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Effect of Low Temperature Pre-annealing on Oxygen Related Donors Formation in N-Doped CZ-Silicon

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Abstract

In view of the interesting informations revealed by the studies of nitrogen in silicon, an attempt has been made to look into the behaviour of low temperature pre-annealing at 480⁰C for shorter duration of 10 h and longer duration of 40 h in N-doped CZ-Si annealed at 650⁰C up to 90 h by subjecting the samples to two basic characterizing tools. Low temperature pre-annealing for a shorter duration followed by annealing at 650⁰C does not register an increase in donor concentration, while reverse is true for pre-annealing of 40 h. Longer pre-annealing time at low temperature brings about a larger increase in the donor concentration during the annealing. Donors generated in N-undoped CZ-Si samples never attain saturation up to 90 h of annealing at 650⁰C, while in N-doped silicon annealed for 60 h, the donors generated reached a saturation stage and no change is observed by annealing for longer duration.

Key Words: Semiconductors; CZ-Silicon; Thermal donors; Nitrogen
PACS: 71.55. - i; 72.20. - i; 72.80. – r

Introduction

Czochralski (CZ) silicon is the most widely used semiconductor for integrated circuit formation. Inherent presence of oxygen and nitrogen plays a crucial role in the formation mechanism of different oxygen related 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 400-1200⁰C produces various kinds of defects [1-4]. The question of formation and diffusion of molecule like oxygen at low temperature 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 650⁰C, preceded by low temperature (480⁰C) pre-annealing schedules.

Materials and Methods

The CZ-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 cm^2 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 650⁰C up to 90 h of annealing. Both groups of sample were annealed at 650⁰C for 90 h preceded by the low temperature pre-annealing at 480⁰C for 10 and 40 h, respectively.

Resistivity of silicon was measured by Four Probe method and then was converted into carrier concentration by Irvin's Curve [5]. 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 SiO_2 complex [6]. 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} [7]. These absorption peaks are superimposed on phonon excitations of the silicon.

Table 1: Specifications of the CZ-Silicon samples

Sample	Resistivity (Ohm-cm)	Initial Concentration (atoms/cm^3)		
		Oxygen	Nitrogen	N-O Complex
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}

Results and Discussion

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^{0}C, respectively preceded by low temperature pre-annealing at 480^{0}C.

From comparative plots of donors concentration in Group A and B samples annealed at 650^{0}C as a function of annealing time for 90 h, as a Fig. 1, it can be inferred that there is a gradual increase in the concentration of donors after 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 [8], and Newman [9]. 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 [10-12]. 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.

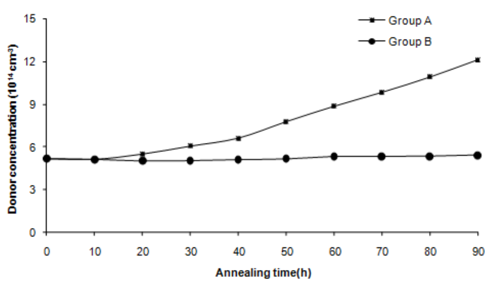

Fig. 1 : Donor concentration of Group A and B samples as a function of annealing time at 650^{0}C

Fig.2 deals with the donor concentration in Group A silicon samples pre-annealed at low temperature of 480^{0}C for a period of 10 and 40 h followed by annealing at 650^{0}C, as a function of annealing time up to 90 h. Low temperature pre-annealing for a shorter duration followed by annealing at 650^{0}C does not register an increase in the donor concentration, while reverse is true for pre-annealing of 40 h. This increase in carrier concentration/ donors may be attributed to the formation of thermal donors during pre-annealing. Thermal donors so formed are likely to be annihilated by annealing at 650^{0}C for shorter duration and subsequent annealing for longer duration may again help to increase donors. The increase of carrier concentration in N-undoped silicon samples pre-annealed for shorter duration meets the same fate as in silicon not subjected to any pre-annealing. This is possibly due to the fact that the number of embryos associated with new donors in 480^{0}C annealed samples for 10 h, is much less than both the numbers of electrically inactive embryos likely to be present initially and those formed during the annealing at 650^{0}C.

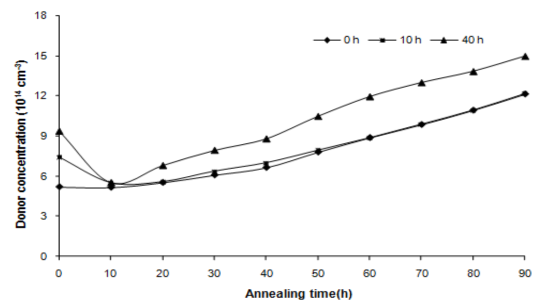

Fig. 2 : Donor concentration of Group A samples pre-annealed at 480^{0}C for 0, 10 & 40 h vs. annealing time at 650^{0}C

The donor concentration in the samples pre-annealed at 10 h and 40 h increased from its initial value 5.2 × 10^{14} cm^{-3} to 8.51 × 10^{14} cm^{-3} and 18.85 × 10^{14} cm^{-3} respectively in Group B silicon samples annealed at 650^{0}C preceded by low temperature pre-annealing at 480^{0}C, as depicted in Fig. 3. The concentration in Group B samples decreased to approach the initial value after 10 h of annealing at 650^{0}C, the behaviour almost identical to that as observed in Group A samples. After annealing for 40-60 h, the concentration in the samples at 650^{0}C for 10 and 40 h reached to 7.46 × 10^{14} cm^{-3} and 19.28 × 10^{14} cm^{-3} respectively. Thereafter, the concentration did not increase with further heat treatment at 650^{0}C up to 90 h, indicating that no more donors are formed. It is also noteworthy that longer pre-annealing time at low temperature 480^{0}C brings about a larger increase in the carrier concentration during the annealing at 650^{0}C, i.e. more donors are formed.

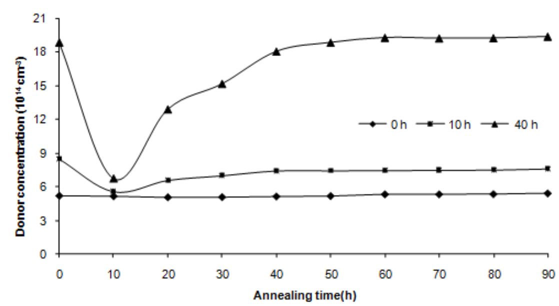

Fig. 3 : Donor concentration of Group B samples pre-annealed at 480^{0}C for 0, 10 & 40 h vs. annealing time at 650^{0}C

As already discussed earlier, the interaction of oxygen with nitrogen results in the formation of electrically active N-O complexes and involvement of more than one oxygen atom may lead to the formation of electrically inactive N-O_m clusters [13-15]. But, the net carrier concentration in N-doped Group B samples pre-annealed at 480^{0}C for 10 and 40 h increases because the process of thermal donor formation dominates. Figures 2 and 3 also clearly reflect that the concentration of oxygen related donors in the pre-annealed Group B samples is higher than that of Group A samples. It may be due to the presence of more initial oxygen concentration in Group B samples.

The optical absorbance by FTIR spectra at 967 cm^{-1} (nitrogen), 1107 cm^{-1} (oxygen) and 249 cm^{-1} (N-O complex) lines in Group B samples annealed at 650⁰C, as a function of annealing time is listed in Table 2. These FTIR studies lend support to the above findings showing that the donors get saturated in Group B samples at 60 h of annealing because the absorbance of N and N-O complexes turn out to be zero. One of the simplest explanations to this behaviour is based on the fact that subsequent annealing beyond 60 h may help in dissociating N-O complexes, making N and O isolated. It appears to help enhance the concentration of nitrogen and oxygen atoms but actually it goes down with annealing time. This happens due to the formation of more and more electrically inactive N-O_m clusters.

Table 2: Optical absorbance of N, O and N-O complexes by FTIR spectra

Annealing time (h)	Absorbance (a.u.)		
	Nitrogen	Oxygen	N-O Complex
0	0.0475	1.320	0.438
10	0.0311	1.301	0.415
20	0.0180	1.291	0.372
30	0.0152	1.284	0.297
40	0.0120	1.275	0.218
50	0.0062	1.259	0.112
60	0.0	1.242	0.0
70	0.0	1.212	0.0
80	0.0	1.186	0.0
90	0.0	1.158	0.0

The FTIR spectra of Group A and B samples annealed at 650⁰C for 1 h shown in Fig. 4. Hara *et al* [16] 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 top nitrogen because these lines do not appear in Group A sample.

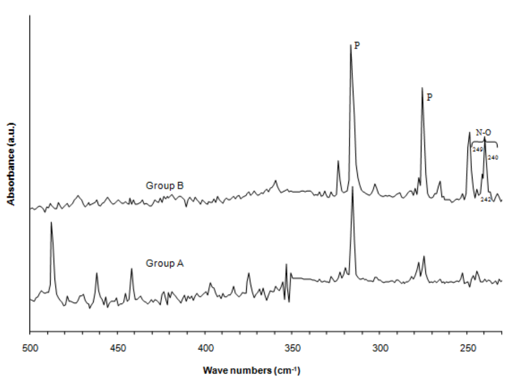

Fig. 4 : FTIR spectra of Group A and B samples annealed at 650⁰C for 1 h in the range 230-500 cm^{-1}

Suezawa *et al* [17] 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 line 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.

Summary

In order to ascertain the effect of nitrogen on the formation of oxygen related donors in step-annealed CZ-Silicon at 650⁰C preceded by low temperature pre-annealing treatments of 10 h and 40 h, 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 650⁰C 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 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 of carrier concentration in N-undoped silicon samples pre-annealed at 480⁰C for shorter duration meets the same fate as in silicon not subjected to any pre-annealing. The carrier concentration of N-doped samples pre-annealed at 480⁰C did not increase after 60 h of annealing at 650⁰C, indicating that no more donors are formed. The two types of oxygen related donors are formed in CZ-Silicon during heat treatment. 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.

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