Solar Grade Silicon by a Direct Metallurgical Process

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Abstract

The paper gives a background on solar grade silicon and presents the SOLSILC concept. A theoretical description of the design criteria for engineering of the refining reactors is given. C, Ti and Al are used in the calculations because they are important with respect to cell efficiency and yield.

Introduction

The global energy consumption is predicted to grow dramatically every year. Higher energy prices and public awareness for the global warming problem have opened up the market for solar cells. The photo-voltaic (PV) industry has a growth rate of about 30% - a situation that many other industries can only dream about. Today, the majority of solar cells are made of silicon, and experts believe that it will take at least a decade before other PV technology based on other materials can hope to be competitive. The dramatic growth in the PV industry has, however, caused a lack of solar grade silicon (SoG-Si), *i.e.*, silicon with the required chemical purity for PV applications, resulting in increased prices for such material. Presently, the shortage of low-cost SoG-Si is the main factor preventing environmentally friendly solar energy from becoming a giant in the energy market in a generation or two.

A direct metallurgical route for production of solar grade silicon can be five times more energy efficient than the conventional Siemens process that uses more than 200kWh/kg Si. A metallurgical route would reduce the payback time (the time during which the solar cell produces the same amount of energy that was used to create it) significantly (of the order of 50% or ~1 year).

The Kyoto agreement aimed at a CO_2 reduction of 3 million tons/year based on PV. The European strategy to achieve this is to decrease module costs to € 1/Wp in 2010 and to have a 3 GWp energy production based on PV installed in 2010. These goals can only be realized if there will be enough feedstock available on the market. Low cost feedstock will also help PV towards being a renewable energy source, independent of public funding.

For producers of metallurgical grade silicon, the increase and cyclic changes in the energy prices are a challenge, and it is necessary to find products with higher value, for which the energy input contributes less to the fixed costs. The strong market pull and

increasing solar grade silicon prices seem to make this a perfect product. However, with the extremely high purity demands and necessity to develop complete new process steps, introduction of this new product into the market involves a great deal of risk.

State of the art – Production of silicon feedstock

Due to the dramatically increased demand for SoG-Si (solar grade silicon) over the last decade, many poly-silicon producers are now using modified or developing new feedstock routes to produce SoG-Si. However, the gap between demand and supply of poly-silicon has so far not resulted in new commercial processes. This means that every producer of silicon based wafers is waiting for a new affordable feedstock that is available in large quantities. The public knowledge of the different process initiatives is limited. The general information is summarized in the following.

Main supply route today

Scrap, rejected, and non-prime material from the semiconductor production is the main supply route of SoG-Si today. For a large part the non-prime polysilicon is deliberately produced by operating the conventional Siemens process with more economical parameters (e.g. faster, lower energy, less quality control).

Modification of the chemical route to semiconductor grade silicon

Several companies (Wacker, REC Silicon, etc) are making a big effort to economise the chemical route further with the aim to produce SoG-Si instead of semiconductor grade. Wacker and REC silicon do this by shifting from rod decomposition of trichloro- or monosilane to deposition in a fluidised bed in the last step of the poly-silicon production. Hemlock is also considering this step. The joint venture of Degussa and Solar World, Joint Solar Silicon (JSSI), is testing a free space reactor. Tokuyama is testing a strongly modified filament reactor for their "Vapour to Liquid Deposition (VLD)" process.

Purification of metallurgical silicon

The metallurgical process route has so far not resulted in a commercially viable process for feedstock to solar cells. Several companies (Elkem, FerroAtlantica, Dow Corning and others) are working on this route in order to produce SoG-Si. Elkem Solar has shown that their SoG-Si may be used to produce cells of an efficiency of 15-16%. Elkem built a pilot-scale plant in the past year. A full scale industrial plant is planned in 2007. Elkem announced that they will have SoG-Si on the market next year. Elkem emphasizes low costs, big volumes and low energy consumption as the main asset. A flow chart presenting the Elkem process is given in Figure 1. Commercial grade Si is treated with a special calcium-silicate slag to remove mainly boron. The metal is cast and leached before it again is melted and further refined [2].
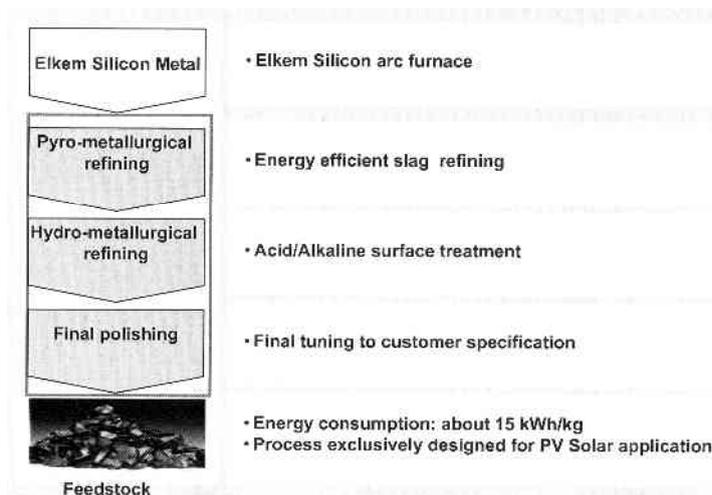
Figure 1: Schematic presentation of the Elkem route for production of solar grade silicon. [1]

Electrolysis/electro chemical purification

This route has only been investigated on a laboratory scale. This could be a viable process on a long term. SINTEF and NTNU are working with the development of this route. The principle of the three layer electro refining of Si in molten oxides at 1500°C is shown in Figure 2. The anode is a mixture of Cu and Si (the Cu makes it denser), and the electrolyte is a mixture of oxides that is less dens than the alloy and the purified silicon is the cathode.
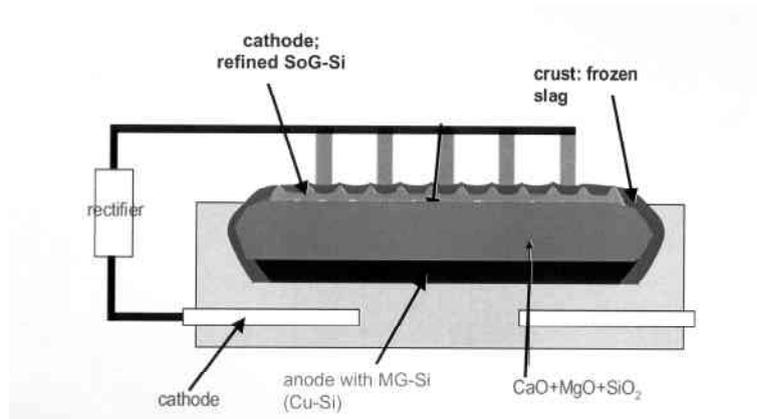

Figure 2: Electro refining of Si in molten oxides at 1500°C. [3]

Supplementary feedstock through recycled material

Approximately 30% of the silicon used to grow a multicrystalline ingot ends up as solar cells. Thanks to the present rapid growth of the photovoltaic industry, the amount of by-products is increasing as well. In this context, reclaim of solar grade silicon by-products from ingot growing, shaping, failed runs, broken wafers and solar cells, etc., becomes more and more interesting from a commercial and scientific point of view. Typically, it

might be sufficient to remove a surface layer of the silicon with accumulated impurities. The largest source of by-product is the saw dust waste from the wafer sawing. The percentage of saw dust increases as the wafers become thinner. However, separation of the Si dust from the SiC used as abrasive in the sawing process is difficult due to sub micron range particles.

Direct carbothermic route

Another route to SoG-Si is the direct carbothermic reduction of quartz and carbon. The SOLSILC technology, in which SoG-Si is produced from clean raw materials, is the major example of this. In the following, the SOLSILC route will be described in more detail.

The SOLSILC concept

A principle sketch of the SOLSILC concept is presented in Figure 3. After reduction of quartz with carbon in the electric arc furnace, the metal goes through several refining steps. It should be noted that purging is usually not necessary.
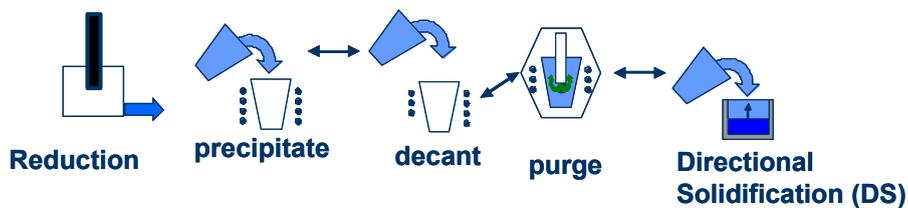

Reduction   **precipitate**   **decant**   **purge**   **Directional Solidification (DS)**

Figure 3. Schematic drawing of the SOLSILC concept.

Knowledge about tolerance for impurities

There is little knowledge about the new feedstock materials, or the accumulation of impurities and their tolerable levels in new feedstock materials, recycling material or in SoG-Si in general. In the, SOLSILC concept, solar grade silicon is produced from clean raw materials to give high purity material directly from the reduction furnace. The SOLSILC concept has chosen to work with carbon with ultra low contents of P, B and other contaminants combined with quartz with very low contamination levels. Silicon production with the SOLSILC concept has resulted in a new standard of cleanliness for a carbothermic reduction process, and has already been running campaigns at a pilot scale of 20kg Si/h. Table 1 shows the specification which is estimated to be necessary for solar grade silicon, based on our own investigations of artificially contaminated material [4], and on recent experiments on highly doped silicon [5]. However, only limited information has been published on this subject and these numbers have a considerable amount of uncertainty.

Table 1: Impurity levels in ppmw (parts-per-million-by-weight) after refining by the direct metallurgical SOLSILC route and impurity levels required to make solar cells are given. For comparison, specification on material used today and results from conventional high-purity metallurgical silicon (Silgrain from Elkem) are also shown.

	Fe	Ti	Al	P	C
SOLSILC Final product estimated	<0.1	<0.1	<0.1	--	<50
Demands[4]	1-10(*)	0.17	0.08	0.1-1(***)	10-50 (**)
Lowest commercial grade [6]	<0.1	<0.1	<0.1	<0.1	<4
Metallurgical (Silgrain, Elkem)	400	21	1100	--	--

(*) see ref [4]: only a limited effect was observed when adding 16 ppmw of Fe to an ingot already contaminated with 10 ppmw of Ti

(**) see ref [4]: 50 ppmw of carbon did not give a significant degradation of fill factor

(***) see ref [5]: <1 Ωcm resistivity appears to be acceptable. This can be obtained by compensation from SoG-Si with a high amount of P.

Note that the requirements for SoG-Si in fact depend on crystallisation technology, wafer thickness, and solar cell process, and possibly on a slight trade-off between cost and cell efficiency (however, only very little reduction of cell efficiency will be allowed in exchange for a cost reduction of the silicon). When impurity levels are close to requirements a silicon quality should therefore eventually be verified carefully by industrial production of wafers and cells.

The impurity levels from the SOLSILC direct route are close to the presently estimated requirements. This means that the need for additional cleaning of raw materials is limited, and therefore also the cost of cleaning. This carbothermic production route can therefore, in principle, reduce the production cost of feedstock to below € 20/kg.

Inclusions

Formation of inclusions

In a direct carbothermic route, the liquid silicon leaves the reduction furnace at a temperature between 1600°C and 1800°C. At this temperature the equilibrium level of dissolved C is 500 ppmw, according to the C-Si phase diagram in Figure 4. In addition to the dissolved carbon, SiC, C particles and oxide films can be found in the tapped material. Depending on removal of particles in the next step, and on the final application of the SoG-Si, it is required that all particles above a certain size are removed. The SiC particles are hard and may conduct electricity by co-precipitation of other impurities. This can give short circuiting in the solar cells and create problems in the wafer sawing process. To clean silicon, advanced refining techniques are necessary where high melting point and high reactivity towards refractories are extra challenges.

Removal of inclusions by settling

From the phase diagram in Figure 4, it can be seen that by lowering the temperature towards the melting point, the concentration of dissolved C will be reduced by precipitation of SiC particles. The first step to remove the particles is by settling.
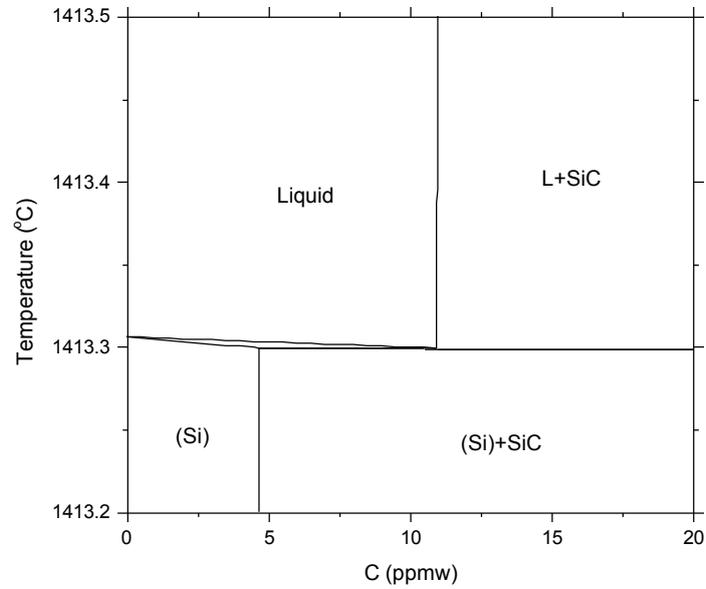
Figure 4: The Carbon rich side of the C-Si phase diagram. At the melting point the solubility of C in the liquid silicon is 11ppmw [7-14].

Settling can be modeled by Stokes law, in which the force on particles by difference in density (specific) weight of SiC and Si is balanced with the drag on the particles as shown schematically in Figure 5.

The resulting equation for the settling velocity can be derived:

$$u_r^2 = \frac{2\Delta\rho g a^2}{\rho\phi 9} \tag{1}$$

where $\Delta\rho$ =770kg/m^3 is the difference in density between silicon and SiC, *a* is the particle radius, *g* is the acceleration due to gravity, and ø is an empirical friction factor.
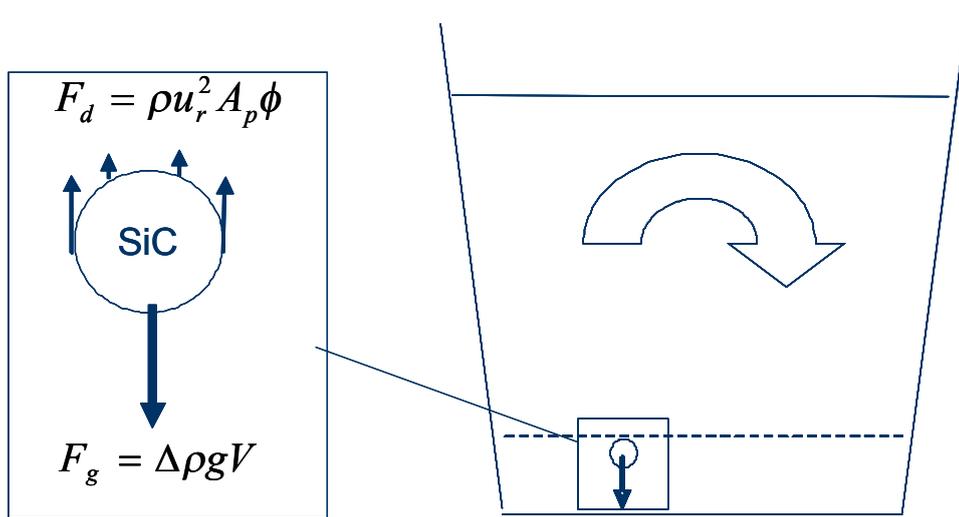
Figure 5: Forces that acts on a particle (left) and a schematic drawing of the settling reactor (right). (V is the volume of the particle.)

Using the settling velocity as mass transfer coefficient and assuming complete mixing in the reactor, the refining efficiency for spherical particles is given by[1]:

$$\frac{C}{C_0} = \exp\left(-\frac{Au_r}{V}t\right)$$

(2)

The term A is the area of the bottom of the reactor and V is the volume of the reactor, C_0 is initial concentration of particles, C is the concentration at a given time t. In Figure 6, the refining efficiency for different settling times is presented as a function of particle size. We can see from the Figure that after one hour, 10 μm particles are removed down to 15% of the initial concentration while almost all 20 μm are removed. These numbers were used to design a pilot scale reactor. Experiments were performed with SOLSILC material, initially containing 700 ppmw of C. After the settling process, the concentration of carbon in liquid silicon was less than 50ppm.

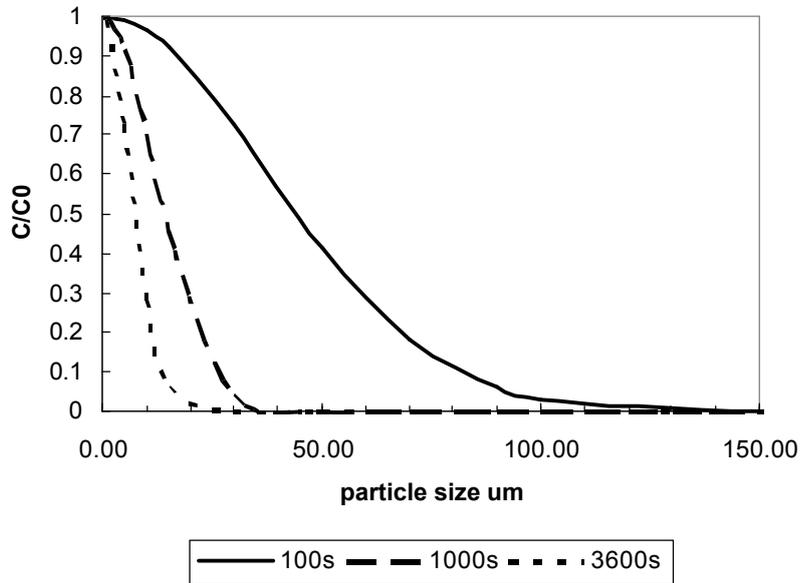[1] For more details se Reference 12.

Figure 6. Theoretical settling curves for SiC in Si and the ratio A/V=1.8m^{-1}.

Refining by solidification

As a part of solar grade silicon production, it is necessary to cast the material after refining. A substantial refining effect can be attained if planar front is achieved during the solidification. The solubility of major impurities is higher in liquid silicon than in solid silicon. In directional solidification with a planar front, there will be a clearly defined interface between solid and liquid silicon.

At the solid/liquid interface, the concentration of the impurities in the Si to solidify will be in equilibrium with the molten metal. The ratio between the two concentrations are defined as the partition coefficient given by $K = C_s/C_l$. C is the concentration in solid (subscript s) and liquid (subscript l). For K values less than 1 there will be a refining effect. Assuming that there is thermodynamic equilibrium at the solid/liquid interface, no diffusion of impurities in solid, and complete mixing in the liquid, the maximum refining effect is given by the well-known Scheil equation:

$$\frac{C}{C_0} = \left(1 - f_s\right)^{K-1} \tag{4}$$

where C is the concentration in the liquid at a given fraction solid, f_s, and C_0 is the nominal (average) concentration of the silicon.

For $K \ll 1$ the Scheil equation simplifies to:

$$\frac{C}{C_0} = \frac{1}{1 - f_s} \tag{5}$$

8

From this equation it can be seen that after 50% solidification, the concentration C is doubled, after 75% doubled again etc. The reason is the relatively much lower solubility in solid than in liquid and therefore the total amount of solute in the liquid remains practically constant, while the volume is reduced as solidification proceeds. Notice that the segregation pattern in Eq (5) is independent of K, under the given assumptions. The principle is shown in Figure 8. Obviously, Scheil's equation (predicting an infinite solute concentration when the solid fraction becomes 1) is invalid above a certain system-specific liquid concentration, where the remaining liquid solidifies by some eutectic reaction.
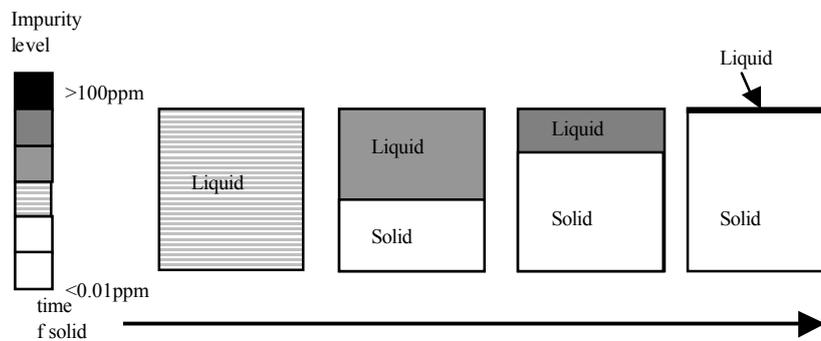

Figure 8: Principle for refining by directional solidification. The dark colour indicates level of impurity (white is <0.01ppm and black is > 100ppm).

Ti and Al

The refining of aluminium was studied by addition of 8 ppm Al to electronic grade silicon. The metal was solidified by directional solidification in SINTEFs Crystalox DS 250 lab pilot furnace. The concentration of Al in the solid silicon was determined by resistivity measurements.

Figure 9 shows the concentration of Al in the solidified Si at different positions and the corresponding concentration of Al in the liquid Si.
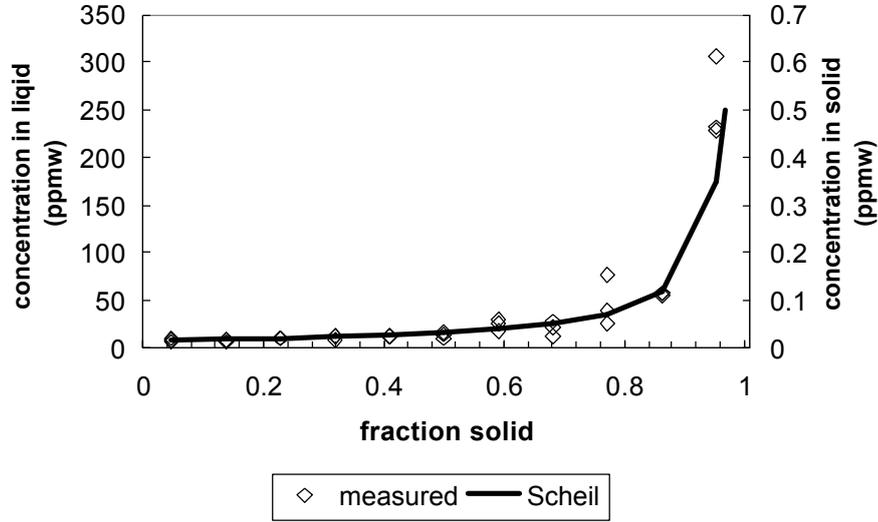
Figure 9: Si with addition of 8ppm Al cast by directional solidification. K=0.002

The curve corresponds well to Scheils's equation, indicating the solute build up at the solidification front is negligible (ie. the assumption regarding complete mixing in liquid is valid). A similar relationship can be given for Ti with $K = 10^{-5}$ [6]. Because the diffusion coefficients for Al and Ti in solid are in the same range ($\sim 10^{-10}$ cm/s [16,17]), we should expect that also Ti follows Eq. (4).

In the industrial process, we want to cut off the high concentration area and use the remaining material. The average concentration in the remaining material for a given cut-off fraction is given by integration of the Scheil equation. Replacing f_s with $1\text{-}f$ where f is fraction remaining liquid gives

$$\frac{C_s}{C_{in}} = Kf^{K-1} \tag{6}$$

Integrating 3 from $f = 1$ to f gives the refining ratio [12], where $\overline{C}_s$ is the mean relative impurity content in the solid, C_{in} is the initial concentration in the metal to be refined.

$$\frac{\overline{C}_s}{C_{in}} = \frac{K}{1-f}\int_f^1 f^{K-1}df = \frac{1-f^K}{1-f} \tag{7}$$

For double solidification, the mean relative impurity content in the cut-off fraction becomes the initial concentration in the second solidification process, giving:

$$\frac{\overline{C}_{s2}}{C_{in}} = \frac{\overline{C}_{s1}}{C_{in}} \frac{\overline{C}_{s2}}{\overline{C}_{s1}} = \left(\frac{1 - f^K}{1 - f}\right)^2 \tag{8}$$

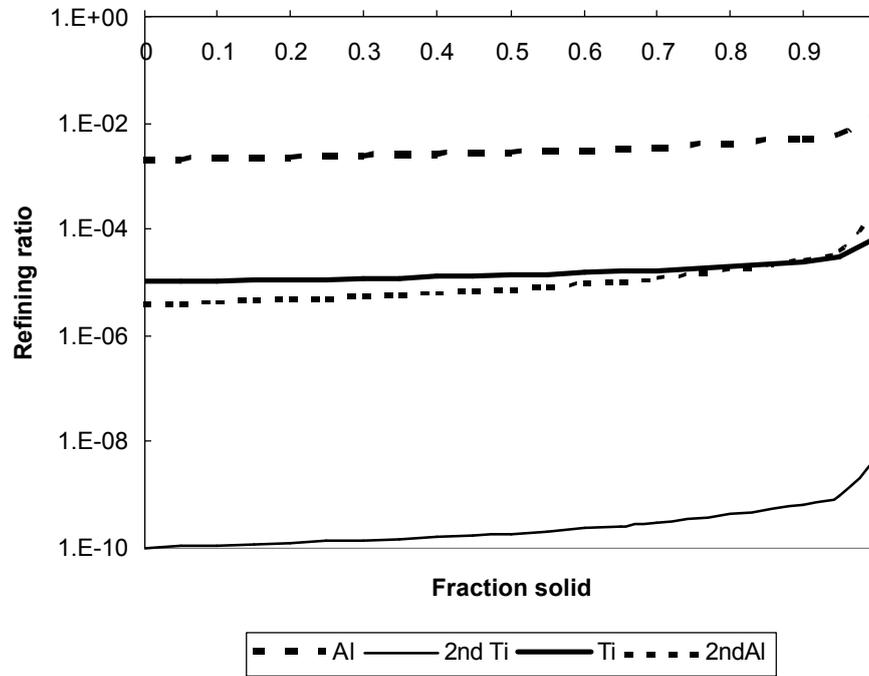Eqs. (7) and (8) is presented graphically in Figure 10.

Figure 10: Refining ratio $\overline{C}/C_0$ given by Eqs. (7) and (8), for single and double solidification with Ti and Al impurities.

We can see from Figure 10 that a single solidification reduces the Al content by a factor 100 while the Ti content is removed by a factor 10000.

Conclusion

It has been shown that theoretically, it is possible to make clean enough material with the refining steps in the Solsilc process. Based on composition of the raw materials and furnace parameters, the metal that leaves the furnace will contain some impurities. These are mainly Ti, Al, Fe and C. In previous work [4,5] we have given some limits for tolerable levels in solar grade silicon. The paper shows that we can reduce the impurities below these levels with settling and directional solidification.

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