

Home Search Collections Journals About Contact us My IOPscience

Electrically active defects in irradiated n-type Czochralski silicon doped with group IV impurities

This article has been downloaded from IOPscience. Please scroll down to see the full text article. 2005 J. Phys.: Condens. Matter 17 S2255 (http://iopscience.iop.org/0953-8984/17/22/013) View the table of contents for this issue, or go to the journal homepage for more

Download details: IP Address: 129.252.86.83 The article was downloaded on 28/05/2010 at 04:55

Please note that terms and conditions apply.

J. Phys.: Condens. Matter 17 (2005) S2255-S2266

# Electrically active defects in irradiated n-type Czochralski silicon doped with group IV impurities

M L David<sup>1,4</sup>, E Simoen<sup>1</sup>, C Claeys<sup>1,2</sup>, V Neimash<sup>3</sup>, M Kras'ko<sup>3</sup>, A Kraitchinskii<sup>3</sup>, V Voytovych<sup>3</sup>, A Kabaldin<sup>3</sup> and J F Barbot<sup>4</sup>

<sup>1</sup> IMEC, Kapeldreef 75, B-3001 Leuven, Belgium

<sup>2</sup> EE Dept KU Leuven, Kasteelpark Arenberg 10, B-3001 Leuven, Belgium

<sup>3</sup> Institute of Physics NANU, 46, Nauki Avenue, Kiev, Ukraine

<sup>4</sup> Laboratoire de Métallurgie Physique, 86962 Chasseneuil-Futuroscope cedex, France

E-mail: marie-laure.david@univ-poitiers.fr

Received 6 October 2004 Published 20 May 2005 Online at stacks.iop.org/JPhysCM/17/S2255

#### Abstract

n-type Czochralski silicon was doped or co-doped in the melt with various group IV elements (Sn, C, Pb) and has been irradiated with 1 MeV electrons to a fluence of  $1 \times 10^{16}$  cm<sup>-2</sup>. The irradiation-induced electrically active defects have been studied by deep level transient spectroscopy (DLTS). It is shown that while Sn is an efficient vacancy trap, leading to the formation of SnV centres, no specific Pb-related deep levels have been found in the upper half of the bandgap. The dominant electron trap is the A centre, while similar concentrations of SnVs are formed in Sn- and Pb + Sn-doped n-Cz material. A number of as yet unidentified deep levels with smaller concentrations has also been observed, together with some grown-in peaks, whereof some could be hydrogen or carbon and lead related.

## 1. Introduction

In the field of silicon material, developments are needed to increase the quality, perfection and performance of microelectronics devices. In particular, the development of radiation hard silicon for various types of applications has received significant attention [1, 2]. Following this objective, considerable attention has recently been given to silicon doped with Sn [3, 4]. It is indeed by now well known that Ge and Sn introduce electrically active defects in irradiated silicon by forming GeV or SnV complexes at the expense of the A and the V<sub>2</sub> centres [5–7]. So, depending on the balance between the formation of electrically active defects and the reduction of the A and V<sub>2</sub> centres, a material hardening can be expected. However, it has been derived that four deep levels are associated with the VSn centre [5–7] and that Sn doping is not so effective from a material hardening viewpoint [8, 9]. In this paper, we investigate the influence

Label	[Pb] $(10^{18} \text{ cm}^{-3})$	[Sn] $(10^{17} \text{ cm}^{-3})$	[C] (10 <sup>16</sup> cm <sup>-3</sup> )	n (300  K) $(10^{15} \text{ cm}^{-3})$	Particle energy (MeV)	Fluence $(10^{16} \text{ cm}^{-2})$
Silicon2	0	0	<2	3.1	e <sup>-</sup> 1	1.1
EPb5	1–5	0	7–8	2.7	e <sup>-</sup> 1	1.1
EPb7	1–5	$\sim 2$	7–8	1.8	e <sup>-</sup> 1	1.1
Pb7	1–5	$\sim 2$	7–8	1.8	_	_
(back side of EPb7)						
ESn9	0	$\sim 2$		1.8	e <sup>-</sup> 1	1.1
Reference [3]	0	0	7–8	2.3	e <sup>-</sup> 1	1.1

 Table 1.
 Sample parameters and irradiation conditions of the n-Cz silicon doped with various amounts of group IV elements. The Pb and Sn concentrations were derived from SIMS on similar material.

of Pb, also a group IV impurity. Therefore, n-type Czochralski silicon samples have been doped in the melt with different group IV impurities (Pb + C, C, Sn, Sn + Pb + C) and have subsequently been irradiated with 1 MeV electrons. Deep level transient spectroscopy (DLTS) experiments have been carried out on these samples to identify the possible new electrically active defects and to evaluate their hardening potential.

## 2. Experiments

n-type Czochralski silicon ([P] =  $2 \times 10^{15}$  cm<sup>-3</sup>) has been doped in the melt with various group IV elements, namely Pb, Sn and C. The characteristics of each sample are summarized in table 1. The Pb and Sn concentrations ([Pb], [Sn]) were derived by secondary ion mass spectrometry (SIMS) and the carbon concentration [C] was derived from absorption measurements (16.5  $\mu$ m band). When doped with Pb, the samples have been co-doped with carbon to suppress any Pb precipitation. It is indeed believed that the strain compensation between Pb and C stabilizes the Pb atoms in lattice positions, preventing it from forming precipitates [10].

1 MeV electron irradiation with a fluence of  $1 \times 10^{16}$  cm<sup>-2</sup> has been performed at room temperature on these samples with typical size of 3 mm × 3 mm × 10 mm. In the case of electron exposures, the particles were stopped halfway through the 3 mm thick material [11, 12], so that the backside could be considered as unirradiated reference material.

Au has been deposited by thermal evaporation to form the 2 or 3 mm diameter Schottky contacts. The large area Ohmic contacts have been made by InGa eutectic and a thin foil of In on the backside of the samples. Prior to the Au evaporation, the material has been etched for 1 min in CP4, which is a mixture of acids consisting of  $C_2H_4O_2$ :HNO<sub>3</sub>:HF = 1:7:1. On a few occasions, once the sample front side was studied, the Ohmic and Schottky contacts have been removed, the samples have been etched again by a 1 min dip in CP4 and a new barrier has been formed on the back side to investigate the non-damaged reference material.

The DLTS experiments have been carried out on a DL8000 apparatus with a helium cryostat at the University of Gent using different reverse biases  $V_R$  to a pulse bias  $V_P$ , for a fixed sampling time  $t_w$  during the temperature scan. The free electron concentration n(T) has been derived from a capacitance–voltage (C-V) plot at 1 MHz at each peak temperature T and at 300 K.

## 3. Results and discussion

#### 3.1. Starting material

Figure 1(a) shows the spectra obtained on an undamaged sample co-doped with C, Pb and Sn (Pb7). As seen, at least three as-grown peaks are revealed in the low temperature part (below 100 K) of the spectra. In the literature, many studies have reported electron traps located between 0.11 and 0.16 eV below the conduction band edge ( $E_C$ ) [13, and references therein]. One of these, located at 0.15–0.16 eV below  $E_C$ , has been assigned to the CH centre [13, 14], whereas two others, located in the range 0.11–0.13 eV below  $E_C$ , have been assigned to CO complexes [13]. Later on, one of these levels was identified as the COH complex [15]. In this context, our  $E_1$  and  $E_2$  levels can be tentatively assigned to the CH and COH centres respectively, implying the presence of hydrogen in our samples. Atomic hydrogen may have been introduced either during the crystal growth as in [16–19] or during the sample preparation and more precisely during the chemical etching as is the case in [13, 20]. The third peak, associated with a very low defect concentration, is revealed in the temperature range where the VO centre is known to appear in irradiated materials [21]. It is however difficult to state its origin since this peak is an as-grown peak.

The CH centre is a nice example of the activation of neutral substitutional impurities by hydrogen in the bond-centred (BC) position between the substitutional silicon and carbon atoms [22], whereby the donor activity stems from the hydrogen donor level at  $E_{\rm C} - 0.16 \, {\rm eV}$  [23, 24]. Such a donor activity should give rise to a Poole–Frenkel shift, although some works [13, 14] found hardly any shift in electric fields below  $1 \times 10^4 \, {\rm V} \, {\rm cm}^{-1}$ . In our case, the average electric field is about  $5 \times 10^4 \, {\rm V} \, {\rm cm}^{-1}$ , and as seen in figure 1(a)  $E_1$  and  $E_2$ show a strong dependence on the electric field with a shift towards lower temperature for higher field (higher  $V_{\rm R}$ ), consistent with a Poole–Frenkel shift. It is indeed by now well established that in case of a donor-like trap (the trapped electron leaves a centre charged positively) the electron-defect interaction potential is modelled by a Coulomb attractive well. In the simplest approximation corresponding to a one-dimensional well from a singly positively charged trap, the potential energy, E(x), is given by

$$E(x) = \frac{-e^2}{\varepsilon x} - eFx \tag{1}$$

where *F* is the electric field in the space charge region,  $\varepsilon$  is the semiconductor permittivity, *e* is the elementary charge and *x* is the distance from the Schottky contact within the depletion region *W*. It lowers the potential barrier for emission from the Coulomb attractive trap by the amount  $\Delta E_m = e \sqrt{\frac{eF}{\pi \varepsilon}}$ . The activation energy for ionization is thus reduced by  $\Delta E_m$ . The emission rate  $(e_n(F))$  is now a function of the electrical field and will be much higher than with zero electrical field  $(e_n(0)):e_n(F) = e_n(0) \exp(\frac{\Delta V_m}{kT})$ .

It turns out, however, to be difficult to formally establish the donor nature of the  $E_1$  and  $E_2$  peaks, since when plotting the Arrhenius plots for  $E_1$  it appears that not only is the energy of the trap changing with the electric field but also the capture cross section (see table 2). This is not clear for the moment and complementary experiments such as filling pulse experiments are needed to understand this point.

Another interesting phenomenon is observed in figure 1(a): a negative peak is revealed around 170 K, which is rather unusual for DLTS experiments performed on a Schottky contact. However, as seen in figure 1(b), the reverse current and the reverse capacitance do not show any anomaly during the temperature scan. The presence of minority peaks has already been observed in p<sup>+</sup>n diodes under majority carrier injection but also in Schottky contacts [25–27]. By assuming the presence of minority carrier (holes) near the metal/semiconductor junction,



**Figure 1.** (a) DLTS spectra normalized by the quiescent capacitance  $C_R$  and corresponding to different reverse biases to a fixed pulse bias ( $V_P = 0$  V) and a sampling time  $t_w = 51.2$  ms, for a C + Pb + Sn doped n-type Cz sample. (b) The reverse capacitance (straight line) and current (dashed line) recorded during the temperature scan from 40 K to room temperature and corresponding to  $V_R = -1$  V.

**Table 2.** Energy position and capture cross section of the E1 level observed in the as-grown C + Sn + Pb doped sample as a function of the reverse bias.

$V_{\rm R}~({ m V})$	$E_{\rm C} - E_{\rm T}  ({\rm eV})$	$\sigma_a \ (\mathrm{cm}^2)$
-10	0.087	$3 \times 10^{-17}$
-8	0.105	$3 \times 10^{-16}$
-4	0.123	$7 \times 10^{-16}$
-1	0.141	$4 \times 10^{-15}$

it has been explained in terms of capture/emission from this tail [25, 26]. Indeed, we can assume that the barrier height is high enough to create an inversion layer in a small region located near the metal/semiconductor junction. If a minority carrier trap level in the bottom half of the bandgap is crossing the hole quasi-Fermi level in this region, the traps become filled during the bias pulse to 0 V. During the following capacitance transient, hole emission from the minority trap will be observed, giving rise to a minority carrier peak. Interestingly, this peak corresponds well with the position of a peak located at 0.33 eV above the valence band ( $E_V$ )

found in p-type Si and assigned to the acceptor level of the CH centre [20]. It is thought to result from the 'anti-bonding of carbon' configuration of hydrogen in the CH complex [20, 22]. This would confirm the presence of hydrogen in our samples and therefore the presence of the CH and COH centres.

Another possibility is that the as-grown  $E_1$  and  $E_2$  centres are related to oxygen thermal donors. These centres have two associated levels, the singly ionized oxygen thermal donor (OTD) located at  $E_{\rm C} - 0.07$  eV and observed in DLTS between 30 and 40 K if no freeze-out of the dopants occurs, and a level located at  $E_{\rm C} - 0.15$  eV, associated with the doubly ionized oxygen thermal double donor detected around 70 K [28, 29]. These OTDs have already been observed in similar materials [3]. They could have been formed during the crystal pulling as the crystal cools down slowly to room temperature and passes through the 450 °C OTD formation regime.

#### 3.2. Radiation-induced deep levels

Figure 2 shows a comparison between the backside (undamaged) of the Pb + C + Sn doped sample (Pb7) and the front side (electron irradiated) of the same sample (EPb7). As seen, electron irradiation gives rise to at least five new peaks above 80 K; three of them are dominant: the peak due to the VO centre, which most probably overlaps the  $C_sC_i$  peak, and the peaks due to the two acceptor states of the SnV complex located at about 0.31 and 0.59 eV below  $E_C$  [4]. This also follows from the three freeze-out steps observed in the capacitance in figure 2(d) and corresponding to the three deep acceptor levels.

At this point, attention has to be given to the concentrations that could be extracted from such a spectrum. As seen in figure 2(d), the concentrations of the A and VSn centres created by irradiation are so high that they induce strong compensation in the sample. The sum of the deep centre concentrations  $\sum N_{\text{Ti}}$  being no longer much smaller than the uncompensated donor density  $N_{\text{D}}^+$ , the DLTS formalism which supposes  $\sum N_{\text{Ti}} \ll N_{\text{D}}^+$  is no longer valid and the concentrations extracted from such a spectrum become inaccurate. A way to avoid this disagreement is to perform constant capacitance DLTS measurements (CCDLTS) [30], which does not show such a limitation. These measurements are currently undertaken in order to extract the correct concentration of each deep level. However, it is still possible to derive an estimation of these concentrations from CV measurement before and after the peak temperature, as will be shown in the following.

Three other peaks are revealed in figure 2(b). As expected, two of them correspond to the two charge states of the divacancy; the peak at 240 K corresponding to the emission from  $V_2^{-/0}$  may also contain a contribution from the PV centre. The third one, labelled  $E'_1$ , is located in the same temperature range as the as-grown peaks. However, as shown in figure 2(c), this peak is not located in the same temperature position as  $E_1$  or  $E_2$ . In this irradiated sample, at temperatures below 80 K, the free electron density is much smaller than at RT or for the unirradiated sample at the same temperature, due to the huge concentration of shallower acceptor levels:  $n (60 \text{ K}) = 3.2 \times 10^{14} \text{ cm}^{-3}$ ,  $n (300 \text{ K}) = 1.8 \times 10^{15} \text{ cm}^{-3}$ . From the maximum electric field, given by the relation

$$F = \frac{eN_{\rm D}^+(x-W)}{\varepsilon} \tag{2}$$

it is derived that F is smaller in the electron-irradiated sample (EPb7) than in the as-grown one (Pb7) for the same values of  $V_R$  and thus that in the case of the Poole–Frenkel shift the peak position of the as-grown level should be shifted towards higher temperature after irradiation. Since  $E'_1$  appears at lower temperature than  $E_1$  and  $E_2$ , it can be stated that  $E'_1$  is not the same centre as  $E_1$  or  $E_2$  and is probably a radiation-induced level.



**Figure 2.** DLTS spectrum corresponding to a bias pulse from  $-1 \rightarrow 0$  V and a sampling time  $t_w = 51.2$  ms, for a C + Pb + Sn doped n-type Cz sample, as grown (straight line, backside of sample) and subjected to a  $10^{16}$  cm<sup>-2</sup> 1 MeV electron irradiation (dashed line, front side of the sample); (b) an expanded view of spectrum (a) to show more clearly the peaks  $E_1$ ,  $E_2$ ,  $V_2^{-/0}$  + VP and  $V_2^{-/-/-}$ ; (c) an expanded view of spectra (a) between 40 and 90 K to show the different positions of the  $E_1$ ,  $E_2$  and  $E'_1$  peaks; (d) the C-T plot at  $V_R = -1$  V.

A rather speculative explanation for the nature of the  $E'_1$  peak is that it could be related to a PbH or SnH complex. In analogy to the case of CH (or CH and SiH in germanium [22]) the electrical activity of the PbH or SnH centre would be determined by the hydrogen donor level and should, therefore, be not much different from the CH position at  $E_{\rm C} - 0.16$  eV. According to the literature, the stability of the CH centre is charge-state dependent. In the positive charge state, the centre is stable and an activation energy of 1.3 eV is needed for the atomic jump of H leading to the dissociation of the complex [31, 32]. In the neutral charge state, the centre is unstable without any bonding, so a smaller activation energy is needed for its dissociation. This energy depends on whether the annealing is done in the dark or under illumination [32]. Illumination would provide electron-hole pairs from which electrons will be captured by the CH centre leading to its neutralization and then its dissociation; the activation energy is the smallest in this case. Thus, an annealing at 2 °C for 10 min under light is sufficient to anneal half of the CH centre whereas 50 min at 60 °C is necessary in the dark. Since irradiation is also creating electron-hole pairs by the ionization part of the 1 MeV electron energy loss, the same dissociation mechanism as the one observed under annealing with light can be assumed. The H released by this mechanism could then be trapped by Pb or Sn, leading to PbH or SnH complexes or even PbOH or SnOH complexes. If this hypothesis is true, then the peaks  $E_1$ and  $E_2$  are already present in the starting material before Schottky barrier preparation, and are, therefore, grown-in defects.



Figure 3. DLTS spectrum corresponding to a bias pulse from  $-2 \rightarrow 0$  V and a sampling time  $t_w = 51.2$  ms, for C + Pb, C-doped and undoped n-type Cz silicon samples subjected to a  $10^{16}$  cm<sup>-2</sup> 1 MeV electron irradiation; (b) an expanded view of spectra (a) to show more clearly the peaks  $E_3$ ,  $E_4$ ,  $E_5$ ,  $V_2^{-/0}$  + VP and  $V_2^{--/-}$ ; (c) the C-T plot at  $V_R = -2$  V.

At this point some insights have to be given about the possible ways to confirm our different hypothesis. First of all, in as-grown samples, it has to be checked whether the CH centre, the oxygen thermal donors or both are observed. The presence of OTDs could be checked by performing an annealing at temperatures above 500 °C. It is indeed well known that the OTDs become unstable in this range of temperature and form larger, electrically inactive aggregates by a coarsening reaction, yielding their disappearance from the DLT spectrum [29].

On the other hand, as detailed above, annealing under light/dark should resolve the problem of the CH centre [32]. Then, if the CH centre is really observed in the as-grown samples, an irradiation under reverse bias, even if difficult to realize, could give some inputs on the possible existence of the PbH or SnH complexes. Indeed, when a reverse bias is applied to the sample during annealing under light, no dissociation occurs because the electrons are swept out from the space charge region avoiding the neutralization of the CH centre. This should be the same during the irradiation, leading to the observation of the CH centres only, while no other deep levels should be formed.

Figure 3 compares the front side spectrum of the 1 MeV electron-irradiated Pb + C silicon (EPb5) with those of electron-irradiated carbon-doped [3] and undoped (Si2) samples. Four peaks are observed in all the samples: the VO +  $C_sC_i$  peak, the two divacancy charge states and a last peak labelled  $E_3$ , which is most probably also present in the Sn-doped material but hidden by the VSn<sup>-/--</sup>-related peak (unless its formation is suppressed by the Sn doping). Comparing with the Pb + Sn + C doped samples, the VSn peaks are not created, confirming

that these peaks are related to the presence of Sn in the n-Cz material. In the high temperature part of the spectra two different peaks appear depending on the group IV doping of the n-Cz silicon. In the Pb + C doped and undoped samples, a peak labelled  $E_4$  is revealed, whereas in the carbon doped samples a peak appears at higher temperature and is labelled  $E_5$ . As seen, no other electron traps than those observed in the undoped silicon have been found in the Pb + Cdoped samples, suggesting that, in contrast to Sn or Ge, Pb does not create VPb-related deep levels in the upper half of the bandgap in a sufficient concentration to be detected by our DLTS measurements. This would imply that the cross section for vacancy capture by substitutional Pb centres is much smaller than for Sn, since the group IV doping concentration is ten times higher, according to table 1.

The nature of the  $E_3$  and  $E_4$  peaks is unresolved for the moment; however, some speculations can be made about it. Quite often, a radiation defect at  $E_{\rm C} - 0.32$  eV has been reported in the literature [33-41]. In many instances, it has been assigned to the VOH centre, i.e., the A centre partially passivated by a hydrogen atom. Actually, it has been shown that there are two defects having nearly the same activation energy, the VOH centre and another unknown defect located at  $E_{\rm C} - (0.29-0.31)$  eV [38, 39]. The latter, stable up to temperatures around 300 °C, has been observed in both proton-irradiated FZ and Cz silicon. Its depth profile, close to the vacancy peak, has also been found to be narrower than the ones of VO and  $V_2$  [38]. It has thus been proposed that this defect is related to a higher-order defect of either vacancy or interstitial type, possibly decorated by some impurity. At the moment, it is not clear whether we are observing the VOH centre or not. Three further experimental facts should be mentioned in this respect: one, the trap concentration profile seems to reduce for higher depletion depths, and two, there appears to be a shift of the peak position towards lower T for higher  $V_{\rm R}$ ; see figure 4. This could indicate that we are dealing with a deep donor, although a more systematic study is necessary to confirm this idea. It should be mentioned that similar deep donors have been reported in pre-amorphized and B- or BF<sub>2</sub>-implanted silicon  $p^+$ -n junctions [42–44]. They were ascribed to the interface states of small self-interstitial clusters. Finally, the spectrum of figure 5 has been obtained by using another correlation function. As seen, another small peak is most likely revealed on the high temperature side of the  $E_3$  level.

As seen in figure 4, the  $E_4$  level does not show any shift with reverse bias. This strongly suggests that we are dealing with a deep acceptor. Most probably this peak is showing a profile (a higher defect concentration near the surface), but more accurate profiling experiments are needed to confirm this fact. A level that could correspond to the  $E_4$  level has been observed at the same time as the level attributed to the VOH centre, either in proton-implanted [36] or in electron-irradiated and chemically etched silicon [34]. In [38], its concentration has been found to increase during annealing under light as well as the concentration of a level attributed to the VOH centre. Due to the simultaneous decrease of the V<sub>2</sub> concentration, this level has been proposed to be associated with a complex involving V<sub>2</sub> and hydrogen. Moreover, the authors have shown that these transformations can occur with light illumination during the evaporation process to form the Schottky contact (optical radiation from the tungsten wire).

Based on this hypothesis, the  $E_4$  level should be observed whatever the doping. As seen in figure 3(b), the C-doped sample also shows a high temperature peak but shifted slightly compared to the one observed in the Pb + C-doped and undoped samples. Figure 4(b) shows the DLTS spectra obtained on the C-doped sample and recorded with different  $V_R$ . It shows that different peaks are observed depending on the reverse bias, suggesting that a defect is observed in the near surface region and another defect is revealed deeper in the bulk.

It should be mentioned here that the DLTS spectra are strongly influenced by the high A-centre concentration. This can give rise to significant errors not only in the energy and



**Figure 4.** Expanded view of DLTS spectra between 100 and 300 K corresponding to a different reverse bias to a fix pulse bias ( $V_P = 0 V$ ) and a sampling time  $t_w = 51.2 ms$ , for (a) a C + Pb-doped n-type Cz sample and (b) a C-doped sample subjected to a  $10^{16} cm^{-2} 1$  MeV electron irradiation.

capture cross section extracted by Arrhenius plots but also in the concentration profiles that could be obtained by performing profiling experiments without keeping the capacitance at a constant value. At this point it is difficult to firmly identify the nature of these peaks, but further investigations of the defect stability and annealing behaviour on less irradiated samples should elucidate their origin.

Finally, a few words need to be said about the concentration of the dominant electron traps created in the upper half of the bandgap. The highest concentrations are summarized in table 3 as derived by *CV* measurements at different temperatures. These preliminary results show the following trend from the viewpoint of the amount of radiation-induced electron traps: Pb + C-doped Si  $\leq$  undoped Si  $\leq$  C-doped Si < Sn-doped Si  $\approx$  Pb + Sn-doped Si. Moreover, in the C + Sn + Pb-doped sample (Epb7), the oxygen concentration ( $\approx 8 \times 10^{17}$  cm<sup>-3</sup>) is more than three times the Sn concentration. Comparing the VO and VSn centre concentration in this sample, one can derive that the capture cross section for the vacancy capture is about



**Figure 5.** DLTS spectrum corresponding to a bias pulse from  $-8 \rightarrow 0$  V and a sampling time  $t_w = 51.2$  ms of the undoped sample (silicon2) subjected to a  $10^{16}$  cm<sup>-2</sup> 1 MeV electron irradiation. This spectrum is displayed with another correlation function:  $a_{1m} = t_0 + T_W/16 + \cos(4\pi t/T_W)$ .

**Table 3.** Concentration derived from CV-measurements of the A centre and the two charge states of the VSn centre,  $VSn^{-/-}$  and  $VSn^{-/0}$ , as a function of the sample doping.

Samples (cm <sup>-3</sup> )	Silicon2	Reference [3]	EPb5	EPb7	ESn9
[VO] or [VO + CsCi]	$7 \times 10^{14}$	$9 \times 10^{14}$	$\begin{array}{c} 4\times10^{14}\\ 0\\ 0\end{array}$	$4 \times 10^{14}$	$5 \times 10^{14}$
[VSn <sup><math>-/</math></sup> ]	0	0		$6 \times 10^{14}$	$6 \times 10^{14}$
[VSn <sup><math>-/0</math></sup> ]	0	0		$5 \times 10^{14}$	$5 \times 10^{14}$

six times higher for Sn than for O. This is in agreement with the observation of Nylandsted Larsen *et al* [4].

The comparison of the VO concentration in the C-doped and undoped samples,  $7 \times 10^{14}$  cm<sup>-3</sup> in Silicon2 and  $9 \times 10^{14}$  cm<sup>-3</sup> in [3], gives an idea about the concentration,  $2 \times 10^{14}$  cm<sup>-3</sup>, of the C<sub>s</sub>C<sub>i</sub> peak, which should overlap with the VO peak in the C-doped samples. Measurements as a function of the filling pulse duration are currently being undertaken to separate the contribution of the 'slow' C<sub>s</sub>C<sub>i</sub> peak from the fast (higher electron capture cross section) VO centre.

Since the concentration of VSn centres in the Sn + C + Pb (EPb7) and the Sn-doped (ESn9) samples are similar, it can be concluded that Pb does not seems to form any VPb-related complexes in the upper half of the bandgap within the detection limit. Remarkably, the Pb + C sample (EPb5) shows the lowest VO + C<sub>s</sub>C<sub>i</sub> peak concentration. This seems to indicate that both the formation of VO and C<sub>s</sub>C<sub>i</sub> centres are suppressed in this material, compared with the silicon reference and the C-doped n-Cz silicon. The apparent absence (or reduction) of the C<sub>s</sub>C<sub>i</sub> level and the concomitant observation of peak  $E'_1$  lends some credence to the idea that it could be related to some Pb<sub>s</sub>C<sub>i</sub> centre, whereby the two decades larger Pb<sub>s</sub> centres are competing with C<sub>s</sub> for C<sub>i</sub> capture. Surprisingly, the total concentration of the dominant vacancy-related peaks is smallest for the Pb + C material, implying some hardening potential. The question arises of where the missing vacancies have gone, if not in PbV centres. It is still possible that the PbV levels occur in the bottom half of the bandgap or that PbV is an electrically inactive or an unstable complex.

Before more firmly drawing the conclusion that Pb doping may yield radiation-harder material, CCDLTS on these samples or DLTS on new uncompensated samples is needed to give more accurate trap level concentrations and profiles.

## 4. Summary

Electrically active defects have been investigated before and after 1 MeV electron irradiation on n-type silicon doped with different group IV elements. Before irradiation, the DLTS study has revealed two peaks that are ascribed either to the CH and VOH centres or OTD(D) centres. After irradiation a whole set of centres is observed. In all the samples, the A centre has been found to be the major defect created. The two acceptor levels of the divacancy have also been observed in all the samples. In the Sn + C + Pb material, the two charge states of the VSn centre have been detected in high concentration. In the undoped, Pb + C and C-doped silicon, a peak located at  $E_{\rm C} - 0.31$  eV was observed. Due to its strong profile observed in the electron-irradiated samples, this peak is thought to be associated with H, most likely injected during HF etching. Whereas the undoped and Pb + C-doped silicon show a peak at 260 K, a peak occurring at 270 K was observed in the C-doped sample. These two peaks are not yet identified. No other electron traps than those observed in the undoped silicon have been found in the Pb + C-doped samples, suggesting that, in contrast to Sn or Ge, Pb does not create VPb-related deep levels in the upper half of the bandgap in sufficient concentrations to be detected within the resolution of our DLTS set-up. Our samples being highly compensated, it is difficult to derive from the standard capacitance DLTS measurements accurate concentrations. However, preliminary results based on the free electron concentration extracted from the CV measured at each capacitance plateau show the following trend from the viewpoint of the amount of radiation-induced electron traps: Pb + C-doped Si  $\leq$  C-doped Si  $\leq$  undoped Si < Sn-doped Si  $\approx$  Pb + Sn-doped Si. Constant capacitance DLTS measurements are currently being undertaken to confirm this trend.

## Acknowledgments

M-L David is grateful to the European Union for granting her a Marie Curie post-doctoral fellowship (FP6-501343). The authors are thankful to Dr A Kuznetsov from KTH in Stockholm for performing SIMS on Pb-doped samples. Professor P Clauws and Mr J Versluys are gratefully acknowledged for use of the DLTS system at the University of Ghent and for their interest and assistance during the measurements. Partial financial support was provided by the Fonds voor Wetenschappelijk Onderzoek (FWO) under project no G.0344.03.

## References

- [1] Khan A, Yamaguchi M, Kaneiwa M, Saga T, Abe T, Annzawa O and Matsuda S 2000 J. Appl. Phys. 87 8389
- [2] Ruzin A, Casse G, Laser M, Lemeilleur F, Matheson J, Watts S and Zanet A 2000 Mater. Sci. Semicond. Process. 3 257
- [3] Simoen E, Claeys C, Neimash V B, Kraitchinskii A, Kras'ko M, Puzenko O and Clauws P 2000 Appl. Phys. Lett. 76 2838
- [4] Nylandsted Larsen A, Goubet J J, Mejholm P, Sherman Christensen J, Fanciulli M, Gunnlaugsson H P, Weyer G, Wulff Petersen J, Resende A, Kaukonen M, Jones R, Öberg S, Briddon P R, Svensson B G, Lindström J L and Dannefaer S 2000 *Phys. Rev.* B 62 4535
- [5] Brelot A 1971 IEEE Trans. Nucl. Sci. 19 220
- [6] Brelot A and Charlemagne J 1971 Radiat. Eff. 9 65
- [7] Claeys C, Simoen E, Neimash V B, Kraitchinskii A, Kras'ko M, Puzenko O, Blondeel A and Clauws P 2001 J. Electrochem. Soc. 148 G738

- [8] Simoen E, Claeys C, Privitera V, Coffa S, Nylandsted Larsen A and Clauws P 2001 Physica B 308-310 477
- [9] Simoen E, Claeys C, Privitera V, Coffa S, Kokkoris M, Kossionides E, Fanourakis G, Nylandsted Larsen A and Clauws P 2002 Nucl. Instrum. Methods Phys. Res. B 186 19
- [10] Milants K, Verheyden J, Barancira T, Deweerd W, Pattyn H, Bukshpan S, Williamson D L, Vermeiren F, Van Tendeloo G, Vlekken C, Libbrecht S and Van Haesendonck C 1997 J. Appl. Phys. 81 2148
- [11] Simoen E, Rafi J M, Claeys C, Neimash V, Kraitchinskii A, Kras'ko M, Tischenko V, Voitovych V, Versluys J and Clauws P 2003 Japan. J. Appl. Phys. 42 7184
- [12] Neimash V, Kras'ko M, Voytovych V, Tischenko V, Simoen E, Rafí J M, Claeys C, Versluys J, De Gryse O and Clauws P 2004 Phys. Status Solidi 201–203 509
- [13] Yoneta M, Kamiura Y and Hashimoto F 1991 J. Appl. Phys. 70 1295
- [14] Endrös A 1989 Phys. Rev. Lett. 63 70
- [15] Hara A, Aoki M, Fukuda T and Ohsawa A 1993 J. Appl. Phys. 74 913
- [16] Chantre A, Bouchet L and Andre E 1988 J. Electrochem. Soc. 135 2867
- [17] Hara A, Aoki M, Fukuda T and Ohsawa A 1993 J. Appl. Phys. 74 913
- [18] Hara A, Koizuka M, Aoki M, Fukuda T, Yamada-Kaneta H and Mori H 1994 Japan. J. Appl. Phys. 33 5577
- [19] Tokuda Y, Katoh I, Ohshima H and Hattori T 1994 Semicond. Sci. Technol. 9 1733
- [20] Kamiura Y, Tsutsue M, Yamashita Y and Hashimoto F 1995 J. Appl. Phys. 78 4478
- [21] Watkins G D and Corbett J W 1961 Phys. Rev. 121 1001
- [22] Maric Dj M, Meier P F and Estreicher S K 1993 Phys. Rev. B 47 3620
- [23] Holm B, Bonde Nielsen K and Bech Nielsen B 1991 Phys. Rev. Lett. 66 2360
- [24] Johnson N M, Herring C and Van de Walle C G 1994 Phys. Rev. Lett. 73 130
- [25] Meijer E, Ledebo L Å and Wang Z-G 1983 Solid State Commun. 46 255
- [26] Meijer E, Grimmeiss H G and Ledebo L Å 1984 J. Appl. Phys. 55 4266
- [27] Simoen E, Clauws P, Huylebroeck G and Vennick J 1987 Semicond. Sci. Technol. 2 507
- [28] Kimerling L C and Benton J L 1981 Appl. Phys. Lett. **39** 410
- [29] Benton J L, Kimerling L C and Stavola M 1983 Physica B 116 271
- [30] Stiévenard D, Lannoo M and Bourgoin J C 1985 Solid-State Electron. 28 485
- [31] Kamiura Y, Fukuda K, Ohyama S and Yamashita Y 2000 Japan. J. Appl. Phys. 39 1098
- [32] Kamiura Y, Hayashi M, Nishiyama Y, Ohyama S and Yamashita Y 1997 Japan. J. Appl. Phys. 36 6579
- [33] Feklisova O V and Yarykin N A 1997 Semicond. Sci. Technol. 12 742
- [34] Tokuda Y 1998 Japan. J. Appl. Phys. 37 1815
- [35] Omura Y, Hayakawa C, Suzuki T and Tajima K 1999 Japan. J. Appl. Phys. 38 4047
- [36] Tokuda Y, Shimada H and Ito A 1999 J. Appl. Phys. 86 5630
- [37] Tokuda Y and Seki T 2002 Semicond. Sci. Technol. 15 26
- [38] Lévêque P, Pellegrino P, Hallén A, Svensson B G and Privitera V 2001 Nucl. Instrum. Methods Phys. Res. B 174 297
- [39] David M-L, Oliviero E, Blanchard C and Barbot J F 2001 Nucl. Instrum. Methods Phys. Res. B 186 309
- [40] Evans-Freeman J H, Kan P Y Y and Abdelgader N 2002 J. Appl. Phys. 92 3755
- [41] Pellegrino P, Lévêque P, Lalita J, Hallén A, Jagadish C and Svensson B G 2001 Phys. Rev. B 64 195211
- [42] Brotherton S D, Gowers J P, Young N D, Clegg J B and Ayres J R 1986 J. Appl. Phys. 60 3567
- [43] Brotherton S D, Ayres J R, Clegg J B and Gowers J P 1988 J. Electron Mater. 18 173
- [44] Ayres J R, Brotherton S D, Clegg J B, Gill A and Gowers J P 1989 Semicond. Sci. Technol. 4 399