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Trivacancy-oxygen complex in silicon: Local vibrational mode characterization

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ABSTRACT

FTIR study of the evolution of multivacancy-oxygen-related defects in the temperature range 100–350 °C in Czochralski-grown Si samples irradiated with different particles (10 MeV electrons and 5 MeV neutrons) has been carried out. Appearance of two absorption bands positioned at 833.4 and 842.4 cm^{-1} has been found upon annealing of the divacancy related absorption band at 2767 cm^{-1}. The 833.4 cm^{-1} band is assigned to a divacancy-oxygen defect. 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 formed via interaction of mobile V_3 with O_i atoms.

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1. Introduction

Infrared (IR) absorption spectroscopy has been known to be a very powerful tool in studies of oxygen-related defects in Si (e.g. see Refs. [1–5] and references therein). However, regarding the multivacancy-oxygen-related defects (V_nO, $n \geq 2$) previous IR absorption 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 the vacancy-oxygen defect (VO or A-center). The vibrational bands of V_nO centers appear in a close vicinity of the main VO band and they are hardly distinguishable in the absorption spectra.

In the present work a careful local vibrational mode (LVM) study of the evolution of multivacancy-oxygen-related defects in the temperature range 100–350 °C in Czochralski-grown Si samples irradiated with different particles (MeV electrons and neutrons) has been carried out. 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. A clear correlation between disappearance (upon annealing) 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 [6,7]. 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.

2. Experimental

The samples used in this investigation were prepared from phosphorus doped n-type Cz-Si crystals ($\rho = 5$–$50\,\Omega\,cm$). The concentrations of interstitial oxygen ($[O_i] = (0.8$–$1.3) \times 10^{18}\,cm^{-3}$) and substitutional carbon ($[C_s] = (1$–$50) \times 10^{15}\,cm^{-3}$) were determined from measurements of intensities of absorption bands at 1107 and 605 cm^{-1} using the calibration coefficients 3.14×10^{17} and $0.94 \times 10^{17}\,cm^{-2}$, respectively [8,9]. The samples were polished to an optical surface on two sides and the dimensions were $10 \times 6 \times 3$ or $10 \times 6 \times 5\,mm^3$.

Irradiations with 10 MeV electrons and fast neutrons (5 MeV) were performed at nominal room temperature ($\leq$ 350 K) with doses in the range 1×10^{16}–$1 \times 10^{18}\,cm^{-2}$ and the samples were kept at RT usually for several weeks before measurements. Isochronal annealing studies have been carried out in the temperature range 75–350 °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

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and the samples were measured at about 20 K (low temperature—LT), and at room temperature (RT).

3. Results and discussion

Fitting procedure: It was noted previously [7] that a band assigned to the V_2O defect appears as a low-frequency shoulder of a much stronger VO band. The separation of the absorption bands due to V_2O and VO is only possible with the use of a fitting procedure. However, the V_2O band appears just in the same region where the VO sub-bands related to ^{29}Si and ^{30}Si isotopes are expected to emerge (Natural silicon is made up of ^{28}Si (92.23%), ^{29}Si (4.68%), and ^{30}Si (3.09%) isotopes [10]). To minimize possible errors upon fitting the knowledge of exact positions of the VO sub-bands is highly desirable. Such positions were found by us using two approaches. It is known that there are differences of only about 0.1 cm^{-1} or less in A_{2u} mode frequencies for an interstitial oxygen atom between the same Si–O_i–Si units embedded in the lattice of natural or monoisotopic crystals [11,12]. The latter result allows us to neglect the possible differences in the *B*1 mode frequencies for the VO defect (for the same Si–O–Si unit) in natural and monoisotopic silicon and infer the geometry (internal angle) of Si–O_s–Si unit and interaction mass, similar to what was done recently to describe Ge isotope effects for the VO center in Ge [13]. The ratio of ν_3 vibration frequencies of two Si–O–Si units with different isotopic composition is

$$\frac{\nu_3(^k\text{Si}_2^l\text{O})}{\nu_3(\text{Si}_2\text{O})} = \sqrt{\frac{Mm(m_l + M_k \sin^2\alpha)}{M_k m_l(m + M\sin^2\alpha)}} \quad (1)$$

where m and M are the masses of the O and neighboring Si atoms, ^{k}Si or ^{l}O stands for an isotope of Si or O and 2α is the internal angle of the Si–O–Si chain. Actually, M is an effective Si mass, which includes also an interactive mass m^*, i.e. $M_{Si} = m_{Si}+m^*$. It is assumed that in Eq. (1) both the force constant and the angle are identical for different isotopic combinations. If the frequencies for at least three different isotopic combinations are known then it is possible to find out the values of m^* and α when solving the system of two equations (1). Presently, for the A-center, the frequencies of the combinations ^{28}Si–^{16}O–^{28}Si (835.8 cm^{-1}), ^{28}Si–^{18}O–^{28}Si (799.9 cm^{-1}) and ^{30}Si–^{16}O–^{30}Si (829.8 cm^{-1}) are known [7,12]. We have solved an appropriate system of linear equations and found that $m^* = 4$ amu and $\alpha = 62°$.

It is known that the asymmetric quasimolecule ^{m1}Si–O–^{m2}Si is nearly equivalent to a symmetric ^{m3}Si–O–^{m3}Si, where m_3 is the arithmetic mean of m_1 and m_2 [13]. So, it is possible to estimate the *B*1 mode position for the composition ^{28}Si–^{16}O–^{29}Si and a combined mode for the ^{28}Si–^{16}O–^{30}Si and ^{29}Si–^{16}O–^{29}Si compositions using again Eq. (1) and to calculate the isotopic shifts. The shifts obtained are 1.55 cm^{-1} for a ^{28}Si–^{16}O–^{29}Si unit and 3.0 cm^{-1} for a ^{28}Si–^{16}O–^{30}Si unit as compared with the main ^{28}Si–^{16}O–^{28}Si line position at 835.8 cm^{-1}.

We have also tried to estimate the isotopic shifts of the *B*1 mode due to the VO defect in a semiempirical way, i.e. to fit the shape of the VO absorption band using Lorenzian type function for three main isotope compositions (^{28}Si–^{16}O–^{28}Si, ^{28}Si–^{16}O–^{29}Si, ^{28}Si–^{16}O–Si^{30}) with the fixed amplitude ratios corresponding to calculated relative concentrations of the appropriate Si–O–Si sites in natural Si (found as 1, 0.1015, and 0.0695 for the ^{28}Si–^{16}O–^{28}Si, ^{28}Si–^{16}O–^{29}Si, and ^{28}Si–^{16}O–^{30}Si+ ^{29}Si–^{16}O–^{29}Si combinations, respectively). A great number of experimentally measured absorption spectra for different samples irradiated with relatively low doses of MeV electrons (when VO concentration was much lower than that of O_i) were analyzed. As an example, Fig. 1 shows one of such spectra.

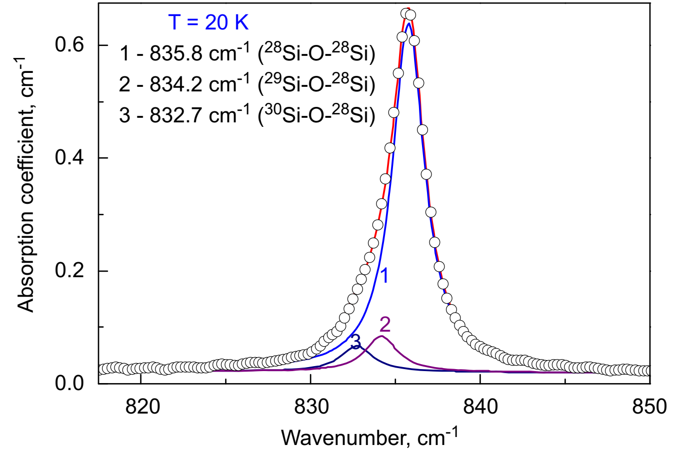

Fig. 1. (Color online). Fragments of the LT absorption spectrum for a Cz-Si sample ($[O_i] = 8.3\times10^{17}$, $[C_s] = 5\times10^{16}$, $[P] = 5\times10^{13}$ cm^{-3}) irradiated with 10 MeV electrons to a dose of 3×10^{17} cm^{-2}. Solid lines are fitting curves.

The fitting parameters were the band positions and their full width at half of maximum (FWHM) under assumption that the FWHM is the same for all VO-related sub-bands. The average values of isotopic shifts and FWHM were found to be the following: 1.51 cm^{-1} for a ^{28}Si–^{16}O–^{29}Si unit, 2.92 cm^{-1} for a ^{28}Si–^{16}O–^{30}Si, and 2.34 cm^{-1} for the FWHM. In the further analysis of more complicated spectra we have used the mean values of the shifts obtained via calculations and fitting (1.55 cm^{-1} for ^{28}Si–^{16}O–^{29}Si and 2.95 cm^{-1} for ^{28}Si–^{16}O–^{30}Si) as fixed ones for V_nO (≥ 2) related bands. The values of FWHM were taken usually as free parameters, but being the same within the sub-band group for a certain defect.

Assignment of the 833.4 *and* 842.4 cm^{-1} *bands*: 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 ⇒ VO, V+VO ⇒ V_2O, V+V_nO ⇒ $V_{n+1}O$. However, in Cz-Si, where the oxygen concentration is normally of about 10^{18} cm^{-3}, the generation of V_nO ($n\geq2$) may be efficient only at very high doses of irradiation when VO concentration is comparable with that of O_i. At low doses when the concentration of radiation-induced defects is much lower than that of O_i, the production of V_2O appears to be negligible even in the case of neutron irradiation. As an example, Fig. 2 shows the LT absorption spectrum around the VO band for a sample irradiated with neutrons to a dose of 1×10^{17} cm^{-2}. The band shape was analyzed using a fitting procedure described above. One can see that there is an excellent agreement between the calculated spectrum 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. 2).

Divacancies in silicon are mobile at temperatures above 200 °C and in Cz-Si crystals the interstitial oxygen has been suggested [14] 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 ⇒ V_2O. It is worth noting here that the occurrence of such a reaction has been confirmed in detailed DLTS studies [15]. Appearance of new defects upon the elimination of V_2 has also been clearly observed in the present infrared absorption studies. Fig. 3 shows a fragment of the LT spectrum measured for the sample used for measurements shown in Fig. 2 after annealing at 250 °C for 1 h. Such treatment resulted in a strong decrease (~90%) of the V_2 related absorption band at 2767 cm^{-1} [14] and the appearance of a complex structure around the main VO band. A fitting procedure

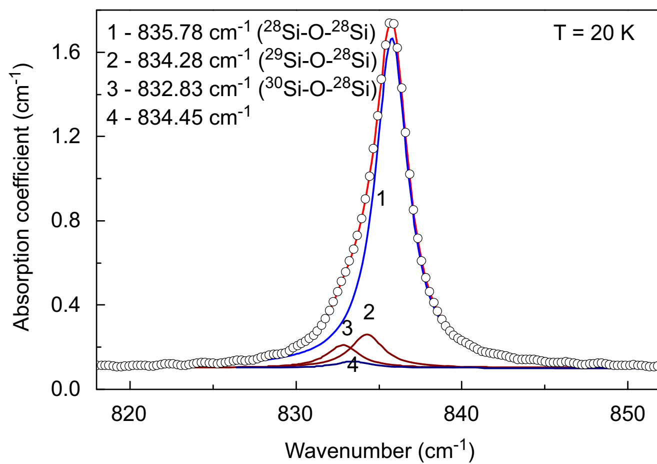

Fig. 2. (Color online). Fragment of absorption spectrum measured at 20 K for a Cz-Si sample ($[O_i] = 1.3 \times 10^{18}$, $[C_s] \leq 1 \times 10^{15}$, $[P] = 7 \times 10^{13}\,cm^{-3}$) irradiated with 5 MeV neutrons to a dose of $1 \times 10^{17}\,cm^{-2}$. Solid lines are fitting curves.

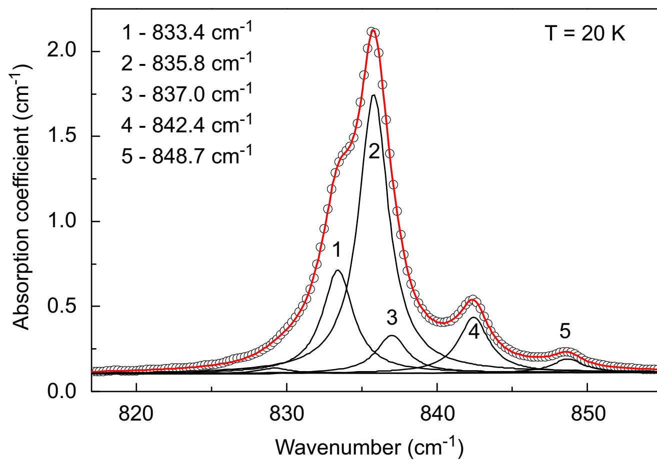

Fig. 3. (Color online). Fragment of the LT absorption spectrum for the Si sample used for Fig. 2, after annealing at 250 °C for 1 h. Solid lines are fitting curves.

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–^{16}O–^{28}Si units are shown in Fig. 3, but the main fitting curve accounts for all the contributions.

It should be noted here that the 848.7 cm^{-1} band has not been observed in the RT spectra. 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 LT measurements with a Ge filter showed a significant decrease in the intensity of the 837.0 cm^{-1} band 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 (most likely, to the singly negative charge 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.

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

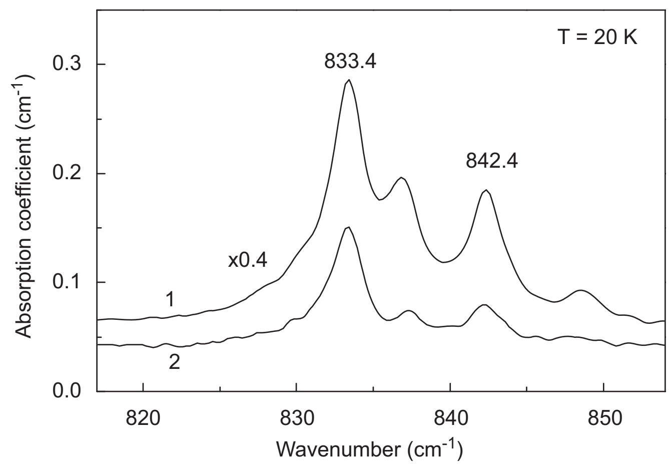

Fig. 4. Fragments of difference-absorption spectra obtained by subtracting the spectra measured after irradiation from the spectra measured after annealing for 30 min at 275 °C for the Si samples ($[O_i] = 8.3 \times 10^{17}$, $[C_s] = 5 \times 10^{16}$, $[P] = 5 \times 10^{13}\,cm^{-3}$): 1—irradiated with neutrons to a dose of $7.5 \times 10^{16}\,cm^{-2}$; 2—irradiated with 10 MeV electrons to a dose of $3 \times 10^{17}\,cm^{-2}$.

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 min) 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 upon anneals 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 is a crucial fact that does not support such a suggestion. We have found that the ratio of intensities of these bands depends on the type of irradiation. As an example, Fig. 4 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 cannot 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 [16] on the thermal stability of V_3. It is interesting to note at this point that the V_2H and V_3H defects detected in EPR and FTIR studies are also not distinguishable by their annealing behavior [17]. On the other hand, according to the EPR data by Lee and Corbett [18] 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 [18] 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.

4. Conclusions

In conclusion, employing high resolution LVM spectroscopy two absorption bands positioned at 833.4 and 842.4 cm^{-1} (at 20 K) are found to appear upon annealing of divacancies in irradiated Cz-Si samples. The experimentally observed band shapes can be closely fitted by calculations using Lorentzians where

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 ascribed to the V_2O pair, only the 833.4 cm^{-1} band is assigned to V_2O, 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 the V_3O center.

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