INTERFACE KINETICS OF THE GROWTH AND EVAPORATION OF ICE SINGLE CRYSTALS FROM THE VAPOUR PHASE

1. Experimental techniques

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In order to measure the interface kinetics of the growth and evaporation of ice single crystals from the vapour phase, two improved substrate chambers have been designed. The chambers allowed measurements under well controlled parameters as temperature, supersaturation and foreign gas pressure. The critical point in the experiments was the determination of the supersaturation. The supersaturation was calculated from the measurements of the temperature difference between the substrate and the ice source that saturated the chamber with water vapour. The determination of this difference was better than 5 mK. However, the absolute value of the difference (zero point of supersaturation) could not be determined directly but was deduced from rate data. A copper substrate was used on which the crystals were randomly orientated. The rate of growth and evaporation was measured by a photogrammetric technique, which allows the three dimensional reconstruction of the crystals.

1. Introduction

The growth of ice crystals from the vapour phase shows some interesting peculiarities. Ice crystallizes in a hexagonal lattice. The growth form can either be a column or a plate, i.e. either the (0001) or {1010} face is the faster growing. The growth form is a function of the temperature and changes at $-9^\circ\mathrm{C}$ from plates to columns to plates and back to columns.

Investigations of this behaviour date back to 1938 [1]. These early experiments as well as most of the following [2] were performed in cloud chambers with 1 bar of air present. Later Gonda and others [3,4] built cloud chambers for measurements under partial pressures of various gases. A chamber for pressures of up to 10 bar was introduced by Gonda [4]. The foreign gas imposes at least a transport resistance (heat and mass) on the interface kinetics.

Shaw and Mason [5] introduced the concept of the substrate chamber into ice research. The crystals grew on a copper substrate and could be continuously monitored. Still 1 bar of air was present; the heat of sublimation was conducted into the substrate. Lamb [6] built the first substrate chamber that could be evacuated, allowing experiments in a pure water vapour environment as well as in an environment of foreign gases (in this case air) to be made. The control of the growth parameters was very advanced. The crystals grew on a stainless steel substrate.

For a careful study of the interface kinetics of ice crystal growth from the vapour phase, measurements in a pure water vapour environment are necessary. Working under these conditions avoids the problems of evaluating the transport resistances as well as the possible influence of the foreign gases as impurities. This entails that only substrate chambers can be used. In addition in substrate chambers, the crystals can be continuously monitored.

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2. Chambers

The construction principle of the substrate chambers designed has been given by other authors: A circular chamber contains a large surface of ice kept at the temperature $T_s$. The ice saturates the chamber with its equilibrium pressure $p = p_e(T_s) = p_s$. The middle of the chamber is occupied by a substrate or growth stage which is maintained at temperature $T_g$. The resulting subcooling of the substrate is defined as $\Delta T = T_s - T_g$ and the supersaturation as $\Delta p = p_e(T_s) - p_e(T_g)$. The entire chamber with the source ice – which is thermally slow – is temperatured by a cryostat (Lauda), whereas the substrate is temperatured by a thermoelectric cooling element (Peltier element). The latter unit is thermally fast and therefore it is used to control the supersaturation.

In this work, polycrystalline copper was used as substrate material on which the crystals grew with a random orientation. By using a variety of orientations, it should be possible to eliminate orientational effects. Epitaxially active substrate materials were not used, as, first, the crystals nucleate with a preferential orientation so that only this orientation can be evaluated, and second, the epitaxial
layer has to be bonded to the base material of the substrate which may lead to heat transfer and contamination problems under pure water vapour conditions.

Two different cells have been designed: One large cell constructed of aluminium and for some parts of polyamide (fig. 1). As the results obtained in this cell did not correspond with results given in the literature, the source ice was analysed for contaminations originating from the polyamide. The surface of the ice showed a contamination of 1 ppm and the bulk of 6 ppm paraffines. In order to analyse the influence of the contaminations, a smaller cell made entirely out of glass (except for the substrate) (fig. 2) was set up. The measurements in both cells showed no significant differences in results, so that an influence of the materials can be neglected.

The glass cell has several drawbacks: as glass is a poor thermal conductor, the source ice cannot be easily temperatured, and since ice expands during freezing the glass cell often broke. Therefore the metal cell was more often used. As can be seen from fig. 2, the glass cell has a ring slit between the source ice and the substrate. In the presence of foreign gases, this slit may limit the transport of water molecules and thereby limit the growth. As the slit cannot be easily avoided, this is a further reason for using the metal cell.

Both cells were connected to the same vacuum system. A dual chamber mechanical vacuum pump was connected to the cells via two liquid nitrogen cooled traps, one filled additionally with a molecular sieve (X13). The vacuum system and the cells were connected through a needle valve.

By controlled renewal of the atmosphere of the cells, the level of trace amounts of foreign gases could be kept at a minimum. The controlled pumping ensured that the surface cooling of the ice never exceeded 1 mK. The trace level of foreign gases was less than 1 Pa. No rubber tubing was used for connections.

Depending on the range, the pressure of the system could be measured by either a Pirani thermal conductance gauge (Balzers, 0–20 mbar) or a mechanical gauge (Leybold, 0–1000 mbar).

The system allowed the controlled introduction of gases from a steel cylinder using a needle valve. The partial pressure was manually monitored and adjusted to within 10%.

Thoroughly outgassed distilled water was supplied directly to the chamber in the case of the glass cell, and in the case of the metal cell via a flask that could be discharged into the chamber.

A small flask partially filled with distilled water was connected to both cells via a valve. This flask provided the necessary water vapour for the nucleation of crystals (fig. 3).

Both cells were thoroughly cleaned; the glass cell by using chromic sulfuric acid and distilled water and the metal cell by using acetone, trichloroethane and distilled water for the metal parts.

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**Fig. 3.** Schematic drawing of the vacuum system. On the left: vacuum generation; upper right: connection to the metal cell; lower right: connection to the glass cell.
The polyamide as well as the cables for the electric connections were rinsed for 24 h with hot and cold water.

Prior to the measurements, the chambers were pumped out to the residual pressure of the pump of 0.6 Pa. The bake-out temperature during the pumping could not exceed 70 to 80°C, as this is the upper temperature limit for the thermoelectric cooling device (a Peltier element, which is a semiconductor).

3. Nucleation

The nucleation of ice on the substrate is achieved by a relatively high supersaturation of the substrate. At temperatures above −20°C it is not practicable to reach the supersaturation by a corresponding subcooling of the substrate. The nuclei are grown out before the subcooling of the substrate has been reduced to a level at which the experiments are to be run.

The technique used here is to maintain the substrate at the desired (low!) subcooling (supersaturation) and then to introduce small amounts of water vapour of about 30 mbar into the system. The pressure rise in the cells is estimated to be between 50 and 300 Pa. Thereby the necessary supersaturation is achieved. Since the amount of vapour is limited, the supersaturation is reduced to the normal low level by condensation onto the source ice within seconds. During nucleation, crystals do not grow very much, so that small crystals are obtained.

With this technique very well developed crystals with hexagonal symmetry and with no rounded edges or corners have been grown. These crystals did not show any faults under 100 × magnification and under specular incident light.

For experiments in foreign gases it was necessary to nucleate the crystals under pure water vapour conditions and to admit the gas later. The introduction had to be slow (\( \dot{p}/p \ll 1/s \)), otherwise the compression wave would also have entailed nucleation.

4. Surface temperature

In a substrate chamber, the heat of sublimation is conducted through the ice into the substrate. The heat conductivity of ice is nearly isotropic with \( \lambda \approx 3 \text{ W/k} \cdot \text{m} \) and the heat of sublimation is roughly \( \Delta H \approx 50 \text{ kJ/mole} \), i.e. high amounts of heat have to be conducted through a relatively poor conductor. Especially in a pure water vapour environment where the growth rates are high, this may give rise to a self-heating of the surface of the crystals which in turn reduces the effective subcooling.

Although a mathematical modelling of the self-heating is possible, it is unpracticable in two ways:

1. Each crystal has at least a slightly different orientation on the substrate so that the boundary conditions for the problem have to be altered each time;
2. The mean length of surface diffusion is of the order of magnitude of the crystal dimensions, so that the place of liberation of the heat (condensation) and growth may be different.

In a very rough approximation, the temperature gradient through the crystal is taken to be constant. With \( T_0 \) as the surface temperature and \( T_g \) the substrate temperature, the surface heating \( T_0 - T_g \) is given by:

\[
T_0 - T_g = h \frac{\Delta H R}{\lambda V_m} \frac{1}{\cos \beta} \approx 10^5 \frac{\text{Ks}}{\text{cm}^2} h R \frac{1}{\cos \beta},
\]

where \( h \) is the height of the face over the substrate, \( R \) the rate of growth and \( \beta \) the angle of inclination of the face. \( V_m \) denotes the molar volume of the ice.

With a mean angle of inclination of \( \beta = 40^\circ \) and a condensation coefficient (as referred to by the Hertz–Knudsen equation) of \( \alpha = 0.13 \), one obtains:

\[
\frac{T_0 - T_g}{\Delta t} \approx 20\% \times \frac{h}{100 \mu \text{m}},
\]

so that a crystal height of about 100 \( \mu \text{m} \) should not be exceeded in order to keep the surface...
heating of the crystal in an acceptable region.

An undue self-heating is revealed by a rounding of the upper corners and edges of the crystals. By only investigating crystals with sharply developed corners and edges, most of the problems of self-heating can be avoided.

The heat of sublimation is further conducted through the substrate into the Peltier element. By assuming a high growth rate of 500 nm/s and a substrate coverage of 10%, the temperature gradient in the copper substrate is 8 mK/cm. As the temperature probe is situated very near to the surface, this can be regarded as a sufficiently low value. On the other hand, if less good conductors are used as materials for the substrate, this gradient will be steeper and may give rise to problems with regard to the correct measurement of the substrate surface temperature.

5. Parameter control

As indicated above, the control of the growth parameters is essential (especially in pure water vapour environment). The following parameters have to be controlled: absolute temperature, supersaturation and foreign gas pressure.

With the modern electronic measuring techniques, the absolute temperature can easily be measured and controlled to within 0.1 K. This imposes no further problems (see below). The partial pressure of the foreign gas is controlled manually to within 10%. This turned out to be a sufficient good value.

The supersaturation necessary for measurements under a pure water vapour environment is of the order of $\Delta p \approx 2$ Pa. In principle, the supersaturation can be measured semi-directly via a differential pressure gauge, as shown by Lamb [6]. This technique, however, has to rely on correct temperature measurements between the substrate and a reference chamber. Since this temperature difference is of crucial importance and a "real" direct technique [7] is very difficult to realize, in this work temperature measurements were directly used for the calculation of the supersaturation. That is, the temperature of the substrate $T_s$ and source ice $T_s$ are measured, and using the equilibrium vapour pressure equation, $\Delta p$ is computed:

$$\Delta p = p_e(T_s) - p_e(T_g) \approx \frac{d p_e}{d T} \Delta T,$$

where $p_e$ denotes the equilibrium vapour pressure. In addition only this technique is applicable under foreign gas pressures.

The parametric sensitivity of the supersaturation with the (absolute) temperature measurements is given by:

$$\frac{\sigma_{\Delta p}}{\Delta p} = \frac{0.1}{K} \sigma_T,$$

whereas the sensitivity with the temperature dif-

![Fig. 4. Schematic drawing of the electronic circuit. Cell with two Pt 100 preamplifiers and differential amplifier, constant current (1 mA) source, control circuit and Peltier element driver.](image)
ferential $\Delta T = T_i - T_s$ is given by:

$$\sigma_{\Delta p} = \frac{0.1}{K} p_e(T_g) \sigma_{\Delta T}.$$ 

An error in the absolute temperature of 1 K changes the supersaturation by 10%. In order to control the supersaturation to within 10% of the assumed maximum $\Delta p = 2$ Pa, the subcooling has to be controlled within less than 8 mK. Going to smaller supersaturations, this requirement becomes even stricter.

Due to their long term stability and low hysteresis, match stick size Pt 100 (Herawit, Heraeus, Hanau) temperature probes were employed to measure the temperature of the substrate and source ice. The temperature difference $\Delta T$ is computed by an operational amplifier circuit. A three-wire constant current technique is used to connect the resistance thermometers. This technique reduces errors in $\Delta T$ due to fluctuations in the current source (fig. 4). A 1 mA feed current was chosen. This is the upper limit where the electrically generated heat (100 $\mu$W) can be dissipated through the ice without an undue heating of the ice (< 1 mK).

The voltage drop over the resistance thermometers is 50-fold amplified and the difference of both channels is again 50-fold amplified. The output of the amplifiers is used as the input for the control circuits for the substrate temperature (Peltier element driver) and the source ice temperature (cryostat). The 2500-fold amplification can easily be checked by shunting one Pt 100 by a 10 to 100 kΩ resistance and monitoring the change in output.

The approximated errors in the measurements and the control of $T_s$ and $\Delta T$ are:

$$\sigma_T < 80 \text{ mK}, \quad \sigma_{\Delta T} = 5 \text{ mK}.$$ 

From these errors the errors in $\Delta p$ were calculated with $\Delta p/Pa = 1.3$ and 2.6 (see fig. 5). A 1% error is due to the error in $T_s$ and the larger remaining part of the error is due to $\sigma_{\Delta T}$.

Although these values seem to be high, no easy improvement seems possible (temperatures at two different points have to be measured simultaneously). In addition, these values provide an acceptable basis.

Precise temperature difference measurements with two probes bear another problem: the synchronousness of the output of both probes and amplifiers. The differential amplifier will yield $\Delta T + \text{constant}$. This constant has to be evaluated by using a common constant temperature bath for both probes. However, since the Pt 100 have a small, but for these measurements important, drift (over weeks), and since they are permanently built into the chambers, this method cannot be used. As no other reliable technique is at hand, the constant was not evaluated. $\Delta T$ was assumed to be zero at the point where the curve of the measured growth and evaporation rates versus $\Delta T$ passes through zero. For this evaluation the inclusion of evaporation measurements proved especially useful.

### 6. Reconstruction of the crystals – taking growth data

The growth data were evaluated from photographs taken from the growing or evaporating crystal. The two techniques used were first a photogrammetric one which gave a three-dimensional reconstruction of the crystals but was very time consuming and second for bulk data an approximate technique. The latter shall be discussed first.

Assuming an angle of the crystal faces with the substrate, the growth rate can be calculated from
the change in diameter of one or more crystal axes. This technique is quite reliable if the growth (or evaporation) is isotropic which turned out to be the case in most experiments.

The photogrammetric technique gives the opportunity of a three-dimensional reconstruction of the objects [8]. Two pictures taken under different angles or with a known replacement are necessary for this reconstruction. Here a stereomicroscope (Wild, Heerbrugg, Switzerland) provides both images which are commonly recorded on one frame using a SLR camera (Minolta, Ahrensburg).

Using an analytical plotter or a stereo comparator [9], the two images can be used to yield the three coordinates \(x, z, h\) of edges and corners of the crystal. Assuming that the faces are flat, these coordinates can be used to compute the coefficients \(A, B, C\) for each face of the crystal corresponding to the equation:

\[
Ax + Bz + Ch = 1.
\]

By taking a series of frames of a growing crystal and evaluating the equation for the faces, precise growth data for the individual faces – as the change in central distances – can be obtained [10]. It is possible to compute the angle between the faces (nominally 90° and 120°) and thereby check the hexagonal symmetry.

The measurements are possible for all faces, even for those who share no edge with the substrate (which is impossible in all other techniques introduced so far).

The growth rates of the \(\{0001\}\) and \(\{10\overline{1}0\}\) axes are measured simultaneously. Thereby the ratio of the growth rates (i.e. the habit) can be determined independently of the absolute supersaturation.

The error in the central distances is typically 0.5 \(\mu m\) and has a maximum of 4 \(\mu m\). With typical crystal diameters of 50 to 200 \(\mu m\), or times between two evaluated frames of 100 s, this indicates an error of less than 1% or 5 nm/s, respectively.

The angles between two prism faces (nominally 120°) were determined to be between 110° and 130°, and the angles between a prism and a basal face (nominally 90°) to be between 80° and 100°. The errors increased with decreasing crystal size. The most time consuming procedure of the photogrammetric technique is the determination of the heights (e.g. of corners). As an alternative, after having established that the angles are close to their nominal values, these heights \((h)\) may be determined by using only the lateral coordinates \((x, z)\) and minimizing the angle deviations from their nominal values.

7. The crystals

The crystals obtained with the techniques described were of very good hexagonal symmetry. Crystals evaluated for rate data showed no rounded edges and corners (i.e. no undue surface heating or cooling had occurred). As a substrate was used that entailed no epitaxy, the crystals showed a random orientation [10,11]. Fig. 6 shows a reproduction of one specimen. The photograph gives a poor reproduction of the crystal, as the second image for a stereoscopic viewing is missing. This drawback is inherent in all paper reproductions. Colour slides made of the crystal show much more details.

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References

[7] A cavern in the substrate is filled with ice. A differential pressure gauge connected to both the cavern and the cell gives directly the supersaturation.