Chemical and structural characterization of oxygen precipitates in silicon by infrared spectroscopy and TEM

O. De Gryse\textsuperscript{a,}\textsuperscript{*}, P. Clauws\textsuperscript{a}, O. Lebedev\textsuperscript{b}, J. Van Landuyt\textsuperscript{b}, J. Vanhellemont\textsuperscript{c}, C. Claeys\textsuperscript{d}, E. Simoen\textsuperscript{d}

\textsuperscript{a}University of Gent, Krijgslaan 281 (S1), B-9000 Gent, Belgium
\textsuperscript{b}RUCA-EMAT, Groenenborgerlaan 171, B-2020 Antwerpen, Belgium
\textsuperscript{c}Ministry of Flanders, AW1, Boudewijnlaan 30, B-1000 Brussels, Belgium
\textsuperscript{d}IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

Abstract

Infrared absorption spectra of polyhedral and platelet oxygen precipitates are analyzed using a modified Day–Thorpe approach (J. Phys.: Condens. Matter 11 (1999) 2551). The aspect ratio has been determined by TEM measurements. The reduced spectral function and the stoichiometry are extracted from the absorption spectra and the concentration of precipitated interstitial oxygen. One set of spectra reveal a Fröhlich frequency around $1100 \text{cm}^{-1}$ and another around $1110–1120 \text{cm}^{-1}$. It is shown that the shift in the Fröhlich frequency is not due to a different stoichiometry, but due to the detailed structure in the reduced spectral function. The oxygen precipitates consist of SiO$_{\gamma}$ with $\gamma \approx 1.1–1.2 \pm 0.1$.

© 2001 Elsevier Science B.V. All rights reserved.

PACS: 61.72.Qq

Keywords: Silicon; Oxygen precipitation; Infrared spectroscopy; TEM

1. Introduction

Oxygen is one of the dominant impurities in Czochralski grown crystalline silicon (Cz). Depending on the thermal treatment oxygen precipitates (SiO$_{\gamma}$) with different morphology are formed in Cz silicon [1]. In the literature different values of $\gamma$ have been reported, ranging from 0.95 to 2 [2–4]. The precise phase, however, has an impact on the precipitate growth kinetics and thus on the interstitial oxygen depletion from the bulk [2]. Therefore, the identification of this phase is highly desirable.

The infrared absorption spectra can be reconstructed using an effective medium theory [3,5–7], only requiring the dielectric functions of the medium and the particles, the volume fractions and the aspect ratio. However, in the former approach [3,4] the analysis depends almost entirely on the availability of dielectric functions of SiO$_{\gamma}$, which limits the certainty of the statements.

It is assumed that the SiO$_{\gamma}$ precipitates consist of two phases [4]: amorphous silicon and amorphous SiO$_2$. The effective dielectric function of a composite depends both on the geometry of the composite and on the dielectric functions of the components. The geometrical information can be summarized in the Bergman–Milton (BM) spectral density function [8,9], which is independent of the material parameters. If the spectral function can be extracted from experimental absorption spectra, the volume fractions of the components can be easily obtained, and thus the $\gamma$ in SiO$_{\gamma}$. Day and Thorpe [10] showed that the spectral functions can be extracted from reflectance data if known properties of the spectral function are incorporated as constraints in the optimization problem. We will make use of their algorithm, but add more constraints, which will allow to obtain the spectral functions and volume fractions in the case of the SiO$_{\gamma}$ precipitates in silicon.
2. Experimental

The investigated Si specimens contained an initial interstitial oxygen concentration between 7.5 and \(10.2 \times 10^{17}\) cm\(^{-3}\) (Table 1) and are divided into four groups of annealing schemes.

The first set of samples (i) received a nucleation step (800°C in N\(_2\) for 24 h) followed by a high-temperature step (3 h, 1100°C in wet oxygen) (samples SD1 and SD2). The second group (ii) received a series of pretreatment followed by a high-temperature step at 1000°C for a duration ranging from 1 to 32 h (samples SD3 and SD4). The third group (iii) received nucleation step (16 h at 500°C), followed by a stabilization step (16 h at 800°C) and a growth step (8 h at 1050°C) (sample SD5) [11]. The last group (iv) received a very long treatment at 750°C in N\(_2\) ambient for 265 h in (sample SD5) [11]. The third group (iii) received nucleation step (3 h, 1100°C) followed by a high-temperature step at 750°C for 24 h) followed by a high-temperature step at 1050°C in Ar for 2 h (samples SD6, S1 and S2) [4]. The interstitial oxygen remaining after annealing was determined by measuring the height of the absorption peak at 1107 cm\(^{-1}\) at 300 K, using the I0C88 standards calibration conversion factor \((3.14 \times 10^{17})\) cm\(^{-2}\) [12]. The interstitial oxygen remaining after annealing was determined at 6 K by measuring the height of the 1206 cm\(^{-1}\) peak [13]. In this way, the broad absorption peak at 300 K belonging to the remaining interstitial oxygen could be removed by subtracting a scaled 1107 cm\(^{-1}\) absorption peak from the experimental spectrum, leaving the spectrum of precipitated oxygen only [4]. Transmission electron microscopy (TEM) observations were performed at 200 keV along the [001] direction (plan view) and along the [0 1 1] direction (cross-section) on two samples (SD6 and S2).

3. Theory, model and simulations

The dielectric function can be obtained by assuming that the particles themselves are composites of inert amorphous silicon (a-Si) \((\epsilon_m = 11.7)\) and thermal oxidized SiO\(_2\) \((t\text{-SiO}_2)\), and thus can be approximated with an effective medium theory. Because representation of the dielectric function of SiO\(_2\) with damped harmonic oscillators is a rather crude approximation for amorphous solids [4,15], the dielectric function of t-SiO\(_2\) was re-extracted using a Gaussian broadened harmonic oscillator model [15,16].

In the BM spectral representation the effective dielectric function of a two component material is given by [10]:

\[
\epsilon_p = \epsilon_{pm} \left( 1 - \frac{\sigma_{pp}}{\epsilon_{pm}} - \frac{1}{\epsilon_{pm}} \int_0^1 g(x) \frac{dx}{x(\epsilon_{pm} - x)} \right)
\]  

with \(\epsilon_{pm}, \epsilon_{pp}\) the effective dielectric function of the composite, the dielectric function of the host (a-Si) and of the inclusion in the composite (t-SiO\(_2\)), \(\sigma_{pp}\) the weight of the delta function of the spectral function at the origin, \(g(x)\) is the reduced spectral function [10], and \(\epsilon_{pm} = \left[ 1 - \epsilon_{pp}/\epsilon_{pm} \right]^{-1}\). The reduced spectral function has some interesting properties [10], \(g(x)\) is zero at \(x = 0\) and 1, and \(g(x) \geq 0\) on the interval [0,1]. Furthermore the zeroth moment gives the volume fraction of the inclusion \(\rho_{pp}\):

\[
\rho_{pp} = \sigma_{pp} + \int_0^1 g(x) \frac{dx}{x}
\]

and for an isotropic material the first moment satisfies:

\[
\mu_1 = \int_0^1 g(x) \frac{dx}{x} = \rho_{pp}(1 - \rho_{pp})/3.
\]

The absorption spectrum for oxide particles in a silicon matrix is given by [3,6]:

\[
\alpha = 2\pi \text{Im}(\epsilon_{eff})/\text{Re}(\epsilon_{eff}),
\]

where \(\nu\) is the wave number \((\text{cm}^{-1})\), and \(\epsilon_{eff}(\nu, f_s, f_d, \epsilon_m, \epsilon_p, y)\) the effective dielectric function [16] according to the continuum theory of Genzel and Martin [7] for spherical and oblate spheroidal [3,6] particles, where \(f_s\) and \(f_d\) are the volume fractions of polyhedral and platelet precipitates, \(\epsilon_m\) and \(\epsilon_p\) the dielectric function of the silicon matrix and the unknown effective dielectric function for the SiO\(_2\) particles (see Eq. (1)), and \(y\) is the aspect ratio. The resonance wave number is given by the Fröhlich wave number \((\nu_s)\) for a sphere and by the longitudinal optical (LO) wave number \((\nu_{LO})\) for a perfect disk, while for an oblate spheroid the resonance wave number \((\nu_{d})\) lies between \(\nu_s\) and \(\nu_{LO}\), depending on \(y\). The absorption spectrum of the oxide precipitates is located in the reststrahlen region (the region between transverse optical wave number \(\nu_{TO}\) and \(\nu_{LO}\)) of t-SiO\(_2\). In the case of SiO\(_2\) particles the medium consists of a rather inert medium (a-Si) and a medium with a strong resonance in the reststrahlen region. These two conditions should allow the extraction of the reduced spectral function.

The spectral functions are extracted by minimizing the following chi-squared function

\[
\chi^2 = \chi^2_z + \chi^2_p,
\]

where \(\chi^2_z = \sum |\nu_s - \nu_s(\nu, \sigma_{pp}, g(x), f_s, f_d, y)|^2\) and \(g(x)

Table 1

<table>
<thead>
<tr>
<th>Sample name</th>
<th>([O_i]) (initial) ((10^{17}) cm(^{-3}))</th>
<th>([O_i]) (final) ((10^{17}) cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>SD1</td>
<td>10.3</td>
<td>1.5</td>
</tr>
<tr>
<td>SD2</td>
<td>10.5</td>
<td>4.9</td>
</tr>
<tr>
<td>SD3</td>
<td>10.2</td>
<td>6.1</td>
</tr>
<tr>
<td>SD4</td>
<td>9.81</td>
<td>2.7</td>
</tr>
<tr>
<td>SD5</td>
<td>8.09</td>
<td>6.23</td>
</tr>
<tr>
<td>SD6</td>
<td>10.17</td>
<td>2.13</td>
</tr>
<tr>
<td>S1</td>
<td>7.52</td>
<td>1.37</td>
</tr>
<tr>
<td>S2</td>
<td>7.94</td>
<td>0.94</td>
</tr>
</tbody>
</table>
approximated as a histogram with 64 bins. As the heart of the problem is an inhomogeneous Fredholm equation of the first kind (Eq. (1)), the problem will be ill-conditioned [10]. The standard strategy to tackle such a problem is to insert a priori knowledge into the chi-squared equations by means of a set of constraints:

$$\chi^2 = \lambda_1 (\mu_1 - \frac{1}{2}p_{pp}(1 - p_{pp}))^2 + \lambda_4 (\nabla g(x))^2 + \lambda_2 (\Delta [O_l] - [O]_{pp})^2 + \lambda_3 [\Delta v^2 + v_d^2],$$

where $\Delta [O_l]$ is the disappeared interstitial oxygen, $[O]_{pp} = (f_s + f_d)p_{pp}C_{SiO_2}$ is the concentration of oxygen in the precipitates, and $C_{SiO_2} = 4.6 \times 10^{22} \text{ cm}^{-3}$ is the oxygen in SiO$_2$. The solution has to satisfy the first-moment relation (first term in Eq. (3)) [10]. The second term is a smoothing term, to prevent wild oscillations in $g(x)$ [10]. The third term states that all the disappeared interstitial oxygen ($\Delta [O_l]$) is in the precipitates ($[O]_{pp}$). The last term gives the differences between the experimental and the simulated $v_l$ and $v_d$, as those are closely related with $v_{TO}$ and $v_{LO}$, which in turn determine the dielectric function [5]. Tests on simulated spectra demonstrated that the algorithm is capable of extracting the volume fractions $f_s, f_d, p_{pp}$ accurately and $g(x)$ with a modest accuracy, while the estimates on $y$ were somewhat underestimated [16]. The accurate determination of $p_{pp}$ allows to determine the stoichiometry.

4. Results and discussion

The samples can be divided into two sets (Table 1). The first set of samples (set I, SD1-SD6) reveals two resonance wave numbers in the absorption spectra around 1115–1120 cm$^{-1}$ and 1215–1225 cm$^{-1}$, traditionally assigned to polyhedral and platelet precipitates, respectively [1,6]. The second set (set II, S1-S2) consists of samples with only one resonance wave number around 1100 cm$^{-1}$, due to polyhedral precipitates [1]. As this resonance wave number is clearly shifted with regard to the samples of set I, one might expect that this is due to a different phase or to a different geometry of the medium.

One sample from set I (SD6) and one from set II (S2) were investigated with TEM. The first sample contained polyhedral and platelets, the latter having an aspect ratio around 0.04–0.02. No platelet precipitates were observed in the second (S2) sample, as expected.

The algorithm is applied on the two sets of samples. For set I a volume fraction ($p_{pp}$) of 0.71 ± 0.04 and for set II a slightly lower value of 0.66 ± 0.03 were obtained. This is equivalent with SiO$_2$, with $\gamma = 1.20 \pm 0.10$ and 1.08 ± 0.07, respectively. The difference in $p_{pp}$ for the two sets is less than 7%, which is not significant, and their 95% confidence regions overlap. Hence, the shift of the Fröhlich wave number from 1110 to 1100 cm$^{-1}$ is not related to a change in volume fraction but is rather due to the detailed picture of $g(x)$, and thus due to a slightly different geometrical structure of the composite. For the samples of set I $g(x)$ has a maximum around $x \approx 0.55$ (Fig. 1(b)), while for the samples of set II the maximum is located around $x \approx 0.3–0.4$ (Fig. 2(b)). The error bars...
of \( g(x) \) for set II are somewhat larger, because the corresponding \( g(x) \) has a rather narrow peak, which is much harder to resolve.

In Fig. 1(a) the absorption spectrum of sample SD6, together with the best fit is given. The obtained aspect ratio is 0.02, which is at the lower border of the error interval determined from the TEM measurements. In Fig. 2(a) an example of set II is given. In both cases the fits to the absorption spectra are good. Deviations can be due to the uncertainty on the dielectric function and to the use of an oscillator model to approximate the dielectric function. Generally, the constraints on the oxygen concentration (third term in Eq. (3)) agreed to within 15%, while the constraint on the first moment (first term in Eq. (3)) agreed to within 25%.

5. Conclusions

The modified Day–Thorpe algorithm has been adapted to the case of absorption spectra of SiO\(_2\) precipitates in silicon and was more severely constrained. This permitted to determine the volume fraction of SiO\(_2\) in the precipitates quite accurately. Also the reduced spectral functions for two sets of specimens with different Fröhlich wave number could be obtained with a moderate accuracy. The shift in the Fröhlich wave numbers is related to a different geometrical structure, of which the reduced spectral function is the emanation. The precipitates consist of SiO\(_2\), with \( \gamma = 1.1 - 1.2 \). Regarding the wide range of experimental situations, the latter result seems to be quite general.

Acknowledgements

This work was performed with financial support from the National Science Foundation (FWO).

References