# LOCAL VIBRATIONAL MODES OF RADIATION-INDUCED OXYGEN-VACANCY COMPLEXES IN SILICON: CALIBRATION FACTORS

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Combined electrical (Hall effect) and optical (infrared absorption) studies of similar silicon crystals irradiated with fast electrons have been carried out. On the base of analysis of the data obtained the calibration factors for the determination of concentrations of radiation-induced oxygen-vacancy complexes in silicon crystals by infrared absorption are deduced. The calibration coefficient for the determination of the oxygen dimer concentration is estimated as well.

***Keywords:*** silicon; radiation; vacancy-oxygen complexes; vibrational absorption bands; calibration factors.

## Introduction

Oxygen is one of the most abundant and technologically important impurities in silicon. In as-grown Si crystals oxygen is mainly present in the form of interstitial ($O_i$) atoms. The $O_i$ concentrations are usually determined from room temperature (RT) measurements of the intensity of the infrared (IR) absorption band at 1107 cm$^{-1}$ [1]: $[O_i] = 3.14\times10^{17}\times\alpha_{1107}$ cm$^{-3}$ [2]. Although interstitial oxygen atoms in Si are electrically neutral and immobile at RT, they contribute to formation of a large variety of oxygen-related radiation- and thermally-induced defects [1, 3, 4]. All these centers give rise to local vibrational modes [1] and Fourier-transform infrared spectroscopy (FTIR) has been successfully used in the studies of many oxygen-related aggregates including vacancy-oxygen complexes $VO_n$ ($n \geq 1$) [5] and oxygen dimer ($O_{2i}$) [6]. Among the above-mentioned defects only VO (A-center) in n-type Si and $VO_2$ complex (in a metastable state [7]) can be detected by electrical measurements. On the other hand, absorption lines due to all of these defects can be observed in FTIR absorption spectra. In many cases it is important to know the absolute values of defect concentrations. However, the available information on calibration coefficients for the determination of the $VO_n$ ($n$ = 1- 4) and $O_{2i}$ concentrations by IR absorption is very limited [8, 9].

In 1986 Oates and Newman [10] determined the calibration coefficient for the VO absorption peak at 830 cm$^{-1}$ (measurements at room temperature). According to their work, $[VO] = 6.1\times10^{16}\times\alpha_{830}$ cm$^{-3}$, where $\alpha_{830}$ is an amplitude of the vibrational absorption band at 830 cm$^{-1}$. Oxygen-rich Si samples doped with tin and irradiated with 2 MeV electrons at RT were studied in the work. After the irradiation the main vacancy-related defects were SnV complexes. Upon further annealing at about 160 °C these complexes started to dissociate and the released vacancies were captured by $O_i$ atoms to form VO defects. The concentration of removed $O_i$ was measured and assumed to be equal to the concentration of generated VO. Such procedure seems to be rather reliable. A very similar calibration factor for the determination of the VO concentration in Si was obtained also by Davies et al. [8] in their work on modeling the generation kinetics of radiation-induced defects. However, in both cases [8, 10] the IR absorption measurements were carried out with a rather low spectral resolution, the measured full width at half of maximum (FWHM) of the 830 cm$^{-1}$ band was about 9 cm$^{-1}$ in the spectra presented. The actual FWHM of this band in the spectra measured at RT is less than 6 cm$^{-1}$ (of about 5.6 cm$^{-1}$ [11]) and to get a correct value of the absorption coefficient of the band ($\alpha_{830}$), measurements with a higher resolution are required.

In this work, in order to determine the calibration coefficient, direct measurements of the concentration of A centers by the Hall effect method were carried out, and IR absorption spectra were measured on similar samples irradiated with the same dose of fast electrons.

## Experimental details

In the present work we have used two similar sets of oxygen-rich (Czochralski-grown) phosphorus-doped n-type Si crystals with a resistivity of about 1 Ω cm. Both sets were irradiated with 6 MeV electrons at RT with the same doses in the range of $(1\text{-}5)\times10^{16}$ cm$^{-2}$. The VO concentration (concentration of the defect with $E_C$ – 0.18 eV level) in one set of samples was determined by an analysis of the temperature dependences of free carriers *n* obtained by means of the Hall effect measurements in the temperature range 77-400 K. To determine the parameters of radiation-induced defects in a semiconductor material, the differential method (Hoffman method) [12, 13] is also used, according to which the position of the levels and the concentration of defects (N) are determined from the dependence of the value $Y = kT\ (dn/dF)$ on $F = E_C - E_F$, where $E_F$ is the Fermi level position. If the levels of various defects are located far enough from each other (> 5 kT), then the dependence Y(F) has the form of spectral bands. For ordinary defects, the ordinate of the band maximum is $Y_m = 1/4\ N$, the abscissa of the band maximum $F_m$ corresponds to the level position.

Another set of samples was used for FTIR absorption measurements. For optical measurements the samples were polished to an optical surface on two sides and the dimensions were 10×6×3 mm$^3$. The concentrations of interstitial oxygen ($[O_i] = 1\times10^{18}$ cm$^{-3}$) and substitutional carbon ($[C_s] = 2\times10^{16}$ cm$^{-3}$) were determined from measurements of intensities of absorption bands at 1107 and 605 cm$^{-1}$ [2, 4]. The IR absorption spectra were measured using a Bruker IFS 113v spectrometer at temperatures of 20 K and 300 K with a spectral resolution of 0.5 or 1 cm$^{-1}$, respectively.

## Results and discussion

Figure 1 shows the temperature dependences of the charge carrier concentration (TDCCs) measured for an as-grown Si sample (curve 1), and a sample irradiated at room temperature to a dose of $1.3\times10^{16}$ cm$^{-2}$ (curve 2) and annealed at 150 °C for 30 minutes (curve 3). It is known that the irradiation of Cz-Si crystals with fast electrons results in the formation of A-centers, divacancies and defects with an energy level at $E_C$ - 0.125 eV which is related to an $IO_2$ complex consisting of the Si self-interstitial atom and two oxygen atoms [14].

A precise determination of the A-center concentration by an analysis of the TDCCs measured after irradiation was rather difficult due to the presence of the $IO_2$ defect.

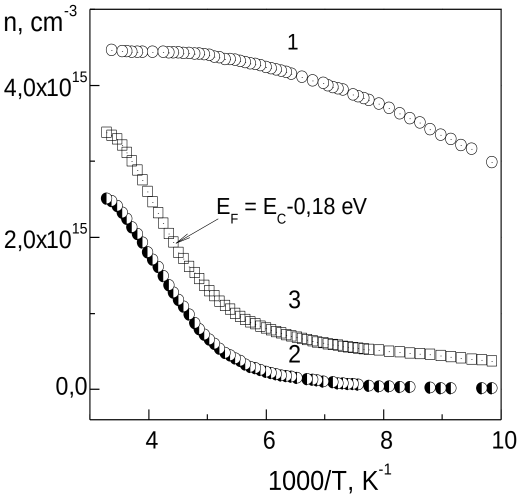

Fig. 1. Temperature dependences of carrier concentration in Cz-Si crystal: 1 - before irradiation, 2 - after irradiation with 6 MeV electrons at T = 293 K to a dose of 1.3 $=10^{16}$ cm$^{-2}$, 3 – after 30-min annealing at T = 150 °C

It is known that it is annealed out in the temperature range of 100 - 125 °C. To eliminate the effect of this defect, the 30-min annealing was performed at 150 °C. After that we have carried out an analysis of the measured TDCC (Fig. 1, curve 3), taking into account the well-known position of the A-center level being located at $E_C$ – 0.18 eV [15]. The concentration of A-centers determined from an analysis of TDCC was found to be $N_A = (3.0 \pm 0.2)\times10^{15}$ cm$^{-3}$.

There is another way to determine the concentration of A-centers [12, 13]. The Y(F) dependence presented in Figure 2 for the Si sample irradiated and annealed at 150 °C indicates the presence of only one peak at about $E_C$ - 0.18 eV. The presence of divacancy [15] leads only to a slight change in the shape of the peak. Based on the fact that for ordinary defects the ordinate of maximum $Y_m$ = 1/4 N, a value of the concentration of the radiation-induced A-centers was found to be $N_A = (3.2 \pm 0.2)\cdot10^{15}$ cm$^{-3}$. Accordingly, an average value of the A-centers deduced when analyzing the data obtained by means of electrical measurements is of about $N_A = 3.1\cdot10^{15}$ cm$^{-3}$.

The absorption bands related to VO in the neutral charge state (lines with maxima at 830 and 836 cm$^{-1}$ in the spectra measured at room temperature and low temperature, respectively) as well as in the negative charge state (lines at 877 and 885 cm$^{-1}$ in the RT and LT spectra, respectively [1]) were detected (Figure 3).

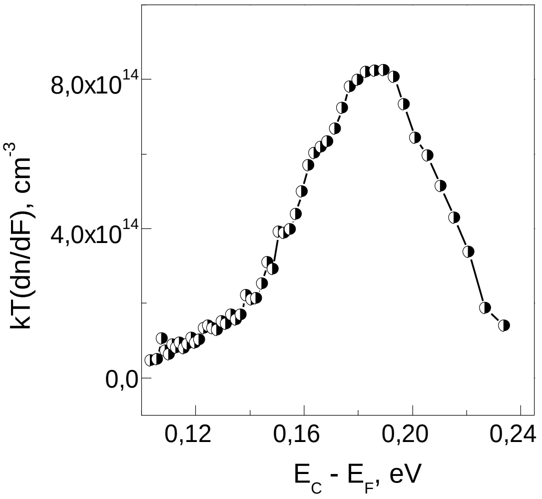

Fig. 2. Dependence of the quantity Y = kT (dn/dF) on $F = E_C - E_F$, obtained by a numerical differentiation of the dependence 3, shown in Figure 1

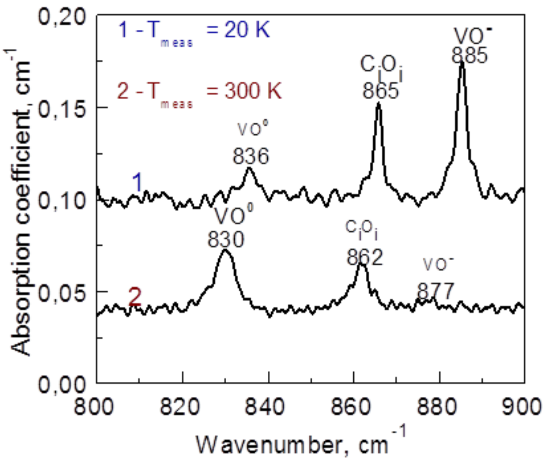

Fig. 3. Fragments of absorption spectra measured at 20 K (1) and at room temperature (2) for a Cz-Si sample ($[O_i] = 1.0\times10^{18}$, $[C_s] = 2\times10^{16}$, $[P] = 5\times10^{15}$ cm$^{-3}$) irradiated with 6 MeV electrons to a dose of $1.3\times10^{16}$ cm$^{-2}$

The combined analysis of the electrical and optical data obtained has allowed us to deduce the following calibration for the determination of the VO concentrations in silicon by IR absorption: RT measurements - $[VO] = 8.5\times10^{16}\times(\alpha_{830} + \alpha_{877})$ cm$^{-3}$, LT measurements (≤ 20K) – $[VO] = 3.5\times10^{16}\times(\alpha_{836} + \alpha_{885})$ cm$^{-3}$. We have estimated also the calibration coefficients for the VO integrated absorption.

Based on the calibration data obtained for the VO center and assuming that the oscillator strength of the oxygen atom vibrations as well as the shape of absorption bands are the same for the oxygen atoms located in the Si vacancy with different environments we have also estimated calibration factors for the determination of concentrations of the $VO_2$ (band at 895 cm$^{-1}$), $VO_3$ (bands at 910 and 975 cm$^{-1}$), $VO_4$ (band at 991 cm$^{-1}$), $V_2O$ (band at 833.4 cm$^{-1}$) and $V_3O$ (band at 842.4 cm$^{-1}$ [11]) complexes in silicon by infrared absorption measurements at low temperatures. The concentrations of the above mentioned complexes can be determined as: $[VO_2] = 4.25\times10^{16}\times\alpha_{895}$ cm$^{-3}$, $[VO_3] = 8.5\times10^{16}\times(\alpha_{910} + \alpha_{975})/2$ cm$^{-3}$, $[VO_4] = 4.25\times10^{16}\times\alpha_{991}$ cm$^{-3}$, $[V_2O] = 8.5\times10^{16}\times(\alpha_{833.4} + \alpha_{837})$ cm$^{-3}$, $[V_3O] = 8.5\times10^{16}\times(\alpha_{842.4} + \alpha_{848.7})$ cm$^{-3}$.

One of the most important oxygen-related defects in silicon is the oxygen dimer. It contributes substantially to enhanced oxygen diffusion and clustering at elevated temperatures. In addition, the oxygen dimer is expected to play a key role in the formation of the center responsible for the light-induced degradation of silicon-based solar cells [16, 17]. We have used different approaches including statistical ones [6, 17] and considered critically various assumptions to deduce the calibration coefficient for a determination of the oxygen dimer concentration from intensity of the absorption band at 1013 cm$^{-1}$ (measured at RT), which is related to a local vibrational mode due to $O_{2i}$ [4, 6]. It has been concluded that the dimer concentration can be estimated as $[O_{2i}] = 7.2\times10^{16}\times\alpha_{1013}$ cm$^{-3}$. However, further studies are required to confirm the value given above.

## Conclusions

Comparison of the data obtained from electrical and optical measurements made it possible to derive the following expressions for determining the concentration of A-centers by IR absorption: for measurements at room temperature: $N_{VO} = 8.5\times10^{16}$ $(\alpha_{830} + \alpha_{877})$ cm$^{-3}$, in the case of low-temperature measurements, $N_{VO} = 3.5\times10^{16}$ $(\alpha_{836} + \alpha_{885})$ cm$^{-3}$. The calibrations factors for a number of more complex vacancy-oxygen related defects ($VO_2$, $VO_3$, $VO_4$, $V_2O$ and $V_3O$) and for the oxygen dimer have been estimated as well.

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