

AREA II.
PREPARATION OF NEW MATERIALS

AREA II: PREPARATION OF NEW MATERIALS

Faculty: M.P. Dudukovic´
J.L. Kardos (MRL)
P.A. Ramachandran

Our past research in this area consisted of expanding the reaction engineering methodology to describe the transport-kinetic interactions involved in manufacturing of new materials. Both modeling, based on fundamentals, and experimental work were pursued. Our goal has always been to facilitate the transfer of bench scale science to manufacturing and to improve the manufacturing processes. We have utilized this approach in the past in four areas:

- i) preparation of semiconductor grade silicon,
- ii) autoclave process for curing of high performance composites,
- iii) microencapsulation and production of biomaterials,
- iv) preparation of long carbon fibers.

Our research in the semiconductor silicon area has been dormant during the past few years (except for proprietary contract studies which cannot be reported here) but we may want to revitalize some new environmental aspects of it. A project was initiated in 1997 to quantify the effect of sonification on the reactivity, effectiveness and specificity of aqueous etching and in cleaning chemistries commonly used in the electronic materials industry. Unfortunately, the graduate student involved, Rebecca Smith, departed for personal reasons without completing her work.

We have perfected our models for devolatilization and resin flow during cure of long carbon fiber composites and we have extended their use to an increased number of polyimide systems with remarkable success. Using independently determined kinetic and mass transfer data, our model has the capability of relating operating procedure and composite quality, and is a useful tool in manufacturing. This success represents a good example of the virtues of team work involving specialists in composites (**J.L. Kardos**), reaction engineering (**M.P. Dudukovic´**) and control and optimization (**B. Joseph**). Work has been completed on modeling the manufacturing of carbon fibers and their carbonization in collaboration with the **Materials Research Laboratory** (MRL). This work is a joint effort of Professors **Kardos, Ramachandran** and **Joseph**.

Our microencapsulation project was completed several years ago and will not be reported on here. Electrophoretic purification of pancreatic islets of Langerhan has also been completed and provides a good quantification of the achievable degree of purification. This project was executed in the **Biological Transport Laboratory** (BTL) with input from CREL. The project of developing a new model and material for release system has been completed. This project also is executed in the BTL with input from CREL.

A brief report is included on the following project:

II-1. Semiconductor Grade Silicon: CREL know-how is reviewed. (**M.P. Dudukovic´** and **P.A. Ramachandran**)

II-1. SEMICONDUCTOR GRADE SILICON

A. Problem Definition

Many aspects of manufacture of semiconductor grade silicon can benefit by utilizing the reaction engineering methodology. Some of these are listed below through past accomplishments and suggested future work.

B. Research Objectives

No specific objectives are set at present other than the overall goal to continue contributing via reaction engineering to improved and cleaner processes for silicon manufacture.

C. Research Accomplishments

CREL contributed over the years to solution of the following problems in Si manufacture:

1. Polysilicon crystal growth in Siemens decomposers by silicon deposition via hydrogen reduction of chlorosilanes was modeled. Optimal operational window for industrial practice was identified.
2. Polysilicon crystal growth via silane pyrolysis was modeled. The model provided guidance for design and optimal operation of Komatsu decomposers.
3. Aerosol (free space reactor) for silicon production via silane pyrolysis was modeled. The model indicated that excessive staging would be needed to reach particle size of the order of 20 μm .
4. Fluidized bed for silicon production via silane pyrolysis was modeled. Model was used to identify operating and design conditions that minimized the formation of dust (fines) and maximized CVD growth.
5. A complete heat transfer model was developed for the Czochralski crystal puller. The model related the production rate and crystal quality to operating and design variables.
6. Improved model based CZ puller control was developed. Simultaneous crystal diameter and interface shape control was achieved. Innovative idea of jet cooling was introduced. Two NASA certificates of recognition were received for the work in this area.
7. A novel etcher for large wafers was developed and implemented in industry (contract work).
8. The analysis of IPA wafer drying has been completed and suggestions for improvement of particle removal made (contract work).

D. Future Work

We are seeking opportunities to continue the work on the following topics:

- A. Improved model based control of CZ pullers.
- B. Novel acid etcher design.
- C. Environmental control and contaminant elimination in various process steps of Si-manufacture.

E. References

1. "Reactor Models for CVD of Silicon", Proc. Flat Plate Solar Arrat Workshop on the Science of Silicon Material Preparation, JPL Publication 83-13, 199-226 (1983).
2. "Interface Shape in Czochralski Grown Crystals: Effect of Conduction and Radiation", R.K. Srivastava, P.A. Ramachandran, and M. P. Dudukovic', J. Crystal Growth, 73, 487-504 (1985).
3. "Radiation View Factors in Czochralski Crystal Growth Apparatus for Short Crystals", R.K. Srivastava, P.A. Ramachandran and M.P. Dudukovic', J. Crystal Growth, 79, 281-291 (1986).
4. "Czochralski Growth of Crystals: Simple Models for Growth Rate and Interface Shape", R.K. Srivastava, P.A. Ramachandran and M.P. Dudukovic', J. Electrochem. Soc.: Solid-State and Technology, 133(5), 1009-1015 (1986).
5. "Simulation of Jet Cooling Effects on Czochralski Crystal Growth", R.K. Srivastava, P.A. Ramachandran and M.P. Dudukovic', J. Crystal Growth, 76, 395-407 (1986).
6. "Aerosol Reactor Design: Effect of Reactor Type and Process Parameters on Product Aerosol Characterization", S.E. Pratsinis, T.T. Kodas, M.P. Dudukovic', and S.K. Friedlander, I&EC Process Design & Develop., 25, 634-642 (1986).
7. "The Effect of Aerosol Reactor Residence Time Distribution on Product Aerosol Characteristics", S.E. Pratsinis, T.T. Kodas, M.P. Dudukovic' and S.K. Friedlander, Chem. Eng. Science 41(4), 693-702 (1986).
8. "Transport-Kinetic Effects in Manufacture of Polycrystalline Silicon", Y.B. Yang, D.Sc. Thesis, Washington University, St. Louis, MO, December, 1988.
9. "Modeling of Czochralski Crystal Growth", P.A. Ramachandran and M.P. Dudukovic', Final Technical Report, EPRI Contract RP-8001-1, (1990).

II-2. Melt Dynamics in Czochralski Crystal Growth of Silicon

A. Problem Definition

Silicon single crystals produced by the Czochralski (CZ) process provide a majority of silicon substrates for the fabrication of microelectronic devices. Buoyancy force is inevitable in melt because of temperature difference in the crucible. Marangoni forces are acting at gas-melt interface due variation of surface tension with temperature. Generated flow under these conditions is turbulent or transition to turbulent in nature. External forces such as Coriolis, centrifugal force (due to crystal and crucible rotation) and Lorentz forces (due to applied magnetic field) are used for stabilizing the flow. Careful balance of between Lorentz force and Coriolis force is essential to achieve better control over melt flow. Knowledge of interaction among these forces is important to study the effect of flow on heat and mass transfer rates in the crucible. Thus, quality of a CZ crystal, determined by its oxygen content, dislocation and defect distribution, is affected by the flow, heat and mass transfer rates in the silicon melt from which the crystal is grown.

Many multi-scale efforts (experimental as well as theoretical) are under way to understand the complexities involved in the crystal growth process [1-2]. Numerical simulation is gaining a lot of attention due to improved computational speed provided by technological evolution. In view of the continuous efforts to predict flow characteristics of the melt in presence of the magnetic field, it is essential to study the predictive capabilities of such numerical models. Prediction of interface shape is still a crucial step in the Czochralski crystal growth process. It depends upon the accuracy of quantification of the effects of magnetic field and turbulence in the system [3]. Although 2D axisymmetric models do not mimic the actual flow, these models are useful for preliminary analysis and parametric sensitivity studies. Time dependent 3D simulations are more computationally demanding but essential for accurate prediction of the flow field of CZ silicon melts.

B. Research Objectives

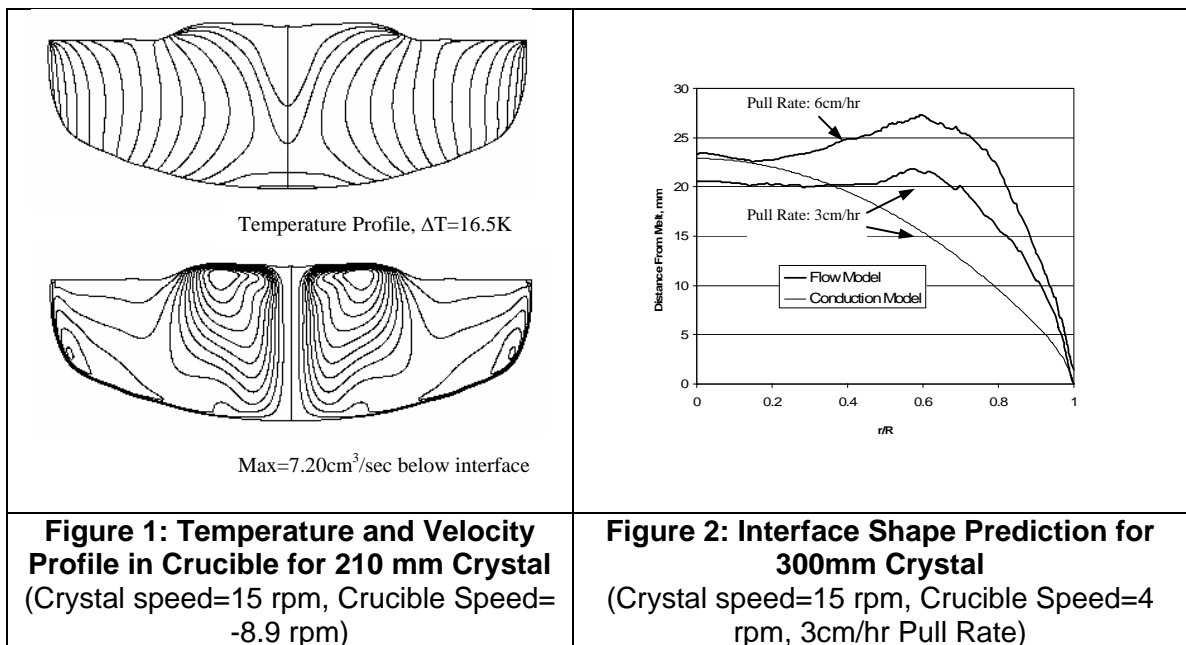
The objective of this work is to develop computational fluid dynamics (CFD) based model for simulation of the melt flow in the Czochralski crystal growth process in order to study the effect of operating parameters such as rotational speed and magnetic field on flow characteristics of the melt, interface shape and oxygen content in the melt and crystal.

C. Accomplishments and Current Work

In this work, a comprehensive mathematical model was developed, which accounts for natural convection (modeled using The Boussineque approximation), forced convection due to crystal/crucible rotation and the Lorentz force, due to motion of electrically conducting liquid induced by the applied magnetic field. Resultant multiphysics model equations, i.e. conservation of mass, energy and momentum and Maxwell's equation along with the phase change phenomenon (crystallization) were solved Czochralski crystal growth process using FLUENT 6.2. In order to study the effect of turbulence and magnetic field, melt flow simulations were carried out in 2D axisymmetric (40K computational cells) and 3D (using $>10^6$ hexahedral cells) domain. Turbulence is modeled using k- ϵ model with Low Reynolds Number Turbulence Model (LRT) [4] and some simulations were also carried out using Reynolds Stress Model (RSM) [5]. The temperature profile along the boundaries of the crucible and crystal were implemented using the results of a global simulation in which convection and radiation heat loss from crystal and

crucible were taken into account. The Marangoni stresses generated due to thermocapillarity were considered at gas-melt interface. Oxygen balance in melt flow was modeled as a diffusion-convection process with appropriate mass transfer boundary conditions i.e. dissolution rate at crucible wall and evaporation rate at melt-gas interface.

Simulations were carried out for industrial 210 and 300mm diameter crystal growth over a wide range of operating conditions ($Re= 3-5 \times 10^4$, $Gr=4-6 \times 10^5$ and $Ra=1-5 \times 10^8$) at different crucible rotation speed and different magnetic field intensity. Effects of the magnetic field and the crucible rotational speed on the flow field and the melt/crystal interface shape were studied using different turbulence models. The calculated temperature profile and flow field (in terms of stream function) are shown in Figure 1. The temperature profile shows high temperature near the edge of the crucible. Effect of conduction and convection and effect of pull rate on interface shape can be seen from Figure 2. Model results show that the temperature is more uniform under the crystal due to convection which lowers the interface shape in the melt.



D. Future Work and Milestones

Flow in Cz crucible is associated with various flow instabilities which makes flow non-symmetric and time dependent. Hence complete three dimensional time-dependent simulations will be carried out in order to understand the effect of local fluctuations of flow on heat and mass transfer rates in the melt.

For further information, please contact Prashant R. Gunjal at gunjal@wuche.wustl.edu

E. Acknowledgement: MEMC Inc. St. Peters, MO 63376.

F. References:

- a. Kumar V., Basu B., S. Enger, G. Brenner and F. Durst, Role of Marangoni convection in Si-Czochralski melts—PartII: 3D predictions with crystal rotation. *Jou. of Crystal Growth*, **255**, 27 (2003).
- b. Kalaev, V.V., D. P. Lukanin, V. A. Zabelin, Yu. N. Makarov, J. Virbulis, E. Dornberger, W. von Ammon, Calculation of bulk defects in CZ Si growth: impact of melt turbulent fluctuations. *Jou. Crystal Growth*, **250**, 203 (2003).
- c. Th. Wetzel, J. Virbulis, A. Muiznieks, W. von Ammon, E. Tomzig, G. Raming, M. Weber., Prediction of the growth interface shape in industrial 300mm CZ Si crystal growth. *Jou. of Crystal Growth*, **266**, 34 (2004).
- d. Launder, B. E. and Sharma, B. I., "Application of the Energy-Dissipation Model of Turbulence to the Calculation of Flow Near a Spinning Disc", *Letters in Heat and Mass Transfer*, **1**, (2), 131-138 (1974).
- e. Launder B. E., G. J. Reece and W. Rodi, Progress in Development of a Reynolds Stress Turbulence Closure, *J. Fluid Mech.*, **68**(3), 537-566, April, (1975).