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Growth of Various Species of Oxygen Related Donors as A function of Annealing Temperature in Czochralski Grown Silicon

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ABSTRACT

Generation and behaviour of various species of oxygen related donors (ODs) as a result of annealing of carbon-rich boron-doped (p-type) Czochralski (CZ) silicon has been studied, as function of annealing temperature, by Hall studies and by FTIR studies. Formation of thermal donors (TDs), Recombination of TDs and chemical acceptors, annihilation of TDs and transformation of TDs into new donors (NDs) is studied. Total nine species of TDs and nine species of NDs are identified, each absorption line being very sharp, suggesting that each originates from a donor with a well-defined structure.

Key Words: CZ- Silicon, Thermal donor, New donor, Annealing, Species of TDs and NDs, Interstitial Oxygen.

INTRODUCTION

Silicon is at present the most widely used semiconductor for integrated circuit fabrication using MOS and bipolar technologies. 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. Oxygen is the most abundant non-intentional impurity incorporated in the growth process of CZ-Si, which is of the order of $10^{18}cm^{-3}$. As low-temperature (<$800^{O}C$) heat treatments are used in device fabrication processes, the oxygen present in CZ-Si induces various defects like ODs and other complexes during fabrication. These electrically active defects may lead to degradation of device performance and to a lowering of device yield. Supersaturated concentration of oxygen is reduced either by out diffusion or by forming complexes or precipitates depending upon the thermal treatments. Formation of precipitates and secondary defects is rather useful in internal gettering to remove metallic impurities in the device active region, since SiO_2 precipitates formed by post - growth diffusion act as sink for inadvertently introduced fast diffusing metallic contaminants that must be excluded from the active regions of integrated circuits. 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. Oxygen is one of the most common do pants 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 $450^{O}C$. 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 $500^{O}C$. 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^{O}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^{O}C[5]. Short term annealing at ≈550^{O}C causes most of the donors in Si to disappear. At higher temperatures, 500-800^{O}C, another group of donors called new donors (NDs) are formed [6].

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, 7]. 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[8], also showed that the ionization energy of TD decreases gradually with the annealing duration at 450^{O}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 [9,10] 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^{O}C. Many absorption lines were observed after annealing of 1250min. 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 temperatures and analyzed for the presence of different species of thermal donors and new donors in the annealed samples.

MATERIAL AND METHODS

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 1x2 cm^{2} size and then subjected to heat treatment in Muffel furnace in air ambient. They were annealed at different temperatures from 480°C to 650^{O}C for 10 hrs each, as per schedule given in table below:

Table 1: Annealing schedule of samples

S.No.	Sample number	Annealing temperature (in ^{O}C)
1.	O	Unannealed
2.	A	480
3.	B	550
4.	C	600
5.	D	650

Fourier Transform Infra-Red (FTIR) Spectroscopy

Optical transmission spectrum from FTIR show many absorption peaks whose position and intensity varies with annealing temperature. 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 OD with well-defined structure. So, each group of lines represents one species of OD. So, we can know the number of different OD species and their ionisation energies.

A rough estimation of absorption coefficient of each species is obtained by FTIR absorption method, described by lizuka *et al.* [11] for absorption coefficient of oxygen.

The relative transmittance of any absorption band with respect to the base line is expressed as

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

Where α corresponds to absorption coefficient for the respective band, which does not include the multiple reflection effect.

RESULTS AND DISCUSSION

Identification Of Various Species Of TDs and NDs

Infra-Red spectra of different samples show small peaks of varying absorptions between 400 and 550cm^{-1}. These absorption peaks can be classified into different groups of lines, those associated with namely TD-1 through TD-9 and ND-1 through ND-9, which can be seen on the transmittance spectra of different samples in figs 1and 2. Different species of TDs obtained are tabulated along with their ionisation energies in table 2 and the identified species of NDs are tabulated in table 3.

Table 2: **Species of Thermal donors and their ionisation energies**

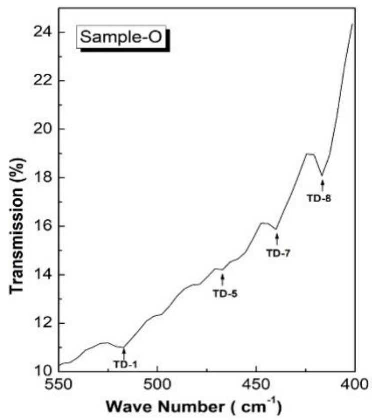
Species of thermal donor	Wave number in cm^{-1}	Ionisation energy in meV
TD-1	517	64.47
TD-2	502	62.12
TD-3	490	60.63
TD-4	473	58.53
TD-5	467	57.79
TD-6	455	56.30
TD-7	438	54.20
TD-8	416	51.48
TD-9	409	50.61

Table 3: **Species of New donors and their ionisation energies**

Species of thermal donor	Wave number in cm^{-1}	Ionisation energy in meV
ND-1	544	67.32
ND-2	536	66.33
ND-3	533	65.95
ND-4	521	64.35
ND-5	506	62.61
ND-6	482	59.64
ND-7	478	59.15
ND-8	452	55.93
ND-9	413	51.10

Discussion of results obtained

IR spectrum of sample no. O (un-annealed sample in Fig.1) shows small peaks corresponding to few TDs like TD-1, TD-5, TD-7 and TD-8, the one corresponding to TD-8 being the strongest. This is because the crystals used were as-grown without any donor-killer heat treatment, so the un-annealed samples already contained some TDs with densities of the order of 10^{14}cm^{-3}, as opined by Kamiura *et al.*[12]. As the annealing temperature increases, the depth of various species of TDs changes. Also, the lines appear and disappear with the change in annealing temperature.



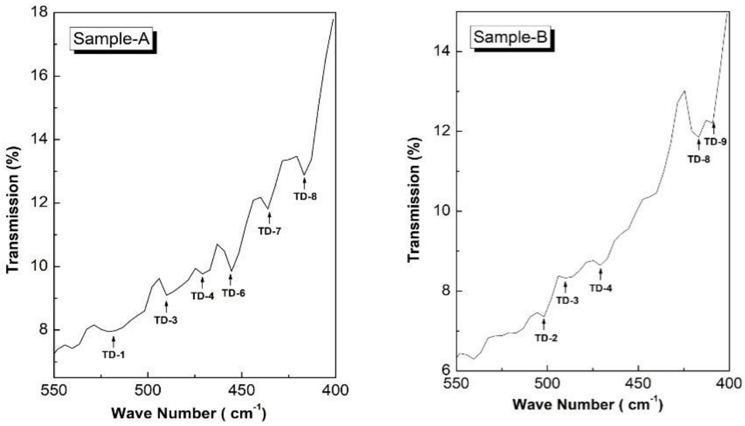


Fig. 1: Variation in species of TDs with temperature

We see in Fig. 1, for sample A, that after ten hours of annealing at 480^{O}C, new species of donors i.e. TD-3, TD-4 and TD-6 appear and TD-5 disappear with TD-6 being the strongest, but all the peaks become sharper as compared to those in un-annealed. 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 initially, resulting in the decrease in carrier concentration. But after annealing, the concentration decreases by large amount, suggesting the formation of thermal donors, so almost all the peaks become sharper. As for sample B, annealed for 10 hours at 550^{O}C 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. Table 4 shows the absorption coefficients of various species of thermal donors at different temperatures.

Table 4: **Absorption Coefficients of different Species of Thermal donors**

Species of thermal donor	Absorption coefficient for un-annealed (O)	Absorption coefficient at 480^{O}C (A)	Absorption coefficient at 550^{O}C (B)	Absorption coefficient at 600^{O}C (C)	Absorption coefficient at 650^{O}C (D)
TD-1	1.785	0.547	-	-	-
TD-2	-	-	0.357	-	-
TD-3	-	1.357	0.142	-	-
TD-4	-	0.428	0.333	-	-
TD-5	0.071	-	-	0.452	-
TD-6	-	1.976	-	-	3.166
TD-7	1.357	0.738	-	-	-
TD-8	1.095	1.047	2.261	-	-
TD-9	-	-	0.166	-	-

The table shows comparative growth and decay of TD-1 through TD-9 as the temperature changes from 480^{O}C to 650^{O}C. Maximum number of species are obtained for annealing at 480^{O}C and as the temperature reaches 600^{O}C, all the species except TD-5 and TD-6 for 650^{O}C remain. Samples annealed in this temperature range show different peaks, slightly different than the peaks for TDs, suggesting the transformation of TDs into NDs. This is clearly seen in figure 2.

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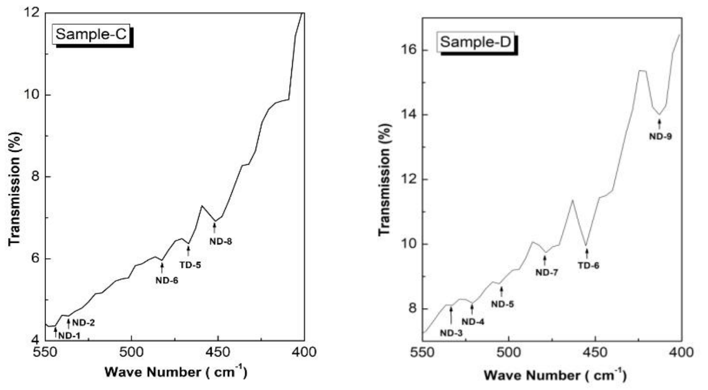

Fig. 2: Variation in species of NDs with temperature

We see in Fig. 2, for sample C, that after ten hours of annealing at 600^{O}C, all the species of TDs, except TD-5 disappear and new species appear at different wave numbers. It can be concluded clearly that they correspond to new donors (NDs) and can be named as ND-1, ND-2, ND-6 and ND-8. For sample D, i.e. for annealing at 650^{O}C, another species of ND appear as ND-3, ND-4, ND-5, ND-7 and ND-9, while retaining TD-6 also. Table 5 shows the absorption coefficients of various species of New donors at temperatures 600^{O}C and 650^{O}C.

Table 5: **Absorption Coefficients of different Species of New donors**

Species of New donor	Absorption coefficient at 600^{O}C (C)	Absorption coefficient at 650^{O}C (D)
ND-1	0.595	-
ND-2	0.119	-
ND-3	-	0.095
ND-4	-	0.357
ND-5	-	0.142
ND-6	0.357	-
ND-7	-	0.785
ND-8	1.285	-
ND-9	-	2.238

It is evident from the table 5 and fig. 2 that the generation and annihilation of donors is dynamic. The donors which are created at 600^{O}C, get annihilated or converted to another form at 650^{O}C and new species of donors appear at 650^{O}C. It can be understood because NDs are formed when the electrically inactive TDs formed earlier get fragmented into smaller clusters and this process continues. Also the Hall studies show that the sample C and D which are annealed for 10 hours at temperatures 600^{O}C and 650^{O}C, respectively again convert to p-type, while sample B annealed at temperature 550^{O}C is n-type, whereas the un-annealed sample and the sample annealed at 480^{O}C is a p-type. It is evident that the TDs which would have been created at temperatures lower than 480^{O}C, have been annihilated, as we know the formation of TDs start at around 300^{O}C and their annihilation starts at around 430^{O}C[13,14]. From 550^{O}C to 650^{O}C temperature, NDs are generated in large numbers.

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 64.47 meV to 50.61meV and nine species of new donors: ND-1 to ND-9 having ionisation energies from 67.32 meV to 51.1 meV. The spectra shows that the energy levels of TD-1 through TD-9 and ND-1 through ND-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 and NDs are not very different. Absorption spectra for different annealing temperature show that the dominant species of

TDs and NDs change with annealing temperature. Initial annealing causes recombination of existing TDs and chemical acceptors, but further annealing causes formation of thermal donors and after 550^{O}C of annealing temperature TD annihilation takes place and the appearance of new peaks exhibits the formation of new type of donors called New Donors (NDs).

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