



Effect of High Temperature Pre-Annealing on Thermal Donors in N-Doped CZ-Silicon

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Abstract: Role of high temperature pre-annealing at 1000°C for shorter duration of 10 h and longer duration of 40 h, followed by annealing at 650°C up to 90 h, has been studied in N-undoped /doped CZ-Silicon. Four Probe and FTIR Spectroscopy tools have been employed in this study. The increase in carrier concentration in N-doped CZ-Silicon occurs at and above 20 h of annealing and the rate of increase is quantitatively more in sample without pre-annealing as compared to pre-annealed at 1000°C. It is also observed that neither the shorter nor the longer high temperature pre-annealing time has any effect on carrier concentration in N-doped CZ-Silicon.

Keywords: Semiconductors, CZ-Silicon, Thermal Donors, Nitrogen

PACS: 71.55.-I; 72.20.-I; 72.80.-r

I. 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. Presence of oxygen in silicon for device processing helps to promote internal gettering process, while a certain level of oxygen concentration is quite essential to provide mechanical strength to the wafer [1], [2], [3]. However, excessive amount of oxygen leads to the degradation of device yield. In the recent past optical and electrical properties of nitrogen doped/ implanted silicon have been carried out and this material showed a great promise for future device application. A lot of self-contradicting experimental data are 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. Inherent presence of oxygen and nitrogen 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. Annealing treatment of the silicon crystal with high oxygen contents in the temperature range 400-1200°C produces various kinds of defects [4], [5], [6], [7]. The question of formation and diffusion of molecule like oxygen 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 nitrogen in donor formation in CZ-Silicon annealed at temperature 650°C, preceded high temperature pre-annealing at 1000°C.

II. MATERIALS AND METHODS

The silicon wafers are n-type with orientation <111> and thickness 500 µm. Some other specifications are given in Table 1. The wafers were cut into small pieces of the size 1 × 2 cm² and then subjected to heat treatment in ambient air. We do not anneal the samples continuously at constant temperature, but step annealing schedules of 10 hours are fixed for Group A and B samples at constant temperature of 650°C up to 90 h of annealing. Both groups of samples were annealed at 650°C for 90 h preceded by the high temperature pre-annealing at 1000°C for 10 h and 40 h, respectively.

Table 1 : Specifications of the CZ-Silicon samples

Sample	Resistivity (Ohm-cm)	Initial concentration (atoms/cm ³)		
		Oxygen	Carbon	Nitrogen
Group A	8	4.8×10^{17}	3.0×10^{15}	–
Group B	8	7.3×10^{17}	2.5×10^{15}	5.9×10^{15}

Resistivity of silicon was measured by Four Probe method and then was converted into carrier concentration by Irvin's Curve [8]. The results are also supplemented by Hall measurement in order to ascertain the carrier concentration. FTIR studies have been used to identify the presence of N, O and N-O complexes. Interstitial oxygen in silicon causes absorption at wave number 1107 cm⁻¹ at room temperature due to asymmetric vibration of SiO₂ complex [9]. Nitrogen in silicon causes absorption at wave number 967 cm⁻¹ while N-O complexes has absorption peaks at wave number 240, 242 and 249 cm⁻¹ [10]. These absorption peaks are superimposed on phonon excitations of the silicon.

III. RESULTS AND DISCUSSION

The collinear four probe method used for resistivity measurements on the un-annealed and annealed CZ-silicon samples in air ambient showed that the resistance differs from point to point in as grown silicon sample while in annealed at 650°C for 1 h, the resistance is almost constant throughout the sample which leads us to conclude that the inhomogeneties present in as grown silicon samples are reduced to a greater extent. The results to be followed relate to the donors generated in N-undoped (Group A) and N-doped (Group B) CZ-silicon annealed at 650°C respectively, preceded by at high temperature pre-annealing 1000°C.

From comparative plots of donors concentration in Group A and B samples annealed at 650°C as a function of annealing time for 90 h, as in Fig. 1, it can be inferred that there is a gradual increase in the concentration of donors after the first 10 h of step annealing in Group A samples, while the donor concentration remains almost unchanged in Group B samples. This, in turn, leads to infer that the presence of nitrogen suppressed the donors formed in the Group A samples. The results are in good agreement with Prakash and Singh [11], Alt et al [12] and Newman [13]. During the course of crystallization of silicon in the presence of nitrogen it is quite natural to expect that the nitrogen atoms occupy substitutional sites in silicon and may exist in N-N pairs. The possibility of the formation of N-O complexes and electrically inactive N-O clusters, having more than one oxygen atom, can not be ruled out [14]. Further heat treatment of the samples changes the agglomeration process of the constituent atoms of the clusters and hence may suppress the formation of new donor in the Group B samples due to the formation of electrically inactive embryos.

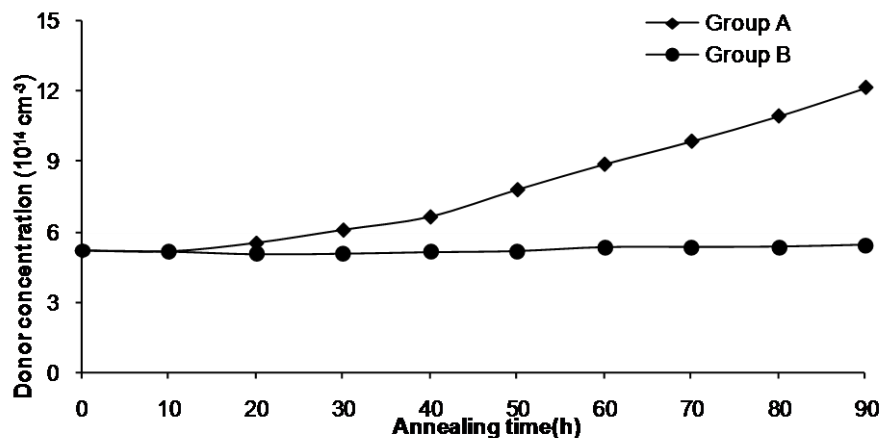


Fig. 1: Donor concentration of Group A and B samples as a function of annealing time at 650°C

The behaviour of donors generated in Group A samples pre-annealed at 1000°C for 0 h, 10 h and 40 h followed by annealing at 650°C, as a function of annealing duration up to 90 h is shown in Fig. 2. An increase in pre-annealing duration helps in maintaining the constancy of carrier concentration almost equal to the initial value throughout the entire cycle of annealing treatment. The increase in carrier concentration occurs at and above 20 h of annealing and the rate of increase is quantitatively more in the samples without pre-annealing as compared to pre-annealed ones. Even high temperature pre-annealing at 1000°C, complete annihilation of parent nuclei having radii less than or more than critical radius, does not take place. Nuclei having radii greater than critical radius are in a position to attract more number of oxygen atoms resulting in the elimination of donors and formation of oxygen precipitates. Longer high temperature pre-annealing duration is suicidal to the existence of as grown nuclei of donors. This is expected on logical grounds also.

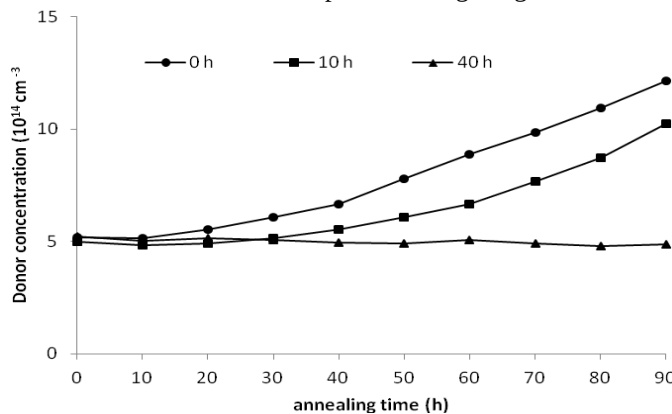


Fig. 2: Plot of donor concentration of Group A samples pre-annealed at 1000°C for 0 h, 10 and 40 h as a function of annealing time at 650°C

The carrier concentration in Group B samples pre-annealed at 1000°C for 10 h and 40 h followed by annealing at 650°C, as a function of annealing time up to 90 h is shown in Fig. 3. It is observed that neither the shorter nor the longer pre-annealing time has any effect on carrier concentration. In the samples without pre-annealing as shown in Fig. 4, the satellite peaks are associated with nitrogen and the major peak is due to presence of oxygen. The pre-annealing at 1000°C for 10 h results in the disappearance of nitrogen related peaks and a subsequent reduction in the magnitude of oxygen related peak at 1107 cm⁻¹. This is clearly indicative of the oxygen out diffusion process leading to the formation of more and more electrically inactive clusters. Because no nuclei of donors exist in the high temperature pre-annealed samples, donors are not generated in the annealing at 650°C as also suggested by Yang *et al* [15], Fujita *et al* [16] and Dubey and Singh [17].

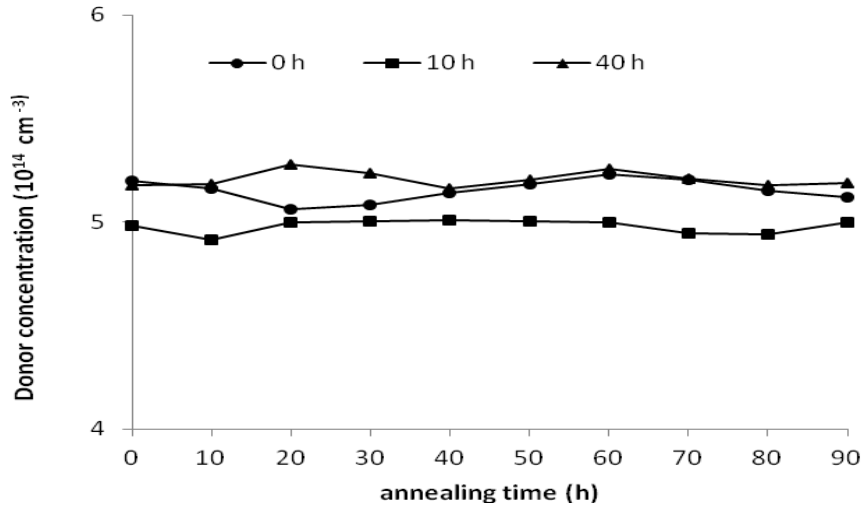


Fig. 3: Variation of donor concentration of Group B samples pre-annealed at 1000°C for 0 h, 10 and 40 h as a function of annealing time at 650°C

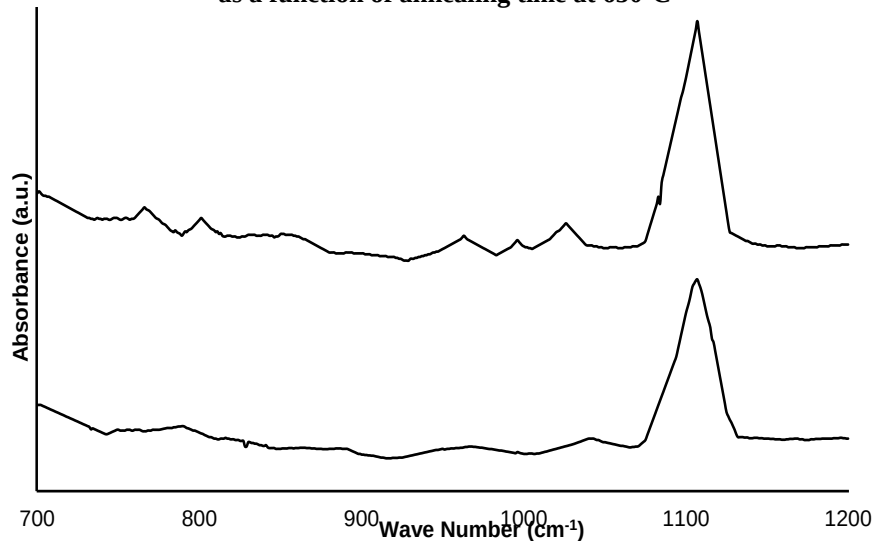


Fig. 4: FTIR spectra of Group B samples (a) without pre-annealing (b) high temperature pre-annealing for 10 h

The FTIR spectra of Group A and B samples annealed at 650°C for 1 h are shown in Fig. 5. Hara *et al* [18] and Wagner *et al* [19] suggested that the optical absorbance lines in the range 350-500 cm⁻¹ are considered to be related to the thermal donors in silicon. As can be seen from the figure (350-500 cm⁻¹), there is no absorbance peak in Group B sample, while Group A sample exhibits the appearance of several absorbance peaks. This means that the presence of nitrogen assists in the suppression of thermal donors. The appearance of optical lines at 240, 242 and 249 cm⁻¹ in IR spectra of Group B sample is due to nitrogen because these lines do not appear in Group A sample.

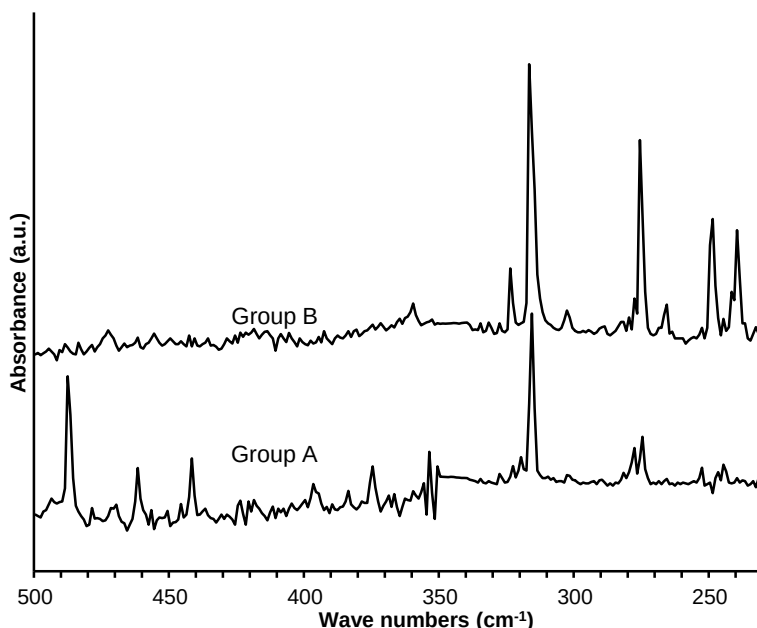


Fig. 5: FTIR spectra of Group A and B samples annealed at 650°C for 1 h in the range 230-500 cm⁻¹
 Suezawa *et al* [20] and Dubey [21] studied the properties of oxygen-nitrogen complexes in nitrogen doped silicon and considered that the oxygen-nitrogen complexes related to 240, 242 and 249 cm⁻¹ optical lines have the properties of the shallow thermal donors. Our results agree with their conclusion. The above discussion leads us to conclude the existence of two types of oxygen related donors. The first of its kind is shallow thermal donor associated with the N-O complexes and the second one is thermal donor related to the oxygen impurity only assisted by silicon self-interstitialcy.

IV. CONCLUSION

In order to ascertain the effect of nitrogen on the formation of oxygen related donors in step-annealed CZ-Silicon at 650°C preceded by high temperature pre-annealing treatments of 10h and 40h, resistivity measurement and FTIR have been used as two basic tools. It is found that donors generated in Group A and B samples annealed at 650°C as a function of annealing time for 90 h, it can be inferred that there is a gradual increase in the concentration of donors after the first 10 h of step annealing in Group A samples, while the donor concentration remains almost unchanged in Group B samples. This, in turn, leads to infer that the presence of nitrogen suppressed the donors formed in the Group A samples. The increase in carrier concentration in N-doped CZ-Silicon samples occurs at and above 20 h of annealing and the rate of increase is quantitatively more in sample without pre-annealing as compared to pre-annealed at 1000°C. It is also observed that neither the shorter nor the longer high temperature pre-annealing time has any effect on carrier concentration.

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