Characterization of Oxide Precipitates in Heavily B-Doped Silicon by Infrared Spectroscopy

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Infrared absorption spectra of oxygen precipitates in boron-doped silicon with a boron concentration between 10^{17} and 10^{19} cm^{-3} are analyzed, applying the spectral function representation of composite materials. The aspect ratio of the platelet precipitates is determined by transmission electron microscopy measurements. The analysis shows that in samples with moderate doping levels (<10^{17} B cm^{-3}) SiO_{2} precipitates are formed with the same composition as in the lightly doped case. In the heavily boron-doped (10^{19} B cm^{-3}) samples, however, the measured spectra of the precipitates are consistent with a mixture of SiO_{2} and B_{2}O_{3}, with a volume fraction of B_{2}O_{3} as high as 0.41 in the most heavily doped case.

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Interstitial oxygen is the main grown-in impurity in Czochralski-grown silicon. Being highly supersaturated it agglomerates into oxide precipitates of various morphologies during thermal treatments. The precipitation kinetics and the resulting precipitate morphology depend on the experimental conditions and material parameters, the doping level being one of them. Although relatively well understood in moderately doped silicon, oxygen precipitation kinetics and precipitate morphology are strongly different in low-resistivity silicon. To use the internal gettering properties of oxide precipitates in a controlled way, a quantitative understanding of oxygen precipitation and of the chemical composition of the oxide precipitates in heavily doped silicon is needed.

As shown previously for moderately doped silicon absorption spectra related with oxide precipitates can be analyzed quantitatively using a modified Day-Thorpe approach, providing the precipitate matrix consists of two phases. When the aspect ratio of the platelet precipitates is determined from transmission electron microscopy (TEM) analyses and the dielectric functions of the constituents of the precipitate are known, the algorithm proposed in Ref. 5 computes the reduced spectral function, together with the volume fractions of the two phases. In case of lightly doped silicon the precipitates were shown to consist of composite SiO_{2} with γ = 1.17 ± 0.14.

In the present paper the precipitate absorption spectra of boron-doped samples with boron concentrations [B_{2}] ranging between 10^{17} and 10^{19} cm^{-3} are analyzed.

Experimental

Two sets of samples with increasing boron concentration are used in this study as shown in Tables I and II. The samples in Table I received a two-step heat-treatment (32 h at 700°C + 16 h at 900°C under Ar flow) and are labeled set I. The samples in Table II received a three-step heat-treatment (500°C/16 h + 800°C/16 h + 1050°C/8 h under Ar flow) and are labeled set II. The latter set was already used in a different study, but the chemical composition of the precipitates was not analyzed at that time.

For the determination of the interstitial oxygen concentration [O_{i}], specimens with a thickness between 10−30 μm were prepared and measured at low temperature. In the case of the samples B3A2 and B6A2, the oxygen concentration after annealing was determined from the absorption bands due to interstitial oxygen and the A center in the low-temperature absorption spectra of 2 MeV electron irradiated samples. The latter approach was followed because the remaining interstitial oxygen concentration ([O_{i}]) after anneal was expected to be very low, making the ultrathin sample method difficult to apply as the detection limit is around 2 · 10^{17} cm^{-3}. Also, because of the small [O_{i}] after anneal, the absolute error on Δ[O_{i}] (difference between initial and final [O_{i}]) due to irradiation was expected to be rather low. The initial oxygen concentration and the precipitated oxygen concentration [O_{i}] are shown in the third and the fourth columns of Tables I and II.

The absorption spectra of the oxide precipitates are obtained from equivalent pieces of material that are subsequently irradiated with a high dose of 2 MeV electrons to obtain transparency. The remaining [O_{i}] is determined from 6 K infrared measurements and a scaled 1107 cm^{-1} absorption peak is then subtracted from the absorption spectrum at room temperature, resulting in the oxide precipitate absorption spectrum. As was shown in Ref. 9 the absorption spectrum of the oxide precipitates is not altered by the irradiation itself.

TEM observations were performed with a 4000EX microscope operated at 400 kV along the [001] direction (plan-view samples) and along the [011] direction (cross section samples) on the four heat-treated samples of set I, and the aspect ratio, defined as the ratio of the thickness to the edge length, was measured (Table I).

Theory, Model, and Simulations

An algorithm was developed which permits the extraction of the volume fraction of one phase in a two-component material from the room-temperature absorption spectrum of the oxide precipitates. The key is to use the Bergman-Milton spectral representation of the dielectric function of a two-component material, or the numerically more accessible reduced spectral function g(x) as introduced by Day and Thorpe. This permits the separation of the optical parameters of the two components from the geometrical information of the composite, the latter represented by the spectral function. Although the determination of the reduced spectral function from a reflectance or absorption spectrum is an ill-conditioned problem, it is shown to be reliable if a priori knowledge is introduced as additional constraints in the minimization procedure.

In electron-irradiated silicon broad absorption bands due to irradiation occur, rendering isolation of precipitate-related absorption bands less obvious. Therefore, the algorithm is extended with a baseline, i.e., the experimental absorption spectrum is then fitted with the absorption due to precipitates superimposed on a non-a priori defined straight baseline. So, it is assumed that the absorption
due to irradiation damage can be treated as a straight baseline in a limited wave number region. This turns out to be only the case for due to irradiation damage can be treated as a straight baseline in a limited wave number region. This turns out to be only the case for due to irradiation damage can be treated as a straight baseline in a limited wave number region. This turns out to be only the case for due to irradiation damage can be treated as a straight baseline in a limited wave number region. This turns out to be only the case for due to irradiation damage can be treated as a straight baseline in a limited wave number region. This turns out to be only the case for due to irradiation damage can be treated as a straight baseline in a limited wave number region. This turns out to be only the case for

<table>
<thead>
<tr>
<th>Sample name</th>
<th>([B_1])</th>
<th>([O_1])</th>
<th>(\Delta[O_1])</th>
<th>(v_i)</th>
<th>(v_d)</th>
<th>(y\text{ (TEM)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B14A</td>
<td>1.0</td>
<td>8.24</td>
<td>7.30</td>
<td>1123</td>
<td>1226</td>
<td>4.3 ± 2</td>
</tr>
<tr>
<td>B12A</td>
<td>4.8</td>
<td>8.00</td>
<td>6.93</td>
<td>1123</td>
<td>1226</td>
<td>2.7</td>
</tr>
<tr>
<td>B3A2</td>
<td>39</td>
<td>6.8</td>
<td>5.2</td>
<td>1220</td>
<td>3.5 ± 2</td>
<td></td>
</tr>
<tr>
<td>B6A2</td>
<td>91</td>
<td>9.2</td>
<td>9.1</td>
<td>1224</td>
<td>5.5 ± 2</td>
<td></td>
</tr>
</tbody>
</table>

The simulated absorption spectral function, while the variable 

\[
\chi^2 = \chi^2_{\text{before}} - \chi^2_{\text{constraints}} \quad \text{with} \quad \chi^2_{\text{constraints}} = \lambda_1 (\Delta m_i)^2 + \lambda_2 (\Delta O_i)^2 + \lambda_3 (v_i - v_d)^2 + \lambda_4 (v_i - v_f)^2 + \lambda_5 (\nabla g(x))^2
\]

The standard strategy to tackle this is to insert \textit{a priori} knowledge 

\[
g(x) = \begin{cases} 
C(x - x_i)^{-\alpha} & 0 < x_i < x < x_U \\
0 & \text{otherwise}
\end{cases}
\]

This is an extension of the analytic function of Ghosh and Fuchs that can produce a more skewed form. This function allows accurate computations of integrals using Jacobi-Gauss quadrature.
rules. \( \sigma_p \) can be found from Eq. 2 and 6. The goal of this first fit is (i) to find an accurate baseline, to find a solution (ii) that reproduces the resonance frequencies of the polyhedral and platelet precipitates in the absorption spectrum, and (iii) that satisfies the first-moment relation. The last requirement is automatically fulfilled. In the second step this solution is used as the initial value. In this case the reduced spectral function is approximated by a histogram with 64 bins. This two-fit approach is rather robust and always leads to a solution.

The dielectric function of \( \text{SiO}_2 \) was re-extracted (see Table III) from experimental data of Grosse et al.\(^{17}\) using the analytic solution of a Gaussian-broadened Lorentzian-oscillator model.\(^{18}\) In the Appendix a robust formula for the Gaussian-broadened Lorentzian-oscillator model is given. For vitreous \( \text{B}_2\text{O}_3 \) the dielectric function of Galeener et al.\(^{19}\) is used, and for Si \( \varepsilon = 11.7 \), as at 900°C, the silicon phase is crystalline in composite suboxides close to \( \text{SiO}_2\).\(^{20}\)

The algorithm was first tested extensively. It is robust against uncertainties of 15% in \( \Delta [\text{O}_1] \) and against approximations in the shape (sphere instead of a truncated polyhedron, oblate spheroid instead of a square platelet) for both \( \text{SiO}_2 / \text{Si} \) and \( \text{SiO}_2 / \text{B}_2\text{O}_3 \) mixtures. It is always capable of finding the volume fraction \( p_p \) to within 7% or better, except for a \( \text{SiO}_2 / \text{Si} \) mixture with platelets with a large aspect ratio (\( y = 0.06 \)), where the absence of a clearly distinct resonance \( \nu_d \) is responsible for a 12% deviation in \( p_p \).

**Results and Discussion**

**Morphology of the oxide precipitates.**—The morphology of the oxide precipitates in moderately doped and in heavily boron-doped silicon are different for the medium (900°C) as well as for the high (1050°C) temperature heat-treatments. In the moderately doped samples of set I both polyhedral/globular-shaped and platelet precipitates are found in the absorption spectra (see Table I). This is analogous to the low-doped case.\(^{5,21}\) In the heavily boron-doped case the platelet morphology is dominant in the absorption spectra after a medium temperature heat-treatment (set I), while after a high-temperature heat-treatment only polyhedral precipitates are observed (set II).

**Table III. Parameters for the dielectric function of \( \text{SiO}_2 \) describing the antisymmetric stretching (AS) modes with notations as in Ref. 18 and with \( \varepsilon_\infty = 2.23 \).**

<table>
<thead>
<tr>
<th>Mode</th>
<th>( \nu_{0} )</th>
<th>( \nu_{p} )</th>
<th>( \nu_{r} )</th>
<th>( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
<td>(cm(^{-1}))</td>
</tr>
<tr>
<td>AS1</td>
<td>1070</td>
<td>788</td>
<td>5</td>
<td>21</td>
</tr>
<tr>
<td>AS2</td>
<td>1178</td>
<td>232</td>
<td>20</td>
<td>36</td>
</tr>
</tbody>
</table>

**Table IV. Set I: results for the experimental spectra.** The fitted absorption spectra were calculated, assuming spherical and oblate spheroidal particles.

<table>
<thead>
<tr>
<th>Solution</th>
<th>( \Delta [\text{O}_1] )</th>
<th>Mix</th>
<th>( p )</th>
<th>( f_s )</th>
<th>( f_l )</th>
<th>( y )</th>
<th>( [\text{O}]_{pp} )</th>
<th>( \delta m_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>B14A</td>
<td>7.3</td>
<td>( \text{SiO}_2 ) + Si</td>
<td>[-0.04, 1.9]</td>
<td>0.003</td>
<td>8.3</td>
<td>3.4</td>
<td>4.5</td>
<td>1.3</td>
</tr>
<tr>
<td>B12A</td>
<td>6.9</td>
<td>( \text{SiO}_2 ) + Si</td>
<td>[-0.04, 1.9]</td>
<td>0.003</td>
<td>8.3</td>
<td>3.4</td>
<td>4.5</td>
<td>1.3</td>
</tr>
<tr>
<td>B3A2</td>
<td>5.2</td>
<td>( \text{SiO}_2 ) + ( \text{B}_2\text{O}_3 ) &amp; 0.003</td>
<td>8.3</td>
<td>3.4</td>
<td>4.5</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B6A2</td>
<td>9.1</td>
<td>( \text{SiO}_2 ) + ( \text{B}_2\text{O}_3 ) &amp; 0.003</td>
<td>8.3</td>
<td>3.4</td>
<td>4.5</td>
<td>1.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Results for the samples of set I.**—Analogous to the low-doped case, the oxide precipitates were assumed to consist of a mixture of \( \text{SiO}_2 \) and Si. In the moderately doped materials (B14A and B12A) this turns out to be the case. However, in the heavily doped samples (\( \geq 10^{18} \) B/cm\(^3\) the concentration constraint (Eq. 4) cannot be met; the oxygen concentration in the precipitates underestimates \( \Delta O \) by a factor of 2.5–3. This indicates that the mode strength of \( \varepsilon_{pp} \) is too strong or, equivalently, that not all the oxygen vibrates with a mode in the Reststrahlen region of the AS-mode of \( \text{SiO}_2 \). The above suggests that the oxide precipitates consist of \( \text{SiO}_2 \) and another material with a low dielectric constant and that not all the oxygen in the precipitates contributes to the absorption spectrum between 1050 and 1250 cm\(^{-1}\). This means that if the oxide precipitates consist of two components, then the second component probably contains oxygen and its dielectric constant should be rather low. As the samples are heavily doped with boron, \( \text{B}_2\text{O}_3 \) should be considered the prime candidate. First, boron is the only dominant impurity available, next to oxygen. Second, \( \text{B}_2\text{O}_3 \) has a low dielectric constant (\( \varepsilon_{pp} \approx 3.1 \) around 1000 cm\(^{-1}\)).\(^{19}\) Third, the Reststrahlen region of \( \text{B}_2\text{O}_3 \) lies between 1260 and 1550 cm\(^{-1}\), which is outside the Reststrahlen region of \( \text{SiO}_2 \) (1070–1245 cm\(^{-1}\)).

The results of the fits are summarized in Table IV. The results on the moderately doped samples B14A and B12A fall in the uncertainty region of volume fractions in the case of lightly doped material.\(^{5} \( p_{\text{SiO}_2} \approx 0.71 \pm 0.04 \). The precipitated oxygen concentration is retrieved to within 15% and the deviations from the first moment of the spectral function (\( \delta m_1 \)) are within 5%. In the algorithm we gave this restriction a large weight in order to pursue internal consistency of the solution. It is also this restriction that is, at least partly, responsible for the rather narrow confidence intervals of the results in Table IV. In Fig. 1 and 2 we give the fit to the absorption spectrum of B14A and B12A, respectively, together with the corresponding reduced spectral function.

The accuracy of the results for the heavily boron-doped samples is comparable to the moderately doped case. The oxygen concentration found in the precipitates agrees to within 15% with the precipitated oxygen concentration, the deviations from the first moment of the spectral function (\( \delta m_1 \)) are less than 5%, and the aspect ratios agree with the results as obtained from TEM (see Table I). The absorption spectrum and corresponding reduced spectral function of B3A2 and B6A2 are shown in Fig. 3 and 4, respectively.

**Extension of the solution for B6A2 to the Reststrahlen region of \( \text{B}_2\text{O}_3 \).**—B6A2 was constrained fitted between 1030 and 1300 cm\(^{-1}\). Using the resulting particle parameters (\( f_s \), \( f_l \)) and the reduced spectral function [\( \sigma_p \), \( g(s) \)] of B6A2 in Table IV and Fig. 4 we calculated the precipitate absorption spectrum between 1000 and 1600 cm\(^{-1}\) and compared this to the experimental absorption spectrum in Fig. 5. The experimental absorption spectrum is corrected...
with one straight baseline between 1000–1600 cm$^{-1}$, in order to
avoid any distortion of the line shape of the various contributions.
The two-particle surface modes due to $\text{B}_2\text{O}_3$ are clearly resolved in
the experimental absorption spectrum, and the simulated spectrum
agrees qualitatively over the Reststrahlen regions of the two compo-
nents $\text{SiO}_2$ and $\text{B}_2\text{O}_3$. The strong absorption band at 1400 cm$^{-1}$
also occurs in the B3A2 absorption spectrum, although less pro-
nounced. The latter is according to expectations since there is less
$\text{B}_2\text{O}_3$ incorporation (see Table IV). On the other hand it did not
occur in any of the room temperature absorption spectra of other
irradiated samples (as-grown or heat-treated), indicating it is not an
irradiation-induced absorption band. The additional absorption
peaks at the high wave number side in Fig. 5 are probably due to
irradiation-induced defects. The reasonable agreement between the
experimental and simulated absorption spectrum between 1030 and
1450 cm$^{-1}$ lends additional support to the $\text{SiO}_2$/B$_2$O$_3$ composite
precipitate hypothesis.

Influence of the uncertainty with regard to the dielectric function of
$\text{SiO}_2$ and $\text{B}_2\text{O}_3$ on the results of set I.—The fit to the absorption
spectrum is also dependent on the dielectric functions. To estimate

the influence of the choice of the dielectric function of SiO$_2$ we repeated the fits with the dielectric function for thermal oxidized silicon, grown at 900°C, as determined by Ishikawa et al.\textsuperscript{22} The results are shown in the second to the fourth column of Table V. The obtained volume fractions of SiO$_2$ in the precipitates deviate by less than 5% as compared to the first fit \textsuperscript{~see Table IV!}, except for the most heavily doped sample, where the deviation amounts to 8%.

In a last test the influence of the choice of the dielectric function of B$_2$O$_3$ is estimated. For this test we used the dielectric function that we extracted from an absorbance spectrum, measured by Wong.\textsuperscript{23} This B$_2$O$_3$ film was first grown on a silicon substrate at 350°C and subsequently heated at 700°C for 10 min.\textsuperscript{23} At this temperature the fraction of building units that consists of boroxol rings is already reduced as compared to B$_2$O$_3$ grown at low temperature.\textsuperscript{24} Again, from the last three columns in Table V we see that the deviation to the original solution is comparable to the analogous deviation for a different dielectric function of SiO$_2$.

Estimate of the SiO$_2$ volume fraction in the precipitates of the samples of set II.—A SiO$_2$ spherical particle would give a Fröhlich frequency around 1090 cm$^{-1}$, while in the case of SiO$_x$ precipitates in lightly doped silicon the Fröhlich frequency lies between 1100–1125 cm$^{-1}$ \textsuperscript{~Ref. 5!}. However, in the present samples of set II Fröhlich frequencies are as low as 1083–1086 cm$^{-1}$ \textsuperscript{~see Table II!}. This indicates a difference in the chemical and/or structural composition, compared to the oxide precipitates in low-doped material. In order to find an explanation for this, the minimum Fröhlich frequency for
SiO₂/Si and SiO₂/B₂O₃ composites in silicon was sought. How-
ever, the use of an effective medium approximation implies an a
cpriori choice regarding the geometry of the composition. In order to
avoid such an a priori choice, the analytical model (Eq. 6) was used
to search for the minimum Frohlich frequency for a spherical par-
ticle in a silicon host (see Fig. 6). As shown in Fig. 6, both the
SiO₂/Si and the SiO₂/B₂O₃ system can have a geometry with de-
creasing Frohlich frequency as the volume fraction \( p_{\text{SiO}_2} \) decreases,
and based on Fig. 6 it is not possible to exclude either of the two
possible mixtures. However, the low values of the Frohlich fre-
quency as compared to the lightly doped case⁵ and the analogous
resistivities of the samples of set I and II support the assumption that
also in the case of set II the precipitates consist of SiO₂/B₂O₃ pre-
cipitates. As the position of the Frohlich frequency in the samples of
set II is found between 1083 and 1086 cm⁻¹ (see Table II), it fol-
lows from Fig. 6 that the upper limit of \( p_{\text{SiO}_2} \) is at 0.85, in the
assumption that the oxide precipitates consist of a SiO₂/B₂O₃ com-
posite. There are not enough data to confirm a strong dependence of
\( p_{\text{SiO}_2} \) on the substitutional boron concentration for the high-
temperature anneals (1050°C).

Comparison with the literature.—There are not so many results
in the literature that can be compared with ours, at least not directly.
Different mechanisms have been put forward to explain the en-
hancement of the precipitation and of the nucleation in heavily
boron-doped silicon. The boron atom size effect, due to Ono et al.,
owns the enhancements to a strain relief mechanism;² if a substitu-
tional boron atom is incorporated into the oxide precipitate instead
of a substitutional silicon atom, then this will cause a strain relief, as
the boron atom is smaller than the silicon atom.²⁴ As the solid
solubility of boron is higher in SiO₂ than in Si,²⁵ boron will segre-
gate into the oxide precipitates.² The linear misfit \( \delta \) is then given by⁴

\[
\delta = \left[ \frac{v_{\text{SiO}_2}}{(1 + 2u + 2v) v_{\text{Si}} + 2R \Delta v_{\text{Si}}} \right]^{1/3} - 1
\]

with \( u \) and \( v \) the number of absorbed vacancies and emitted in-
terstials, \( R \) the number of absorbed boron atoms for each oxygen
atom, and with \( \Delta v_{\text{Si}} = 0.58v_{\text{Si}} \) the volume difference between a
silicon and a boron atom,³⁹ and \( v_{\text{SiO}_2} \) and \( v_{\text{Si}} \) the volume of a SiO₂
molecule and silicon atom, respectively.

Takeno et al.³ assumed that \( R \) is proportional to the boron con-
centration. The incorporation of this strain relief mechanism (based
on Eq. 7) into a precipitation model indicates the explanation that
two-step anneals with a nucleation step between 600 and 700°C. For
boron concentrations of 4 · 10¹⁸ and 9.1 · 10¹⁸ cm⁻³ the corre-
sponding \( R \) values are 0.10 and 0.23, respectively. These are some-
what lower than those obtained in this paper. But from our analysis
of both sets of samples it is already clear that \( R \) is not only depen-
dent on the boron concentration, but also on the temperature.
Ono et al. performed TEM studies on the oxygen precipitates in heavily boron-doped silicon after prolonged one-step heat-treatments.\textsuperscript{2} They used thermodynamic relationships to calculate the linear misfit from the size and aspect ratio of the precipitates. In the moderately doped (40 m\(\Omega\) cm, \(-5 \cdot 10^{17}\) B cm\(^{-3}\)) sample the linear misfit is rather high, and does not change during the thermal treatment. Contrary to the moderately doped case Ono et al. showed, based on thermodynamic calculations and TEM observations, that the linear misfit is lower in heavily boron-doped silicon and decreases as the heat-treatment is prolonged. For the most heavily doped sample (6 m\(\Omega\) cm) the substitutional boron transport is high enough to explain the strain relief by the boron atom size effect.\textsuperscript{2} However, only the diffusion coefficient of substitutional boron was used in the calculations, thereby neglecting the possible impact of other mechanisms (e.g., diffusion of interstitial boron).

In order to compare the results of Ono et al.\textsuperscript{2} with our results based on the analysis of absorption spectra, the formula as proposed by Takeno et al.\textsuperscript{4} (Eq. 7) was used to calculate \(R\), in the assumption that the boron-size effect is responsible for the strain relief and that the number of absorbed vacancies and ejected interstitials are not altered

\[
\left(1 + \frac{v_{Si}}{\lambda_S} + \frac{v_{Si}}{\lambda_{pp}} + \frac{v_{Si}}{\lambda_{pp}}ight)^2 \approx \frac{(1 + 2u + 2v) v_{Si} + 2R \Delta v_{Si}}{v_{SO_2}}.
\]

The resulting \(R\) values are shown in Fig. 7, together with the results from the quantitative analyses of the absorption spectra. From Fig. 7 it is clear that the agreement between the spectroscopic analysis and the strain analysis from the TEM data of Ono et al.\textsuperscript{2} at the end of the oxygen precipitation process is remarkably close for each temperature and for each resistivity. From the analysis of the TEM results of Ono et al. it is also clear that in the high-temperature case (1000°C) the dependence of \(R\) on the substitutional boron concentration is indeed smaller than in the 900°C temperature heat-treatments. This is also consistent with the results for the samples of set II. The oxide precipitates in the investigated samples are grown during a two-step or a three-step heat-treatment. In the case of Ono et al. the samples received a single heat-treatment. The close agreement between the results from the different analyses in Fig. 7 indicates that it is the high-temperature step that determines the final value of \(R\), i.e., the value for large precipitates.

Conclusions

The analysis of the absorption spectra of annealed and subsequently irradiated heavily boron-doped silicon, following the removal of the contribution of interstitial oxygen in the absorption spectra, combined with the measurement of the interstitial oxygen concentration in ultrathin samples, has allowed for the first time a quantitative analysis of the chemical (\(\text{SiO}_2/\text{Si}\) or \(\text{SiO}_2/\text{B}_2\text{O}_3\)) and structural \([g(x), p_{pp}]\) composition of the oxide precipitates in heavily boron-doped silicon.

The morphology of the oxide precipitates in moderately doped and in heavily boron-doped silicon are different for the medium (900°C) as well as for the high (1050°C) temperature heat-treatments. In the moderately doped samples both polyhedral and platelet precipitates are found in the absorption spectra. In the heavily boron-doped case the platelet morphology is dominant in the absorption spectra after a medium temperature heat-treatment, while after a high-temperature heat-treatment only polyhedral precipitates are observed.

Using the extended algorithm, the spectral function and the corresponding volume fraction of \(\text{SiO}_2\) in the \(\text{SiO}_2/\text{Si}\) mixture in the moderately doped samples of set I as well as in the \(\text{SiO}_2/\text{B}_2\text{O}_3\) mixture in the heavily boron-doped samples of set I was obtained. The assumption of oxide precipitates consisting of a \(\text{SiO}_2/\text{B}_2\text{O}_3\) mixture is shown to be a plausible one. The reasonably good agreement of the experimental and simulated absorption spectrum of sample B6A2 over the Reststrahlen regions (1000–1600 cm\(^{-1}\)) of both components (see Fig. 5) and the absence of the broad, strong 1400 cm\(^{-1}\) absorption band in all the other room-temperature absorption spectra of electron-irradiated silicon, also contributes to the \(\text{SiO}_2/\text{B}_2\text{O}_3\) precipitate hypothesis.

The value of the Frohlich frequency of the oxide precipitates in heavily boron-doped silicon after a three-step heat-treatment is low when compared to the moderately doped counterpart,\textsuperscript{5} and it is shown that a \(\text{SiO}_2/\text{B}_2\text{O}_3\) mixture is plausible, although an analysis based solely on the position of the Frohlich frequency cannot exclude the possibility of \(\text{SiO}_2\) precipitates. Based on the position of the Frohlich frequency of the polyhedral precipitates in the heavily boron-doped samples of set II, the upper limit of \(p_{pp}\) is determined, assuming the precipitate material consists of a \(\text{SiO}_2/\text{B}_2\text{O}_3\) mixture.

Independently of the spectroscopic analysis of our samples, an analysis of the strain relief data of Ono et al.,\textsuperscript{2} assuming that the boron atom size effect is responsible, shows close quantitative and consistent agreement in equivalent material, i.e., material with an initial interstitial oxygen and substitutional boron concentration in the same range, and heated to the same temperature.
We may conclude that this presented detailed analysis of infrared absorption spectra strongly supports the hypothesis that oxide precipitates in heavily boron-doped silicon are composed of a SiO\textsubscript{2}/B\textsubscript{2}O\textsubscript{3} mixture with a substantial volume fraction of B\textsubscript{2}O\textsubscript{3}.

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Appendix

The Gaussian-broadened Lorentzian oscillator is given by

\[ \epsilon(v) = \epsilon_\infty + \frac{1}{\sqrt{2\pi} \sigma} \int_{-\infty}^{\infty} \exp\left(-\frac{(x-v\gamma_j)^2}{2\sigma^2}\right) \frac{v_j^2}{x^2 - v^2 - i\gamma_j v} \, dx, \]

where \( x \) in the integrand is the space of TO-resonance wave numbers, \( v\gamma_j \), the resonance frequency of the \( j \)th TO mode, \( \gamma_j \) its Lorentzian width, and \( \sigma \) its Gaussian width.

In 1992 Brendel and Bormann solved this equation analytically\(^{18}\)

\[ A_j = \sqrt{x^2 + i\gamma_j v} \]
\[ c_+ = \frac{A_j - v\gamma_j}{i\sqrt{2}\sigma_j} \quad c_- = \frac{A_j + v\gamma_j}{i\sqrt{2}\sigma_j} \]
\[ \epsilon_f(v) = \frac{i\sqrt{\pi} v\gamma_j}{2\sqrt{2}\sigma_j} \left[ \exp(c_+^2)\text{erfc}(c_+) + \exp(c_-^2)\text{erfc}(c_-) \right] \]

with the complementary error function defined as

\[ \text{erfc}(z) = \frac{2}{\sqrt{\pi}} \int_{z}^{\infty} \exp(-t^2) dt \]

This analytical solution is exact, but poses some problems. First, it is necessary to use a fast algorithm to calculate the complementary error function for complex \( z \). Second, the product of an exponential and the complex complementary error function can suffer from under- and overflow.

Crandall\(^{20}\) proposed an accurate formula for the erfc function, based on the formula of Chiarella and Reichel\(^{27}\)

\[ \text{erfc}(z) = \frac{\exp(-z^2)\pi}{2\pi} \left\{ \frac{1}{z^2} + 2 \sum_{n=1}^{\text{m}_\text{max}} \frac{\exp(-m^2z^2)}{m^2 \pi^2 + z^2} \right\} + \frac{2}{1 - \exp\left(\frac{2\pi^2}{\epsilon}\right)} \]

with \( \epsilon = 10^{\text{prec}} \) and \( m_{\text{max}} \) given by \( m_{\text{max}} = \lceil \text{prec} \sqrt{\ln(10)} \rceil \), with \( \lceil \rceil \) the floor function.

Now, a function \( h(z) \) is defined

\[ h(z) = \exp(z^2)\text{erfc}(z) \] \hspace{1cm} \[ \text{A-5} \]

Substituting Eq. A-4 into Eq. A-5 gives

\[ h(z) = \frac{\epsilon}{\pi} \left( \frac{1}{z^2} + 2 \sum_{n=1}^{\text{m}_\text{max}} \frac{\exp(-m^2z^2)}{m^2 \pi^2 + z^2} \right) + \frac{2\exp(z^2)}{1 - \exp\left(\frac{2\pi^2}{\epsilon}\right)} \] \hspace{1cm} \[ \text{A-6} \]

This formula can now be used in Eq. A-2.

References