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Numerical and Experimental Study of Hydrodynamic Effects in Crystal Growth from Melts

1. Introduction

Microelectronic devices like integrated circuits (ICs) as well as optoelectronic devices like lasers, light emitting diodes and photo-detectors are manufactured from semiconductor (Si, GaAs, etc.), and in some cases from oxide, single crystals. These crystals are produced from the melt, using special techniques called "crystal growth" at temperatures between 1000°C and 1800°C by controlling the liquid/solid phase transition. The production volume of Si, the most commonly used material, is more than 3000 metric tons a year with a market value of around 1 billion dollars.

The main technique for growing these crystals is the Czochralski process which is sketched in Fig. 1. The semiconductor or oxide is melted in a crucible with dimensions up to 500 mm in diameter and depth. The crystal is "pulled" from the top of the melt, starting with the dipping of a small seed crystal and increasing the crystal diameter up to 300 mm, always keeping its interface in contact with the melt. Pulling rates for Si are of the order of millimeters per minute. This rate is limited by the heat of crystallisation which has to be removed from the growth interface via the growing crystal. Another limitation follows from the requirements of crystal imperfection, which is an even more serious problem with compound semi-conductors (e.g. GaAs) and oxides. It is evident from numerous experimental studies that the relevant properties of the growing crystals are mainly determined by the transport process in the melt, i.e. heat and species transfer (for details see review articles by M u l l e r [1] and B r o w n [2]).

In the case of the Czochralski method (cf. Fig. 1) the transport mechanisms are: (i) buoyancy driven convection, originating from the side wall heating and top cooling (crystal); (ii) thermocapillary (Marangoni) convection, originating from the temperature gradients in the free melt surface between crucible wall and crystal, and (iii) forced convection, induced by the crystal and the

crucible rotation. Beside the Czochralski (CZ) process, the floating zone (FZ) and Bridgman methods are also in use for melt growth. The main differences to the CZ is that in the FZ no crucible is used, whereas in the Bridgman method the crystal grows in contact with the crucible, which is either vertically (VB) or horizontally adjusted (HB). (For more details see text books on crystal growth or [3].) In both VB and HB no forced convection occurs; in VB also the thermocapillary convection is avoided and buoyancy is considerably reduced by growing the crystal downwards (stable stratification in the melt).

In the first part of this paper it will be shown how the various hydrodynamic effects occurring in the melt affect the relevant properties of the growing crystal. This knowledge leads to the conclusion that an optimization of the crystal properties requires control of the convection dominated transport processes, i.e. mainly the thermal boundary conditions. Such a process modelling can be done on the basis of numerical simulations of the transport processes in the melt. In the second part of this paper we will discuss the present limitations and future possibilities for the numerical simulation of the melt growth processes.

2. Experimental studies

The growth rate is mainly determined by the heat transport through the growth interface. In the CZ of Si the relatively large amount of heat can only be removed from the growing crystal via its periphery, making a strongly concave interface necessary. With compound semiconductors, lower growth rates (10mm per hour) and smaller crystal diameters allow a convex or even a plane interface to be established. Flat interfaces, i.e. flat isotherms, are optimum with respect to avoiding thermal stresses in the growing crystal, which are an important source of crystallographic defects [4]. Convective flows determine the shape of the interface as illustrated for three different examples in Fig. 2. The shape of the interface can be visualized in the grown crystals by the striations as will be discussed later. The S-shaped interface of the GaAs crystal is typical for melt growth configurations dominated by buoyancy convection, which creates non-axi-symmetric roll cells. In CZ-configurations, the rotational forced convection yields a more axi-symmetric flow and the interface is typically convex for LEC-growth [6] and concave for CZ-growth of Si [7].

The species transport in the melt is also of high relevance for a growing crystal, as the electronic and optical properties of semiconductor and oxide crystals are determined by small amounts (10^{-2}% — 10^{-4}%) of impurity atoms called dopants.These dopants are distributed as solutes in the melt and are transported by convection and diffusion to the growth interface. However, the solute atoms reaching the interface are not all incorporated into the crystal but are partly rejected according to thermodynamic laws (distribution/segregation coefficient [8]). Some of the rejected species leave the region of the growth interface by the transport mechanisms and are then brought back to it again. It is clear, that both the intensity and the spatial variation of the convective flow strongly influence concentration and spatial distribution of species in the growing crystal. Figure 3 shows two extreme

experimental examples, correlated to strong convection and weak convection, together with the theoretical curves. These results present only the axial variation in one coordinate of the crystal (one-dimensional). It is clear that any spatial variation of the flow velocities causes differences in the concentration distribution according to Fig.3, resulting in the so-called radial or lateral non-uniformity of crystals [1].

The impacts of the hydrodynamic effects on the growing crystals discussed above do not depend on whether the flow is steady or unsteady. However, flow unsteadiness causes another problem in a growing crystal, namely temperature fluctuations near the growth interface. The heat transport determined growth rate therefore becomes also unsteady i.e. it fluctuates. This effect causes a variation of the incorporation of the dopants which is called doping striations, as illustrated in Fig.4. According to this principle the striations depicted in Fig. 2 can be explained. In principle, the buoyancy, thermo capillary and forced convection can each be unsteady or their interaction can cause unsteadiness. An experimental study of the different origins is possible for example after making a Fourier analysis of the frequency spectrum of the temperature fluctuations [9]. From these results it follows clearly that the hydrodynamic state of the melt in usual research or production Czochralski apparatus is far from being steady but comes closer to a turbulent state.This statement has two important consequences:

. A numerical simulation, which should come close to reality, has to consider unsteady turbulent - like flows, i.e. three - dimensional time-dependent calculations are necessary, as will be discussed in section 3.

. It is necessary and important to consider measures reducing the flow velocities (i.e. Reynolds number) in order to come close to a steady state of convection. This will be discussed in the following section.

First of all, a reduction of the melt height would be effective in CZ-growth with respect to buoyancy. This contradicts the increasing crystal dimensions, unless a continuous liquid feed technique [10] can be technically established.

From the point of view of the thermal boundary conditions, top heating and seeding from below would be optimum. This leads to the vertical Bridgman (VB) configuration and the submerged heater technique [11]. Neither method can be used for silicon but VB is now in progress for GaAs and InP growth [12].

Most effective for semiconductors and universal for all growth methods is the use of magnetic fields for suppressing unsteady flow and reducing convective transport [15]. Figure 5 illustrates this effect impressively. Magnetic fields are also useful to control the incorporation of oxygen during CZ-growth of Si [13].

It should also be mentioned that a reduction of gravity ("microgravity") has been demonstrated to be effective in reducing the driving force of buoyancy convection [14]. However, this possibility cannot be considered in the foreseeable future as a technically and economically useful solution.

Finally it has been demonstrated experimentally and confirmed theoretically that the action of the Coriolis force on a centrifuge can be used to stabilize convection [15].

3. Numerical simulation of transport processes

Transport processes in the melt are governed by the conservation laws for mass, momentum, enthalpy and chemical species. A representative transport equation may be written in integral form as:

$$\frac{d}{dt}\int_{CV} \rho\phi dV + \int_{CS} \phi\rho(V - V_s)\, dS - \int_{CS} \Gamma_\phi \, \mathrm{grad}\phi \, dS = \int_{CV} q_\phi \, dV$$

where ρ stands for density, V is the fluid velocityvector, V_s is the velocity of the control surface, Γ_ϕ is the diffusion coefficient and q_ϕ is the volumetric source of the transported quantity ϕ. The first term on the left hand side describes the rate of change of the quantity ϕ in the control volume (CV) which may move and change its shape and size. The second term describes the convection flux of ϕ through the boundary of the CV (a closed surface, called control surface, CS). The convection process is determined by the fluid velocity relative to the control surface, $V - V_s$. The third term describes the diffusion flux of ϕ through the CS - here taken to obey the Fourier (or Fick's) law. The term on the right hand side contains all other terms relevant for the conservation of ϕ within the control volume. In the case of momentum equations ($\phi = U_i$), there are additional diffusion flux terms when ρ and μ (the dynamic viscosity) are not constant, and the pressure and buoyancy terms are the major source terms (see [16] for more details).

A convenient way for a numerical simulation of transport processes is to use the finite-volume (FV) approach to discretize the transport equations and obtain systems of algebraic equations. Other approaches, like finite - difference (FD) or finite-element (FE) are also suitable; the advantage of the FV method is its - simplicity and inherent conservativeness. It offers the possibility to use volumes of arbitrary shape and unstructured grids, as is the case of the FE approach; indeed, these two methods usually lead on the same grid to the same discretized form of the equations. It is beyond the scope of this paper to describe the discretization process. Interested readers may find more information on FV methods in [17] and on FE methods in [18].

An important issue in the numerical simulation are the boundary conditions and their implementation in the solution scheme. The crystal growth process is characterized by

- non-trivial geometry which changes with time and is not a priori known (curved crucible walls, free surface meniscii, non-planar crystal/melt interface);

- complex boundary conditions (heat transfer by conduction through the

cruicible wall and by convection and radiation through the free surface, chemical species being added through the free surface and released by crucible walls etc.).

. unsteady three-dimensional flow (initial conditions needed).

In a large CZ apparatus turbulence is likely to be present, which makes the direct simulation very complex. In addition, the temperature differences are such that the Boussinesq approximation is usually not valid and the dependence of fluid properties (μ, ρ, Pr, C_p, Sc,...) on temperature should be known; unfortunately, most of the properties of metal melts are only approximately known, making accurate full simulation even more difficult.

All numerical methods provide only approximate solutions; they are affected by the following errors:

. *Modelling errors* (the difference between the exact solution of the mathematical model and the actual flow);

. *Discretization errors* (the difference between exact solution of the discretized equations and the exact solutions of the partial differential equations);

. *Solution errors* (the difference between the approximate and the exact solutions of the discretized equations, including round-off errors).

Typical modelling errors in crystal growth simulations result from the use of the Bousinesq approximation at high temperature differences, where the dependence of all melt properties on temperature should be considered. Whereas the solution error is easily controlled (through the level of residuals and relative variable changes in the iteration process), the discretization can only be estimated by performing systematic grid refinement. The order of the approximations used in the discretization process indicates only the rate of error reduction for sufficiently fine grids and gives no information about the magnitude of errors on a given grid. One can distinguish between space and time discretization errors; they can be estimated if the solutions on different systematically refined grids are available, cf. [19].

Due to the extreme complexity of the growth process, numerical simulations are often performed for simplified models. In some cases only heat conduction is considered, but the model incorporates the whole apparatus, cf. [20]. The aim of such simplified models is to predict e.g. the effect the pooling rate and heater output have on the diameter of the growing crystal. By specifying the crystal diameter as a controlling parameter, the models can be used for process control.

Most of the numerical crystal growth studies solve the two-dimensional (2D), i. e. axi-symmetric, coupled equations describing the heat transfer by conduction, convection and radiation, cf. [21,22,23]. The inclusion of convection into the model makes the simulation more realistic, as the heat

transfer rates are significantly higher when convection is present than in pure heat conduction. However, the model is limited to steady flows at small Rayleigh and Reynolds numbers, since at higher values of these parameters the flow becomes unsteady and three-dimensional, and a 2D axi-symmetric model will fail to converge under such circumstances [23]. There are only a few comparisons of predictions and experiments; the agreement is not always very satisfactory (e.g. the predicted shape of the crystal/melt interface does not agree with experiment when convection is included, cf. [23]).

Results with three-dimensional (3D) models are not as numerous as the 2D ones, and are usually limited to studying the transport processes in melt only and under simplified boundary conditions [24,25,26]. M i l e c i c and W i n g e r a t h [24] studied the influence of various parameters (crystal and crucible diameter, melt height, temperature difference between crystal and crucible wall) on the flow in an idealized Czochralski geometry (cylindrical crucible with plane bottom wall, flat crystal/melt interface and free surface). They showed that the buoyancy driven flow is highly unstable for all conditions that approach the real crystal growth process. Several authors simulated also the effect of magnetic forces on the flow and found that they reduce the velocity magnitudes. The Marangoni convection flows in a FZ melting process were studied by R u p et al [26]. They determined numerically the critical Marangoni number at which the oscillating convections starts.

Due to the scarcity of detailed experimental data on crystal melt flows and excessive computing times of the presently used solution methods, most of the numerical studies lack the conclusive validation of the results. In some papers the authors do not even mention the size of the grid used (e. g. [25]).

During the first NATO Workshop on computer modelling in crystal growth from melts, the definition of several bench-mark test cases for CZ crystal growth was initiated; those were later published in [27]. Two research groups in Erlangen, using different FV solution methods and very fine grids with up to320 x 320 CV, obtained identical results for all four test cases. Figure 6 shows predicted streamlines for the flow induced by crystal and crucible rotation (a,b) and by combined forced and natural convection (c). The flow patterns in Fig. 6 (a,c) are very similar, indicating that at the given crystal rotation and Rayleigh number the forced convection dominates. The effect of counter-rotation of the crucible is demonstrated in Fig. 6 (b): the flow induced by the rotation of crystal is limited to a small region near the crystal edge, and only a weak counter-rotating roll is formed beneath it. The accuracy of the results is demonstrated in Fig. 7, where the profiles of the radial velocity (b) and the maximum stream function value (a), obtained on various grids, are presented. From differences between the solutions on the two finest grids it can be concluded that the discretization errors on the finest grid are of the order of 0.1% .

The use of very fine grids is made possible by the introduction of multigrid techniques (cf. [19]). Iterative solution methods are known to eliminate efficiently error components whose wavelength is comparable to the mesh spacing. In an intermediate numerical solution, the solution error is composed of a spectrum of error components with various frequencies. By

operating on a sequence of systematically refined grids, the multigrid method achieves almost a constant convergence rate,irrespective of the fineness of the finest grid. The computing time increases then approximately linearly with the grid size,whereas in a single grid solution method this increase is quadratic. For the above test calculations, computing times of only a few minutes on a CRAY computer or two hours on a SUN workstation were needed for the grid with 320 x 320 control volumes. A classical single grid method would require about 100 times larger computing time. In the case of unsteady flow, the savings are not as dramatic, but they are still significant (factor 2 to 10). A three-dimensional multigrid FV method for studying CZ flows in realistic geometries has been developed by L e i s t e r and P e r i c [28]. Figure 8 shows a typical grid and predicted velocity field for unsteady flow at Grashof number of 7.5×10^9.

The largest problem in the simulation of crystal growth is the consideration of the heat transfer by radiation, which appears to be playing an important role, and the determination of the free surface and crystal/melt interface shapes. Some two-dimensional models (e. g. [23]) incorporate these features, but 3D applications are limited to prescribed shape and heat transfer through the free surface.

The prediction of 3D unsteady flows requires, in spite of the multigrid and other acceleration techniques, enormous computing times. It is a generally accepted view that the required computing power for such flow simulations can only be provided in the future by parallel computing. This is the reason why many research groups worldwide are working on parallelization of the solution methods. The domain decomposition techniques and MIMD (multiple instruction, multiple data) parallel computers are mostly employed in conjunction with implicit solution methods. The efficiency of parallel computing, which takes into account the reduction of convergence rate due to domain decomposition and loss of CPU TIME due to communication, is a function of the grid size and number of processors. The above mentioned bench-mark test case (cf. Fig. 6) was solved on a transputer system with 48 processors using a grid with 512 x 348 CV in 1357 seconds, with an estimated efficiency of 80%. The same calculation took 1190 seconds on a CRAY YMP computer. For a given algorithm, it is possible to create a model for the prediction of parallel efficiency as a function of the number of processors, the setup time and data transfer rates [29]. Fig. 9 shows estimated efficiencies for a problem with 10^6 grid points and two parallel computers. Up to 500 transputers would offer an efficiency of about 80% and a real computing power of over 200 MF lops for type T800 and about 4 GFlops for type T9000.

The parallel processing can be achieved not only in space but also in time; this enables an overall efficiency increase [30]. It is thus expected that more accurate simulations of 3D unsteady flows will soon become possible, at least for laminar regimes. The large eddy simulation of turbulent flows, which is nowadays only being undertaken on academic level, will also become a plausible means for solving engineering problems [31].

4. Conclusions

From the discussion carried out in the preceding sections, the following conclusions can be drawn:

. The quality of crystals grown from melts is determined by the transport processes in the melt. The understanding and control of these processes enables the improvement of crystal properties.

. Due to the hostile environment, a detailed experimental analysis of the transport processes in the melt is not possible. Experimental studies must therefore be comp lemented by numerical simulations.

. Numerical simulations already proved useful in describing the complex transport processes during crystal growth from melt and in determining the parameters at which the flow regime changes (e. g. from steady to unsteady, from symmetric to asymmetric etc.). The development of advanced numerical techniques like multigrid and parallel computing promises accurate simulations of unsteady 3D flows in the near future.

5. Acknowledgements

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7. FIGURES

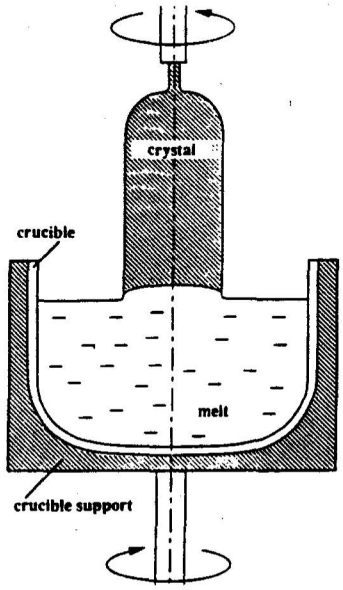


Fig. 1: Principle of the Czochralski growth process.

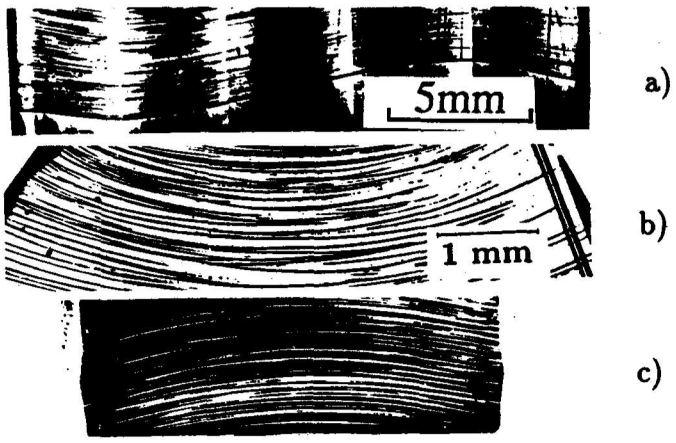


Fig. 2: Different shapes of the solid/liquid interface:
(a) non-axisymmetric buoyancy convection in zone melting of GaAs,
(b) convex-shaped axisymmetric interface in Liquid Encapsulated Czochralsky growth (LEC) of InP
(c) concave-shaped interface in Czochralski growth of Si [7].
Direction of growth from top to bottom.

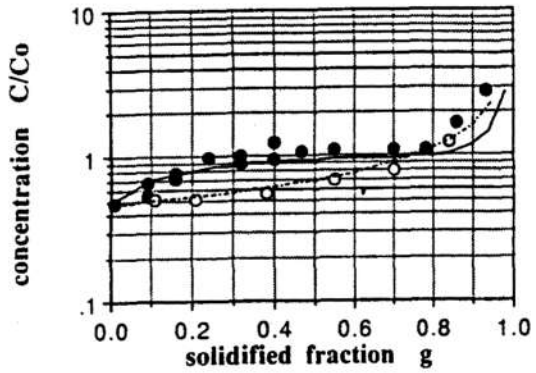


Fig. 3: Concentration C (normalized by initial concentration C_o) along growth direction as a function of the solidified fraction g for two limiting cases: complete mixing (dash-dotted line = theory, empty symbols = experimental results of VB growth of Te-doped GaSb) and weak mixing (solid line = theory, full symbols = experimental results of LEC growth of S-doped InP).

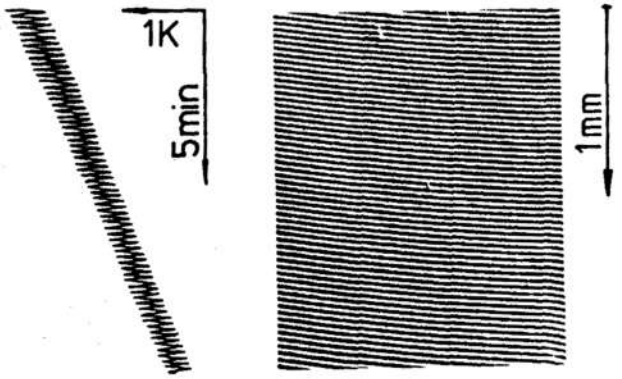


Fig. 4: Longitudinal section of a Te-doped InSb crystal with doping striations (right) and melt temperature recorded during the growth time (left). Growth method: VB with top seeding.

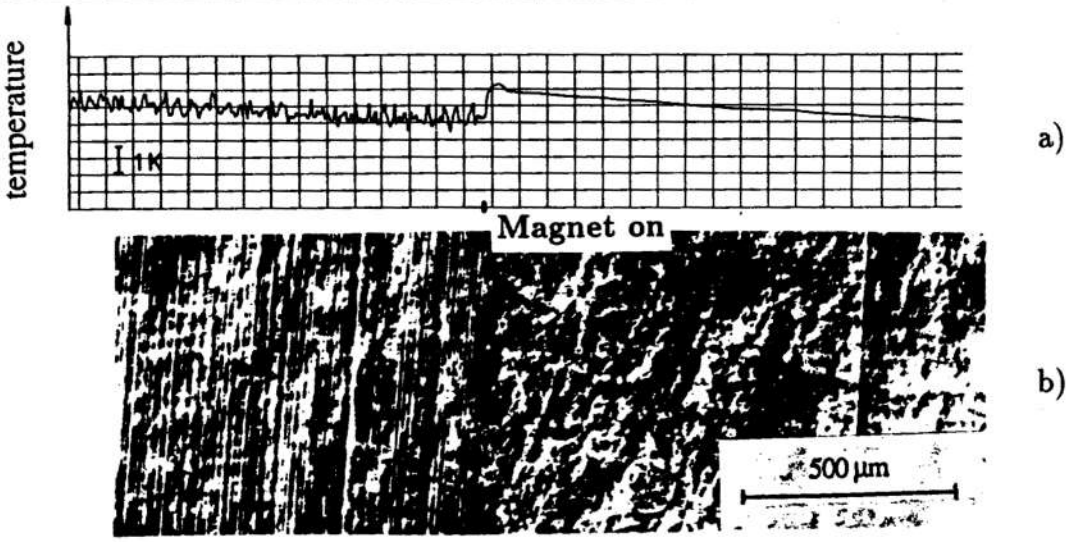


Fig. 5: The effect of laterally applied magnetic field in horizontal zone growth of Te-doped InSb: (a) temperature recorded during the growth time, (b) longitudinal crystal section with doping striations. Growth direction from left to right.

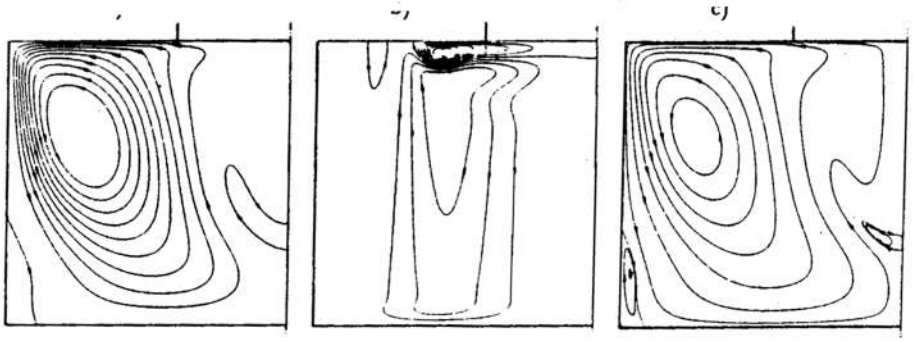


Fig. 6: Predicted streamlines for three benchmark test cases defined in [27], using 320 X 320 CV grid and second-order discretization: (a) $Re_X = 10^4$, $Re_C = 0$, $Gr = 0$,
(b) $Re_X = 10^4$, $Re_C = -Re_X/4$, $Gr = 0$,
(c) $Re_X = 10^4$, $Re_C = 0$, $Gr = 10^5$, Re_C and Re_X - Reynolds numbers based on crucible and crystal rotation, respectively.

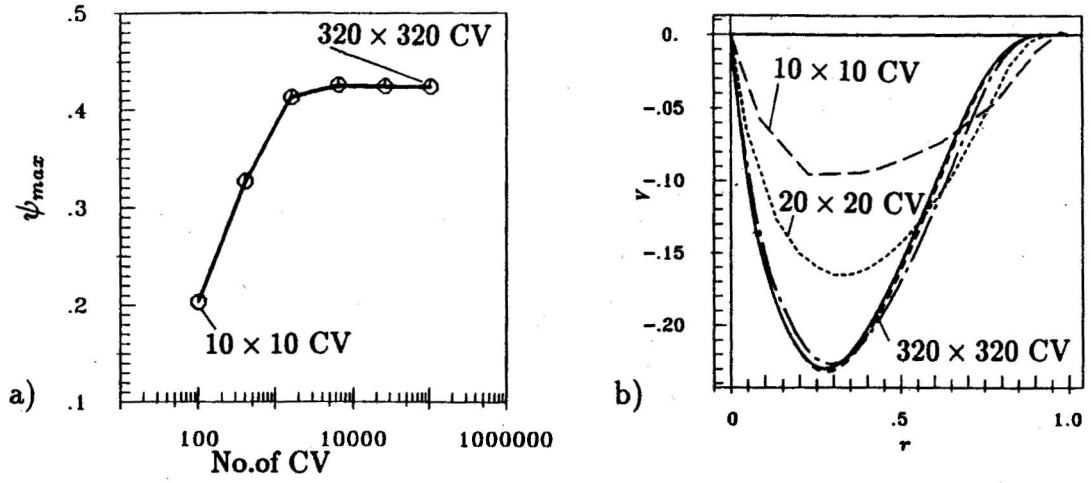


Fig. 7: Dependence of solution in Fig. 6 (a) on the numerical grid: (a) strength of the primary vortex, (b) profile of radial velocity component.

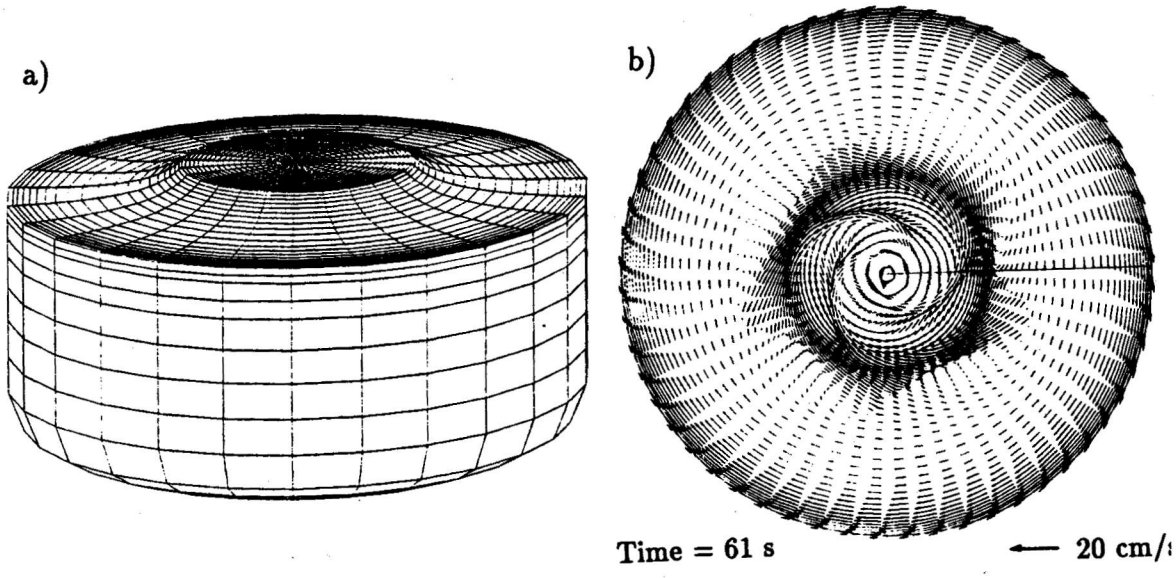


Fig. 8: A typical 3D grid for CZ melt flow calculation (a) and a velocity field in a radial cross-section beneath the crystal for unsteady CZ flow at Gr = 7.5 . 10^9, Re_C = $1.2.10^6$, Re_X = 10^{-6} and Pr = 0.02 (b).

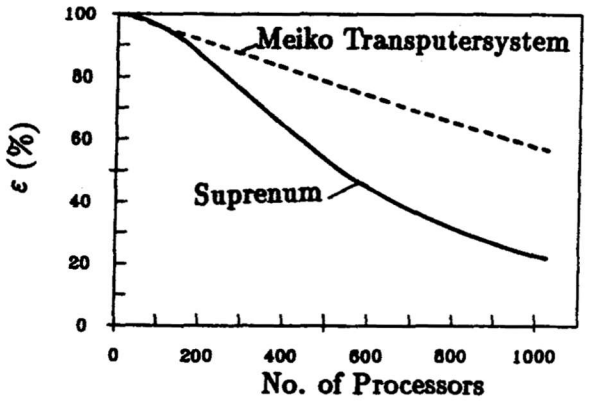


Fig. 9: Predicted efficiency of the parallel solution of fluid flow problems with implicit methods on a grid with 10^6 nodes using domain decomposition technique.Authors' address: