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14. Abstract/Notes

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OPTIMUM CONVECTION CONDITIONS FOR CZOCHRALSKI GROWTH OF SEMICONDUCTORS

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Abstract

Time dependence of flow patterns in conventional Czochralski pulling of semiconductor crystals like silicon and gallium arsenide leads to corresponding temperature (and thus growth rate) fluctuations at the growth interface. In order to minimize the resulting inhomogeneities (striations) the general approach is to reduce convection by either applying damping magnetic fields or by growth in microgravity. An alternate approach is the application of enforced convection which leads to homogenization of the whole melt and thus to well-defined conditions at the growth interface. The advantages and disadvantages of the various approaches are discussed and examples of industrial applications given.

Introduction

For most applications the present quality of quasi-dislocation-free silicon crystals is adequate. However, the increasing degree of device integration from present commercial 64 kbit/chip to forthcoming 256 kbit/chip and forecasted 512 kbits to megabit per chip requires silicon crystals with improved homogeneity (in terms of spreading resistence) and decreased number of swirl-defects in order to enlarge the yield. Many impurities have to be kept below the ppm - and in certain cases below ppb - level whereas the oxygen concentration (originating from the starting material, from the growth atmosphere and from the SiO_2 crucible) has to be kept within narrow specific tolerances. Silicon crystals of special perfection with very low oxygen and

carbon concentrations are essential for high-power devices, these crystals therefore are grown by the more complex vertical float-zone process.
Gallium arsenide for major applications in optical communications and displays and for forthcoming applications in microelectronics (high-speed FET and HEMT devices) and in power devices (FET arrays) could not be grown commercially to the required quality so far. The dislocation problem has been reduced somewhat by doping and by diminishing the temperature gradients in the growth processes (liquid-encapsulated Czochralski "LEC" and horizontal Bridgman "Boat-grown"). Nevertheless GaAs crystals with etch-pit densities (EPD) less than $10^3 cm^{-2}$ are not yet commercially available*, and typical EPDs are between 10^4 and $10^5 cm^{-2}$. Other problems with GaAs are non-stoichiometry, non-homogeneity, swirl-like defects, the deep-level defects EL2, and the required purity for achieving semi-insulating material (without the highly diffusive compensating chromium) for high-speed devices. There is widespread hope that also GaAs can be economically produced by the Czochralski process (yielding preferred round wafers instead of D-shaped wafers of the Bridgman process), and that most of above problems can be solved by proper adjustment of the growth parameters.
One important parameter in Czochralski growth is <u>convection</u> which is responsible for homogeneity and for the distribution (and number?) of swirl-like and EL2 defects. In the following the various convection regimes in the Czochralski process will be described and the most promising approaches to optimization of the convection conditions in Czochralski melts presented.

Convection regimes in the conventional Czochralski process

The hydrodynamics of Czochralski melts is rather complex due to the geometry, the rotation of crystal and crucible, and due to the temperature distribution. The behaviour of specific melts is determined by the ratio of kinematic viscosity to thermal diffusivity defined by the dimensionless Prandtl number Pr, which may vary between typically 0.01 - 0.03 for metals and semiconductors, 0.04 - 0.5 for oxide metals, 7 for water, and above 10 for oils and many other organic liquids. This variety of Pr impedes the transfer of experience and the application of flow simulation results to crystal growth reality.
A further complication due to temperature differences along the free liquid surface was recognized in the solidification experiments in Skylab. The

* Sumitomo announced "dislocation-free" GaAs for 1985

temperature sensitivity of the surface tension causes the thermocapillary or Marangoni convection which may have a significant impact on the hydrodynamic scene depending on the ratios of the respective dimensionless Marangoni, Grashof and Reynolds numbers, the latter two representing natural and forced convection, respectively /1/.

The flow regimes which may occur in the conventional Czochralski process are shown in Fig. 1. Here the Taylor number (defined below) is assumed sub-critical. The angular flow directions and velocities are indicated by circles of various sizes with internal dots for upward flow and with central crosses for downward flow.

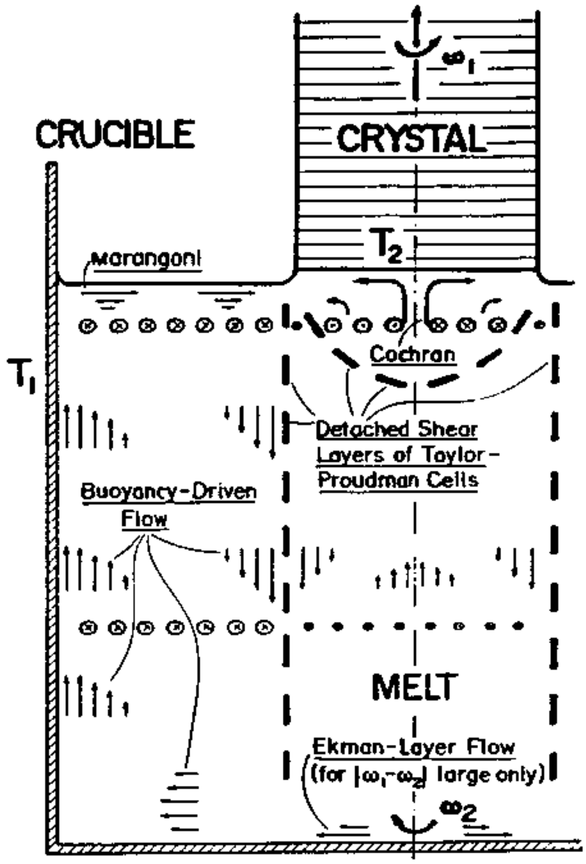

Fig. 1. Flow regimes in conventional Czochralski process with Taylor-Proudman cells and with significant natural convection (low Taylor number)

Natural convection caused by temperature differences consists of the buoyancy-driven regime (Bénard convection) defined by the Grashof number /1/ or by the Rayleigh number Ra = Ga . Pr /2/, and of the Marangoni convection mentioned above. The rotation of the crystal (and often also of the crucible in opposite direction: counterrotation) causes (mechanically) forced convection: the rotating crystal acts as a centrifugal fan, and the resulting flow carries the name of Cochran who analyzed it in 1934. Although the resulting momentum boundary layer somewhat isolates the growth interface from the generally instable flow regimes in the melt /1/, the adjustment of the crystal rotation rate is critical with respect to the hot liquid pulled to the crystal and its effect on the shape of the crystal-melt interface. Critical crystal rotation rates for upward flow have been established /3/, and a sudden transition of the flow regimes observed /4, 5/. Frequently the continuous rotation of crystal and counterrotation of crucible lead to liquid regions with distinctly different angular velocities, the so-called Taylor - or Taylor-Proudman cells. The occurrence of these cells and of other phenomena as a function of the relative rotation rates of crystal and crucible have been recognized by flow visualization experiments /6, 7/. The Ekman flow at the crucible bottom occurs only at significant relative differences of the crystal and crucible rotation rates.

The interaction of the screw-like spatially non-uniform shear flow along the boundaries of the Taylor-Proudman cells with (generally time dependent /8/) natural convection (and/or with Taylor vortices, see below) is one cause of temperature fluctuations at the growth interface. These temperature changes - not the fluctuations of the velocity component of the convection - lead to growth-rate fluctuations and striations /9, 10/.

The relative contributions of the various natural and forced flow regimes can be estimated from the respective dimensionless numbers. Their derivations has been done for the following growth conditions and properties of molten silicon: crystal diameter 5 inches ($r = 6{,}35$cm); crucible diameter 15 inches ($R = 19$cm); aspect ratio of melt (diameter to height) = 1; crucible rotation rate + 10 rpm; crystal rotation rate - 15 rpm; crystal temperature 1685K, crucible wall temperature 1800K, melt density $2.33 g.cm^{-3}$; thermal diffusivity $0.125 cm^2.s^{-1}$; volumetric thermal expansion coefficient $1.41.10^{-5} K^{-1}$; viscosity 0.7 centipoise; surface tension 720 $dynes.cm^{-1}$; thermocapillarity coefficient $14.9 cm.s^{-1}.K^{-1}$.

The resulting dimensionless numbers are:

Prandtl No. (Momentum diffusivity ÷ heat diffusivity) $Pr = 0.024$

Grashof No. (Buoyancy force ÷ viscous force) $Gr = 1.10^8$

Reynolds No. (Inertia force ÷ viscous force) $Re \approx 8.10^4$
Ekman No. (Viscous force ÷ Coriolis force) $E = 1/Re \approx 1.10^{-5}$
Taylor No. (Centrifugal force ÷ viscous force) $Ta \approx 6.10^4$
Marangoni No. (Surface-tension driven force ÷ viscous force) $Ma \approx 9.10^4$
Bond No. (Buoyancy force ÷ surface tension force) $Bo \approx 500$.

These numbers have been derived for the Czochralski geometry by using simplifying assumptions and analogy arguments, therefore they indicate only the order of magnitude for the following discussion on the relative importance of the various flow regimes in above examples of Czochralski growth of silicon. The small Ekman number indicates that a geostrophic core will be formed consisting of the Taylor-Proudman cells /11/. Ekman flow at the crucible bottom, Stewartson layers along the vertical interfaces of the Taylor--Proudman cells, and Cochran flow towards the crystal interface are the dominating forced flows in the liquid center. The large Taylor number indicates instability /12/ with turbulent Taylor vortices in the peripherical part of the melt outside the Taylor-Proudman cells. In view of the very small value for $E^2.Gr(=Gr.Re^{-2})$ in the central region and $Gr.Ta^{-2}$ in the peripherical liquid region the forced convection is dominating in the bulk liquid and buoyancy-driven convection nearly negligible. Thermocapillary convection along the free liquid surface according to the large Marangoni number is not negligible. On the other hand, the data of the surface tension of silicon and its temperature sensitivity may be not sufficiently reliable to give a conclusive indication of the role of the Marangoni convection. However, the effective convection regimes are sensitive to the geometrical and thermal symmetries of the Czochralski system. In addition, the aspect ratio of the melt changes during the pulling process and thus will modify the flow unless the growth parameters are programmed to preserve a desirable flow pattern and interface shape.

The rather comples nature of Czochralski flow can frequently be guessed already from the liquid surface patterns during growth, especially in growth of oxide compounds at high temperatures. The large variety of swirl-like patterns (frequently called "spokes") was reproduced by simulation experiments in order to find relations to the internal flow /13/.

Magnetic fields

The application of a magnetic field to the crystal growth melt was suggested nearly 20 years ago /14/ to suppress oscillatory convection and thus temperature fluctuations and striations. However, the technological realization was achieved only recently, first to silicon /15, 16/, then 1982/1983 to gallium arsenide /17, 18/ in the framework of a Japanese "Big Project" of MITI. The orientation of the magnetic field should be perpendicular to the hot and cold melt interfaces to be most effective. The damping efficiency, i.e. the increase of the critical Rayleigh number for the onset of buoyancy-driven convection, is defined by the Hartmann number Ha. For many liquid metals and semiconductors $Ha = 0.0262\ H_0L$ with H_0 the magnetic field in gauss and L in cm the distance over which the magnetic field acts. A detailed understanding of the action of magnetic field on Czochralski melts is attempted by numerical simulations /19/.

For growth of silicon and gallium arsenide crystals of two and three inch diameter, typically 1200 to 3000 gauss are applied /15 - 17/. A significant reduction in temperature oscillations from 18^0 to 0.1^oC was observed during growth of 2-inch GaAs by liquid-encapsulated Czochralski /18/. Thus the homogeneity could be improved, and the concentration of EL2 defects was reduced, presumably by a reduction of the growth-rate fluctuations. The first experiments were undertaken with normally conducting electromagnets with coils weighing 4.6 to 23 tons. A new approach uses superconducting coils of 36kg weight for achieving the same central magnetic field as above classical magnets. Due to the significant improvement of the quality of crystals grown in magnetic fields, at least one company has started the development of commercial crystal growth equipment using magnets.

Microgravity

The instabilities in buoyancy-driven convection in low-Pr fluids like metals and semiconductors and the related striations as well as the unawareness of the role of thermocapillary convection in crystal growth until the Skylab experiments 1973/1974 established the great interest in crystal growth in zero gravity. Still now there are plans of large US companies to produce certain semiconductor crystals of improved homogeneity in space on a commercial base. These efforts undoubtly will have to compete with crystal production on earth where sufficient to excellent homogeneity has been achieved by magnetic fields (as described before) or by dominating forced convection (next section).

Without doubt, solidification experiments in space are very important for the understanding of the gravity parameter and for the study of the other flow patterns in absence of the disturbing effect of buoyancy-driven convection. Also several specific materials (spheres) and phenomena could only be realized in space. However, for the production of homogeneous structurally perfect semiconductor crystals in space there are, besides the required large efforts, problems, for example:

a) there is no real zero gravity, only "microgravity" and "g-jitter" of 10^{-3} to 10^{-6}g,
b) technological difficulties with process and temperature control,
c) thermocapillary convection for high (economic) solidifications rates (which require large temperature gradients for extraction of the latent heat of crystallization).

Accelerated Crucible Rotation Technique

ACRT had been suggested already in 1971/1972 for homogeneization not only of high-temperature solutions but also of Czochralski melts /20, 21/. However, there was general doubt about the beneficial effect of this stirring technique in melt growth due to the periodically induced fluctuations of magnitude and directions of fluid flow /22, 23/ until it was realized that hydrodynamic fluctuations themselves have a small or negligible effect on homogeneity, and that it is mainly temperature fluctuations that cause striations /10/. This was confirmed experimentally as discussed further below. A typical flow pattern for ACRT-Czochralski for subcritical Taylor number is shown in Fig. 2. Stirring by ACRT is achieved through periodic acceleration and deceleration of the crucible rotation. This induces Ekman-layer flow along horizontal boundaries like the crucible bottom: during acceleration liquid parts in a thin layer ("Ekman-layer" of thickness proportional to $E^{1/2}$) are thrown to the periphery of the melt where the flow bends upwards in the thin Stewartson-layers (thickness α $E^{1/3}$ and/or $E^{1/4}$) along the internal crucible wall. In deceleration the reverse flow occurs, and high-momentum fluid from the periphery moves to the center within the bottom Ekman-layer where due to friction the centrifugal forces are reduced. The optimum ACRT period is related to the spin-up time during which the largest fraction of the liquid is pumped (accelerated) through the Ekman layer /24, 25/.

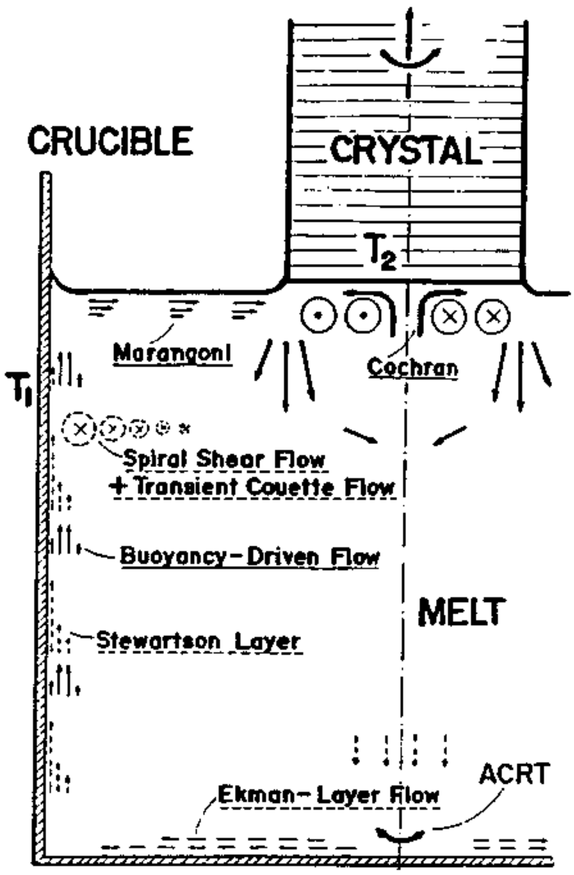

Fig. 2. Flow regimes in Czochralski growth using ACRT.

Another flow of ACRT is the spiral-shear flow caused by the inertia of the liquid when the crucible is accelerated or decelerated /20, 21, 24/. Besides kinematic viscosity and rotation/acceleration rates the aspect ratio of the melt determines the relative importance of Ekman-layer flow and spiral--shearing distortion, the former dominating under typical Czochralski conditions with an aspect ratio of about unity /24/. For high acceleration rates a transient Couette flow was predicted /24/ and also observed in simulation experiments /26/.

The above ACRT-induced flows interact with the flow regimes in conventional Czochralski melts discussed before. The present view is that optimum ACRT--Czochralski conditions would be achieved with a quasi-laminar flow in front of the crystal interface and with efficient mixing of the residual melt. The laminar flow along the growth interface would be achieved by a critical constant crystal rotation rate, the resulting Cochran flow yields a quasi--constant thickness of the momentum - and diffusion boundary layers. The adjustment of the Cochran flow and of the enforced ACRT convection have to be done within the limits dictated by the shape of the solid-liquid interface and by development of flow instability and surface waves. Recent flow visualization has revealed that specific ACRT periods and maximum rotation rates can be found where sufficient mixing is achieved without the formation of surface waves /26/. This is shown in Fig. 3 where the observed flows in forced Czochralski-ACRT convection experiments (neglecting thermal effects) as well as the optimum region of effective mixing are indicated. The flow visualization experiments /26/ as well as computer simulation /27/ demonstrated that by ACRT the formation of Taylor-Proudman cells can be prevented, especially in the ACRT-isorotation regime.

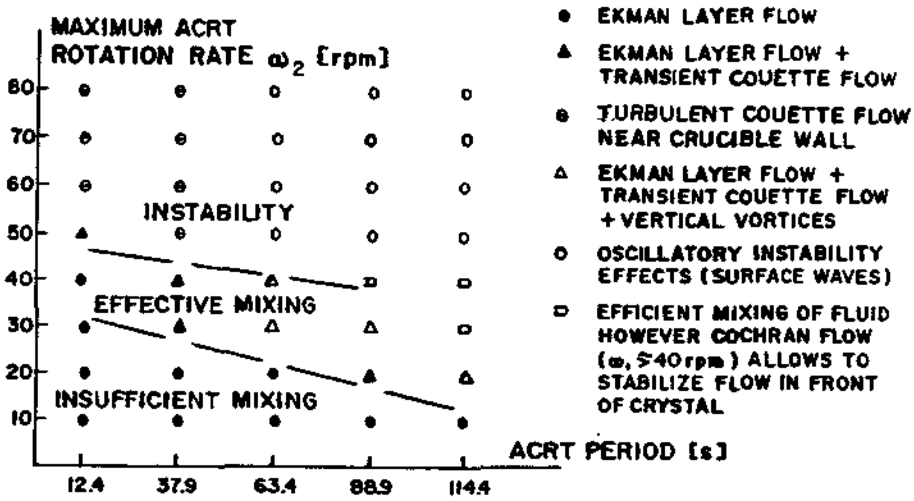

Fig. 3. Regime of ACRT rotation rates and periods for achieving effective mixing in Czochralski simulation experiments using a liquid of high Pr /26/.

The change of the crucible rotation rate causes a quasi instantaneous parabolic deformation of the free liquid surface. Since this would cause changes of the meniscus angle and thus of growth rate and crystal diameter, the liquid level variation effects can be minimized by compensating height corrections of either the crystal or the crucible /28/. ACRT is realized in conventional Czochralski apparatus by electronic control of dc motors /26/ or of step motors, or by frequency programming of ac motors.

ACRT is now applied in silicon production /28, 29/ where the proper change of the ACRT stirring action allows to program the dissolution rate of the SiO_2 crucible and thus to achieve silicon crystals of nearly constant oxygen concentration from seed to tail. At the same time the homogeneity within the wafers is improved. A similar improvement of silicon homogeneity has been achieved by proper adjustment of the crucible rotation rate during the pulling process /30/. For this phenomenon the following explanation is proposed: In large silicon melts the Taylor number is supercritical, and thus Taylor vortices are formed in the peripheral fraction of the melt. The induced flow component along the crucible wall, together with the contribution from Stewartson-layer flow, determines the dissolution rate of the silica crucible in a similar way as ACRT stirring. Another technological application of ACRT is in Czochralski fabrication of garnet solid solutions which are applied as substrates for magneto-optic memory display production /31/.

Discussion

It is difficult to take measures to reduce the striation problem in view of the hydrodynamic complexity of the conventional Czochralski process.

The achievement of excellent thermal symmetry as well as the reduction of thermal gradients (by afterheaters, radiation shields, heat pipes /32/, the height of B_2O_3 encapsulent in case of GaAs growth) have lead to certain improvements. However, the Taylor-Proudman cells causing locally differing flow rates and directions in the liquid region below the edge of the crystal impede significant improvements. In view of the limits of forced convection by Cochran flow (crystal rotation) it would be difficult to find conditions for growth of very homogeneous crystals by conventional Czochralski growth. Further complications are caused by the change of the aspect ratio of the melt and by the required narrow tolerances of the oxygen concentration in silicon. These complications demand a programmed variation of the (steady) rotation rates of crystal and crucible and of the crucible position within the heater. In any case the automatic diameter control is a prerequisite for obtaining high-quality crystals.

Microgravity would reduce buoyancy-driven convection which, however, is anyhow negligible in view of the supercritical Taylor number in typical semiconductor Czochralski growth. The problem of the Taylor-Proudman cells would remain, and also thermocapillary convection would be unaffected. With the occurrence of Taylor vortices in large semiconductor Czochralski melts the main reason for microgravity crystal production by the Czochralski process is eliminated. Nevertheless, solidification research in space and development of crucible-free processes making use of the high-purity vacuum are of utmost interest.

Magnetic fields damp the convective oscillations and have been demonstrated to homogeneize silicon and GaAs crystals. In the latter case also the EL2 defects are reduced although there remains a problem with the so far unexplained high conductivity of GaAs crystals grown by magnetic LEC. At the moment magnetic fields are most promising and thus will be applied in those cases where it is economically justified.

The ACRT-Czochralski method requires by orders of magnitude lower investment compared to magnetic fields and to microgravity. Although it is already applied to Czochralski production of specific technological crystals (silicon: oxygen and garnets), a more deep understanding of its action is required for wide application. In any case the individual optimization of the ACRT parameters for each specific process is recommended to minimize inhomogeneities.

Striations have been a long-standing problem in Czochralski growth: now the solution to this problem seems in sight by optimizing the convection conditions, in addition to careful control of other parameters like temperature/diameter control, temperature gradients, and thermal symmetry. In this connection it may be mentioned that recently the "inherent" or "intrinsic" striation problem in flux growth of oxide solid solutions could be solved /33/.

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