

Loss of oxygen and carbon during donor formation in CZ-silicon

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Abstract. Due to a lack of proper understanding about the formation mechanism of oxygen related donors during the transition temperature range (465–540°C) which exhibits the transition of TDs to NDs, an attempt has been made to study their behaviour in the present context. We have found the formation and diffusion of molecule like oxygen at low temperature annealing of silicon and observed that second order kinetics of oxygen diffusion holds good. A relatively low value of 0.6 eV has been estimated to be the activation energy for the diffusion of oxygen in silicon which is supposed to be due to the hydrogen passivation.

Keywords. Donors; kinetics; activation energy; oxygen precipitation; silicon.

1. Introduction

In view of the potential applications of the silicon, this material has been thoroughly investigated perhaps from all possible angles in order to optimize the material for device fabrication. Annealing of the oxygen rich silicon in the 300–500°C temperature range yields shallow donor states (Fuller *et al* 1954; Fuller and Logan 1957; Kaiser *et al* 1958), generally termed thermal donors. A lot of self-contradicting experimental data is available in the literature. Still there is a wide gap of doubt yet to be bridged up by a more methodical and comprehensive approach harmoniously blended with sound logic.

Annealing of the samples beyond $\approx 480^\circ\text{C}$ results in the gradual disappearance of thermal donors and simultaneous appearance of a new kind of donors called new donors (NDs). However, behaviour of the oxygen related donors (ODs) in the transition temperature range (465–540°C) which witnesses simultaneous existence of both TDs and NDs along with the possible presence of some thermal acceptors, is not yet well understood. Therefore, we have tried here to look at this important aspect.

Inherent presence of oxygen and carbon plays a crucial role in the formation mechanism of different donor species which differ from one another in their composition and electronic structure depending upon the temperature range within which they can be generated. On one hand a certain amount of oxygen is beneficial as it provides matrix hardening and also responsible for internal gettering effect; at the same time high concentration of oxygen in the sample leads to the degradation of device yield. Similarly the presence of carbon suppresses TD concentration while it enhances ND concentration. The question of formation and diffusion of molecule like

oxygen at low temperature in silicon has also been a point of debate for years together. Therefore, the present investigation is aimed to see the role and behaviour of oxygen and carbon in donor formation in CZ-silicon in the temperature range 430–630°C.

2. Materials and methods

Two types of CZ-silicon wafers were used in the study, henceforth referred to as group A and group B. The history of the samples has a great effect during the study of the annealed samples. Therefore, specifications and other information regarding the wafers are listed in table 1 as provided by the suppliers.

The wafers were cut, etched and one side mirror polished. These wafers were cut down into small samples of dimension $1 \times 2 \text{ cm}^2$ and heat treated for different schedules. In one schedule, group A samples were annealed for 26 h as a function of temperature between 465–540°C in regular steps. In the second schedule, groups A and B samples were pre-annealed for 24 h at 455°C. After that, group A samples were heat treated at 470°C for 6–111 h in regular steps and group A+B was given heat treatment for 11 h between 430–630°C in regular steps.

2.1 Resistivity measurement and donor concentration

Resistivity of silicon wafer was measured with a collinear four-probe array at room temperature and the number of carriers derived from Irvin's curve (Sze and Irvin 1968). After that, the wafer was heat treated and subsequently cleaned in hydrofluoric acid in order to eliminate the surface oxide. The resistivity of the annealed samples was again measured at room temperature and

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Table 1. History of the wafers.

Group	Thickness (μm)	Orientation	Dia. (mm)	Resistivity (ohm-cm)	Initial concentrations (ppma)	
					[C _s]	[O _i]
A	380–390	$\langle 100 \rangle$	80.0	80–100	11.0	37.7
B	210	$\langle 100 \rangle$	50.0	8–10	8.4	22.2

the corresponding number of charge carriers derived from the Irvin's curve. Assuming that the mobility remains constant, the difference of two carrier concentrations between unannealed and annealed samples gives the donors generated or annihilated during heat treatment.

2.2 Precipitated oxygen and carbon

Absorption coefficient needed to compute oxygen and carbon contents in the samples has been derived from 1106 cm^{-1} and 605 cm^{-1} bands, respectively, by FTIR measurements using the procedure laid down by Iizuka *et al* (1985). The values of α_o (for oxygen) and α_c (for carbon) so obtained helped to obtain the interstitial oxygen concentration [O_i] and substitutional carbon concentration [C_s] using the expressions:

$$[\text{O}_i] = (3.03 - 0.02) \times 10^{17} \alpha_o \text{ cm}^{-3},$$

$$[\text{C}_s] = 1.1 \times 10^{17} \alpha_c \text{ cm}^{-3}.$$

The initial oxygen and carbon concentrations in the test wafer were measured without any treatment on it. Later, the wafer was given a specific heat treatment to calculate interstitial oxygen and substitutional carbon concentrations. The difference between the two is attributed to precipitated oxygen during heat treatment.

3. Results and discussion

3.1 Donor activity in the temperature range 465–540°C

Annealing of the samples helped in reducing the inhomogeneities present in the unannealed samples up to a greater extent. The resistivity variation along with donor generation as a function of annealing temperature for 26 h of annealing had been observed for group A samples. As the group A sample is *p*-type, annealing for shorter duration (≈ 1 h) generally resulted in an increase of resistivity due to compensation mechanism and thereafter, resistivity fell-off indicating the reversal of the nature of the sample (Om Prakash *et al* 1998). In the present case donors generated at 465°C annealing for 26 h are $1.9 \times 10^{14} \text{ cm}^{-3}$ with a maximum of $1.0 \times 10^{15} \text{ cm}^{-3}$ at 480°C. This behaviour is quite understandable as more

and more oxygen atoms get clustered with silicon self-interstitials Si_i yielding electrically active donors. Annealing of the samples beyond 480°C and up to 510°C helped in the gradual disappearance of donor activity coming down to $2.6 \times 10^{14} \text{ cm}^{-3}$. This is more likely due to joining of more oxygen atoms on the pre-existing TD rendering it electrically inactive. These inactive clusters get fragmented into smaller electrically active clusters i.e. NDs corresponding to $T > 510^\circ\text{C}$ annealing.

As a result of pre-annealing of the group B samples at 455°C for 24 h and subsequent annealing at 470°C for 6–111 h in regular steps, the resistivity decreases at first for annealing duration up to 54 h. This is clearly a region where the TDs are under the process of generation and more and more TDs come into existence as electrically active clusters, a situation similar to that witnessed in the group A samples. The growth pattern of TDs (figure 1) coming up from $1.5 \times 10^{17} \text{ cm}^{-3}$ for 6 h to $4.7 \times 10^{17} \text{ cm}^{-3}$ for 54 h annealing assisted by the pre-annealing treatment is quite expected. This is contrary to the results reported earlier without pre-annealing where no saturation in donor concentration was observed (Tarun Kumar and Singh 1994; Om Prakash and Singh 1995). Beyond 54 h annealing duration the resistivity increases. This is a region where TDs are facing gradual extinction due to the formation of electrically inactive clusters.

3.2 Donor activity in temperature range 430–630°C

Resistivity measurements on group A+B samples revealed that initial region of the rapid growth of TDs has completely lost its entity due to the pre-annealing treatment, which advanced the TD generation process towards the lower annealing temperature. In our studies, annealing in the temperature range 430–630°C clearly indicated the presence of two OD regions: gradual disappearance of TDs and appearance of NDs. Simultaneous existence of thermal acceptors (TAs) along with new donors seems quite plausible. Figure 2 shows trend of the donors generated. The fact that the presence of carbon suppresses the TD formation and accelerates ND formation (Bean and Newman 1972), is clearly reflected herein from our data.

In this temperature range we conclude that: (i) TDs gradually disappear in the temperature range 430–510°C for group A and 430–470°C for group B, (ii) NDs are

formed in the temperature range 510–550°C for group A and 470–510°C for group B, (iii) generation of more and more thermal acceptors as a function of annealing temperature compensates the ND concentration in both groups beyond 550°C and 510°C, respectively and (iv) also the creation of recombination centres and ND like defects cannot be ruled out. Donor generation in group A is lower as compared to group B due to the presence of large amount of carbon, because carbon is known to be an efficient self-interstitial trap (Mathiot 1987).

3.3 Oxygen diffusion at low temperatures $T < 500^\circ\text{C}$

A smooth and gradual decrease in the values of absorption coefficients of oxygen as a function of annealing time has been noticed for groups A and B samples. We found that oxygen and carbon precipitation increases with increase in annealing temperature and duration as well (Cazcarra and Zunino 1980). In a crystal containing only interstitial oxygen atoms the first stage of oxygen aggregation has to be the formation of O_2 dimers (McQuaid *et al* 1995). This is a second order process which is described by the equation:

$$\frac{d[\text{O}_i]}{dt} = -8\pi R_c D_{\text{oxy}} [\text{O}_i]^2,$$

which, in turn, leads to

$$\frac{1}{[\text{O}_i]_t} - \frac{1}{[\text{O}_i]_0} = 8\pi R_c D_{\text{oxy}} t,$$

where R_c is the capture radius associated with dimer formation and is expected to be 5 Å. A plot of difference of the reciprocal values of the actual oxygen concentration $[\text{C}(t)^{-1}]$ and initial oxygen concentration $[\text{C}(0)^{-1}]$ versus annealing time comes to be a straight line (figure 3) suggesting that the oxygen reduction can be described by a second order kinetics, as recently supported by McQuaid *et al* (1995). From the gradient of the straight line equal to $8\pi R_c D_{\text{oxy}}$, the diffusion coefficient of the

oxygen (D_{oxy}), at temperature 470°C comes out to be $\approx 6.18 \times 10^{-19} \text{ cm}^2 \text{ s}^{-1}$. The use of this procedure to analyse measurements relating to anneals at 450°C and 470°C led to normal values of D_{oxy} .

Arrhenius plot of the diffusion coefficient of oxygen as a function of $1/kT$ is shown in figure 4. From the slope of the line we found the activation energy for the normal diffusion of oxygen to be $\approx 0.6 \text{ eV}$, a value close to that reported by Gaworzewski and Schmalz (1980). This value is significantly lower than that estimated by Stavola *et al* (1983) which is $E_a = 2.54 \text{ eV}$. This lower value of E_a can be explained by sinks of diffusing O_i atoms. As grown CZ-silicon may contain hydrogen impurities (Newman 1996) which could catalytically interact with neighbouring O_i atoms and lower the energy of their saddle point configuration during the diffusion process. The activation energy for the diffusion of Si_i atoms, 0.4 eV (Gosele and Tan 1982), is quite comparable to the experimental value of oxygen diffusion estimated by our data. This leads one to conclude that the diffusion of oxygen at low temperatures is characteristic of the transport of self-interstitials chiefly due to the formation of molecule like oxygen clusters. In this process the dimer dissociation rate has been neglected in comparison to dimer formation rate. These dimers having small binding energy (0.1–1.0 eV) diffuse more easily in silicon lattice because dimers have small activation energy (1.4 eV) than single O_i atoms.

In our quantitative analysis we found an average of seven oxygen atoms involved in a single donor formation at low temperatures. For this purpose we took a group of Si samples having negligibly less carbon impurities to avoid the other complex formation like C–O, rather than oxygen related defects during the heat treatment at different temperatures. By comparison between the number of maximum donors generated and the amount of oxygen reduced at different temperatures ($450^\circ\text{C} < T < 500^\circ\text{C}$), we found that it takes an average of seven oxygen atoms for a single donor formation.

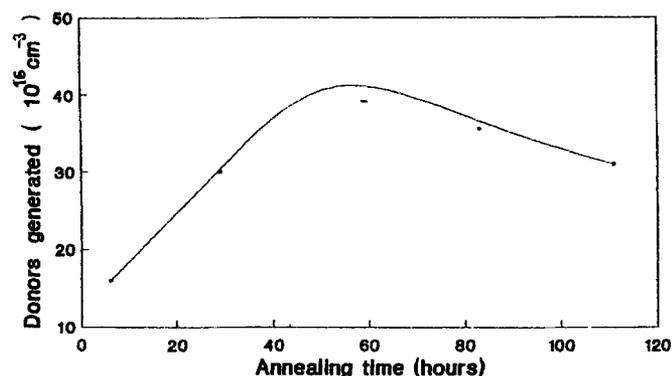


Figure 1. Donors generated as a function of annealing time at 450°C.

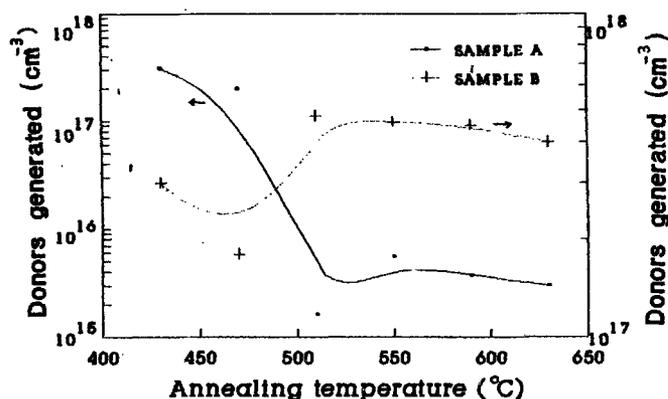


Figure 2. Variation of donors generated as a function of temperature annealed for 11 h.

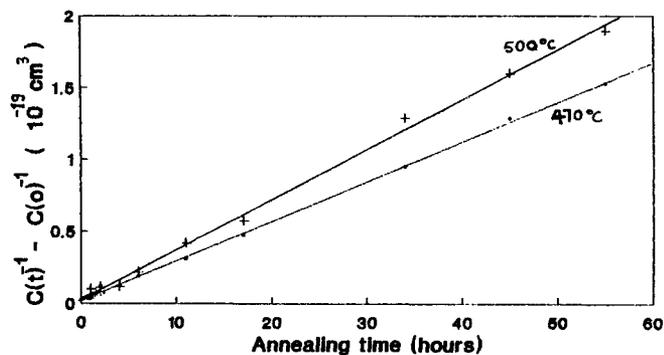


Figure 3. Plot of differences of reciprocal values of oxygen concentration at time t and initial oxygen concentration $[C(t)^{-1} - C(o)^{-1}]$ as a function of annealing time at 470°C and 500°C.

3.4 Role of carbon during donor formation

3.4a Suppression effect of TD formation: At low temperature ($T < 500^\circ\text{C}$) the normal TD annihilation unrelated to carbon has generally been described to further the growth of TD clusters beyond the critical size to induce the change of TD structure to lose its electrical activity (Wagner and Hage 1989). In the present study, carbon induced the gradual disappearance of TDs and carbon itself at 470°C of annealing. However, neither carbon can move at 470°C as long as it occupies a substitutional site (C_s), nor TDs can. It has been proposed that Si_i atoms may play a role in the formation and electrical activity of TDs (Newman 1985). Therefore, we propose the hypothesis that Si_i created during oxygen aggregation process (O_2 formation) ejects C_s into an interstitial site C_i . This C_i rapidly diffuses to various species of TDs to interact them so as to make them electrically inactive. However, exact mechanism of this process is not yet known. The main problem with this explanation is that calculations (Kelly 1989) indicate that there is insufficient strain within a cluster as small as O_2 to cause the ejection of a Si_i .

3.4b Enhancement effect on ND formation: It has been found that presence of carbon leads to the enhancement of new donor formation at higher temperature range ($T > 550^\circ\text{C}$). Carbon has been recognized to provide nucleation sites for oxygen precipitation around 650°C (Gaworzewski and Schmalz 1983). The present results obtained by us have suggested that NDs are carbon related. The resistivity measurements have clearly indicated that both low temperature pre-annealing and carbon enhance the ND generation.

In general, as to the oxygen reduction samples pre-annealed at 455°C and not pre-annealed behave similarly. The absolute values, however, are different in pre-annealed samples. The oxygen reduction starts only after

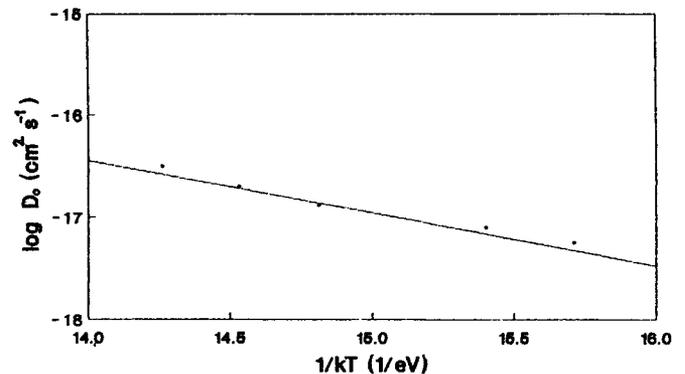


Figure 4. Arrhenius plot of oxygen diffusion coefficient as a function of $1/kT$.

annealing for 6 h at 630°C where the annihilation of TDs is finished and the formation of NDs has begun.

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