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Short Communication

Role of nitrogen on formation of oxygen related donors in step annealed CZ-Silicon

S. SINGH*, B. C. YADAV[a], R. SINGH[a]
Sagar Institute of Technology & Management, Barabanki (U.P.), India
aDepartment of Physics, Lucknow University, Lucknow (U.P.), India

Effect of low temperature pre-annealing at 480°C and high temperature at 1000°C for shorter duration of 10 h and longer duration of 40 h, followed by annealing at 650°C up to 900 h, has been studied in N-undoped/doped CZ-Silicon. Low temperature preannealing for a shorter duration followed by annealing at 650°C does not register an increase in donor concentration, while reverse is true for pre-annealing of 40h. Longer pre-annealing time at low temperature brings about a larger increase in the donor concentration during the annealing. Donors generated in N-un-doped samples never attain saturation up to 90 h of annealing at 650°C, while in N-doped silicon annealed for 60 h, they reached a saturation stage and no change is observed by annealing for longer duration. Neither the shorter nor the longer pre-annealing time has any effect on carrier concentration in N-doped samples pre-annealed at 1000°C. Existence of shallow thermal donors associated with N-O complexes and thermal donors associated with oxygen impurity only assisted by silicon self-interstitialcy has been established.

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1. 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]. However, excessive amount of oxygen leads to the degradation of device yield. In the recent past study on optical and electrical properties of nitrogen doped/implanted silicon has been carried out and this material showed a great promise for future device applications. 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 [2]. 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 behaviors of oxygen and nitrogen in donor formation in CZ-Silicon annealed at temperature 650°C, preceded by low temperature (480 °C) and high temperature (1000 °C) pre-annealing schedules.

2. Materials and methods

The silicon wafers used in the study were n-type with orientation <111> and thickness 500µm. Some other specifications are given in Table 1. The wafers were cut into small pieces of the size 1x2 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 650°C up to 90 h of annealing. Both groups of samples were annealed at 650°C for 90 h preceded by the low temperature pre-annealing at 480°C for 10 and 40 h, respectively. The same process was repeated for high temperature pre-annealing at 1000°C for 10 h and 40 h respectively. Recently rapid thermal processing has been used for oxygen precipitation[3].

Table 1. Specifications of CZ-Silicon samples.

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

2.1. Resistivity measurement and donor generation

The resistivity of silicon wafer was measured with a collinear four probe array at room temperature and the number of carriers is derived from Irvin's Curve [4].Assuming that the mobility remains constant; the difference of the two carrier concentrations between un-annealed and annealed samples gives the donors generated or annihilated during the heat treatment.

2.2 FTIR Measurement

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 the asymmetric vibration of SiO_2 complex [5]. Nitrogen in silicon causes absorption at wave number 967 cm^{-1} while N-O complexes have absorption peaks at wave number 240, 242 and 249 cm^{-1} while N-O complexes have absorption peaks at wave number 240, 242 and 249 cm^{-1} [6]. These absorption peaks are superimposed on phonon excitations of the silicon.

3. Results and Discussion

3.1. Effect of Nitrogen doping

Resistivity of group A silicon samples annealed in the temperature range 650-1000°C as a function of annealing time for 4 h is shown in Fig. 1. The resistivity of N-doped silicon samples annealed at different temperatures first increases with annealing time up to 1 h before attaining a relatively stable value which is higher at higher annealing temperatures [7]. An annealing time to reach relatively stable resistivity in the group A silicon samples annealed at different temperatures is different. Maximum stable resistivity is obtained in the samples annealed at temperature > 900°C.

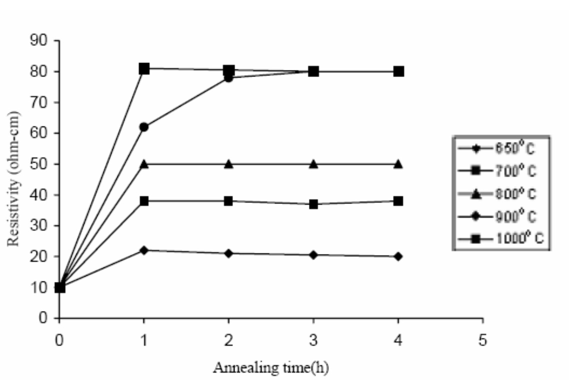

Fig.1. Resistivity of group A silicon sample vs. annealing time in the range 650-10000C.

3.2. Annealing at a reference temperature of 650 °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. 2, 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 [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 cannot be ruled out [10]. 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 donors in the group B samples due to the formation of electrically inactive embryos.

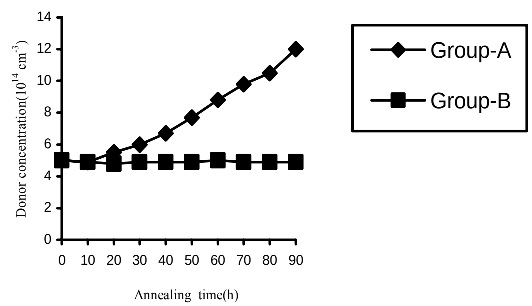

Fig. 2. Comparative plots of donors concentration in group A and B samples annealed at 650°C as a function of annealing time for 90 h.

3.3. Effect of low temperature pre-annealing

Fig. 3 deals with the donor concentration in Group A silicon samples pre-annealed at low temperature of 480°C for a period of 10 & 40 h followed by annealing at 650°C, as a function of annealing time up to 90 h. Low temperature pre-annealing for a shorter duration followed by annealing at 650°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 preannealing. Thermal donors so formed are likely to be annihilated by annealing at 650°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°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°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 and 18.85×10^{14} cm^{-3} respectively in Group B silicon samples annealed at 650°C preceded by low temperature Pre-annealing at 480°C as depicted in Fig. 4. The concentration in Group B samples decreased to approach the initial value after 10 h of annealing at 650°C, the behaviours almost identical to that as observed in Group A samples. After annealing for 40-60 h, the concentration in the samples at 650°C for 10 and 40 h reached to 7.46×10^{14} cm^{-3} and 19.28×10^{14} cm^{-3} respectively.

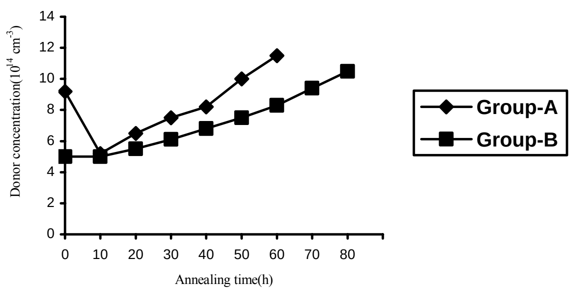

Fig. 3. The donor concentration in group A silicon samples pre annealed at low temperature of 480°C for a period of 10 & 40 h followed by annealing at 650°C, as a function of annealing time up to 90 h.

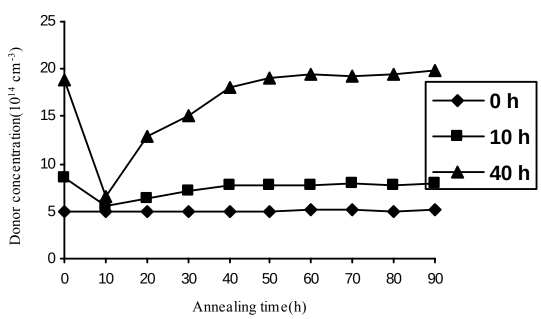

Fig. 4. The donor concentration in the samples pre-annealed at 10 h and 40 h in group B silicon samples annealed at 650°C preceded by low temperature pre-annealing at 480°C.

Thereafter, the concentration did not increase with further heat treatment at 650°C up to 90 h, indication that no more donors as formed. It is also noteworthy that longer pre-annealing time at low temperature 480°C brings about a larger increase in the carrier concentration during the annealing at 650°C, i.e. more donors are formed. 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_n-O_m clusters [11]. But, the net carrier concentration in N-doped Group B samples pre-annealed at 450°C for 10 and 40 h increases because the process of thermal donor formation dominates. Figures 2 and 3 also clearly reflect 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. A close look at Figs. 3 and 4 reveals that the donor concentration in Group A samples never attain saturation up to 90 h of annealing at 650°C, while in Group B samples the donors reached a situation stage at 60 h of annealing and no change is observed by annealing for longer duration. This behaviors may be explained in view of the fact that in the former case each process such as crystal growth, pre-annealing and annealing, adds more and more nuclei vulnerable to the growth of thermal donors while in the later case lesser number of oxygen atoms are available for donor formation due to the generation of N-O complexes, N_n-O_m clusters and electrically inactive embryos [12]. It is also evident from the Fig. 3 that the saturated donor concentration is almost the same as their initial values due to the simultaneous ongoing processes of the dissociation of the clusters and reformation of donors. 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 650°C, as a function of annealing time was recorded. 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 behavior is based on the fact that subsequent annealing beyond 60 h may help in dissociation 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_n-O_m clusters.

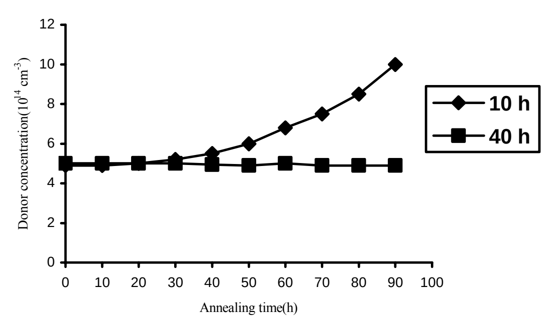

Fig. 5. Donors generated in group A samples pre-annealed at 1000°C for 10 h and 40 h followed by annealing at 650°C as a function of annealing duration up to 90 h.

3.4. Effect of high temperature pre-annealing

The behaviour of donors generated in Group A samples pre-annealed at 1000°C for 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.5. 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 (Fig. 2) as compared to pre-annealed one. 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. 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 reveals that neither the shorter nor the longer pre annealing time has any effect on carrier concentration. In the samples without pre-annealing 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 [13] and Dubey & Singh [14]. Hara et al [15] suggested that the optical absorbance lines in the range 350-500 cm^{-1} are considered to be related to the thermal donors in silicon. In the region 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. Suezawa et al [16] 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.

4. Conclusion

In order to ascertain the effect of nitrogen on the formation of oxygen related donors in step-annealed CZ-Silicon at 650^0C preceded by low and high 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 650^0C 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 of carrier concentration in N-undoped silicon samples pre-annealed at 480^0C 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 480^0C did not increase after 60 h of annealing at 650^0C indicating that no more donors are formed. The increase in carrier concentration occurs at and above 20 h of annealing as compared to pre-annealed at 1000 ^{0}C.It is also observed that neither the shorter not the longer high temperature pre-annealing time has any effect on carrier concentration.

References

[1] Om Praksah, N. K. Upreti, S. Singh, Mater. Sci. & Engg. B, **52,** 180 (1997).
[2] S. A. McQuaid, M. J. Binns, C. A. Londos, J. H. Tucker, A. R. Brown, R. C. Newman, J. Phys. C. Appl. Phys. **77** 1427 (1995).
[3] Liming Fu, D.Yang, Xiangyang Ma, Hanqin Jiang & Dualin Que, Semi. Sci. Tech. **22** 1302 (2007).
[4] S. M. Sze, J.C.Irvin, Solid State Electronics **11,** 599 (1968).
[5] T. Iizuka; S. Takasu; M. Tajima, T. Najaki, N. Inoue, M. Watanake, J. Electrochem. Soc.**132,** 1707 (1985).
[6] P. Wagner, R. Oeiler, Zurhwhner Appl. Phys. A **46**, 73 (1986).
[7] D. Yang, D. Que, K. Sumino, J.Applied Physics **77,** 943 (1995).
[8] Om praksah, S. Singh, J.Phys. Chem. Solids **60,** 353 (1999).
[9] R. C. Newman, J. Phys.: Condens. Matter **12,** 335 (2000).
[10] C. S. Chen, C. F. Li, H. J. Ye, S. C. Shen, D. R. Yand J. Appl. Phys. **76,** 3347 (1994).
[11] D. Yang, M. Klevermann, L. I. Murin, Physica **B 302-303**, 193 (2001).
[12] V. Dubey, S. Singh, J. Phys. Chem. Solids **65,** 1265 (2004).
[13] D. Yang, D. Qu, K. Sumino J. Appl. Phys. **80,** 1493 (1996).
[14] V. Dubey, S. Singh Bull. Mater. Sci.**25,** 589 (2002).
[15] A. Hara, T. Fukuda, T. Miyabo, I. Hirai Appl. Phys. Lett. **54,** 626 (1989).
[16] M. Suezawa, K. Sumino, H.Harada, T. Abe J.Appl. Phys. **25,** L829 (1988).

*Corresponding author: chauhanssingh@rediffmail.com