International Journal of Materials Science ISSN 0973-4589 Volume 12, Number 1 (2017)
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EFFECT OF NITROGEN AND CARBON IN THE FORMATION OF SHALLOW THERMAL DONORS IN CZ-SILICON

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Abstract
Silicon is an important material for fabrication of integrated circuits and optoelectronic devices. Therefore, proper characterization and understanding regarding the role of impurities is essential to optimize the device yield. The shallow thermal donors (STDs) are a family of defects which are generally formed by annealing N-rich CZ-silicon around 650 ^{o}C. STDs can also arise from impurities other than N. At least two families of STDs could co-exist: one is based on N-O defect and other C-O ones.
Both the N and O atoms have one very short Si bond with their mutually shared Si atom. A kinetic study by linking the rate of loss of N-pairs to the increase in STDs based on IR electronic absorption intensities suggested that STDs consisted of an unknown O containing core, with N-pairs attached themselves.

Keywords: CZ-Silicon, Shallow thermal donor, Oxygen defects, Nitrogen defects.

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]. However, excessive amount of oxygen leads to the degradation of device yield. Inherent presence of oxygen, nitrogen, carbon and hydrogen 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 temperature range 400-1200 ^{o}C produces various kinds of defects known as thermal donors. Annealing around 650 ^{o}C leads to the formation of a family of Shallow Thermal Donors (STDs). At least two families of STDs could exist: one is based on N-O and other on C-O ones [3-5]. There are two possible structures for N_i-O_{2i} defect. One has C_{2v} and another C_{1h} symmetries. C_{2v} defect is more stable. On replacing the N by $(CH)_i$ the other family based on C-O is formed. Hydrogen and carbon are common interstitial and substitutional impurities respectively in silicon [6-8]. The single hydrogen defect is highly mobile and is easily trapped by impurities and lattice defects. The greater binding energy of hydrogen with carbon rather than silicon suggests that hydrogen will attach directly to carbon [9]. N-O and C-O defects are briefly explains below:

N-O defects
N-doping in CZ-Si suppresses vacancy and interstitial defects and increases oxygen precipitation. Isolated N_i defects also exist in implanted material at low temperature but lie below detection limit in doped as grown material [10-12]. Nitrogen molecule associates with oxygen. N_xO_y complexes act as nuclei and enhance oxygen precipitation. When nitrogen doped CZ-Si is subjected to high temperature annealing, N-N pair bonds are probably broken and become N_i or N_s. They can not form N_xO_y complexes with oxygen; therefore can not enhance oxygen precipitation. The further precipitation of oxygen is due to interstitial or substituional nitrogen pairing with oxygen.

C-O defects
C_iO_i is a stable defect with an annealing temperature around 350 – 450 ^{o}C. Carbon atom is only slightly affected by divalent or trivalent oxygen [13-14]. Earlier results had found that oxygen atom is trivalent [15-16]. The defect with two H atoms is inert but with a single H atom behaves as a deep acceptor in one form whereas a donor in another form. The defect appears to be first of a family of shallow single donors. There are two configurations of C_iO_iH: R-form, O-form. Hydrogen always prefers to bond with C. C_iH diffuses faster than C_i [17-18]. The binding energies of H with C_iO_i center are reported to be about 2.5 eV. Therefore release of H is unlikely to occur. The interaction between C_iO_iH and a single H passivate the Si & C radicals

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leading to an inert defect. There are no donor or acceptor levels. Hydrogen related STDs are stable upto 520 °C [19], whereas TDDs have broken down by then. In addition, H passivated TDs have been identified and are known to lose hydrogen and reactivate at less than 200 °C [20-21]. The hydrogen is present as an unintensional impurity and the concentrations of these centers are comparable with those of thermal donors. $(C\text{-}H)_i$ is believed to be fast diffusing species in Si [22].

$(C\text{-}H)_iO_{2i}$ acts as N_iO_{2i} defect. It has two possible structures with either one oxygen atom on each side of $(C\text{-}H)_i$ or with both on one side of $(C\text{-}H)_i$. Second structure is more stable than its equivalent with one oxygen atom on either side of $(C\text{-}H)_i$ unit. $(C\text{-}H)_iO_{2i}$ further attracts a oxygen dimer to form$(C\text{-}H)_iO_{4i}$ of C_{1h} symmetry. $(C\text{-}H)_iO_{2i}$ is more stable in a C_1 configuration similar to $C\text{-}O_{2i}$. There is a lack of shallow donor properties in $(C\text{-}H)_iO_{2i}$ in C_{2v} configuration, although it is iso-eletronic with the N_iO_{2i} shallow thermal donor. However (CH) unit is less electronegative than N_i and so the core Si atom is less polarized.

Material and Methods

The CZ-silicon wafer is cut down into small pieces of the size 1×2 cm^2 and then subjected to annealing treatment in ambient air. The specification of the materials is given in the table 1. In sample A, the carbon concentration is almost negligible. Sample B and C are carbon rich.

Table-1: Specifications of samples

Sample Group	Thickness (mm)	Dia. (mm)	Orientation	Resistivity (ohm-cm)	Initial Concentration		
					[O]	[C]	[N]
A	390	75	<111>	9-12	7.9×10^{17}	2.5×10^{14}	7.9×10^{17}
B	600-670	80	<100>	12-22	31.0×10^{17}	1.0×10^{17}	-
C	600-670	80	<100>	12-22	33.5×10^{17}	0.4×10^{17}	-

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 [23]. 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.

FTIR measurement

FTIR studies have been used to identify the presence of N, O, N-O, $(C\text{-}H)_i\text{-}O_i$, $(C\text{-}H)_i\text{-}O_{2i}$ etc complexes. Nitrogen in silicon causes absorption at wave number 967 cm^{-1}. The 240, 242, 249 cm^{-1} absorption lines are main lines related to N-O complexes. The results are in good agreement with previous experiments. These absorption peaks are superimposed on phonon excitations of the silicon.

Results and Discussion

Families of N-O complexes

A comparative study of the figs (1) and (2) clearly reflects that low temperature annealing of CZ-Si does not result in any significant increase in oxygen precipitation, while higher temperature annealing causes quite a reasonable increase. On the other hand oxygen precipitation almost reaches a saturation stage for low temperature annealing 16 hour, but at higher temperature annealing, situation is different and oxygen precipitation goes on increasing as a function of annealing time. From fig. 3 we can see the line intensity of silicon annealed at 650 °C becomes almost constant after 1 h and the line intensity of the sample annealed at 900 °C gradually decreases up to 3 h annealing time. At 900 °C one can think of the non-existence of N-O complexes.

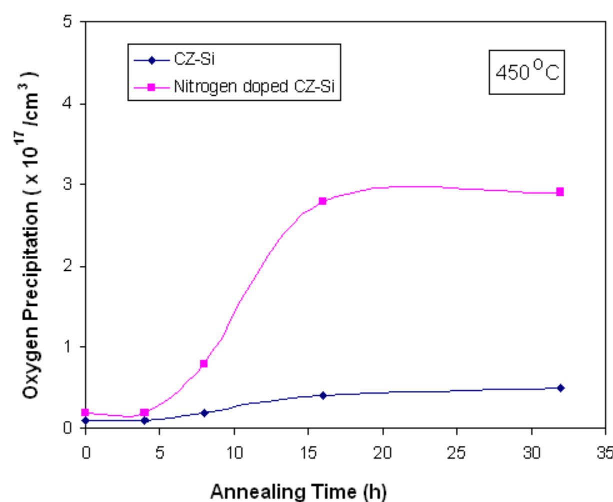


Fig. 1: Precipitation of oxygen in Nitrogen doped CZ-Si

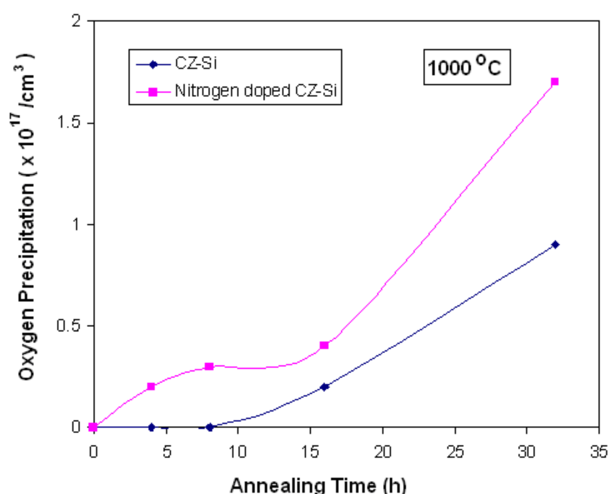


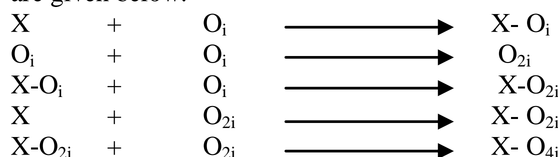
Fig. 2: Increased precipitation of oxygen in Nitrogen doped CZ-Si

Oxygen reduction and donor generation at 650 °C

The behaviour is shown in fig. 4 & 5 for the samples B and C. It is clear that the more donor are generated as a function of annealing time (fig.4) which leads us to a natural conclusion that more oxygen is reduced (fig.5).

Role of $(C\text{-}H)_i$ in the thermal donor formation

Previous theory has indicated that $(C\text{-}H)_i$ diffuses faster than C_i [8]. $(C\text{-}H)_i$ may traps a single oxygen or a dimer and becomes $(C\text{-}H)_i\text{-}O_i$ or $(C\text{-}H)_i\text{-}O_{2i}$ respectively. $(C\text{-}H)_i\text{-}O_{2i}$ defects attract further oxygen atoms to form $(C\text{-}H)_i\text{-}O_{4i}$. This acts as a STD. They may happen through the trapping of a fast diffusing oxygen dimer. Some proposed reactions are given below:



$$X + O_i \longrightarrow X\text{-}O_i$$
$$O_i + O_i \longrightarrow O_{2i}$$
$$X\text{-}O_i + O_i \longrightarrow X\text{-}O_{2i}$$
$$X + O_{2i} \longrightarrow X\text{-}O_{2i}$$
$$X\text{-}O_{2i} + O_{2i} \longrightarrow X\text{-}O_{4i}$$

Where X stands for $(C\text{-}H)_i$.

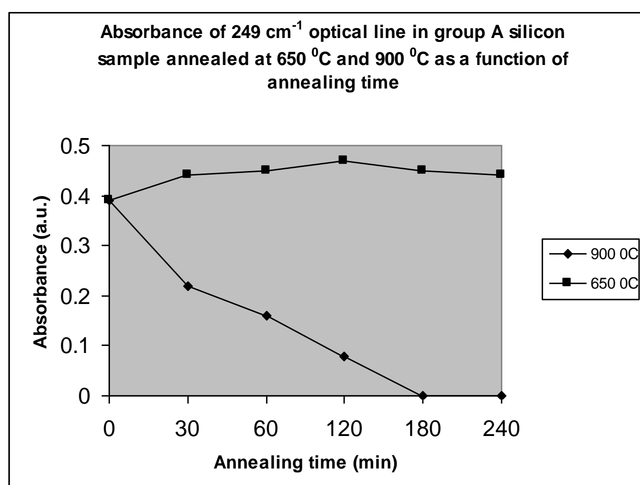


Fig.3: FTIR spctra of Group A silicon samples (a) 650°C annealing for 4 h, and (b) 900°C annealing for 4 h

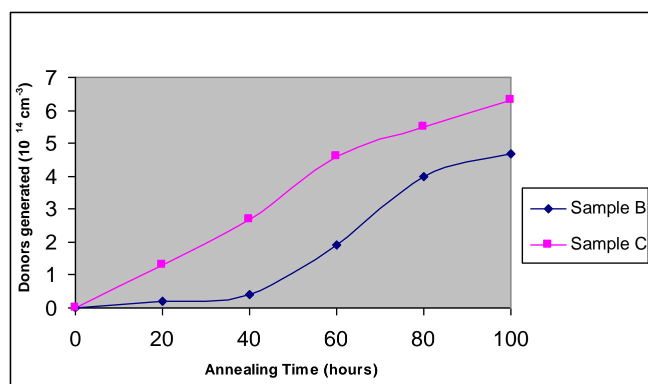


Fig.4: Plot of donors generated as a function of annealing time at 650 °C

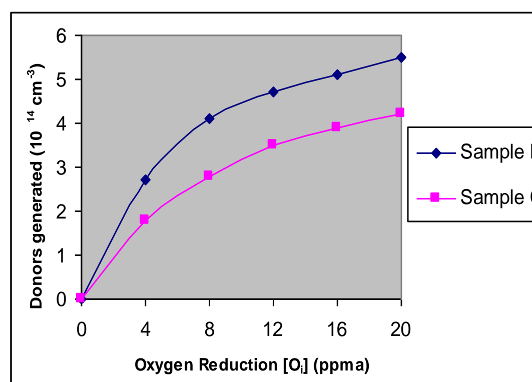


Fig.5: Plot of donors generated as a function of oxygen reduction at 650 °C

Conclusion

As an illustration, $(C\text{-}H)_i$ and oxygen atom, both in interstitial positions, may get associated either with a single interstitial oxygen atom resulting in the formation of $(C\text{-}H)_i\text{-}O_{2i}$ or $(C\text{-}H)_i$ may be associated with an interstitial dimer again meeting the same fate as above. $(C\text{-}H)_i\text{-}O_{2i}$ so formed has every likelihood to be associated with interstitial dimer resulting in the formation of $(C\text{-}H)_i\text{-}O_{4i}$. $(C\text{-}H)_i\text{-}O_i$ may acts as a pre-cursor of $(C\text{-}H)_i\text{-}O_{2i}$. Interaction between $(C_i\text{-}O_i)$ and hydrogen is equally possible, resulting in the formation of $(C_i\text{-}O_i)\text{-}H$, $(C_i\text{-}O_i)\text{-}H_2$ and $(C_i\text{-}O_{2i})\text{-}H$. All these help in the formation of thermal donors. N-doping causes vacancy & interstitial defects to go down and provides a boost to oxygen precipitation. High temperature annealing of CZ-Si:N may break N-N pair bonds pushing the N to interstitial or substitutional positions and unable to form N_xO_y complexes. Further precipitation is possible with oxygen pairing with N_i or N_s. A logical support of experimental findings to theoretical concepts and vice-versa leads one to conclude that the field is still wide open to be supplemented by other studies to ascertain the authenticity of various possibilities.

Some points are given below:

1. There are two types of STDs are existing: one is nitrogen based and another is carbon based.
2. Large N concentrations suppress STD formation.

3. $(C\text{-}H)_i\text{-}O_i$ may exist. This may act as a pre-curser of $(C\text{-}H)_i\text{-}O_{2i}$.
4. Nitrogen enhances the formation of STDs different from conventional new thermal donors.

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