International Journal of Enhanced Research in Science, Technology & Engineering
ISSN: 2319-7463, Vol. 13 Issue 3, March-2024, Impact Factor: 8.375

A Study of the Nature and Concentration of Carriers Generated in Heat Treated Czochralski Grown Silicon

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ABSTRACT

Czochralski-grown (CZ) silicon is preferred over float zone (FZ) silicon commercially in electronic device industry for the economic reasons as well as for the point of view of strength of the device. Hence it needs to be studied thoroughly. During the growth process of CZ Si, oxygen gets trapped at interstitial sites, which on annealing during device fabrication forms clusters. Such clusters are electrically active and are known as thermal donors (TDs). Here in this study, variation in concentration of charge carriers with annealing time is studied 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. It is seen that the presence of carbon slows down the TD formation and enhances TD annihilation and ND formation.

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

INTRODUCTION

Czochralski-grown (CZ) silicon is the primary material for integration of many electronic components after the replacement of Germanium. Now silicon is mostly used material in integrated chips and solar panels manufacturing. Single crystals of silicon are produced primarily by Czochralski method. Many impurities, prominently Oxygen and Nitrogen are in-built in the crystal, which affect the electrical and optical properties. The other method is Float Zone (FZ) method. FZ-Si is very soft for most commercial applications and crumbles very easily because it contains very less oxygen than CZ-Si. The oxygen precipitates help to suppress stacking faults and make silicon more resistant to thermal stress during processing. Therefore, CZ-Si is used for integrated circuit designs having many thermal processing steps. Silicon crystals grown by the CZ method contain oxygen impurities at a concentration close to 10^{18} cm^{-3}. The isolated atoms occupy off-axis bond-centred sites and are electrically neutral [1, 2]. When CZ material is annealed at temperature $>300^{O}C$, isolated interstitial atoms diffuse and form clusters. These clusters are known to be electrically active, which act as double donors [3,4] 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-$500^{O}C$ 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 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 [6, 10]. It is revealed by many studies that the ND generation is enhanced by the low temperature pre-annealing [6,11,12].

In very lightly doped silicon, these oxygen related thermal donors modify the resistivity of material and hence they can affect numerous resistivity dependent device parameters. The number of donors generated or eliminated during heat treatment can be deduced by measuring the resistivity of the specimen. Alternatively, the number of majority charge carriers can be obtained by Hall study and then we can deduce the number of donors generated or eliminated by calculating the difference of number of carriers with the approximation that the mobility remains constant.

In the present study, p-type CZ-silicon, rich in carbon is studied for different annealing durations. 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 charge carriers is noted as the annealing proceeds, using Hall effect measurements.

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 annealed at constant temperature of 480°C for different durations in the range of 1-70 hrs. Following methods are used for study and measurements.

Hall study

Study of Hall effect is used to ascertain the nature of majority carriers in the samples. In the eexperimental 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

$$R_H = \frac{E_y}{j_x B_z} \text{----(1)}$$

where j_x is current density.

As in semiconductors, both types of charge carriers are present and the direction of Hall field as well as of Hall voltage will be opposite for electrons and holes, p-type and n-type semiconductors can easily be differentiated. 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.

The Hall coefficient becomes

$$R_H = -r/nq \quad \text{for } n >> p \text{ [n-type]} \quad \text{----(2)}$$

$$\text{And } R_H = +r/pq \quad \text{for } p >> n \text{ [p-type]} \quad \text{----(3)}$$

where r is called the Hall factor. Its value is usually close to unity. From the equations (2) and (3), carrier concentration can also be obtained.

RESULTS AND DISCUSSION

The results of Hall effect studies are recorded in table below:

Sample no.	Annealing time (hrs.)	Nature of dominant charge carriers	Hall Coefficient R_H x10^4	Hall Factor r	Number of Charge Carriers x10^{13}
0	0	p	6.13	0.91	9.278
1	1	p	9.652	0.95	6.152
2	10	p	6.354	0.94	9.246
3	20	n	1.461	0.94	4.034
4	30	n	9.876	0.92	5.822
5	40	n	1.127	0.94	5.222
6	50	p	1.611	0.95	3.686
7	60	p	1.549	0.94	3.805
8	70	p	1.273	0.93	4.581

Hall studies for the determination of the nature of dominant charge carriers revealed that the un-annealed sample as well as samples annealed up to 10 hrs were p-type. The samples annealed for 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.

Number of majority charge carriers is also evaluated by the experimental values of Hall coefficient using equations 2 and 3 and is given in the last column of the table. Number of majority charge carriers is plotted against annealing time in figure 1. Here positive charge carriers are shown on positive side and negative charge carriers on negative side of y-axis. From the fig 4.1, it is observed that initially (for annealing time of 1hr), the number of positive charge carriers falls. But after that it increases sharply and reaches a maximum for annealing time of 10 hrs. This initial fall in carrier concentration is due to compensation mechanism. As the sample is p-type, initially both type of charge carriers would be present-those of thermal donors and of chemical acceptors and therefore a recombination of both type of carriers would take place, resulting in the decrease in carrier concentration [13, 14, 15].

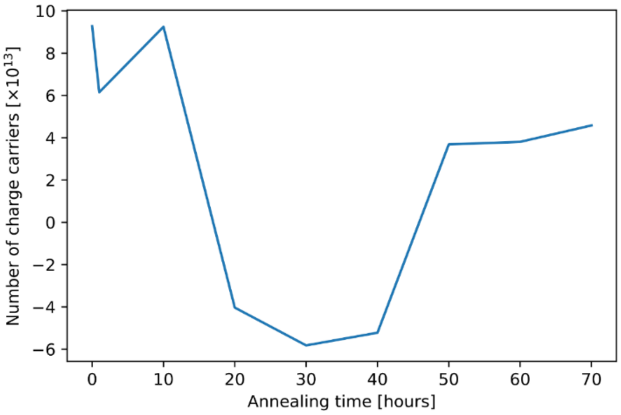

Fig.1: Number of charge carriers vs annealing time

Hall studies have shown that the sample is p-type even after annealing of 10 hrs. So, we can say that the recombination process continues up to 10 hrs. of annealing and the samples are in an unstable situation. Here the growth of TDs appears to be slow, which can be attributed to the presence of carbon in high concentration. It is a well-known fact that the presence of carbon suppresses the TD formation [10].

From annealing of 1 hour duration to 10 hrs duration, the number of impurity atoms i.e. net acceptor atoms increases, which may be due to the breaking up of some already existing TDs, created during crystal growth. The crystals used were as-grown without any donor-killer heat treatment, so they already contained TDs with densities of the order of 10^{14} cm^{-3}, as opined by Kamiura *et al* [16]. After that the concentration decreases by a large amount upto 20 hrs. annealing, suggesting the formation of thermal donors. As the sample is annealed for 20 hrs, it converts into n-type. It shows that the thermal donors created, have completely compensated for the chemical acceptors and now the net charge carriers are n-type, but in small numbers. With the increase in total annealing time, the number of donor impurity atoms increases as more TDs are created. But at 40 hrs of total annealing time, the number of thermal donors begins to decrease and beyond 50 hrs of total annealing, again the reversal of nature of the sample to p-type is observed and the sample retains its p-type nature up to 70 hrs total annealing. Here we observe that the number of positive charge carriers i.e. number of acceptor atoms increases continuously. The initial decrease in carrier concentration with annealing time is quite obvious, as more and more oxygen atoms get clustered with silicon self-interstitials, yielding more and more electrically active thermal donors. Decrease in the number of negative carriers beyond 30 hrs of annealing may be thought due to the joining of more oxygen atoms on the pre-existing TD rendering it electrically inactive. So, the region from 30 hrs to 50 hrs may be said to be the region of TDs annihilation or their conversion to electrically inactive clusters. From 50 hrs to 60 hrs annealing time, the carrier concentration is almost constant, but after that at 70 hrs, it again increases slightly. This increase may be accounted for by the generation of New donors (NDs). These NDs are formed when the electrically inactive TDs formed earlier get fragmented into smaller clusters which are said to be NDs.

Our results are in qualitative agreement with the results of Shyam Singh *et al.* [14, 15]. The difference being that the TD formation in our samples is smaller and slower and TD annihilation and ND formation start early. The reason for that is- our samples contained a higher concentration of initial substitutional carbon compared to their samples and it is a fact that the presence of carbon enhances the TD annihilation and ND formation [6, 10,16].

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, suggesting the formation of some electrically inactive clusters and annihilation of thermal donors. The presence of carbon slows down the TD formation and enhances TD annihilation and ND formation.

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