Transitions in thermocapillary flows: impact on crystal growth

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Summary

A variety of crystal growth methods involve free melt surfaces, including the commercially important Czochralski and Floating-Zone processes. Thus thermocapillary ("Marangoni") convection can be a major source of heat and mass transfer in these processes, and, if time-dependent, leads to dopant striations in the resulting crystals. For the float-zone growth of semiconductors, the transition to time-dependency and the formation of dopant striations has been studied experimentally and numerically. The transition to time-dependence is closely linked to the transition from a 2-D to a 3-D flow configuration. It depends strongly on the Prandtl number. The actual flow configuration also depends on the aspect ratio and the zone shape.

Introduction

Single crystals of a variety of materials are essential for modern technology. The vast majority of semiconductor devices is based on wafers cut from single crystals of either elemental or compound semiconductors. In most cases, these crystals are grown from the melt by the Czochralski (CZ), the Floating Zone (FZ), or the Bridgman and VGF methods. For crystal growth, heat and mass transfer in the melt, and especially in the area close to the solid-liquid interface, are of utmost importance. In addition to diffusion, convection is the main mechanism to be considered. Sources of convection are buoyancy convection and artificially introduced flows (e.g. through counterrotation of crystal and crucible), but in the case of free melt surfaces also thermocapillary convection (also known as Marangoni convection), driven by the temperature dependence of the surface tension. Both the CZ and FZ methods, used for the commercial production of silicon, exhibit free melt surfaces and are thus subject to thermocapillary convection. In the FZ case, shown schematically in fig. 1, the comparatively high surface to volume ratio leads to a pronounced influence of thermocapillary convection.

During crystal growth, controlling the segregation of impurities or dopant on a macroscopic and a microscopic scale is of crucial importance for most applications. Segregation is governed by the phase diagram of a system, growth kinetics, and the heat and mass transfer in the melt, the latter with the contributions of diffusion and convection. In addition to axial and radial segregation acting on the scale of the crystal dimensions, small-scale fluctuations (μm to mm) of the dopant concentration following the interface curvature, the so-called striations, are often found in crystals (fig. 2). They are caused by time-dependent variations either of the growth rate through temperature fluctuations, or of the

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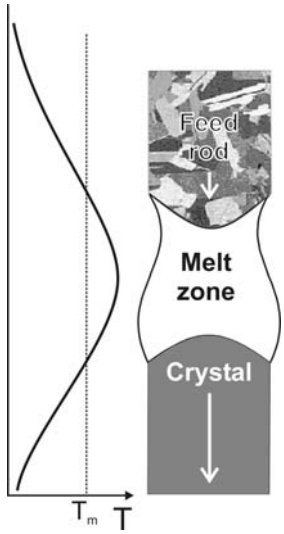


Fig. 1: Schematic setup of the float-zone process. Zone shape is shown for the 1g case.

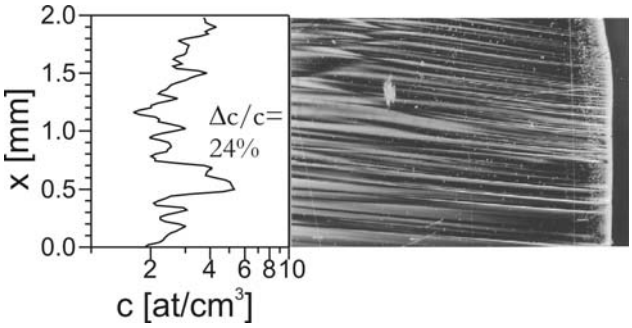


Fig. 2: Surface micrograph of an etched axial cut of a Si FZ crystal. Light and dark areas correspond to different dopant concentrations as shown in the diagram on the left. Growth direction was from bottom to top.

thickness of the concentration boundary layer in front of the interface. Direct sources of these fluctuations are externally imposed variations, such as rotation in an asymmetrical temperature field or an unsteady growth rate due to mechanical problems. The other major source is time-dependent convection in the zone. This includes time-dependent thermocapillary convection, which is usually characterized by the Marangoni number Ma:

$$Ma = -\frac{\partial\gamma/\partial T \cdot \Delta T \cdot z}{\rho\nu\kappa} \tag{1}$$

where $\partial\gamma/\partial T$ is the temperature dependence of the surface tension, ρ the density, ν the kinematic viscosity, κ the thermal diffusivity, ΔT the temperature difference, and z the characteristic length, usually close to half of the zone length *l* for FZ growth.

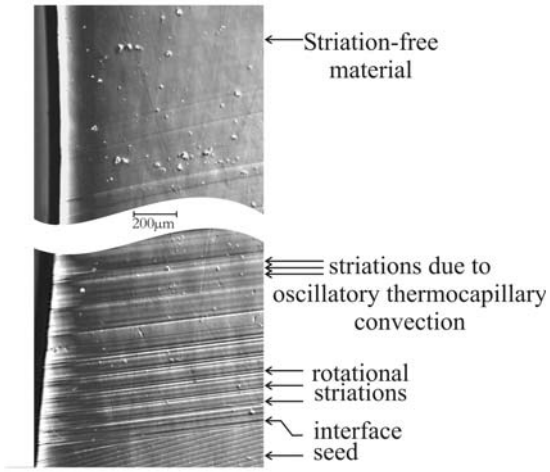
The transition of thermocapillary convection from a laminar to a time-dependent flow is characterized by the critical Marangoni number Ma_{c2}. Early experiments in space and on the ground showed that for radiation-heated small-scale Si floating zones time-dependent thermocapillary convection is the dominant mechanism for the formation of striations [1,2]. However, not even the order of magnitude for Ma_{c2} was known at the time. The same holds for the nature of the transition from laminar to time-dependent convection. Some knowledge existed from transparent model melts like $NaNO_3$ or silicon oil [3,4] but not for semiconductor or metal melts with much lower Prandtl numbers (Pr=0.013 for Si and Pr=0.04 for GaSb).

Experimental determination of Ma_{c2}

The easiest way to determine Ma_{c2} in a float zone experiment is a reduction of the zone length *l* until the striations vanish; this method changes z and ΔT in eq. (1) at the same time. It is, however, limited on the low side of z by the minimum zone length as

determined by the interface curvature and on the high side of z by the maximum zone length obtainable on earth. Therefore it is not always possible to obtain a transition from striated material to a striation-free one or vice versa. The former is the case for silicon, as striations can be found even in material grown from zones of a few mm length, whereas the latter is the case for GaSb. The latter obstacle can be overcome by going into micro-gravity (µg), where much larger zones are possible. At the same time it eliminates the influence of buoyancy convection, so that pure thermocapillary convection is studied. Such an experiment was done for GaSb [5]. Fig. 3 shows the transition from striated material to a striation-free one. The analysis of the temperature profile and the zone

Fig. 3: Surface micrograph of an etched axial cut of a GaSb FZ crystal grown under µg. Growth direction was from bottom to top, the zone length was reduced from 16 to 14mmin during growth.From [5].



height at the transition point resulted in a value of 375±125 for Ma_{c2} in this case.

For Si, Ma_{c2} could be determined by decoupling z and ΔT in eq. (1): a thin (5µm) SiO_2-coating of the crystals and the zone was used, eliminating the free surface and thus thermocapillary convection. Then a ring-shaped part of the coating was removed to obtain a partially confined melt zone with an annular free surface of constant height. Thus z remained fixed and Ma was changed only by the variation of ΔT along the free surface during the movement of the zone. The experiments were performed with different sizes of z, and also under µg to eliminate any influence of buoyancy convection on Ma_{c2}. A detailed description can be found in [6]. With this method it was possible to determine Ma_{c2} = 150±50 for silicon. For comparison, the actual Ma value is about 3000-4000 for a typical radiation heated Si floating zone of 8mm diameter and 10mm height.

Numerical simulations

With numerical simulations, it is also possible to determine Ma_{c2} and at the same time gain more insight into the paths leading to time-dependency. However, the boundary conditions applied must be carefully chosen and compared to experiments to achieve meaningful results. For instance, early simulations of Si floating zones used a 2-D ap-

proach, because of the constraints of computing power and time [7]. This appeared justified, because experiments with transparent materials (i.e. high Pr numbers) showed the symmetric pattern for thermocapillary convection in a floating zone, with good agreement between simulation and experiments for those substances. Using the same approach for low Pr materials resulted in critical numbers two orders of magnitude higher than the ones experimentally determined, however. 3-D simulations (details can be found in [5,8]) gave a very different result for the low Pr number materials, as shown in fig. 4 for Si:

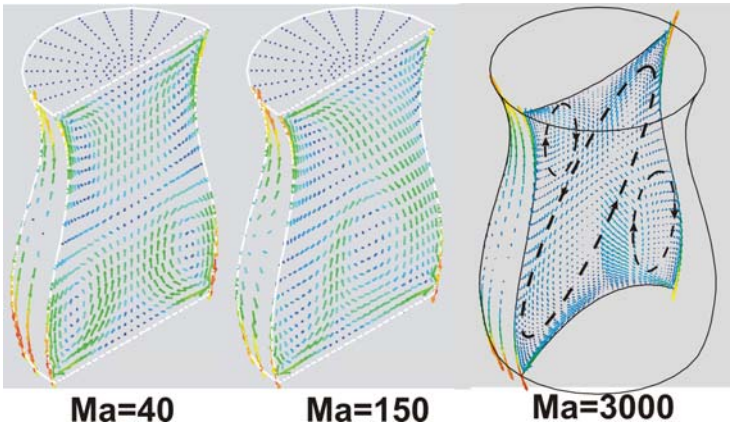


Fig. 4: 3-D numerical simulations of Si float zones for different Ma numbers, from [8,9]. At Ma=40 two independent flow rolls exist. At Ma=150 the upper and lower roll have coupled. At Ma=3000 the rolls are coupled, forming a large diagonal roll and two smaller ones, which are rotating. The simulation for Ma=3000 used curved interfaces, but the same aspect ratio and zone shape as the other two.

The classical two-roll pattern for thermocapillary convection in a floating zone is only present at very small Ma numbers; before a transition to time-dependency, the symmetry is broken, the two rolls unite and form a large diagonally oriented roll plus small secondary rolls. The transition to time-dependency is then mainly due to azimuthal waves. For Si floating zones of 10mm diameter and 12mm length, 3-D simulations resulted in Ma_{c2} values of 150 [8]. Other authors got a value of 115 [10]. Both are close to the experimentally determined value. Typical flow velocities are of the order of 0.1 m/s. A simulation of a Si-FZ experiment with a partially free surface as described above in the experimental section was also done by [10] and resulted in a number of Ma_{c2}=100-200, validating the experimental approach to determine Ma_{c2}. For the GaSb experiment, a value of $Ma_{c2} = 355\pm90$ was determined numerically [5], in good agreement with the experimental values. The 3-D flow pattern with the azimuthal instability varies from that of Si-FZ configurations, showing a direct coupling of the upper and lower roll in a figure "8" pattern, shown in fig. 5. This is explained by the smaller aspect ratio ($h/d\approx0.8$-0.9) of this zone compared to $h/d\approx1.5$ for the Si simulations as well as the barrel shape of the GaSb zone.

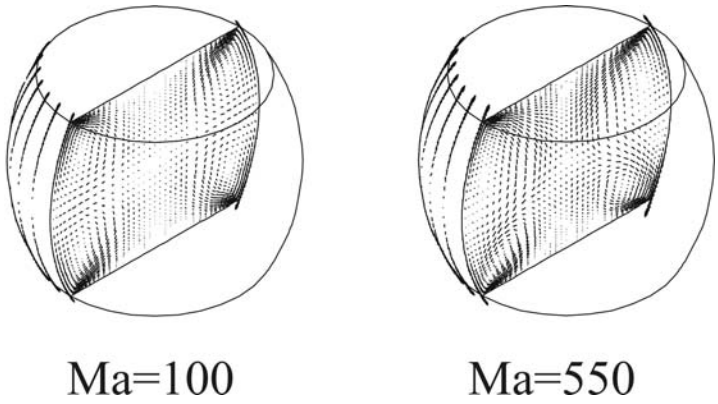
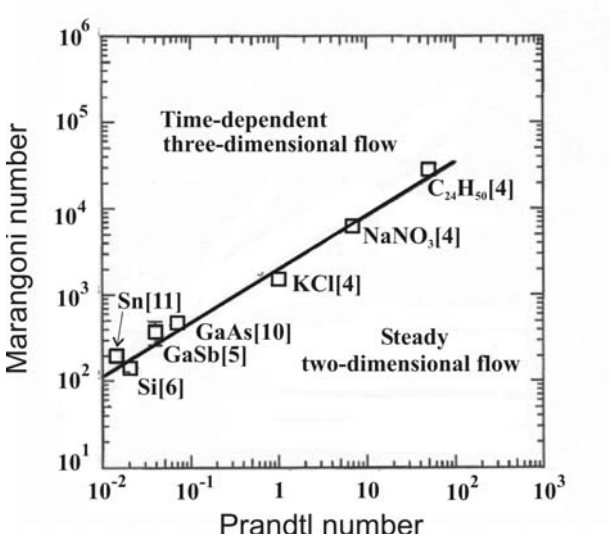


Fig. 5: 3-D numerical simulations of a GaSb float zone under microgravity, for a Ma value below Ma_{c2} (left) and above Ma_{c2} (right). From [5].

Fig. 6: The critical Marangoni number Ma_{c2} versus Prandtl number, after [11].



Both the values for Si and GaSb fit an empirical relationship for Ma_{c2} vs. Pr suggested by Yang and Kou [11]:

$$Ma_{c2} = 2000 \cdot \mathrm{Pr}^{0.6} \tag{2}$$

This relationship together with values for several materials is shown in fig. 6. It is interesting to note that it seems to fit well despite different paths to time dependency, especially taking into account the high Pr number materials like KCl or $NaNO_3$. Finally it should be noted that it is possible to reduce or suppress thermocapillary convection in semiconductor melts, and thus the formation of dopant striations, through the use of ei-

ther static [9,12,13] or dynamic [14] magnetic fields. The transition from a time-dependent to a laminar flow regime in these cases is usually coupled with a resymmetrization of the flow geometry.

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