Carbon concentration variation in polycrystalline silicon wafers

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Even after a long period of studies on defects in silicon, relatively little attention has been paid to the carbon behaviour. From the 1970s this impurity has attracted significant research activities, especially when it was found that a carbon presence having a concentration above $10^{16}$ atoms cm$^{-3}$ strongly affects the crystal perfection of silicon wafers during device fabrication [1, 2].

Although a lot of research in this area has been performed on monocrystalline silicon wafers, relatively little attention has been paid to the polycrystalline wafers often used for solar energy conversion. Since in various types of solar-grade polycrystalline silicon wafers produced the concentration of carbon is rather high, it is interesting to study its behaviour as well as its interactions with other impurities in order to design a suitable technological process resulting in better performances of the solar cells produced.

Due to the low quality of the starting material (solar-grade silicon) and due to the graphite crucible often employed in ingot production processes, silicon polycrystalline wafers used for solar energy conversion are usually very rich in carbon. Since the growth of these types of materials is generally a rapid process, which strongly deviates from thermal equilibrium, it is expectable that the concentration of impurities is not homogeneous throughout the volume of the ingot, that they are "lot dependent" and, due to the specific conditions employed, it can be said that they are even "manufacture dependent" [3].

There are contradictory results on the thermal history dependence of carbon concentration in monocrystalline silicon, for example Regolini et al. [4] found that the carbon concentration in silicon is not dependent on the thermal history, whereas some others [5-7] reported that it is. In order to study this phenomenon in polycrystalline materials, we performed an isochronal annealing at various temperatures on several types of solar-grade polycrystalline silicon wafers, to reveal whether its concentration depends on the thermal annealing in samples supersaturated with carbon at room temperature.

Our experiments were performed on three types of solar-grade polycrystalline silicon produced by various techniques. SILSO (registered trade mark) wafers, produced at Wacker-Chemitronics GmbH, and HEM (heat-exchange method), at Crystal Systems Inc., were produced with casting techniques in ingot form and subsequently sliced into wafers, but with various processes [8, 9]. EFG (edge-defined film-fed crystal growth) type of material was produced in the form of long ribbon at Mobil Solar Co., and then cut into wafers [10].

All samples were degreased before the thermal treatment and then isochronally heated for 6 h in dry N$_2$ atmosphere from 450 to 1250°C. After the heat treatment all wafers were dipped in HF solution in order to remove any oxide layer formed at the surface.

Infrared spectra were taken with a Perkin-Elmer 1710 Fourier-transform infrared spectrometer, at room temperature with 4 cm$^{-1}$ resolution, and the infrared beam diameter was about 1 cm. A differential technique in taking infrared spectra was used with floating zone (FZ) oxygen and a carbon-free sample as a reference. The conversion factor used for carbon concentration calculation was $1.1 \times 10^{17}$ atoms cm$^{-3}$ (ANSI/ASTM F 121-81) and for oxygen it was $2.45 \times 10^{17}$ atoms cm$^{-3}$ (ANSI/ASTM F 121-83).

In spite of the very inhomogeneous distribution of oxygen and carbon in the polycrystalline samples, we performed our measurements after each step on exactly the same position, taking the average information from several grains and therefore obtaining relevant information for the carbon behaviour in the bulk of material.

Table I: Carbon and oxygen concentrations in various samples before thermal treatment

<table>
<thead>
<tr>
<th>Sample</th>
<th>$c(C_s) \times 10^{17}$ atoms cm$^{-3}$</th>
<th>$c(O_i) \times 10^{17}$ atoms cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SILSO</td>
<td>$3.1$</td>
<td>$0.1$</td>
</tr>
<tr>
<td>HEM</td>
<td>$2.0$</td>
<td>$2.8$</td>
</tr>
<tr>
<td>EFG</td>
<td>$9.1$</td>
<td>$0.1$</td>
</tr>
</tbody>
</table>

Values for substitutional carbon, C$_s$, and interstitial oxygen, O$_i$, concentration in the as-received samples are given in Table I.

As indicated in Table I, the O$_i$ concentration for SILSO and EFG samples was below the detection limit, i.e. $\approx 10^{16}$ atoms cm$^{-3}$. As the C$_s$ solubility is about $10^{16}$ atoms cm$^{-3}$, even at 1100°C [11], it can be observed that the carbon was in supersaturation at room temperature in all samples and particularly in the EFG type of material.

The presence of carbon in so high a concentration in these type of polycrystalline wafers is understandable, since the starting material is of solar-grade.
purity, i.e. has a higher concentration of carbon in feedstock material. Furthermore, all processes for producing wafers for solar conversion applications are very rapid and therefore the effective coefficient of segregation for carbon deviates strongly from the equilibrium value, and in particular it is about unity for the growth of EFG samples [10], while for Czochralski growth it is $k = 0.07$.

The behaviour of substitutional carbon concentration with isochronal thermal treatment is shown in Fig. 1. As shown in the figure, thermal treatment did not significantly affect the carbon concentration in SILSO and HEM samples over the whole temperature range. In the case of EFG material a steady and significant decrease can be observed only for very high temperatures. Besides a slight increase of the initial value of $C_s$ and its small decrease at 650 °C, its high value remains substantially the same up to 1050 °C. Only above that temperature does a decrease in $C_s$ concentration occur and it approaches values similar to SILSO and HEM material upon annealing at 1250 °C.

It is very surprising that the thermal treatment performed had no significant effect on the $C_s$ concentration of SILSO and HEM samples over the whole temperature range, and even annealing at the highest temperatures had not decreased the $C_s$ supersaturation.

On the other hand, it was found [5-7] that after heating a highly carbon-doped Czochralski-grown monocrystalline silicon wafers, a reduction in substitutional carbon concentration took place for annealing in the temperature interval 600-800 °C.

![Figure 1](image)

*Figure 1* Substitutional carbon concentration variation with isochronal annealing for (■) SILSO, (●) HEM and (○) EFG material.

Shimura [6] found that after an annealing at 750 °C for 6 h the carbon concentration decreased from 10 p.p.m. to below the detection limit. Livingston et al. [12] also found that for carbon present in material in rather low concentrations ($4 \times 10^{16}$ atoms cm$^{-3}$), annealing at temperatures up to 850 °C led to very rapid removal of carbon from solution so that its presence could no longer be detected by infrared spectroscopy. For annealing above 850 °C, however, the $C_s$ concentration recovers almost completely and no further changes in the concentration were observed, within experimental error, for thermal treatments above this temperature. On the other hand, Bean and Newman [11] found that a single heat treatment of samples containing high concentrations of both oxygen and carbon did not lead to significant precipitation of either impurity. However, the samples irradiated by 2 MeV electrons at room temperature in high doses, and therefore having a high concentration of structural defects, behaved differently. In these samples, even upon single annealing, a precipitation of both carbon and oxygen occurred in the high-temperature region. They found that a FZ-grown material rich in carbon and without structural defects gave no variation in carbon concentration for annealing in a wider temperature range (from 550 to 1300 °C).

Our polycrystalline materials were rich in structural defects, such as grain boundaries, dislocations, stacking faults and point defects. Therefore, it should be expected that these structural defects could serve as a nucleation centre where carbon should segregate and therefore reduce its supersaturation upon annealing.

Although the initial oxygen concentration in some of our materials (SILSO and EFG) was below the detection limit, as reported in Table I, a significant concentration of oxygen seems to be present in solar-grade polycrystalline materials, but in an infrared-inactive form, as was already shown [13-16]. Therefore, carbon and oxygen interaction cannot be ruled out. Still, it is puzzling that in the HEM material, where the $O_i$ and $C_s$ concentrations are almost the same, no significant interaction was observed.

Upon further thermal treatment of EFG material at temperatures higher than 1150 °C only a small decrease in the $C_s$ concentration was observed although the remaining $C_s$ concentration was still much above the equilibrium concentration for that temperature. Carbon removed from substitutional positions upon this high-temperature annealing was found to precipitate in the bulk of material in the form of certain C–O complexes and SiC precipitates that give rise to the characteristic broad peak from 800 to 950 cm$^{-1}$ in the absorbance spectrum [17]. On the other hand, for the SILSO and HEM materials where high-temperature annealing did not change the carbon concentration, this peak in the absorbance spectrum was not observed.

To understand the described behaviour of carbon upon thermal treatment in polycrystalline material, we propose the following model. Due to the specific