# Interaction of Radiation-Induced Self-Interstitials with Vacancy-Oxygen Related Defects $V_nO_2$ (n from 1 to 3) in Silicon

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**Two stage electron irradiation with thermal heat-treatments after each stage is used for vacancy-oxygen-related defect engineering in Czochralski-grown silicon (Cz-Si). The Cz-Si samples are first irradiated at room temperature with 2.5 MeV electrons and then heat-treated at 320 °C to anneal out the VO, $V_2O$, and $V_3O$ centers and generate the $VO_2$, $V_2O_2$, and $V_3O_2$ complexes as the dominant vacancy-oxygen-related defects. Subsequently, the samples are irradiated at room temperature again and subjected to 30-min isochronal annealing in the temperature range 75–350 °C. Defect evolution upon the treatments is monitored by means of the local vibrational mode (LVM) absorption spectroscopy. From an analysis of changes in intensity of the LVM lines it is revealed that the second irradiation results in a noticeable decrease in the concentrations of the $VO_2$, $V_2O_2$, and $V_3O_2$ complexes and an increase in the concentrations of the oxygen dimer and the $VO_2^*$ defect (metastable state of $VO_2$, which consists of the VO and $O_i$ components). The observed defect transformations are argued to be related to interactions of the radiation-induced self-interstitial silicon atoms (I) with the vacancy-oxygen complexes via the following reactions:**
**$VO_2 + I \rightarrow O_{2i}$, $V_3O_2 + I \rightarrow V_2O_2$, $V_2O_2 + I \rightarrow VO_2^*$.**

## 1. Introduction

Processes of radiation-induced defect formation and their elimination in silicon and silicon devices have been a subject of great attention since the 1960s and still are.[1–3] A large number of experimental and theoretical results have already been accumulated in this research field motivated by the control and removal of implant damage and an understanding of defect reactions which has facilitated defect engineering in silicon. In particular, the structural, electronic, optical, and dynamical properties of a number of radiation-induced defects (RIDs) have been determined. These include defects resulting from interactions of primary lattice defects with interstitial oxygen atoms, the most abundant impurity atoms in Czochralski-grown (Cz) Si crystals. The relevance of understanding of effects of radiation-induced oxygen-related defects on performance of silicon-based electronic devices has been underlined recently in a review paper by Chroneos et al.[3] In that review and in an earlier work (ref. [4]) several methods of defect engineering for management of interactions of intrinsic defects with oxygen-related centers and related modifications of electrical and optical properties of Cz-Si crystals have been discussed. In the present work interactions of silicon self-interstitial atoms with some oxygen-vacancy-related defects will be considered in more details.

Oxygen in silicon is one of the most effective traps for mobile mono-vacancies, di-vacancies, and tri-vacancies.[1–12] The vacancy-oxygen complex (VO), also called the A-center, was the first radiation-induced defect identified in irradiated Si crystals.[5] By now, its properties have been thoroughly studied.[3,6] More recently, the properties of the divacancy-oxygen ($V_2O$) and trivacancy-oxygen ($V_3O$) complexes have been studied in detail.[7–11] It is found that the VO, $V_2O$, and $V_3O$ centers disappear upon annealing of the irradiated Si samples at temperatures above 300 °C and their disappearance is accompanied by the appearance of vacancy-oxygen complexes containing two oxygen atoms ($VO_2$, $V_2O_2$, and $V_3O_2$). All of these complexes give rise to vibrational absorption bands which can be observed in the infra-red absorption spectra.[3,4,6,10,12–18]

The $VO_2$ defect plays an important role in processes of aggregation of oxygen atoms and vacancies during growth of silicon crystals by Czochralski techniques and upon formation of oxide films and oxygen precipitates in Cz-Si wafers.[6,19,20]

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Therefore, the formation and elimination mechanisms and properties of this center have been extensively studied.[3,6] According to the $VO_2$ structural model, in the minimum energy configuration two oxygen atoms saturate all four broken bonds of a Si vacancy.[3,6] In this configuration, both oxygen atoms occupy equivalent positions inside the vacancy, each of them is connected with two silicon atoms and gives rise to an absorption band at 895 $cm^{-1}$.[6,12] For a long time it was thought that the $VO_2$ defect could not be electrical active. However, in 2003, bistability of the $VO_2$ complex was discovered.[15] It has been found that there is another, metastable, configuration of this center – $VO_2{}^*$, in which one oxygen atom is inside the vacancy, while the second atom occupies an interstitial position at the center of the nearest Si-Si bond. The total energy of the defect in the metastable configuration is only 0.25 eV higher than the energy of the ground state of the $VO_2$ complex, so at high temperatures a noticeable fraction of the complexes can be in the metastable $VO_2{}^*$ state. Unlike the minimum energy electrically inactive $VO_2$ state, the $VO_2{}^*$ complex is an acceptor with an energy level located at about 0.05 eV below the conduction band edge. The absorption bands at 928 and 1004 $cm^{-1}$ have been assigned to the neutral state of the $VO_2{}^*$ defect, while the bands at 967 and 1023 $cm^{-1}$ have been linked to the negatively charged center.[16,17]

In electron-irradiated Cz-Si crystals, the formation of the $VO_2$ and $VO_2{}^*$ complexes was found to occur either during annealing in the temperature range 300–400 °C of Cz-Si crystals irradiated at room temperature, or upon so-called hot (≈350 °C) irradiation (see ref. [17] and references therein). Recently, it has been argued that two infrared absorption lines at 924 and 1016 $cm^{-1}$, which were observed in absorption spectra of Cz-Si samples subjected to irradiation with fast neutrons and annealing in the temperature range 200–300 °C, are related to the $VO_2{}^*$ defect.[21] It should be noted, however, that the arguments presented in ref. [21] for the assignment of the lines at 924 and 1016 $cm^{-1}$ to the $VO_2{}^*$ center are not very solid. In this paper we give further evidence for the assignment of the absorption bands at 928 and 1004 $cm^{-1}$ to the $VO_2{}^*$ defect and report on the formation of this complex and oxygen dimers ($O_{2i}$) in the room temperature region as a result of irradiation of Cz-Si samples containing the $V_nO_2$ vacancy-oxygen centers, including the recently identified $V_2O_2$ and $V_3O_2$ complexes.[13,14]

## 2. Experimental Details

The samples used in the study were prepared from phosphorus doped *n*-type Czochralski-grown (Cz-Si) crystals ($\rho = 20\ \Omega \cdot cm$) with measured concentrations of interstitial oxygen ($O_i$) and substitutional carbon ($C_s$) atoms being $1 \times 10^{18}\ cm^{-3}$ and $\leq 5 \times 10^{16}\ cm^{-3}$, respectively. Irradiation with fast electrons ($E = 2.5$ MeV) was carried out at nominal room temperature with a dose of $1.28 \times 10^{18}\ cm^{-2}$. To generate the $VO_2$, $V_2O_2$, and $V_3O_2$ defects in high concentrations the samples were annealed at 320 °C for 30 h. Then a second room temperature irradiation was carried out with a dose of $3.5 \times 10^{17}\ cm^{-2}$ and the samples were subjected to 30-min isochronal annealing in the temperature range 75–350 °C with 25 °C increments.

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 spectra were recorded at about 20 K and at room temperature (RT). The shape of the bands was analyzed by fitting the spectra with Lorentzian components with contributions due to silicon isotopes ($^{29}$Si and $^{30}$Si) being taken into account.[22]

## 3. Experimental Results and Discussion

Spectrum 1 in **Figure 1** is a fragment of the low-temperature absorption spectrum for a Cz-Si sample annealed at 320 °C for 30 h after irradiation with 2.5 MeV electrons (the absorption spectrum of this sample measured at room temperature before annealing can be found in ref. [23]). It can be seen from spectrum 1 that the main radiation-induced defects in this sample after annealing are the $VO_2$, $V_2O_2$, and $V_3O_2$ vacancy-oxygen related complexes. This is evidenced by the high intensity of the absorption bands with their maxima located at 895.5 $cm^{-1}$ ($VO_2$),[6,12] 829.3 $cm^{-1}$ ($V_2O_2$) and 844.4 $cm^{-1}$ ($V_3O_2$).[13,14] After the second irradiation of the annealed sample with 2.5 MeV electrons at room temperature, the intensities of all the above mentioned bands have decreased. On the other hand, increases in the intensity of the bands with their maxima at 835.8 $cm^{-1}$ (VO complex),[6] 928.4 and 1003.8 $cm^{-1}$ ($VO_2{}^*$ complex),[15–17] as well as the band with its maximum at 1012.4 $cm^{-1}$, which is an LVM due to the oxygen dimer,[24] occur. It is obvious that a strong increase in the concentration of the VO complex resulting from the second irradiation is related to the capture of the radiation-induced mobile vacancies by interstitial oxygen atoms whose concentration is still rather high in the sample studied. An increase in the oxygen dimer concentration is evidently due to an interaction of the silicon self interstitials (I) with the $VO_2$ defects via a reaction $VO_2 + I \rightarrow O_{2i}$.[25] It is reasonable to expect that not

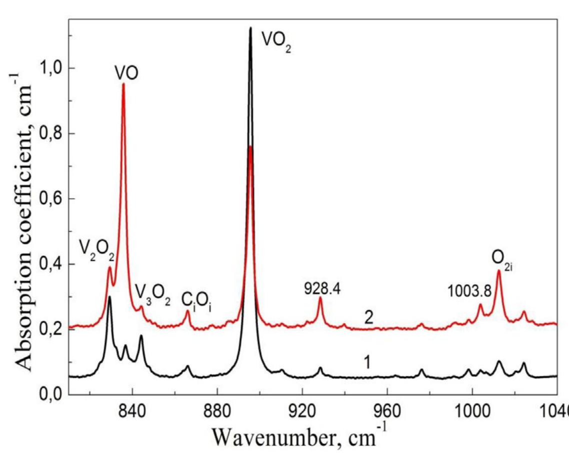


**Figure 1.** Fragments of infrared absorption spectra recorded at 20 K on a Cz-Si sample, which was subjected to the following treatments: 1) irradiation with 2.5 MeV electrons at room temperature to the accumulated dose of $1.28 \times 10^{18}\ cm^{-2}$ with following annealing at 320 °C for 30 h; 2) subsequent irradiation with 2.5 MeV electrons at room temperature to the accumulated dose of $3.5 \times 10^{17}\ cm^{-2}$. The spectra are shifted on the vertical axis for clarity.

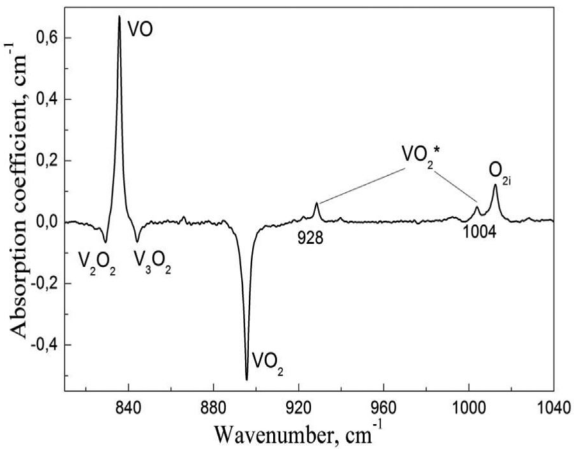


**Figure 2.** Difference absorption spectrum obtained by subtraction of spectrum 1 from spectrum 2 in **Figure 1**.

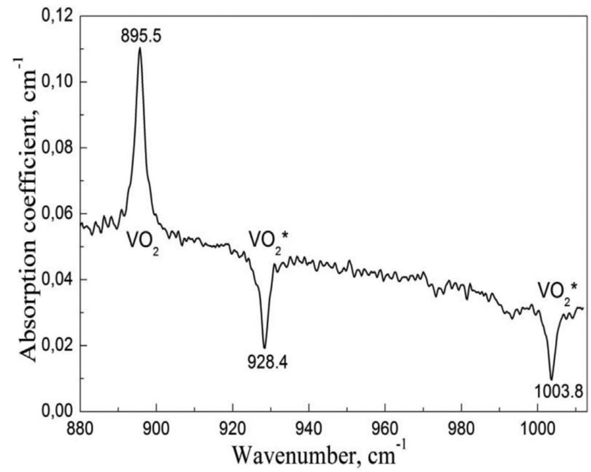


**Figure 3.** Difference absorption spectrum obtained by subtraction of the spectrum recorded after annealing at 250 °C for 30 min from the spectrum recorded after annealing at 275 °C for 30 min for a Cz-Si sample which before these anneals was subjected to a two-stage irradiation with 2.5 MeV electrons with a heat-treatment at 320 °C for 30 h between the irradiation stages. The original spectra were recorded at 20 K.

only $VO_2$ but $V_2O_2$ and $V_3O_2$ complexes are also effective traps for the Si self-interstitials and the following reactions can occur:

$$V_3O_2 + I \rightarrow V_2O_2,$$

$$V_2O_2 + I \rightarrow VO_2*.$$

Evidence for the above reactions is provided by the results shown in **Figure 2**.

To further confirm the assignment of the bands observed at 928.4 and 1003.8 $cm^{-1}$ to the $VO_2^*$ complex, we carried out a 30-min isochronal annealing with steps of 25 °C in the temperature range 75–350 °C using a sample subjected to the second irradiation at RT (see spectrum 2 in Figure 1). An analysis of the absorption spectra measured after each annealing step has showed that heat-treatments at 275 °C and above have resulted in a decrease in the intensity of the bands at 928.4 and 1003.8 $cm^{-1}$ with a correlated increase in the amplitude of the band at 895.5 $cm^{-1}$ (**Figure 3**). This effect is due to the transformation of the $VO_2$ defect from the metastable $VO_2^*$ state to the minimum energy configuration with two oxygen atoms inside a vacancy. An

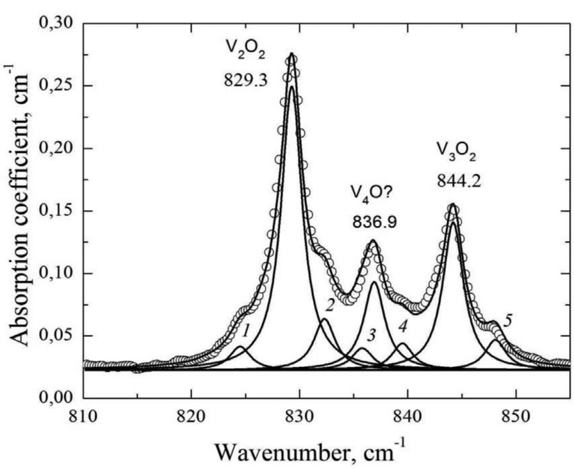


**Figure 4.** Spectral analysis of a fragment of the absorption spectrum recorded at 20 K for a Cz-Si samples which was subjected to irradiation with 2.5 MeV electrons at room temperature to the accumulated dose of $1.28 \times 10^{18}$ $cm^{-2}$ with following annealing at 320 °C for 30 h. Circles are experimentally measured points and solid lines are fitting lines of Lorentzian form. For each band the presence of all three Si isotopes ($^{28}$Si, $^{29}$Si, and $^{30}$Si) is taken into account upon fitting. For clarity, only the fitting sub-curves corresponding to $^{28}$Si-O-$^{28}$Si units are shown, but the main fitting curve accounts for all the contributions.

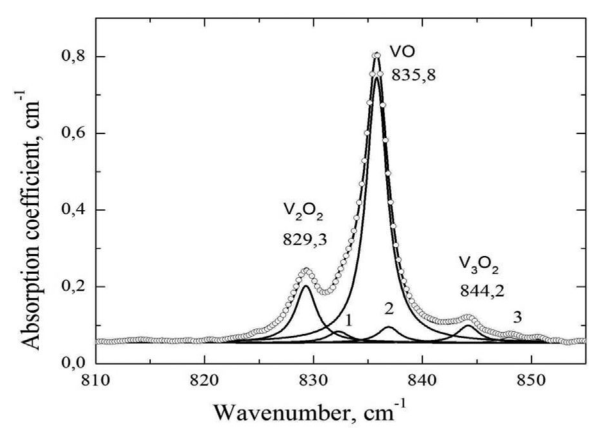


**Figure 5.** Spectral analysis of a fragment of the absorption spectrum recorded at 20 K for a Cz-Si sample which was subjected to irradiation with 2.5 MeV electrons at room temperature to the accumulated dose of $1.28 \times 10^{18}$ $cm^{-2}$ with following annealing at 320 °C for 30 h and subsequent irradiation with 2.5 MeV electrons at room temperature to the accumulated dose of $3.5 \times 10^{17}$ $cm^{-2}$. Circles are experimentally measured points and solid lines are fitting lines of Lorentzian form. For each band the presence of all three Si isotopes ($^{28}$Si, $^{29}$Si, and $^{30}$Si) is taken into account upon fitting. For clarity, only the fitting sub-curves corresponding to $^{28}$Si-O-$^{28}$Si units are shown, but the main fitting curve accounts for all the contributions.

**Table 1.** Absorption coefficients (in $cm^{-1}$) in the maxima of the LVM absorption bands due to oxygen-related defects in a Cz-Si sample which was subjected to irradiation with 2.5 MeV electrons at room temperature to the accumulated dose of $1.28 \times 10^{18}\,cm^{-2}$ with following annealing at 320 °C for 30 h and subsequently to irradiation with 2 MeV electrons at room temperature to the accumulated dose of $3.5 \times 10^{17}\,cm^{-2}$. Positions of the LVMs (in $cm^{-1}$) at 20 K for the analyzed oxygen-related defects are indicated in the Table.

| Sample treatments | $V_2O_2$ 829.3 | VO 835.8 | $V_3O_2$ 844.2 | $VO_2$ 895.5 | $VO_2{}^*$ 928.4 | $VO_2{}^*$ 1003.8 | $O_{2i}$ 1012.4 |
|---|---|---|---|---|---|---|---|
| 1st Irradiation + annealing at 320 °C for 30 h | 0.23 | 0.02 | 0.12 | 1.04 | 0.03 | 0.02 | 0.05 |
| 2nd irradiation | 0.15 | 0.69 | 0.05 | 0.54 | 0.08 | 0.05 | 0.17 |
| Difference in amplitudes of LVMs | −0.08 | +0.67 | −0.07 | −0.5 | +0.05 | +0.03 | +0.12 |

equilibrium distribution between the $VO_2{}^*$ and $VO_2$ states can be attained at annealing temperatures above 275 °C. The presence of a high potential barrier between these states prevents the re-configuration of the defect at lower temperatures.[15–17]

Figures 4 and 5 show the results of a more detailed analysis of the low-temperature absorption spectra (see Figure 1) in the range of wave numbers between 810 and 855 $cm^{-1}$. A fitting procedure using Lorentzians was used to analyze the absorption data. For each band the presence of all three Si isotopes ($^{28}$Si, $^{29}$Si, and $^{30}$Si) was taken into account upon fitting.[22] For clarity, only the fitting sub-curves corresponding to the $^{28}$Si-O-$^{28}$Si vibration units are shown in Figures 4 and 5, but the main fitting curves accounts for all the contributions. On the basis of the data obtained, the absorption coefficients for all main LVM bands observed in the absorption spectra were determined. The absorption coefficient values are presented in **Table 1** alongside the changes in their values as a result of the second 2.5 MeV electron irradiation with a dose of $3.5 \times 10^{17}\,cm^{-2}$. The data on the changes in the absorption coefficients of the LVM bands confirm the suggestion that the increase in the concentration of $VO_2{}^*$ and $O_{2i}$ complexes is due to an interaction of the radiation-induced silicon self-interstitial atoms with the $VO_2$, $V_2O_2$, and $V_3O_2$ vacancy-oxygen complexes.

## 4. Conclusion

The processes of formation of radiation-induced defects upon electron irradiation of Cz-Si crystals containing the $VO_2$, $V_2O_2$, and $V_3O_2$ vacancy-oxygen complexes have been studied. An increase in the concentration of the $VO_2$ complex in the metastable $VO_2{}^*$ configuration as well as in the oxygen dimer $O_{2i}$ concentration occurred in the samples as a result of the irradiation. It is concluded that these phenomena are due to the interaction of the silicon self-interstitial atoms generated by irradiation with the $VO_2$, $V_2O_2$, and $V_3O_2$ vacancy-oxygen complexes. The results obtained on radiation-induced formation of $VO_2{}^*$ complexes are important from the point of view of additional confirmation of the identification of the bands at 829.3 and 844.4 $cm^{-1}$ as related to the $V_2O_2$ and $V_3O_2$ complexes, respectively.

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## Conflict of Interest

The authors declare no conflict of interest.

## Keywords

electron irradiation, local vibrational modes, self-interstitials, silicon, vacancy-oxygen defects

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