CHAPTER 2

DIRECTIONAL SOLIDIFICATION OF mc-Si INGOTS
BY ISO-ROTATION OF THE CRUCIBLE

2.1 INTRODUCTION

The strongly growing photovoltaic market is based on crystalline silicon technology. This requires the wafer manufacturers to produce high quality material in high productivity processes. Crystal quality is the dominating factor in all kinds of solar cells (Sopori et al 1994). The conversion efficiency of any solar cell is determined by the crystal quality. Crystal quality is characterized by the minority carrier lifetime in the absorber region of the solar cell. The life of the minority carriers mainly depends on the impurities and density of the deep defects present in the as-grown substrate (Macdonald and Cuevas 1999).

Basically, four methods are used to grow silicon ingots for commercial PV applications. The Czochralski and floating zone methods produce high quality single crystal material whereas directional solidification and electromagnetic semicontinuous casting produce large grain multicrystalline silicon. The majority of silicon wafers used for the solar cells is Cz grown single crystalline and DS grown multicrystalline materials (Ciszek 2003). At the beginning, mostly Cz grown single crystals were used for solar cells. The Cz process is the standard method employed by the semiconductor industry to make silicon wafer for the integrated circuits. The
same approach was used by the manufacturers to make high-efficiency silicon solar cells.

Casting and DS are two techniques used to produce mc-Si ingots for solar cells. Both casting and DS techniques are less complex compared to the Cz process and yield mc-Si ingots. The purity of the mc-Si wafers depends on the purity of the initial material used for melting and on the interaction between the melt and crucible walls (especially the oxygen content). In these techniques, the molten silicon is poured into a ‘mold’ where the solidification takes place. The solidification takes place in all directions, and unlike the Cz pulling process, the resulting ingot is not single crystalline but contains many grains and grain boundaries. In the DS process, the crucible containing the molten Si is lowered through the RF heating coil and therefore it is the bottom part of the melt that solidifies first (Ciszek et al 1979). In the EMC technique, direct contact between the melt and the crucible is avoided, reducing the contamination and oxygen content (Sivoththaman et al 2006).

This chapter describes the growth of gallium doped mc-Si ingots by DS employing the iso-rotation of the crucible and their carbon concentration measurement using the FTIR spectroscopy. The solidification of mc-Si ingots by the constant heater translation rate of 30 mm/hr, and with various crucible rotation rates of 0, 1 and 30 rpm is discussed in detail. The carbon concentration in mc-Si ingots solidified at various crucible rotation rates was measured by the FTIR spectroscopy. The results are explained on the basis of effect of crucible rotation on the carbon concentration in terms of segregation phenomena.
2.2 SEGREGATION

Segregation is important in crystal growth for a variety of reasons. Firstly, segregation is most effectively used to purify the starting materials used for crystal growth processes. Secondly, one may want to predetermine the composition of a nutrient in order to obtain a specific composition of the growing crystal. In crystallization from a melt, various impurities from the melt are incorporated into the growing crystal. It is known from experimental investigations that as a rule the concentration of an impurity has a different value in a solid phase compared to a co-existing fluid phase. During solidification of melts, the concentration of an impurity in the solid phase is usually reduced while increasing in fluid, i.e. segregated. The equilibrium segregation behavior associated with the solidification of multiple-component systems can be determined from the corresponding phase diagram of the binary system with a solute (impurity) and a solvent (host material) as components (Garandet et al 1994).

Most impurities in silicon lower the melting point $T_m$ of silicon because they form eutectic systems with it. Figure 2.1 represents a portion of such a phase diagram near the melting point of silicon. Because of the different solubilities of impurity A in solid and liquid silicon at the same temperature $T_x$, the binary phase diagram consists of solidus and liquidus lines, which intersect the 100% silicon axis at $T_m$. Both lines can be approximated as linear for low impurity concentrations. Therefore, the ratio of the solubility of impurity A in solid silicon ($C_S$) to that in liquid silicon ($C_L$) remains constant over a certain concentration range. This ratio is referred to as the equilibrium segregation or distribution coefficient and is defined with $k_0$ as

$$k_0 = \frac{C_S}{C_L} \quad (2.1)$$
Table 2.1 shows the equilibrium segregation coefficient for several impurities in silicon.

Table 2.1 Equilibrium segregation coefficients of various impurities in silicon

<table>
<thead>
<tr>
<th>Impurity</th>
<th>$K_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>0.8</td>
</tr>
<tr>
<td>Ga</td>
<td>0.008</td>
</tr>
<tr>
<td>C</td>
<td>0.07</td>
</tr>
<tr>
<td>N</td>
<td>$7 \times 10^{-4}$</td>
</tr>
<tr>
<td>P</td>
<td>0.35</td>
</tr>
<tr>
<td>O</td>
<td>1.25</td>
</tr>
<tr>
<td>Fe</td>
<td>$8 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

The segregation coefficient defined in the above equation actually represents the ratio of the difference in thermodynamic potential due to the interaction and entropy of mixing of the impurity with the host material in the solid and liquid phase. The impurity solubility in liquid silicon is always higher than that in solid silicon ($k_0 < 1$).

![Schematic binary phase diagram for silicon and impurity with $k_0 < 1$](image-url)

Figure 2.1 Schematic binary phase diagram for silicon and impurity with $k_0 < 1$
Equilibrium segregation can be obtained by calculation from the binary phase diagram under the assumption that solidification proceeds very slowly, or the solidification rate can be approximated to be zero. The values of the equilibrium segregation coefficient for silicon have been correlated to the tetrahedral radius of the impurities, which implies that impurities with larger radius have smaller equilibrium segregation coefficient.

2.3 NORMAL FREEZING

Normal freezing experiments are frequently employed for determining the effective segregation coefficients. Depending on the mixing conditions in the bulk melt, one will obtain different impurity concentration profiles in the solid. For the ‘no-mixing, diffusion only’ case after an initial transient, segregation will cease as \( k \to 1 \) for any practical growth rate. Solidification of a liquid from one end to the other is shown in Figure 2.2.

![Solidification by normal freezing](image)

Figure 2.2 Solidification by normal freezing

The normal freezing assumes the following condition

1. Diffusion in the solid is negligible.
2. Impurity concentration in the liquid is uniform.
3. Equilibrium segregation coefficient \( (k_0) \) is constant.
The impurity concentration in the solid ($C_S$) as a function of the fraction solidified $g$ is given by

$$C_S = k_0C_0(1-g)^{k_0-1}$$

(2.2)

where $C_0$ is the initial impurity concentration in the liquid. This relation is known as Pfann relation (Garandet et al 1994). This relation is plotted in Figure 2.3 for various values of $k_0$.

![Graph showing carbon concentration versus solidified fraction of the melt volume for different segregation coefficients](image)

**Figure 2.3** Carbon concentration versus solidified fraction of the melt volume for different segregation coefficients

Normal freezing is a powerful method for material purification if $k_0$ deviates enough from 1 and if high impurity levels have to be dealt with. In principle, by using smaller and smaller fractions of the initial amount of material, each consecutive normal freezing step should result in an even purer substance. In practice, the result of such a chain of processes is limited by the necessity of in between handling of the material that eventually introduces as many impurities as are removed.
2.4 EFFECTIVE SEGREGATION COEFFICIENT

The equilibrium segregation coefficient \( k_0 \) is applicable for solidification only at a negligibly slow growth rate. The actual crystal growth is not at thermal equilibrium, and the portioning of impurities between the crystal and the melt is described by the effective segregation coefficient (\( k_{\text{eff}} \)).

For finite or higher solidification rates, impurity atoms with \( k_0 < 1 \) are rejected by the advancing solid at a greater rate than they can diffuse into the bulk of the melt. In the Cz crystal growth process, with the start of solidification at a given seed-melt interface, segregation takes place and the rejected impurity atoms begin to accumulate in the melt layer near the growth interface and diffuse in the direction of the bulk of the melt (Garandet et al 1993). An impurity concentration gradient thus develops just ahead of the advancing crystal which is shown in Figure 2.4.

![Figure 2.4 Schematic concentration distribution of solute near the solid-liquid interface](image-url)
2.5 CARBON IN mc-Si

The effects of carbon in mc-Si have not been investigated as thoroughly as the effects of oxygen. Several reports have shown that high carbon concentration has an impact on thermal donor activity and on oxygen precipitation and thereby on point defects (Kalejs 1993, Oherlein et al. 1982). It is well known that carbon in silicon melts originated both from the starting material and from the graphite hot-zone components (Carlberg 1983). The carbon level in a Cz grown silicon crystal rises from the seed end to the bottom end. This is due to the segregation, which easily can be accounted for by the normal freeze relation. The constant incorporation of carbon is through the ambient atmosphere originating from the graphite hot-zone parts. Carbon is substitutionally dissolved in silicon and tetrahedrally bonded to silicon atoms, precipitate as in the form of SiC or agglomeration in the form of loose C-Si agglomerates if the concentration exceeds the solubility limit (Taylor et al. 1993).

The efficiency of mc-Si solar cells can be strongly reduced by material-induced shunts (Breitenstein et al. 2003). These shunts are caused by SiC precipitates, which were generated during the crystallization of the mc-Si ingot at the DS process. It is well known that so-called SiC filaments cause dangerous ohmic shunts in solar cells (Bauer et al. 2007). In addition, during the commercial mc-Si wafer production, silicon is molten in a silica crucible in a protected atmosphere and the mc-Si ingot is then grown by a solidification process. After the removal of its edges and head and tail regions, the mc-Si ingot is cut into several bricks, which are then wire sawed into mc-Si wafers for solar cells. Steel wire and SiC grinding powder are used for the wire sawing process of mc-Si. In the wire sawing process of mc-Si ingot in production, foreign inclusions (such as SiC and Si₃N₄) can result in defected wafer surfaces and sometimes even break wires (Du et al. 2007).
Carbon in silicon lattice is electrically inactive, but if the concentration is higher then it will enhance the oxygen precipitation as SiO$_2$ species and form pair defects with interstitial oxygen (Hu 1980). In addition, it will strongly interact with oxygen and form CO complexes. The hypothesis of carbon acting as heterogeneous nucleation centers for oxygen precipitation implied an enhanced oxide precipitation (Leroueille 1981, Sun et al 1990). The two main factors, which appear to influence carbon precipitation in silicon: a large volume decrease and high interface energy. The carbon precipitation process is associated with a volume decrease in the silicon lattice since the size of the carbon atom is small. In contrast, the oxygen precipitation is associated with a volume increase in the silicon lattice. The volume change associated with oxygen and carbon precipitation favors co-precipitation in an approximate ratio of 2:1 (Akiyama et al 1973, Shimura 1986).

2.6 CARBON SOLUBILITY IN LIQUID Si

The only phase to be considered beside liquid and solid solution of Si is β-SiC, and that the three phase equilibrium (liquid) + (Si, solid) + (SiC) is eutectic (Durand and Duby 1999). By measuring the amount of dissolved carbon in the silicon phase at different temperatures a relation for the carbon solubility as a function of temperature is obtained. Many researchers have studied the solubility of carbon in liquid silicon using different experimental set-ups and different analyzing techniques, which is summarized in Table 2.2. However, the experimental measurements with liquid Si are more complex in nature since the interaction with the ambient atmosphere and the graphite crucible may disturb the measurements. Hence it was found from the reported results that the solubility of carbon at the melting point is 40 ppm by mass.
Table 2.2 Solubility of carbon in liquid silicon

<table>
<thead>
<tr>
<th>Investigators</th>
<th>Silicon melting</th>
<th>Method of analysis</th>
<th>Temperature range (K)</th>
<th>Solubility at melting point (mass ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hall</td>
<td>Silica crucible</td>
<td>Gravimetry</td>
<td>1793-1998</td>
<td>41</td>
</tr>
<tr>
<td>Nozaki et al</td>
<td>FZ-Si</td>
<td>IR absorption and charged particle analysis</td>
<td>1685</td>
<td>43</td>
</tr>
</tbody>
</table>

2.7 CARBON SOLUBILITY IN SOLID Si

The solubility of carbon in solid Si was reported by Davies and Newman in the temperature range 873-1623 K. This solubility is limited by the formation of β-SiC precipitates. They have used infrared absorption measurement to estimate the carbon concentration (Davies and Newman 1994). Endo et al measured the solubility of carbon in solid Si using infrared measurement with a modification in the calibration constant used by Davies and Newman (Endo et al 1979). The maximum carbon concentration in solid Si is approximately $5 \times 10^{17}$ atoms/cm$^3$. The equilibrium segregation coefficient of carbon between solid and liquid silicon was determined to be 0.07 by Nozaki et al. This value was determined experimentally by passing a molten zone through carbon painted silicon rods (Nozaki et al 1970).

Silicon melt and graphite parts are not in direct contact; the following reactions between graphite and silica crucible were studied for the SiC precipitation (Khattack 1980).

$$2C + SiO_2 \rightarrow SiC + CO_2$$
$$3C + 3 SiO_2 \rightarrow SiC + 2CO_2 + 2 SiO$$
$$4C + 2SiO_2 \rightarrow SiC + 3CO + SiO$$
$$3C + SiO_2 \rightarrow SiC + 2CO$$
In addition to these reactions, two additional reactions were also considered

\[
\begin{align*}
\text{C} + \text{SiO}_2 & \rightarrow \text{SiO} + \text{CO} \\
\text{C} + 2\text{SiO}_2 & \rightarrow 2\text{SiO} + \text{CO}_2
\end{align*}
\]

The above reactions have positive free energy changes at atmospheric pressure and in the temperature range 1600-1750 K. The standard free energy change for these reactions was found to be more positive at atmospheric pressure.

### 2.8 DIRECTIONAL SOLIDIFICATION FURNACE

The growth experiments were carried out in travelling heater furnace at Toyota technological institute. Figure 2.5 shows the schematic of the DS furnace. The furnace has four independent heaters, among which the upper and left side heaters are used for solidification.

![Figure 2.5 Directional solidification furnace](image)

Figure 2.5 Directional solidification furnace
2.8.1 Crucible

There are many problems which have been found in the development of the DS technology, the major one is the proper choice of the crucible material. The high reactivity of silicon results in the contamination of the melt by the impurities of the crucible and in most of the cases the solidifying melt adheres to crucible materials and consequently the ingot due to the difference in their coefficients of thermal expansion. Hence the proper choice of the crucible is difficult. The crucibles used have been developed to withstand the high temperature during a silicon ingot growth process in order to avoid unwanted failures in the presence of liquid silicon. Crucibles are lined with a silicon nitride based coating to prevent the sticking of liquid silicon with the crucible walls and subsequent cracking of the ingot due to the development of strong stress during solidification and cooling processes. Mainly two types of crucibles are being used for the growth of mc-Si, normal sintered natural quartz crucibles of photovoltaic grade and crucibles made from electronic grade fused synthetic silica. The content of trace elements in the crucible (in ppm) is listed in Table 2.3 (Olsen and Øverlid 2008).

<table>
<thead>
<tr>
<th>Crucible/Impurities</th>
<th>Al</th>
<th>Fe</th>
<th>Ti</th>
<th>Ni</th>
<th>Ca</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sintered quartz crucible</td>
<td>890</td>
<td>100</td>
<td>110</td>
<td>0.61</td>
<td>89</td>
<td>3.7</td>
</tr>
<tr>
<td>Fused silica crucible</td>
<td>15</td>
<td>0.5</td>
<td>1.3</td>
<td>0.03</td>
<td>0.6</td>
<td>0.06</td>
</tr>
</tbody>
</table>

2.9 CRYSTAL GROWTH – ISO-ROTATION

The effective way for the removal of impurities is the efficient use of segregation. To increase the segregation effect, it is important to enhance transport of impurities from the solid-liquid interface to bulk of the melt. In
this section, the growth of gallium doped mc-Si ingots by varying the crucible rotation is discussed.

Silicon feedstock (Off-specification) with gallium dopant ($10^{16}$ atoms/cm$^3$) was placed in a cylindrical quartz crucible of 10 cm diameter. Prior to loading the charge materials, protective $\alpha$-Si$_3$N$_4$ coating was made on the walls of the crucible to prevent sticking of the ingot to the crucible. The temperature in the furnace was raised up to 1550°C, just above the melting point of silicon. During the solidification process, Argon gas was passed over the melt surface with a flow rate of 0.8 l/min under 0.5 atm pressure in order to avoid carbon incorporation through SiO and CO into the melt. The melt was maintained at a high temperature for 2 hrs in order to ensure complete melting and ejection of tiny bubbles, which may cause void or crystal defects. After complete melting of charge, the furnace temperature was lowered to 1450°C. During the solidification, the heaters were moved from the bottom to the top at the rate of 30 mm/hr, and the crucible was rotated at a constant rotation rate, $\omega$. After the heater had reached near the top of the furnace, the temperature was lowered at a rate of 300°C/hr to room temperature. The entire growth cycle is shown in Figure 2.6. The growth details are given in the Table 2.4. The grown ingot was in cylindrical shape with diameter of 10 cm and height of 10 cm, weighing 2 kg. The mc-Si ingots were solidified at rotation rate ($\omega$) of 0, 1 and 30 rpm, which were named as ingot A, ingot B and ingot C respectively. The grown ingot was vertically cut into two half-cylinders. Then the half-cylinders were sliced vertically to a thickness of 0.5mm along the growth direction. The photographs of the grown ingots are shown in Figures 2.7, 2.8 and 2.9.
Figure 2.6 Temperature profile during the growth of mc-Si

Table 2.4 Growth details of mc-Si by DS process

<table>
<thead>
<tr>
<th>Parameters</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crucible diameter [cm]</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>Pressure [atm]</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Gas flow rate [l/min]</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Heater movement rate [mm/hr]</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Crucible rotation [rpm]</td>
<td>0</td>
<td>1</td>
<td>30</td>
</tr>
<tr>
<td>Dopant</td>
<td>Ga</td>
<td>Ga</td>
<td>Ga</td>
</tr>
<tr>
<td>Ingot name</td>
<td>A</td>
<td>B</td>
<td>C</td>
</tr>
</tbody>
</table>
Figure 2.7 Photograph of the DS grown mc-Si at crucible rotation 0 rpm

Figure 2.8 Photograph of the DS grown mc-Si at crucible rotation 1 rpm
2.10 ETCHING

Chemical etching of silicon wafers is accomplished by dipping the wafers in an etchant which is traditionally an acidic mixture of hydrofluoric acid and nitric acid. The mc-Si has multiple crystallographic orientations with crystalline defects such as dislocations, stacking faults and twins (Fathi 2007). Many authors have reported the observation of crystalline defects in mc-Si by chemical etching (Kulkarni and Erk 2000, Sopori 1984). The wafers were roughly etched with a solution of hydrofluoric acid and nitric acid in a ratio of 1:13 for 10 minutes to remove the sawing damage.

2.10.1 Polishing

To obtain mirror like surface, the mc-Si wafers were polished with diamond particles of grain-size 0.5 and 0.3 μm combined with deionized water. Then, the wafers were polished with alumina powder particles of grain-size 0.1 μm. Finally, wafers were washed with acetone, methanol and water sequentially. After polishing, the wafers were etched for 3 minutes using the same etchant described above to remove the polishing damage.
2.11 MEASUREMENT PROCEDURE

A JASCO (MFT-2000) FTIR spectrophotometer was used to measure the carbon concentration in silicon wafers. The measurement was carried out at room temperature in air atmosphere. The thickness of the samples for FTIR spectroscopy was 0.5 mm. The measurement range of wavenumber was set from 500 to 1200 cm\(^{-1}\) with a resolution of 4 cm\(^{-1}\). A non-doped Czochralski silicon sample was used as a reference. Both the test and reference sample was carefully prepared by keeping the thickness variation less than 0.005 mm with identical surface preparation. A background spectrum, which represents the absorption from the atmosphere in the chamber, is collected during each FTIR measurements. All the sample spectrum and reference spectrum are automatically ratioed against this background spectrum. Figure 2.10 shows a typical sample spectrum.

![FTIR spectrum showing substitutional carbon in mc-Si](image)

Figure 2.10 FTIR spectrum showing substitutional carbon in mc-Si
The two-phonon lattice bands of silicon at 610 cm\(^{-1}\) are superimposed on the band of carbon and affect the intensity of the carbon peak. Hence these silicon lattice vibrations were subtracted using a FTIR spectrum of a pure Cz grown silicon sample. The optical absorption line at 605 cm\(^{-1}\), which is associated with the vibration of carbon in the substitutional position, was used for analyzing the carbon concentration (Newman 1996). The following expression from the American society for testing and materials (ASTM) was used to calculate the carbon concentration in a mc-Si ingot. The absorption coefficient (\(\alpha\)) is calculated from the expression below

\[
\alpha = \frac{23.03}{x} (A_p - A_b)
\]

(2.3)

where \(x\) is the sample thickness in mm, \(A_p\) is the peak value of the carbon only absorbance spectrum, and \(A_b\) is the baseline value of the carbon only absorbance spectrum. For room temperature measurements, the substitutional carbon concentration is calculated in atoms/cm\(^3\) as follows (ASTM 2000).

\[
\text{atoms/cm}^3 = 8.2 \times 10^{16} \alpha
\]

(2.4)

### 2.11.1 Important factors influencing the measurements

The test and reference sample should be prepared by keeping the thickness variation less than 0.005 mm with identical surface preparation. The measurement is also influenced by the resistivity. For p-type material, the resistivity of the wafer should be greater than or equal to 3 ohm-cm. Below this resistivity, absorption of probe beam occurs due to significantly high free carrier concentration which in-turn reduces the available energy. Moreover, scattering of the light at the surface reduces the energy that passes through the sample and thereby reduces the sensitivity. Hence it is important to perform the measurements on double side polished wafers.
2.12 RESULTS AND DISCUSSION

Figures 2.11, 2.12 and 2.13 show carbon concentration distribution determined by the FTIR for the ingots solidified at 0, 1 and 30 rpm of crucible rotation, respectively. Figures 2.11, 2.12 and 2.13 (a) show photograph of the vertically sliced mc-Si. The center and edge of the ingot are indicated in the figures. The measurement area of carbon concentration is indicated by dashed lines. Figures 2.11, 2.12 and 2.13 (b) show the distribution of carbon concentration measured by FTIR.

(a) Photograph of the vertically sliced mc-Si (b) Distribution of carbon concentration measured by FTIR
Figure 2.12 (a) Photograph of the vertically sliced mc-Si (b) Distribution of carbon concentration measured by FTIR
Figure 2.13  (a) Photograph of the vertically sliced mc-Si (b) Distribution of carbon concentration measured by FTIR
It is well known that the segregation coefficient of carbon in silicon is 0.07. The carbon concentration increases as crystal growth proceeds. Actually the carbon concentration in each ingot increases from the bottom region towards to the top, and reaches the solubility limit. The segregation coefficient has a strong correlation to the solubility limit, since effective segregation coefficient is changed by the growth rate. Hence the solubility limit in each ingot is also changed. The concentration of carbon in the ingot is also dependent on the carbon concentration in melt at the solid-liquid interface. The change in the carbon concentration is influenced by the strength of melt convection. During the solidification, most important is convection at the growth interface since it controls the chemical composition of the growing crystal. Melt convection may be classified by the physical mechanism driving convective currents. It includes buoyancy driven convection, marangoni convection and rotational forced convection. In the case of travelling heater method (THM), buoyancy convection is weak because low temperature melt is located at the bottom of crucible. The aspect ratio of melt is one; hence marangoni convection is also weak. The momentum, heat and mass transports in a melt are strongly influenced by rotational forced convection.

In the ingot A, the transport of impurities in a melt was mainly due to diffusion and convection. The combination of gravity and temperature distribution produces natural convection in the crucible. As solidification proceeds, carbon concentration in melt increases due to segregation. Hence the ingot A has high and inhomogeneous carbon concentration along the growth direction. Then high carbon concentration leads to the formation of impurity boundary layer near the solid-liquid interface. Since the carbon concentration in the boundary layer is higher than that at the bulk of the silicon melt, and then the nucleation of SiC occurs. After, carbon concentration exceeds its solubility limit, it starts to precipitate as SiC particles. It causes fluctuation of growth rate of silicon which leads to the
formation of smaller grains. In our experiments, smaller grains were found in the center and top of the ingot A. The boundary between the small grain region and large grain region seems convex toward the top. The SiC precipitates appeared on the center and top of the ingot in the smaller grain region where the carbon concentration is relatively high.

The melt convection during the growth of ingot B is stronger than in the case of ingot A. The carbon concentration in the ingot B is homogeneous since the segregation effectively enhanced the transport of carbon from the solid-liquid interface to the top of the ingot. The carbon concentration at the center of the ingot B is approximately $4 \times 10^{17}$ atoms/cm$^3$. However, small grains appear near the top, the boundary between the small and large grain regions seems concave toward the top.

The melt convection during the growth of ingot C is very much stronger than in the case of growth of ingots A and B. The strong convection enhanced the carbon concentration in ingot C. The carbon concentration at the center of the ingot C is approximately $7 \times 10^{17}$ atoms/cm$^3$. This is because of the strong convection which also boosted the carbon contamination from the protective Si$_3$N$_4$ coating. Hence the carbon concentration is high at the peripheral region of the ingot C. During the rotation of the crucible, the carbon in the Si$_3$N$_4$ protective coating dissolves and incorporates into the melt. This observation is supported by the appearance of small grains at the peripheral region in the ingot. Moreover the precipitation of Si$_3$N$_4$ was also appeared and which acted as a trigger for the small grain formation. The small grains appear near the top and peripheral region, and it seems macroscopic crystal morphology is nonaxisymmetric. Figure 2.14 shows the distribution of carbon concentration at the center ($r=25$ mm, $z=5$ to $75$ mm) in each ingot.
Figure 2.14 Distribution of carbon concentration in each ingot

The carbon concentration partly exceeded the solubility limit at the melting point of silicon, and the highest concentration is in the smaller grain regions. It implies that two solid phases exist, one is substitutional carbon in the silicon and other might be silicon carbide. Since the segregation coefficient of carbon is less than one, carbon concentration in the melt is increasing with the growing ingot. When the carbon concentration in the melt exceeds the solubility limit, SiC precipitates may form and stimulate generation of a new grain. In our experiments, we observed needle like SiC and Si$_3$N$_4$ precipitates in the small grains region. Many experimental investigations also reported the precipitation of SiC and Si$_3$N$_4$ particles in mc-Si (Søiland et al 2004, Rifai et al 2004). However in our FTIR spectrum, the peak corresponding to SiC (appears at 794 cm$^{-1}$) was not observed (Engelbrecht 1987). This is may be due to the low concentration of SiC in the ingots. In our experimental results, carbon concentration is low in growth direction and homogenized in the radial direction when the crucible rotation rate is 1 rpm.
2.13 CONCLUSION

Using THM process, mc-Si ingots were grown by directional solidification with various crucible rotation rates. From the cross sectional views of the ingots, many small grains were observed in the center and top of the ingots. In the region of small grains, needle like precipitates were observed visually, which are identified as SiC and Si$_3$N$_4$ particles. The small grains appeared due to the precipitation of SiC which initiated the multicrystalline growth. During solidification, increase of crucible rotation rate enhances segregation effects but at the same time, it accelerates additional contamination from a crucible and its coating material. The grown ingots were evaluated by FTIR spectroscopy for substitutional carbon concentration. In ingot A, the inhomogeneous carbon concentration is due to the natural convection. Also, due to the strong convection in the melt and contamination from the crucible and coating, the carbon concentration is high at the edge of the ingot C. The ingot B, grown at crucible rotation rate of 1 rpm has homogeneous carbon concentration from the bottom to the top ingot. These results suggest that optimized heater transfer rate with a crucible rotation rate of 1 rpm is suitable to grow mc-Si ingots with less carbon concentration.