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Determination of oxide precipitate phase and morphology in silicon and germanium using infra-red absorption spectroscopy

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Abstract

Oxide precipitates in single crystal silicon and in germanium lead to the formation of specific absorption bands in FTIR spectra. A novel methodology is used to interpret and simulate the FTIR spectra. It is based on the assumption that the optical response of the precipitates can be simulated by that of a mixture of two components with known optical properties. The effective dielectric function of such mixture depends on the way the two phases are mixed together. It is shown that both the volume fractions and the spectral functions can be obtained in the case of oxide precipitates in silicon and germanium.

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Keywords: FTIR; Precipitates; Germanium; Silicon; GeO_x; SiO_x

1. Introduction

Oxygen precipitation in silicon has been studied for many decades due to its importance for IC processing and yield. It is therefore well-known that oxide (SiO_x) precipitates in silicon occur as square platelets in the lower-temperature range and as (truncated) octahedra at high-anneal temperatures [1,2]. For the theoretical calculation of the optical response of such particles these shapes are often considered as spheroids. This is a valid assumption if the dielectric loss function of the precipitated phase has broad bands. This approach has been used e.g. by Hu [3] and by Borghesi et al. [4] and by the present authors [5] for the analysis of infra-red (IR) absorption spectra related with silicon oxide precipitates in silicon. Besides the shape of precipitates, the absorption spectra are also determined by the volume fractions of different particle shapes and last but not least by the dielectric functions of both the host lattice and the precipitated phase(s). When the dielectric functions are known, the volume fractions can be determined by determining the best fit between simulated and measured spectra.

The main problem in this approach is that the dielectric function of the precipitated phase is not a priori known. One straightforward solution is to assume that the precipitated phase consists of a mixture of materials with known dielectric functions. Drawbacks are a.o. that the results depend

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strongly on the accuracy of the available dielectric functions and that it is also impossible to estimate the accuracy of x. Borghesi et al. [4], De Gryse et al. [6] and recently also Štoudek and Humlíček [7], modelled the absorption spectra of the precipitated silicon oxide phase as a homogeneous phase of SiO_x yielding an x value of 1.8, 1 and 1.9 ± 0.1, respectively. Homogenous silicon suboxide, however, is unstable at higher temperatures and segregates into silicon and SiO_2 [8,9]. The present authors have used a similar approach assuming however that the precipitated phase is a mixture of SiO_2 and amorphous silicon yielding a x value close to 1 [5]. In the present paper an alternative approach is presented for the interpretation of the precipitate-related absorption bands which is based on the use of the spectral function [10].

2. Experimental set-up and measurement results

2.1. Silicon

Both n- ($\geqslant 1.8\,\Omega\,cm$) and p-type ($(\geqslant 20\,\Omega\,cm$) silicon substrates were used with initial interstitial oxygen concentrations between 7.5 and $10.5 \times 10^{17}\,cm^{-3}$ (Table 1). Three different thermal anneals were performed:

- Treatment (i): various low-temperature pre-treatments followed by an high-temperature anneal at 1000 °C for 1 to 32 h.
- Treatment (ii): a treatment in N_2 at 800 °C for 24 h followed by 3 h in wet oxygen at 1100 °C.
- Treatment (iii): an anneal in N_2 at 750 °C for 265 h followed by a 1050 °C anneal in Ar for 2 to 8 h.

2.2. Germanium

Oxygen-rich Cz-germanium crystals were grown in a nitrogen–oxygen atmosphere. Before the oxygen-precipitation treatment the germanium samples were submitted to a 5 min dispersion at 900 °C followed by a quench to room temperature. The interstitial oxygen concentration after the quench amounted to $C_{OI} = 2.5 \times 10^{17}\,cm^{-3}$ as determined from the amplitude of the absorption band at $856\,cm^{-1}$ using the conversion factor of $5 \times 10^{16}\,cm^{-2}$ of Kaiser and Thurmond [11]. Oxygen precipitation treatments were performed in Ar atmosphere at temperatures between 500 and 620 °C [12]. The anneals were always followed by a quench to room temperature in order to avoid formation of other oxygen agglomerates such as thermal donors.

3. A new interpretation of precipitate-related IR absorption bands based on the use of the spectral function

In the conventional approach the measured infrared absorption spectra are reconstructed using an effective medium theory which requires the dielectric function of the host matrix and of the inclusions as well as their volume fractions and aspect ratio.

In the present work it is also assumed that with respect to their optical behaviour the inclusions can be considered to consist of a mixture of two phases, i.e. the amorphous form of the host matrix and its oxide. The effective dielectric function of such mixture depends both on how both phases are mixed (the ''geometry'' of the precipitated phase) ánd on the dielectric functions of both components. The geometrical information can be summarised in

Table 1
Experimental matrix

Set	Treatment	C^i_{OI}	C^f_{OI}	ΔC_{OI}	ν_s (cm^{-1})	ν_d (cm^{-1})	C_{Oprec}	$\frac{\Delta C_{OI} - C_{Oprec}}{\Delta C_{OI}}$ ($\times 10^{-2}$)
1	ii	10.3	1.5	8.8	1117	1215	8.1	8.7
1	ii	10.5	4.9	5.6	1120	1226	4.5	20
1	i	10.2	6.1	4.1	1116	1217	3.1	25
1	i	9.81	2.7	7.11	1116	1212	6.0	15
1	iii	8.09	6.23	1.86	1103-1115	1229	1.5	19
1	iii	10.17	2.13	8.04	1113	1225	6.8	15
2	iii	7.52	1.37	6.15	1099	No	5.2	15
2	iii	7.94	0.94	7	1100	No	6.5	7.0

All oxygen concentrations are given in $10^{17}\,cm^{-3}$ units [10].