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Study of oxygen clustering in Czochralski silicon at 450 °C–800 °C: correlation with thermal donors formation

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The understanding of the generation-annihilation phenomena of oxygen-related thermal donors (TDs) in p-type Czochralski silicon is of great importance for device fabrication and operation in microelectronic and photovoltaic industry. In this work, we report on oxygen clustering-based activation and partial annihilation of TDs in Cz-Si submitted to thermal annealing under nitrogen at 450 °C-800 °C for different thermal plateau exceeding 4 hours. The effect of thermal annealing on interstitial oxygen and dimer (O_i and O_{2i}) vibration modes appearing in the 580 cm^{-1}-500 cm^{-1} spectral range is studied. We found that heat treatment at 450°C and 650 °C give rise to new thermal donors (NDs) that are located at 540 cm^{-1} and 532 cm^{-1}, respectively. Subsequent to heat treatment above 650 °C, we depict the formation of new thermal oxygen defects having an IR signature in the 1800 cm^{-1}-1500 cm^{-1} spectral range, and which are especially sensitive to the thermal treatment duration**.** Resistivity measurements confirm that several of them are electrically active.

1 Introduction

Heat treatments of Czochralski-grown (Cz) Si crystals in the 350 °C-500 °C temperature range results in the generation of several families of oxygen-related thermal donors (TDs) [1]. It is found that TDs activation is mediated by oxygen dimer (O_{2i}) formation, which presents the first stage of oxygen aggregation in Cz silicon [2]. Some of them are not stable at temperatures above 550 °C and can be annihilated [3-5]. Moreover, small oxygen clusters can be formed after heat treatment at 650 °C giving rise to new thermal donors [6]. However at elevated temperatures (≥ 700 °C) the formation of new TDs and nucleation sites where oxygen precipitation starts, become predominant [5, 6]. The atomic configuration of these oxygen defects is not yet known. Different models have been proposed to explain their formation process. One configuration for oxygen clustering predicts the development of a chain of Si-O molecules at 450 °C [7, 8]. However, despite all these research efforts, the detailed formation mechanisms of TDs in silicon crystals still remain not well understood, and therefore there is no complete model that could account for all experimental data.

In this work, we study the generation dynamic of oxygen aggregation and clustering in boron doped Cz-silicon, following successive thermal treatments at 450 °C, 550 °C, 650 °C and 800 °C. We focus our interest on interstitial and dimer oxygen behaviours and on generation of new thermal donors, which give rise to IR bands in the 500 cm^{-1} -580 cm^{-1} spectral range. Also new thermal oxygen defects associated to oxygen precipitation after heat treatments at temperature ≥ 650 °C, were pointed out in the 1800-1500 cm^{-1} frequency region.

2 Experimental procedures

The starting wafers are p-type, boron-doped monocrystalline Cz silicon having a resistivity in the range of 1-2 Ω cm. The incorporated interstitial oxygen concentrations [O_i] are of about 0.8 to 2×10^{18} cm^{-3}. Prior to thermal annealing, the samples were chemically etched in a solution of (HF: HNO_3: CH_3COOH; 16 %: 24 %: 60 %) for 3 min, rinsed in deionized water and dried under N_2 flux. The formation of oxygen defects is studied by cumulative heat treatments at 450 °C, 550 °C, 650 °C and 800 °C. Hence, four sets of samples can be distinguished as summarized in Table 1. The different treatments were carried out in a closed tubu-

lar furnace using tungsten-halogen lamps under nitrogen ambient. The silicon dioxide forming on both silicon surfaces during thermal annealing is removed by a simple dipping in a diluted HF solution (10%).

Table 1 Samples and their corresponding thermal treatments

Sample type	450°C, 4h	550°C, 4h	650°C, 4h	800°C, 4h
Sample1 (S1)	X	X	X	X
Sample2 (S2)		X	X	X
Sample3 (S3)			X	X
Sample4 (S4)				X

The various oxygen configurations in Cz-Silicon were evaluated by Fourier Transform Infrared spectroscopy (FTIR) at room temperature using a Nicolet instrument Magna system 550 Spectrometer with a resolution of 4 cm^{-1}. The interstitial oxygen concentration is evaluated by FTIR spectroscopy using the well-known absorption band at 1107 cm^{-1} using the IOC88 calibration factor of 3.14 10^{17} cm^{-2} [9, 10]. The resistivity measurements were carried out using the four point probes method.

3 Experimental results

Figure 1 shows the evolution of the FTIR spectrum with thermal annealing (TA) in the 500-580 cm^{-1} spectral region. First, one may notice the existence of two major IR absorption bands located at around 560 cm^{-1} and 513 cm^{-1}, assigned to oxygen-dimer (O_{2i}) and to symmetric stretching of interstitial oxygen [11], respectively. A new IR band located at around 540 cm^{-1} appears subsequent to TA at 450 °C.

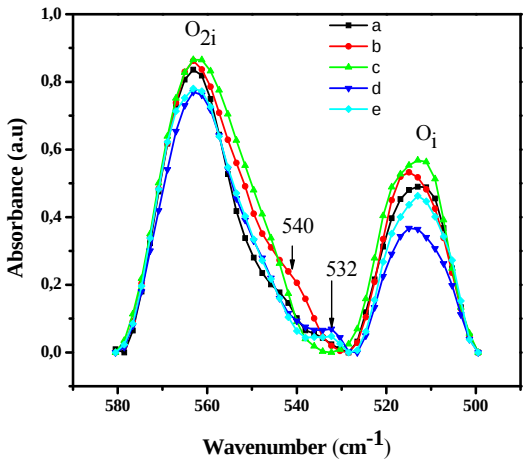

Figure 1 Room temperature FTIR spectra in the 580 -500 cm^{-1} spectral region for (a) as-grown Si, (b) state (a) + TA at 450 °C, (c) state (b) + TA at 550 °C, (d) state (c) + TA at 650°C, and (e) state (d) + TA at 800 °C. The duration of each annealing step is 4 hours.

Heat treatment at 450 °C allows the diffusion of interstitial oxygen atoms (O_i) in the silicon lattice, resulting in the formation of small clusters which apparently act as new thermal donor having an IR absorption mode around 540 cm^{-1} (Fig. 1b). Apparently, further TA at 550 °C (Fig. 1c) would eliminate this new oxygen-related clustering throughout a dissociation phenomenon. This may be explained by the intensity increase of the IR band of interstitial oxygen located at around at 513 cm^{-1} (Fig. 1c). Indeed, we found a partial recovery of the interstitial oxygen concentration after TA at 550 °C, as illustrated in Fig. 2.

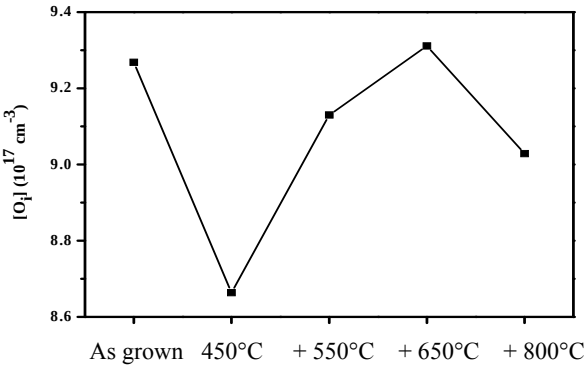

Figure 2 Evolution of the interstitial oxygen concentration in sample 1 (S1) with cumulative thermal annealing during 4 hours.

Cumulative heat treatment at 650 °C generates a new IR absorption band peaking at around 532 cm^{-1} and a clear decrease of the 560 cm^{-1} and 513 cm^{-1} intensity bands associated to oxygen dimer and interstitial oxygen, respectively (Fig. 1d). Furthermore, we observe a little increase in the interstitial oxygen concentration (Fig. 2), which can show that the absorption bands at 1107 cm^{-1} and 513 cm^{-1} are independent [12].

New absorption bands peaking at around 1762 cm^{-1}, 1722 cm^{-1}, 1668 cm^{-1} and 1596 cm^{-1} appear in the 1800 – 1500 cm^{-1} spectral range (Fig. 3); these bands can be attributed to the formation of new oxygen complexes, which increase dramatically after subsequent heat treatment at 800 °C.

First thermal annealing of as grown Si at 550 °C (sample 2, Table 1) allows the annihilation of oxygen-related defects present in as-grown silicon; we observe a net increase of the absorption bands intensity associated to oxygen dimer and interstitial oxygen as regard to as-grown Si (Fig. 4b). Subsequent heat treatment at 650 °C generates more oxygen defects (having IR signatures at around 540 cm^{-1} and 532 cm^{-1}) with a decrease of interstitial oxygen concentration. Subsequent heat treatment at 800 °C does not affect the later complexes but they become more important (Fig. 4).

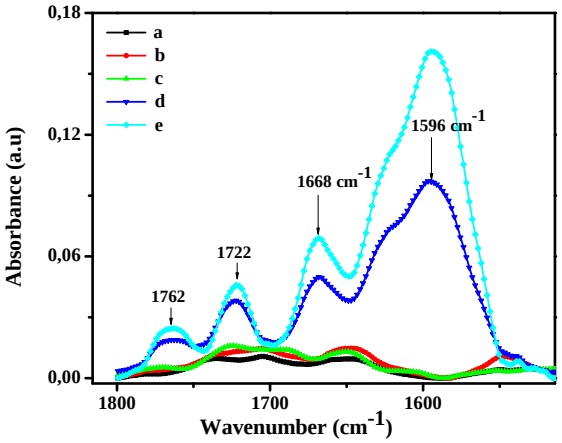

Figure 3 FTIR spectra in the 1800 1500 cm^{-1} spectral region of sample S1 for (a) as-grown Si, (b) state (a) + TA at 450 °C, (c) state (b) + TA at 550 °C, (d) state (c) + TA at 650 °C, and (e) state (d) + TA at 800 °C. The duration of each annealing step is 4 hours.

A decrease of the interstitial oxygen concentration is obtained, which in turn indicate the start of precipitation and the generation of more oxygen clusters. The vibrational modes presented in the 1800-1500 cm^{-1} spectral range present the same behaviour as in sample 1; they become visible following heat treatment at 650 °C.

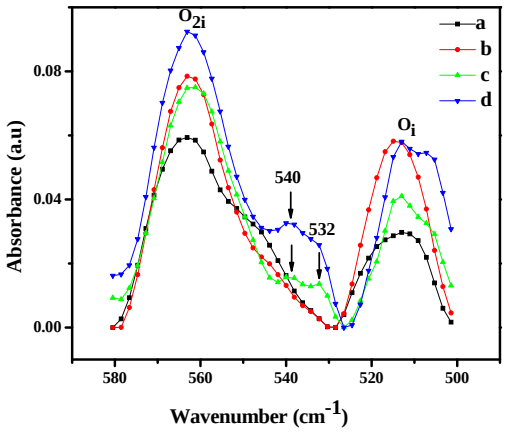

Figure 4 FTIR spectra of sample 2 in the 580-500 cm^{-1} spectral range for (a) as-grown Si, (b) state (a) + TA at 550 °C, (c) state (b) + TA at 650 °C, (d) state (b) + TA at 800 °C . The duration of each annealing step is 4 hours.

In Fig. 4, one may notice that the relative IR band intensities of interstitial oxygen (at 513 cm^{-1}) and oxygen dimer (at 560 cm^{-1}) increase after annealing at 550 °C. Upon heat treatment at 550 °C the infrared vibration band at 545 cm^{-1} disappeared and new thermal oxygen electrically inactive defects are generated. A strengthening of the IR bands peaking at around 1595 cm^{-1}, 1667 cm^{-1}, 1720 cm^{-1} and 1765 cm^{-1} occurs at 650 °C. The corresponding absorption intensity of these bands increases at 800 °C for samples S1, S2 and S3. These modes are recovering and become more dominant after annealing at 800 °C. As the annealing temperature rises up to 800 °C, one may observe that the relative intensity of the vibrational bands located at 560 cm^{-1} and 513 cm^{-1} (corresponding to dimer oxygen and interstitial oxygen), respectively, increase slowly (Fig. 4).

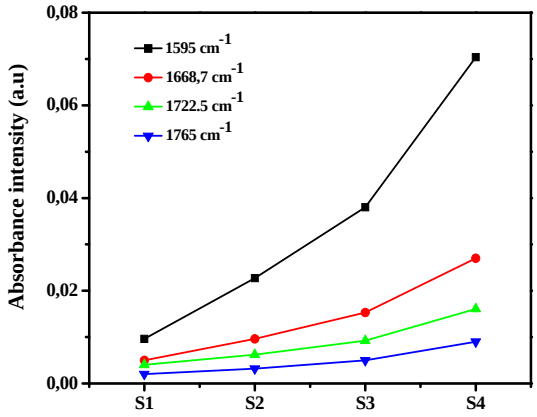

Figure 5 Change in the IR absorbance intensity of the bands related to the various oxygen defects in the 1800 - 1500 cm^{-1} spectral region for samples S1, S2, S3 and S4.

The new oxygen defects observed in the 1800-1500 cm^{-1} spectral region are more pronounced for S4 (Fig. 5). After the first heat treatment at 800 °C (S4), the concentration of interstitial oxygen decreases from 8.5 10^{17} cm^{-3} to 7.9×10^{17} cm^{-3}. It seems to be clear that oxygen defects in the 1800-1500 cm^{-1} spectral region depend on the concentration of interstitial oxygen and the thermal annealing process.

4 Discussions

It seems to be clear that the formation of new oxygen defects is slightly dependent on interstitial oxygen concentration. The first stage of oxygen aggregation in boron-doped Cz-silicon occurs during annealing at 450 °C, through formation of oxygen dimer (O_{2i}), which contains a high concentration of interstitial oxygen.

The experimental data presented in this study support the view that the clustering and aggregation of oxygen can lead to generation of new oxygen defects. It should be mentioned that oxygen precipitation in pre-annealed samples at temperatures ≥ 650 °C is accompanied by an effective generation of new thermal donors having IR absorption bands in the 1800-1500 cm^{-1} spectral range. The

silicon resistivity increases after annealing at 450 °C, which is attributed to the formation of oxygen-related clusters, which are considered as more electrically active oxygen defects at this temperature. Thermal annealing at 650 °C generates new oxygen thermal defects associated to IR vibration modes at around 532 cm^{-1}, 1762 cm^{-1}, 1722 cm^{-1}, 1662 cm^{-1} and 1596 cm^{-1}. It is possible to generate some new electrically active thermal oxygen defects upon annealing at 650 °C. The effect of the heat treatment on the the resistivity is presented in Table 2. A partial recovery of the initial resistivity values is obtained following annealing at 650 °C.

Table 2 Effect of the heat treatment on the resistivity of sample 1.

Sample	As-grown	450°C, 4h	550°C, 4h	650°C, 4h	800°C, 4h
ρ (Ω cm)	1.73	1.81	1.66	1.72	1.67

5 Conclusions

Cumulative heat treatments of Cz-Si samples lead to the activation and formation of new thermal oxygen defects. We studied the oxygen related defects in different spectral ranges: 1800-1500 cm^{-1} and 580-500 cm^{-1}. After annealing at 450 °C and 650 °C new oxygen defects are generated with IR vibration modes located at 540 cm^{-1} and 532 cm^{-1}. After heat treatment at 650 °C, it appears new IR modes located at 1762 cm^{-1}, 1722 cm^{-1}, 1662 cm^{-1} and 1596 cm^{-1}; the intensity of the modes increases after a subsequent heat treatment at 800 °C. We observe an increase of the resistivity after thermal annealing at 450 °C, which may be attributed to clustering of oxygen atoms yielding defects considered as more electrically active thermal donor (TDs) at this temperature.

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