HAL
open science

# Electromagnetic Processing of Materials at SIMaP : focus on Solar Silicon elaboration

Y Delannoy, G Chichignoud, K Zaidat

## To cite this version:

Y Delannoy, G Chichignoud, K Zaidat. Electromagnetic Processing of Materials at SIMaP : focus on Solar Silicon elaboration. 8th International Conference on Electromagnetic Processing of Materials, Oct 2015, Cannes, France. hal-01331357

**HAL Id: hal-01331357**

**https://hal.science/hal-01331357v1**

Submitted on 13 Jun 2016

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

# Electromagnetic Processing of Materials at SIMaP : focus on Solar Silicon elaboration

Y. Delannoy[1,2], G.Chichignoud[2,1] and K.Zaidat[1,2]

[1] Univ. Grenoble Alpes, SIMAP, F-38000 Grenoble, France
[2] CNRS, SIMAP, F-38000 Grenoble, France

*Corresponding author : Yves.Delannoy@simap.grenoble-inp.fr*

**Abstract**
Electromagnetic Processing of Materials (EPM) is studied in SIMaP for applications in nuclear engineering and in the energy sector. Our research concerns the effect of electromagnetic fields on fluid flows, mass transfer and materials micro structures. The fluids on which we act are mainly liquid metals (including molten semiconductors), but also oxides (to be solidified as glass or crystals), or gases (thermal plasmas). A survey of those activities will be presented.
Focusing on two examples concerning solar silicon, we'll present a plasma purification process and studies on the segregation of impurities during solidification. The plasma used to remove boron from liquid silicon is provided by high power (40 to 600kW) induction torches, that were studied both numerically and experimentally as a EPM system acting on gas [1]. When the segregation phenomenon is used to remove metallic impurities from the silicon, a strong stirring improves the productivity, and our studies (experimental and numerical) enable to quantify this performance [2].
Electromagnetic stirring of liquid silicon is also used in the plasma process and generally can be viewed as a means to increase the mass transfer to interfaces (free surface or solidification fronts), raising several questions about turbulence and magnetic fields, complicated by free surface deformations or flow across the solidification front. Some other open questions arise from the impurity distribution in solidified silicon, that do not always follow the classical Scheil law when metallurgical silicon is used in segregation processes.

**Key words :** Silicon purification, Plasma processing, Crystallization, Electromagnetic stirring, Segregation

## Electromagnetic processing of materials

Electromagnetic actuators are used to process solid or liquid materials, especially at high temperature where it avoids polluting the material with intrusive systems. Induction systems provide heating sources and electromagnetic forces in the core of the material,which can heat up, melt, levitate any electrically conducting material, and also stir and deform it if it is liquid. On the contrary, continuous magnetic fields can be used to control the fluid velocity, mainly by making the velocity field uniform along the magnetic lines.
Several processes have been developed in SIMaP using those phenomena, including electromagnetic casting of steel, cold crucible continuous casting of titanium and silicon, high speed metal coating a ceramic fibers, induction melting of glass to encapsulate nuclear waste, purification of molten salts for future nuclear reactors, or silicon purification for photovoltaic applications, that will be detailed below. Our elaboration platform includes several modulable meter-sized containers, where some kilograms of material can be treated at high temperature to study all those processes. Numerical models of the whole process are used to design and optimize such installations.
For all those applications, computational and experimental skills have been developed, to study the electromagnetic phenomena, the magneto-hydrodynamic interactions and their results on heat and mass transfers, which are often the keys points in material processing. Fundamental research use small scale experiments to study materials properties (molten drops on substrates, or in levitation), surface properties (droplets controlled by electric fields, controlled oxidation of liquid metals with a controlled fluid flow), or solidification mechanisms (segregation of impurities, development of freckles, thermoelectric effects on dendrite tips). Theoretical or numerical models are developed in parallel, and adjusted using these experiments.

## Silicon purification

Metallurgical silicon (MG), produced by reducing silica with carbon in high temperature (2000°C) arc remelting furnaces, is widely used as additional element for aluminum alloys, as raw material for the production of silicones, and also as the basic material for electronic grade silicon (EG) and solar grade silicon (SoG). EG and SoG are crystallized and used as semiconductors, which needs an improved quality compared to MG (Figure 1). The purity needed to produce electronic chips (EG) is higher than the required purity for solar cells (SoG), which is now the larger market (in tons) for purified silicon. SoG is presently mainly produced by the chemical route, initially developed for EG, where all the silicon is transformed into silane or chlorosilanes and distillated.

Several groups in the world are seeking for a less expansive metallurgical route, devoted to SoG, where the silicon will remain in solid or liquid phase. This normally includes a solidification step where segregation of impurities is used to remove all the metallic pollutants, and a specific step to remove Boron, for which the segregation effect is very weak.

**Plasma process to remove boron**

The interaction of liquid silicon with gas mixtures containing $H_2$ and $O_2$ or $H_2O$ can remove boron, as was shown by early research using inductive plasma in France [3] [5], arc plasma in Japan [4] or bubbling in the USA [6]. The Nedo process in Japan, and the Photosil process in France, were developped to industrial scale, and the latter is still in development to reduce its cost. Understanding and increasing the rate of purification is still a research subject in our lab [7], but also in Norway [8], China [9], Korea [10], or USA [11].

The purification takes place at the gas/liquid interface (Figure 1), and thus, to get a high purification rate for large reactors, the mass transfer rates should be high in the liquid phase (to bring boron to the surface) and in the gaseous phase as well (to bring oxidizing species and remove reaction products). An optimized design of the induction furnace can provide both the thermal control of the melt (melting, maintaining hot) and a strong electromagnetic stirring so that the mass transfer in the liquid is not limiting. The frequency and power of the induction furnace, the thickness and thermal insulation of the graphite crucible, as well as the type of magnetic field (monophase or travelling) were adapted to a larger and larger batch size during the development of the process.

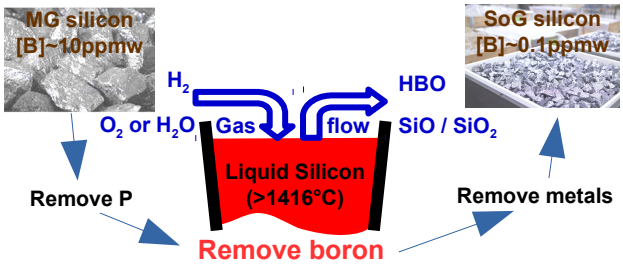


**Figure 1:** Gas-liquid step to remove boron from silicon

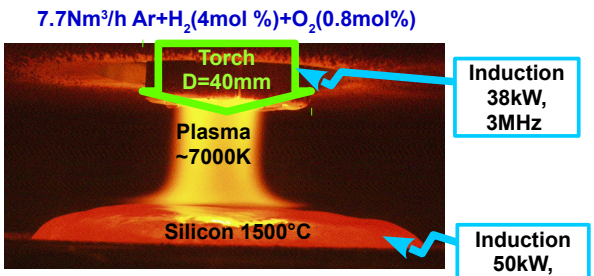


**Figure 2:** Plasma process running at lab scale in SIMaP

The inductive plasma torch is a very special induction system, because of the huge variation of the electric conductivity of the plasma with temperature (0 to 5000 A/V/m). Modeling the gas properties was necessary to obtain predictive models, that were validated with spectroscopic measurements of temperature and composition. Starting an inductive plasma is also a special procedure, because the cold gas is electrically insulating. A lighting procedure was developed and adapted to solid state generators with our industrial partners, and this work is presented to this conference [13].

The purification rate can be measured by sampling the liquid or by on line gas analysis (Figure 3), and the challenge for industrial development is to increase it, knowing that the limiting step is the surface reaction or the mass transfer in gases. The plasma was supposed to provide radicals and atomic species that could increase the surface reaction kinetics compared to cold gas processes, but this is now questionable since it was shown that the boron to silicon oxydation ratio follows an equilibrium law [7] when the silicon temperature (Figure 4) or hydrogen pressure varies. The plasma jet also provides a positive gradient of gas temperature in the gas boundary layer close to the silicon, that prevents the formation of silica fumes in this reaction zone (silica fumes are formed later, when the SiO gas produced at the interface cools down). All in all, the plasma can be designed to optimize the heat flux provided to the silicon surface as shown in another presentation [14].

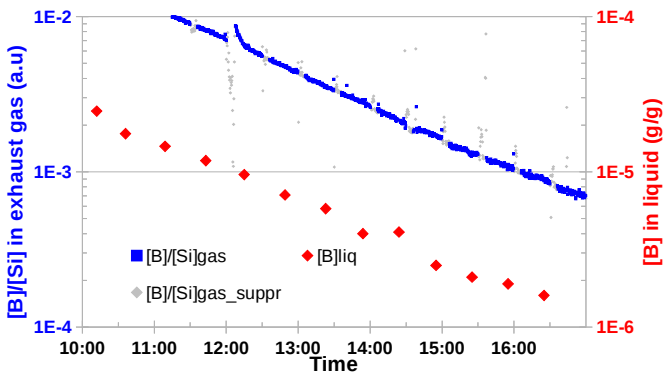


**Figure 3:** Boron fraction measured in both phases

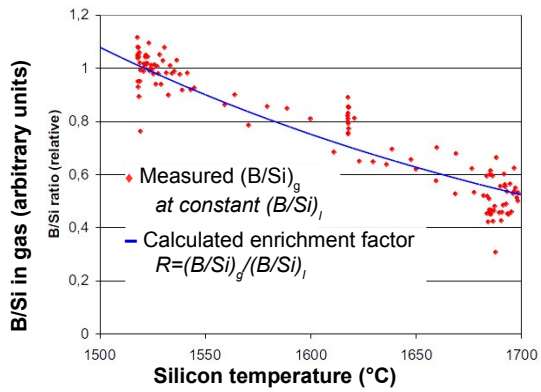


**Figure 4:** Equilibrium effect of the silicon temperature

**Removing metallic impurities by segregation**

Segregation of impurities has long been an unwanted phenomenon because it leads to a nonuniform distribution of dopants in monocrystaline semiconductors, often grown by the Czochralski process (CZ). The local distribution of dopant in the liquid boundary layer, which drives the dopant fraction in the solid, is related to the segregation coefficient (an equilibrium property coming from the phase diagram), to the crystallization velocity, to the diffusion coefficient of the dopant, and to the fluid flow [15]. In idealized CZ situations, the fluid flow normal to the front is homogeneous on the whole interface, and is known from the rotation of the crystal. Therefore the dopant fraction in the solid is also known, and its ratio against the liquid fraction (the effective segregation coefficient $k_{eff}$) can be calculated from the crystal rotation.

A generalization is possible using the local mass transfer coefficient across the boundary layer to define $k_{eff}$, or the slope of the dopant fraction at the interface as in [16], in place of the uniform normal flow due to the rotation in CZ systems. This can be used for turbulent boundary layers, where the mass transfer is driven by the turbulence level and not by the flow normal to the wall. Generalizing is also possible on interfaces with stagnation and detachment points or lines [17], [2], i.e with normal liquid velocity towards the melt in some places, and towards the front in other places (with a normal velocity larger than the crystallisation rate). In this general case, $k_{eff}$ is no longer uniform on the whole interface and the dopant contents in the crystal does not relate only to the solidified fraction of the ingot as predicted by the Scheil's law. Furthermore, metallic impurities are sometimes incorporated in multicrystalline ingots as intermetallic precipitates at grain boundaries [18]. In other situations this phenomenon was found negligible [19]. Anyhow it is generally accepted that a sufficient liquid convection will increase the segregation effect, and therefore improve the purity of the solidified silicon (except the last solidified material, which is eliminated).

Our team is working on the quantification and understanding of the role of a strong liquid stirring, which was found necessary to reduce significantly the metallic contents during a high speed solidification (several cm/h, or some dm/h). In such situations [20] the flow is turbulent, and its main effect is to increase the mass diffusivity in the diffusion layer near the front, even if the flow is parallel to the front. The effect of normal components also exist as in laminar situations, but they always play in both directions (somewhere decreasing $k_{eff}$, elsewhere increasing it), because any normal flow towards the front (higher than the solidification velocity) is balanced by a normal flow out of the front (detachment zones), where the concentration is much higher than in other zones.

A laboratory furnace (VB2) was equipped by an electromagnetic stirrer (using travelling magnetic field) to control the convection direction and intensity during solidification of metallurgical grade silicon [2]. A numerical model was developed in parallel [21], using the Fluent code to describe the whole furnace, with a home made induction module for electromagnetic stirring, and interface tracking with remeshing to describe the front and its boundary layer. The effect of stirring is clearly seen for aluminum in the VB2 experiments (Figure 5): from the concentration in the lower part of the ingot, the effective segregation coefficient $k_{eff}$ is around 0.2 without stirring, and below $7.10^{-3}$ with upwards or downwards TMF. The numerical model (Figure 6) gives correctly $k_{eff}$=4.4 $10^{-3}$ with downwards TMF, but it also predicts a rather good segregation without TMF ( $k_{eff}$=9.1 $10^{-3}$), which is not obtained in experiments.

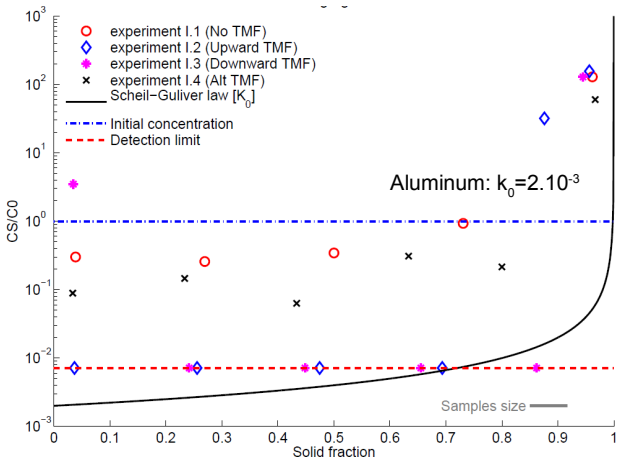


**Figure 5:** Experimental segregation of aluminum in the VB2 furnace with or without stirring (TMF up, down or alternate).

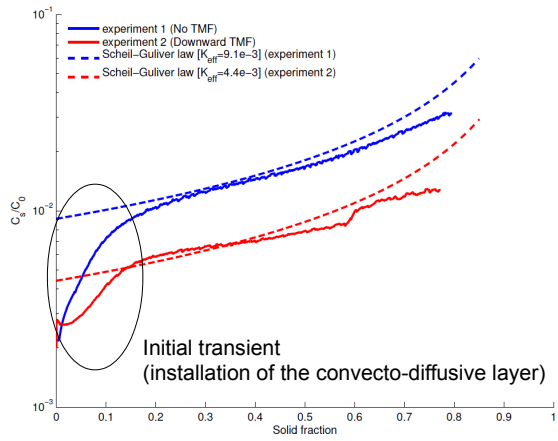


**Figure 6:** Calculated segregation for aluminum in the VB2 furnace with or without stirring

Additional experiments and modeling were done in the VB2 furnace to characterize the fluid flow. With TMF, the fluid flow calculated by our axisymmetric model was compared to measurements in cold liquid metals: the measured and calculated velocity range are similar, but the flow structure are very different due to a fluid instability yet documented in high aspect ratio cylinders stirred by TMF [22]. Without TMF, natural convection was calculated, and validated using

the shape of the solidification front, that compares fairly well to in situ marking made during the experiments. With a good prediction of the fluid flow, the higher aluminum contents in experiments than in simulations could be due to intermetallic precipitates at grain boundaries, but this was not yet quantified.

**Conclusion**

Silicon purification by the metallurgical route is a good example of high temperature material processing that could be improved with electromagnetic systems. This route produces solar grade silicon which fulfills the market needs, including for high efficiency cells when monocrystals are grown from this material. However, the processing cost has still to be reduced, and the use of inductive plasmas to increase the boron removal rate, or electromagnetic stirrers to enable high speed segregation with turbulent fluid flows, could help reaching this goal.

Fundamental research is needed to better understand and control the effect of electromagnetic fields on interface mass transfer in liquid metals, or in inductive plasmas, either to free surfaces or to solidification fronts. The reaction rates in purification systems, or the segregation of impurities at planar fronts, could help to characterize this mass transfer.

**References**


[1] J.Altenberend, G.Chichignoud, Y.Delannoy (2013) Spectrochimica Acta Part B 89, 93-102
[2] M.Cablea, K.Zaidat, A.Gagnoud, A.Nouri, Y.Delannoy (2014) J. Crystal Growth 401, 883-887
[3] D.Morvan, J.Amouroux, M.C.Charpin, H.Lauvray (1983) Revue de physique appliquée 18, 239-251
[4] H.Baba, N.Yuge, Y.Sakaguchi, F.Aratani, Y. Habu (1991) Proc.10th Eupvsec Lisbon, 286–290
[5] C.Alemany, C.Trassy, B.Pateyron, K-I.Li, Y.Delannoy (2002) Solar energy mater. & solar cells 72, 41-48
[6] C.P.Khattak, D.B.Joyce, F.Schmid (2002) Solar energy materials & solar cells 74, 77–89
[7] J.Altenberend (2012) PhD, Univ.Grenoble, lab.SIMaP
[8] O.S.Sortland, M.Tangstad (2014) Metallurgical and materials transactions E 1, 211-225
[9] J-J.Wu, W-H.Ma, B.Yang, Y-N.Dai, K.Morita (2009) Trans. Nonferrous Met. Soc. China 19, 463-467
[10] B.P.Lee, H.M.Lee, D.H.Park, J.S.Shin, T.U.Yu, B.M.Moon (2011) Solar Energy Mater.& Solar Cells 95, 56–58
[11] W.R.Imler, R.E.Haun, R.A.Lampson, M.Charles, P.Meese (2013) Proc. 39th Ieee Pvsc Tempa, 497-501
[12] J.Altenberend, G.Chichignoud, Y.Delannoy (2013) Spectrochimica Acta Part B 89, 93–102
[13] G. Chichignoud, Y. Delannoy, F. Cocco, P. Rivat, L. Natale (2015) 8th EPM conference, Cannes, oct.2015
[14] M. Vadon, Y.Delannoy, G. Chichignoud (2015) 8th EPM conference, Cannes, oct.2015
[15] J.A.Burton, R.C.Prim, W.P.Slichter (1953) The Journal of Chemical Physics 21, 1987-1991
[16] L.O.Wilson (1978) Journal of Crystal Growth 44, 247—250
[17] J.P.Garandet, N.Kaupp, D.Pelletier, Y.Delannoy (2012) Journal of Crystal Growth 340, 149–155
[18] D.Macdonald, A.Cuevas, A.Kinomura, Y.Nakano, L.J.Geerligs (2005) J. of Applied Physics 97, 033523/1-7
[19] R.Kvande, L.J.Geerligs, G.Coletti, L.Arnberg, M.DiSabatino, E.J.Øvrelid, C.C.Swanson (2008) J.Appl.Phys.104, 064905/1-8
[20] F.Santara, Y.Delannoy, A.Autruffe (2012) Journal of Crystal Growth 340, 41–46
[21] M.Cablea (2015) PhD, Univ.Grenoble, lab.SIMaP
[22] A.Y.Gelfgat (2005) Journal of Crystal Growth 279 (3–4), 276 – 288