Interactions of self-interstitials with interstitial carbon-oxygen center in irradiated silicon: an infrared absorption study

L.I. Murin^{1,a}, B.G. Svensson^{2,b}, V.P. Markevich^{3,c}, A.R. Peaker^{3,d}

¹Scientific-Practical Materials Research Center of NAS of Belarus, Minsk 220072, Belarus

²Oslo University, Department of Physics/Centre for Materials Science and Nanotechnology, N-0318 Oslo, Norway

³The University of Manchester, Manchester M13 9PL, United Kingdom

^amurin@ifttp.bas-net.by, ^bb.g.svensson@fys.uio.no,

^cv.markevich@manchester.ac.uk, ^dpeaker@manchester.ac.uk

Keywords: Silicon, defects, $I_nC_iO_i$ complexes, IR absorption, vibrational modes.

Abstract. The evolution of radiation-induced carbon-oxygen related defects with the fluence of MeV electrons and upon subsequent isochronal annealing (75-350 °C) in Si crystals with different carbon and oxygen content has been studied by means of Local Vibrational Mode (LVM) spectroscopy. In particular, the generation kinetics of the bands at 998 and 991 cm^{-1} is considered and additional arguments supporting their previous assignment to the $I_2C_iO_i$ and $I_3C_iO_i$ complexes are found. An annealing behaviour of the LVMs related to the C4 (IC_iO_i) defect has been studied in the various Si crystals irradiated with different particles. In all the samples studied the bands at 940 and 1024 cm^{-1} are found to disappear at about 200 °C while three new LVM bands, at 724 cm^{-1} (O-related) and at 952 and 973 cm^{-1} (both C-related) are emerging. Further increase in annealing temperature up to 250-275 °C results in a transformation of the latter bands into another set of LVM bands at 969 cm^{-1} (O-related) and at 951 and 977 cm^{-1} (both C-related). These bands disappear upon annealing in the temperature range 300-325 °C. The ratios of all the bands intensities as well as their transformation rates do not depend on the oxygen and carbon content in the Si samples nor on the kind of irradiation (2.5 and 10 MeV electrons, fast neutrons) and irradiation doses. These facts confirm our previous conclusion that all the above-mentioned LVMs arise from the C4 defect being in different configurations (IC_iO_i , $IC_iO_i^*$, and $IC_iO_i^{**}$).

Introduction

Along with oxygen, carbon is one of the most abundant impurities in Si crystals. In Czochralski grown silicon (Cz-Si) it is present normally in concentration of about 10^{15} - 10^{16} cm^{-3} and sometimes higher. The presence of carbon can affect significantly many of the oxygen-related defect reactions that occur upon heat-treatments at elevated temperatures or irradiations with high-energy particles [1-3]. In the latter case a major role of carbon is the trapping of the Si self-interstitials. Interstitial carbon atoms (C_i), generated via the Watkins displacement mechanism, are mobile at room temperatures and can interact with other defects and impurities. In Cz-Si the main sink for diffusing C_i is interstitial oxygen (O_i) and as a result the C_iO_i complex (C3 defect) [4-7] is generated as one of the dominant radiation-induced centers. The C_iO_i defect, in turn, appears to be a very effective trap for the Si self-interstitial atoms (I) and at doses when the C_iO_i concentration becomes comparable with that of C_s the so-called C4 defect (IC_iO_i) is generated efficiently. This defect has been detected only in infrared (IR) absorption studies [4, 5]. It gives rise to two main bands located at low temperature at about 940 and 1024 cm^{-1} (936 and 1020 cm^{-1} at room temperature). The first band is carbon related while the second one is mainly oxygen related [7, 8].

Upon further increase in the irradiation dose the C4 defect appears to be a trap for the Si interstitial atoms as well and a successive formation of $I_nO_iC_i$ ($n \geq 2$) centers is expected [5]. It was suggested by us earlier [7, 9] that the absorption bands at 998 and 991 cm^{-1} are related to the $I_2C_iO_i$

and $I_3C_iO_i$ defects, respectively. However, in the references [10, 11] these vibrational bands were assigned to the IC_iC_s complex. In present work the generation kinetics of the bands at 998 and 991 cm^{-1} has been studied and further arguments supporting their previous assignment to the $I_2C_iO_i$ and $I_3C_iO_i$ complexes have been found.

Another problem discussed in this paper is related to configurational transformations of the C4 defect upon isochronal annealing [9]. There is no consensus between experimental data [9] and the results of *ab-initio* modeling [12]. We will present some additional results on the C4 annealing behavior, which confirm our previous assignments.

Experimental details

The samples used in this investigation were prepared from n-type Cz-Si crystals ($\rho = 10\text{-}50\ \Omega\text{-cm}$, $[O_i] = (0.8\text{-}1.3)\times 10^{18}\ cm^{-3}$, $[C_s] = (0.5\text{-}3.0)\times 10^{17}\ cm^{-3}$). The concentrations of O_i and C_s were determined from measurements of intensities of absorption bands at 1107 and 605 cm^{-1} using the calibration coefficients 3.14×10^{17} and $0.94\times 10^{17}\ cm^{-2}$, respectively [1]. The samples were polished to an optical surface on two sides and the dimensions were $10\times 5\times 3\ mm^3$.

Irradiation with 2.5 and 10 MeV electrons was performed at room temperature (RT) by different fluencies in the range $1\cdot 10^{16}\text{-}2\cdot 10^{18}\ cm^{-2}$ and the samples were kept at RT for several months before measurements. A few samples were irradiated with 5 MeV neutrons. Isochronal annealing studies have been carried out in the temperature range 75-350 °C in 25 °C steps for 30 min at each temperature. IR absorption analysis was carried out using a Bruker IFS 113v spectrometer. A spectral resolution of 0.5 or 1.0 cm^{-1} was used and the samples were measured at 20 and 300 K.

Experimental results

$I_2C_iO_i$ and $I_3C_iO_i$ defects. Figure 1 shows the development of the IR absorption spectra in the wavenumber range 800-1040 cm^{-1} with accumulated dose of 2.5 MeV electrons for a Cz-Si sample with an intermediate carbon concentration ($[C_s] = 5\times 10^{16}\ cm^{-3}$). Along with the dominant and well known absorption band at 830 cm^{-1} related to vacancy-oxygen complex (A-center) several weaker vibrational bands positioned at 862, 936, 988, 994 and 1020 cm^{-1} are seen in the spectra. All of the latter bands are associated with the radiation-induced centers involving carbon since none of them could be observed in the absorption spectra of Cz-Si with low carbon content ($[C_s] < 10^{15}\ cm^{-3}$) [13]. Apparently, the well known band at 862 cm^{-1} is related to C_iO_i defect [1, 4-7], the bands at 936 and 1020 cm^{-1} are due to IC_iO_i [1, 5, 7]. Most likely, the absorption bands at 998 and 991 cm^{-1} are associated with $I_2C_iO_i$ and $I_3C_iO_i$ defects, respectively [7].

Evidently, formation of all the abovementioned centres should occur via the following sequential reactions [5]:

Figure 2 shows the generation kinetics of the corresponding centers studied. An analysis of the data obtained supports the previously suggested mechanism of the successive formation of the defects giving rise to the bands at 994 and 988 cm^{-1} in accordance with the above given reaction scheme.

A strong evidence that the centers responsible for the bands at 988 and 994 cm^{-1} (991 and 998 cm^{-1} at low temperatures) involve an oxygen atom has been presented in Ref. 7. In that study a few samples were enriched with ^{18}O oxygen isotope and a clear oxygen isotopic shift was observed for these bands (from 991 and 998 cm^{-1} in ^{16}O -doped Si to 948 and 954 cm^{-1} in ^{18}O -doped Si). So, most

Fig. 1. Fragments of absorption spectra measured at 300 K for a Cz Si sample ($[O_i] = 1.0 \times 10^{18}$, $[C_s] = 5 \times 10^{16}$, $[P] = 1 \times 10^{14} \text{ cm}^{-3}$), as-grown (1) and irradiated at room temperatures with the following accumulate doses of 2.5 MeV electrons: (2) 4×10^{16} , (3) 8×10^{16} , (4) 1.6×10^{17} , (5) 3.2×10^{17} , (6) 6.4×10^{17} , and (7) $1.28 \times 10^{18} \text{ cm}^{-2}$.

Fig. 2. Generation kinetics of C_iO_i and $I_nC_iO_i$ defects upon electron irradiation at room temperature (see Fig 1).

likely the bands at 998 and 991 cm^{-1} are related to oxygen vibrations in the $I_2C_iO_i$ and $I_3C_iO_i$ defects, respectively. Unfortunately, no corresponding C_i -related LVMs have been detected yet. Perhaps, their intensity is very low, as it does occur for the LVMs of some other carbon involving centres [1].

Isochronal annealing studies carried out by us have shown that the $I_2C_iO_i$ and $I_3C_iO_i$ defects possess slightly different thermal stabilities: $I_2C_iO_i$ is stable up to 400 °C while $I_3C_iO_i$ anneals out at about 300 °C (see also figures in the next subsection).

IC_iO_i , $IC_iO_i^*$, and $IC_iO_i^{}$ defects.** A complicated annealing behavior of the LVMs related to the C4 (IC_iO_i) defect has been revealed [9]. At about 200 °C the bands at 940 and 1024 cm^{-1} are transformed into 3 new LVM bands at 724 cm^{-1} (O-related) and at 952 and 973 cm^{-1} (both C-related). Further increase in annealing temperature up to 250-275 °C results in a transformation of the latter bands into a new set of LVM bands at 969 cm^{-1} (O-related) and at 951 and 977 cm^{-1} (both C-related). These bands disappear at about 300-325 °C. It has been argued that all the above-mentioned LVMs arise from the C4 defect being in different configurations (IC_iO_i , $IC_iO_i^*$, and $IC_iO_i^{**}$, respectively). However, this conclusion has been questioned later [11, 12]. LVMs calculated for the (meta)stable $IC_iO_i^*$ and $IC_iO_i^{**}$ structures found in an *ab-initio* study have not matched the wavenumbers of the absorption lines assigned by us to the corresponding defects [12]. Another reason is an absence of the $IC_iO_i^*$ LVMs in the IR absorption spectra measured at RT temperature [11, 14, 15]. To solve this puzzle we measured IR spectra at different temperatures in the range 20-300 K for a Cz-Si sample containing IC_iO_i defect after annealing at 200 °C.

Fig. 3 shows evolution of the spectra with the measurement temperature. The vibrational lines assigned to $IC_iO_i^*$ are clearly observed in the spectra measured at 20 K and 80 K, but they are not observable at room temperature at all. The origin of this phenomenon is not clear and requires a further investigation.

the observed appearance/disappearance of the C4 related bands are very similar in all the cases and, obviously, should be related to configurational transformations of the IC_iO_i defect since the

Fig. 5. The changes in amplitudes of the most intense absorption lines associated with the IC_iO_i , IC_iO_i^* , and $\text{IC}_i\text{O}_i^{**}$ structures [9], normalized to the amplitude of the 1024.2 line after irradiation upon isochronal annealing for the Cz-Si samples: $\blacklozenge$ - spectra of which are shown in Fig. 4a, $\blacksquare$ - see Fig. 4b, $\circ$ - see Fig. 4c.

ratios of their intensities are approximately the same. The latter is clearly demonstrated in Fig. 5 where the changes upon isochronal annealing in amplitudes of the most intense absorption lines (1024.2, 973.2 and 969.3 cm^{-1}) assigned to the IC_iO_i , IC_iO_i^* , and $\text{IC}_i\text{O}_i^{**}$ structures [9], normalized to the amplitude of the 1024.2 cm^{-1} band after irradiation, are presented for different samples. Independence of observed changes on carbon content and kind of irradiation (fast electrons or neutrons) provides a strong support to our earlier conclusion on the existence of different configurations of the C4 defect. At this point it should be noted that the initial C4 structure (formed upon irradiation) is not a structure with minimum energy. It appears to be a metastable state, and a structure consisting of the C3 defect with a nearby I atom can be suggested. The most stable configuration corresponds to the $\text{IC}_i\text{O}_i^{**}$ center. This information and the above presented new experimental data will be helpful if the problem with the IC_iO_i structures will be revisited in an *ab-initio* modeling study.

Summary

We have studied the generation kinetics of the vibrational absorption bands at 998 and 991 cm^{-1} and found strong additional arguments supporting their previous assignment to the $\text{I}_2\text{C}_i\text{O}_i$ and $\text{I}_3\text{C}_i\text{O}_i$ complexes. An annealing behaviour of the LVMs related to the C4 (IC_iO_i) defect has been compared in different Si crystals irradiated with different particles (electrons and/or neutrons). In all the samples studied the bands at 940 and 1024 cm^{-1} are found to disappear at about 200 °C while three new LVM bands, at 724 cm^{-1} (O-related) and at 952 and 973 cm^{-1} (both C-related) are emerging. Further increase in annealing temperature up to 250-275 °C results in a transformation of the latter bands into another set of LVM bands at 969 cm^{-1} (O-related) and at 951 and 977 cm^{-1} (both C-related). These bands disappear upon annealing in the temperature range 300-325 °C. The ratios of all the bands intensities as well as their transformation rates do not depend on the oxygen and carbon content in the Si samples nor on the kind of irradiation and a dose. These facts confirm the previous conclusion that all the above-mentioned LVMs arise from the C4 defect being in different configurations (IC_iO_i , IC_iO_i^* , and $\text{IC}_i\text{O}_i^{**}$).

Acknowledgments

We thank Prof. C.A. Londos for a help with irradiation of some Si samples with fast neutrons. Fund for Fundamental Research of the Republic of Belarus (grant F12MC-009) and the Norwegian Research Council (FRINATEK program) are thanked for a partial financial support.

References

- [1] G. Davies and R.C. Newman, Carbon in monocrystalline silicon, in: T.S. Moss (Ed.), Handbook on Semiconductors, Vol. 3b, Elsevier Science, Amsterdam, 1994, pp. 1557-1635.
- [2] F. Shimura (Ed.), Oxygen in Silicon, Semiconductors and Semimetals, Vol. 42, Academic, London, 1994.
- [3] J.L. Lindström, T. Hallberg, J. Hermansson, L.I. Murin, V.P. Markevich, M. Kleverman, and B.G. Svensson, Oxygen and carbon clustering in Cz-Si during electron irradiation at elevated temperatures, Solid State Phenomena, 69-70 (1999) 297-302.
- [4] G. Davies, A.S. Oates, R.C. Newman, R. Woolley, E.C. Lightowers, M.J. Binns, and J.C. Wilkes, Carbon-related radiation damage centres in Czochralski silicon, J. Phys. C: Solid State Phys. 19 (1986) 841-855.
- [5] G. Davies, E.C. Lightowers, R.C. Newman, and A.S. Oates, A model for radiation damage effects in carbon-doped crystalline silicon, Semicond. Sci. Technol., 2 (1987) 524-532.
- [6] J. Coutinho, R. Jones, P.R. Briddon, S. Oberg, L.I. Murin, V.P. Markevich, and J.L. Lindstrom, The interstitial carbon-oxygen center and shallow thermal donors in Si, Phys. Rev. B, 65 (2002) 014109 (1-11).
- [7] L.I. Murin, V.P. Markevich, J.L. Lindstrom, M. Kleverman, J. Hermansson, T. Hallberg, and B.G. Svensson, Carbon-oxygen-related complexes in irradiated and heat-treated silicon: IR absorption studies, Solid State Phenomena, 82-84 (2002) 57-62.
- [8] G. Davies, S. Hayama, S. Hao, B. Bech Nielsen, J. Coutinho, M. Sanati, S.K. Estreicher, and K.M. Itoh, Host isotope effects on midinfrared optical transitions in silicon, Phys. Rev. B, 71 (2005) 115212 (1-7).
- [9] L.I. Murin, J.L. Lindström, G. Davies, V.P. Markevich, Evolution of radiation-induced carbon-oxygen-related defects in silicon upon annealing: LVM studies, Nucl. Instrum. Methods Phys. Res. B, 253 (2006) 210-213.
- [10] C.A. Londos, M.S. Potsidi, G.D. Antonaras, A. Andrianakis, Isochronal annealing studies of carbon-related defects in irradiated Si, Physica B, 376-377 (2006) 165-168.
- [11] M.S. Potsidi, C.A. Londos, The $C_iC_s(I_{Si})$ defect in silicon: An infrared spectroscopy study, J. Appl. Phys. 100 (2006) 033523 (1-4).
- [12] D.J. Backlund, S.K. Estreicher, C4 defect and its precursors in Si: First principles theory, Phys. Rev. B, 77 (2008) 205205 (1-8).
- [13] J.L. Lindstrom, T. Hallberg, J. Hermansson, L.I. Murin, B.A. Komarov, V.P. Markevich, M. Kleverman, B.G. Svensson, Interaction between self-interstitials and the oxygen dimer in silicon, Physica B: Condensed Matter, 308-310 (2001) 284-289.
- [14] A.S. Oates, M.J. Binns, R.C. Newman, J.H. Tucker, J.C. Wilkes, A. Wilkinson, The mechanism of radiation-enhanced diffusion of oxygen in silicon at room temperature, J. Phys. C: Solid State Phys. 17 (1984) 5695-5705.
- [15] C.A. Londos, M.S. Potsidi, E. Stakakis, Carbon-related complexes in neutron-irradiated silicon, Physica B, 340-342 (2003) 551-555.

Gettering and Defect Engineering in Semiconductor Technology XV

10.4028/www.scientific.net/SSP.205-206

Interactions of Self-Interstitials with Interstitial Carbon-Interstitial Oxygen Center in Irradiated Silicon: An Infrared Absorption Study

10.4028/www.scientific.net/SSP.205-206.218