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Divacancy-oxygen and trivacancy-oxygen complexes in silicon: Local Vibrational Mode studies

L.I. Murin[1,a], B.G. Svensson[2,b],J.L. Lindström[3,c]
V.P. Markevich[4,d] and C.A. Londos[5,e]

[1]Scientific-Practical Materials Research Centre of NAS of Belarus, BY-220072 Minsk, Belarus

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

[3]Lund University, Division of Solid State Physics, SE-22100 Lund, Sweden

[4]University of Manchester, School of Electrical and Electronic Engineering, Manchester M60 1QD, UK

[5]Physics Department, Athens University, 15784 Athens, Greece

[a]murin@ifttp.bas-net.by, [b]b.g.svensson@fys.uio.no, [c]Lennart.Lindstrom@ftf.lth.se
[d]v.markevich@manchester.ac.uk, [e]hlontos@phys.uoa.gr

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Abstract. Fourier transform infrared absorption spectroscopy was used to study the evolution of multivacancy-oxygen-related defects in the temperature range 200-300 °C in Czochralski-grown Si samples irradiated with MeV electrons or neutrons. A clear correlation between disappearance of the divacancy (V_2) related absorption band at 2767 cm^{-1} and appearance of two absorption bands positioned at 833.4 and 842.4 cm^{-1} at 20 K (at 825.7 and 839.1 cm^{-1} at room temperature) has been found. Both these two emerging bands have previously been assigned to a divacancy-oxygen defect formed via interaction of mobile V_2 with interstitial oxygen (O_i) atoms. The present study shows, however, that the two bands arise from different defects since the ratio of their intensities depends on the type of irradiation. The 842.4 cm^{-1} band is much more pronounced in neutron irradiated samples and we argue that it is related to a trivacancy-oxygen defect (V_3O) formed via interaction of mobile V_3 with O_i atoms or/and interaction of mobile V_2 with VO defects.

Introduction

Local Vibrational Mode (LVM) spectroscopy has appeared to be a very powerful tool in studies of the oxygen-related defects of different type in Si [1-13], including small oxygen clusters [9], self-interstitial- [10] and vacancy-oxygen aggregates [11]. Among the latter defects are the well known vacancy-oxygen (VO) complex or A-center [2], VO_2, VO_3 and VO_4 defects [3-8]. More recently, LVM signatures of more complicated defects, VO_5 and VO_6, have been found [12]. However, there is another group of vacancy-oxygen aggregates, the so-called multivacancy-oxygen (V_nO, $n \geq 2$) defects, for which the previous LVM studies have not led to a clear and self-consistent picture.

One of the main reasons is that all members of the V_nO family contain a Si-O-Si bonding structure like that for VO, and as it was already noted in Ref. 13 the oxygen-related vibrational bands of V_nO in some cases could hardly be resolved from the more intensive 836 cm^{-1} band due to the A-center. This is in agreement with the *ab-initio* calculations [14, 15], which have also predicted that the frequencies of LVMs of such defects as VO and V_2O should be very close. Since concentrations of the V_nO defects are lower than that of VO the vibrational bands of V_nO are expected to appear as satellites to the main VO band. In 1964 Ramdas and Rao [4] reported a number of lines appearing around the main VO band, upon annealing in the temperature range 200-400 °C of neutron-irradiated Cz-Si. The most pronounced satellites were positioned at about 829, 833 and 842 cm^{-1} at low temperature and were labeled as S_1, S_2 and S_3, respectively. The centers

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responsible for the latter two bands were generated without any expense of the VO defect, and were suggested to arise from multivacancy-oxygen complexes with a V_2O center as a very likely candidate.

Studies employing high resolution Fourier transform infrared (FTIR) absorption spectroscopy have confirmed the results of Ref. 4 and show that the picture is even more complicated with a very rich satellite spectrum of VO [16]. A number of satellite lines were also observed in electron irradiated Cz-Si upon annealing in the temperature range 200-400 °C [17, 18]. However, no attempts were undertaken in Refs. 16-18 to elucidate the origin of the defects giving rise to the satellite bands. A more straightforward and rather extensive study of V_nO defects in neutron-irradiated Cz-Si has been done by the Athens group [7, 19, 20]. Based on annealing studies and semi-empirical modeling, Londos et al. [7, 19, 20] assigned the bands positioned at about 839 and 884 cm^{-1} at room temperature to V_2O and V_3O complexes, respectively. The 839 cm^{-1} band was produced during anneals at temperatures above 230 °C, when divacancies are known to become mobile and the appearance of the band was linked to the trapping of V_2 by O_i. However, V_2 annealing was not monitored in Ref. 19. Further, the identification of the V_3O band is also rather tentative. A side-band at 884 cm^{-1} was found only as a shoulder of the more intense VO_2 band at 887 cm^{-1} via a fitting procedure [20]. In general, appearance of such shoulders can occur due to the presence of ^{29}Si and ^{30}Si isotopes in natural silicon, and in this context it can be noted that earlier [1, 13] the 887 cm^{-1} band itself was erroneously assigned to V_3O.

There is no consensus on identification of the V_2O bands either. Low-temperature FTIR studies by Lindström et al. [8] showed a correlation between the disappearance of V_2, monitored through its electronic transition observed at 2767 cm^{-1}, and the growth of the S_2 shoulder at 833.4 cm^{-1} in 2.5 MeV electron-irradiated Cz-Si samples. Accordingly, the 833.4 cm^{-1} band was assigned to V_2O.

In the present work an attempt is made to obtain more solid identifications of LVMs due to V_2O and V_3O defects via comparative FTIR studies of the VO satellite lines in electron- and neutron irradiated Czochralski-grown (Cz) Si materials with measurements carried out at both, low and room temperatures.

Experimental details

The samples used in this investigation were prepared from phosphorus doped n-type Cz-Si crystals (ρ = 1-50 Ω-cm),). The concentrations of interstitial oxygen ($[O_i] = (0.8\text{-}1.3)\times10^{18}$ cm^{-3}) and substitutional carbon ($[C_s] = (1\text{-}50)\times10^{15}$ cm^{-3}) were determined from measurements of intensities of absorption bands at 1107 and 605 cm^{-1} using the calibration coefficients 3.14×10^{17} and 0.94×10^{17} cm^{-2}, respectively [11]. The samples were polished to an optical surface on two sides and the dimensions were 10×6×3 mm^3 or 10×6×5 mm^3.

Irradiations with 2.5 MeV electrons and fast neutrons (5 MeV) were performed at nominal room temperature (≤ 350 K) with fluencies in the range $1\cdot10^{16}$-$1\cdot10^{18}$ cm^{-2} and the samples were kept at RT at least for several weeks before measurements. Isochronal annealing studies have been carried out in the temperature range 75-400 °C with 25 °C increments 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 about 20 K (low temperature - LT), and at room temperature (RT).

Experimental results

Evidently, upon room temperature irradiation the V_nO defects in silicon can be generated via sequential trapping of mobile vacancies by O_i, VO, V_2O etc, i.e., via the reactions $V + O_i \Rightarrow VO$, $V + VO \Rightarrow V_2O$, $V + V_nO \Rightarrow V_{n+1}O$. However, in Cz-Si, where the oxygen concentration is normally of about 10^{18} cm^{-3}, the generation of V_nO ($n \geq 2$) may be efficient only at very high doses of irradiation when VO concentration is comparable with $[O_i]$. At low fluencies when the

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concentration of radiation-induced defects is much lower than [O_i], the production of V_2O appears to be negligible even in the case of neutron irradiation. As an example, Figures 1a and 1b show the absorption spectra around the VO band measured at 20 K and at RT for a sample irradiated with neutrons to a fluence of 1×10^{17} cm^{-2}. The band shapes are analyzed using a fitting procedure where the effect of silicon isotopes (^{29}Si and ^{30}Si) has been taken into account. In the case of the LT spectrum an excellent agreement is observed between the calculated spectrum obtained with the use of Lorentzians and the measured one. The presence of an additional peak at 834.45 cm^{-1}, which could be related to V_2O has been found upon fitting, but its intensity is very low (see curve 4 in Fig. 1a). Also for the RT measurements a reasonable agreement is obtained between the measured and calculated values (Fig. 1b), although the correspondence of the spectra was worse than that for the LT spectra. In the following, we will concentrate mainly on the LT spectra with the additional benefit of monitoring the divacancy annealing via changes in the intensity of the 2767 cm^{-1} band related to V_2 electronic excitations [21,22]. In all the samples studied the 2767 cm^{-1} band was strong and clearly observed, e.g., in the case of neutron irradiation its amplitude amounted up to about 5 cm^{-1}.

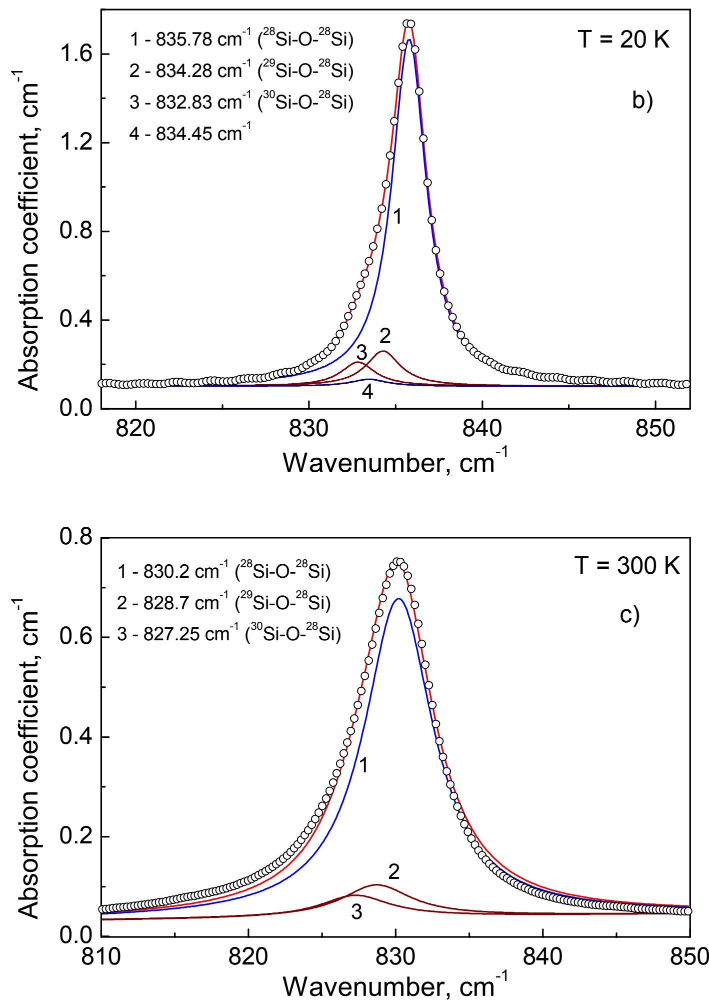

Fig. 1 Fragments of absorption spectra measured at 20 K (a) and at room temperature (b) for a Cz-Si sample ([O_i] = 1.3×10^{18}, [C_s] $\leq$ 1×10^{15}, [P] = 7×10^{13} cm^{-3}) irradiated with 5 MeV neutrons to a dose of 1×10^{17} cm^{-2}. Solid lines are fitting curves.

Divacancies in silicon are mobile at temperatures above 200 °C and in Cz-Si crystals the interstitial oxygen has been suggested [21] to be the main trap of mobile V_2, i.e., a transformation of V_2 into V_2O can be expected to occur via the reaction $V_2 + O_i \Rightarrow V_2O$. It is worth noting here that the occurrence of such a reaction has been confirmed in detailed DLTS studies [23]. Appearance of new defects upon the V_2 elimination has also been clearly observed in the present infrared absorption studies.

Fig. 2 shows a fragment of the LT spectrum measured for the sample used for measurements shown in Fig.1 after annealing at 250 °C for one hour. Such treatment resulted in a strong decrease (~90%) of the V_2 related absorption band at 2767 cm^{-1} and the appearance of a complex structure around the main VO band.

A fitting procedure using Lorentzians was used again to analyze the data. In addition to the main absorption band related to VO, four relatively strong bands appeared in the spectra. For each band the presence of all three Si isotopes was taken into account upon fitting. For clarity, only the fitting sub-curves 1-5 corresponding to ^{28}Si-O-^{28}Si units are shown in Fig. 2, but the main fitting curve accounts for all the contributions. For further validation the fitting results we have analyzed also

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difference absorption for all the bands. The corresponding difference absorption spectrum is shown in Fig. 3.

For completeness, Fig. 4 shows the spectra measured at RT for the sample used for the spectra in Figs. 2 and 3. Two main satellite bands positioned at about 826 and 839 cm^{-1} appear in the RT spectra. Apparently, these bands correspond to the 833.4 and 842.4 cm^{-1} bands observed in the LT spectra. It should be noted here that the 848.7 cm^{-1} band observed at LT has disappeared at RT. This band disappears also in the LT spectra when optical excitation from the spectrometer is suppressed by using a Ge filter and concurrently, the intensity of the 842.4 cm^{-1} band increases. Also measurements with a Ge filter showed a

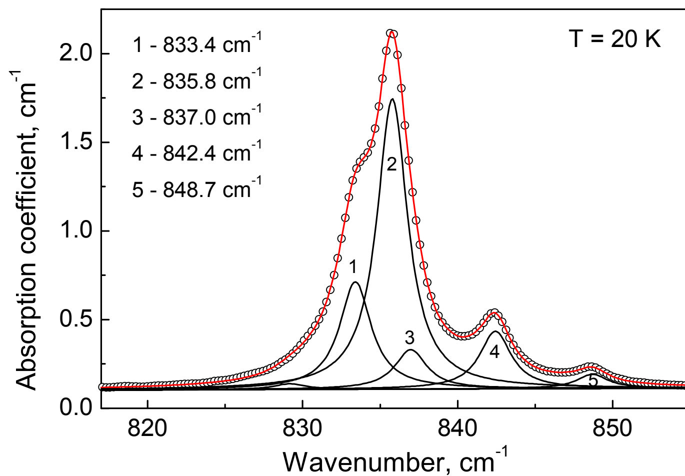

Fig. 2. Fragment of the LT absorption spectrum for the Si sample used for Fig. 1, after annealing at 250 C for 1 h. Solid lines are fitting curves.

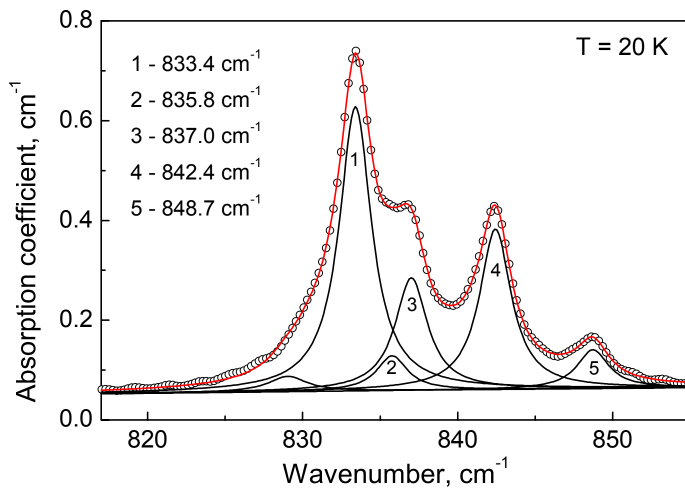

Fig. 3. Fragment of a difference-absorption spectrum obtained by subtracting the spectrum measured at 20 K after irradiation from the spectrum measured after annealing for 1h at 250 C for the Si sample used for Fig. 1. Solid lines are fitting curves.

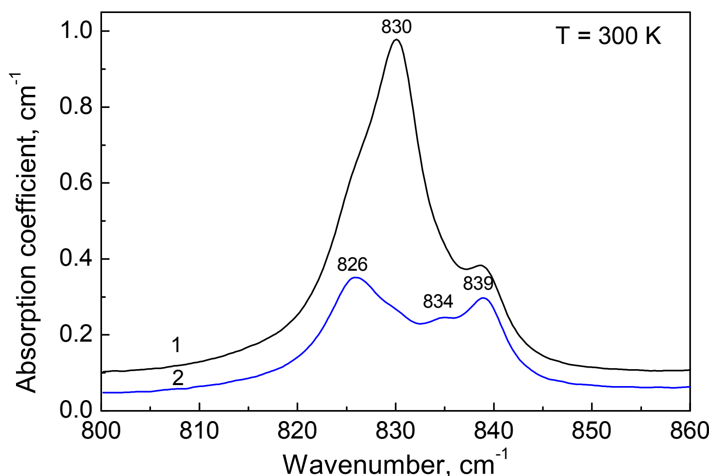

Fig. 4. Curve 1 - fragment of the RT absorption spectrum for the Si sample used for Fig. 1, after annealing at 250 °C for 1 h. Curve 2 - fragment of a difference-absorption spectrum obtained by subtracting the spectrum measured at 300 K after irradiation from the spectrum measured after annealing for 1h at 250 C for the same Si sample.

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significant decrease in the intensity of the band 837.0 cm^{-1} and a corresponding growth in intensity of the 833.4 cm^{-1} band. These facts demonstrate that the 837.0 and 848.7 cm^{-1} bands are related to optically excited states of the defects giving rise to the 833.4 and 842.4 cm^{-1} bands, respectively. For the 837.0 cm^{-1} band there is also another defect which contributes since the band can be partly observed at RT and has a higher thermal stability as compared with the 833.4 cm^{-1} band.

Discussion

Thus, in agreement with the previously published results, our data demonstrate that the annealing of divacancies in neutron-irradiated Cz-Si is accompanied by the appearance of new absorption bands. The most intense of them are located at 833.4 and 842.4 cm^{-1} (826 and 839 cm^{-1} at RT). Isochronal (30 minutes) annealing studies have shown that not only their formation processes but also annihilation kinetics are very similar. The bands at 833.4 and 842.4 cm^{-1} disappear simultaneously in the temperature range 300-350 °C.

One can suggest that both bands arise from the same defect, namely V_2O, being in different configurations. However, there are some crucial facts that do not support such a suggestion. Firstly, the ratio of intensities of these bands is the same at LT and at RT. It is difficult to imagine two different configurations of the V_2O defect that are equal in total energy. Besides, only one V_2O center has been observed in DLTS studies and practically full transformation of V_2 into this center occurs. The second and, probably, the most important fact is that the ratio of intensities of these bands depends on the type and fluence of irradiation. As an example, Fig. 5 shows fragments of the absorption spectra with these bands for electron- and neutron-irradiated samples. Evidently, the 842.4 cm^{-1} band is much more pronounced after neutron irradiation and so, it originates most likely from a more complex defect than that responsible for the 833.4 cm^{-1} band. A possible candidate is the V_3O defect which may be generated via interaction of mobile divacancies with A-centers, i.e., via the reaction $V_2 + VO \Rightarrow V_3O$.

However, it appears that this reaction can not account for the observed overall generation of V_3O (the 842.4 cm^{-1} band), especially in samples with relatively low VO concentration. It is very likely, that V_3, produced mainly as a primary defect, has the same migration ability as V_2, and V_3O can be also generated via the reaction $V_3 + O_i \Rightarrow V_3O$. Such a suggestion is in agreement with EPR data [24] on the thermal stability of V_3. On the other hand, according to the EPR data by Lee and Corbett [25] the V_3O defect is likely responsible for the P4 spectrum which appears upon annihilation of VO and V_2O at about 350 °C and that is at variance with our assignment of the 842.4 cm^{-1} band. However, Lee and Corbett [25] have noted that a V_3O_2 defect, being in a certain configuration, can also give rise to the P4 spectrum and this assignment is more consistent with our interpretation.

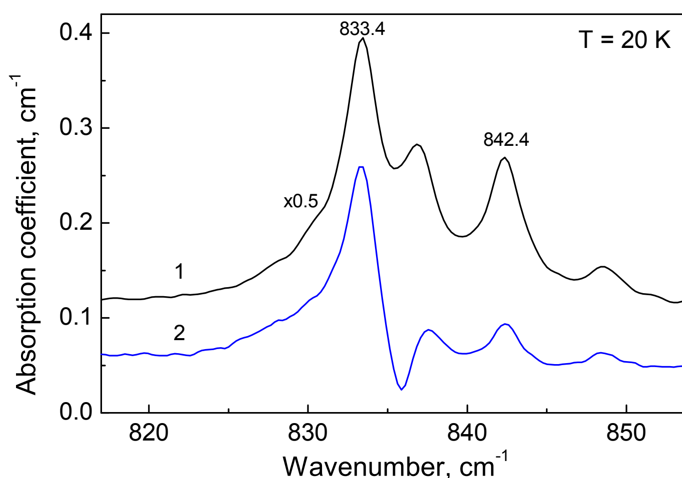

Fig. 5. Fragments of difference-absorption spectra. Curve 1 is the same as shown in Fig. 3, but with intensity of the peaks scaled down by a factor of 2. Curve 2 was obtained by subtracting the spectrum measured at 20 K after irradiation from the spectrum measured after annealing for 30 min at 280 °C for a sample irradiated with 2.5 MeV electrons to a dose of 1×10^{18} cm^{-2}.

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Conclusions

In conclusion, high resolution LVM spectroscopy have shown that two absorption bands positioned at 833.4 and 842.4 cm^{-1} (at 20 K) appear simultaneously with the elimination of divacancies in irradiated Cz-Si samples. The experimentally observed band shapes can be nicely fitted by calculations with the use of Lorentzians, in which contributions from all the three stable Si isotopes are taken into account. In contrast to previous studies reported in the literature, where both these bands have been attributed to the V_2O center, we have assigned only the band at 833.4 cm^{-1} band to V_2O, which is formed via trapping of mobile V_2's by O_i. The relative intensity of the 842.4 cm^{-1} band is substantially enhanced in neutron-irradiated samples compared to that in electron-irradiated ones and hence, this band is associated with a higher order complex than that responsible for the 833.4 cm^{-1} band. A likely candidate is V_3O center.

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