

Interaction of oxygen with thermally induced vacancies in Czochralski silicon

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Complexes consisting of a vacancy and four oxygen atoms, VO_4 , were found in oxygen-rich Czochralski silicon wafers subjected to rapid thermal annealing (RTA) at 1250 °C for 30 s in Ar/O_2 atmosphere by means of Fourier transform infrared spectroscopy with enhanced sensitivity. An absorption band at 985 cm^{-1} , previously observed only in irradiated Si and assigned to a local vibration mode of VO_4 , was measured reproducibly in all RTA treated wafers examined. A concentration of about $1.4 \times 10^{13} \text{ cm}^{-3}$ of thermally induced VO_4 was estimated from the integrated intensity of the band at 985 cm^{-1} using the known calibration factor for interstitial oxygen. © 2009 American Institute of Physics. [DOI: 10.1063/1.3090486]

The precipitation of supersaturated interstitial oxygen (O_i) in Czochralski (CZ) silicon is widely used for internal gettering of metallic impurities in silicon device technology.¹ Numerous investigations were made to clarify the nature of nucleation centers for the oxide precipitates.² High temperature annealing followed by quenching or rapid thermal annealing (RTA) are reliable processes to reach the precipitation of oxygen in the bulk of the wafer with a defect denuded zone below the surface.^{3,4} Theories for this phenomenon are based on the formation of VO_2 complexes, that are believed to act as nucleation centers for oxygen precipitates.⁵⁻⁷ From the experimental side, as far as we know, there are no direct observations of the formation of VO_2 complexes by RTA treatments. On the other hand, such complexes are well known from radiation experiments, where a family of V_nO_m complexes [$1 \leq (n,m) \leq 6$] was revealed by selective methods.⁸⁻¹³ A certain set of the local vibration modes was identified in infrared absorption for such radiation induced V_nO_m complexes.⁸⁻¹⁰ The main reason for the lack of observation of RTA induced VO_2 complexes was assumed to be the relatively low concentration of these defects after RTA treatment compared to radiation treatments.

The aim of this work was to find the traces of the first stages of RTA induced interaction between O and V on the point defect level by means of Fourier transform infrared (FTIR) spectroscopy with enhanced sensitivity. Due to a significant improvement of the photometric accuracy of the measurements of differential transmittance, this method allows to detect weak absorption bands with a sensitivity, which is approximately two orders of magnitude higher than by conventional FTIR.^{14,15} However, this method cannot prevent the measured spectra from parasitic contributions from residual surface absorption due to not ideal chemical and structural states of the surface. Therefore, we paid special attention to clearly distinguish the weak bulk differential absorption arising after RTA from a possible surface related absorption.

Double side polished (100) oriented wafers with a diameter of 150 mm manufactured from oxygen-rich p -type

B-doped CZ silicon with a resistivity of about 40 $\Omega \text{ cm}$ were used in the experiments. The concentration of interstitial oxygen measured by FTIR using a calibration factor of $2.45 \times 10^{17} \text{ cm}^{-2}$ (DIN 50438/1) was $8.5 \times 10^{17} \text{ cm}^{-3}$. The wafers were cleaved along the diameter into two halves. Only one half of each wafer was subjected to a RTA treatment at 1250 °C for 30 s in oxygen containing Ar atmosphere with a cooling rate of approximately 70 K/s in the temperature interval 1250–900 °C. Two half wafers were mounted, instead of one entire wafer, in one plane in the RTA chamber in order to reach similar conditions than with a complete wafer. The untreated wafer halves served as the individual references for the FTIR measurements. In order to estimate the degree of surface related absorption and to extract the bulk changes in the absorption after RTA from the whole differential absorption spectra measured by FTIR, two essentially different conditions of measurements were applied. They consist of different geometries for measurements in connection with essentially different sample preparation procedures as demonstrated in Fig. 1. Using both conditions, different partial weights of the surface absorption in the measured differential spectra under the same state can be obtained.

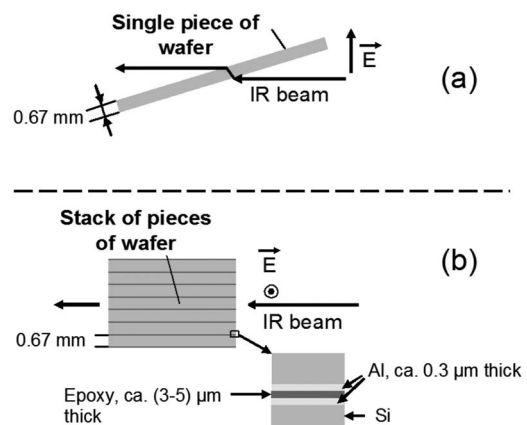


FIG. 1. Two geometries used for FTIR transmission measurements on (a) single plate under Brewster angle of incidence and (b) on stack of plates at normal incidence. All samples are cut from Si wafers.

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In the arrangement in Fig. 1(a), single pieces of wafers were measured under Brewster angle of incidence, with the electric field lying in the plane of incidence. Under such conditions, the interference fringes from the double side polished samples were strongly suppressed. Immediately before the FTIR measurements, the chosen pair of samples, RTA treated and reference, was subjected to a cleaning procedure simultaneously in order to minimize possible deviations in the state of surfaces between two samples. The samples were cleaned from both residual organic contamination and native oxide in organic solvents followed by HF dipping, with subsequent rinsing in de-ionized water and air drying. Just a few minutes later, the pair of samples was mounted on a moving stage in the sample chamber of the FTIR spectrometer BOMEM DA8. Then, the whole volume of the spectrometer was evacuated to approximately 2 Torr using an oil-free membrane pump.

The more complicated geometry, shown in Fig. 1(b), was designed to enlarge the bulk-to-surface absorbance ratio, under the condition of an unchanged thickness of samples. In this geometry, the infrared beam propagates along the surface of wafer, and the length of beam path in Si can be chosen deliberately. We chose this length approximately one order longer as for the thickness of the samples. In this way, an increase by one order of the weight of the bulk absorbance in the recorded absorbance spectra was reached. Coating the surfaces of the samples with the highly reflective Al layers in conjunction with choosing the electric field in the beam parallel to the Al/Si interface suppressed a possible contribution from the absorption by the Al/Si at grazing reflection. Due to the opposite directions of the electric field in the incident and reflected waves on Si/Al boundary under grazing angle of incidence, the resulting electric field at this interface is almost zero. After cutting the Al-coated half wafers into the pieces with a size of about $10 \times 15 \text{ mm}^2$, stacks of samples were mounted from these pieces using epoxy glue. The stacks were ground, polished, and finalized by chemo-mechanical polishing. The cleaning procedure of the open Si surfaces was carried out immediately before the beginning of the FTIR measurement, analogously to the case of the single piece cleaning for Brewster measurements.

The FTIR measurements with enhanced sensitivity were carried out at room temperature with a resolution of 1 cm^{-1} , using a mercury cadmium telluride detector cooled by liquid nitrogen. Several thousands of periodical changes of samples, RTA treated and reference sample, were carried out to provide an enhanced photometric quality of the resulting average differential spectra. A slight Fourier filtration of the high frequency noises was applied to the collected spectra. As the result, the effective spectral resolution for the presented spectra corresponds to approximately 2 cm^{-1} . In order to present clearly the achieved photometric accuracy, the whole set of measured spectra was treated as four subsets for each pair of measured samples.

The spectra obtained from both single pieces and stacks of pieces are presented in Fig. 2. It is clearly seen that the shape of the spectra is similar for all presented spectra obtained from three different wafers under two significantly different conditions of measurement. In each spectrum, three clearly pronounced peaks appear with their maxima located at 985, 1005, and 1013 cm^{-1} . The amplitude of the peak at 985 cm^{-1} is positive, whereas the amplitude of the doublet at 1005 and 1013 cm^{-1} has the opposite sign. The absolute

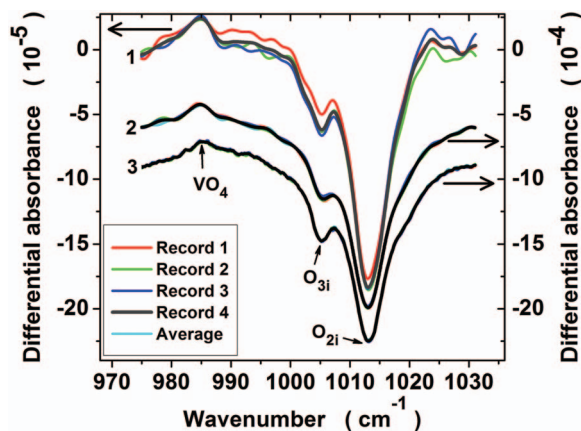


FIG. 2. (Color) Differential absorption spectra of three wafers subjected to RTA 1250°C for 30 s in oxygen containing Ar atmosphere. 1—wafer #1, measured on a single sample under Brewster angle of incidence; 2, 3—wafers #2, #3, respectively, measured on stacks of samples at normal incidence. The lengths of the beam paths in the samples are 1–0.7, 2–7.6, and 3–6.4 mm. For each wafer, four sequential records and their average are shown. Thermally untreated single samples or stacks of samples were used as the references. Straight line subtraction and vertical shifting are applied for clarity.

amplitudes of the spectra 2 and 3 exceed the amplitude of the spectrum 1 by approximately one order of magnitude. The stack geometry used for the spectra 2 and 3 increased the optical path by approximately one order of magnitude and thus increased the intensity of the spectra compared to the single sample geometry used for spectrum 1. The invariability of the shape of spectra recorded by the considerably different thicknesses of samples and the linear increase in amplitude with increasing thickness clearly indicate that all three peaks observed originate from the bulk, irreversibly from the sign of differential absorbance in the peaks. According to their spectral position in correlation with their shape, the peaks 1005 and 1013 cm^{-1} were identified as local vibration modes of O_{3i} and O_{2i} , respectively.^{10,16,17} The observed negative amplitudes of O_{2i} and O_{3i} correspond to a reduction in the initial amplitude of O_{2i} and O_{3i} measured before the RTA treatment by approximately 20%.¹⁸ Corresponding results of the FTIR measurements of the full intensity of peaks 1005 and 1013 cm^{-1} before and after RTA using a reference from float zone Si with low oxygen content were presented in Ref. 18. Both position and half width of the positive peak at 985 cm^{-1} correspond to the local vibration mode of a defect, which was previously observed in irradiated Si and interpreted first, in the year 1964, as VO_n complex with $n \geq 3$.⁸ Later, this band was assigned more definitively to VO_4 .¹⁰ A second previously identified local vibration mode of VO_4 at $(1004\text{--}1009) \text{ cm}^{-1}$ (Refs. 10, 19, and 20) is not clearly seen in our spectra due to overlapping by the more intense doublet of O_{3i} and O_{2i} at 1005 and 1013 cm^{-1} , respectively. The observed negative amplitude of the peak 1005 cm^{-1} , instead of the expected positive peak from the band $(1004\text{--}1009) \text{ cm}^{-1}$ of VO_4 , can be explained by the more intensive decrease in the intensity of O_{3i} peak at 1005 cm^{-1} . Such suppose is based on the considerably higher absorption in the doublet 1005 and 1013 cm^{-1} ($\text{O}_{3i}, \text{O}_{2i}$) before RTA (Ref. 18) compared with the observed amplitude of the peak 985 cm^{-1} (VO_4) arising after RTA. Moreover, a remarkable scattering of the position of the band $(1004\text{--}1009) \text{ cm}^{-1}$ observed in irradiated then annealed

Si^{10,19,20} can be partially explained by the contribution from O_{3i} band 1005 cm⁻¹.

Until now, as far as we know, VO₄ complexes were never detected without radiation treatments with energies of particles, which are higher than the threshold for Frenkel pair generation. We have estimated the absolute concentration of the observed VO₄ on the basis of the assumption that the apparent charge²¹ of the local vibration mode 985 cm⁻¹ is nearly the same as for the well-known local vibration mode 1107 cm⁻¹ of interstitial oxygen. The relatively moderate shift in the frequency of vibration of oxygen in VO₄ in comparison with oxygen in the O_i state, $\Delta\omega/\omega = (1107 - 985 \text{ cm}^{-1})/1107 \text{ cm}^{-1} \cong 11\%$, implies a corresponding moderate shift in the force constant of Si–O bond for both these defects. The similarity of the force constant lets us expect a similar apparent charge. Under this assumption, the concentrations of O_i and VO₄ should be proportional to the areas of the corresponding absorption peaks with the same proportionality factor.²¹ The half widths of the bands at 985 and 1107 cm⁻¹ were measured to be equal to 5 and 33 cm⁻¹, respectively. We used a calibration factor of $2.45 \times 10^{17} \text{ cm}^{-2}$ (DIN 50438/1) for the determination of O_i from the amplitude of the band at 1107 cm⁻¹ and multiplied it by the ratio of the half widths, 5/33, as the peak factor for the determination of concentration of VO₄. The absorption coefficient calculated from the absorbance of the band at 985 cm⁻¹ in spectrum 2 taking into account the thickness of the measured stack of samples is equal to $3.9 \times 10^{-4} \text{ cm}^{-1}$. Using the half width corrected peak factor of $3.71 \times 10^{16} \text{ cm}^{-2}$, we derived a concentration of about $1.4 \times 10^{13} \text{ cm}^{-3}$ for the RTA induced VO₄ complexes. If more than one oxygen atom in VO₄ would be involved in the vibrational band at 985 cm⁻¹, the whole apparent charge of VO₄ would be larger than for O_i. In such a case, the estimated concentration of VO₄ would be lower.

The obtained concentration of VO₄ agrees reasonably with the vacancy concentration of about $1 \times 10^{13} \text{ cm}^{-3}$ measured by platinum diffusion in silicon wafers, which were rapidly cooled from 1250 °C.⁵ Similar concentrations of stored vacancies were obtained by simulation of RTA cooling from 1250 °C.⁶ Until now, it was believed that the thermally induced vacancies are stored in silicon by formation of VO₂.^{5,6} However, according to our findings in this work, VO₄ is the dominating defect containing vacancies and oxygen atoms. No reliable indications on the presence of vibration bands of other complexes containing V and O were found, such as the bands attributed to VO complexes at 830 and 885 cm⁻¹ in neutral or negative state, respectively, VO₂ complexes at 889, 924, and 1000 cm⁻¹, in neither the ground nor the metastable configuration,²² or the bands attributed to VO₃ and VO₅₍₆₎ complexes.¹⁰ Assuming nearly the same apparent charges of the local vibrations of oxygen in VO_n ($n=1-6$) and taking into account nearly the same half width of the corresponding absorption bands, a conclusion can be drawn that VO₄ dominates in concentration, among other VO_n complexes, after the RTA treatment.

Moreover, no indications on the formation of oxide precipitates and on remarkable changes of the concentration of O_i after RTA were found in the spectra. Both spectra were practically identical. When analyzing the O_i difference more into detail from the measurements with the untreated reference part of the CZ Si wafers, we observed only very small

differences in the O_i concentration with a negative or positive sign on a level of 10^{15} cm^{-3} . Additional differential measurements of two untreated parts taken from the same wafer revealed that this level is comparable to natural fluctuations of the O_i concentration on the wafer. Therefore, only an upper estimation can be made that RTA induced changes in the concentration of O_i do not exceed a level of 10^{15} cm^{-3} or $\sim 0.1\%$ of the initial concentration of O_i. Nevertheless, we have found fully reproducible signs of changes in the absorption for the bands 985, 1005, and 1013 cm⁻¹, as it is shown in Fig. 2.

In summary, the formation of the vacancy and oxygen containing complex VO₄ was found in oxygen-rich CZ silicon wafers subjected to a RTA treatment at 1250 °C for 30 s in oxygen containing Ar atmosphere by means of sensitive FTIR combined with additional tests to separate the weak absorption bands of VO₄ in bulk Si from a possible surface absorption. The concentration of VO₄ as estimated from the observed absorption band at 985 cm⁻¹ amounts to $1.4 \times 10^{13} \text{ cm}^{-3}$. No traces of other VO_n complexes with $n \neq 4$ were found.

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