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IR studies on the interaction between thermal and radiation defects in Silicon

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Abstract. Fast neutron irradiations on pre-treated Cz-grown silicon were carried out. The pre-treatments involved thermal anneals at 450 ^{o}C and 650 ^{o}C under high hydrostatic pressure. We mainly examined, by means of IR spectroscopy, the effect of pre-treatments on the production of the oxygen-vacancy (VO) pair. The amplitude of the VO band was found independent on the 450 ^{o}C treatment although the amplitudes of the TDs bands were reduced. On the other hand, the amplitude of the VO band was found lower in the samples treated at 650 ^{o}C, indicating an influence on the production of the oxygen-vacancy defects. The results are discussed and explanations are suggested concerning possible interactions between thermal and radiation defects.

Introduction

A considerable amount of work has been expending in the last 50 years in trying to elucidate the nature, the structure, the formation, the annealing kinetics and generally the behavior of the various defects induced in Cz-Si upon heat treatments at elevated temperatures. Such defects are mainly [1,2] thermal donors, oxygen precipitates and structural defects as dislocation loops and stacking faults. An important issue in this field of research is the effect of the thermally-induced defects on the behavior of other defects present or/and produced in the material upon various processes. In this respect, the effect of thermal donors and new thermal donors/ precipitates on the defects produced by the irradiation and vice versa, is of high technological and scientific interest.
Thermal anneals of Cz-Si at 450 ^{o}C leads to the formation of small oxygen clusters with donor behavior, called thermal donors. A main family of these oxygen-related clusters is that of the double thermal donors (TDDs) which comprise [3] a series of at least seventeen double donor species sequentially formed upon heating. Recent models [4] consider (TDDs) as chain-like structures of oxygen atoms (O_n), where different numbers of oxygen atoms characterize the various species of the family. Localized vibrational mode (LVMs) bands in the regions 945-1000, 700-730 and 575-580 cm^{-1} have been reported [4] as related to TDDs. At higher temperatures, i.e. 650 ^{o}C, TDDs annihilate mainly by: dissociation, which is the main mechanism ($O_n \rightarrow O_{n-1}+O_i \rightarrow \ldots$) [1,2], and/or transformation [5] into VO_n complexes ($O_n \rightarrow VO_n + Si_I$, n>4).
Thermal anneals of Cz-Si at 650 ^{o}C lead [1,2], besides the elimination of any existing TDDs in the material, to the nucleation of oxide particles finally evolving to oxygen precipitates and to the generation [6,7] of a new family of thermal donors, the so-called new thermal donors (NTDs). LVM bands related to these defects have not been reported so far. (NTDs) are most probably related [2,8]

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to oxygen precipitates. In any case the exact structure of NTDs is not known. Also the microscopic mechanism of the oxygen precipitation process is not well established and understood. Moreover, oxygen precipitates are defects with complicated atomic structures due to the polymorphism of the silicon dioxide, the final form of oxygen precipitate.

The dominant defects formed in Cz-grown Si upon irradiation are the vacancy-oxygen pair VO, the well-known A-center, and the divacancy V_2. In neutron irradiated silicon disordered regions are formed, as well. They contain [9] a core mainly from divacancies surrounded by silicon self interstitials, vacancies and other impurities in the periphery. The A-center in the neutral charge state gives rise [10] to an IR band at 830 cm^{-1}. The center is stable up to 300 ^oC where its signal in the spectra begins to disappear with the concomitant growth of another band at 895 cm^{-1} attributed [10] to the VO_2 defect.

The use of Si for technological applications requires processing stages that involve both thermal treatments and irradiations. The detailed knowledge of the oxygen aggregation processes and of the behavior of oxygen-related defects, either of thermal or/and radiation origin, is very crucial for technological purposes. In many cases, the spectroscopic signals of these defects are very weak, obstructing proper investigation. It is well known that high hydrostatic pressure strongly enhances [11] oxygen agglomeration processes in Si. The phenomenon has been attributed either to the activation [11] of additional nucleation centers or to the enhancement [12] of the diffusivity of the oxygen atoms in Si. Due to this effect of the pressure, the concentrations of the thermal donors and oxygen precipitates are substantially larger so that any possible interaction between thermal and radiation defects is expected to become observable. Conceptually, the application of pressure opens a new window for engineering and control of the oxygen impurity in Si. Notice in addition, that high pressure treatments are highly relevant to the new generation of strained-silicon devices. Strain for example is inevitable in the materials in the course of fabrication processes of silicon integrated circuits and can cause severe degradation of device characteristics. It is therefore an important parameter of Si devices and any information concerning the effect of this variable on the material would be valuable. In our case, hydrostatic pressure is expected to improve our understanding of oxygen-related thermal and radiation defects and their mutual influence. This study is a continuation of a previous work [13] concerning the behavior of radiation defects in the presence of thermal defects in Si.

Experimental details

We used five Cz-grown Si samples with initial oxygen content of 1.4×10^{18} cm^{-3}. We used commercially available material of p-type conductivity with a concentration of 1×10^{15} cm^{-3}. The carbon concentration was beyond IR detection limit, thus smaller than 1×10^{16} cm^{-3}. Besides the untreated sample labeled A_o, the other four samples were subjected to thermal treatments under high hydrostatic pressure - the method is described elsewhere [11] - and are labeled as follows: A_2 (450 ^oC, 10.5 kbars, 5 h), A_3 (450 ^oC, 10.7 kbars, 10 h), A_6 (650 ^oC, 10.9 kbars, 5 h) and A_7 (650 ^oC, 11 kbars, 10 h). The two temperatures of the thermal treatments were deliberately selected for the purpose of this paper. The temperatures T_1=450 ^oC and T_2=650 ^oC are characteristic [1,2] for the generation of thermal donors and new thermal donors, correspondingly. The applied hydrostatic pressure was chosen to be ~ 11 kbars, since it is known that pressures larger than 10 kbars enhance [12,14] the formation of donors at 450 ^oC and 650 ^oC. We chose short time durations for the high temperature-high pressure treatments (HTHP) that is $t\leq10$ h, in order that the oxygen precipitation process is restricted at the early stages and the associated generation of the dislocation loops and stacking faults is negligible. The thermal donor concentrations of the samples were extracted from Hall effect measurements and were found to be 8×10^{15} cm^{-3} for the sample A_2, $\sim1\times10^{16}$ cm^{-3} for the sample A_3, 2×10^{14} cm^{-1} for the sample A_6, and $< 2\times10^{14}$ cm^{-3} for the sample A_7. Then the samples were irradiated by fast neutrons with a fluence of 8×10^{16} n/cm^2. The temperature of irradiation was $\approx$ 50 ^oC. Afterwards, 30 min isochronal anneals were carried out in open furnaces from 200 ^oC to 600 ^oC, in approximately 10 ^oC steps. After each annealing step the IR spectra were taken by

employing a Jasco IR spectrometer of dispersive kind. The two phonon absorption was subtracted by using a Float-zone Si sample of equal thickness as reference. We mainly measured the [O_i] after each treatment and the amplitude of the VO peak in the spectra immediately after irradiation.

Experimental results and discussion

Fig.1 shows fragments of the IR spectra of the A_o, A_3 and A_7 samples after the pre-treatments as well as after the neutron irradiation. It is well-known that initial stages of oxygen precipitation give rise [1] to IR bands that convolute with the 1104 cm^{-1} band of O_i. We note that the shape of the O_i band for the A_3 sample (Fig $1b_1$) does not exhibit any distortion indicating that no observable precipitates are formed in the material treated at 450 ^oC under pressure. The decrease of the amplitude of the oxygen band (compare figures $1(a_1)$ and $1(b_1)$) is attributed to the formation of thermal donors. In the case of the A_7 sample a small distortion in the shape of the oxygen band is observed at the side of the lower wavenumber region of the band verifying the formation of oxygen precipitates. Lorentzian deconvolution shows a weak band around 1074 cm^{-1} indicating that the concentration of these precipitates is quite small. Notice that an IR band at 1230 cm^{-1} related [1] also to oxygen precipitates in Cz-Si treated for long times is not present in our spectra.

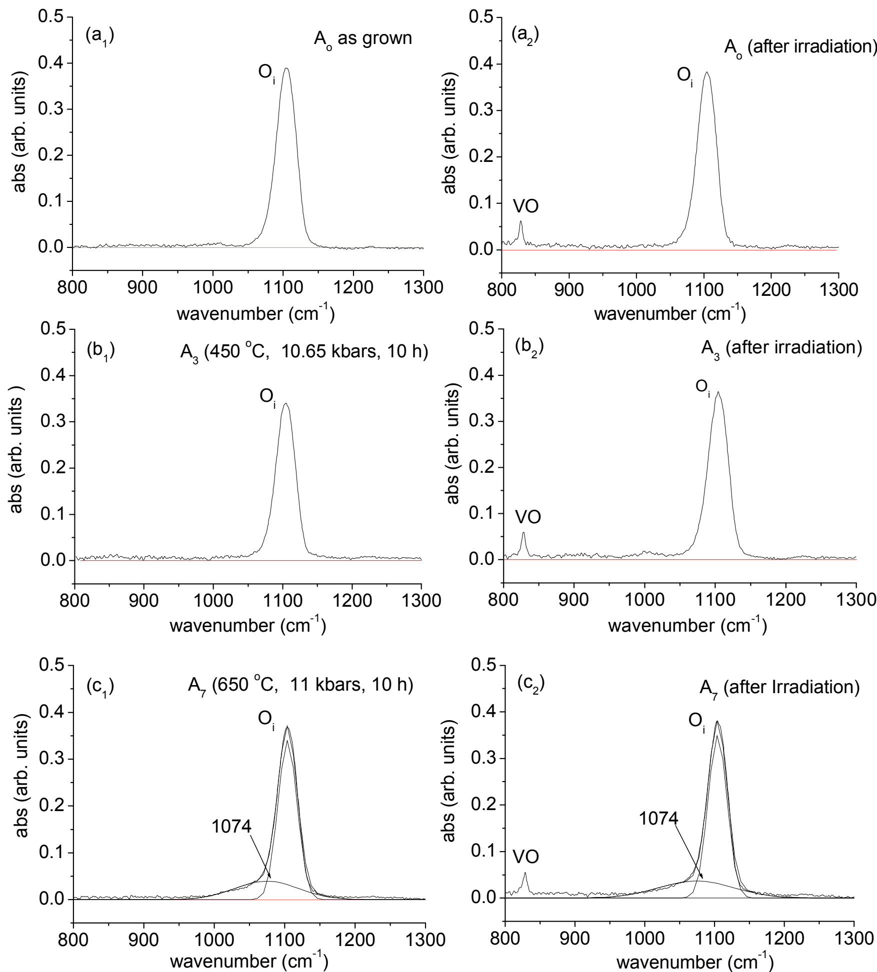

Fig.1 Fragments of the IR spectra of the samples A_o, A_3 and A_7 after the pre-treatments (a_1, b_1, c_1, correspondingly) and after the irradiation (a_2, b_2, c_2, correspondingly).

Fig.2 presents the amplitudes of the VO defect, immediately after irradiation, for the untreated sample and for the samples pre-treated at 450 ^oC and 650 ^oC, under pressure, for 5 h and 10 h, correspondingly. All the information concerning these samples is summarized in Table 1. The concentration of the produced A-centers in the samples pre-treated at 450 ^oC it appears to be the same as that of the initially untreated sample, although the corresponding concentrations for the samples pre-treated at 650 ^oC are smaller. The so far published results on the issue of interactions between thermal defects and radiation defects are contradictory. It has been reported [15,16] that TDs can be annihilated by electron irradiation and also that the formation of the VO-center is enhanced. This enhancement was attributed to the release of oxygen atoms from thermal donors centers. It has also been suggested [17] that complexes between thermal donors and VO defects are formed in the temperature range of 300-400 ^oC in samples subjected to thermal pre-treatments at

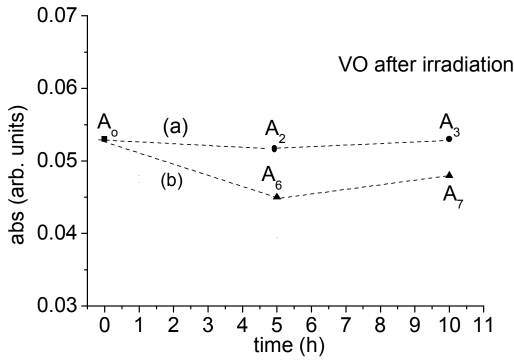

Fig. 2 The amplitudes of the VO defect in the untreated sample and the samples pre-treated at 450 °C (a) and 650 °C (b) under pressure, for 5 and 10 h, correspondingly.

450 °C. On the other hand, there are other reports argued [18,19] that the components of the Frenkel pairs, that is vacancies and self-interstitials produced by the irradiation, do not interact with thermal donors. It was suggested [18] that a potential barrier is created near thermal donors preventing the migration of vacancies towards them. It was also reported [18,19] that the initial introduction of A-center was not affected by the presence of thermal donors. Our results concerning treatments at 450 °C verify the latter conclusion. However, for treatments at 650 °C the VO concentration immediately after the irradiation is smaller. In the case of the later treatment small precipitates form [1,2] and therefore Si_I's are trapped at their interface with the Si matrix. Rodlike defects are also produced [1,2]. Their presence may affect the production of vacancies, due to the irradiation, resulting in smaller VO concentrations.

Table 1 Parameters of the HTHP treatments, the O_i concentration after various treatments, the VO amplitudes and the TDs concentrations of the samples used.

Sample	$[O_i]_o$ ($\times 10^{18}$ cm^{-3})	$[O_i]$ after treatment ($\times 10^{18}$ cm^{-3})	$[O_i]$ after irr. ($\times 10^{18}$ cm^{-3})	VO (arb. units)	[TDs] ($\times 10^{15}$ cm^{-3})
A_0 (As-grown)	1.4	1.4	1.37	0.053	
A_2 (450 °C, 10.5 kbars, 5 h)	1.4	1.38	1.28	0.052	8
A_3 (450 °C, 10.7 kbars, 10 h)	1.4	1.18	1.25	0.053	10
A_6 (650 °C, 10. 9 kbars, 5 h)	1.4	1.39	1.35	0.045	0.2
A_7 (650 °C, 11 kbars, 10 h)	1.4	1.33	1.38	0.048	<0.2

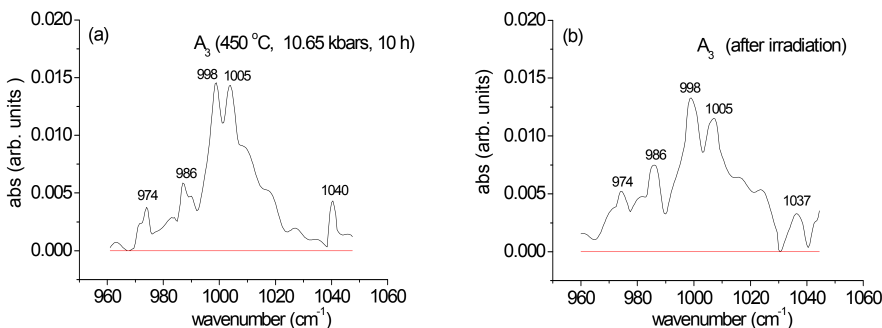

Fig. 3 Fragments of the IR spectra of the sample A_3 (a) after treatment and (b) after irradiation.

Fig.3 shows segments of the IR spectra of the sample A_3 in the region 950-1050 cm^{-1}. The bands at 974, 986, 998 and 1005 cm^{-1} shown in Fig. 4a most probably originate [20] from TDD_1, TDD_2, TDD_3 and TDD_4, respectively. Sample A_3, treated at 450 °C, for 10 h under high pressure, contains a large amount of TDDs (Table 1). After the irradiation the heights of the corresponding peaks are slightly diminished. Any definite conclusion about an interaction between TDDs and the VO defect cannot be possibly drawn from Figs 2, 3a and 3b. However, as it is seen from Table 1 the oxygen concentration after irradiation is larger than that after the 10 h treatment, despite the fact that oxygen atoms are spent for the production of the VO defects. The origin of the surplus oxygen atoms is not clear. It may be argued that a portion of the TDDs dissociates as a result of the

irradiation thus providing the additional oxygen atoms. Although the mechanism of this radiation-assisted dissociation of TDDs is not clear, we note that the idea of oxygen interstitial atoms emanated from TDDs has already been suggested [15,21] in the literature. For the sample A_2 treated at 450 ^oC for 5 h, the gain of oxygen atoms due to any possible TDDs dissociation seems not to overbalance the loss of O_i atoms due to the formation of VO defects and therefore the oxygen concentration after irradiation is smaller than that after treatment (Table 1).

In the A_7 sample treated at 650 ^oC NTDs are expected to form. NTDs are oxygen-related defects of unknown structure. They are considered to be larger oxygen clusters than those of TDs acting as nuclei of oxygen precipitates [6]. IR bands correlated with NTDs have not been reported so far, to the best of our knowledge. No LVM bands were observed in our spectra, especially in the region 950-1050 cm^{-1}. However, the oxygen concentration was higher after irradiation than after treatment for the A_7 sample, while the opposite is observed for the sample A_6 subjected to a 5h treatment under pressure (Table 1). Following the previous line of thought as for the A_3 sample, the same arguments concerning the surplus of oxygen interstitial atoms could be put forward. Any direct interaction between NTDs and radiation defects can not be concluded. Notice also that the amplitude of the precipitate-related peak at 1074 cm^{-1} remains unchanged after HTHP treatment and after irradiation (Fig. 1(c_1) and Fig. 1(c_2)).

Thus from our IR measurements concerning studies of the production of the VO defects only and the observable changes in their concentration due to the presence of thermal defects after HTHP treatments at 450 ^oC and 650 ^oC, we cannot definitely conclude about any direct interaction between radiation and thermal defects in Cz-Si. On the other hand, studies of the evolution of the VO defects and their conversion to the VO_2 defects have indicated interactions between thermal and radiation defects [13].

It is worth noting, at this point, that measurements on material initially irradiated and then subjected to heat treatments have led also to contradictory results concerning interaction between thermal and radiation defects. In particular, it was concluded that the production of TDDs in neutron-irradiated Si followed by HTHP treatment at 450 ^oC is strongly reduced [22]. On the other hand, results on Si material implanted with He ions and subsequently annealed up to 500 ^oC showed that the induced radiation damage substantially enhances the thermal donor formation [23].

Summary

We have studied, by means of IR spectroscopy, the production of the VO defect in neutron-irradiated Si samples pre-treated at 450 ^oC and 650 ^oC under high hydrostatic pressure for various time durations. The primary purpose was to detect any influence of the presence of thermal defects, in particular TDDs and NTDs or precipitates on the production of the VO defect. Our experimental results for treatments at 450 ^oC support the view of liberation of oxygen interstitial atoms from thermal donors in the course of the radiation process. We tend to believe that no direct interaction between TDDs and radiation defects occurs. In the case of treatments at 650 ^oC the reduction of the produced VO centers upon irradiation could be related to Si_I's trapped at the interface of the oxygen precipitates and the Si matrix. Any direct interaction of NTDs or precipitates with radiation defects is not definitely confirmed. The issue needs further investigation and most possibly a combination of optical and electrical experimental techniques would provide additional information to clear up the picture.

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