SPECTROSCOPIC STUDY OF OXYGEN AGGLOMERATION IN STEP-ANNEALED CZOCHRALSKI SILICON

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Abstract- **Czochralski-grown silicon being the chief material for the fabrication of electronic devices, needs to be studied thoroughly. During the growth process of CZ Si, oxygen gets trapped at interstitial sites. Here in this study, variation in concentration of interstitial oxygen 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. Oxygen concentration is determined by evaluating absorption coefficient of oxygen from the IR spectrum of the specimens with successive annealing in steps of 10 hrs. It is seen that more and more oxygen gets precipitated with the increase in annealing time due to the formation of TDs and NDs. It is also seen that the concentration of interstitial oxygen after annealing is higher than the initial concentration. An attempt has been made to explain the reasons behind this.**

Key Words: **CZ- Silicon, Thermal donor, New donor, Thermal acceptor, Interstitial Oxygen, Pre-annealing.**

1. Introduction

Silicon has maximum impact on semiconductor industry. About 90% of the silicon crystal used in semiconductor industry is CZ silicon. Though FZ-silicon is purer, CZ-silicon is preferred because of cost consideration and strength. Virtually all the silicon used for fabricating integrated circuits belongs to CZ type. Oxygen is the most abundant non-intentional impurity incorporated in the melt during the growth process of CZ-Si crystals from the walls of the crucible. Heat treatment of the silicon crystal with high oxygen contents of the order of 10^{18} cm^{-3} at interstitial sites in the temperature range 400-1200 ^{O}C produces various kinds of defects. Various models have been given by Ourmazd *et al* [1], Mathiot *et al* [2] and McQuaid *et al* [3] to understand the actual mechanism of device degradation by these defects. Although interstitial oxygen atoms in their dispersed state are neutral [4,5], they play a crucial role in conductivity by forming clusters on heat treatment, which act as nuclei for SiO_2 precipitates. 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°C) heat treatments. The clusters formed due to annealing at temperatures above 300°C are known to be electrically active, which act as double donors [6,7] and are termed as oxygen related donors (ODs). Depending upon the temperature range and annealing time, various types of ODs are generated in CZ-Si. Annealing in the range of 300-500°C produces thermal donors (TDs) [7], which get annihilated by the additional annealing at temperatures above 500°C [8]. They are also annihilated on extending annealing time at a temperature of about 450°C. At higher temperatures, 500-800°C, another group of donors called new donors (NDs) is formed [9]. Formation of NDs is also thought to be accompanied by the formation of acceptors under certain conditions [10]. A new kind of thermal donors, new thermal donors (NTDs) are also reported, which survives even after extremely long duration of annealing at 450°C, when all the species of TDs are annihilated [11,12]. 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 [9,13,14]. It has been proposed by Newman [15] 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 concentration of interstitial oxygen is noted as the annealing proceeds.

2. 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 20 -70 hrs. in steps of 10 hrs. Following methods are used for different measurements.

2.1 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.

2.2 FTIR Measurement

Absorption coefficient needed for determining the oxygen concentration is determined by FTIR absorption method, described by lizuka *et al.* [16].

Concentration of interstitial oxygen (O_i) in silicon can be derived from 1106 cm^{-1} absorption band of the IR spectrum, using the following expression:

$$[O_i] = (3.03 \pm 0.02) \times 10^{17}. \alpha_o \quad \text{-------- (1)}$$

Where α_o is the peak absorption coefficient for the 1106 cm^{-1} band corresponding to oxygen, which can be determined for unannealed and different annealed samples. The relative transmittance of the oxygen absorption band with respect to the base line is expressed as

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

The α'_o term corresponds to the absorption coefficient which does not include the multiple reflection effect. The relationship between α'_o and the actual absorption coefficient, α_o for oxygen is given by lizuka *et al* [16], as given in fig 1.

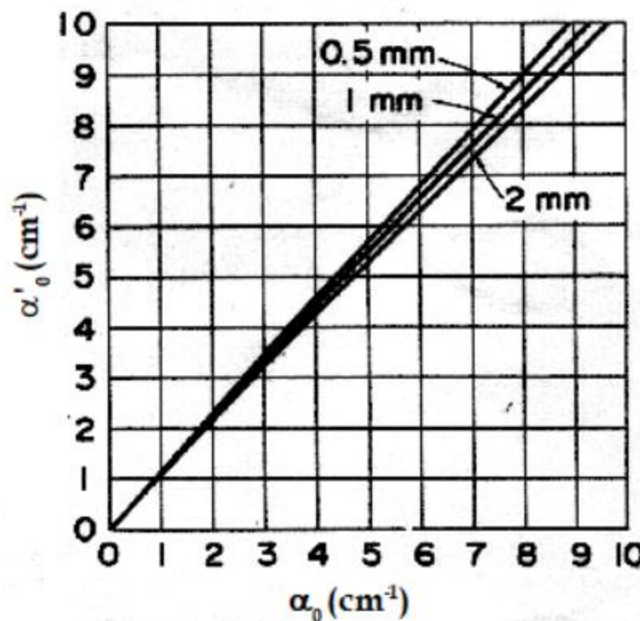

Figure 1: Relationship between α'_o and α_o for different sample thicknesses

So the procedure to determine the absorption coefficient is- draw base line on the transmission spectra between 1300 and 900 cm^{-1}, calculate $T_{rel.}$ and then α'_o using equation (2), then obtain value of α_o 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.

3. Results and Discussion

3.1 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.

3.2 Absorption Coefficient and Concentration of Interstitial Oxygen

The absorption coefficient and then concentration of interstitial oxygen is calculated from the IR spectra obtained from Fourier Transform Infra-Red (FTIR) spectroscopy using the method given for the absorption coefficient of oxygen by Iizuka *et al.* [16] and the relation 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 1. Oxygen loss or the amount of oxygen precipitated is found out by taking the difference in concentration of oxygen, taking 20 hours i.e. 10 hours annealing after 10 hours of pre-annealing is taken as reference, as this is the point where the donor formation starts and the sample changes from p-type to n-type.

Table 1: Oxygen Concentration with variation in annealing time for step-annealing

Sample no.	Total annealing (pre-annealing + annealing) time (hrs.)	$T_{rel} = T_{peak}/T_{bg}$	Absorption coefficient of oxygen α'_o* (cm^{-1})	α_o** (cm^{-1})	Oxygen Concentration $[O_i]=(3.03\pm0.02)\times10^{17}\alpha_o$ (cm^{-3})	Oxygen Loss (cm^{-3})
0	0	0.8392	4.1728	3.7092	11.239×10^{17}	-
1	10 + 10 = 20	0.6410	10.5876	9.4112	28.516×10^{17}	-
2	20+10 = 30	0.6588	9.9407	8.8361	26.773×10^{17}	1.743×10^{17}
3	30+10=40	0.7163	7.9448	7.0620	21.398×10^{17}	7.118×10^{17}
4	40+10=50	0.7167	7.9339	7.0523	21.368×10^{17}	7.148×10^{17}
5	50+10=60	0.7508	6.8208	6.0629	18.371×10^{17}	10.145×10^{17}
6	60+10=70	0.8123	4.9456	4.3961	13.320×10^{17}	15.196×10^{17}

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

**Actual value determined from fig.1

Absorption coefficient and oxygen concentration determined in this way may be defined qualitatively, if not quantitatively. Variation in absorption coefficient of oxygen with time in step annealing schedule is plotted in figure 2, while variation in amount of oxygen precipitated i.e. oxygen loss is plotted in figure 3.

The absorption coefficient and hence the concentration of interstitial oxygen at 20 hours total annealing (including 10 hrs. of pre-annealing), exceeds that in un-annealed sample. But beyond this, annealing induces continuous decrease in oxygen concentration upto 70 hrs. total annealing time. It is quite expected in the initial stage of TD formation. It is justified in the region of TD annihilation also, as TD annihitation does not mean breaking up of TD, but rendering it electrically neutral by aggregation of more and more oxygen atoms on it. As, it is evident that the oxygen concentration is almost constant between 40 and 50 hrs. of annealing, it can be said that a saturation in donor concentration is reached. This saturation in TD concentration is due to pre-annealing which is not observed in the samples without pre-annealing, according to Om prakash and Shyam Singh [17]. Beyond 50hrs. annealing, the oxygen concentration again falls, suggesting ND formation.

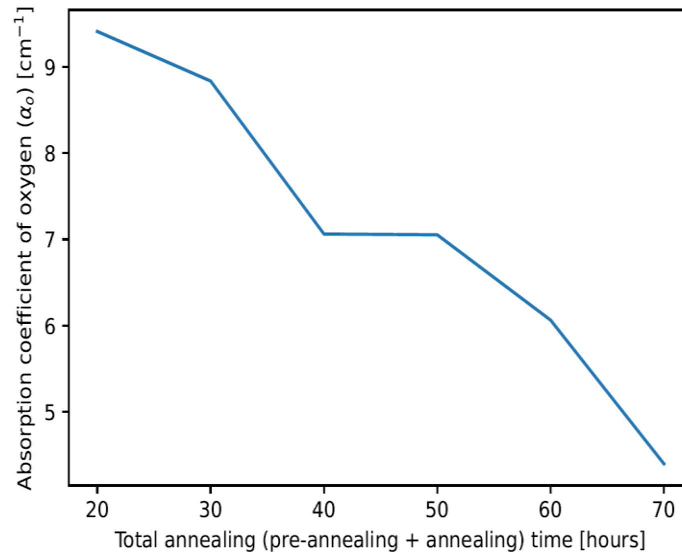

Fig. 2 : Variation in absorption coefficient of oxygen with annealing time

The concentration of interstitial oxygen is maximum at 20hrs annealing time. It is seen that after this point, as the step of annealing proceeds, there is a gradual decrease in oxygen concentration. Hence this point can be taken as reference point and for further readings in the annealing schedule, oxygen loss can be calculated by taking difference from the value at 20hrs point (assumed as initial oxygen concentration here). So it is seen that more and more oxygen gets precipitated with the increase in annealing time due to the formation of TDs and NDs.

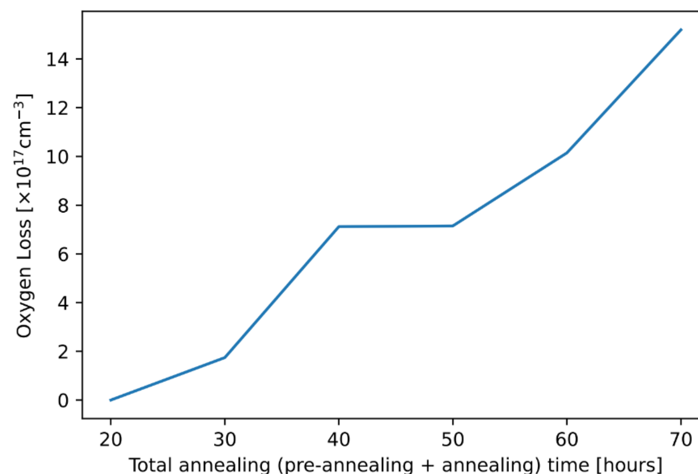

Fig. 3 : Variation in oxygen loss with annealing time

Now the question remains: Why the concentration of interstitial oxygen in annealed samples is higher than the initial concentration? This increase is observed for all the samples and for the sample annealed for 10 hours after a pre-annealing of 10hrs. i.e. annealed for total 20hrs, oxygen concentration reaches to its maximum value. A few possible reasons that come to mind, are listed below:

i) According to Kamiura *et al.* [18], Carbon-rich crystals already contain some TDs in their as grown-state. So, it may be possible that with the increase in annealing time, these TDs might break up, releasing the oxygen, which then diffuses to interstitial sites.

ii) Oxygen might be present in un-annealed samples in other forms also than as interstitial atom. One such form may be oxide precipitate, studied by M. Ataka [19]. According to him, Si-O pairs are generated in the cooling stage after the crystal growth. So, it may be hypothesized that these Si-O pairs are broken up by long annealing, again liberating oxygen.

Other type of oxide precipitate has been proposed by Katayama *et al.* [20]. They detected some microdefects using Transmission Electron Micorscopy (TEM), which act as the nuclei for oxygen precipitates. They may be platelet oxygen precipitates or C_i-O_i complexes. Again it may be thought that the observed increase in concentration of O_i may be due

to release of oxygen from these nucleation sites.
Jastrzebski *et al.* [21] have also suggested that oxygen is not only present as isolated atom O_i , but also exists in the form of small complexes undetectable by IR measurements. In their view, these complexes may be O_3 complexes. So again, under the prolonged annealing these complexes may release oxygen to increase the concentration of O_i.
iii) The presence of surface oxides that might be created due to long annealing or high temperature annealing, can not be ruled out as the source of extra oxygen.
iv) The relative study of IR spectra of different samples reveal that the absorption peak of O_i shifts towards lower wave number and the absorption band broadens, as the annealing time is increased. This may be due to the mixing of absorption band of O_i with that of SiO_2, which is at 9.3 mm i.e. 1075 cm^{-1}. R. C. Newman [22] has pointed out this problem, by stating that the measurements of the peak absorption coefficient at 4.2K instead of room temperature 300K, might be necessary to separate the absorption of O_i from the broad absorption of precipitated SiO_2 particles.

4. Conclusion

The carbon-rich p-type sample changes its nature to n-type after annealing for 20 hrs, suggesting that donor formation starts there and then the samples again converting to p-type after being annealed for 50 hrs, suggest the formation of some electrically inactive clusters and annihilation of thermal donors.
A decrease in concentration of oxygen is observed with annealing time due to formation of TDs and NDs. But there is a considerable increase in oxygen concentration after annealing of 20 hours from un-annealed one, possibly due to already existing TDs in carbon-rich crystal or due to oxide precipitates in the form of Si-O pairs or C_i-O_i complexes or O_3 complexes in un-annealed sample or due to presence of surface oxides.

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