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Infrared studies of oxygen-related defect formation in neutron-irradiated Cz-silicon after annealing at $T = 450–650$ °C under hydrostatic pressure

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Abstract

The infrared absorption technique was used for the studies of oxygen aggregates and related defects in 5 MeV neutron-irradiated Czochralski-grown silicon after heat treatment (HT) at 450 and 650 °C under hydrostatic pressures (HP) of 1 and 1.1 GPa, respectively. The results obtained showed that the formation processes of classical thermal double donors (TDDs) are reduced in neutron-irradiated Si subjected to HP–HT treatment. This result can be explained in terms of higher formation rates of V–O defects, the so-called A-centres. The enhanced oxygen precipitation and shallow thermal donor formation are observed after HP–HT treatment at $T = 650$ °C.

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1. Introduction

Formation processes of thermal donors (TDs) in Czochralski-grown silicon (Cz-Si) have been studied since more than 40 years (see review [1]). In spite of this fact, the atomic structures of TDs and their formation kinetics still remain under study. The TD families are not uniform in their nature but in all cases, oxygen, present in Cz-Si crystals in concentrations up to 10^{18} atoms cm^{-3}, is an impurity taking part in the processes of TD formation. In the temperature range $350 < T < 550$ °C, electrically active small oxygen aggregates with discrete donor states from $E_c = -0.04$ to -0.07 eV and from $E_c = -0.16$ to -0.11 eV are formed, the so-called thermal double donors (TDDs). At least 16 members of the TDD family have been studied up to now [2,3]. The individual members of this family are resolved by infrared (IR) absorption measurements of their electronic transitions from the neutral (TDD^0) or singly ionised (TDD^+) ground states [3]. At present, it is commonly accepted that TDD_n for $n \geq 3$ are formed by joining oxygen atoms one by one to the TD core in the (1 1 0)-plane [4]. Recently, two groups of IR vibrational bands (VBs) in the regions 975–1105 cm^{-1} and 724–748 cm^{-1}, related to small oxygen clusters of TDDs, were discovered [5]. The discussion is still going on concerning the TDD cores as well as atomic structures of TDD1 and TDD2. There is experimental evidence confirming that the smallest agglomerations of oxygen atoms are dimers O_{2i}, the dioxygen complex formed of two O_i sharing a common silicon neighbour [6]. Vibrational IR absorption bands at 1012, 1060 and 1105 cm^{-1} were shown to arise from this complex. Some indications that these complexes can be precursors for TDD1 and TDD2 were found in Ref. [7]. Short annealing of Cz-Si at $T \geq 600$ °C leads to the disappearance of TDDs, the so-called donor killing annealing. However, after prolonged annealing new donors (NDs) with ionisation energies between $E_c =$

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−0.03 and −0.2 eV [8] are produced. It has been established that NDs consist of several TD families: shallow TDs with energy of ionisation $E_c - E_i \leq 30$ meV (STDs), TDDs and deep donors (DDs) [8]. Recent studies showed that the temperature range of production of each TD family is not so critical and different kinds of TDs can be formed in a wide temperature range depending on the annealing time [8,9]. It has also been stated that factors such as hydrostatic pressure (HP) applied during heat treatment (HT) [10], hydrogenation [11] and the presence of radiation defects [12] can modify the formation processes of TDs or the structures of oxygen aggregates. In this paper, some oxygen-clustering effects in neutron-irradiated Cz-Si subjected to HT at 450 and 650 °C under external argon pressure (HP) were studied by IR absorption measurements.

2. Experimental

Phosphorous-doped Cz-Si samples with electron concentrations $n = 8 \times 10^{14}$ cm^{-3} at room temperature (RT) were used in this study. The interstitial oxygen [O$_i$] and substitutional carbon [C$_s$] contents, determined from the intensity of IR absorption bands at 1107 and 605 cm^{-1}, were 8.5×10^{17} and $< 2 \times 10^{16}$ atoms cm^{-3} making use of the calibration factors of 3.14×10^{17} and 1×10^{17} atoms cm^{-2}, respectively. The amount of precipitated oxygen Δ[O$_i$] was calculated as a difference between the [O$_i$] concentrations in initial materials (reference samples) and heat-treated ones. The samples were divided into two groups. One of them was irradiated with 5 MeV neutron at RT with a dose of 5×10^{16} neutrons cm^{-2}. Then both groups of samples, irradiated and non-irradiated, were subjected to HT under external argon HP of 1–1.1 GPa at 450 and 600 °C, respectively (see Table 1). Following the HP–HT treatment, IR absorption measurements with a resolution of 4–0.5 cm^{-1} were carried out at 300–11 K over a spectral range 1500–200 cm^{-1} with the aid of a Brucker IFS 113v Fourier Transform Infrared Spectrometer (FTIR). An additional external lamp of 250 W was used for higher intensity of illumination in the case of sample NS4 to increase the population of shallow donors with electrons by moving the quasi-Fermi-level up. The concentrations of shallow impurities were estimated from the intensity of absorption lines associated with the 1s–2p$_{+/-}$ electronic transitions [13]. The total concentration of TDDs was derived from four-point resistivity measurements at RT. The concentration of shallow impurities was estimated from IR data. The concentration of a specific member of the TDD family was calculated based on the intensity of the absorption line due to the 1s–2p$_0$ transition, in accordance with [14]. The spectra in all figures have been vertically displaced for clarity.

3. Results

In the IR absorption spectra taken over a spectral region of 250–550 cm^{-1} at 11 K, many sharp lines are observed in samples heat-treated at 450 °C (Fig. 1). They are identified as the electronic transitions from the neutral ground state to excited ones of phosphorous [13]

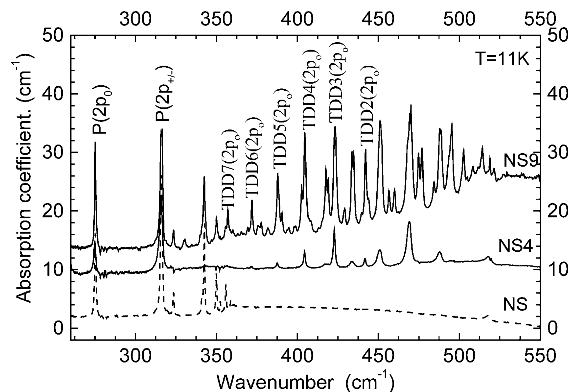

Fig. 1. IR absorption lines of the electronic transitions of TDD^0 and P^0 at $T = 11$ K for the NS4 and NS9 samples treated at 450 °C under HP of 1 GPa and for the reference sample NS.

Table 1
Basic parameters of studied samples and the parameters of the treatments

Sample name	Irradiation ($\times 10^{16}$ neutron cm^{-2})	HP–HT, treatment temperature (°C)/time (h)/pressure (GPa)	n at 300 K ($\times 10^{14}$ cm^{-3})	[P] from absorption ($\times 10^{14}$ cm^{-3})	[O$_i$] ($\times 10^{17}$ atoms cm^{-3})	Δ[O$_i$] ($\times 10^{17}$ atoms cm^{-3})
NS	–	Initial material	8.2	5	8.5	–
NS4	5	450/10/1	2.4	3.7	7.7	0.8
NS4[a]				3.75[a]		
NS4[b]				2.4[b]		
NS9	–	450/10/1	84.8	5	8.6	–
NS5	5	650/5/1.1	17.8	5	5.1	3.4
NS10	–	650/5/1.1	12.3	4.8	5.8	2.3

[a] Measured with additional illumination.
[b] Measured in darkness (without illumination).

and TDDs [2]. For clarity, only the lines used in concentration calculations are labelled in Fig. 1. For comparison, the spectrum of a reference sample denoting NS is also shown. No lines related to the presence of any other residual impurity were observed in the samples studied. The concentrations of phosphorous [P] obtained from IR absorption and resistivity measurements are gathered in Table 1. The concentrations of some specific members of TDDs ($n = 2$–5) estimated from absorption data are given in Table 2. In the NS sample, the value of [P] obtained from IR spectra differs by 3.2×10^{14} cm^{-3} from that estimated from electrical data. It means that an additional source of electrons already exists in the starting material. As seen in Fig. 1, no trace of TDDs was observed in the NS4 sample. The IR spectrum displayed in Fig. 2 over a spectral range 1000–1200 cm^{-1} shows the presence of an absorption line at 1012 cm^{-1} and weaker one at 1105 cm^{-1}. Both lines are attributed to the vibrational modes of O_{2i} [7]. For this reason, the line at 1012 cm^{-1} cannot be assigned to vibrational mode of electrically active oxygen aggregates [5]. Besides, the calculated integrated intensity (IA) of a line at 1012 cm^{-1} in the NS sample appears to be very close to the quasi-equilibrium value of oxygen dimers in Cz-Si with $O_i = 8.5 \times 10^{17}$ atoms cm^{-3} found in Ref. [7]. No trace of STDs in the NS sample is seen in absorption spectra.

The [P] concentration estimated from an absorption spectra in the NS4 sample was 3.7×10^{14} atoms cm^{-3}. This value suggests that only 75% of phosphorous atoms has been detected in absorption measurements. No difference in the intensities of absorption lines related to P and TDDs was observed when additional illumination was used (see Table 1). To reach the Fermi-level position in the NS4 sample at 11 K, absorption measurements without illumination were taken using a germanium filter. In this case, [P] is equal to 2.4×10^{14} atoms cm^{-3}. This value is half of the total [P]. It means that the Fermi-level at 11 K was pinned closely on the phosphorous level. For TDDs deeper than phosphorous, the population with electrons should not be lower. So, one can estimate that the real [TDDs] in sample NS4 should be $\leq 7.35 \times 10^{14}$ cm^{-3}. This value is about four times lower than the TDD concentration in sample NS9.

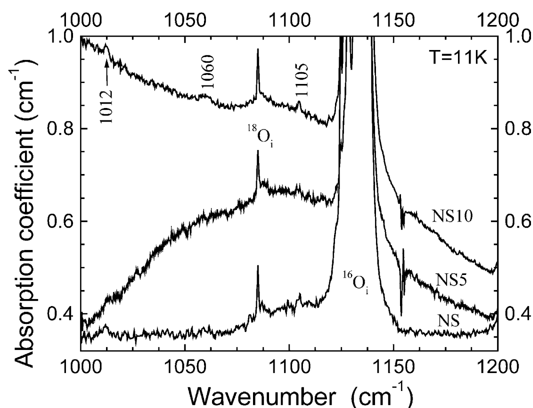

Fig. 2. Absorption spectra of oxygen dimer modes for the NS, NS5 and NS10 samples. A broad absorption band is related to the large, close to spherical shape oxygen precipitates.

It can be concluded that the production of TDDs in neutron-irradiated Cz-Si during HP–HT treatment at 450 °C is strongly reduced.

The IR absorption spectra taken over a spectral range 1250–600 cm^{-1} at 300 K are depicted in Fig. 3 (spectra 3 and 4) for the samples heat-treated at 450 °C. In sample NS4, several lines related to the vibrational modes of V_nO_m centres, TDDs and other TDs are observed. The lines are labelled according to Stein [15].

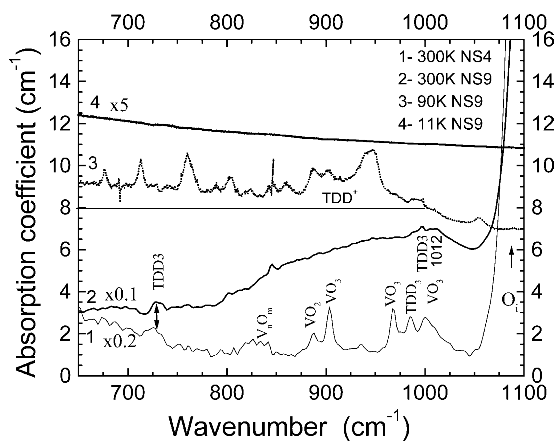

Fig. 3. Temperature change in the absorption spectrum in the spectral range 600–1350 cm^{-1} for the NS9 sample and absorption spectrum for the NS4 sample at RT.

Table 2
TDs concentration calculated from FTIR and electrical measurements

Sample name	n at 300 K from STD ($\times 10^{14}$ cm^{-3})	[TDD] ($\times 10^{14}$ cm^{-3})					IA of band at 1080 cm^{-1} 11 K/300 K (cm^{-2})
		[TDD2]	[TDD3]	[TDD4]	[TDD5]	$[TDD]_{total}$	
NS	3.2	–	–	–	–	–	–
NS4	?	0.29	1.34	3.45	0.78	5.86	–
NS9	25.9	7.26	8.86	7.49	3.36	27.0	–
NS5	12.8	–	–	–	–	–	61/56
NS10	7.3	–	–	–	–	–	23/22

A broad absorption band in the NS9 sample, whose sharper lines assigned to LVMs of TDs can be resolved, is thought to be related to the electronic transitions from the ground state of singly charged $TDDs^{+}$ to exited states and the conduction band. To confirm this fact the evolution of absorption spectra with temperature was investigated in sample NS9 (see Fig. 3, spectra 1, 2 and 3). At temperatures >70 K due to lowering of the Fermi level, a set of discrete absorption lines related to the electronic transitions from the ground state of singly ionised TDDs to exited states [2] start to appear in IR spectra of the NS9 sample. Thermal widening of the lines results in the appearance of a wide broad band at RT. This broad band is much more intensive in sample NS9 as compared with that in sample NS4. This fact confirms unambiguously that the concentration of TDDs in sample NS9 is much higher than that in the NS4 sample.

After HP–HT treatment at 650 °C an increase in the electron concentration at 300 K and a sizeable reduction in the interstitial oxygen concentration in both the samples NS5 and NS10 (irradiated and non-irradiated ones) are observed (see Table 1). The spectra taken over a spectral range 1200–1000 cm^{-1} at $T = 11$ K are presented in Fig. 2 for the HP–HT samples annealed at 600 °C. Except the typical lines related to the vibrational modes of interstitial oxygen $^{16}O_i$ and its natural isotope $^{18}O_i$, a broad band with a maximum at $\sim$1080–1070 cm^{-1} at 11 K and three vibrational modes at 1105, 1060 and 1012 cm^{-1} assigned to O_{2i} are seen. IA of this broad band, calculated after deconvolution of the absorption spectrum between 1300 and 900 cm^{-1}, remains constant with temperature (see Table 2). Its IA corresponds to the amount of precipitated oxygen. According to Halberg and and Lindström [16], such a broad band with a maximum at $\sim$1080 cm^{-1} is attributed to the presence of larger spherical-like oxygen precipitates.

An increase in the electron concentration in samples NS5 and NS10 at 300 K indicates that STDs are formed during HP–HT treatment. The IR spectra recorded on samples NS5 and NS10 in a range 200–500 cm^{-1} at 11 K are depicted in Fig. 4 after subtraction of the absorption in sample NS. Two bands, a weak broad band with a maximum at $\sim$250 cm^{-1} and a second one with a maximum at $\sim$350 cm^{-1}, were found. As [P] is same in samples NS, NS5 and NS10, a band at $\sim$350 cm^{-1} should not be due to the transitions from excited phosphorous states to the conduction band. An agreement between the intensities of these bands and the electron concentration at RT suggests that these two bands can be attributed to the presence of shallow TDs formed during HP–HT treatment, although further investigations should be conducted. The appearance of two broad bands, close to the spectral range originated from optical transitions at the neutral and singly ionised

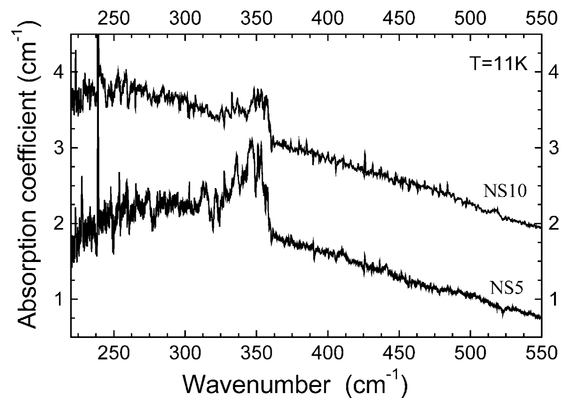

Fig. 4. IR absorption spectra at 11 K related to STDs for the samples NS5 and NS10 obtained after subtraction of the absorption of the reference sample NS.

states of many species of shallow TDDs with slightly different ground state energies (labelled NTDs), has already been observed by Kamiura et al. [9]. They also found that the different annealing conditions led to the formation of several families of STDs.

4. Discussion and conclusions

The obtained results showed that the formation process of TDDs in neutron-irradiated Si during applied HP–HT treatment at 450 °C is substantially reduced. It is well known that neutron irradiation of Si results in the appearance of point-defect clusters in the silicon lattice. Oxygen atoms strongly interact with vacancies producing V–O defects. The annealing of V–O complexes gives rise to the formation of higher-order defects belonging to a family of V_nO_m defects. It has been shown [12] that the TDD formation kinetics in electron-irradiated materials is the same as that in standard Cz-Si and, hence, the [V–O] defects should be ruled out as the "core" of TDDs. From this it follows that the formation processes of TDDs and [V–O] complexes should be competing processes. The reaction rates of these reactions are determined by the concentrations of oxygen and defects (TDD nucleation sites and vacancies) as well as their capture radii. It has been calculated [17] that the average concentration of vacancies $[V_{av}]$ in a so-called supercluster after neutron irradiation is 5.5×10^{19} cm^{-3}, and the average size of the supercluster is 1.8×10^{-17} cm^3. At a neutron dose of 5×10^{16} neutrons cm^{-2} superclusters concentration should be $\approx 6 \times 10^{15}$ cm^{-3} assuming that introduction rate of superclusters is $\beta = 0.12$ per neutron cm^{-1} [17] and interaction cross-section of 5 MeV neutrons with Si is 2.4054 barn [18]. For initial oxygen concentrations of $[O_i]_0 = 8.5 \times 10^{17}$ atoms cm^{-3}, there are about 15 oxygen atoms per cluster. The concentration of oxygen dimers, using the calibration procedure proposed in Ref. [7], is 2.3×10^{16} atoms cm^{-3}

in sample NS. It gives about 0.41 oxygen dimers per cluster. It means that the vacancy concentration should be several orders of magnitude higher than concentrations of other defects and impurities taking part in these competing reactions. As a consequence, the production rate of V–O defects, converted into [V_nO_m] defects upon annealing at 450 °C, can be much higher than that of TDDs assuming that the capture radii of the two processes cannot differ by many orders of magnitude. The presence of V_nO_m defects in sample NS4 was demonstrated by absorption measurements (see Fig. 3). Thus, the reduced formation of TDDs can be explained in terms of the higher formation rates of V–O defects. Although the TDD concentration in NS4 is much lower compared with that in NS9, the concentration of precipitated oxygen is larger (see Table 1). This fact also confirms that the number of oxygen atoms interacting with vacancies is much higher than that taking part in the TDD formation.

It is interesting to note that the distribution of TDD_n is different in samples NS4 and NS9. A significant increase in the concentration of lower-numbered TDDs is observed in sample NS4 (see Table 2). It means that the formation of TDD precursors, most probably O_{2i}, is retarded. It can be explained in terms of the higher rates of interactions between oxygen atoms and vacancies in sample NS4. Detailed studies of the TDD formation kinetics in HP–HT materials are needed.

The conclusion given above also explains the enhanced oxygen precipitation in sample NS5 as compared with that in sample NS10. It has been shown [16] that VO_2 defects act as nuclei for oxygen precipitates. In this model, the presence of V–O centres in sample NS5 after irradiation, subsequently transformed into [V_nO_m] complexes, contributes to increasing concentration of nuclei for oxygen precipitation. This process is accompanied by an increase in concentrations of shallow TDs. One can conclude that STDs are formed due to generation processes of higher-order oxygen clusters, this being an intermediate stage of the growing oxygen precipitates. In such a case, V_nO_m defects can be considered as nuclei sites for STD formation during HP–HT treatment.

References

[1] F. Shimura (Ed.), Oxygen in Silicon, Academic Press, Boston, 1994.
[2] P. Wagner, J. Hage, J. Appl. Phys. A 49 (1989) 123.
[3] W. Götz, G. Pensl, W. Zulehner, Phys. Rev. B 46 (1992) 4312.
[4] J.W. Corbett, H.L. Frisch, L.C. Snyder, Mater. Lett. 2 (1984) 209.
[5] T. Halberg, J.L. Lindström, J. Appl. Phys. 79 (1996) 7570.
[6] S. Öberg, C.P. Ewels, R. Jones, T. Halberg, J.L. Lindström, L.I. Murin, P.R. Briddon, Phys. Rev. Lett. 81 (1998) 2930.
[7] L.I. Murin, T. Halberg, V.P. Markevich, J.L. Lindström, Phys. Rev. Lett. 80 (1998) 93.
[8] V.V. Emtsev, G.A. Oganesyan, K. Schmalz, Solid State Phenom. 47/48 (1996) 259.
[9] Y. Kamiura, M. Suezawa, K. Sumino, F. Hashimoto, Jpn. J. Appl. Phys. 29 (1990) L1937.
[10] A. Misiuk, W. Jung, B. Surma, J. Jun, M. Rozental, Solid State Phenom. 57/58 (1997) 393.
[11] A.B. Brown, M. Claybourn, R. Murray, P.S. Murray, P.S. Nandhra, R.C. Newman, J.H. Tucker, Semicond. Sci. Technol. 3 (1988) 591.
[12] J. Svensson, B.G. Svensson, J.L.L. Lindström, Appl. Phys. Lett. 21 (1986) 1435.
[13] S.C. Barber, Thin Solid Films 72 (1980) 201.
[14] P. Wagner, Mater. Res. Soc. Symp. Proc. 59 (1986) 125.
[15] H.J. Stein, Mater. Sci. Forum 10–12 (1986) 935.
[16] T. Halberg, J.L. Lindström, J. Appl. Phys. 72 (1992) 5130.
[17] Z. Li, H.W. Kramer, ROSE Collaboration Meeting, CERN, June 1, 1999, p. 108.
[18] T-2 Nuclear Information Service, Los Alamos National Laboratory.