

# Infrared spectroscopy of oxygen interstitials and precipitates in nitrogen-doped silicon

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## Abstract

We have used infrared absorption to study interstitial oxygen and oxygen precipitates in a series of nitrogen-doped silicon (Si:N) samples. Transmittance spectra have been measured in the temperature range from 10 to 300 K. This allowed us to separate reliably the contributions of interstitial oxygen ( $O_i$ ) and oxygen precipitates, obtained in the single-step (16 h at 1050 °C) and two-step (4 h at 750 °C, followed by 16 h at 1050 °C) heat treatment. In the data analysis, we focus on the amount of oxygen available initially in the unannealed material, and its redistribution following the two thermal treatments. The absorption spectra of the precipitates are analysed using effective-medium models; we have used infrared ellipsometric spectra of amorphous silicon dioxide, optimized for the range of weak absorption at high frequencies, and their modifications for different stoichiometries. The resulting concentration of  $O_i$  and the oxygen atoms in the precipitates is found to depend rather significantly on the nitrogen doping.

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*Keywords:* Silicon; Interstitial oxygen; Precipitate; Nitrogen doping

## 1. Introduction

Silicon single crystals used for device fabrication are grown either by floating zone (FZ) or the Czochralski (CZ) technique. Oxygen is incorporated in CZ-grown Si crystal during manufacturing from a silica crucible. Oxygen atoms are electrically neutral and occupy bond-centred interstitial sites in the lattice with the typical concentration  $[O_i] \sim 10^{18} \text{ cm}^{-3}$ . A much lower concentration  $[O_i] \sim 10^{16} \text{ cm}^{-3}$  is usually present in FZ Si [1].

At room temperature (RT), highly supersaturated CZ Si is stable as the  $O_i$  atoms are immobile. During subsequent treatments at elevated temperatures, diffusion of  $O_i$  atoms leads to their aggregation and formation of silicon oxide precipitates. Wafers are first annealed at a lower temperature ( $T < 750 \text{ °C}$ ) to nucleate small  $\text{SiO}_x$  precipitates, and a series of later treatments at higher temperatures cause the precipitates to grow.

There are two main reasons for nitrogen doping of Si crystals: first, the enhancement of oxygen precipitation leads

to improvements of the intrinsic gettering ability, and second, locking dislocations result in an increased mechanical strength of both CZ and FZ wafers. Nitrogen doping during crystal growth, at levels comparable to the vacancy concentration, is used to create N–V and N–V–O complexes (nitrogen, N; vacancy, V; and oxygen, O). These complexes enhance the nucleation of oxygen precipitates due to increasing density of the precipitate nuclei [2,3]. In the infrared (IR) range these complexes manifest themselves in a series of absorption peaks. This fact can be used to determine the nitrogen concentration in silicon [4,5].

IR measurements of CZ Si performed at RT reveal a broad absorption band at a wavelength  $\lambda$  close to 9  $\mu\text{m}$  (the wavenumber of  $1107 \text{ cm}^{-1}$ ). This band is related to the antisymmetric stretching of the Si– $O_i$ –Si quasimolecule and has been commonly used for the determination of  $[O_i]$  present in the sample [6]. At the sample temperature of 77 K, the band sharpens and shifts to  $1136 \text{ cm}^{-1}$ .

The contribution of  $\text{SiO}_x$  (with  $x$  close to 2) precipitates to the absorption spectra is expected to span the range from about  $1080 \text{ cm}^{-1}$  (for spheres, resonating near the TO mode of the oxide) to  $1250 \text{ cm}^{-1}$  (for plates, with the resonance near the LO mode of the oxide). The LO mode is

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normally infrared inactive, but can become infrared active for particles of a size smaller than  $\lambda/2\pi n_m$  (where  $\lambda$  is the vacuum wavelength of the incident radiation, and  $n_m$  is the refractive index of the embedding matrix) [7].

In spite of considerable effort devoted to the precipitation, the problem is far from being solved, see e.g. the recent papers [8,9].

## 2. Calculation of absorption spectra

Following Hu [7], we assume that the shape of precipitates can be approximated by ellipsoids which, in various ratios of their axes ( $a_1, a_2, a_3$ ), include the disc, sphere, and needle. Accordingly, we consider just the shape of a spheroid ( $a_2 = a_3$ ). If the spheroid is smaller than  $\lambda/2\pi n_m$  (about  $0.4\mu\text{m}$  in the case of interest, since the refractive index of silicon is about 3.4), the electric field  $\mathbf{E}$  can be written as

$$\mathbf{E}_p = \hat{\mathbf{g}} \cdot \mathbf{E}_m, \quad (1)$$

where  $\hat{\mathbf{g}}$  is a tensor, and subscripts p and m refer to the precipitate and the matrix, respectively. We assume isotropic complex dielectric constants  $\varepsilon_p$  and  $\varepsilon_m$ . Then  $\hat{\mathbf{g}}$  becomes diagonal (if the axes of the ellipsoid coincide with that of the coordinate system), and has the elements

$$g_j = \varepsilon_m / [L_j \varepsilon_p + (1 - L_j) \varepsilon_m], \quad (2)$$

where  $L_j$  is the depolarization factor along the  $a_j$  axis of the ellipsoid ( $L_1 + L_2 + L_3 = 1$ , and, approximately,  $L_1 : L_2 : L_3 = 1/a_1 : 1/a_2 : 1/a_3$ ). After averaging over all orientations of ellipsoids [7], it is possible to replace  $\hat{\mathbf{g}}$  by the scalar

$$g = \frac{1}{3}(g_1 + g_2 + g_3). \quad (3)$$

We use the continuum model of average dielectric constant  $\varepsilon_{av}$ , leading to the following result:

$$\varepsilon_{av} = 1 + \frac{(1-f)(\varepsilon_m - 1) + f(\varepsilon_p - 1)g}{(1-f) + fg}, \quad (4)$$

where  $f$  is the volume fraction of the precipitates. The absorption coefficient  $K$  as a function of wavenumber  $\nu$  is then calculated as

$$K(\nu) = \frac{\text{Im } \varepsilon_{av}(\nu)}{\text{Re } n_{av}(\nu)} 2\pi\nu, \quad (5)$$

where  $n_{av}$  is the average complex index of refraction obtained from  $\varepsilon_{av}$ . For the calculation of complex dielectric constant  $\varepsilon_m$  we use the parabolic approximation  $n(\nu) = 3.41626 + 1.443 \times 10^{-9} \nu^2$  for intrinsic silicon [10] and results of our transmission measurements on FZ Si (providing the extinction coefficient  $k$ ). For  $\varepsilon_p$  we use the optical constants of vitreous  $\text{SiO}_2$  from our own IR ellipsometric measurements (see Fig. 1), modified for different oxygen content. We assume a linear dependence between the positions of TO mode in  $\text{SiO}_x$  and the value of  $x$ . For the TO range in non-crystalline  $\text{SiO}$ , we have used the dielectric function from Ref. [11].

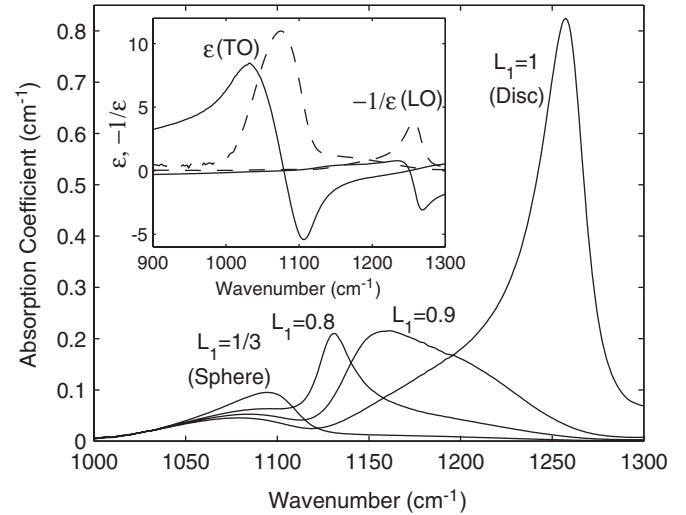


Fig. 1. Calculated contributions of randomly oriented  $\text{SiO}_2$  spheroids of various shapes to the infrared absorption spectra of Si. The volume fraction of the spheroid inclusions was  $2 \times 10^{-6}$ ;  $L_1$  is the depolarization factor along the rotational axis of the spheroid. Real (solid lines) and imaginary (dashed lines) of  $\varepsilon$  and  $-1/\varepsilon$  of vitreous  $\text{SiO}_2$  are plotted in the inset; the TO (LO) position is about 1070 (1260) wavenumbers, respectively.

## 3. Experimental

Measurements of transmittance were performed in the IR spectral range from  $6000$  to  $400\text{ cm}^{-1}$  using a Fourier transform spectrometer BRUKER IFS 55 EQUINOX with a Globar source, a KBr beam splitter, and a DTGS detector. The measurements were performed with  $2\text{ cm}^{-1}$  resolution at RT and 77 K using a liquid nitrogen cryostat GRASEBY SPECAC. Some samples were also measured at 10 K using a liquid helium cryostat JANIS ST-100-FTIR with  $0.25\text{ cm}^{-1}$  resolution.

The samples were (100) CZ silicon slices 100 mm in diameter, slightly doped with boron. They were cut from both nitrogen-doped and standard ingots grown by the Czochralski technique at ON Semiconductor Czech Republic; slices from a standard silicon ingot without nitrogen doping served as the reference. The reference samples were grown at conditions identical to the growth of the studied samples. The thickness of all slices was about 3 mm. Concentration of  $\text{O}_i$  was measured at RT according to Ref. [6] using IOC-88 calibration factor of  $3.14 \times 10^{17}\text{ cm}^{-2}$ ; concentration of N in the Si:N samples was calculated using the segregation coefficient of  $7 \times 10^{-4}$  [5] and measured at RT according to Ref. [4], see Table 1.

The samples were annealed according to the ASTM standard precipitation tests A ( $1050^\circ\text{C}$  for 16 h) and B ( $750^\circ\text{C}$  for 4 h followed by  $1050^\circ\text{C}$  for 16 h) [12]. Three samples (denoted by A, B, C) from the beginning (N39A-C), middle (N604A-C), and end (N1157A-C) of the N-doped ingot as well as from the beginning (25A-C), middle (819A-C), and end (1233A-C) of the standard ingot make a series of 18 different samples; 12 of them are listed

Table 1

Characteristics of the non-annealed Si:N samples: the measured  $[O_i]$  (the error  $\sim 0.01 \times 10^{17} \text{ cm}^{-3}$ ), the measured  $[N]$  (the error  $\sim 0.1 \times 10^{15} \text{ cm}^{-3}$ ) and the nitrogen concentration calculated from the growth conditions

Sample	Measured $[O_i]$ ( $10^{17} \text{ cm}^{-3}$ )	Measured $[N]$ ( $10^{15} \text{ cm}^{-3}$ )	Calculated $[N]$ ( $10^{15} \text{ cm}^{-3}$ )
N39C	10.48	0	0.3
N604C	8.51	0.2	0.5
N1157C	8.57	1.1	1.3

Table 2

Samples studied: annealing steps, decrease of  $[O_i]$  in percent of the starting value (the error  $\sim 0.3\%$ ), volume fraction of precipitates  $f$  from simulations (the procedure differentiates between spherical ( $f_s$ ) and disc-shaped ( $f_d$ ) particles ( $f = f_s + f_d$ ), the error of  $f \sim 0.1 \times 10^{-6}$ ) and (in percent of the starting value) the oxygen concentration necessary to build the precipitates (the error  $\sim 0.5\%$ )

Sample	Anneal.	$[\Delta O_i]$ (%)	$f(f_s + f_d)$ ( $10^{-6}$ )	$[O_p]$ (%)
25A		5.6	1.0 (0.8 + 0.2)	4.1
N39A		34.2	8.0 (7.2 + 0.8)	33.6
819A	16 h at	2.7	0	0
N604A	1050 °C	21.7	2.8 (2.0 + 0.8)	14.2
1233A		2.2	0	0
N1157A		8.1	1.2 (0.9 + 0.3)	6.1
25B		82.0	17.8 (17.0 + 0.8)	72.2
N39B	4 h at	83.8	17.9 (17.3 + 0.6)	75.1
819B	750 °C and	2.3	$\sim 0.2$ (0.2 + 0)	$\sim 1$
N604B	16 h at	23.4	3.1 (2.3 + 0.8)	15.7
1233B	1050 °C	3.8	$\sim 0.2$ (0.2 + 0)	$\sim 1$
N1157B		14.8	1.7 (1.4 + 0.3)	8.6

in Table 2. Samples C, not subjected to any thermal treatment, have been used as the reference. Recently, a more complex, three-step annealing process has been reported in Ref. [8].

In the range from 400 to about  $1500 \text{ cm}^{-1}$  silicon exhibits a non-negligible multi-phonon absorption. We have therefore used the data obtained on FZ Si, essentially  $O_i$ -free, to subtract this background.

#### 4. Results and discussion

In general, the measured values of  $[N]$  are in a good agreement with the calculated estimates, see Table 1. Small differences can be explained e.g. by means of nitrogen steaming from the melt. As expected, the presence of N was not confirmed for annealed samples due to the formation of oxygen precipitates [13].

Fig. 1 shows the calculated infrared absorption spectra of silicon samples with diluted  $\text{SiO}_2$  spheroids of various eccentricities, characterized by the depolarization factor  $L_1$ . We can see that the disc-shaped particles give rise to an absorption band at about  $1250 \text{ cm}^{-1}$ , and spherical precipitates at about  $1100 \text{ cm}^{-1}$ . Close to the latter, the absorption band due to  $O_i$  in silicon occurs ( $1107 \text{ cm}^{-1}$  at

RT). By using the transmission spectra taken at low temperatures we can identify the contributions of precipitates and interstitial oxygen, see Fig. 2. Namely, the difference spectrum of Fig. 2 represents the contribution of the precipitates.

Simulations of the absorption spectra resulting from various shapes of the  $\text{SiO}_x$  precipitates, compared to the measurements on the N39A sample, are presented in Fig. 3. Both disc-shaped and spherical-shaped particles apparently coexist in this sample. The peaks at  $\sim 1120$  and  $1220 \text{ cm}^{-1}$  correspond to the spherical and disc-shaped precipitates, respectively.

Using samples C (non-annealed), we have determined the decrease of interstitial oxygen concentration in the

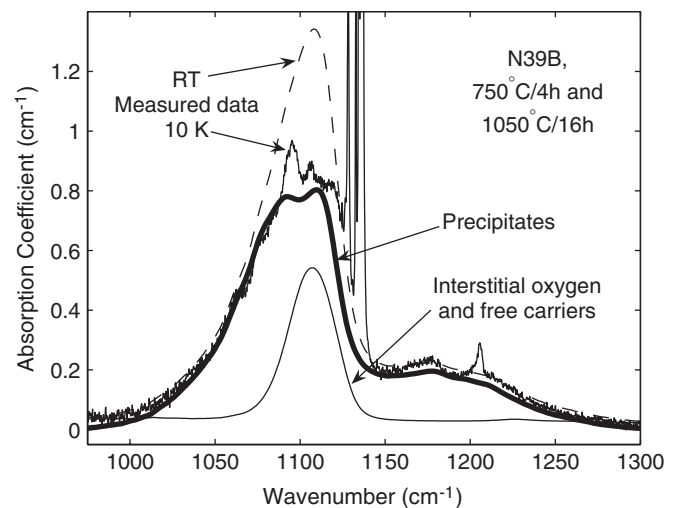


Fig. 2. Decomposition of the RT absorption spectra of the sample N39B. The sum of the contributions of  $O_i$  and free carriers (thin line), the contribution of precipitates (thick line). The 10 K spectrum exhibits a series of sharp lines of very high absorption coefficient, not shown on this scale.

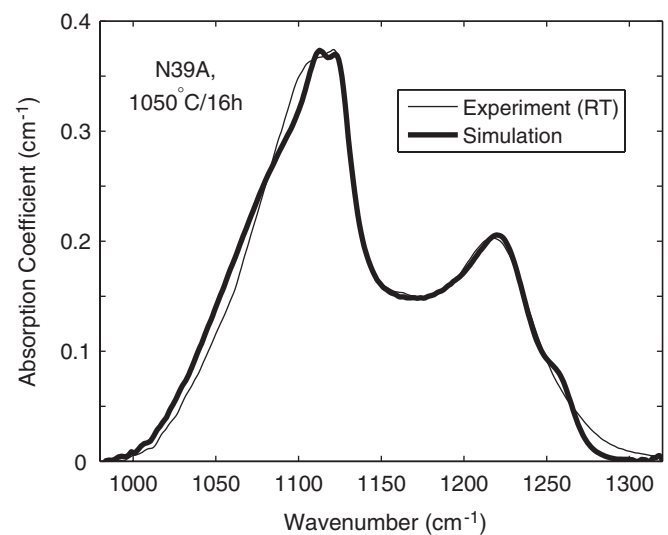


Fig. 3. Comparison of the contribution of the precipitates (i.e., free carriers subtracted) with the effective-medium simulation.

annealed series of samples, A and B. On the other hand, from simulations of the absorption spectra we have obtained the volume fraction, shape and stoichiometry  $x$  of the  $\text{SiO}_x$  precipitates. The stoichiometry was established to be  $x = 1.9 \pm 0.1$ ; this value agrees well with the results of Ref. [14], but differs significantly from the value  $x = 1.17 \pm 0.14$  reported in Ref. [9]. This stoichiometry was subsequently used to determine the amount of  $\text{O}_i$ , which was necessary to build the precipitates, see Table 2.

The precipitates were not detected in the as-grown samples serving as the reference. Further, we found only two annealed samples with no traces of precipitates in the IR spectra: samples A from the middle and the end of the standard CZ Si ingot. Thus, the data witness the favourable influence of the nitrogen doping on oxygen precipitation.

## 5. Conclusion

Using the low temperature IR absorption spectra, we are able to differentiate between the contribution of interstitial oxygen and  $\text{SiO}_x$  precipitates, and determine the concentration of  $\text{O}_i$  in the CZ Si samples. The effective-medium model of average dielectric constant makes it possible to determine the shapes, volume fractions and stoichiometry of the precipitates. The amount of oxygen in the precipitates is in good agreement with the observed decrease of  $[\text{O}_i]$ .

A higher volume fraction of precipitates was found in the nitrogen-doped samples, with the maximum in samples of the B series, i.e., from the beginning of the crystals. We are also able to differentiate between spherical and disc-shaped particles. The latter are identified in all samples from the

nitrogen-doped crystal, and in the samples from the beginning of the standard crystal. Our extensive study proves that the nitrogen doping has a favourable influence on the oxygen precipitation.

## Acknowledgements

The present work was supported by the project MSM 0021622410 of the Ministry of Education of Czech Republic.

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