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IDENTIFICATION OF VARIOUS SPECIES OF TDs IN CZOCHRALSKI SILICON AND A STUDY OF THE EFFECT OF ANNEALING ON THEIR RELATIVE CONCENTRATION

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Generation and behaviour of various species of thermal donors (TDs) as a result of annealing of carbon-rich boron-doped (*p*-type) CZ-silicon has been studied, as function of annealing time at a constant temperature of 480°C, by Hall studies and by FTIR studies. Recombination of TDs and chemical acceptors and transformation of TDs into NDs is studied. It is seen that the conversion of incoming *p*-type sample to *n*-type is slow initially due to the compensation mechanism. Total nine species of TDs are identified, each absorption line being very sharp, suggesting that each originates from a thermal donor with a well-defined structure.

KEYWORDS : CZ- Silicon, Thermal donor, New donor, Annealing, Species of TDs.

INTRODUCTION

Silicon is at present the basic material for electronic device fabrication. Hence quite a large number of studies have been conducted to thoroughly investigate the properties of silicon and the effect of impurities and defects in it. Next to oxygen, silicon is the second most common element found in the upper layer of the earth's crust. Silicon is usually not found free, but mainly in its oxide form. So before using it in semiconductor device engineering, its extraction, purification and subsequent crystallisation is necessary. Silicon used in semiconductor industry has to meet stringent specifications of purity and perfection. There are two types of silicon used in industry depending upon the method of their crystallisation-Float-zone (FZ) Silicon and Czochralski (CZ) Silicon. Although FZ-silicon is purer than CZ-Si, latter is preferred over FZ-Si because of economic criterion and also because CZ wafers are less susceptible to mechanical rupture.

Crude silicon is first purified to the highest purity level possible, by chemical methods. Silicon obtained through such purification is of semiconductor grade in the form of polysilicon rods in which the concentration of troublesome impurities is about 1 in 10^9 silicon atoms and the resistivity of this silicon is very high for most of the applications. So, it has to be purified further, which is done by a method called zone refining. It is based on the tendency of most impurities to remain in the liquid part when the melted semiconductor gradually solidifies.

Purified polysilicon rods may be converted to single crystal by a technique called float zone (FZ) method of crystal growth. Here the polyrod is mounted vertically over a piece of single crystal silicon, called the seed, that is pre-cut in the desired crystallographic orientation. A current carrying coil is slowly moved vertically, so that the region of the polyrod in front of it melts. As the molted zone passes the polyrod it transforms the rod's polycrystalline structure into a single crystal. During this growth process both the rod and the seed are slowly rotated to preserve uniformity.

But, the most common method for crystal growing in use, is the Czochralski pulling technique. The purified Si is remelted in a quartz-lined graphite crucible. The seed, attached to a holder is dipped into the molten Si and then very slowly pulled up again, rotating at the same time to preserve uniformity. The temperature is properly controlled so that the molten Si sticking to the seed starts solidifying following the crystal structure of the seed. Large single crystals can be grown using this technique.

Important advantage of the FZ-method is the purity of the resulting crystals because of the absence of contamination from containers. Crystals obtained from CZ-technique possess impurities due to contamination from the crucible, but still, it has advantage over FZ-technique in other points, like-the growth of large crystals is easier in CZ-technique because here the mechanical growth conditions are more favourable as a result of self-stabilization of the hanging CZ-crystals. The thermal conditions are also better during CZ-growth. That’s why most of the semiconductor devices used in the field of communication, entertainment etc., use CZ-Si, therefore there is a need to study more and more about different aspects of CZ-Si.

Impurities and defects play essential roles in determining the electrical and optical properties of semiconductors. Hence quite a large number of studies have been conducted to clarify the electrical and optical properties related to impurities and defects in semiconductors. In the course of these studies, it has been recognised that clusters and complexes, such as pairs and large aggregates of impurities and defects have properties much different from those of isolated impurities and defects. The effect of impurities and defects on electrical and optical properties is usually determined by their energy levels, but the clusters have spatial extension which provide them with some other properties also which cannot be derived from the energy levels alone.

About 30 elemental impurities such as P, As, Bi, Sb, B, Al, Ga, In etc. have been tried in silicon so far. Oxygen is perhaps one of the most common dopants being introduced from the walls of the fused silica crucible during the growth of the CZ-crystal.

Oxygen atoms in a silicon crystal show a peculiar behaviour as member of group VI impurities. They reside on interstitial sites and are electrically inactive when they are dissolved in the lattice [1, 2]. Supersaturated oxygen atoms in a silicon crystal become clustered due to annealing at temperatures around 450°C. Such clusters are known to be electrically active as donors [3]. They are termed as thermal donors (TDs). They are annihilated due to annealing above 500°C. The generation and annihilation of TDs are thought to be related to generation and dissociation of some kind of clusters of oxygen atoms or/and self-interstitial atoms of Si generated by the formation of SiO_2. Different annealing schedules produce electrically active centres varying in nature. Thermal donors were first reported by Fuller *et al.* in 1954[4]. TDs are obtained by low temp annealing (300-500°C) of CZ Silicon single crystal. TDs are shallow double donors having slightly different energy levels, which exhibit sharp absorption lines, showing the presence of various species of TDs with different ionisation energies. On increasing annealing time, shallower species of TDs become dominant, but on extending annealing time further (> 10^5 min), all the species of TDs are annihilated at a temperature of about 450°C [5]. Short term annealing at ≈550°C causes most of the donors in Si to disappear.

Infrared studies of the electronic transitions associated with the thermal donors show the presence of at least nine different double donor species. The energy levels associated with the donors form a succession of increasingly shallow states with nearly constant separation (~2meV) [5, 6]. At constant annealing temperature, the concentration of each donor species was determined by Oeder and Wagner [5] as a function of the annealing time. The species appear successively with shallower energy levels on increasing annealing duration. The concentration of each species reaches a maximum and decays. Out of the nine species, the third and the fourth attain the highest maximum concentration.

The KFR model proposed by Kaiser, Frisch and Reiss[7], also showed that the ionization energy of TD decreases gradually with the annealing duration at 450°C. This may again be interpreted to be due to change in the species of dominant TD with the duration of annealing.

Suezawa and Sumino [8, 9] proposed their model of thermal donors in 1984. They showed how each kind of TD is related to the number of oxygen atoms involved in it. It was shown that the optical absorption spectra depended upon the duration of annealing at a constant annealing temperature of 471.3°C. Many absorption lines were observed after annealing of 1250 min. These were classified into six groups of lines-those associated with namely TD-1 to TD-6. Each absorption line being very sharp, suggesting that each originates from TD with a well-defined structure. The spectra shows that the energy levels of TD-1 through TD-6 are rather close to each other.

In the present study, *p*-type CZ-silicon is studied for different annealing durations and analysed for the presence of different species of thermal donors in the annealed samples.

MATERIAL AND METHODS

2.1 Sample preparation

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 1 × 2 cm^2 size and then subjected to heat treatment in Muffel furnace in air ambient. They were annealed at constant temperature of 480°C for different durations in the range 1-70 hrs, as per schedule given in table below:

S. No.	**Sample number**	**Annealing time (In Hours)**
1.	O	0
2.	A	1
3.	B	3
4.	C	5
5.	D	8
6.	E	10
7.	F	20
8.	G	30
9.	H	40
10.	I	50
11.	J	60
12.	K	70

2.2 Fourier Transform Infra-Red (FTIR) Spectroscopy

Optical transmission spectrum from FTIR show many absorption peaks whose position and intensity varies with annealing time. By careful observation of the spectra of different samples, these absorption lines can be classified into different groups & lines. Each absorption line is sharp, suggesting that each originates from a TD with well-defined structure. So, each group of lines represents one species of TD. So, we can know the number of different TD species and their ionisation energies.

RESULTS AND DISCUSSION

3.1 Identification of Various Species of TDs

Infra-Red spectra of different samples show small peaks of varying absorptions between 400 and 520 cm-1. These absorption peaks can be classified into nine groups of lines, those associated with namely TD-1 through TD-9, which can be seen on the transmittance spectra of different samples in figs 1-3. Different species of TDs obtained are tabulated along with their ionisation energies in table 1.

Table 1 : Species of Thermal donors and their ionisation energies

Species of thermal donor	**Wave number in cm^{-1}**	**Ionisation energy in meV**
TD-1	514	63.85
TD-2	508	63.10
TD-3	495	61.48

TD-4	489	60.74
TD-5	473	58.76
TD-6	463	57.51
TD-7	455	56.52
TD-8	436	54.16
TD-9	415	51.55

3.2. Discussion of results obtained

IR spectrum of sample no. O (un-annealed sample, Fig. 1(a)) shows small peaks corresponding to all the TDs except TD-2 and TD-4, the one corresponding to TD-9 being the strongest. This is because the crystals used were as-grown without any donor-killer heat treatment, so that the un-annealed samples already contained some TDs with densities of the order of 10^{14} cm^{-3}, as opined by Kamiura *et al.*[10]. As the annealing proceeds, the depth of various species of TDs changes. Also, the lines appear and disappear with the change in annealing time.

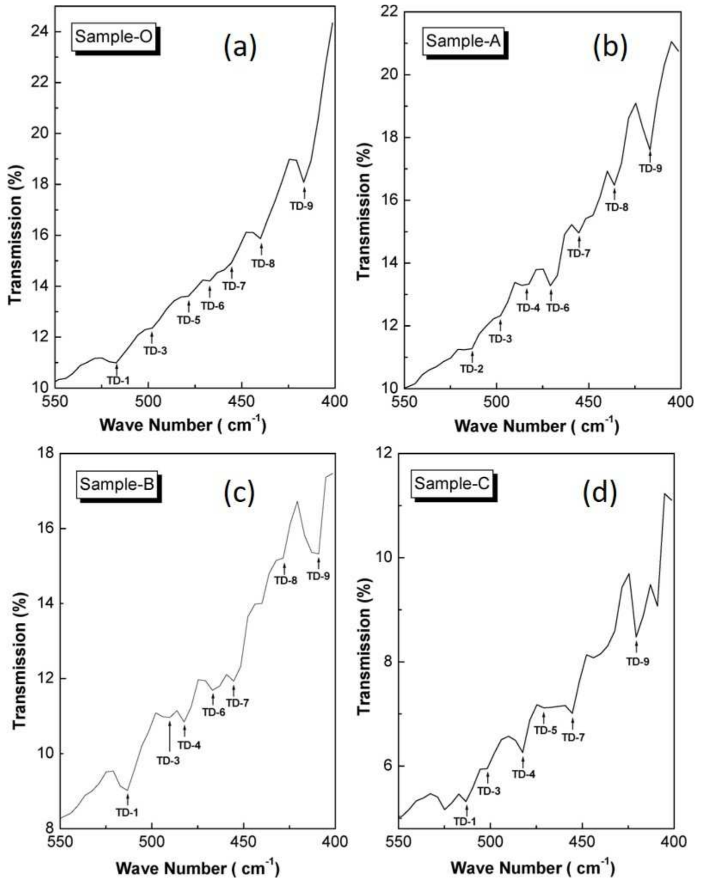

Fig. 1

We see in Fig. 1(b), that after one hour of annealing, new species of donors *i.e.* TD-2 and TD-4 appear and TD-1 and TD-5 disappear with TD-9 still being the strongest. As annealing proceeds further to three and five hours, peaks become sharper. As our sample is *p*-type, initially both types of charge carriers would be present-those of thermal donors and of chemical acceptors and therefore a recombination of both types of carriers would take place, resulting in the decrease in carrier concentration. From un-annealed sample to annealing of 1hr. duration, the number of impurity atoms *i.e.* net acceptor atoms increases, which may be due to breaking up of some already existing TDs, created during crystal growth. After that the concentration decreases by large amount up to 5 hrs. annealing, suggesting the formation of thermal donors, so almost all the peaks become sharper. This increase in concentration of acceptor impurities shows the neutralisation of charge carriers, the situation being non-equilibrium.

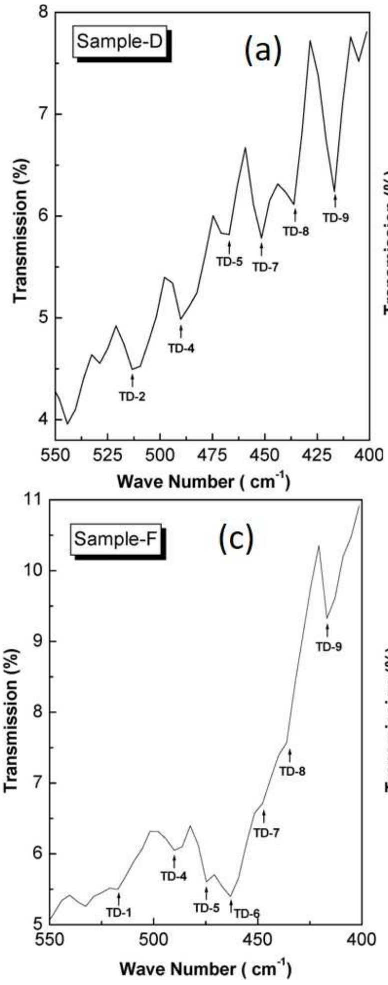

Fig. 2

Almost all the lines have their maximum intensity for the sample annealed for 8 hrs *i.e.* sample D (Fig. 2 a), suggesting maximum donor concentration. This recombination of charge carriers continues up to 10 hours of annealing and the samples are in unstable situation. At 20 hrs annealing (sample F), almost all the TDs disappear except small peaks of TD-4, TD-5, TD-6 and a strong peak of TD-9. These results are in agreement with Oeder & Wagner [5] and Pajot *et al*. [6].The Hall studies on the samples have shown that the sample remains *p*-type up to 10 hours of annealing and converts to *n*-type after 20 hours of annealing. 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 number. With the increase in total annealing time, the number of donor impurity atoms increases as more TDs are created. More and more oxygen atoms get clustered with silicon self-interstitials, yielding more and more electrically active thermal donors.

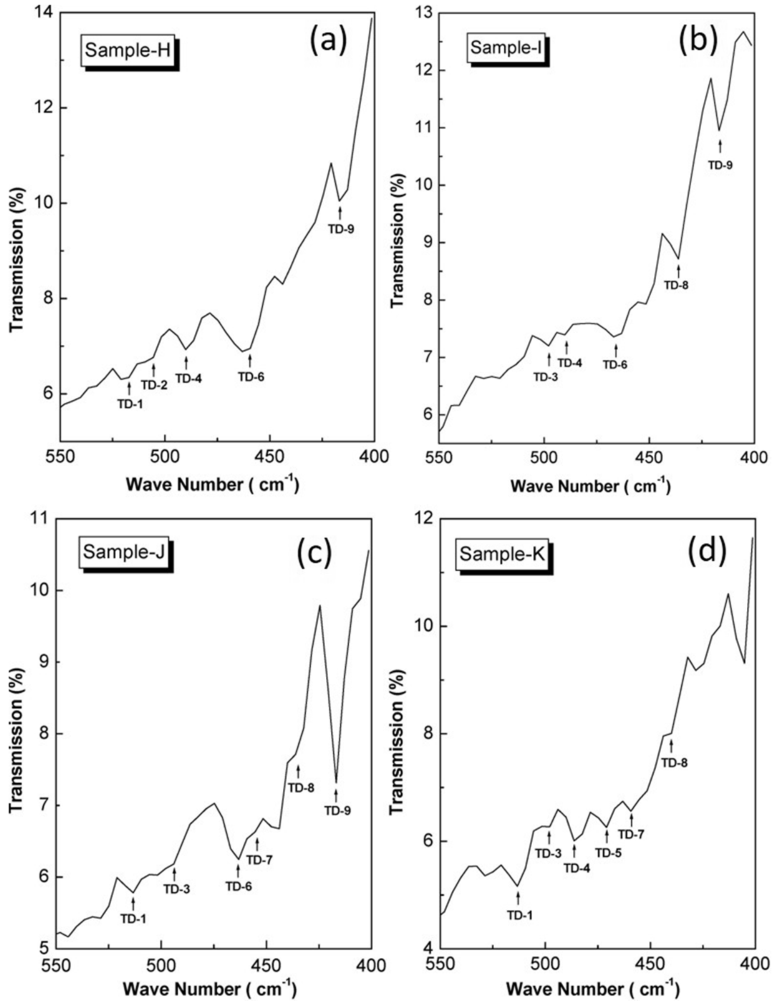

Fig. 3

But at 40 hrs and 50 hrs of total annealing time, almost all the peaks diminish, suggesting annihilation of TDs due to joining of more oxygen atoms on the pre-existing TDs rendering them electrically inactive. Beyond 50 hrs of annealing, again the reversal of nature of sample to *p*-type is observed, in Hall study. 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, there is little increase in size of each peak, but after 70 hrs. of annealing, new peaks are obtained, which are different than the nine observed species of TDs. They 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.

CONCLUSION

Infra-Red spectrum of unannealed as well as annealed samples show various peaks at different wavelengths, corresponding to total nine species of thermal donors: TD-1 to TD-9 having ionisation energies from 63.85 meV to 51.55 meV. The spectra shows that the energy levels of TD-1 through TD-9 are rather close to each other and therefore suggest that the extensions of the wave functions of donor electrons belonging to all kinds of TDs are not very different. Absorption spectra for different annealing time show that the dominant species of TDs change with annealing time. Initial annealing causes recombination of existing TDs and chemical acceptors, but further annealing causes formation of thermal donors and after 30 hrs of annealing, TD annihilation takes place, which continues till 50 hrs. It is also seen, by the appearance of new peaks that 70 hrs of annealing produce new type of donors called New Donors (NDs).

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