International Journal of Materials Science
ISSN 0973-4589 Volume 19, Number 1 (2024), pp. 1-08

http://www.ripublication.com

Effect on the Carbon Concentration of Step-Annealing in Carbon-Rich Czochralski Silicon

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Abstract

Variation of Substitutional Carbon with annealing time is studied as a result of pre-annealing at moderate temperature 480°C in carbon-rich boron-doped (p-type) CZ-silicon. Correlation of this concentration with the generation and annihilation of thermal donors (TDs) and new donors (NDs) has been studied using Hall Effect and FTIR studies. Carbon concentration is determined by evaluating absorption coefficient of carbon from the IR spectrum of the specimens with successive annealing in steps of 10 hrs. It is seen that the pre-annealing slows down the TD formation, but enhances ND formation. The study also shows that TD and ND formation increases concentration of substitutional Carbon, but TD annihilation is accompanied by a decrease in concentration of C_S.

Keywords: CZ- Silicon, Thermal donor, New donor, Thermal acceptor, Substitutional Carbon, Pre-annealing, Silicon self-interstitial.

INTRODUCTION

Silicon is the most important material for electronic industry, at present. It is the chiefly used semiconductor in Bipolar or MOS technologies and is an essential ingredient of solar cells. Silicon, in nature is found mainly in its oxide form. So to make it of device grade quality, it has to pass through various stages of extraction, purification and finally crystallisation. Commercially available silicon is of two types, mainly differing in their crystallisation process. The two types are float zone or FZ silicon and Czochralski grown or CZ silicon. Whereas FZ-silicon is pure form of silicon, free from any impurity or contamination, CZ silicon picks up contamination from the fused silica crucible during its growth process. Even then, CZ-silicon is mostly used in common electronic devices because of cost consideration and strength. The main component of contamination from the walls of the crucible during the growth process of CZ-Si crystals is oxygen. These grown-in oxygen impurities occupy bond-centred intersititial sites in CZ-Si. Their concentration in CZ-Si is of the order of 10^{18} cm^{-3}, which is several orders of magnitude greater than the concentration of electrically active donors and acceptors intentionally introduced to fabricate semiconductor devices. Although interstitial oxygen atoms in their dispersed state are neutral [1, 2], they play a crucial role in obtaining high device yields since SiO_2 precipitates, formed by post-growth diffusion, act as sinks for inadvertently introduced fast diffusing metallic contaminants which must be excluded from the device active regions. The presence of oxygen also leads to a hardening of Si matrix, so that plastic deformation is prevented during device fabrication. On the other hand, the presence of oxygen in CZ-Si, induces various defects during the fabrication of devices, which is carried out by low temperature ($< 800^{o}$C) heat treatments. Supersaturated oxygen atoms in a silicon crystal become clustered due to annealing at temperatures above 300^{o}C. Such clusters are known to be electrically active, which act as double donors [3, 4] and are termed as oxygen related donors (ODs). These donors are generally undesirable because they prevent the determination of intentionally doped dopant in the sample and hinders with its properties leading to device degradation. Depending upon the temperature range and annealing time, various types of ODs are generated in CZ-Si. Annealing in the range of 300-500^{o}C produces thermal donors (TDs) [4], which get annihilated by the additional annealing at temperatures above 500^{o}C [5]. They are also annihilated on extending annealing time at a temperature of about 450^{o}C. At higher temperatures, 500-800^{o}C, another group of donors called new donors (NDs) is formed [6]. Formation of NDs is also been thought to be accompanied by the formation of acceptors under certain conditions [7]. A new kind of thermal donors, new thermal donors (NTDs) are also reported, which survives even after extremely long duration of annealing at 450^{o}C, when all the species of TDs are annihilated [8, 9]. Inherent presence of carbon plays a crucial role in the formation mechanism of different donor species. It is revealed by many studies that the ND generation is enhanced by the low temperature pre-annealing and the presence of carbon [6, 10, and 11]. Carbon is also found to suppress the TD formation and enhance TD annihilation [12]. Prakash and Singh [13] have also seen that the carbon induced gradual disappearance of TDs and carbon itself at 470^{o}C of annealing. But the carbon occupies substitutional site in silicon, so it cannot move at 470^{o}C from its site. It has been proposed by Newman [14] that interstitial silicon atom may play a role in the formation and electrical activity of TDs.

In the present study, p-type CZ-silicon, rich in carbon is studied for different annealing durations in a step-annealing schedule. The annealing temperature is in the moderate region, but the extended annealing induces TD annihilation and transformation of TDs into NDs. Corresponding change in the carbon concentration is noted as the annealing proceeds.

MATERIAL AND METHODS

The sample used is Czochralski (CZ)-grown p-type (Boron doped) silicon crystal wafer of about 80 mm diameter and 420 mm thickness. These wafers are cut into pieces of 1x2 cm^2 size and then subjected to heat treatment in Muffel furnace in air ambience. They were step-annealed at constant temperature of 480°C for different durations in the range of 10 -70 hrs in steps of 10 hrs. Following methods are used for different measurements.

Hall study

Study of Hall Effect is used to ascertain the nature of majority carriers in the samples. In the experimental set-up for Hall study, a semiconductor sample carries a current 'I' along x-axis under the action of a steady electric field E_x. When a constant magnetic field B_z is applied along the Z-direction, a hall voltage V_H is developed between the faces of the crystal along the y-direction due to the deflection of charge carriers by the Lorentz force. The Hall coefficient is expressed as

$$R_H = \frac{E_y}{j_x B_z}$$

Where j_x is current density.

If Hall coefficient comes out to be positive then the sample is p-type and if it comes out to be negative then the sample should be n-type.

FTIR Measurement

Absorption coefficient needed for determining the carbon concentration is determined by FTIR absorption method, just as we can measure oxygen concentration, described by lizuka *et al.* [15].

Concentration of substitutional carbon (Cs) in silicon can be derived from 605 cm^{-1} absorption band of the IR spectrum, using the following expression:

$$[C_s] = 1.1 \times 10^{17}.\ \alpha_c\text{--------}\ (1)$$

Where α_c is the peak absorption coefficient for the 605 cm^{-1} band corresponding to carbon [16, 17], which can be determined for unannealed and different annealed samples. The relative transmittance of the carbon absorption band with respect to the base line is expressed as

$$T_{rel} = T_{peak} / T_{bg} = \exp(-\alpha'_c\, d)\ \text{--------}\ (2)$$

The α'_c term corresponds to the absorption coefficient which does not include the multiple reflection effect. The relationship between α'_c and α_c can be related to that given by lizuka *et al* [15] for relationship between absorption coefficients for oxygen, as given in Fig 1.

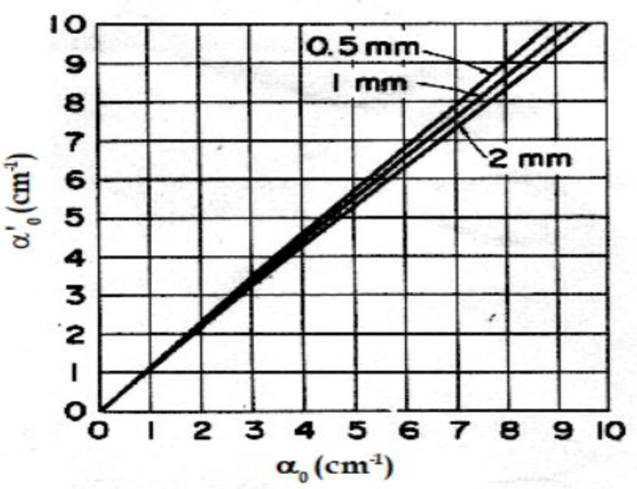

Figure 1: Relationship Between α'_o and α_o for Different Sample Thicknesses

So the procedure to determine the absorption coefficient is- draw base line on the transmission spectra between 800 and 400 cm^{-1}, calculate $T_{rel.}$ And then α'_c using equation (2), then obtain value of α_c using fig.1. We choose line on the graph corresponding to 0.5 mm for our calculations, as our sample thickness is 0.42 mm, which is closest to that, of all the three lines.

RESULTS AND DISCUSSION

Hall Effect Study

Hall studies for the determination of nature of dominant charge carriers revealed that the un-annealed sample as well as sample annealed for 10 hrs were p-type. Step-annealed samples, annealed for total 20-40 hrs are n-type, while the samples annealed for 50-70 hrs are again p-type. As we already know that the un-annealed samples used by us are p-type, so the study shows that the sample annealed up to 10 hrs. at 480°C maintains its nature as p-type. It is only after 10 hrs, that the sample changes its nature to n-type, suggesting the donor formation. The samples annealed for 50 hrs. or more are again converted to p-type, suggesting the formation of some electrically inactive clusters and annihilation of thermal donors.

Concentration of Substitutional Carbon

The absorption coefficient and then concentration of substitutional carbon is calculated from the IR spectra obtained from Fourier Transform Infra-Red (FTIR) spectroscopy. The same method is adopted for the determination of absorption coefficient of carbon as for the absorption coefficient of oxygen, given by Iizuka *et al.* [15]. Also it is assumed that the same relation holds between α'_c and α_c as that between α'_o and α_o [15] as shown in fig 1, using the line for sample thickness of 0.5mm (close to our value, d = 0.42mm). The results are recorded in table below:

Sample no.	**Total annealing (pre-annealing + annealing) time (hrs.)**	**T_{rel} = T_{peak}/T_{bg}**	**Absorption coefficient of carbon**		**Carbon Concentration $[C_s]=1.1 \times 10^{17}\alpha_c$**
			$\alpha'_c{}^*$ (cm^{-1})	**$\alpha_c{}^{**}$ (cm^{-1})**	**(cm^{-3})**
0	0	0.7500	6.848	6.087	6.696×10^{17}
1	0 + 10 = 10	0.7666	6.552	5.824	6.406×10^{17}
2	10 + 10 = 20	0.7738	6.108	5.429	5.972×10^{17}
3	20+10 = 30	0.7723	6.152	5.468	6.015×10^{17}
4	30+10=40	0.7714	6.179	5.493	6.042×10^{17}
5	40+10=50	0.7843	5.785	5.142	5.656×10^{17}
6	50+10=60	0.7659	6.349	5.644	6.208×10^{17}
7	60+10=70	0.7558	6.667	5.926	6.519×10^{17}

*Calculated value from the relation $T_{rel} = \exp(-\alpha'_c d)$

**Actual value determined from Fig. 1

Absorption coefficient and carbon concentration determined in this way may be defined qualitatively, if not quantitatively. Variations in absorption coefficient and carbon concentration with annealing time in step annealing schedule are plotted in Fig 2 and 3, respectively.

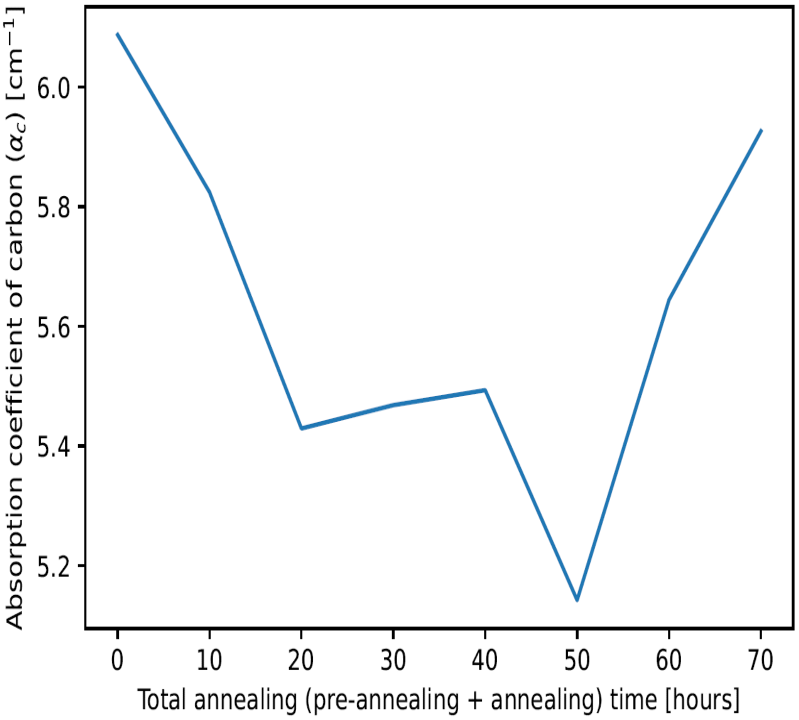

Figure 2: *Variation in absorption coefficient of Carbon with annealing time*

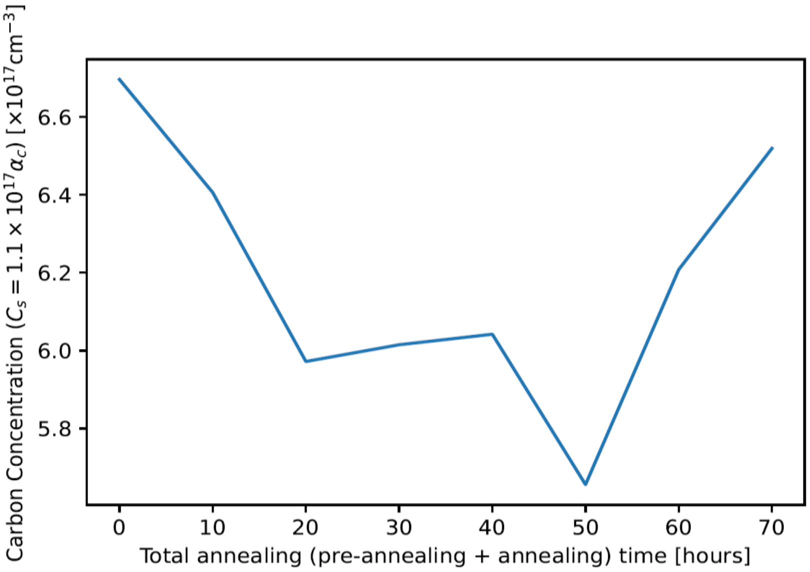

Figure 3*: Variation in carbon concentration with annealing time*

As can be seen from the results and correlating them with earlier results of resistivity and donors generated and annihilated, the concentration of substitutional carbon seems to be increasing for TD formation stages and decreasing for TD annihilation stages. It is observed by Kamiura *et al.* [18, 19] that carbon rich Cz-Si shows anomalously rapid annihilation of TDs, accompanied with the substantial decrease in substitutional carbon density. They proposed the hypothesis that the Si self-interstitials created during the oxygen aggregation (TD formation) process, eject substitutional carbon into an interstitial site, when this self-interstitial is liberated on TD annihilation. This interstitial carbon rapidly diffuses to TDs to aggregate with them, forming electrically inactive clusters. So our observation about the decrease in concentration of C_s while TD annihilation, is in perfect agreement with Kamiura *et al.*

For TD formation case, I propose just the reverse of it. As the TDs are formed, Si self-interstitials are created, vacating their lattice sites. Carbon atoms, either at interstitial sites or at any other defect-trap, may fit itself in these vacant lattice sites, transforming into substitutional carbon.

For ND formation, Leroueille [20] and Ohsawa *et al.* [21] observed, simultaneous annihilation of substitutional carbon atoms. But Fukuoka *et al.* [22] detected no participation of carbon atoms directly in the formation of ND. In the present study, no decrease in concentration of C_s is observed, rather an increase is observed. This can be explained, as I propose, as follows: formation of NDs follow the annihilation of TDs, which is accompanied by the transformation of C_s into $C_{i,}$ the C_i being aggregating with TD to form electrically inactive cluster. Now when the ND formation takes place then these clusters are broken into small clusters, which are NDs. This process must be, then, accompanied by the liberation of C_i, which can again transform into C_s.

Therefore, presence of carbon enhances the ND formation, but carbon itself does not take part in this formation. This observation is in contradiction with Leroueille [20] and Ohsawa *et al.* [21], but in agreement with Fukuoka *et al.* [22].

CONCLUSION

In carbon-rich p-type sample the growth of thermal donors is slow, due to the presence of initial carbon in high concentration and due to pre-annealing. Pre-annealing is also seen to enhance TD annihilation and ND formation. As for carbon concentration, it is seen that the concentration of substitutional carbon increases for TD formation stages and decreases for TD annihilation stages. An increase in concentration of C_S is observed with the formation of ND.

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