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Abstract
Results are presented on the photoluminescence (PL) characterization of heavily doped p^+ Czochralski silicon, which has been subjected to a two-step, oxygen precipitation heat treatment. It will be shown that the presence of oxygen precipitates gives rise to the D1, D2 and D5 lines, where the energy of the D1 line shifts to lower values for a stronger degree of precipitation. The occurrence of these PL features is also a function of the boron concentration in the p^+ material. The PL results are compared with Fourier transform infrared absorption data and with transmission electron microscopy results. From this, it is concluded that PL has a good potential for use in the assessment of oxygen precipitation in heavily doped silicon.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Currently, there is a strong drive to use epitaxial ('epi'-) silicon wafers in the volume production of advanced microelectronic circuits. Epilayers on both heavily (p^+) and lightly doped (p^-) substrates yield high-quality wafers, which are able to meet the ever tighter material requirements of the 'SIA roadmap' [1]. One of the major advantages of epi-material is the absence of so-called crystal-originated particles (COPs), occurring in pulled Czochralski (Cz) silicon, which consist of large vacancy clusters formed during the cooling of the crystal from the melt temperature. These COPs have a strong impact on the gate oxide integrity (GOI) of MOS devices and can also enhance the junction leakage current, when they exist in the vicinity of the depletion region [2].

Table 1. Description of the epi-samples used in the study. The epilayer thickness was 3 μm. A1 refers to a single HT at 700 °C, while A2 refers to a two-step treatment.

Label	Resistivity (mΩ cm)	Doping density (cm^{-3})	Heat treatment
B3–A1	19	3.7×10^{18}	700 °C/50 h
B6–A1	10.1	9.1×10^{18}	700 °C/24 h
B3–A2	19	3.7×10^{18}	700 °C/32 h + 900 °C/16 h
B6–A2	10.1	9.1×10^{18}	700 °C/32 h + 900 °C/16 h
B12–A2	68	4.8×10^{17}	700 °C/32 h + 900 °C/16 h
B14–A2	200	1.0×10^{17}	700 °C/32 h + 900 °C/16 h

It is well established that the oxygen precipitate density in heat-treated Cz silicon is increased by heavy boron doping [3]. This enhances the internal gettering capability of p/p$^+$ epi-material. Key to the understanding of the oxygen precipitation behaviour is the assessment of the interstitial oxygen concentration, denoted by [O$_i$], and the amount of oxygen in SiO$_x$ precipitates, which requires a dedicated analysis, based on infrared absorption spectroscopy [4, 5].

One route to gaining information on precipitated oxygen is by investigating the absorption peaks around 1100 cm^{-1} at 300 K [6]. For heavily doped p$^+$ silicon this is possible by irradiating the sample with a high fluence ($(1–3) \times 10^{19}$ cm^{-2}) of 2 MeV electrons at room temperature [4]. In this way, the material becomes transparent in the mid-infrared region due to a deactivation of the B dopant atoms, through the creation of radiation damage. Alternatively, it has recently been demonstrated that the study of the well-known D1–D2 photoluminescence (PL) lines [7] in heat-treated Cz silicon could provide further insight into oxygen precipitation [8, 9]. It has in fact been shown that the line position (energy) depends sensitively on the details of the oxygen precipitation treatment [8, 9].

Therefore, it is the aim of this work to investigate by means of PL the oxygen precipitation behaviour in heavily doped p$^+$ silicon. Materials with different starting resistivities have been used for that purpose. If successful, this would allow study of the optical properties of oxygen precipitates in p$^+$ silicon without the need for heavy electron irradiation. One complicating factor when dealing with heavily doped material is the associated band-gap narrowing, which causes a shift and a broadening of the PL lines of excitons bound to the dopants [10–12]. The results of this initial PL study will be compared with Fourier transform infrared (FTIR) data obtained on thinned and/or electron-irradiated samples. The former method yields [O$_i$] and Δ[O$_i$] (the concentration of precipitated oxygen after heat treatment (HT)), while the latter provides information on the presence of SiO$_x$ precipitates ($1 < x < 2$) [4]. Structural defects have been characterized by transmission electron microscopy (TEM).

2. Experimental details

p$^+$ silicon wafers with a 3 μm thick epilayer and four different resistivities, ranging from 10.1 to 200 mΩ cm, have been heat treated. The relevant electrical parameters of the starting material are summarized in table 1. The samples received different HTs, as described in table 1. As there was no trace of precipitate bands for the B3 and B6 material after a 700 °C anneal only, a second set of samples was prepared, which underwent a two-step HT, consisting of 32 h at 700 °C and 16 h at 900 °C under Ar flow. Results corresponding to the single-and double-anneal treatments are labelled A1 and A2, respectively.

For the PL measurements, the samples were mounted in a liquid helium cryostat. Excitation by a 488 nm Ar laser was utilized. Different excitation power densities P ranging from 5 to 50 mW mm^{-2} were applied.

Table 2. Peak energy for the main PL lines in the p$^+$ epi-material, before and after HT (50 mW mm^{-2}; T = 5.5 K). A1: a single HT at 700 °C, A2: two-step HT 700 °C/32 h + 900 °C/16 h (bd = below detection limit).

| Sample	D1 (meV)	D5 (meV)	D2 (meV)	B^{TO} (meV)
B14	bd	bd	bd	1086.9
B14–A2	806	844	875	1088.0
B12	823.5	—	876.5	1082.5
B12–A2	811.3	847	875.5	1087.8
B3	819	—	—	1059.6
B3–A1	820	—	—	1056.0
B3–A2	~850	—	—	1053.0
B6	825	—	—	1043.5
B6–A1	825	—	—	1055.0

Complementary FTIR and TEM analysis has also been performed in order to facilitate the interpretation of the PL results. In the case of heavily doped silicon, problems arise due to the high free carrier absorption in the mid-IR region, i.e., around the 1106 cm^{-1} peak position of O$_i$ at 300 K. In order to solve these, a method has been developed which relies on a special procedure of thinning of the samples, down to a thickness in the range 10–30 μm. It is important to maintain the original material properties, which precludes heating the specimens, and to achieve a stress-free state [4]. The sensitivity of the method is further enhanced by performing measurements of the 1136.3 cm^{-1} absorption peak of O$_i$ at 6 K, using an optimized conversion factor reported in [5].

3. Results

The first set of experiments was performed with the 3 μm epilayer on top. Removing the epilayer by polishing 40 μm off and etching did not markedly affect the PL spectra, except for the B^{TO} 1092 meV line, which disappears from the spectrum for some of the polished p$^+$ samples. This indicates that the 1092 meV line originates from the lightly doped epilayer, while in the p$^+$ material, the B^{TO} line is shifted towards lower energies, as indicated in table 2. As can be seen there, the shift increases for increasing doping density. At the same time, a broadening of the lines occurs, which can be expected from the band-gap narrowing, occurring at higher doping levels [10–12].

Figure 1 focuses on the energy region below 1 eV, where the features related to oxygen precipitates and/or dislocations are expected. It corresponds to the 68 mΩ cm material before and after annealing A2 (see table 1). As can be seen, before HT, weak bands already exist and are tentatively assigned to the D1 and D2 lines. However, the corresponding peak position reported in table 2 is clearly higher than 807 meV for the D1 dislocation line and close to the expected value of 874 meV for D2. According to the interpretation put forward by Pizzini *et al* [8, 9] and following upon an original suggestion by Tajima *et al* [13], this points to the presence of oxygen precipitates in the B12 starting material. Furthermore, the high energy of the D1 line suggests an early stage of precipitation, leading to small SiO$_x$ particles. In the 200 mΩ cm starting material B14, no PL lines above the detection limit of the technique were observed in the same spectral region (table 2).

Using the two-step anneal A2 results in the development of clear D1 and D2 lines in figures 1 and 2. While the D2 line remains at the same position, D1 has shifted close to its saturation value around 807 meV [8]. This indicates the injection of silicon interstitials in
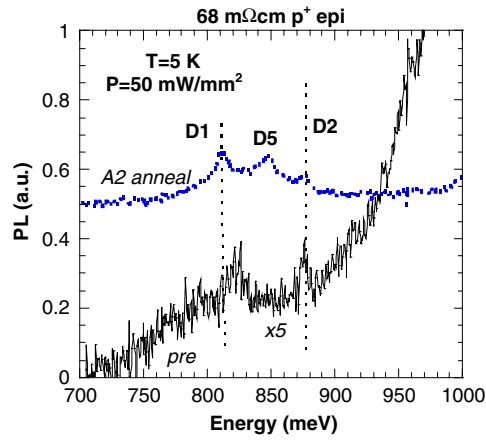
Figure 1. The PL spectrum of a 68 mΩ cm p+ sample before and after a two-step HT. The PL spectrum corresponding to the starting material has been multiplied by a factor of 5.
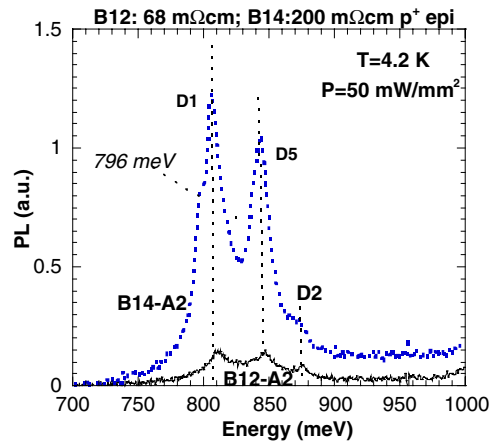
**Figure 2.** Comparison of the PL spectra for a 68 and a 200 mΩ cm p+ sample after a two-step HT.

the lattice upon proceeding with oxygen precipitation, in order to relax the strain around the growing precipitate. Eventually, when the stress becomes high enough, dislocation loops can be punched out. In fact, weak features around 958 and 1000.8 meV in the spectrum of the two-step-annealed 200 mΩ cm sample could well correspond to the D3 and D4 dislocation lines. They are below the detection limit in B12.

In addition to D1 and D2, a peak around 845 meV labelled D5 is also discerned after annealing in figures 1 and 2. A similar feature has been reported in Au-doped [14] and Er-doped silicon [8]. It has tentatively been ascribed to metal atoms (Me) captured by oxygen (precipitate), leading to Me–O optically active bonds. It should also be recalled that p+ material is very effective in gettering transition metals such as Fe, where they can be bound to oxygen precipitates during the HT.

Finally, a shoulder is clearly evident on the low-energy flank of the D1 line of the annealed 200 mΩ cm material. It could correspond to the D1a line at 802 eV of [9].

Figures 3(a) and (b) exhibit the dependence of the PL on the excitation power at $T = 6.8$ K and on the temperature for $P = 10$ mW cm^{-2}, for the annealed 200 mΩ cm material B14. The
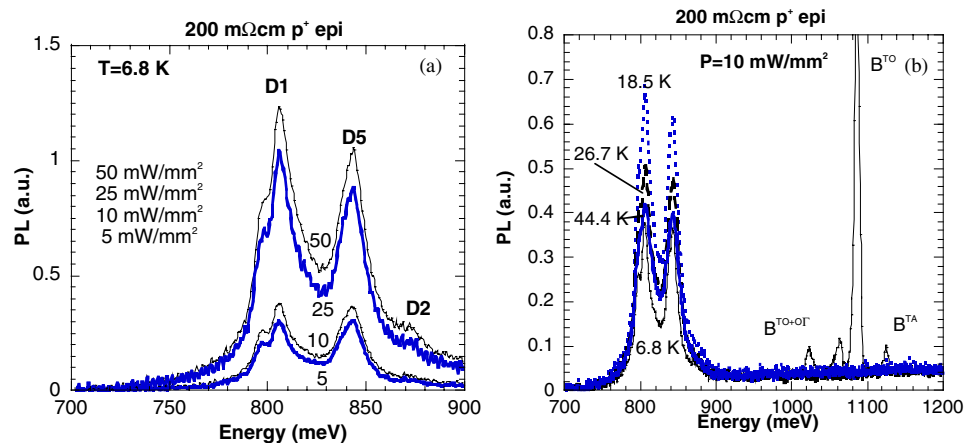
Figure 3. (a) PL spectra for different excitation power densities P and (b) at $P = 50$ mW mm^{-2} for different temperatures, for the annealed 200 mΩ cm p$^+$ material.
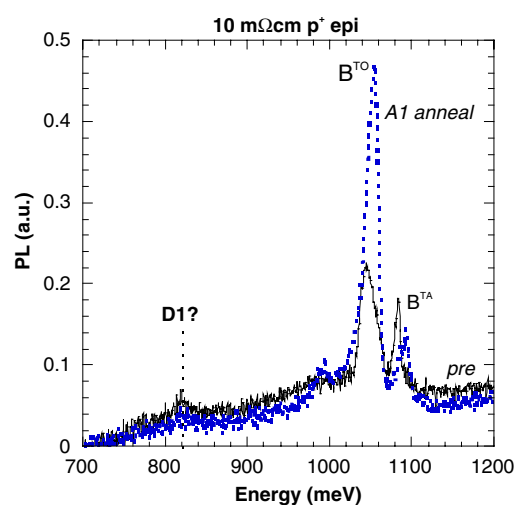
Figure 4. The PL at $T = 5.5$ K and $P = 50$ mW mm^{-2} for the 10 mΩ cm material before (full curve) and after (dotted curve) a 700 °C anneal for 24 h.

796 meV shoulder shows different behaviour with excitation power and with temperature. It becomes less pronounced with respect to the D1 peak for higher T and/or P. It is also clear that the D1, D5 and D2 luminescence is retained at much higher temperatures than the B-related excitonic PL. One special feature is that the 6.8 K spectrum has a lower intensity than for the higher temperatures, which is rather unexpected from the literature [15]. At the moment, no explanation is available for this phenomenon.

For the 10 and 19 mΩ cm materials, the following results have been obtained. As mentioned above, no oxygen precipitation was found after the 700 °C treatment just by FTIR investigation of the thinned samples. This is also confirmed by the PL spectra of figure 4. The peak at ~825 meV is hardly affected by the 700 °C anneal and no evidence of a D2 or D5 line is found. It was, therefore, decided to prepare a second set of samples receiving the two-step anneal A2. The corresponding PL spectrum for the 19 mΩ cm material is represented in
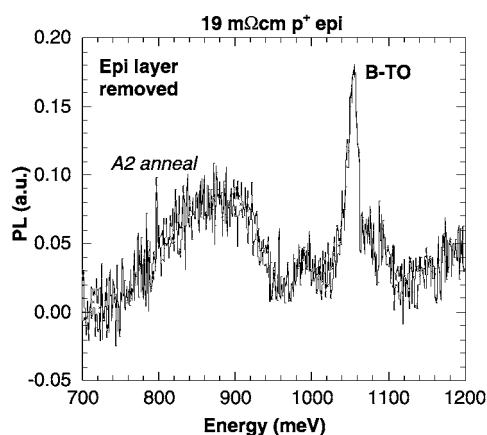
Figure 5. The PL at $T = 6$ K and $P = 50$ mW mm^{-2} for a 19 mΩ cm material after annealing A2, consisting of 32 h at 700 °C and 16 h at 900 °C under an Ar flow.

Table 3. Initial interstitial oxygen concentration determined from the height of the 1136 cm^{-1} local vibrational mode using the IOC-88 standard [17]. The samples were first thinned and polished to an appropriate thickness [4, 18]. The presence and type of oxygen precipitates after a two-step annealing were measured using FTIR for 10^{19} cm^{-2} 2 MeV electron-irradiated samples [4] using the analysis method of [6].

Sample	$[O_i]$ (10^{17} cm^{-3})	$\Delta[O_i]$ (10^{17} cm^{-3})	Precipitate bands
B14	8.2 ± 0.5	7.3	Platelike + polyhedral
B12	8.0 ± 0.5	6.9	Platelike + polyhedral
B3	6.8 ± 0.8	5.2	Platelike
B6	9.2 ± 1.2	9.1	Platelike

figure 5; it shows a broad feature in the 800–900 meV region. This is clearly different to the 820 meV D1 line found in the starting material. As will be shown below, there is strong additional evidence of oxygen precipitation after the two-step anneal for all p$^+$ substrates studied.

4. Discussion

From the foregoing, some conclusions can be drawn regarding the PL of heavily doped p$^+$ silicon subjected to an oxygen precipitation treatment. First, in the energy range of interest PL lines can already be found for the starting material, which could correspond to the D1–D2 emission bands in oxygen-precipitated Cz silicon. These lines grow after a two-step anneal in B12 and B14, where the D1 line shifts to a lower position—in line with the observations of [8, 9]—while D2 remains at approximately the same energy. In addition, some new peaks at ~845 and 796 meV may develop for the 'lightly' doped samples B12 and B14 studied here.

In order to interpret the data more clearly, the PL results of table 2 are compared with the results revealed by the FTIR analysis and the findings summarized in table 3. More details will be published elsewhere [16]. There exists a distinction between the B12–B14 material on the one hand and the B3–B6 substrates on the other. While the former show a mixture of platelike and octahedral precipitates in the absorption spectrum of figure 6(a), only platelike precipitates are found for the 10 and 19 mΩ cm material (figure 6(b)). This is confirmed by the TEM results for B12 of figure 7. TEM also reveals the presence of bulk stacking faults (SFs) in all samples.
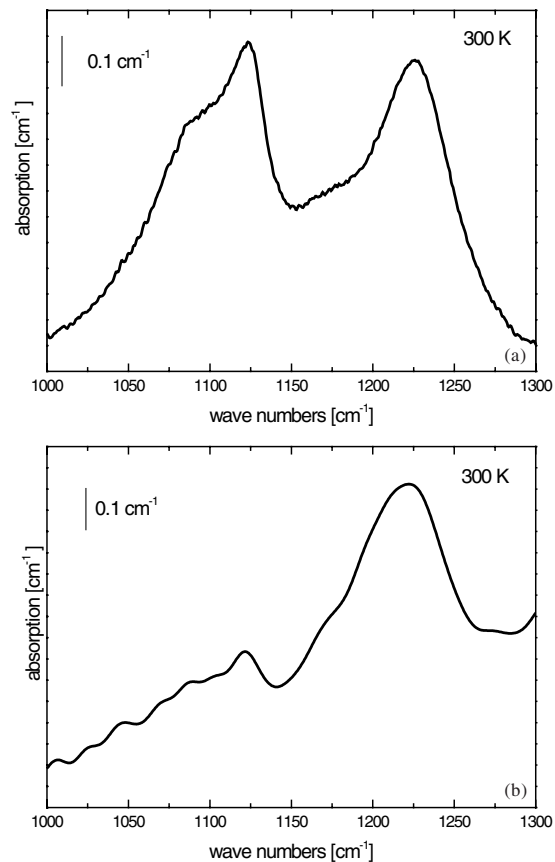
Figure 6. (a) The absorption spectrum due to the precipitates for the two-step-annealed 200 mΩ cm sample. The double resonance stems from polyhedral (1110–1120 cm^{-1}) and platelet precipitates (1225 cm^{-1}) [6]. (b) The absorption spectrum due to the precipitates for the two-step-annealed 19 mΩ cm sample. The absorption band with a maximum around 1225 cm^{-1} corresponds to platelet precipitates.

It remains to explain the impact of the B concentration on the oxygen precipitation behaviour. In this context, it should be noted that the presence of a high boron concentration has a strong effect on the strain relaxation around an oxide precipitate, which results in a change in the precipitate morphology from platelike to polyhedral and the emission of silicon interstitials [3]. It is, therefore, expected that precipitate strain relaxation by interstitial injection in the matrix will happen earlier for the less heavily doped material B12–B14 compared with B3–B6. This probably explains the nature of the PL spectra reported here: for the 68 and 200 mΩ cm material, D1, D2 and D5 lines develop, whereby the D1 line shifts to the energy which is thought to correspond to dislocations/interstitials. One curious fact calling for further investigations is the observation of SFs in the heavily doped B3–B6 material by TEM, without any clear evidence of the D1–D2 lines developing after the two-step anneal.

5. Conclusions

It has been shown that PL is a promising technique for the study of oxygen precipitation in heavily doped Cz silicon, which requires no special sample preparation, i.e., no high-fluence
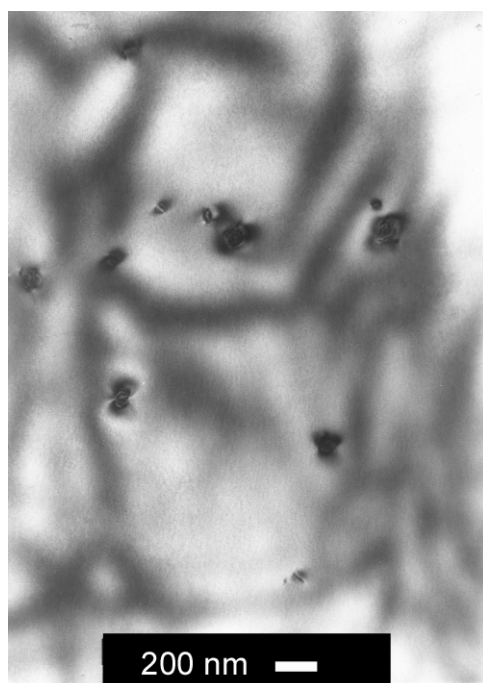
Figure 7. A plan-view TEM image of the two-step-annealed 68 mΩ cm p$^+$ material, showing the presence of platelet oxygen precipitates.

irradiation. From the observation of D1–D2 lines in some of the starting material, without any corresponding evidence for precipitation found by TEM or FTIR, it may be concluded that the PL technique is probably more sensitive than the others. A detailed correlation study between the three techniques should result in a more quantitative analysis of oxygen precipitation in heavily doped silicon by means of PL.

Acknowledgments

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