = \Delta \Phi \, \frac{\lambda}{4\pi} \frac{1}{\cos(\theta/2)}.\tag{1}$$

Here λ is the wavelength of the laser beam ($\lambda = 632.8$ nm), θ is the angle between the incoming laser beam and the beam reflected from the facet, and $\Delta \Phi$ is the value of the phase difference between the interference patterns of two consecutive interferograms.

We have chosen the maximal frame-taking rate enabled by our setup, i.e. 25 frames per second, for two reasons: to prevent the frame-to-frame phase difference to acquire values higher than 2π , and to access as wide range of growth rates as possible.

We will describe our method of analysing two-dimensional (2D) digitised interferograms (256 grey levels, on a square grid of 64×64 pixels) only briefly. The detailed discussion of this method may be found in Refs. [9,20]. We have used the refined Fourier-transform method for fringe-pattern analysis, which approximates each interferogram by a function [24]

$$g(\mathbf{r}) = a(\mathbf{r}) + b(\mathbf{r}) \cos[2\pi \mathbf{q} \cdot \mathbf{r} + \Phi(\mathbf{r})]$$
(2)

in which the desired information is contained in the phase field $\Phi(\mathbf{r})$, while $a(\mathbf{r})$ and $b(\mathbf{r})$ are the functions whose spatial dependencies originate from experimental imperfections, and $\mathbf{r} = (x, y)$. The method is based on the assumption that $\Phi(\mathbf{r}), a(\mathbf{r})$ and $b(\mathbf{r})$ are spatially slow-varying functions on the scale established by the spatial-carrier frequency $\mathbf{q} = (q_x, q_y)$, which is given by the number of pixels per interference line. Then, the Fourier spectrum of each interferogram contains localised features separated by **q**. The standard procedure [24] includes the extraction of one of the first-order maxima, centred either at **q** or at $-\mathbf{q}$, and its shift to the origin of the inverse space. Then one does the inverse Fourier transform back to the real space, and extracts the phase field $\Phi(\mathbf{r})$. We have then unwrapped the phase field by the procedure described in Ref. [25], and averaged it over the grid to obtain the value $\bar{\varPhi}$. The difference of averaged phases between two consecutive interferograms $\bar{\Phi}_2 - \bar{\Phi}_1 = \Delta \Phi$ then gives, by means of Eq. (1), the vertical facet displacement Δz .

Our refinements of this method are related to the automatic, dynamic method of removal/subtraction of the background (i.e. of a component of noise) from the interferograms, and to the use of the sampling theorem for determining the exact (subpixel) position of the first-order maxima, i.e. the exact value of **q** [20]. These refinements have enabled us to achieve nanometre resolution in vertical facet displacement. We have recently made new improvements to the method applied [26].

4. Results and discussion

In Fig. 1a and b we present the growth, i.e. the vertical advancement of (111) facets of two of our crystals (which we shall refer to as crystal crA and crystal crB) as a function of time for 24 (crA) and 72 (crB)h of growth. These crystals grew at a temperature around 800 K, i.e. some 30 K below the roughening temperature for (111) facets. Such temperature is a compromise between crystals with well-developed facets and with still reasonably fast shape relaxation processes. The former is better satisfied at lower temperatures (since step energy and consequently nucleation barrier vanish approaching $T_{\rm R}$), further from roughening temperature, where the facets are more pronounced. The latter condition is better fulfilled closer to $T_{\rm R}$. The crystals grew under nearly the same imposed total chemical potential difference, at constant volume growth rate, being 0.191 and 0.024 mm³/h, for crystals crA and crB, respectively. Average surface advancement rates have correspondingly continuously decreased during the growth, from about 100 down to 0.6 nm/s. Different volume growth rates have been a consequence of different capillary tip orifice diameters (cf. Fig. 1 in Ref. [27]). We note that the origin of the time axes has been set at the beginning of the recording of the interference pattern, and this moment has been taken as zero of the vertical facet displacement as well ($t = t_0, z = z_0$). As may be seen from Fig. 1a and b, the facet height does not exhibit monotonic advancement in time.

Our measurements have been influenced by noise originating from various sources associated with the specificities of experiments conducted at high temperatures. In spite of the antivibrational table, the vibrations of the capillary tip onto which the crystal grows remain the most obvious source of "purely **Fig. 1.** Vertical facet displacement as a function of time of growth (raw data) for crystals crA (1a) and crB (1b). The origin of time axis depicts the beginning of facet monitoring ($z = z_0$ for $t = t_0$).

mechanical" vibrations. We expect that these contribute primarily to higher-frequency noise, i.e. that their frequencies considerably surpass the vibrational frequency of our antivibrational table (being approximately 5–10 Hz). However, the thermally induced noise seems to appear at much lower frequency range than purely mechanical one, and it contributes substantially to the overall noise, interfering with the effects that we want to resolve.

In our earlier measurements we have found that during the growth of copper selenide crystals at temperatures of approximately 800 K, i.e. close to the roughening temperatures $(T_{\rm R} \approx 830 \,{\rm K})$, the (111) facet size (i.e. its radius, L) exhibits oscillations superimposed on the global behaviour related to linear volume increase. Moreover, we have found the indications that the facet height (z) is correlated to facet size (L) oscillations [19]. In Fig. 2 we plot the idealised outline of the observed oscillatory behaviour of L. Together with this we plot the behaviour of z that we expect, exhibiting delays in advancement (plateaux) during the intervals of the increase of L, while during its increase L decreases. The derivative of z, i.e. the velocity of facet advancement, is plotted in Fig. 2 as well. We now analyse the directly measured facet height curves of Fig. 1a and b in order to see whether they incorporate the plateaux-like behaviour as outlined in Fig. 2.

To this end we have performed the Fourier analysis of the curves presented in Fig. 1a and b. The low-frequency parts of the



а



Fig. 2. Schematic drawing of behaviour of facet size (L), vertical facet advancement (z) and facet vertical velocity (dz/dt) that we expect. Full lines in lower two plots describe a more realistic behaviour.

results are plotted in Fig. 3a and b for crystals crA and crB, respectively. Apart from the peaks at approximately 5 Hz and their higher harmonics (not shown in Fig. 3), the Fourier spectra are almost featureless for frequencies higher than 0.004 Hz (≈ 4 min), containing predominantly the noise. Prior to Fourier transformation, we have removed the trends from the vertical facet displacements by subtracting from facet advancement curves the functions $z_{\text{trend}} = ct^{1/3}$, corresponding to average radial growth of crystals growing at constant volume growth rate. We have written on abscissa the times corresponding to frequencies as well.

Guided by the expected facet height behaviour, we have analysed which features in Fourier spectrum shown in Fig. 3a contribute to the structure of the facet height curve, specifically which parts of this spectrum could build the expected plateaux in facet height curve. To this end, we have identified some pronounced frequency ranges (whose upper end frequencies are denoted by letters A, B, and C in Fig. 3a) by making use of the following procedure. Starting from the low-frequency side of the spectrum we notice a pronounced spectral range, and use the upper limit frequency of this feature as the upper cut-off frequency of the spectrum, and Fourier transform such restricted spectrum back to the real space. Upon comparing the so reconstructed facet height curve with the raw data, we repeat the procedure by adding the next pronounced frequency sequence of the spectrum, until we find the cut-off frequency which defines the frequency range sufficient for reconstruction of the expected plateaux in facet height curve. The results of the Fourier transform back to the real space are shown in Fig. 4a, together with the raw data. For the sake of clarity of these figures, we have plotted the parts of the curves corresponding to 1 h of growth only. Nevertheless, as discussed later, our conclusions do not depend on any time interval during the growth of any particular crystal, but rather on their growth rate. The frequency denoted by A in Fig. 3a has thus been identified as cut-off frequency defining part of the spectrum which yields the trend of the facet height curve (dotted line in Fig. 4a). Upon setting the cut-off frequency at a value denoted by B in Fig. 3a, we obtain the curve plotted by dashed lines in Fig. 4a. This curve approaches the experimental data, but still does not exhibit the plateaux that we expect. Only by inclusion of frequency range BC of the Fourier spectrum (corresponding to time interval between approximately 21 and 35 min), i.e. by taking a value denoted by C as the cut-off frequency, we have been able to obtain curve plotted by full line in Fig. 4a that exhibits the expected plateaux in facet height behaviour. In Fig. 4a we have also emphasised, by thick solid lines and as a guide to the eye, the idealised shapes of these plateaux.

We have followed the same procedure for crystal crB (cf. Figs. 3b and 4b) as well. Here, much broader spectral intervals have to be taken into account to obtain the same features in facet height curve than in the case of crystal crA. The cut-off frequencies *A*, *B* and *C* are at much higher values for crystal crB, which has grown at much lower (constant) volume growth rate than crystal crA. The frequency range BC responsible for the appearance of plateaux in facet height curve now corresponds to much shorter times than for crystal crA, i.e. to times between approximately 7 and 15 min. The plateaux are now more frequent and shorter than for crystal crA.

In Fig. 5a and b we present the vertical facet displacement curves emerging from Fourier spectra with cut-off at frequencies C for 6 h of crystals' growth, together with the measured raw data, in order to show that the plateaux-like behaviour presented in Fig. 4 is characteristic for much longer time intervals. In Fig. 6a and b we plot the facet vertical velocity during 6 h intervals of Fig. 5. In these figures we have depicted the average facet velocities by dashed lines corresponding to these 6 h's growth intervals, with $\langle v_A \rangle \approx 5.3$ nm/s and $\langle v_B \rangle \approx 1.8$ nm/s, for crystals crA and crB, respectively. As may be seen from Figs. 4, 5, and, especially, Fig. 6, the vertical advancement of the facet is not monotonic. The rate of facet vertical advancement ranges from 0 to approximately 15 and 5 nm/s for crystals crA and crB, respectively, i.e. the facet advancement comprises intervals in which the facet grows vertically with higher-than-average velocity, alternating with the intervals during which the facet does not advance, or does so with growth rate much slower than the average rate. Moreover, the exchange of such intervals is quicker for crystal crB, which has grown at the lower constant volume growth rate.

To the best of our knowledge, this is the first *direct* indication of such growth mode at high temperatures. As has been mentioned in Section 1, the experiments on ⁴He single crystals at mK temperatures have revealed a growth mode of the c-facet, in the direction perpendicular to it, termed burst-like growth mode [1,9], in which the periods of facet advancement alternate with the intervals during which the facet does not grow, or grows very slowly, at the rate of less than two monolayers per second. The average frequency of this alternation is approximately two-three orders of magnitude higher for He crystals than for our copper selenide crystals.

For our crystals, which grow at about 800 K, i.e. near the roughening temperature for (111) facets ($T_R \approx 830$ K), it seems natural to assume that the 2D thermal nucleation is the basic mechanism behind the observed mode of vertical facet advancement. Such facet growth implies facets without dislocations [9]. A facet may advance vertically only if critical size nucleus of a new



Fig. 3. Fourier transform of vertical facet displacement of Fig. 1, for crystals crA (1a) and crB (1b). Letters A, B, and C denote upper cut-off frequencies (the lower being 0) for various parts of the spectra, as defined in text.

layer is formed on top of it. This formation is regulated by 2D nucleation barrier [10]. The key issue is the relation between the values of the local driving force for facet advancement, i.e. the chemical potential difference across the formed facet felt by the Cu atoms just beneath the facet, and the step formation energy. Note that the growth of the crystal takes place under the circumstances in which the imposed chemical potential gradient across the surface diminishes on an average (since our crystals grow under the conditions of constant volume growth rate).

The probability for the nucleation barrier penetration is proportional to the exponential factor $\exp[-k\beta^2/(d_{111} \cdot k_{\rm B}T \cdot \Delta\mu_{\rm sst})]$,

where *k* is a numerical factor, β is the step formation energy per unit step length, d_{111} is the interplanar separation, $k_{\rm B}T$ is the thermal energy and $\Delta\mu_{\rm sst}$ is the chemical potential difference (per unit volume) across the facet, i.e. the local supersaturation on the growing crystal surface [10]. By using a simple model of stationary diffusion of Cu atoms, injected at the centre of the spherical crystal, towards the crystal surface, we have shown that the concentration of Cu atoms beneath the facet, whose nucleation barrier prevents Cu atoms from forming a new layer, may cause the local chemical gradient $\Delta\mu_{\rm sst}$ to acquire values that are high enough to penetrate the barrier [27].



Fig. 4. Vertical facet displacement for 1 h of growth corresponding to parts of Fourier spectrum 0A (dotted line), 0B (dashed line), and 0C (full line), for crystals crA (1a) and crB (1b). Thick lines are drawn as a guide to the eye for possible plateaux. "0" denotes zero frequency. Pale lines: raw data.

On this basis we propose the following scenario of facet advancement. With facet formed, the Cu atoms travel to the kink sites at steps on rough and stepped area. Particularly, the growth of the steps near the facet edge causes pronounced and fast facet lateral spreading. This process is readily accompanied by accumulation of Cu atoms beneath the facet, which enhances the value of the local supersaturation far above the imposed supersaturation. When this value becomes sufficient to penetrate the nucleation barrier, the growth proceeds, owing to the Cu atoms accumulated beneath the facet, by facet's faster-thanaverage advancement. During this facet vertical advancement the concentration of the Cu atoms beneath the facet depletes, and thus the local chemical potential gradient across the facet drops until it acquires a value that is again lower than the one needed to form a critical nucleus of new layer, and the vertical advancement of the facet stops. The process repeats itself with the facet (with its nucleation barrier) in its newly established vertical position.

From Figs. 4 and 5 one may notice that the plateaux in the vertical facet displacement corresponds to time intervals between 21 and 35 min for crystal crA, and between 7 and 15 min for crystal crB. This means that the average frequency, with which the time intervals of fast and slow growth show the absence of growth exchange, is approximately three times higher for crystal B (i.e. for the crystal whose volume growth rate is approximately eight times lower than the corresponding rate for crystal A, cf. Fig. 6 as



Fig. 5. Vertical facet displacement for 6 h of growth, corresponding to part OC of Fourier spectrum (full line), for crystals crA (1a) and crB (1b). Pale lines: raw data.

well). This finding may at first glance look a bit contradictory, but may be understood within our proposed scenario.

The deviations of the growth shapes from equilibrium are larger the higher volume growth rate is [2]. As long as the facet advancement proceeds via the 2D nucleation, the same is valid for shape deviations from the growth shape determined by the particular volume growth rate, i.e. from the average growth shape. Correspondingly, more time would be needed for such system to restore its average shape. In other words, since the crystals grow at the constant volume growth rate, for crystal A in each time interval more Cu atoms reach the crystal surface, where they have to be accommodated, either increasing the size of the rough area and of the facet, or, upon the penetration of the nucleation barrier, contributing to facet vertical building, i.e. to its vertical advancement. This process would last longer for crystal A, for which more new layers have to be built on the facet (since its average facet vertical growth rate is higher, cf. Fig. 6). The observed behaviour is in agreement with the proposed proportionality of the nucleation barrier and the facet size [28].

We note that in our measurements this average frequency with which the intervals of the facet's vertical and lateral advancement exchange vary very little during the growth of any particular crystal, i.e. our measurements indicate that this frequency is determined mainly by the volume growth rate of the crystals. More quantitative arguments would require more systematic



Fig. 6. Velocity of vertical facet displacement for 6 h of growth, corresponding to part OC of Fourier spectrum, for crystals crA (1a) and crB (1b). Dashed lines: Average radial growth rate.

experimental investigations within the accessible range of volume growth rates.

5. Conclusions

Using the DLI method we have recorded the growth of facets of spherical copper selenide single crystals at temperatures around 800 K, under the conditions of constant volume growth rate. Our aim has been to investigate the possibility that the facets advance with plateaux-like behaviour at high temperatures, which would imply that the basic mechanism of facet growth is the 2D thermal nucleation. By direct interferometric measurements we have found the indication of facet growth mode consisting of alternating time intervals during which the facet does not advance vertically but rather grows laterally enlarging its area, with intervals during which it advances at a rate much higher than the average one. Such facet growth mode necessarily implies facets free of dislocations and resembles the burst-like growth mode of c-facet of ⁴He crystals at temperatures below 1 K. Moreover, we have found that the frequency of this alternation is higher for crystals whose volume growth rates are smaller. These findings are explained in terms of the Cu atoms diffusion, by nucleation barrier-induced build-up of local supersaturation (under the circumstances of the decrease of global supersaturation with time), and subsequent penetration of the nucleation barrier.

Acknowledgement

We gratefully acknowledge the financial support by the Ministry of Science, Education and Sport of the Republic of Croatia.

References

- J.P. Ruutu, P.J. Hakonen, A.V. Babkin, A.Y. Parshin, J.S. Penttilä, J.P. Saramäki, G. Tvalashvili, Phys. Rev. Lett. 76 (1996) 4187.
- [2] S. Balibar, H. Alles, A.Ya. Parshin, Rev. Mod. Phys. 77 (2005) 317.
- [3] H.J. Maris, A.F. Andreev, Phys. Today (February 1987) 25.
- [4] M. Wortis, Equilibrium crystal shapes and interfacial phase transitions, in: R. Vanselow, R. Howe (Eds.), Chemistry and Physics of Solid Surfaces, Vol. 7, Springer, Berlin, 1988 (and references therein).
- [5] A.A. Chernov, Modern Crystallography III (Crystal Growth), Springer, Berlin-Heidelberg-New York-Tokyo, 1984.
- [6] M. Elbaum, Phys. Rev. Lett. 67 (1991) 2982.
- [7] A. Pavlovska, D. Nenov, J. Crystal Growth 12 (1972) 9;
 A. Pavlovska, J. Crystal Growth 46 (1979) 551.
- [8] T. Ohachi, I. Taniguchi, J. Crystal Growth 65 (1983) 84;
 T. Ohachi, I. Taniguchi, in: P. Vashista, J.N. Mundy, G.K. Shenoy (Eds.), Fast Ion Transport in Solids, Elsevier North Holland, Amsterdam, 1979, p. 597.
- [9] J.P. Ruutu, P.J. Hakonen, A.V. Babkin, A.Ya. Parshin, G. Tvalashvili, J. Low Temp. Phys. 112 (1998) 117.
- [10] A.A. Chernov, Modern Crystallography III (Crystal Growth), Springer, Berlin-Heidelberg-New York-Tokyo, 1984 (Chapters 2 and 3).
- [11] K. Thürmer, J.E. Reutt-Robey, E.D. Williams, M. Uwaha, A. Edmundts, H.P. Bonzel, Phys. Rev. Lett. 87 (2001) 186102.
- [12] T. Ohachi, S. Imai, T. Tanaka, I. Taniguchi, Solid State Ionics 28–30 (1988) 1160.
 [13] M. Horvatić, Z. Vučić, Solid State Ionics 13 (1984) 117:
- [13] M. Horvatić, Z. Vučić, Solid State Ionics 13 (1984) 117;
 O. Milat, Z. Vučić, B. Ruščić, Solid State Ionics 23 (1987) 37;
 - M. Horvatić, Z. Vučić, J. Gladić, M. Ilić, I. Aviani, Z. Ogorelec, Solid State Ionics 27 (1988) 31;
 - M. Horvatić, I. Aviani, M. Ilić, Solid State Ionics 34 (1989) 21.
- [14] Z. Vučić, J. Gladić, J. Crystal Growth 205 (1999) 136.
- [15] Z. Vučić, D. Lovrić, J. Gladić, B. Etlinger, J. Crystal Growth 263 (2004) 590.
- [16] S. Balibar, B. Casraing, Surf. Sci. Rep. 5 (1985) 87.
- [17] C. Rothman, M. Wortis, J.C. Heyreaud, J.J. Métois, Phys. Rev. Lett. 52 (1984) 1009;
 - J.J. Métois, J.C. Heyreaud, J. Crystal Growth 57 (1982) 487.
- [18] H. Rau, A. Rabenau, J. Solid State Chem. 1 (1970) 515.
- [19] Z. Vučić, J. Gladić, Fizika A 9 (2000) 9.
- [20] D. Lovrić, Z. Vučić, J. Gladić, N. Demoli, S. Mitrović, M. Milas, Appl. Opt. 42 (2003) 1477.
- [21] S.G. Lipson, E. Polturak, in: D.F. Brewer (Ed.), Progress in Low Temperature, Vol. XI, Elsevier Science Publishers B.V., Amsterdam, 1987.
- [22] F. Gallet, S. Balibar, E. Rolley, J. Phys. (Paris) 48 (1987) 369.
- [23] D. Lovrić, Z. Vučić, J. Gladić, S. Mitrović, M. Milas, N. Demoli, in: W. Osten, W. Jüptner (Eds.), Proceedings of the Fourth International Workshop on Automatic Processing of Fringe Patterns, Elsevier, Paris, 2001, p. 259.
- [24] M. Takeda, H. Ina, S.J. Kobayashi, J. Opt. Soc. Am. 72 (1) (1982) 156.
- [25] W.W. Macy Jr., Appl. Opt. 22 (1983) 3898.
- [26] J. Gladić, Z. Vučić, D. Lovrić, Opt. Lasers Eng. 45 (2007) 868.
 [27] D. Lovrić, Z. Vučić, J. Gladić, J. Crystal Growth 304 (2007) 497.
- [28] W.W. Mullins, G.S. Rohrer, J. Am. Ceram. Soc. 83 (2007) 249
- G.S. Rohrer, C.L. Rohrer, W.W. Mullins, J. Am. Ceram. Soc. 84 (2001) 2099.