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Formation of oxygen related donors in step-annealed CZ-silicon

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Abstract. The effect of step-annealing necessitated by the difficulties being faced in the long duration annealing treatments to be given to CZ–silicon has been studied. One pre-anneal of 10 h followed by annealing of 10 h causes a decrease in the absorption coefficient for carbon (a_c). Oxygen and carbon both accelerate thermal donor (TD) formation process but oxygen plays a dominating role. Three anneals of 10 h each followed by one anneal of 10 h support the view that carbon suppresses the donor formation. The absorption coefficient for carbon decreases after a few number of step-anneals resulting in the transformation of TD to new donor (ND) as brought about by annealing at temperature, > 500°C. It is quite logical to conclude that step-annealing may bring about the same results as obtained on continuous annealing for a longer duration.

The results have been fully supported by proper interpretation in the light of existing theories.

Keywords. Semiconductors; annealing; thermal donors; new donors; activation energy.

1. Introduction

Silicon has maximum impact on semiconductor industry. About 90% of the silicon crystal used in semiconductor industry is CZ–silicon. Virtually all the silicon used for fabricating integrated circuits belongs to this class. Silicon and oxygen both separately are of paramount importance. Union of these two is inevitable in most silicon devices. But it leaves some problems with a mark of interrogation, such as the exact kinetics of thermal donor formation, behaviour of oxygen related donors (ODs) in the transition temperature range, average number of oxygen atoms involved in a single donor, fine structure of thermal donors (TDs) etc, are still surrounded by an air of uncertainty and excitement.

Oxygen is the most abundant non-intentional impurity incorporated in the melt during growth process from the walls of the fused silica crucible. Oxygen impurities influence strongly the electrophysical and mechanical properties of CZ–Si. Heat treatment of the silicon crystal with high oxygen contents ($O_i \approx 3{\cdot}0 \times 10^{17}$ to $1{\cdot}5 \times 10^{18}$ cm^{-3}) in the temperature range 400–1200°C produces various kinds of defects. Various models (Ourmazd *et al* 1984; Mathiot 1987; McQuaid *et al* 1995) have been put forth to understand the actual mechanism of device degradation by these defects, but the actual state of affair is not yet well understood. Annealing process of the CZ–Si at low temperature (< 800°C) is of increasing importance for prospective applications of low temperature cycles to device technologies as well as for fundamental researches on the behaviour of oxygen in silicon. In view of a few problems stated above and difficulties being faced in long duration annealing treatments, an effort has been made to see the effect of step-annealing in order to obtain the same results as achieved by continuous annealing for a longer duration.

2. Materials and methods

Proper interpretation of the data obtained from the measurement of the properties of the sample is dependent on the nature of the sample, its previous history and imperfections. Babitskii *et al* (1991) and Oehrlein *et al* (1984) have shown that the pre-heat treatment history has large effect on initial thermal donor growth rate. Two groups of grown silicon wafers used in the study were obtained from SSPL, Delhi and SIMCO Materials International, New Delhi. The wafers are *p*-type boron doped with orientation ⟨111⟩ and thickness 500 μm. Some other specifications are given in table 1.

The wafers were cut into small pieces of size 1 × 2 cm^2 and then subjected to heat treatment in ambient air. We did not anneal the samples continuously at constant temperature but step-annealing schedules of 10 h each were fixed for different samples at constant temperature of 450°C up to 70 h followed by annealing as shown in table 2.

2.1 *Resistivity measurement and donor generation*

The resistivity of a silicon wafer is measured with the most commonly used collinear four-probe array at room

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temperature and the number of carriers is derived from the Irvin's curve (Sze and Irvin 1968). Afterwards, the sample receives the desired heat treatment in ambient air and is cleaned in hydrofluoric acid in order to eliminate the surface oxide. Now, by measuring its new resistivity the corresponding number of carriers is obtained from Irvin's curves. The results are also supplemented by Hall measurement in order to ascertain the carrier concentration. From the difference of number of carriers and approximating that the mobility remains constant, we deduce the number of donors generated or eliminated during heat treatment.

2.2 *FTIR measurement*

The FTIR is primarily used to detect certain impurities (oxygen and carbon) in silicon. Interstitial oxygen in silicon causes absorption at $l = 9{\cdot}05\ \mu m$ ($1106\ cm^{-1}$) at 300°K and at $8{\cdot}87\ \mu m$ ($1227{\cdot}6\ cm^{-1}$) at 77°K due to the antisymmetric vibration of SiO_2 complex. The expression for interstitial oxygen concentration is given as

$$O_{i\,=}\,(3{\cdot}03 \pm 0{\cdot}02) \times 10^{17}{\cdot}a_0,$$

where a_0 is the peak absorption coefficient for $1106\ cm^{-1}$ band (Iizuka *et al* 1985).

The expression for carbon concentration is

$$C_s = 1{\cdot}1 \times 10^{17}{\cdot}a_c,$$

where a_c is the peak absorption coefficient for $605\ cm^{-1}$ band (Regolini *et al* 1986; ASTM Standard 1988).

The initial oxygen (O_o) and carbon (C_o) concentrations are measured on the incoming wafer without any special heat treatment, using infrared absorption bands at $1106\ cm^{-1}$ due to interstitial oxygen. Afterwards the wafer is given desired heat treatment and the concentrations of oxygen (O_i) and carbon (C_s) are again measured with same IR technique. The difference between (O_o) and (O_i) and between (C_o) and (C_s) are attributed to the precipitated oxygen and carbon during heat treatment. Absorption coefficient needed for calculating the oxygen concentration is determined with Fourier transform infrared (FTIR) absorption method.

Table 1. A few specifications of the samples.

Group	Diameter (mm)	Concentration (atoms/cm^3)	Resistivity (ohm–cm)
A	50	$B \sim 1{\cdot}1 \times 10^{15}$	12
B	100	$B \sim 0{\cdot}9 \times 10^{15}$	20

Table 2. Annealing schedule of the samples.

Sample No.	Step-annealing (h)	Annealing (h)	Total annealing time (h)
1.	–	10	10
2.	10	10	20
3.	10 + 10	10	30
4.	10 + 10 + 10	10	40
5.	10 + 10 + 10 + 10	10	50
6.	10 + 10 + 10 + 10 + 10	10	60
7.	10 + 10 + 10 + 10 + 10 + 10	10	70

3. Results and discussion

3.1 *Resistivity measurement and donor generation*

The resistivity of the sample annealed up to ≈ 1 h, increased; but thereafter, for longer annealing period, the resistivity fell off exponentially. This behaviour clearly showed that *p*-type sample was converted to *n*-type due to generation of thermal donors (Prakash and Singh 1997). From the comparative plots of resistivity variation as a function of annealing time for group A and B samples as shown in figure 1, it can be inferred that for the group A samples, there is a sharp fall in the resistivity in first 20 h, i.e. first 10 h step-annealing followed by a 10 h annealing at a constant temperature of 450°C. Beyond this, the resistivity falls slowly up to 40 h of annealing and then above 40 h, it almost becomes constant. Similar results have been obtained for the samples belonging to group B.

The primary motive of the resistivity measurement is to determine the carrier concentration which helps us to find out the donor concentration. Figure 2 clearly reflects that for group A samples, generated donor steadily grows in number as the annealing time (step-annealing + annealing) increases. This steady growing trend of donors slows down after four successive step-annealing each of 10 h duration. Similar results have been obtained for the other samples belonging to group B. However, even for heat treatment of 70 h, the maximum is not attained but as per trend of curve at 70 h it can be safely concluded

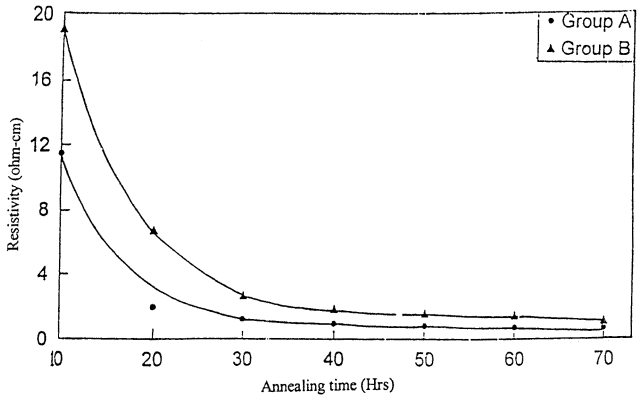

Figure 1. Resistivity vs annealing time at 450°C.

that longer heat treatments would bring a saturation in donor generation. Above results are in agreement with Capper *et al* (1977), Cazacarra and Zunino (1980) and Prakash and Singh (1997).

3.2 *Absorption coefficient*

Absorption coefficient needed for calculating the oxygen and carbon concentrations were determined by performing FTIR measurements at room temperature on unannealed and step-annealed samples. The plots of absorption coefficients, a_0 vs annealing time and a_c vs annealing time at 450°C are shown in figure 3. A smooth and gradual decrease in values of absorption coefficients of oxygen is noticed. A decrease in the absorption coefficient results in the corresponding decrease in the oxygen concentration as is clear from the relation $O_i = 3{\cdot}03 \times 10^{17} \cdot a_0$ shows that the oxygen atoms are shifted from their original positions to form electrically active clusters i.e. TD, due to heat treatment.

While in case of carbon, first step-anneal of 10 h followed by annealing for 10 h, the absorption coefficient goes down resulting in the subsequent decrease in the C_s concentration. The presence of carbon in CZ–Si is known to suppress the TDs formation while presence of oxygen enhances the TDs formed. In this case it appears as if the presence of carbon accelerates the TD formation process but the fact remains that oxygen assisted TD formation process is still dominant as compared to carbon assisted TD formation process. As a result the net outcome is that the TDs have a growing trend during this step-annealing and annealing schedule. After this, up to three step-anneals followed by one anneal the absorption coefficient of carbon increases, which in turn, supports the adopted view that the carbon suppresses the donor formation. Beyond this the absorption coefficient decreases which suggests that the donors generated again start increasing. We feel that this is the region of new donors (NDs), for which the carbon acts as a promoter. Electrically inactive embryos generated as a result of heat treatment in the temperature range 350–550°C, become electrically active between 650°C and 750°C and thus further help in the growth of NDs (Fukuoka *et al* 1987). In other words one may conclude that a few number of step-anneals may bring about the transformation of TD to ND as brought about by the annealing at temperature > 500°C (Prakash *et al* 1997). The fractional change of the IR absorption coefficient, a_0, as a function of heat treatment at 450°C shows an increasing trend, which is in tune with the result shown in figure 2. Our results are in agreement with Prakash and Singh (1995).

3.3 *Oxygen and carbon precipitation*

The initial oxygen and carbon concentrations of unannealed samples for group A have been found to be $4{\cdot}72 \times 10^{17}$ cm^{-3} and $3{\cdot}85 \times 10^{17}$ cm^{-3}, respectively. The values of absorption coefficients have been used to determine the oxygen concentration and carbon concentration. The difference in oxygen concentration with respect to the reference sample gives the oxygen precipitation. We may say that oxygen precipitation increases with increase in heat treatment. Our results are in agreement with Cazacarra and Zunino (1980) and Kumar and Singh (1994).

3.4 *Diffusion coefficient and activation energy*

A plot of the difference of the reciprocal values of the actual and initial oxygen concentration $[C_t^{-1} - C_0^{-1}]$ as a function of annealing time at 450°C gives a straight line (figure 4), which suggests that the oxygen reduction can

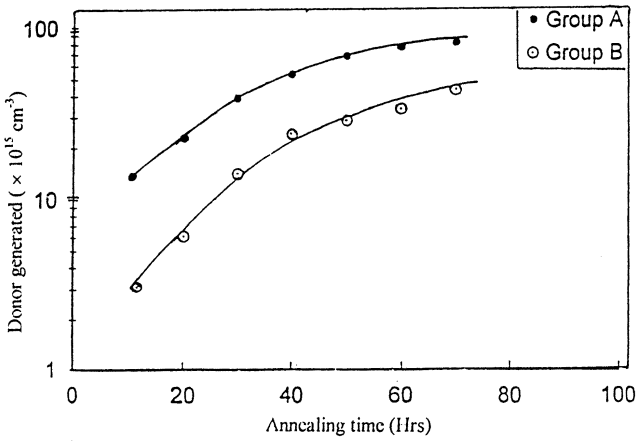

Figure 2. Plot of donor generated as a function of annealing time at 450°C.

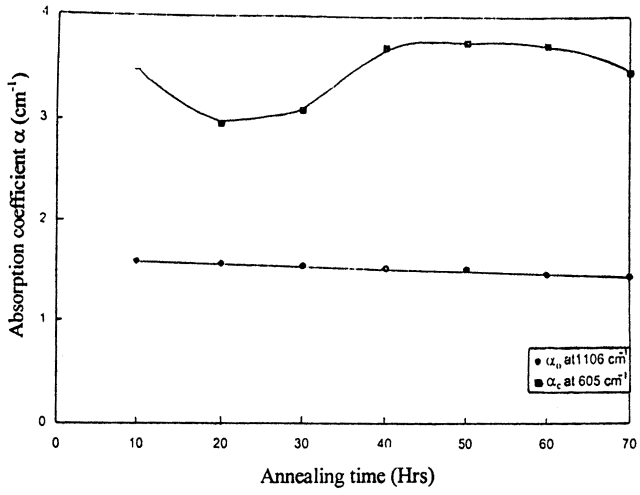

Figure 3. Effect of heat treatment at 450°C for different duration on IR absorption coefficient of group A samples.

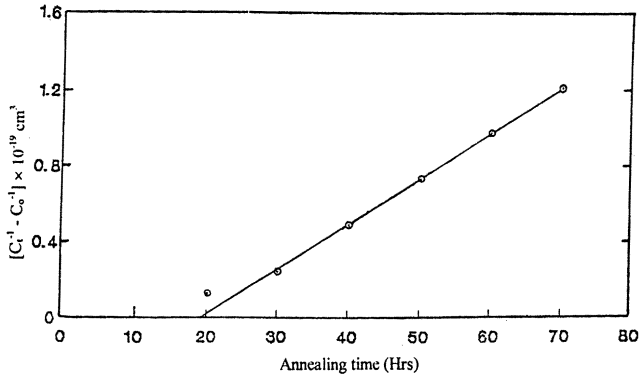

Figure 4. Difference of the reciprocal values of the actual oxygen concentration and initial concentration vs annealing time at 450°C of group A samples.

be described by second order kinetics (Reiche *et al* 1988). From the gradient of the straight line equal to $8pDR$, the diffusion coefficient (D) of oxygen has been determined to be = $2{\cdot}3 \times 10^{-15}$ cm^2/s. Here R is the distance at which the oxygen atoms bind together to form a complex; $R = 5{\cdot}0 \times 10^{-8}$ cm (Newman 1985). The value of D so obtained is substituted in the expression

$$D = 0{\cdot}17 \exp(-E/KT) \text{ cm}^2 \text{ s}^{-1},$$

which yields the value of activation energy for the diffusion of oxygen to be ~ 1·84 eV. The migration energy of interstitial oxygen atoms has been reported to be 2·4–3·5 eV (Gosele and Tan 1982), so the formation process of NDs is not controlled by the diffusion of interstitial oxygen atom but may be due to the presence of embryos.

4. Conclusions

From the results of the study, it can be concluded that step-annealings may play the same role as that of continuous annealing in order to make the CZ–silicon wafer to meet the device requirements. It has also been found that the ambients whether nitrogen or air do not have any influence on the behaviour of the parameters calculated. The difference whatsoever observed is attributed to the presence of the initial oxygen and carbon concentrations of the incoming wafers, as reported by Prakash *et al* (1998) and also supported earlier by Bean and Newman (1972). Our results are in tune with the earlier findings that carbon suppresses the donor formation. Second order kinetics has been found to be followed by oxygen reduction. The thermal diffusion coefficient of oxygen comes out to be $2{\cdot}3 \times 10^{-15}$ cm^2/s and activation energy ~ 1·84 eV.

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