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Thermal double donor annihilation and oxygen precipitation at around 650 °C in Czochralski-grown Si: local vibrational mode studies

L I Murin[1,5], J L Lindström[2], V P Markevich[1], A Misiuk[3] and C A Londos[4]

[1] Institute of Solid State and Semiconductor Physics, National Academy of Sciences of Belarus, P Brovki Street 17, 220072 Minsk, Belarus
[2] Division of Solid State Physics, Lund University, Lund, Sweden
[3] Institute of Electron Technology, Warsaw, Poland
[4] Physics Department, Athens University, Athens, Greece

E-mail: murin@ifttp.bas-net.by

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Abstract

We have used local vibrational mode (LVM) spectroscopy to monitor the formation of oxygen-related thermal double donors (TDDs) at 450 °C and their annihilation at 650 °C in carbon-lean Czochralski-grown (Cz-) Si crystals. A few samples were treated at 650 °C under high hydrostatic pressure. It is found that the annihilation of TDDs at 650 °C results not only in a partial recovery of the interstitial oxygen, but also in the appearance of a number of new O-related LVM bands in the range 990–1110 cm^{-1}. The positions of these lines and their shapes are identical to those observed for Cz-Si irradiated with electrons or neutrons and annealed at 600–700 °C. Since the lines appear upon annealing out of VO_3 and VO_4 defects in irradiated samples, they are suggested to arise from VO_m ($m > 4$) complexes. In both kinds of samples, pre-annealed and pre-irradiated, the new LVM bands disappear upon prolonged annealing at 650 °C while enhanced oxygen precipitation occurs. The VO_m defects are suggested to serve as nuclei for oxygen precipitates developing at around 650 °C. High hydrostatic pressure is found to enhance further (up to 4–5 times) the oxygen precipitation process at 650 °C in the samples pre-annealed at 450 °C.

1. Introduction

Heat treatment of Czochralski-grown (Cz) Si crystals in the temperature range 350–550 °C results in the generation of several families of oxygen-related thermal donors. Among them

[5] Author to whom any correspondence should be addressed.

the thermal double donors (TDDs) are the most well known and they have been intensively investigated since 1954 [1–5]. TDDs comprise a series of species with a helium-like excitation spectrum. They are formed sequentially upon heating and are distinguished by their increasingly shallow levels. The electronic transitions of 17 neutral (TDD0–TDD16) [6, 7] and ten positively charged TDDs (TDD0–TDD9) [2, 7] were observed in infrared absorption spectra. According to present models of TDDs they are oxygen clusters (chains) involving different numbers of interstitial oxygen atoms (O_i) [8, 9]. It is argued that the sequential formation of the TDD family occurs mainly via a migration of the oxygen chains (dimers, trimers and TDD species) and their interaction with single O atoms.

TDDs are not stable at temperatures above 550 °C and annihilate rather rapidly. The kinetics of TDD annihilation has been studied in a number of works (e.g., see [10–14] and references therein). It has been established that the main mechanism of the TDD elimination is their dissociation, as a substantial recovery of interstitial oxygen has been normally observed in carbon-lean Cz-Si crystals. However, as a rule this recovery has not been complete and the transformation of some of the TDDs into other centres has been suggested. Besides this, it was noted that in such samples an enhanced generation of the new thermal donors (NTDs) and oxygen precipitate nuclei occurred upon following heat treatments in the range 600–700 °C, but a microscopic mechanism of this phenomenon was not established.

Local vibrational mode (LVM) spectroscopy has recently appeared to be a very powerful tool in studies of small oxygen-related clusters in Si [8, 15–19]. In this work, LVM spectroscopy is used to explore a possible origin of oxygen-related defects formed upon TDD annihilation at 650 °C.

2. Experimental details

The samples used in this investigation were prepared from n-type commercial Cz-Si crystals ($\rho = 50\ \Omega$ cm, $[O_i] = 1.3 \times 10^{18}$ cm^{-3}) with low content of carbon ($[C_s] \leqslant 1 \times 10^{15}$ cm^{-3}). The concentrations of O_i and C_s were determined from measurements of intensities of absorption bands at 1107 and 605 cm^{-1} [20, 21]. The samples were polished to an optical surface on two sides and the dimensions were $10 \times 5 \times 3$ mm^3. To generate TDDs the samples were annealed at 450 °C for 60, 120 and 240 h. The thermal donor killing treatments were performed at 650 °C in air for different durations up to 40 h. Some of the samples were treated at 650 °C under high pressure (10.6 kbar) in purified argon for 1 and 10 h. A few as-grown samples were irradiated with fast electrons or neutrons at room temperature and then annealed isochronally up to 700 °C.

IR absorption analysis was carried out using a Bruker IFS 113 v spectrometer. A spectral resolution of 0.5–1.0 cm^{-1} was used and the measurements on the samples were made at 20 and 300 K in the range 400–4000 cm^{-1}. Resistivity of the samples was measured by the four-probe technique at room temperature (RT).

3. Experimental results and discussion

3.1. TDD generation at 450 °C

Figure 1 shows fragments of infrared absorption spectra of Cz-Si samples in the as-grown state (spectra 1) and after treatments at 450 °C for 60, 120 and 240 h (spectra 2, 3 and 4 respectively). In the spectra of the as-grown samples, absorption lines with maxima at about 514, 560, 1013, 1107 and 1226 cm^{-1} can be seen. All these lines except the one at 1013 cm^{-1} are associated with local vibrational modes due to single interstitial oxygen atoms in the

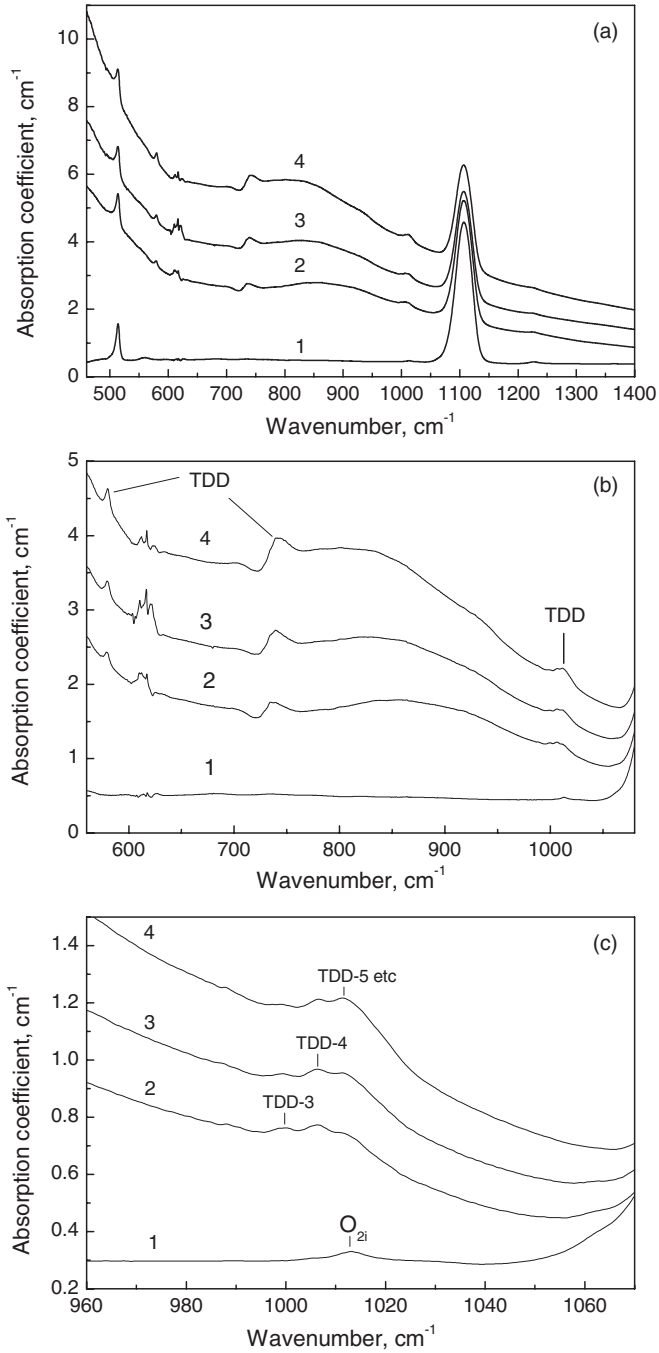

Figure 1. Fragments of absorption spectra at 300 K of Cz-Si samples in the as-grown state (spectra 1) and after treatment at 450 °C for 60 h (spectra 2), 120 h (spectra 3) and 240 h (spectra 4).

Si lattice [22]. The line at 1013 cm^{-1} was identified recently as attributable to an LVM of the oxygen dimer [23]. The treatment at 450 °C resulted in the growth of an overall absorption

due to the increase in free electron concentration (the sample resistivities were 0.31, 0.23 and 0.21 Ω cm after anneals for 60, 120 and 240 h respectively) and the appearance of the LVM bands at about 580, 730 and 1000 cm^{-1} related to TDDs [8, 15]. The broad band centred at about 900–950 cm^{-1} is also related to TDDs but originates from electronic transitions in TDDs being in a positive charge state. Due to the high concentration of introduced donors some of the thermal donors are not ionized at room temperature.

It should be pointed out that a noticeable decrease in the intensity of the O_i-related bands with increasing heat treatment time at 450 °C is observed while the integrated intensity of the TDD bands increases and their peak positions are shifted to higher energies probably due to an increase in the number of oxygen atoms involved in the TDD chains [8]. No other oxygen-related bands, except those of TDDs and O_i, could be detected even after annealing for 240 h.

3.2. Heat treatments at 650 °C

3.2.1. TDD annihilation. Figure 2(a) shows fragments of the infrared absorption spectra of a Cz-Si sample in the as-grown state (spectrum 1), after treatment at 450 °C for 240 h (spectrum 2) and following annealing at 650 °C for 1 h (spectrum 3). The latter treatment results in the disappearance of all the features related to TDDs and a recovery of interstitial oxygen atoms. However, the recovery is not complete and a significant content of O_i should be present in other forms. Careful analysis of the spectra measured after short time treatments at 650 °C has shown that a number of new LVM bands located in the range 990–1110 cm^{-1} appear upon TDD annihilation (figures 2(b) and (c)). In the room temperature spectra (figure 2(b)), the bands positioned at about 1036 and 1051 cm^{-1} appear to be the most prominent. In the low temperature spectra (figure 2(c)) a greater number of bands can be detected (resolved) and the most intense of them are positioned at about 1040, 1056 and 1108 cm^{-1} at 20 K.

Evidently, some oxygen-related defects should give rise to these bands. When seeking for a possible origin of such defects we found a very useful hint from annealing studies of radiation-induced defects (RDs) in Cz-Si. Figure 3 shows fragments of infrared absorption spectra of Cz-Si samples irradiated with 10 MeV electrons at room temperature and then isochronally (30 min) annealed up to 700 °C. For simplicity only the spectra after anneals at 600, 650 and 700 °C are presented. After annealing at 600 °C the bands related to VO_3 (at 910, 975 and 1005 cm^{-1}) and VO_4 (at 991 and 1014 cm^{-1}) defects [16, 17, 19] are still dominant ones. With temperature increasing to 650 °C they disappear, while bands similar to those shown in figure 2 are generated. The identity of the bands generated upon TDD annihilation and RD transformation is more clearly manifested in figure 4 where the spectra of some pre-irradiated and pre-annealed samples after anneals at 650 °C for 1 h are shown. Since the lines appear upon annealing of VO_3 and VO_4 defects in irradiated samples it is reasonable to suggest that they arise from VO_5 and/or VO_6 defects. Transformation of VO_3 and VO_4 defects into VO_5 and VO_6 may occur via capture of mobile interstitial oxygen atoms and oxygen dimers, i.e. via reactions

$$VO_3 + O_{2i} \rightarrow VO_5$$
$$VO_4 + O_i \rightarrow VO_5$$
$$VO_4 + O_{2i} \rightarrow VO_6.$$

Formation of the latter defects in pre-annealed crystals can occur most probably via injection of Si self-interstitials by O_{im} ($m > 4$) defects, i.e. via the reaction

$$O_{im} \rightarrow VO_m + I_{Si}.$$

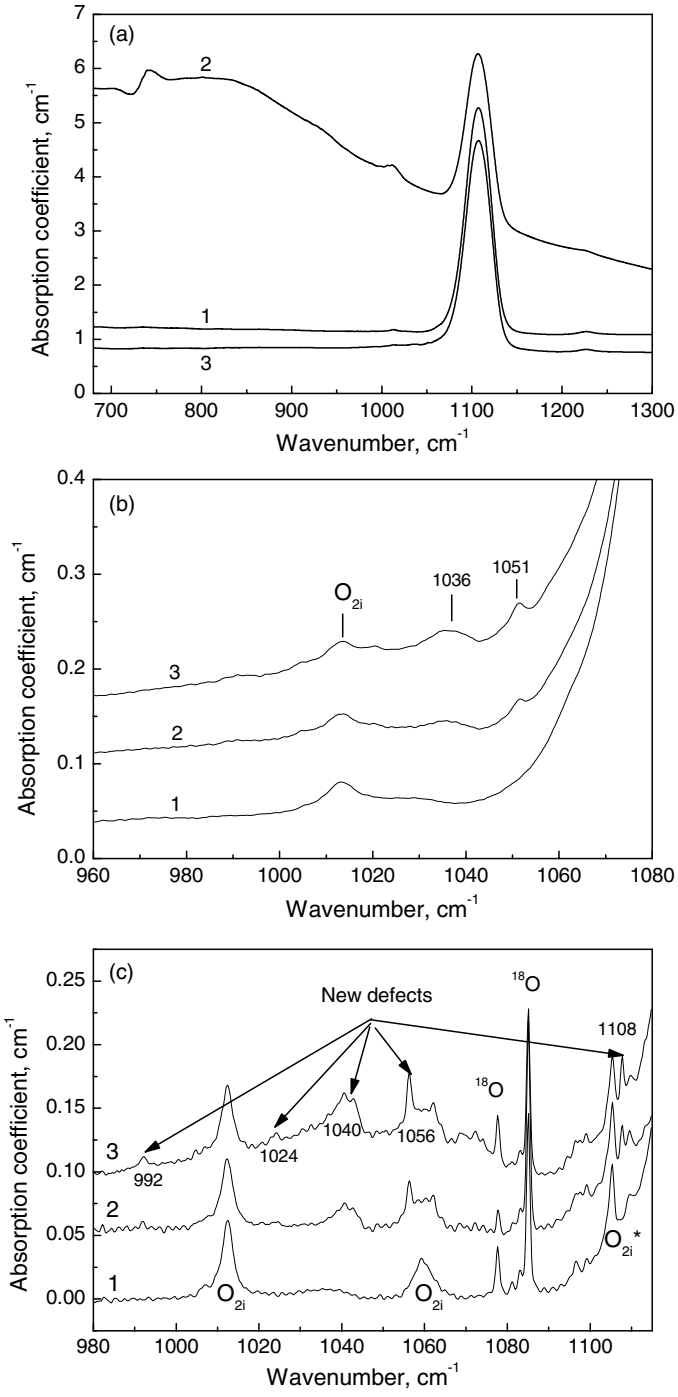

Figure 2. Fragments of absorption spectra at 300 K ((a), (b)) and 20 K (c) of Cz-Si samples in the as-grown state (spectra 1) and after treatments at: 2a—450 °C for 240 h; 3a—450 °C for 240 h followed by 650 °C for 1 h; 2b, 2c and 3b, 3c—650 °C for 1 h after 450 °C for 120 and 240 h, respectively.

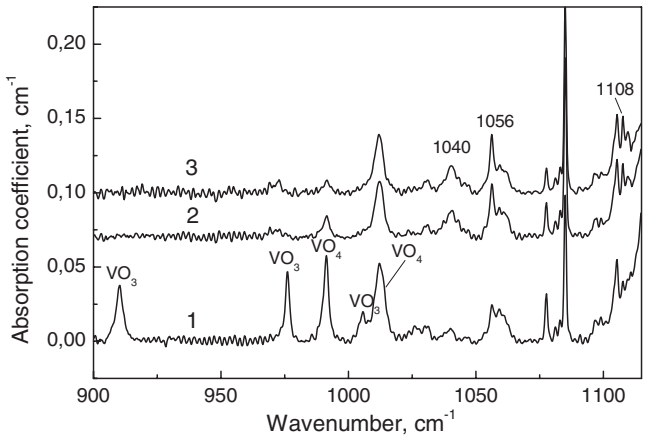

Figure 3. Fragments of absorption spectra at 20 K for a Cz-Si sample irradiated with 10 MeV electrons ($F = 3 \times 10^{17}$ cm^{-2}) at RT and annealed for 30 min at: 1—600 °C; 2—650 °C; 3—700 °C.

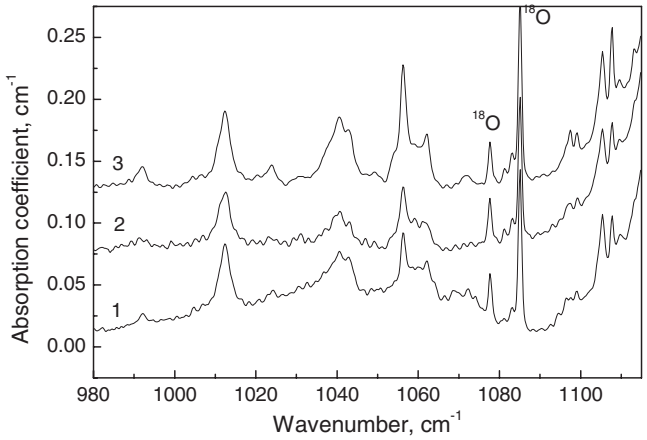

Figure 4. Fragments of absorption spectra at 20 K of Cz-Si samples annealed at 650 °C for 1 h after: 1—annealing at 450 °C for 240 h; 2—irradiation with 2 MeV electrons at RT ($F = 1 \times 10^{18}$ cm^{-2}); 3—irradiation with 5 MeV neutrons at RT ($F = 1 \times 10^{17}$ cm^{-2}).

Apparently, there are two parallel ways of the TDD annihilation occurring: dissociation and transformation into VO_m.

3.2.2. Oxygen precipitation. In both kinds of samples, pre-annealed and pre-irradiated, the new LVM bands disappear upon prolonged annealing at 650 °C while enhanced oxygen precipitation occurs. Figure 5 shows fragments of infrared absorption spectra of Cz-Si samples, as-grown and pre-heat treated at 450 °C, which were annealed at 650 °C for 40 h. An enhanced removal of interstitial oxygen (manifested via a decrease in the strength of the 1107 cm^{-1} band) is observed in the pre-heat treated samples along with the formation of oxygen precipitates giving rise to a broad band with a maximum at about 1080–1085 cm^{-1}. There is a clear correlation between an enhancement of these processes and the duration of the pre-heat

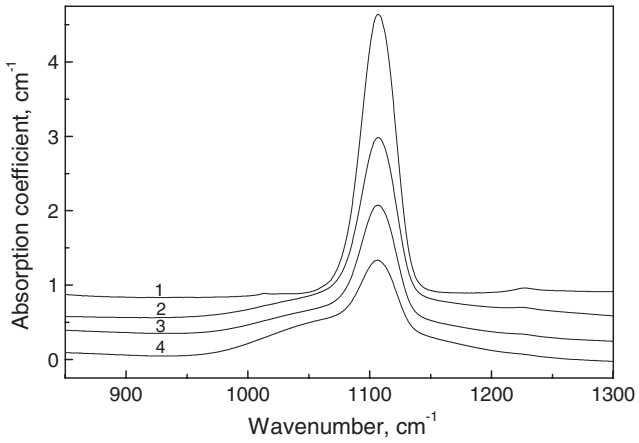

Figure 5. Fragments of the absorption spectra at 300 K for Cz-Si samples annealed at 650 °C for 40 h: 1—as-grown; 2—after annealing at 450 °C for 60 h; 3—after annealing at 450 °C for 120 h; 4—after annealing at 450 °C for 240 h.

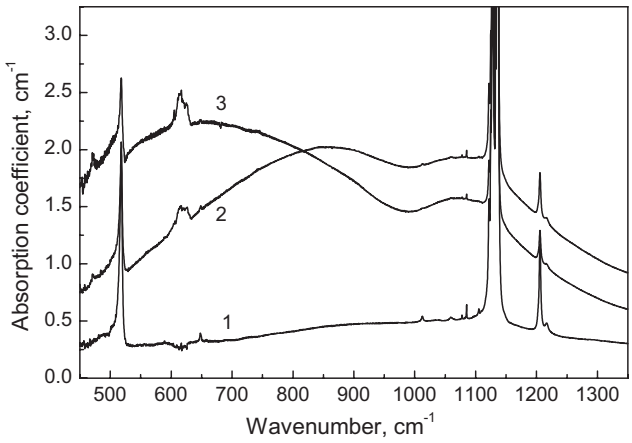

Figure 6. Fragments of the absorption spectra at 20 K for Cz-Si samples annealed at 650 °C for 40 h: 1—as-grown; 2—after annealing at 450 °C for 60 h; 3—after annealing at 450 °C for 120 h.

treatment at 450 °C: the greatest interstitial oxygen loss and precipitate growth correspond to the longer duration.

It should be mentioned that oxygen precipitation in the pre-annealed samples is accompanied by an effective generation of new thermal donors. The material resistivity, which recovered after TDD annihilation practically to that of the initial material, i.e. up to about 50 Ω cm, decreased again to about 3 Ω cm after 40 h at 650 °C. The NTD generation is manifested also in the low temperature absorption spectra (figure 6) via increase in the absorption by free carriers and the appearance of a broad band due to electronic transitions in the new TDs. These donors are known [24] to give rise to a continuous spectrum of electronic states. The position of the maximum density of these states appears to be a function of the duration of both treatments: at 450 and 650 °C. For a given annealing time at 650 °C it is shifted to lower energies with increase in the pre-annealing time at 450 °C and it is shifted to

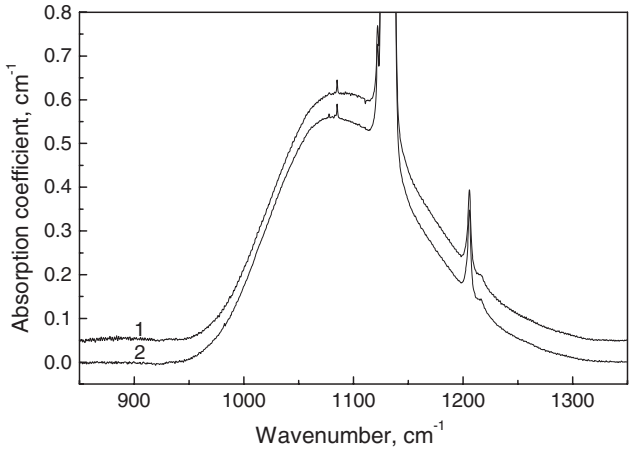

Figure 7. Fragments of the absorption spectra at 20 K for Cz-Si samples annealed at 450 °C for 240 h followed by treatment at 650 °C for: 1—40 h under normal conditions; 2—10 h under high pressure (10.6 kbar).

lower energies with increase in the annealing time at 650 °C for a given length of treatment at 450 °C.

In agreement with the previous findings (e.g. see [25] and references therein), we have found that preliminary irradiation of the Cz-Si samples also results in a strong enhancement of oxygen precipitation and of new TD generation at 650 °C. The shapes of the absorption bands related to oxygen precipitates appear to be very similar for pre-irradiated and pre-annealed samples. This implies that the origins of the enhancement effect are the same in the two cases and are most probably associated with the formation of VO_m defects, which can serve as nuclei of oxygen precipitates developing at around 650 °C.

3.2.3. High pressure effects. It has been found previously that the oxygen agglomeration processes in Si at elevated temperatures are enhanced strongly under high hydrostatic pressure (HP) [26–28]. In the present work some of the samples pre-annealed at 450 °C and a few as-grown ones were treated at 650 °C under high pressure (10.6 kbar) in purified argon for 1 and 10 h. Optical and electrical characterizations of the samples have shown that high hydrostatic pressure, in accordance with the previous data, significantly enhances (4–5 times) the oxygen precipitation process and the NTD generation at 650 °C for all the samples studied.

An important finding of the present work is that in both cases (high and normal pressure) the origins of the oxygen precipitates appear to be the same as they give rise to identical IR absorption spectra. As an example, figure 7 shows fragments of spectra of two samples pre-treated at 450 °C for 240 h and annealed at 650 °C. One of the samples was annealed at 650 °C under atmospheric pressure for 40 h and another one under HP for 10 h. It is clearly seen that the shapes and intensities of the bands arising from the oxygen precipitates are practically identical for the two cases. This means that not only the origins but also the sizes and concentrations of the precipitates should be the same [29]. This conclusion is also consistent with the similar values of the sample resistivities (∼3 Ω cm), which indicate equal amounts of the NTDs generated in the two cases.

Evidently, in samples pre-heat treated at 450 °C the subsequent oxygen precipitation at 650 °C under normal as well as under high pressure conditions occurs predominantly on the

nucleation centres created upon the TDD annihilation. In that case, the precipitation process should be diffusion limited and the observed HP enhancement effect appears to be mainly related to an enhancement in the oxygen diffusion under high pressure [30].

4. Conclusions

LVM studies have shown that the dominant oxygen-related defects developing in carbon-lean Cz-Si upon heat treatment at 450 °C for up to 240 h are the thermal double donors. Their annihilation at 650 °C is found to result not only in a partial recovery of the interstitial oxygen, but also in the appearance of a number of new O-related LVM bands in the range 990–1110 cm^{-1}. The positions of the lines and their shapes are identical to those observed for Cz-Si pre-irradiated with electrons or neutrons and annealed at 600–700 °C. For irradiated samples these new lines appear upon annealing out of VO_3 and VO_4 defects and they are suggested to arise from VO_m ($m > 4$) defects. In both kinds of samples, pre-annealed and pre-irradiated, the new LVM bands disappear upon prolonged annealing at 650 °C while highly enhanced oxygen precipitation occurs. Seemingly, the VO_m defects can serve as nuclei for oxygen precipitates developing at around 650 °C.

High hydrostatic pressure is found to enhance further (up to 4–5 times) the oxygen precipitation process and the generation of new TDs at 650 °C in the samples pre-annealed at 450 °C. The observed effect is related most probably to the enhancement of the oxygen diffusion induced by high pressure.

Acknowledgments

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