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Determination of the effective distribution coefficient (K) for silicon impurities

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For the production of photovoltaic cells, the silicon purity can be intermediate between metallurgical grade silicon (MG-Si, 98%–99.9% pure) and electronic grade silicon (>99.9999% pure). This silicon, with intermediate purity and that still meets solar cell requirements, is called upgraded metallurgical grade silicon (UMG-Si). One method of producing UMG-Si is applying a controlled solidification process, like unidirectional solidification (heat exchange method), zone melting (or zone refining), or Czochralski growth to MG-Si. These processes use the impurities solubility difference in solid and liquid silicon known as effective distribution coefficient (K). For these reasons, to study the solidification process, it is necessary to determine K for silicon impurities, which is the objective of this study. MG-Si (99.85% purity or 1500 ppm of impurities) was processed by 1 pass of zone melting at 1 mm/min using an electron beam furnace with water cooled copper crucible. The effective distribution coefficient (K) for impurities with $\mathrm{Ko} \leq 10^{-1}$ was found to follow the relation $K = 0.03\ \mathrm{Ko}^{-0.063}$. For boron, $\mathrm{K} = 0.8$. Impurities with Ko between 10^{-3} and 10^{-8} presented similar effective distribution coefficients ($\mathrm{K} = 0.07 \pm 0.02$), meaning that the effective distribution coefficient of a specific impurity depends on the total amount of impurities. The measured impurities profiles in silicon were compared with those obtained by Pfann's equations using the effective distribution coefficients and showed comparative results. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4739759]

I. INTRODUCTION

The Siemens process is used all over the world to purify silicon. This process produces high-purity silicon with less than 1 ppm impurities (>99.9999% pure), known as electronic grade silicon (EG-Si). It is also used by the microelectronics industry and in the production of solar cells.

For the production of photovoltaic cells, the silicon purity can be intermediate between metallurgical grade silicon (MG-Si, 98%–99% pure) and EG-Si. Silicon with intermediate purity is called upgraded metallurgical grade silicon (UMG-Si) or solar grade silicon (SG-Si). As silicon represents up to 25% of the panel price, global research is underway to obtain this silicon by alternative process to Siemens, at lower costs, but still meeting the requirements for solar cell manufacture.[1]

One alternative is to apply a controlled solidification process, such as unidirectional solidification (or HEM = heat exchange method), zone melting (or zone refining), or Czochralski growth

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in MG-Si to obtain silicon that meets solar cell requirements. These processes use the difference of solubility of an impurity in solid and liquid phases, known as distribution coefficient.

For a binary alloy, assuming negligible diffusion in the solid, the equilibrium distribution coefficients (Ko) at a determinate temperature (Eq. (1)) is defined as the relation between the concentration of the solute in the solid phase (C_S) and the concentration of the solute in the liquid phase (C_L).[2] The equilibrium distribution coefficient (Ko) is obtained from the equilibrium diagram (Figure 1)

$$\mathrm{Ko} = C_S/C_L, \tag{1}$$

where C_S = solute concentration in the solid and C_L = solute concentration in the liquid.

The solidification occurs in equilibrium when the solidification speed is slow enough to allow the solute to reject in the liquid (supposing $\mathrm{Ko} < 1$). This can be uniformly distributed in all liquid remaining. The solute in the solidified fraction can also be uniformly distributed by diffusion. In this case, the entire ingot formed will have a uniform composition Co (Figure 2).

In industrial processes, time is too scarce to obtain equilibrium conditions, as the diffusion in solids is very low and there is no uniform distribution of the solute in the liquid. Part of the reject solute (supposing $\mathrm{Ko} < 1$) remains near the solid/liquid interface (region δ in Figure 2) and the composition of solid formed will be a function of the liquid composition in this region. In this case, the composition of solid formed in the interface (C_{SI}) will be related to the bulk liquid composition ($C_{L\infty}$) by the effective[2] distribution coefficient (K), as seen in the equation

$$K = C_{SI}/C_{L\infty}, \tag{2}$$

where C_{SI} = solute concentration in the solid at the S/L interface and $C_{L\infty}$ = solute concentration in the bulk liquid.

If an impurity has $K > 1$, this means that it is more soluble in the solid than in the liquid silicon. Therefore, during the ingot solidification, this impurity is concentrated in first portion

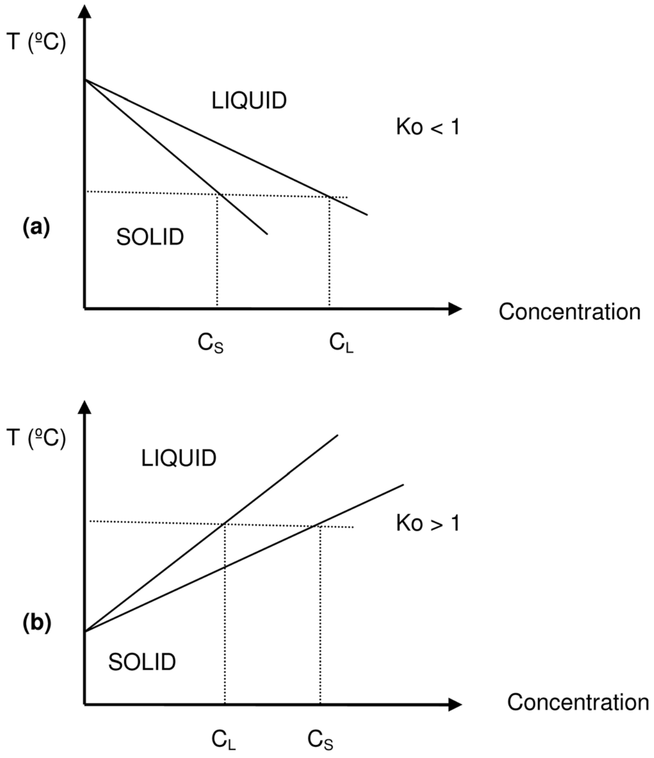

FIG. 1. Schematic representation of equilibrium diagram for binary alloy. (a) $\mathrm{Ko} < 1$; (b) $\mathrm{Ko} > 1$.

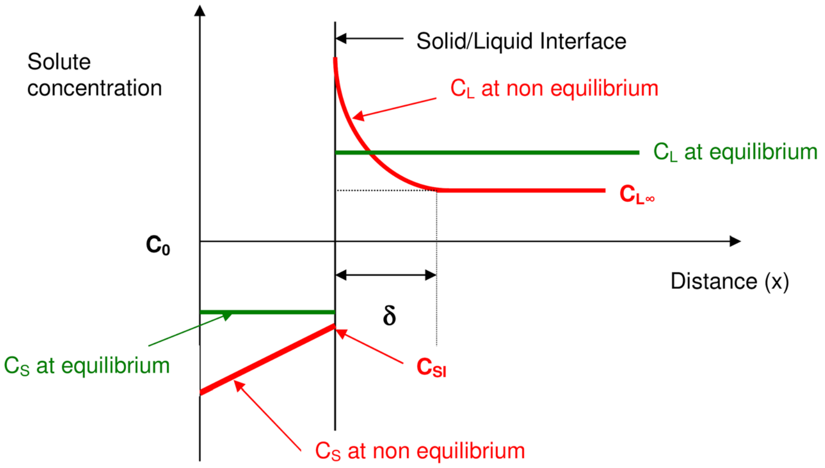

FIG. 2. Schematic illustration for solid and liquid concentrations during equilibrium and non equilibrium conditions. δ is a region where diffusion in the liquid contributes to solute transportation during a non equilibrium solidification. $Ko = C_S/C_L$ and $K = \mathbf{C_{SI}/C_{L\infty}}$.

solidified. If the impurity has $K < 1$, this means that it is more soluble in the liquid than in the solid. So, during the ingot solidification, this impurity is concentrated in the liquid, and the last portion solidified is enriched with this impurity. If an impurity has $K \approx 1$, this means that the impurity has almost the same solubility in solid and liquid, signifying that, after solidification, it keeps the same level in the whole ingot. To study solidification processes, it is necessary to determine the effective distribution coefficient (K) for an alloy.[2]

This work proposes a method to determine K for silicon using the horizontal zone melting process. The advantages of the horizontal zone melting process (with crucible) over the vertical zone melting or floating zone (without crucible) process is the control over the size of the zone which is much simpler in the horizontal zone melting process, and that it allows the use of silicon in any shape (stones, granulated, or ingots), while only silicon bars can be used in the floating zone process. The technique produces a small liquid zone in the ingot and moves it slowly along this, producing a redistribution of solute in the ingot.[3]

II. EXPERIMENTAL PROCEDURE

We used an 80 kW EBM (electron beam melting) EMO-LEW furnace, as previous research carried out by our group demonstrated the technical viability of the process, with excellent results in terms of final purity of the silicon and cell efficiency.[4–7] The starting material was MG-Si stones (200 g) supplied by Liasa Alumínio S/A, with diameters from 20 to 50 mm. The stones were placed in the copper crucible inside the furnace, and the vacuum of the entire system was activated. When the internal pressure reached 10^{-3} Pa, the sample was gradually heated by slowly increasing the power of the electron beam until the material was completely melted. When the entire mass of silicon was melted, the working power was kept constant between 11 and 13 kW for 20 min. The process was performed in a water-cooled copper crucible (in the bottom part of the crucible) with internal dimensions of 150 mm in length, 40 mm in width, and 15 mm in height. The silicon was solidified in the same copper crucible. The ingot was then turned over 180° and remelted in the same way to ensure its homogeneity. Details of the furnace and crucible are described elsewhere.[5]

Processing by zone melting (ZM) occurred in 135 min in the same copper crucible used for preparing the initial ingots. As each ingot was 150 mm long, the zone speed was, approximately, 1 mm/min. It is important to point out that the crucible remained stationary and the beam moved at a constant speed, "scanning" over the ingot. The beam was adjusted electronically, allowing for the formation of a zone 10 mm thick by 15 mm wide. Table I shows the chemical composition (mass ppm) of the MG-Si used as starting material and the ingot in

TABLE I. Chemical composition (mass ppm) of the MG-Si and the different regions in the ingot after 1 pass of zone melting at 1 mm/min. Co is the initial impurity concentration in the MG-Si.

		Solidified fraction			
Element	Co	0.1	0.3	0.6	0.9
Al	175	13	40[a]	60[a]	62[a]
B	12.5[b]	11	12	12	15
Ca	35	0.75	1.1	4.2	1.3
Co	0.27	0.03	0.12	0.2	1.9
Cr	2.2	0.35	1.2	1.9	14
Cu	7.0	0.8	0.24	2.6	8.5
Fe	980	190	1050[a]	2200[a]	10 000[a]
Mn	100	5.5	15	25	10
Mo	0.30	<0.05[c]	0.2	0.4	0.8
Nb	0.22	<0.05[c]	<0.05[c]	0.15	0.5
Ni	1.7	0.4	0.65	2	19
P	50	9.4	14	11	0.75
Ti	75	4	17	35[a]	185[a]
V	2.7	0.25	0.60	1.1	7
W	0.15	<0.1[c]	<0.1[c]	<0.1[c]	0.2
Zr	3.6	0.25	0.95	1.6	10
Other elements	12.71	0.50	2.20	2.53	14.13
Total impurities	1454.05	235.88	1155.26	2359.68	10367.18
Purity (%)	99.86	99.976	99.884	99.764	98.963

[a] Nonhomogeneous region.
[b] Calculated by mass balance.
[c] <x not added to the total amount of impurities.

different regions after 1 pass of zone melting at 1 mm/min. The chemical analysis was conducted at the Northern Analytical Laboratory (USA) using the glow discharge mass spectrometry (GDMS) technique.

III. RESULTS AND DISCUSSIONS

For a binary alloy, the solute concentration in the solid after one pass of zone melting can be described by Pfann[3] equation

$$C_S = Co\ [1\text{–}(1-K)\exp(-K\cdot fs/Z)], \tag{3}$$

where C_S = solute concentration in the solid at a distance x, Co = initial solute concentration in the binary alloy, K = effective distribution coefficient of solute in the alloy, fs = solidified fraction = x/L, x = distance from the beginning of the solidification, L = length of the ingot, Z = relative zone length = ℓ/L, and ℓ = liquid zone length.

Conditions:

1. Valid in the range $0 \le fs < 1-Z$.
2. K and Z are constant.
3. Solute concentration in the liquid zone is uniform.
4. Ingot has a uniform concentration (Co) before the zone melting process.
5. Solid and liquid densities are the same.
6. Diffusion in the solid is negligible.

For this work, the ingot had 15 cm and the zone length 1.5 cm, which means that $Z = 1.5/15 = 0.1$. For K determination, it was selected impurities that appeared in great amounts on the metallurgical silicon and solar efficiency which deteriorated more.[8]

Using Eq. (3) with Ko, the concentration was calculated at $fs = 0.1$ and compared with the measured values obtained after 1 pass of zone melting (Table II).

The results from Table II show that

1. The measured concentration for phosphorus is lower than that calculated by Pfann's equation. The reason for this is that this element had a huge evaporation during the process, due to its vapor pressure being much higher than the furnace chamber (10^{+8} and 10^{-3} Pa, respectively). As the reduction of phosphorus concentration is not only caused by zone melting, but also by evaporation, Pfann's equation cannot be used because it assumes no evaporation of the alloy elements.
2. The measured concentration for boron is nearly the same as calculated by Pfann's equation, because its equilibrium distribution coefficient is near the unit ($Ko = 0.8$), which means that boron has nearly the same solubility in liquid and solid silicon. Boron also does not evaporate during the process, as its vapor pressure is lower than the furnace chamber (10^{-4} and 10^{-3} Pa, respectively).
3. For all other elements measured, except for boron and phosphorus, the level measured was much higher than the calculation by Pfann's equation using the equilibrium distribution coefficient (Ko). For this reason, it is important to determine the effective distribution coefficient (K).

Burton[2] working with germanium single crystal grown obtained a correlation (Eq. (4)) between the effective distribution coefficient (K) and the equilibrium distribution coefficient (Ko)

$$K = \frac{1}{\left[1 + \left(\frac{1}{Ko} - 1\right) \cdot \exp -\frac{R\delta}{\mathrm{DL}}\right]}, \tag{4}$$

TABLE II. Equilibrium distribution coefficient (Ko) of impurities in silicon[9] and vapor pressure of these impurities[10] at 1500 °C. Co is the initial impurity concentration in the MG-Si. Calculated (calc) and measured (meas) values for impurities concentration after 10% of solidified fraction ($fs = 0.1$).

Element	Ko	Vapor pressure (Pa)	Co (ppm)	$C_{(fs=0.1\ \mathrm{meas})}$ (ppm)	$C_{(fs=0.1\ \mathrm{calc\ Ko})}$ (ppm)	$C_{(fs=0.1\ \mathrm{meas})}/C_{(fs=0.1-\mathrm{calc\ Ko})}$
Al	2.0×10^{-3}	70	175	13	0.70	18.6
B	0.8	4×10^{-4}	12.5	11	10	1.1
Co	2.0×10^{-5}	3	0.27	0.03	1.08×10^{-5}	2.8×10^{3}
Cr	1.1×10^{-5}	11	2.2	0.35	4.84×10^{-5}	7.2×10^{3}
Cu	4.0×10^{-4}	53	7.0	0.80	5.60×10^{-3}	143
Fe	8.0×10^{-6}	5	980	190	1.60×10^{-2}	1.2×10^{4}
Mn	1.3×10^{-5}	4×10^{3}	100	5.5	2.60×10^{-3}	2×10^{3}
Mo	4.5×10^{-8}	3×10^{-7}	0.30	0.05	2.70×10^{-8}	2×10^{6}
Nb	4.4×10^{-7}	3×10^{-9}	0.22	0.05	1.94×10^{-7}	2.6×10^{5}
Ni	1.0×10^{-4}	1.3	1.7	0.40	3.40×10^{-4}	1.2×10^{3}
P	0.35	$>10^{8}$	50	9.4	27	0.35
Ti	2.0×10^{-6}	5×10^{-2}	75	4.0	3.00×10^{-4}	1.3×10^{4}
V	4.0×10^{-6}	8×10^{-3}	2.7	0.25	2.16×10^{-5}	1.2×10^{4}
W	1.7×10^{-8}	10^{-11}	0.15	0.10	5.10×10^{-9}	2×10^{7}
Zr	1.6×10^{-8}	10^{-6}	3.6	0.25	1.15×10^{-7}	2×10^{6}

where R = solidification speed (cm s^{-1}), δ = length of the region in the liquid between the interface and the point where the liquid concentration (C_L) is uniform (cm). In this region, the diffusion also contributes to impurities in transport and likewise the liquid flow, and DL = diffusion coefficient of the element in the liquid silicon (cm^2 s^{-1}).

Equation (4) shows that

If $R\delta \rightarrow \infty$, [exp – $(R\delta)/DL$] $\rightarrow 0$ and K $\rightarrow$ 1 (no segregation),

If $R\delta \rightarrow 0$, [exp – $(R\delta)/DL$] $\rightarrow 1$ and K $\rightarrow$ Ko (efficient segregation).

To have an effective purification, the product Rδ should be as low as possible. But if the solidification speed is lowered, the cost of the purification process is raised, because it takes more time. Therefore, a balance between solidification speed and process cost should be achieved. For silicon purification and crystal growth, typical values are 0.07 mm/min for HEM, 1 mm/min for Czochralski growth (CZ), and 7 mm/min for floating zone (FZ).[11–13]

Also, if the stirring is improved in the liquid, the δ value is reduced and the purification process is more effective. In our case, working with an electron beam furnace is practically impossible to impose stirring methods for the liquid phase, and it occurs only by convection currents.

In the controlled solidification, the heat flow is oriented in one direction, so the grains in a polycrystal or the grain in monocrystal grow in the opposite direction of the heat flow. To keep a plane solid-liquid interface, without formation of dendrites and cells, a low solidification speed is required. When dendrites or cells are formed, the impurities are segregated in the interdendritic or intercellular spaces and the efficiency of the purification is drastically reduced. To keep the plane interface during the unidirectional solidification of a binary alloy, the solidification speed (or growth speed) could be described in Fleming's[14] equation

$$R < \frac{[G \cdot Ko \cdot DL]}{[-m \cdot Co \cdot (1 - Ko)]}, \tag{5}$$

where G = actual temperature gradient in the liquid; D_L = diffusion coefficient of the element in the liquid silicon; and $m = dT_{Liquidus}/dC_L$.

As m, Ko, and DL are characteristics of the binary alloys, Eq. (5) shows that when the impurity concentration is raised, the solidification speed should be reduced to keep the plane interface. If the temperature gradient imposed is raised, the speed can be increased, and process cost is also reduced. In our case, we used a water cooled copper crucible, which imposed a very high heat extraction rate (200 °C/mm).

Calculating K from Burrton's equation (Eq. (4)) is not easy, since it is necessary to have the δ value. In our case, it is impossible, because the solidification occurs in a vacuum chamber under an electron beam. We therefore used another approach.

For phosphorus, it is not possible to calculate K in the present case due to the high vaporization of this element during the zone melting.

For boron, Table III shows a very good approximation between the measured value and the calculated one using Eq. (3) with Ko. As boron does not vaporize during the process, this means that K should be very near to Ko or 0.8.

TABLE III. Correlation between K and $\left[1 - \left(\frac{1-K}{\exp K}\right)\right]$.

K	$\left[1 - \left(\frac{1-K}{\exp K}\right)\right]$
10^{-1}	0.18564
10^{-2}	0.01985
10^{-3}	0.00199
10^{-4}	2×10^{-4}
10^{-5}	2×10^{-5}
10^{-6}	2×10^{-6}

Using Eq. (3) for $Z = 0.1$ and $fs = 0.1$, we have the real value of Cs, or the measured value obtained experimentally

$$CS\ \ (fs = 0.1\ \ meas) = \ Co \cdot \left[1 - \frac{1-K}{\exp K}\right], \tag{6}$$

Table III shows that the term $[1 - (1-K)/\exp K)]$ converges to $2\mathrm{K}$ when $\mathrm{K} \leq 0.1$, as expressed by

$$\left[1 - \frac{(1-K)}{\exp K}\right] = 2K \quad \text{for} \quad \mathrm{K} \leq 0.1. \tag{7}$$

In our case, except for boron and phosphorus, all other metallic impurities have $\mathrm{Ko} \leq 0.1$ which also suggests that $\mathrm{K} \leq 0.1$. Using Eqs. (6) and (7), we have

$$\mathrm{C}_{\mathrm{S(fs\,=0.1\,meas)}} = \mathrm{Co} \cdot 2\mathrm{K}. \tag{8}$$

By analogy:

$$\mathrm{C}_{\mathrm{S(fs\,=0.1\,calc\,Ko)}} = \mathrm{Co} \cdot 2\mathrm{Ko}, \tag{9}$$

$$[\mathrm{C}_{\mathrm{S\,(fs\,=0{,}1\,meas)}}]/[\mathrm{C}_{\mathrm{S\,(fs\,=0{,}1\,calc\,Ko)}}] = [\mathrm{Co} \cdot 2\mathrm{K}]/[\mathrm{Co} \cdot 2\mathrm{Ko}] = \mathrm{K}/\mathrm{Ko}. \tag{10}$$

Plotting $[\mathrm{C}_{(\mathrm{fs}=0.1\ \ \mathrm{meas})}/\mathrm{C}_{(\mathrm{fs}=0.1-\mathrm{calc}\mathbf{Ko})}]$ against Ko (Figure 3), we obtain

$$[\mathrm{C}_{(\mathrm{fs}=0.1\,\mathrm{meas})}/\mathrm{C}_{(\mathrm{fs}=0.1-\mathrm{calc\,Ko})}] = 0.03\,\mathrm{Ko}^{-1.063} = \mathrm{K}/\mathrm{Ko}, \tag{11}$$

$$\mathrm{K} = 0.03\,\mathrm{Ko}^{-0.063} \quad \text{valid for} \quad \mathrm{Ko} < 0.1. \tag{12}$$

Using Eq. (12), K was calculated for elements with $\mathrm{Ko} \leq 0.1$ (Table IV). It is observed that impurities with Ko between 10^{-3} and 10^{-8} have nearly the same effective distribution coefficient (0.07 ± 0.02), which shows that K of a specific impurity depends on the total amount of impurities. Yuge *et al.*[15] working with silicon unidirectional solidification in a water cooled copper crucible, using an electron beam furnace, with solidification speed of 0.9 mm/min (the same of our work), found $\mathrm{K} = 0.3$ for iron, much higher than its Ko (10^{-5} in silicon).

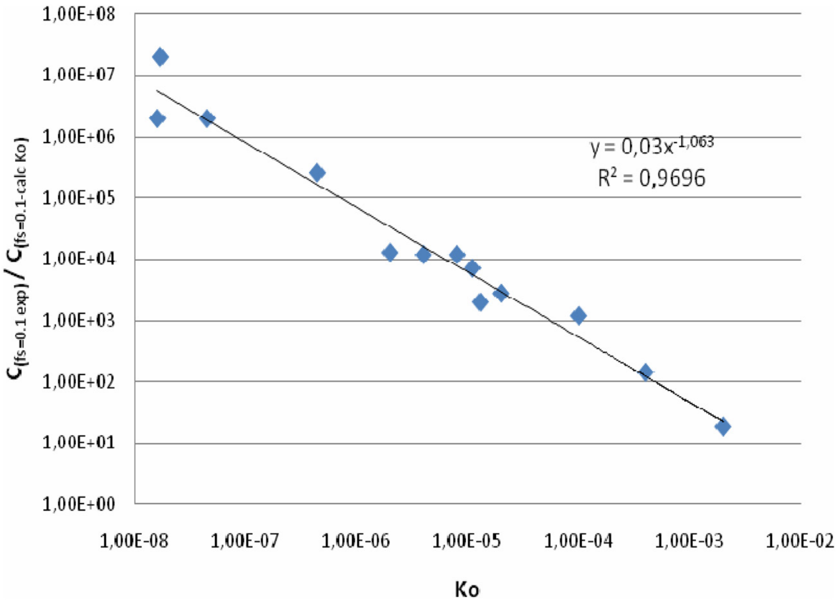

FIG. 3. $[\mathrm{C}_{(\mathrm{fs}\,=\,0.1\ \ \mathrm{meas})}/\mathrm{C}_{(\mathrm{fs}\,=\,0.1-\mathrm{calc}\ \ \mathrm{Ko})}]$ as a function of Ko.

TABLE IV. Equilibrium distribution coefficient (Ko) of impurities in silicon[9] and effective distribution coefficient (K) calculated with Eq. (12). Co is the initial impurity concentration in the MG-Si. Calculated (calc) and measured (meas) values for impurities concentration at 10% of solidified fraction (fs = 0.1) after 1 pass of zone melting at 1 mm/min.

Element	Ko	K	Co (ppm)	$C_{(fs = 0.1\ meas)}$ (ppm)	$C_{(fs = 0.1\ calc\ K)}$ (ppm)
Al	2.0×10^{-3}	0.044	175	13	15.4
Co	2.0×10^{-5}	0.059	0.27	0.03	0.03
Cr	1.1×10^{-5}	0.061	2.2	0.35	0.27
Cu	4.0×10^{-4}	0.049	7.0	0.80	0.69
Fe	8.0×10^{-6}	0.063	980	190	123
Mn	1.3×10^{-5}	0.061	100	5.5	12.2
Mo	4.5×10^{-8}	0.087	0.30	0.05	0.05
Nb	4.4×10^{-7}	0.075	0.22	0.05	0.03
Ni	1.0×10^{-4}	0.053	1.7	0.40	0.18
Ti	2.0×10^{-6}	0.068	75	4.0	10.2
V	4.0×10^{-6}	0.065	2.7	0.25	0.35
W	1.7×10^{-8}	0.092	0.15	0.10	0.03
Zr	1.6×10^{-8}	0.092	3.6	0.25	0.66

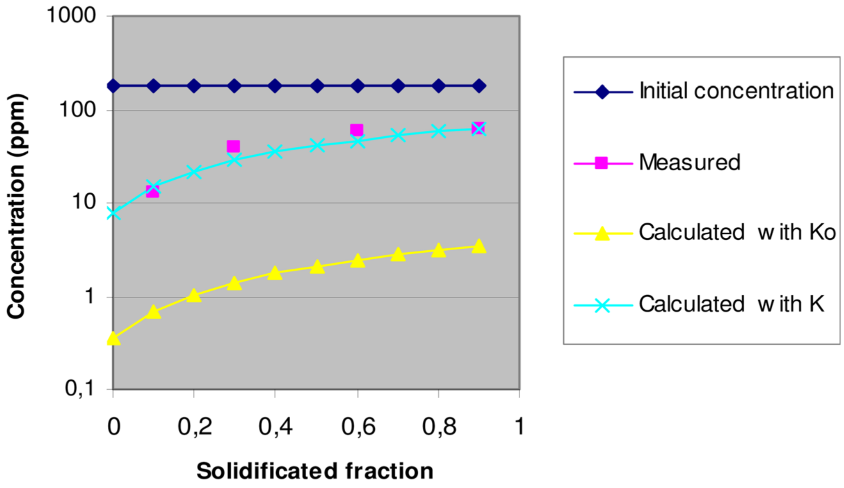

FIG. 4. Aluminum profile after 1 pass of zone refining at 1 mm/min measured and calculated by Pfann's equations using Ko and K obtained from Eq. (12).

The calculated (calc) and measured (meas) values for impurities concentration after 10% of solidified fraction (fs = 0.1) appeared to agree with the majority of impurities (Table IV), indicating that Eq. (12) can be applied for zone melting of metallurgical silicon.

Figure 4 shows that there is a good correlation between the measured concentrations of aluminum and the calculated values with Pfann's equation (Eq. (3)) using the effective distribution coefficient (K). Although the calculation for K was done for fs = 0.1, Figure 4 shows that it is valid for 90% of the solidified ingot.

IV. CONCLUSIONS

Using metallurgical grade silicon (99.85% purity in mass, or 1500 ppm of impurities) processed by 1 pass of zone melting at a speed of 1 mm/min, it was concluded that

1. The effective distribution coefficient (K) for impurities with $K_0 \leq 0.1$ was found to follow the relation $K = 0.03\ Ko^{-0.063}$. For boron, K = 0.8.

2. Impurities with Ko between 10^{-3} and 10^{-8} presented nearly the same effective distribution coefficient ($K = 0.07 \pm 0.02$), which means that the effective distribution coefficient of a specific impurity depends on the total amount of impurities presented in the silicon.
3. The measured impurities profiles in silicon were compared with those obtained by Pfann's equations using the effective distribution coefficients and showed to be in agreement.

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