

# An Analysis of Oxygen Diffusion and Aggregation in Step-Annealed Czochralski Silicon

Dr. Ritu Agarwal (Associate Professor)

Physics department, Bareilly College, Bareilly-243001  
Affiliated to M.J.P.Rohilkhand University, Bareilly-243006 (India)  
E-mail: rituag2767@gmail.com

## Abstract

Oxygen is incorporated in Czochralski silicon crystals during the crystal pulling process and is generally present in the as-grown material in a supersaturated state. Hence during thermal treatments it will tend to form clusters and precipitates. 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. In this work important information about TDs has been obtained by IR absorption due to the electronic transitions, by which the change in concentration of oxygen with annealing time is studied in a step-annealing schedule rather than a continuous one. 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.

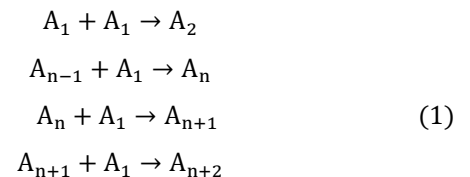
**Keywords:** CZ- Silicon, Thermal donor, Interstitial Oxygen, Oxygen loss, Diffusivity, Activation energy, Pre-annealing.

## INTRODUCTION

During the process of semiconductor device fabrication Si wafer is subjected to heat treatments. CZ-Silicon, rich in oxygen due to their growth process, on being subjected to heat treatment above 300 °C temperature yields donor like defects of many kind or species, collectively called as oxygen related donors or ODs. Fuller *et al.* [1] first exposed this problem in 1954 to the workers in the field to further investigate in view of the technological as well as industrial importance. Since then many workers have tackled this problem from different angles and with the help of much more sophisticated instruments.

The oxygen atoms occupy interstitial positions and are bonded to two silicon lattice atoms. The defects produced as a consequence of clustering of oxygen atoms in the temperature range 300-500 °C are double donors [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]. There is also an indirect evidence that this is associated with the emission of silicon interstitials even at temperature 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 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 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 (SiO<sub>2</sub>) 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-



Here,  $A_n$  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<sub>2</sub> 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-

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

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-

$$K = 8\pi r_c D_{oxy} \quad (3)$$

Where the capture radius  $r_c$  is about  $5\text{\AA}$  and  $D_{oxy}$ , the normal thermal diffusivity of dispersed interstitial oxygen is given by [12]-

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

Where E is the activation energy of oxygen diffusion.

## MATERIAL AND METHODS

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  $1 \times 2 \text{ cm}^2$  size and then subjected to heat treatment in Muffel furnace in air ambience. They were step-annealed at constant temperature of  $480^\circ\text{C}$  for different durations in the range of 20-70 hrs in steps of 10 hrs. Following methods are used for different measurements.

### 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

$$R_H = \frac{E_y}{j_x B_z} \quad (5)$$

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.

### 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  $1106 \text{ cm}^{-1}$  absorption band of the IR spectrum, using the following expression:

$$[O_i] = (3.03 \pm 0.02) \times 10^{17} \cdot \alpha_o \quad (6)$$

Where  $\alpha_o$  is the peak absorption coefficient for the  $1106 \text{ cm}^{-1}$  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

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

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

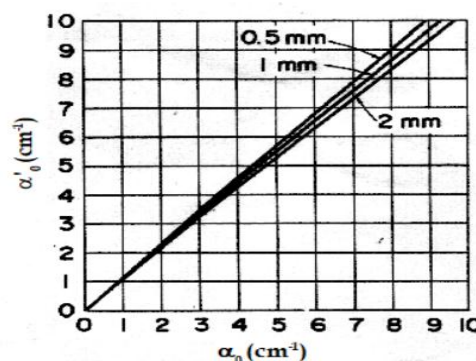


Figure 1: Relationship between  $\alpha'_o$  and  $\alpha_o$  for different sample thicknesses

So the procedure to determine the absorption coefficient is- draw base line on the transmission spectra between  $1300$  and  $900 \text{ cm}^{-1}$ , calculate  $T_{rel}$ . And then  $\alpha'_o$  using equation (7), then obtain value of  $\alpha_o$  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.

### 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 reciprocal of  $[O_i]_t$  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 as  $5\text{\AA}$  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.-

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

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

## RESULTS AND DISCUSSION

### 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 10 hrs were p-type. Step-annealed samples, annealed for total 20-40 hrs are n-type, while the samples annealed for 50-70 hrs are again p-type. As we already know that the un-annealed samples used by us are p-type, so the study shows that the sample annealed up to 10 hrs at  $480^\circ\text{C}$  maintains its nature as p-type. It is only after 10 hrs, that the sample changes its nature to n-type, suggesting the donor formation.

### 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  $\alpha'_o$  and  $\alpha_o$  [10] as shown in fig 1, using the line for sample thickness of 0.5mm (close to our value,  $d = 0.42\text{mm}$ ). The results are recorded in table 1. The concentration of interstitial oxygen at 20 hours total annealing (including 10hrs. of pre-annealing), is maximum and even exceeds that in un-annealed sample. But beyond this, annealing induces continuous decrease in oxygen concentration upto 70 hrs total annealing time. It is quite expected in the initial stage of TD formation. It is justified in the region of TD annihilation also, as TD annihilation does not mean breaking up of TD, but rendering it electrically neutral by aggregation of more and more oxygen atoms on it.

### Diffusion coefficient and activation energy

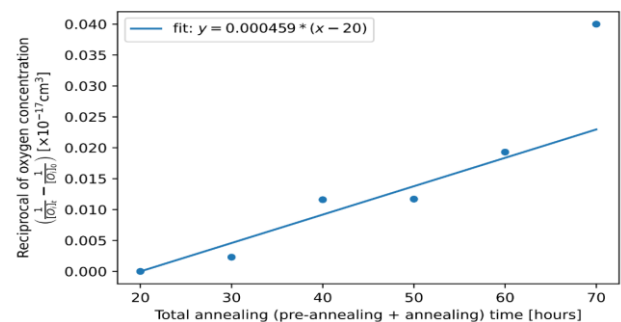
As it is already seen that the concentration of interstitial oxygen is maximum at 20hrs annealing time and after this point, as the step of annealing proceeds, there is a gradual decrease in oxygen concentration. Hence this point (i.e. 20hrs. annealing time) can be taken as reference point and for further readings in this annealing schedule, oxygen loss can be calculated by taking difference from the value at 20hrs point (assumed as initial oxygen concentration here). So for the difference in the

reciprocal values of concentration,  $[O_i]_0$  corresponds to the concentration at 20 hrs annealing in table 1.

**Table 1: Reciprocal of Oxygen Concentration against total annealing time**

| Sample no. | Total annealing (pre-annealing + annealing) time (hrs.) | Oxygen Concentration $[O_i]$ $\times 10^{17} \text{ (cm}^{-3}\text{)}$ | $1/[O_i]$ $\times 10^{-17} \text{ (cm}^3\text{)}$ | $1/[O_i]_t - 1/[O_i]_0$ $\times 10^{-17} \text{ (cm}^3\text{)}$ |
|------------|---|--|---|---|
| 1          | 10 + 10 = 20  | 28.516   | 0.0351  | 0   |
| 2          | 20+10 = 30  | 26.773   | 0.0374  | 0.0023  |
| 3          | 30+10=40  | 21.398   | 0.0467  | 0.0116  |
| 4          | 40+10=50  | 21.368   | 0.0468  | 0.0117  |
| 5          | 50+10=60  | 18.371   | 0.0544  | 0.0193  |
| 6          | 60+10=70  | 13.320   | 0.0751  | 0.0400  |

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  $5\text{\AA}$ , given by Newman and Mcquaid *et al.* [14, 15] as,

$$D_{oxy} = 10.15 \times 10^{-19} \text{ cm}^2/\text{sec at } 480^\circ\text{C}.$$

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

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

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

$$E = 2.576 \text{ eV}$$

This value of activation energy for oxygen diffusion is in very good agreement with the value (2.54 eV) estimated by Stavola *et al.* [12] and also with the value (2.4 - 3.5 eV) reported by Gosele and Tan [16].

## CONCLUSION

The carbon-rich p-type sample changes its nature to n-type after annealing for 20 hrs, suggesting that donor formation starts there and then the samples again converting to p-type after being annealed for 50 hrs, suggest the formation of some

electrically inactive clusters and annihilation of thermal donors. A decrease in concentration of oxygen is observed with annealing time due to formation of TDs and NDs.

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. Diffusivity of oxygen in silicon is calculated by the equation of second order kinetics, which comes out to be  $10.15 \times 10^{-19} \text{ cm}^2/\text{sec}$  at  $480^\circ\text{C}$ . Also the activation energy of the process is found out to be 2.576 eV.

## REFERENCES

- [1] C.S. Fuller; J.A. Ditzenberger; N.B. Hannay and E. Buehler, Phys. Rev. 96, p. 833 (1954).
- [2] R. Oeder and P. Wagner, Defects in semiconductor, ed. S. Mahajan and J.W. Corbett, Elsevier Publication Co., New York, p. 171 (1983).
- [3] D. Wruck and P. Gaworzewski, Phys.Stat. Solidi a 56, p. 557(1979).
- [4] C.S. Fuller and R.A. Logan, J. Appl. Phys. 28, p. 1427 (1957).
- [5] R. C. Newman; A. S. Oates and F. M. Livingston, J. Phys. C. 16, p. L 667 (1983).
- [6] W. Kaiser, Phys. Rev. 105, p. 1751 (1957).
- [7] B. Pajot; H. Compain; J. Lerouille and B. Clerjand, Physica (Utrecht) B 177/118, p. 110(1983).
- [8] W. Kaiser; H. L. Frisch; H. Reiss, Phys. Rev. 112, p. 1546(1958).
- [9] M. Suezawa and K. Sumino, Phys.Stat.Sol. (a) 82, p. 235(1984).
- [10] R. C. Newman, J. Phys. C: solid St. Phys. 18, p. L 967 (1985).
- [11] D. Mathiot, Appl. Phys. Lett. 51(12), p. 904(1987).
- [12] M. Stavola; J. R. Patel; L. C. Kimerling and P. E. Freeland, Appl.Phys. Lett. 42, p. 73(1983).
- [13] T. Iizuka; S. Takasu; M. Tajima; T. Arai; T. Nozaki; N. Inoue and M. Watanabe, J.Electrochem. Soc. 132(7), p. 1707 (1985).
- [14] R. C. Newman and R. Jones, 'Oxygen in Silicon', F. Shimura (ed.), Semicond. and Semimetals (Academic; San Diego) 42, p. 289(1994).
- [15] S. A. McQuaid; M. J. Binns; C. A. Londos; J. H. Tucker; A. R. Brown and R. C. Newman, J. Appl. Phys. 77(4), p. 1427(1995).
- [16] U. Gosele and T.Y. Tan, Appl. Phys. A 28, p.79 (1982).