DLTS and PL studies of proton radiation defects in tin-doped FZ silicon

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Abstract

In this paper, deep level transient spectroscopy (DLTS) is applied to study the deep levels in tin-doped and high-energy proton irradiated n-type float-zone (FZ) silicon. The results will be compared with irradiated tin-free FZ reference material, in order to evaluate the hardening potential. It will be shown that in Sn-doped silicon (FZ:Sn), a number of additional deep levels can be observed, two of which have been identified as acceptors associated with Sn–V. Furthermore, optically active recombination centres have been probed by photoluminescence (PL) spectroscopy. The PL results confirm the reduction of electrically active radiation-defect formation in FZ:Sn. At the same time, no Sn-related optically active centres have been found so far. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Tin-doped silicon; Proton-irradiation; DLTS; Photoluminescence; Tin-vacancy complexes

1. Introduction

Currently, there is strong interest in using impurity enriched silicon for radiation hard detectors. One of the candidate dopants is tin, which is known for its ability to trap vacancies, thereby suppressing the formation of regular radiation defects like the V–O or V–V centres. However, one should also assess the electrical activity of the formed Sn–V complexes. Here it is the aim to elaborate further on a previous study, which identified two new acceptor levels, related to Sn–V [1,2] in high-energy proton-irradiated Sn-doped Czochralski (Cz) n-type silicon. At the same time, it was demonstrated that the total introduction rate of radiation defects in Cz:Sn was up to a factor 2 lower than in float-zone (FZ) samples without tin-doping (abbreviated FZ:0). In addition to deep level transient spectroscopy (DLTS) measurements, photoluminescence (PL) is applied for the first time on irradiated tin-doped silicon.
2. Experimental

The Sn-doped FZ silicon has been obtained from TOPSIL and was doped in the melt, to a tin concentration in the range \(10^{18}\) cm\(^{-3}\) [3]. Gold Schottky barriers (2 mm diameter) were evaporated and covered by a thin In foil for protection. An In–Ga eutectic ohmic contact was applied to the back of the sample. For comparison purposes, p–n junctions fabricated on standard FZ material without tin doping have been irradiated as well. The doping concentration \(N_D\) of the n-type substrates has been derived from capacitance–voltage (C–V) measurements at 1 MHz on the reverse biased Schottky barriers or p–n junctions. The PL was excited by an 488 nm Ar laser, using a power of 50 mW. The sample temperature was 12 K. The Schottky barrier or the p–n junction were removed by polishing and etching, before PL investigation.

Proton irradiations have been performed using the TANDEM accelerator at Demokritos (8 MeV) or at the Cyclone facility in Louvain-la-Neuve (60 MeV). The fluences have been indicated in Table 1. DLTS analysis was applied as described previously [1,2]. A typical spectrum before irradiation is shown in Fig. 1 for an FZ:Sn sample; no deep levels were observed within the sensitivity limit in the p–n junctions.

3. Results and discussion

3.1. DLTS results

Before irradiation (Fig. 1), a number of grown-in deep levels have been found, which are typical for high-purity FZ silicon [4,5]. The \(E_c - 0.073\) and \(E_c - 0.563\) eV centres are believed to have the same origin. The fact that the trap concentration \(N_T\) corresponding with the two peaks is the same \((1.4 \times 10^{12} \text{ cm}^{-3})\) is in line with this assumption. According to Lefèvre [5], the levels originate from a self-interstitial related defect, possibly a di-interstitial. The third level \((E_c - 0.143\) eV) could be the same as in [4]. There is in fact a shoulder to the low-temperature side of this peak, which could coincide with the \(E_c - 0.11\) eV interstitial carbon-related centre found previously [4,5]. Both the \(C_i\) and \(S_{ii}\)-related peaks were found to anneal at rather low temperatures, i.e. \(\sim 175\) °C [4], implying a fairly simple structure.

After high-energy proton irradiation, a number of radiation-induced deep levels have been observed, both in the reference and the tin-doped FZ material (Fig. 2). However, the grown-in peaks are still present for the low-fluence 60 MeV exposure. One of the interesting observations is that the trap concentration \(N_T\) of the grown-in mid gap level is 20% smaller after irradiation, i.e. \(\sim 1.2 \times 10^{12} \text{ cm}^{-3}\). Even if account is made for a relative error on \(N_T\) of about 10%, this is a significant reduction, as it is expected that also the radiation-induced peaks corresponding to \(V\)–\(V_0\) and \(Sn\)–\(V_0\) will contribute to the peak height. In other words, an

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Experimental radiation matrix</th>
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<tbody>
<tr>
<td>([\text{Sn}]) (cm(^{-3}))</td>
<td>(N_D) (cm(^{-3}))</td>
</tr>
<tr>
<td>0</td>
<td>(1.0 \times 10^{14})</td>
</tr>
<tr>
<td>0</td>
<td>(1.2 \times 10^{14})</td>
</tr>
<tr>
<td>(\sim 10^{18})</td>
<td>(2.7 \times 10^{14})</td>
</tr>
<tr>
<td>(\sim 10^{18})</td>
<td>(2.6 \times 10^{14})</td>
</tr>
</tbody>
</table>

Fig. 1. DLTS spectrum of a \(10^{18}\) cm\(^{-3}\) Sn-doped n-type FZ substrate before irradiation. Bias pulse from \(-4 \rightarrow 0\) V and time constant window \(\tau \sim 6\) ms.
The data suggest thus a recombination between the interstitial-related grown-in peaks and the radiation-induced point defects (vacancies?), leading to a reduction of their concentration. This is further supported by the 8 MeV data, where no trace is found of the grown-in deep levels (Fig. 3). Note also that the activation energy for the double acceptor level of Sn–V is in good agreement with previously reported values [1–3]. The single-negative charge state could not be revealed in this case, as it is masked by the presence of the grown-in mid gap level.

With respect to the trap introduction rates, the difference between irradiated FZ material with and without tin-doping is less pronounced than for the case of Cz:Sn, reported before [1,2]. One reason could be the lower fluence used here. By contrast, comparing the results for the 8 MeV exposure, it is clear that the Sn-doped FZ material is less degraded than its tin-free counterpart. This follows from the fact that a complete freeze-out of the capacitance of the p–n junction is observed below 200 K for FZ:0, while the Schottky barrier of Fig. 3 is measurable down to 20–30 K. The corresponding doping density has reduced to $5 \times 10^{12}$ cm$^{-3}$. This points to the fact that in both cases the shallow donor concentration is compensated by the radiation-induced deep-levels. It should finally be noted that in addition to the four levels of the Sn–V complex, some additional traps have been found, which seem to be typical for irradiated tin-doped silicon. These are the $E_c - 0.074$ and $E_c - 0.086$ eV electron traps of Fig. 3 and a hole trap H2 at $E_v + 0.181$ eV. The origin of these levels is not clear for the moment, but they could be related to the higher order Sn$_n$V$_m$ centres, which have recently been found by electron paramagnetic resonance [6].

3.2. PL results

The PL spectra before and after a 60 MeV $\times$ $10^{11}$ cm$^{-2}$ proton irradiation are represented in Figs. 4 and 5, respectively. Before exposure, the PL lines of the phosphorous donors (transverse acoustical – TA and transverse optical – TO) dominate the excitonic region. The origin of the broad PL between 0.7 and 0.9 eV is not clear for the moment. The line at $\sim 0.980$ eV could be in the range of the D4 dislocation line [7]. Considering that the material may contain A swirl defects (dislocation loops) this identification is not so
unlikely, though a more firm correlation should be established. The 0.980 feature could also be related to a small interstitial cluster, if the hypothesis regarding the origin of the grown-in deep levels is correct. Recently, strong interest has developed in this matter and a number of PL lines, like the W and I₃ line and a broad peak at \( \sim 0.97 \) eV for self-implanted silicon have been identified [8].

After proton irradiation, two carbon-related PL lines have been clearly identified in both materials. They are the 0.97 eV G-line ascribed to \( \text{C}_i-\text{C}_s \) [7,9–11] and the 0.79 eV line associated with the \( \text{C}_i-\text{O}_i \) complex [7,12–14]. Similar results have been reported before for the FZ reference material [15]. In addition, it can be noted in Fig. 5 that the P-related luminescence is higher in the Sn-doped material, compared with the non-doped sample. This demonstrates that the non-radiative recombination by radiation-induced point or cluster defects is lower in FZ:Sn. In other words, the created traps have a smaller \( N_T \) and/or are less recombination active. It is believed that this is due to the vacancy capture by Sn, which suppresses the formation of divacancies (V–V), A(V–O)- and E(P–V)-centres [16,17]. This confirms the previous observations on Cz:Sn [1,2]. Apparently, from PL follows that the introduced Sn–V centres are less effective as non-radiative recombination centres than the V–V or V–O, for example. However, one should not overlook the role of the grown-in defects in the FZ:Sn material studied here. If they are indeed interstitial-related, they can contribute to the capture of radiation-induced vacancies by recombination, thereby reducing their concentration. This could in fact be a more favorable mechanism for hardening, compared with the Sn-doping, though it is limited by the maximum concentration of the grown-in centres. It should finally be remarked that so far, no Sn-related PL lines have been observed before or after proton irradiation.

4. Conclusions

It has been shown that high-energy proton irradiation introduces a number of Sn-related radiation defects in Sn-doped FZ silicon. However, the introduction rate of the standard radiation defects is reduced, particularly for higher damage levels. PL spectroscopy reveals no specific Sn-related lines, but confirms the lower recombination activity of the deep radiation-induced levels in tin-doped FZ material.
Acknowledgements

Guy Berger and his co-workers from the cyclone facility in Louvain-la-Neuve are gratefully acknowledged for assistance during the 60 MeV proton irradiations. A. Blondeel is thanked for help during the DLTS measurements. This work has been performed in the frame of the European Training and Mobility of Researchers Network ENDEASD (ERB 4061 PL 97-0645).

References