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Effect of carbon on oxygen precipitation in Czochralski silicon

C. A. Londos[*1], **M. S. Potsidi**[1], and **V. V. Emtsev**[2]

[1] Solid State Section, Physics Department, University of Athens, Panepistimiopolis, Zografos, 157 84 Athens, Greece
[2] Ioffe Physico-Technical Institute of the Russian Academy of Sciences, Politekhnicheskaya ul. 26, 194021 St. Petersburg, Russia

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Isochronal anneals were performed in Cz-Si samples of high and low carbon concentrations, from room temperature up to 1200 °C. We report infrared studies on the thermal evolution of various bands of oxygen precipitates formed in the course of the annealing process. The effect of carbon on their spectral behavior is examined. It was observed that in the carbon-rich material the oxygen impurity appears to anneal out at a lower temperature than in the carbon-lean material, in agreement with earlier reports that carbon enhances the oxygen precipitation process in Si. In relation with that, two bands at 1060 and 1080 cm^{-1} attributed to spheroidal precipitates and another band at 1099 cm^{-1} related to the dissolution of platelet precipitates and the formation of microprecipitates make appearance in the spectra of carbon-rich Si at slightly lower temperatures and display higher intensities. This indicates that the enhancement of oxygen precipitation process is due to the effective formation of spheroidal precipitates having the lowest interfacial energy. The role of carbon in the enhanced precipitation process is discussed.

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1 Introduction

Oxygen and carbon are the two dominant impurities unintentionally added in the Si matrix during growth. Their properties and generally their behavior during processing affect the quality of the crystals used in the fabrication of the Si-based electronic devices.

During thermal processing of Si at elevated temperatures the diffusion of oxygen atoms leads to their agglomeration and the formation [1–3] of SiO_x precipitates. The yield and properties of very large scale integration devices are extensively affected by the behavior of oxygen. The use of oxygen precipitates (OPs) for intrinsic gettering and the subsequent removal of the various contaminants from the active region of the silicon substrate is a practically important issue in Si technology. Additionally, it is well-known that the presence of carbon has a significant influence [4] on oxygen precipitation. However, the exact role of carbon in the oxygen aggregation processes, due to its complexity, is not completely understood. It has been reported that carbon enhances [2, 5], inhibits [6] or even has no influence [7] on the oxygen precipitation. It has also been found [2, 8] that the role of carbon depends on many factors, among them the temperature range of the treatment, the initial carbon and oxygen concentrations [9] of the material, as well as the size [10] of the precipitates. It is therefore obvious that there is a need to deep our understanding of the behavior of both impurities and especially their interactions under various conditions over a broad temperature range, where the oxygen aggregation process takes place.

[*] Corresponding author: e-mail: hlontos@phys.uoa.gr, Phone: +003 210 7276726, Fax: +003 210 7276726

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In this work we report infrared spectroscopic data on heat-treated carbon-lean and carbon-rich Cz-grown Si samples subjected to isochronal anneals at temperatures up to 1200 °C. We monitor the evolution of the various bands attributed to the OPs, corresponding to the various shapes and morphologies they acquire on increasing the temperature, in an attempt to gain further insights on the role of carbon in the oxygen precipitation process.

2 Experimental details

Two groups of samples ($[O_i] = 1.1\times10^{18}$ cm^{-3}, $[C_s] < 10^{16}$ cm^{-3}) and ($[O_i] = 7\times10^{17}$ cm^{-3}, $[C_s] = 7.1\times10^{16}$ cm^{-3}) with low and high carbon concentration respectively, were used. Their typical dimensions were 18×10×2 mm^3. These thick samples were mechanically polished on both sides to be suitable for IR spectroscopy measurements. Fifteen minute isochronal anneals of ~ 10 degree steps were performed in conventional open furnaces, from room temperature up to 1200 °C. To avoid contamination, the samples were inserted within quartz ampoules and these ampoules were put inside quartz tubes prior to being placed in the furnaces. Infrared absorption measurements were carried out at room temperature, after each annealing step, to monitor the amplitudes of the observed IR bands in the spectra. Relative changes in the O_i and C_s concentrations were monitored by the intensities of the 1107 cm^{-1} and 604 cm^{-1} absorption lines, respectively. The two-phonon absorption background was subtracted by using a float-zone reference sample of equal thickness.

3 Experimental results and discussion

Figures 1 (a) and (b) present the variation with temperature of the intensity of the $[O_i]$ in carbon-lean Cz-Si (C(L)) and in carbon-rich Cz-Si (C(R)), respectively. Figure 1 (c) displays the variation with tempera-

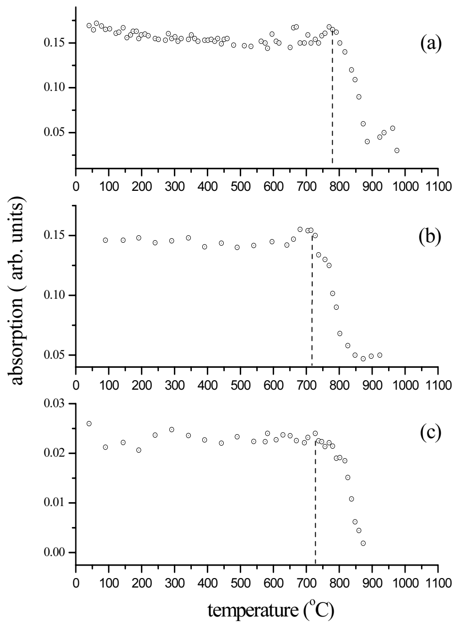

Fig. 1 Temperature-dependent evolution of $[O_i]$ in the carbon-lean *(a)* and carbon-rich *(b)* Cz-Si samples. Temperature-dependent evolution of $[C_s]$ in the carbon-rich Cz-Si sample *(c)*.

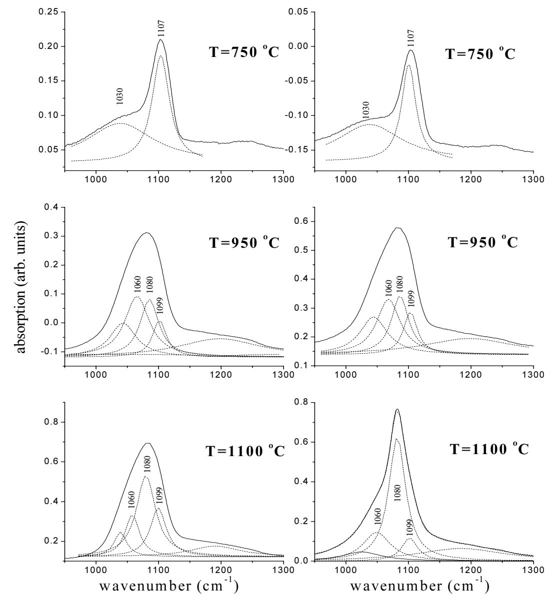

Fig. 2 Several IR spectra in the temperature ranges of 450 °C to 750 °C, 750 °C to 950 °C and 950 °C to 1100 °C in the carbon-lean *(left column)* and carbon-rich *(right column)* materials.

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ture of the [C_s] in the C(R) material. Fig. 2 presents selective IR spectra of the oxygen interstitial 1107 cm^{-1} band at selective temperatures of the temperature ranges (450-750 °C), (750-950 °C) and (950-1100 °C), both for the C(R) and the C(L) sample. Due to the thermal treatments the shape of the band is distorted as a result of the emergence in the spectra, in the same frequency range, of other bands related to oxygen precipitates. The individual contribution of each constituent band was revealed by computer deconvolution using Lorentzian profiles. The presence of three well-pronounced bands at 1060, 1080 and 1099 cm^{-1}, is evident.

Figure 3 depicts the evolution with temperature of the IR bands at 1080 cm^{-1} and 1060 cm^{-1} attributed to spheroidal precipitates [11] for the C(L) and the C(R) material. Fig. 4 shows the evolution with temperature of the 1099 cm^{-1} band, which has been connected [2] from TEM results with the dissolution of platelet precipitates and the formation of microprecipitates.

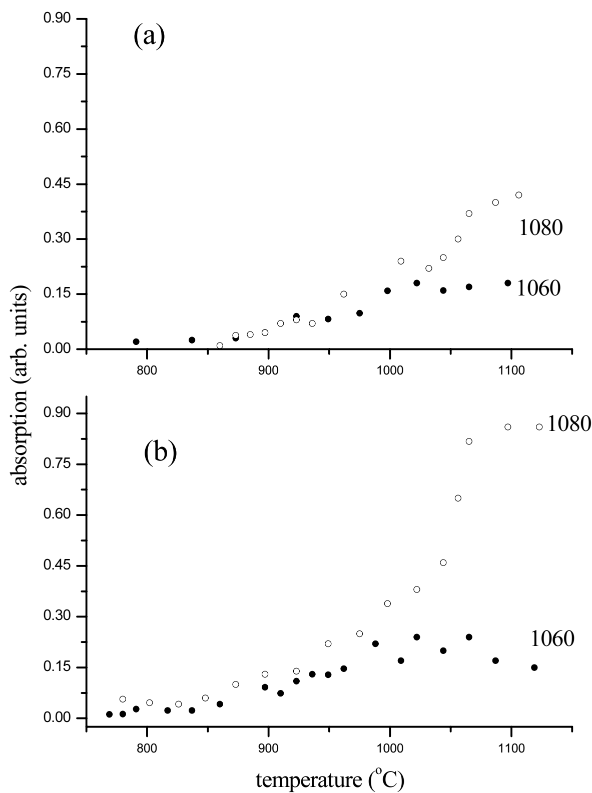

Fig. 3 Temperature-dependent evolution of the 1060 cm^{-1} and the 1080 cm^{-1} bands related to spheroidal precipitates in the carbon-lean *(a)* and carbon-rich *(b)* Cz-Si samples.

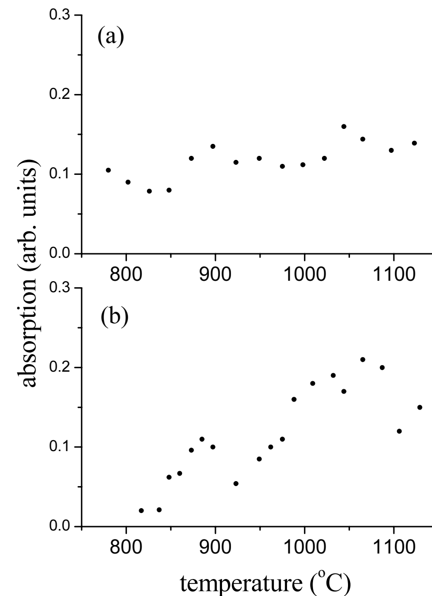

Fig. 4 Temperature-dependent evolution of the 1099 cm^{-1} band related to microprecipitates in the carbon-lean *(a)* and carbon-rich *(b)* Cz-Si samples.

As it is seen from Fig. 1 the O_i, as well as the C_s impurity, begin to anneal out at a lower temperature (~ 720 °C) in the C(R) compared to that of the C(L) sample (800 °C). This is in agreement with previous reports [1] on the anneal out of the oxygen impurity in Si at ~ 750 °C in C(R) silicon material. The phenomenon has been attributed [12, 13] to the ability of C and O atoms to form C-O complexes. These complexes are fast-diffusing molecular-like C-O species [13], formed as a result of the great enhancement of carbon and oxygen diffusion [13] at 750 °C, offering effective heterogeneous seeding sites for

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oxygen precipitation [8]. Another explanation [14] is based on the fact that co-precipitation of C atoms and Si_I's is likely to occur if both components are in supersaturation. However, in our experiment and for temperatures below ~ 800 °C, we consider that the dominant [15] role of carbon is to offer heterogeneous seeding sites for oxygen precipitation.

Concerning the oxygen precipitation process the following observations are made from the inspection of from Figs. 2, 3 and 4: i) up to ~750 °C, the appearance of the 1030 cm^{-1} band indicates [2] that oxygen precipitation occurs mainly through the formation of needle-shaped precipitates, in both C(R) and C(L) material, ii) the higher intensities of the 1060 cm^{-1} and 1080 cm^{-1} bands in the C(R) material for temperatures above ~ 950 °C show that the density of the spheroidal precipitates, is much larger than the precipitate density in the C(L) sample and iii) the higher intensity of the 1099 cm^{-1} band in the C(R) material at temperatures above ~ 950 °C shows that the dissolution of the disc-shaped precipitates and the formation of microprecipitates is more pronounced in the C(R) than in the C(L) sample. The results clearly demonstrate that the presence of carbon strongly affects the formation and the evolution of the OPs indicating an influence in the mechanisms involved in the precipitation process. In what follows, the enhanced formation of spheroidal OPs in the C(R) sample is discussed.

Previous reports [16] straight connect the formation of OPs with the presence of proper nuclei formed during growth in the crystal. These nuclei may consist [17] of small numbers of carbon atoms and Si_I's, which become effective [18] in the temperature range 650 °C-800 °C. Moreover, the evolution of the OPs is dictated [19] mainly by the minimization of the interfacial energy. Within the framework of our model, we suggest that the fast-diffusing C-O species that form at ~ 720 °C, when C_s and O_i impurities start to simultaneously anneal out in the C(R) sample contribute to the appearance and evolution of the oxygen precipitates during the isochronal annealing sequence. We distinguish two ways of this contribution: i) the carbon atoms of the complex provide the volume required for the Si_I trapping so that strains around the OPs are relieved [19] and ii) these impurity atoms help the OPs minimize in taking a spherical shape thus minimizing their interfacial energy. Indeed, from Figs. 2, 3 and 4 it is seen that up to ~ 950 °C the intensities of the 1060 and 1080 cm^{-1} bands, corresponding to spheroidal precipitates are definitely higher in the C(R) material, but the intensities of the two bands are comparable in the C(R) and the C(L) materials, in this temperature range. However, above ~ 950 °C the picture appears to be changed. From Fig. 3 it is seen that the intensity of the 1060 cm^{-1} band in the C(R) sample, i.e at 1050 °C, is noticeably higher than that in the C(L) sample. Also, the intensity of the 1080 cm^{-1} band is also significantly higher in the former material. This indicates that the transformation rate of the OPs towards their spherical shape is higher in the C(R) material compared to the C(L) material. Thus the minimization of the interfacial energy becomes the dominant process in the C(R) sample, at lower temperatures. It is therefore reasonable to conclude that above ~ 950 °C the C atoms would not provide the additional volume sufficient for the emission of Si_I's but rather contribute to a reduced interfacial energy of the Si/SiO_x interface in the C(R) sample, while the OPs are driven towards a spheroidal shape. Thus, our results support the previously suggested role of carbon [4], reporting on the enhancement of the oxygen precipitation process in Si, by providing new sites for precipitation at temperatures below ~ 800 °C, while at temperatures above 850 °C carbon has a catatytic role. In the latter case carbon atoms are not directly incorporated in the growing precipitate. Notice, that in the case of the fifteen minute isochronal anneal sequence of our experiment, the characteristic temperature at which the role of carbon changes is ~ 950 °C. Tracing for the first time the evolution of the relevant LVM bands in the IR spectra, we have established that this enhancement effect is associated with a rapid formation of the spherical-like precipitates. In addition, the higher intensities of the 1099 cm^{-1} band in the C(R) sample give clear evidence that the dissolution of the disc-shaped precipitates run at higher rates in the presence of carbon impurity.

4 Conclusion

Infrared absorption studies on carbon-doped Czochralski Si samples showed that carbon enhances the formation of the spheroidal precipitates, since the IR bands related to these extended structural defects

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display higher intensities in the carbon-rich material. More specifically, carbon in silicon, affects the oxygen precipitation process in two ways: In the temperature range below ~ 950 °C carbon assists the precipitation process by providing additional seeding sites for heterogeneous precipitation, through the formation of C-O complexes. Above ~ 950 °C carbon plays a catalytic role contributing to the minimization of the interfacial energy. The latter process is a decisive factor of the enhancement of the oxygen precipitation, manifested by the faster formation of spheroidal-shape precipitates.

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