ISSN: 2582-8118 ***Volume 3, Issue 5; Sept 2023***

INTERNATIONAL JOURNAL OF RESEARCH AND ANALYSIS IN SCIENCE AND ENGINEERING

Web: https://www.iarj.in/index.php/ijrase/index

2. Effect of The Presence of Carbon on the Course of Oxygen Related Donors (ODs) in Czochralski Silicon in Transition Region

Dr. Ritu Agarwal
Associate Professor,
Physics department, Bareilly College,
Bareilly.

ABSTRACT

Generation and behaviour of thermal donors (TD) and new donors (ND) as a result of annealing in transition temperature range (450°C-650°C) of carbon-rich boron-doped (p-type) CZ-silicon has been studied, as function of annealing time as well as of annealing temperature, by Hall studies, resistivity measurements and by FTIR studies. Transformation of TDs into NDs is studied with simultaneous appearance of thermal acceptors (TAs). It is seen that the conversion of incoming p-type sample to n-type is slow due to the compensation mechanism. Presence of carbon is found to suppress the growth of TDs, but to enhance TD annihilation. Carbon is also seen to enhance ND formation but not taking part in ND formation, itself.

KEYWORDS:

CZ- Silicon, Thermal donor, New donor, interstitial oxygen, substitutional carbon.

1. Introduction:

Czochralski (CZ) silicon is the backbone of electronic industry at present being the chiefly used semiconductor in bipolar or MOS technologies. CZ silicon picks up contamination from the fused silica crucible during its growth process. The main component of contamination from the walls of the crucible during the growth process of CZ-Si crystals is oxygen. These grown in oxygen impurities occupy bond-centred interstitial sites in CZ-Si. Their concentration in CZ-Si is of the order of 10^{18} cm^{-3}, which is several orders of magnitude greater than the concentration of electrically active donors and acceptors intentionally introduced to fabricate semiconductor devices. Although interstitial oxygen atoms O_i in their dispersed state are neutral [1,2], they play a crucial role in obtaining high device yields, since SiO_2 precipitates, formed by post-growth diffusion, act as sinks for inadvertently introduced fast diffusing metallic contaminants, which must be excluded from the device active regions - the process known as internal gettering. The presence of oxygen

also leads to a hardening of Si matrix, so that plastic deformation is prevented during device fabrication. On the other hand, presence of oxygen in CZ-Si induces various defects during the fabrication of devices, which is carried out by low temperature (<800°C) heat treatments. Supersaturated oxygen atoms in a silicon crystal become clustered due to annealing at temperatures above 300°C. Such clusters are known to be electrically active [3], which act as double donors and are termed as oxygen related donors (ODs). These donors are generally undesirable because they prevent the determination of intentionally doped dopant in the sample and hinders with its properties leading to device degradation. Depending upon the temperature range and annealing time, various types of ODs are generated in CZ-Si. Annealing in the range of 300-500°C produces thermal donors (TDs) [4], which get annihilated by the additional annealing at temperatures above 500°C [5] or by extending annealing time at a temperature of about 450°C. At higher temperatures 500-800°C, another group of donors called new donors (NDs) is formed [6], which is also thought to be accompanied by the formation of acceptors under certain conditions [7]. Many studies have indicated that the ND generation is enhanced by the low-temperature pre-annealing and the presence of carbon [6]. Carbon is also found to suppress the TD formation and enhance TD annihilation [8]. In the present study, p-type CZ-silicon, rich in carbon is studied for different annealing temperatures and annealing durations, the annealing temperature lying in the transition region, where TDs transform into NDs.

2. 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 1x2 cm^2 size and then subjected to heat treatment in Muffel furnace in air ambient. They were annealed either at constant temperature of 480°C for different durations in the range 1-20 hrs or for fixed duration of 10 hrs. at different temperatures from 450°C to 650°C.

2.1 Hall study and Resistivity Measurement:

Study of Hall effect is used to ascertain the nature of majority carriers in the samples. Resistivities of un-annealed and annealed samples are measured with a collinear four point probe technique. The impurity concentration is deduced from the measured resistivity with the help of Irvin's curves [9].

2.2 FTIR Measurement:

Absorption coefficients needed for determining the oxygen and carbon concentration is determined by FTIR absorption method, described by lizuka *et al.* [10]. Concentration of interstitial oxygen (Oi) can be derived from 1106 cm^{-1} absorption band whereas concentrations of substitutional carbon (C_s) in silicon can be derived from 605 cm^{-1} absorption band of the IR spectrum, using the following expressions, respectively :

$$[O_i] = (3.03 \pm 0.02) \times 10^{17} \alpha_O$$

and $[C_s] = l.l \times l0^{17}. \alpha_c$

Where α_O and α_c are peak absorption coefficients of the bands corresponding to oxygen and carbon, respectively.

3. Results and Discussion:

3.1 Resistivity Measurement and Donor Activity:

Resistivity measurements on un-annealed and annealed samples are performed to ascertain the number of donors generated or annihilated. It is observed that initially for annealing time of 1 hr. at temperature 480°C, the resistivity falls, but after that it increases sharply and reaches a maximum for annealing time of 5 hrs, as shown in fig. 1.

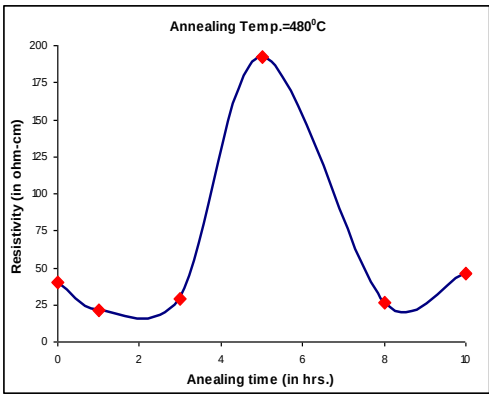

Fig.1: Resistivity v/s Annealing time

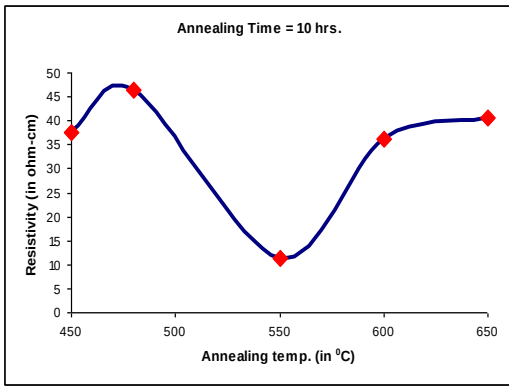

Fig.2: Resistivity v/s Annealing temperature

The initial rise in resistivity with annealing time is due to compensation mechanism. As the sample is p-type, initially both type of charge carriers would be present-those of thermal donors and of chemical acceptors and therefore a recombination of both type of carriers takes place, resulting in the decrease in carrier concentration [11,12,13]. Hall studies have showed that the sample is p-type even after annealing of 10 hrs, indicating that the recombination continues upto 10 hrs. of annealing and the samples are in unstable situation. The sample converts to n-type after annealing of 20 hrs. Here the growth of TDs appear to be slow, which can be attributed due to presence of carbon in high concentration (initial concentration of substitutional carbon as determined by FTIR measurements is about $6.7xl0^{17}$ cm^{-3}), confirming the fact that the presence of carbon suppresses the TD formation [8].

Actual number of donors generated can not be deduced as both type of impurities are present simultaneously and the dominant nature of sample is p-type upto 10 hrs. of annealing [11]. What we measure by Irvin's curves is the number of impurity atoms, which are majority acceptor atoms here. Upto 1 hr. of annealing the number of net acceptor atoms increases, which may be due to breaking up of some already existing TDs, created during crystal growth, as the crystals used were as grown without any donor-killer heat treatment so that they already contained TDs with densities of the order of 10^{14} cm^{-3}, as opined by Kamiura *et al.* [14]. After that, upto 5 hrs. of annealing, the concentration of impurity atoms decreases

by large amount, suggesting the formation of thermal donors. Again the increase in concentration of net acceptor impurities upto 10 hrs. of annealing show the neutralisation of charge carriers. Only after 20 hrs. of annealing, we get the concentration of donors as the TDs now have completely compensated for chemical acceptors and the sample has converted to n-type.

Variation in resistivity with temperature as shown in fig. 2, shows that first the resistivity increases from 450°C to 480°C, suggesting the decrease in concentration of TDs due to TD annihilation. This is also evident by the fact that the sample reverses its nature to p-type at 480^0C. From 480^0C to 550^0C, the resistivity of the sample decreases, which can be attributed to the generation of NDs, the sample again converting to n-type. Beyond 550^0C upto 650^0C, the resistivity again increases and the sample again converts to p-type, this time it can be due to the generation of more and more thermal acceptors (TAs) with increase in temperature. There is also a possibility of creation of recombination centres and ND like defects which act as electrically inactive centres, as suggested by Babich *et al.* [7] and also observed by Prakash and Singh [13].

3.2 FTIR Measurement and Oxygen Precipitation:

Results of FTIR studies for interstitial oxygen show that initially the absorpiton coefficient and hence the concentration of interstitial oxygen decreases and the amount of oxygen precipitated increases, with the increase in annealing time (fig. 3). Clearly, this region indicates the formation of thermal donors and the loss in interstitial oxygen is due to the clustering of more and more oxygen atoms to from TDs. But after 8 hours of annealing, the oxygen concentration increases, suggesting that some TDs might have been broken releasing oxygen that shifts to interstitial sites.

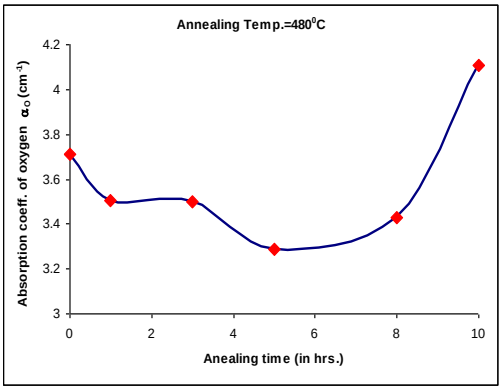

Fig.3: Absorption coeff. of oxygen v/s annealing time

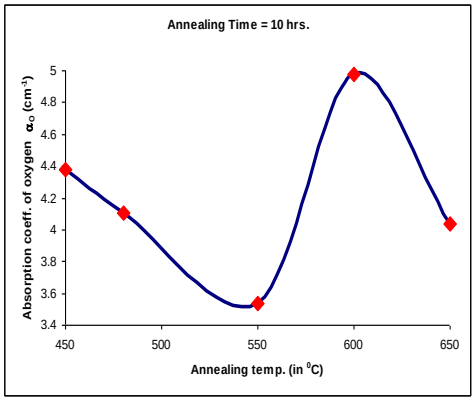

Fig.4: Absorption coeff. of oxygen v/s annealing temperature

Variation in oxygen concentration with annealing temperature (fig. 4) indicates that the region from 450^0C to 550^0C, which is the region of TD annihilation upto 480^0C and ND formation after that, witnesses a reduction in oxygen concentration, which is obvious as the TD annihilation means rendering of TDs into electrically inactive clusters by aggregation of more and more oxygen atoms to the TDs, reducing the concentration of interstitial

oxygen. Same is the case with ND formation. But after this, as the annealing temperature is increased further upto 600^0C, a remarkable increase in oxygen concentration is observed, suggesting breaking up of clusters of NDs and simultaneous release of oxygen. As this region has been assigned as the region of formation of thermal acceptors (TAs) and recombination centres, on the basis of Hall and resistivity measurements, it may be thought that the formation of TAs may accompany breaking up of NDs, releasing oxygen.

3.3 Role of Carbon in Donor Formation:

Analysing FTIR spectra for concentration of substitutional carbon, it is seen that the concentration of carbon increases for TD formation stages and decreases for TD annihilation stages (fig. 5 & 6). This decrease in concentration of Cs with TD annihilation is in perfect agreement with Kamiura *et al.* [14, 15], who proposed the hypothesis that the Si self - interstitials created during the TD formation, are liberated on TD annihilation and simultaneously eject substitutional carbon into an interstitial site, reducing the concentration of Cs. This interstitial carbon rapidly diffuses to TDs to aggregate with them, forming electrically inactive clusters.

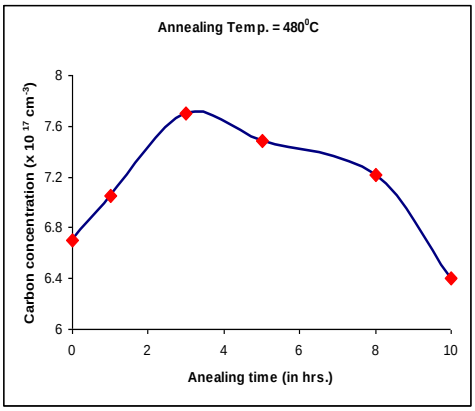

Fig.5: Concentration of substitutional carbon v/s annealing time

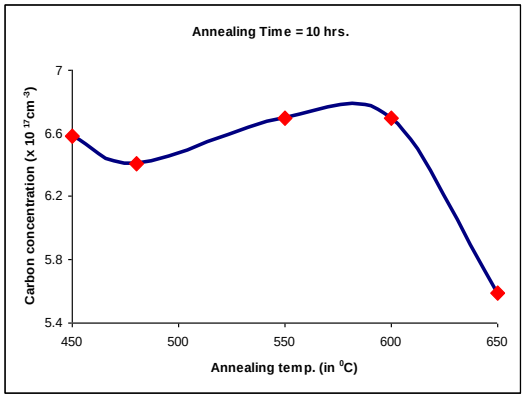

Fig.6: Concentration of substitutional carbon v/s annealing temperature

Increase in concentration of Cs with TD formation can be explained as follows-As the TDs are formed, Si self- interstitials are created, vacating their lattice sites. Carbon atoms, either at interstitial sites or at any other defect trap, may fit itself in these vacant lattice sites, transforming into substitutional carbon.

For ND formation, Leroueille [16] and Ohsawa *et al.* [17] observed, simultaneous annihilation of substitutional carbon atoms. But Fukuoka *et al.* [18] detected no participation of carbon atoms directly in the formation of ND. In the present study, no decrease in concentration of C_s is observed, rather slight increase is observed, which can be explained as follows : formation of NDs follow the annihilation of TDs, which is accompanied by the transformation of C_s into C_i and C_i being aggregating with TD to form electrically inactive clusters. These clusters are then broken into small clusters, which are NDs. This process, therefore, must be accompanied by the liberation of interstitial carbon,

C_i, which can again transform into C_s. Therefore carbon, itself does not take part in ND formation but as already seen in this study, its presence enhances the ND formation. So the results are in agreement with Fukuoka *et al.* but contradict the observations of Leroueille and Ohsawa *et al.*

4. Conclusion:

In carbon-rich p-type sample the stability in donor formation is not attained for initial annealing time (upto 10 hrs at 480°C temp.) due to compensation mechanism. The growth of thermal donors is slow, due to the presence of initial carbon in high concentration. Presence of carbon is seen to enhance TD annihilation and ND formation, but carbon does not take part in ND formation itself. Formation of thermal acceptors accompany breaking up of new donors.

References:

1. J.R. PATEL, in: 'Semiconductor Silicon 1981', Ed. H.R. Huff, R.J. Kriegler, and Y. Takeishi, The Electrochemical Society, Pennington (N.J.), p. 189 (1981).
2. U. GOSELE and T.Y. TAN, Appl. Phys. A 28, p.79 (1982).
3. C.S. FULLER and R.A. LOGAN, J. Appl. Phys. 28, p. 1427 (1957).
4. C.S. FULLER; J.A. DITZENBERGER; N.B. HANNAY and E. BUEHLER, Phys. Rev. 96, p. 833 (1954).
5. R. OEDER and P. WAGNER, Defects in semiconductor, ed. S. Mahajan and J.W. corbett, Elsevier Publication Co., New York, p. 171 (1983).
6. A. KANAMORI and M. KANAMORI, J. Appl. Phys. 50(12), p. 8095 (1979).
7. V.M. BABICH; N.P. BARAN; A.A. BUGAI; A.A. KONCHITS; V.B. KOVALCHUK; V.M. MAKSIMENKO and B.D. SHANINA, Phys. Stat. Sol. (a) 109, p. 537 (1988).
8. A.R. BEAN; R.C. NEWMAN, J. Phys. Chem. Solids. 33, p. 255 (1972).
9. S.M. SZE and J.C. IRVIN, Solid State Electron. 1l, p. 599 (1968).
10. T. IIZUKA; S. TAKASU; M. TAJIMA; T. ARAI; T. NOZAKI; N. INOUE and M. WATANABE, J.Electrochem. Soc. 132(7), p. 1707 (1985).
11. M. SUEZAWA and K. SUMINO, Phys. Stat. Sol. (a) 82, p. 235 (1984).
12. OM PRAKASH AND S. SINGH, Indian J. Phys. 69A(5), 509-515 (1995)
13. OM PRAKASH AND SHYAM SINGH, Bull. Mater. Sci. 21(5), p. 399 (1998)
14. YOICHI KAMIURA; TAKASHI MAEDA; YOSHIFUMI YAMASHITA and MINORU NAKAMURA, Jpn. J. Appl. Phys. 37, p. L 101 (1998).
15. Y. KAMIURA; Y. UNO and F. HASHIMOTO, Jpn. J. Appl. Phys. 32, p. L1715 (1993).
16. J. LEROUEILLE, Phys. Status Solidi (a) 67, p. 177 (1981).
17. A. OHSAWA; R. TAKIZAWA; K. HONDA; A. SHIBATOMI and S. OHKAWA, J. Appl. Phys. 53, p 5733 (1982).
18. NOBORU FUKUOKA; KAZUHIKO NAKATA; MAKOTO HONDA; KOZO ATOBE and TETSUYA KAWAKUBO, 'Defects control in Semiconductors' K. Sumino (ed.), Elsevier Science Publishers B.V. (North-Holland), p. 547 (1990).
19. R.SINGH; P.B. NAGABALASUBRAMANIAN; Int. J. of Appl. Engg. Research ISSN 0973-4562 Volume 14(2) p. 43(2019).
20. KAZUHISA TORIGOE; TOSHIAKI ONO; AIP advances, 10,045019 (2020); https://doi.org/10.1063/1.5140206.