# Cold-Container Crystal Growth of “Last-to-Freeze” Silicon Samples, and Enhanced Detection of Metallic Impurities by ICP-MS

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***Abstract* — Inductively-coupled cold containers are used to melt silicon samples of various shapes, and the electromagnetic forces on the melt form an isolated, well-controlled last-to-freeze region where impurities in the sample are concentrated by their small segregation coefficients. Inductively-coupled plasma mass spectrographic (ICP-MS) values for impurity concentrations in the ~0.1 g enriched region are related back to the ~30 g original sample, providing lower limits for impurity concentrations that are below the typical ICP-MS 0.1 ppb detection limit. There is no rod or granular sample geometry restriction as with float-zone impurity concentration techniques, and no obfuscating impurity introduction from quartz crucibles or graphite hot zones.**

***Index Terms* — crystal growth, ICP-MS, impurity analysis, metal impurities, silicon, silicon feedstock.**

## I. BACKGROUND AND INTRODUCTION

Silicon PV module prices have recently fallen much faster than historically expected from the industry learning curve, which plots the change in PV module cost as a function of amount of material produced. The reasons for this are based in the imbalance between supply and demand for silicon feedstock material. Following a substantial scarcity of feedstock in 2003 – 2008 (with accompanying module prices above the trend line), a recent and reactionary glut of feedstock (and PV modules) emerged in 2011 -2013 (with low feedstock prices, and PV module prices below the learning curve trend line). While good for consumers, the downward price pressure is demanding new R&D focus directions for commercial viability [1]. There is no fundamental shortage of silicon, as it comprises 27% of the Earth’s crust, and the lower prices are expected to be somewhat stable.

To remain competitive, PV feedstock and crystalline ingot producers will need to increase the quality/cost ratio of their products. Monitoring, reduction, and control of lifetime-killing impurities are areas of importance in this effort. As was shown early by Davis and co-workers [2], even sub-ppb levels of some contaminants can have an influence on Si solar cell performance. But measuring impurity concentrations at such low levels is an onerous task.

Fortunately, the small effective segregation coefficient of many impurities in silicon can be used to concentrate a large fraction of these impurities into one or several last-to-freeze regions of a silicon melt. This technique has been used for some time where rod-shape feed stock samples or core-drilled rod samples could be obtained and float zoned [3]. An example of a controlled last-to-freeze region in a float-zoned (FZ), core-drilled sample from up-graded metallurgical-grade (MG) silicon is shown in Fig. 1 (left). The concentration of impurities into the last-to-freeze tip is obvious from the texture change shown at higher magnification in Fig. 1 (right).

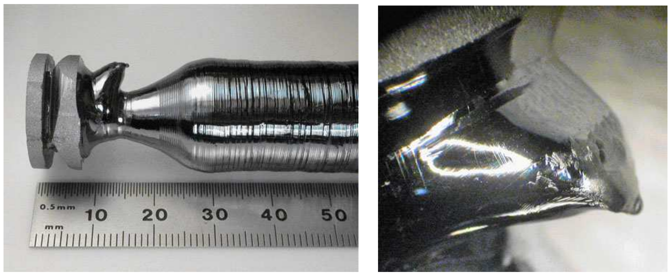

Fig. 1. Last-to-freeze region with concentrated metal impurities in a FZ, core-drilled sample from up-graded MG silicon.

This technique could likely be extended to analysis of metal impurities in fluidized-bed granular polysilicon, float-zoned with controlled last-to-freeze regions by the techniques in [4] or [5]. However, most silicon feedstock used for PV is not readily available in either a rod shape or bead-like granular form. Czochralski (CZ) growth could be used to concentrate metal impurities by melting more general shapes of silicon, but has numerous disadvantages. Usually there are a number of last-to-freeze regions, some on the crystal and a number on the residual silicon in the crucible. In addition, impurities can be introduced from the crucible and hot zone, obscuring the true concentration in the starting silicon itself.

We show here that radio frequency (RF) induction-coupled, cold-container techniques can be used to melt various-shaped samples of silicon (chips, chunks, rods, etc.), and that the electromagnetic forces are a convenient aid in forming a well-defined last-to-freeze region that can be removed for Inductively-Coupled Plasma Mass Spectrographic (ICP-MS) analysis of the concentrated impurity levels. These can readily be related back to the original impurity concentrations in the samples. This provides enhanced sensitivity of the conventional ICP method for impurities present below the typical detection limit of about 0.1 ppb atomic. Various cold-container methods can be used (cold crucible, cold boat, electromagnetic casting, etc). A review of the cold-container approaches for melting silicon was made by Mühlbauer [6].

## II. IMPURITY SEGREGATION IN SILICON

The equations governing impurity segregation determine the distribution of an impurity that results after solidifying a silicon sample with presumed uniform initial distribution of that impurity. We'll assume just one solidification step and will ignore impurity evaporation since the growth is done in argon near room pressure. Then for zone solidification (either FZ or boat zoning),

$$C(x)/C_o = 1-(1-k)e^{-kx} , \qquad (1)$$

where k is the effective segregation coefficient, C(x) is the impurity concentration at position x along the ingot (x is in units of melt zone length), and $C_o$ is the initial, uniform concentration of that impurity in the feedstock. In the last melt zone to freeze of an ingot that is N melt zones long (i.e., for N-1 < x < N), the impurity concentration profile is expressed by

$$C(x) = C(N-1)\cdot(N-x)^{(k-1)}. \qquad (2)$$

Equation (2), taken by itself, is essentially the normal freezing equation, usually written for CZ or directional solidification as

$$C(g) = C_o k(1-g)^{(k-1)}. \qquad (3)$$

with g being the fraction solidified (0 to 1).

A convenient lab-scale impurity concentration set-up uses a ~30g charge of the source material and harvests a ~0.1g last-to-freeze sample for ICP-MS analysis – a ratio of ~300:1. In our cold-boat zone solidification process (described later), the ~30g ingot is solidified with a 3cm zone length and is 18cm or 6 zone lengths long. Segregation coefficients of impurities in silicon range from 0.8 (boron) to 1.6 x $10^{-8}$ (zirconium). The expected distribution for an impurity with moderate k (e.g. indium with k = 4 x $10^{-4}$), zone solidified in the cold boat, is plotted in Fig. 2a using (1) and (2). The impurity concentration in the last 1/300 to freeze (i.e. the tip which is to be analyzed by ICP-MS) is plotted in Fig. 3.

The ratio of the area under a curve like the one in Fig. 2b to the area under 1 vs. x for x = 0 to 6 (i.e. 6) gives the fraction q of original impurity in the ~30 g sample that ends up in the ~ 0.1g last-to-freeze tip for any given impurity with it's associated k value. This ratio is (1/6) times the integral of (2) evaluated between 5.98 and 6. For a general k value, the solution is

$$q = (1-(1-k)e^{-5k})\cdot((0.02)^{k})/ 6k. \qquad (4)$$

Fig. 3 is a plot of q vs. k. For segregation coefficients less than 1 x $10^{-3}$, more than 99% of the original impurity in the ~30g Si source sample ends up in the ~0.1g last-to-freeze tip which is analyzed by ICP-MS. This gives 300X improvement in the detection limit for those impurities. Lesser, but still significant, improvement occurs for k as low as 0.1.

These governing equations describe an idealized situation, and in reality a number of factors (elaborated in the discussion section) can lead to deviations from the predicted detection limit improvement. Most of these tend to lessen the improvement. Thus, impurity concentrations obtained by this method are represented as a lower limit and actual values are probably higher.

For CZ growth, directional solidification, or other normal freezing processes, the situation is similar because (3) has the

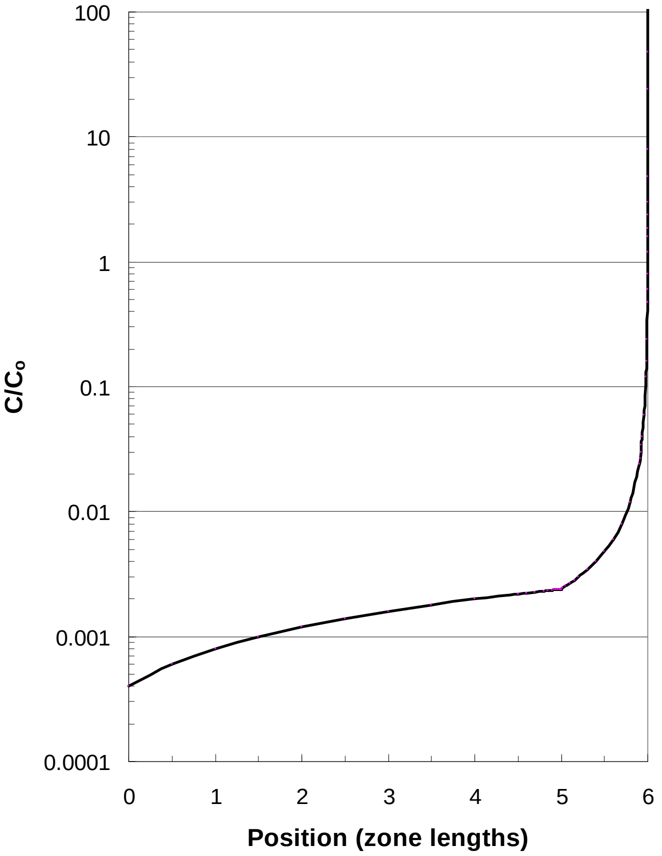

Fig. 2a. Expected distribution of an impurity with moderate k of 4 x $10^{-4}$ after zone solidification.

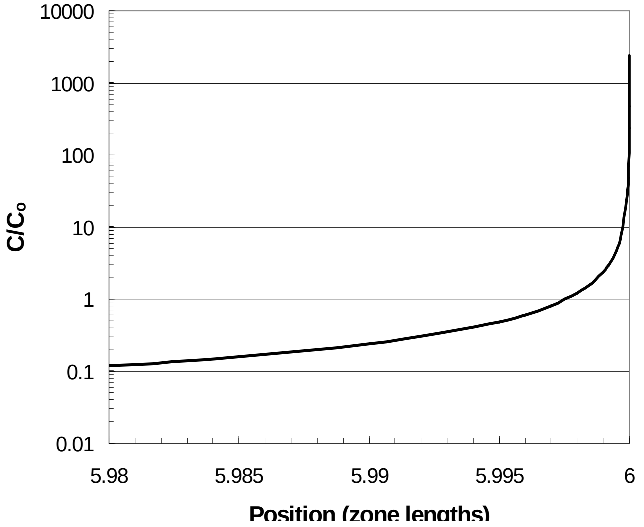

Fig. 2b. A magnified view of the impurity distribution in the region of the last zone length between 5.98 and 6.00.

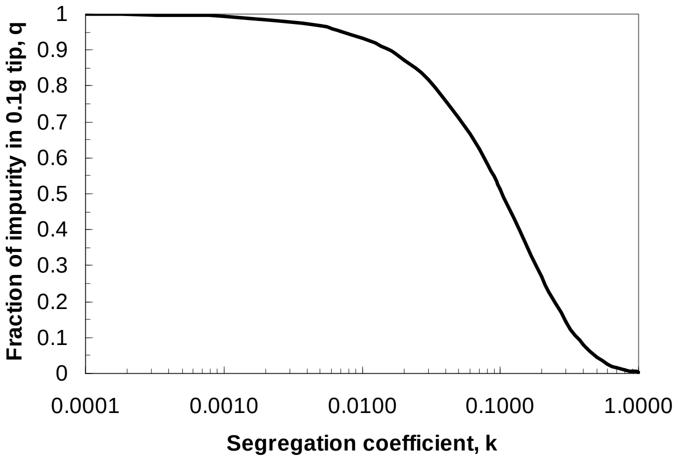

Fig. 3. Predicted fraction q of the original impurity in a 30g Si source sample zone solidified with a 3cm zone length and 18cm ingot length that will be concentrated into the last 0.1g to freeze, as a function of segregation coefficient k for the impurity.

same form as (2). Again, we will consider the case of the ~0.1g last-to-freeze tip directionally solidified from a ~30g initial Si charge. Then the solution of the integral of (3) evaluated between g = 0.99666… and 1 is

$$q = k(0.003333\ldots)^{k} \qquad (5)$$

and essentially overlaps the plot in Fig. 3, differing only in the 3rd decimal place for any k <0.1. The difference increases progressively between k = 0.1 and k = 1, but there is not much detection limit enhancement in that region anyway.

## III. ELECTROMAGNETIC COLD-CONTAINER PREPARATION OF LAST-TO-FREEZE SILICON SAMPLES

Either zone solidification or normal freezing results in the concentration of essentially all impurities with $k < 1\text{x}10^{-3}$ into the last few tenths or less of a gram to freeze. FZ sample generation requires rod or granular feedstock. Normal freezing in hot crucibles can accommodate a variety of sample geometries but can introduce extraneous impurities from the crucible or hot zone. Here, we used either normal freezing in a cold crucible [7] (Fig. 4) or zone solidification in a cold boat [8] (Fig. 5) applied to silicon chip and chunk feedstock.

Approximately 30 g samples with individual chip and chunk piece sizes between ~2mm (~.01 g) and ~20mm (~2 g) were studied. They were produced by the Siemens process as polysilicon “logs” that were subsequently chipped by the manufacturer for convenient crucible loading. The water-cooled boat or cold crucible was made of copper and was housed in a quartz tube chamber with stainless steel end fittings. For zone solidification, the chips and pieces were distributed uniformly along the boat. Growth at 2.5mm/min was conducted in a 1.75 l/min, 5-nines-pure argon flow after rough pumping the system and melting one end of the charge. The chamber was moved through a 6-turn RF coil operating at 660 kHz to effect zone melting and solidification. Near the end of solidification, the electromagnetic forces of the RF coil and induced current in the cold container assisted in achieving an isolated last-to-freeze zone. In Fig. 6, some examples of last-to-freeze tips are shown. Fig. 7 illustrates a typical cold-boat charged with Siemens’ process polysilicon chips and pieces.

Fig. 4. Cold crucible melt and solidified, last-to-freeze region

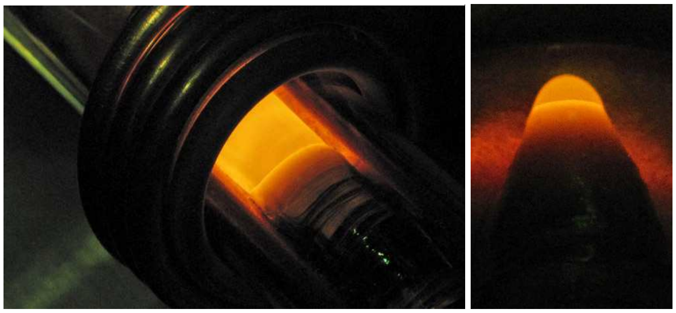

Fig. 5. Cold-boat zone solidification and last-to-freeze region

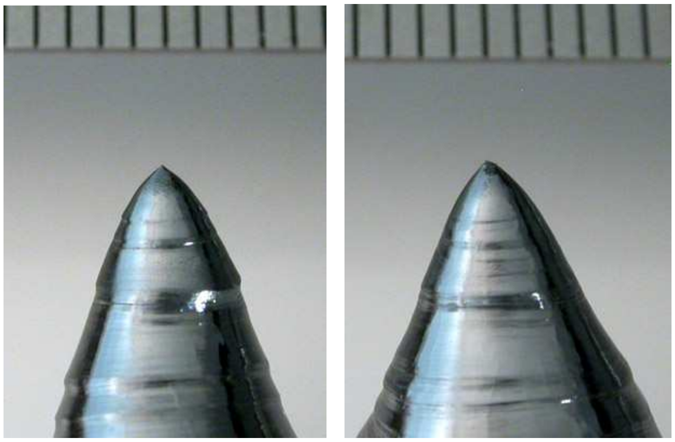

Fig. 6. Examples of last-to-freeze tips from zone solidification of Siemens’ process CVD polysilicon chip source material. The scale markers are 1mm.

Fig. 7 Copper cold boat with typical 30g polysilicon chip and chunk charge

## IV. INDUCTIVELY-COUPLED PLASMA MASS SPECTROSCOPY

Iso Guide 34 NIST traceable ICP-MS standards were used to prepare working standards in the appropriate concentration range, per SEMI PV049-00-0613. The samples were analyzed utilizing a PerkinElmer NexIon 300 system and standard conditions. The small samples were surface cleaned with 1% nitric acid produced from concentrated semiconductor grade nitric acid, prior to sample digestion. Silicon samples were digested utilizing a small amount of concentrated high-purity HF and $HNO_3$ acids. Typically, 0.1 g of sample material is weighed into a clean, dry PTFE bottle, followed by the addition of 1 mL of HF and 0.5 mL of $HNO_3$. The addition of $HNO_3$ was performed utilizing small, successive aliquots because of the high reactivity involved. No heating is necessary; the addition of HF and $HNO_3$ dissolves the silicon. Samples were subsequently evaporated utilizing high concentrations of HF to reduce the silicon background. The residue was re-suspended in a 2% $HF/H_2O_2/HNO_3$ solution for introduction into the plasma.

## V. RESULTS

We worked with randomly selected pieces of chip and chunk polysilicon material from a single lot provided by a commercial vendor. Seven (7) different chips in the ~0.1g weight range were selected from the as-received material for ICP-MS analysis of 32 impurity species. Fifteen (15) of these 32 impurities were present at or below the 0.1 ppb detection limit by at least one of the 7 measurements and were the focus of further study by the cold boat enhancement procedure described above. For the other 17 impurities, the average standard deviation of the 7 measurements was 81% of their average concentration value, and the range was 40% to 117% of their average concentration value. The rather large standard deviations may have contributions from material variations within the lot and from measurement reproducibility.

Four cold-boat runs of ~30g each were made with polysilicon pieces from this lot. Last-to-freeze tip pieces ~0.1g in weight were removed from the grown ingots and analyzed by ICP-MS. The value obtained was multiplied by the ratio of analyzed tip weight to initial silicon charge weight and by the expected fraction of impurities concentrated into the tip sample (from (4) and Fig. 3) to get the new (and generally lower) levels for concentrations of those impurities.

The first column of Table 1 lists the 15 impurities that showed a concentration at or below the 0.1 ppb detection limit in at least one of the 7 determinations made on the as-received polysilicon chips. The following four columns show the ICP-MS results on the last-to-freeze tips from the four cold-boat zone solidification runs to concentrate impurities into the tips. The last two columns are the average calculated concentrations $C_o$ of each impurity and their standard deviations obtained as

$$C_o = \text{Conc. in tip x (tip weight/ingot weight) x q.} \qquad (6)$$

The averages are presented as lower limits because there are a number of factors that can lead to less impurities being concentrated into the tip than the idealize calculations take into consideration. These will be discussed below.

## VI. DISCUSSION AND CONCLUSIONS

We've described a technique for enhancing the detection limit for low-level impurities in silicon by a factor of about 300. It involves concentrating impurities into a last-to-freeze region and using calculations describing impurity segregation behavior to relate ICP-MS analysis of last-to-freeze tips back to the concentrations in the silicon source material. While this has been done previously by FZ growth using feed rods core-drilled from the source material or bead feedstock, our method using cold-containers allows more flexibility in the geometry of the source material to be analyzed. In particular, chips and chunks of source material can be used – common forms supplied for crystal growth. The boat zoning process is easier to carry out than float zoning. An advantage over concentrating impurities by directional solidification in a hot crucible is that impurity introduction from the quartz crucible and graphite hot-zone is avoided. On the other hand, copper is incorporated from the cold container at a level of about 0.07 to 0.5 ppm. To refine the method, high-purity copper, gold-plated copper, or high purity silver should be explored as cold container materials. The cold boat used in this work was made from commercial-grade copper.

TABLE I

IMPURITY CONCENTRATIONS IN LAST-TO-FREEZE TIPS OF 4 ZONE-SOLIDIFIED SI INGOTS AND THE AVERAGE SOURCE SI LEVELS OF THOSE IMPURITIES $C_O$ CALCULATED FROM THE TIP VALUES

| **Impurity** | **Concentration in Last-to-Freeze Tip (ppb)** | | | | **Calculated Concentration $C_O$ in Source (ppb)** | |
|---|---|---|---|---|---|---|
| | Run 1 | Run 2 | Run 3 | Run 4 | Average | Std. Dev. |
| As | 13.1 | 21.8 | 13.6 | 0.13 | ≥ 0.015 | 0.012 |
| Be | <0.1 | <0.1 | 4.0 | <0.10 | - | - |
| Cd | 0.2 | 0.4 | 0.4 | 0.71 | ≥ 0.002 | 0.001 |
| Co | 1.0 | 2.3 | 2.5 | 2.15 | ≥ 0.008 | 0.002 |
| Ga | 7.5 | 0.9 | 0.5 | 1.1 | ≥ 0.015 | 0.023 |
| Ge | 0.1 | 0.1 | <0.1 | <0.10 | - | - |
| In | <0.1 | <0.1 | <0.1 | 0.61 | - | - |
| Li | 0.1 | <0.1 | <0.1 | 0.17 | - | - |
| Mn | 5.2 | 16.5 | 15.8 | 9.58 | ≥ 0.046 | 0.012 |
| Mo | 1.8 | 4.5 | 2.2 | 6.54 | ≥ 0.017 | 0.011 |
| Nb | 1.0 | 2.2 | 2.7 | 1.52 | ≥ 0.007 | 0.001 |
| Sr | 4.1 | 10.5 | 11.3 | 6.74 | ≥ 0.032 | 0.005 |
| Ta | 62.6 | 103.2 | 133.5 | 86.51 | ≥ 0.396 | 0.041 |
| V | 2.8 | 19.3 | 5.0 | 2.03 | ≥ 0.029 | 0.030 |
| Zr | 100.2 | 2448.2 | 767.2 | 55.82 | ≥ 3.050 | 4.214 |

There are a number of reasons why fewer impurities may be concentrated into the last-to-freeze tip than the equations predict:

- The ingots have a small grain structure and some impurities may be trapped at grain boundaries.
- Some impurities may evaporate from the molten zone.
- The effective segregation coefficients k may be less for cold-boat zoning than for more conventional techniques.
- Constitutional super cooling may alter the segregation behavior as the last-to-freeze tip is approached.
- The geometry of the molten zone is altered by repulsive inductive forces as the last-to-freeze tip is formed.
- The extreme last-to-freeze tip is a singularity in the mathematical sense, with C going to ∞ as the remaining material to freeze approaches 0, and the actual physical behavior is uncertain.

There are also reasons why post-growth sample preparation may reduce levels of some of the impurities:

- In some cases, metallic impurities “sweat out” of the surface near the tip as tiny beads that are loosely adhered and may be lost in handling.
- Use of acid solutions for pre-analysis sample preparation may preferentially remove enriched metals at the surface.

For these reasons, the calculated average concentrations are presented as lower limits for actual $C_o$ values in the source Si.

The standard deviation of the measured concentration values and of the average calculated concentrations from them are rather large, sometimes on the same order as the average value itself. More work is needed to sort out the reasons for this.

The rather large calculated concentration values for Zr and to a lesser extent for Ta are unusual, but not entirely unexpected. Even though one or two of the 7 direct determinations on the source material chips were below the 0.01 ppb detection limit, others were high (up to 4.8 ppb for Zr and 30 for Ta). The levels for Be, Ge, In, and Li were extremely low, usually below the detection limit, even in the impurity-concentrated tip region.

## ACKNOWLEDGEMENT

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