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A Survey of Oxygen Loss and Kinetics of TD Formation in Short-Annealed CZ-Silicon at 450°C

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ABSTRACT

Czochralski silicon (CZ-Si) is the primary material for integrated circuits and CMOS industry. Oxygen gets incorporated in silicon during the crystal-pulling process and is present in the grown crystal material in a supersaturated state. Hence during thermal treatments, it will tend to form clusters and precipitates.

Therefore, thermal donor formation during heat treatment of CZ silicon is important to study. In this work, important information about TDs formed in short annealing durations at 450°C has been obtained by IR absorption due to the electronic transitions, by which the change in concentration of oxygen with annealing time is studied. Then by knowing the amount of oxygen loss in the process, diffusivity and hence the activation energy for the formation of TD clusters is presented successfully.

KEYWORDS:

CZ- Silicon, Thermal donor, Interstitial Oxygen, Oxygen loss, Diffusivity, Activation energy, Pre-annealing.

1. Introduction:

Single crystals of silicon are produced commercially by Czochralski (CZ) method. During the process of semiconductor device fabrication Si wafer is subjected to heat treatments. CZ-Silicon absorbs oxygen from the crucible during its growth process.

The oxygen atoms occupy interstitial positions and are bonded to two silicon lattice atoms. The oxygen diffuses in the silicon by an interstitial hopping mechanism. During low temperature annealing (300-500°C) of CZ silicon, shallow donors are formed, known as thermal donors (TDs), which act as double donors [1,2,3].

The donor activity of the cluster (TD) is destroyed by annealing at a temperature higher than 500°C with an activation energy of 2.5-2.8eV [4]. This is associated with the emission of silicon interstitials even at temperatures as low as 450°C [5]. Infrared studies of the electronic transitions associated with the thermal donors show the presence of different double donor species. At constant annealing temperature, the concentration of each donor species was determined by Oeder and Wagner [2] as a function of the annealing time. The initial rate of donor formation is proportional to the fourth power of the initial oxygen concentration [6]. On the basis of systematic studies of the IR-absorption band, the donors are supposed to be oxygen complexes with an increasing number of oxygen atoms being attached to them during heat treatment [7]. It is a generally accepted view about TD formation that the small aggregate formation is due to mobile interstitial oxygen impurity atoms. One of the basic models of TD formation was proposed by Kaiser, Frisch and Reiss [8], known as KFR model. According to this model, polymerization of oxygen i.e. the formation of silica (S_iO_2) observed at high temperatures begins in the course of heat treatment at temperatures as low as a several hundred °C. Certain intermediates in this polymerization are electrically active donors. Among the intermediate complexes formed, those containing more than a certain number of oxygen atoms no longer act effectively as donors at room temperature. Extending the treatment of KFR model, Suezawa and Sumino [9] described the chemical rate equations for the formation of oxygen clusters as–

$$\begin{array}{c} A_1 + A_1 \rightarrow A_2 \\ A_{n-1} + A_1 \rightarrow A_n \\ A_n + A_1 \rightarrow A_{n+1} \\ A_{n+1} + A_1 \rightarrow A_{n+2} \end{array} \quad \text{-----------(1)}$$

Here, An is the density of oxygen clusters consisting of n oxygen atoms.

R. C. Newman [10] proposed a model, according to which, oxygen atoms diffuse at their normal rate to form di-oxygen molecules (O_2 dimers) and during this process, self-interstitials so generated are mobile. This results in the formation of clusters during the heat treatment. This model states that one silicon atom is displaced into an interstitial site to accommodate two oxygen atoms that were originally in bonded interstitial sites. In his work, Newman has not found any evidence for interactions between interstitial oxygen atoms and self-interstitials. The model suggests that thermal donors might be identified with aggregates of self-interstitials rather than oxygen clusters. The process follows second order kinetics which can be described by the equation for rate of loss of O_i atoms from solution as-

$$\frac{d[O_i]}{dt} = -\,8\pi\, r_c\, D_{oxy}\, [O_i]^2 \quad \text{----------(2)}$$

Where r_c is the separation at which the two atoms bind together, called the capture radius and D_{oxy} is diffusion coefficient of oxygen.

D. Mathiot [11] carried on the Newman's idea of self-interstitial aggregates to put forward his model in 1987. This kinetic model is based on self-interstitial agglomeration which allows good simulation of TD formation. He also showed that the reaction of oxygen agglomeration proceeds with the rate constant K given by-

$$K = 8\pi\, r_c\, D_{oxy} \qquad \text{------------(3)}$$

where the capture radius r_c is about 5Å and D_{oxy}, the normal thermal diffusivity of dispersed interstitial oxygen is given by [12]-

$$D_{oxy} = 0.17 \exp(-E/kT)\ \mathrm{cm^2 s^{-1}} \qquad \text{------------(4)}$$

Where E is the activation energy of oxygen diffusion.

In the present work, the early stage of oxygen precipitation is studied in n-type CZ-silicon at 450^{o}C and an effort is made to understand the kinetics of thermal donors for short annealing cycles through measurement of diffusion constant and activation energy of the process.

2. Material and Methods:

The sample used is Czochralski (CZ)-grown n-type 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 1-10 hrs. Following methods are used for different measurements.

2.1 Hall Study:

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

$$R_H = \frac{E_y}{j_x B_z} \qquad \text{---------(5)}$$

where j_x is current density.

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.

2.2 FTIR Measurement:

Absorption coefficient needed for determining the oxygen concentration is determined by FTIR absorption method, described by lizuka et al. [13].

Concentration of interstitial oxygen (O_i) in silicon can be derived from 1106 cm^{-1} absorption band of the IR spectrum, using the following expression:

$$[O_i] = (3.03 \pm 0.02) \times 10^{17} . \alpha_o \qquad \text{-------- (6)}$$

Where α_o is the peak absorption coefficient for the 1106 cm^{-1} band corresponding to oxygen, which can be determined for unannealed and different annealed samples. The relative transmittance of the oxygen absorption band with respect to the base line is expressed as

$$T_{rel} = T_{peak} / T_{bg} = \exp(-\alpha'_o d) \qquad \text{--------(7)}$$

The α'_o term corresponds to the absorption coefficient which does not include the multiple reflection effect. The relationship between α'_o and the actual absorption coefficient, α_o for oxygen is given by lizuka *et al* [13], as given in fig 1.

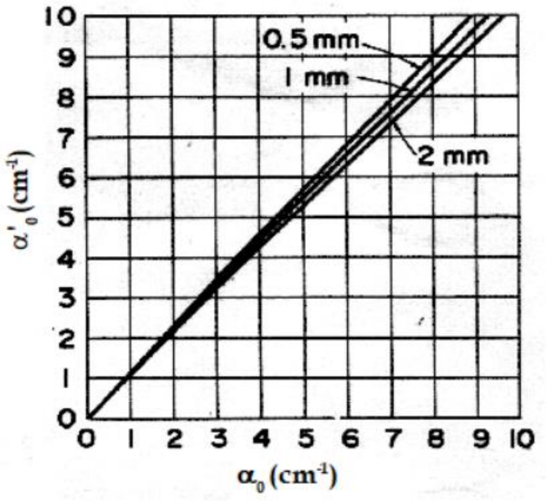

Figure 1: Relationship between α'_o and α_o for different sample thicknesses

So, the procedure to determine the absorption coefficient is- draw base line on the transmission spectra between 1300 and 900 cm^{-1}, calculate $T_{rel.}$ and then α'_o using equation (7), then obtain value of α_o using Fig.1. We choose line on the graph corresponding to 0.5 mm for our calculations, as our sample thickness is 0.42 mm, which is closest to that, of all the three lines.

2.3 Determination of Diffusion Coefficient and Activation Energy:

In a crystal containing only dispersed interstitial oxygen (O_i) atoms, the first stage of oxygen aggregation is the formation of O_2 dimers [10] which follows second order kinetics described by equation (2), i.e.-

$$\frac{d[O_i]}{dt} = - 8\pi r_c D_{oxy} [O_i]^2$$

Integrating this equation from time t = 0 to t, we get the relation between the differences of the reciprocal values of the actual and initial oxygen concentration and annealing time so that a plot of the difference of reciprocals of $[O_i]_t$ and $[O_i]_0$ versus time(t) should yield a straight line with a slope equal to $8\pi\ r_c D_{oxy}$, where 'r_c' is the capture radius, whose value is given by Newman and Mcquaid *et al.*. [14, 15], as 5Å and 'D_{oxy}' is the diffusion coefficient of O_i atoms. Therefore, by plotting a graph between the differences of the reciprocal values of the actual and initial oxygen concentration as a function of annealing time, and from the gradient of the straight line obtained, we can calculate the value of 'D_{oxy}' at a given temperature.

The value of 'D_{oxy}' so obtained is substituted in equation (4), i.e.-

$$D_{oxy} = 0.17\exp(-E/kT)\ \mathrm{cm^2 s^{-1}}$$

to calculate the value of activation energy, 'E' of oxygen diffusion.

3. Results and Discussion:

3.1 Hall Effect Study:

Hall studies for the determination of nature of dominant charge carriers revealed that the un-annealed sample as well as sample annealed for 1 to10 hrs, all were n-type. As we already know that the un-annealed samples used by us are n-type, so the study shows that the sample annealed up to 10 hrs. at 480°C maintains its nature as n-type, suggesting some donor formation might have started.

3.2 Concentration of Interstitial Oxygen:

The absorption coefficient and then concentration of interstitial oxygen is calculated from the IR spectra obtained from Fourier Transform Infra-Red (FTIR) spectroscopy using the method given for the absorption coefficient of oxygen by Iizuka *et al.* [13] and the relation between α'_o and α_o as shown in fig 1, using the line for sample thickness of 0.5mm (close to our value, d = 0.42mm). The results are recorded in table 1. The concentration of interstitial oxygen for un-annealed sample is maximum. But annealing induces continuous decrease in oxygen concentration upto 10 hrs total annealing time. It clearly indicates the initial stage of thermal donor formation as there will be loss of interstitial oxygen due to the clustering of more and more oxygen atoms to form TDs.

3.3 Diffusion Coefficient and Activation Energy:

As it is already seen that the concentration of interstitial oxygen is maximum at 0 annealing time i.e. for un-annealed sample and after this point, as the annealing proceeds, there is a gradual decrease in oxygen concentration. Hence oxygen loss is calculated by taking difference from the value of initial oxygen concentration and the concentration for annealed samples for different durations. So for the difference in the reciprocal values of concentration, $[O_i]_0$ corresponds to the concentration of un-annealed sample, in table 1

Table 1: Reciprocal of Oxygen Concentration against total annealing time

Sample No.	**Total annealing time (hrs.)**	**Oxygen Concentration $[O_i]$ xl0^{17} (cm^{-3})**	**$1/[O_i]$ xl0^{-17} (cm^3)**	**$1/[O_i]_t$ - $1/[O_i]_0$ x l0^{-17} (cm^3)**
1	0	20.432	0.0489	0
2	1	19.961	0.0501	0.0012
3	3	18.762	0.0533	0.0044
4	5	18.083	0.0553	0.0064
5	8	16.611	0.0602	0.0113
6	10	15.848	0.0631	0.0142

The loss in oxygen can be described by second order kinetics, as a plot of the difference of the reciprocal values of the concentration at time 't' and initial oxygen concentration, as a function of annealing time, gives a straight line. This is shown in fig. 2, where a graph is plotted using table 1

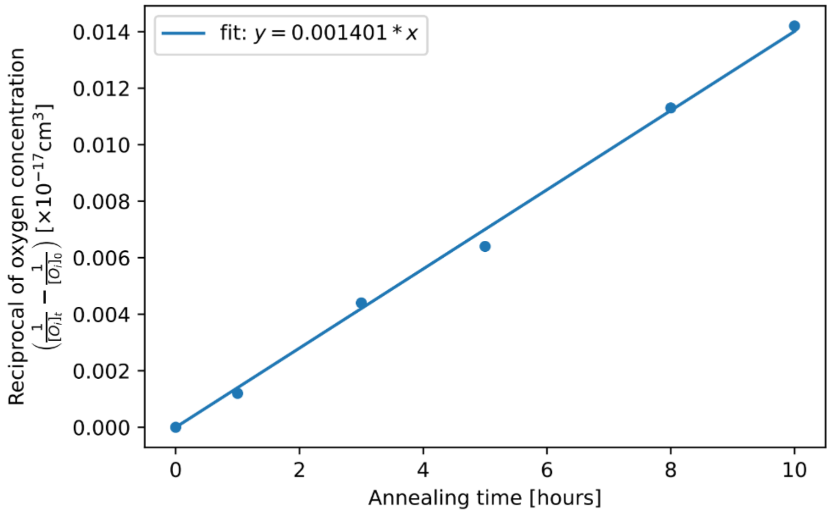

Figure 2: Plot of differences of reciprocal of oxygen concentration with annealing time

From the gradient of straight line in fig. 2 equal to $8\pi\ r_c D_{oxy}$ (from equation 2), the diffusion coefficient, 'D_{oxy}' of oxygen has been determined (using value of capture radius, r_c as 5Å, given by Newman and Mcquaid *et al.*. [14, 15] as,

$$\mathbf{D_{oxy} = 30.96 \times 10^{-19}\ cm^2/sec\ at\ 450\ ^oC.}$$

This value of D_{oxy} is substituted in the expression

$$D_{oxy} = 0.17\exp(-E/kT)\ cm^2 s^{-1}$$

yielding the value of activation energy for the diffusion of oxygen as-

$$\mathbf{E = 2.404\ eV}$$

This value of activation energy for oxygen diffusion is in very good agreement with the value (2.4 - 3.5 eV) reported by Gosele and Tan [16].

4. Conclusion:

The n-type sample after annealing for 10 hrs maintains its nature as n-type with considerable decrease in oxygen concentration, suggesting continuous donor formation as the annealing proceeds.

The plot of the difference of the reciprocal values of the concentration at time 't' and initial oxygen concentration, against annealing time gives a straight line, suggesting that the loss in oxygen can be described by second order kinetics. The diffusivity of oxygen in silicon is calculated by the equation of second order kinetics, which comes out to be 30.96 x 10^{-19} cm^2/sec at 450°C. Also the activation energy of the process is found out to be 2.404 eV.

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