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## Formation and evolution of oxygen-vacancy clusters in lead and tin doped silicon

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Infrared spectroscopy (IR) measurements were used to investigate the effect of lead (Pb), tin (Sn), and (Pb, Sn) codoping on electron radiation-induced defects in silicon (Si). The study was mainly focused on oxygen-vacancy ( $VO_n$ ) clusters and in particular their formation and evolution upon annealing. It was determined that Pb causes a larger reduction in the production of the VO defect than Sn. In (Pb, Sn) co-doped Si isochronal anneals revealed that the evolution of VO increases substantially at  $\sim 170^\circ\text{C}$ . This is attributed to the release of V from the SnV pair. Interestingly, in the corresponding evolution curves of VO in the Sn- and the Pb-doped samples, this inverse annealing stage is also present for the former while it is not present for the latter. This is attributed to the formation of PbV pairs that do not dissociate below  $280^\circ\text{C}$ . The partial capture of V by Sn in co-doped samples is rationalized through the higher compressive local strain around Pb atoms that leads to a retardation of vacancy diffusion. The conversion of VO to the  $VO_2$  defect is substantially reduced in the Pb-doped sample. The evolution curves of VO and  $VO_2$  clusters in the isovalent doped Si samples hint the production of  $VO_2$  from other mechanisms (i.e., besides  $VO + O_i \rightarrow VO_2$ ). For larger  $VO_n$  clusters ( $n = 3, 4$ ), the signals are very weak in the Pb-doped sample, whereas for  $n \geq 5$ , they are not present in the spectra. Conversely, bands related with the  $VO_5$  and  $VO_nC_s$  defects are present in the spectra of the Sn-doped and (Pb, Sn) codoped Si. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4729573>]

### I. INTRODUCTION

Czochralski-grown Si (Cz-Si) is a mainstream material for numerous photovoltaic and microelectronic applications. The need to improve the quality of relative devices demands a comprehensive understanding of impurities and defects in Cz-Si.<sup>1–7</sup> Oxygen is the main impurity in Cz-Si and is unintentionally introduced during growth. Oxygen is accommodated initially at interstitial sites ( $O_i$ ) and is electrically inactive. Upon annealing  $O_i$  participates in a manifold of defect reactions, the products of which can affect the electrical and the optical properties of Si.<sup>8</sup> Oxygen is a major trap for V forming the VO pair (also known as A-center), which is besides the divacancy ( $V_2$ ) the most significant defect in irradiated Si. Due to its electrical activity, the A-center can act as an important recombination<sup>9</sup> center, affecting the performance of Si-based devices. Due to this behavior, the A-center was studied with numerous experimental techniques.<sup>8–15</sup> These results coupled with extensive theoretical investigations<sup>16,17</sup> led to a detailed understanding of the VO pair with its electrical and optical behavior being characterized completely. Upon thermal treatments, oxygen participates in a number of reactions, some of which lead to the formation of  $VO_n$  clusters<sup>18–20</sup> through the addition of  $O_i$  atoms in the initial VO pair. The next member of the family is the  $VO_2$  cluster formed *via* the reaction  $VO + O_i \rightarrow VO_2$ . This center has been extensively studied due to its unique properties, includ-

ing its metastability.<sup>21,22</sup> Importantly, it has been suggested<sup>23</sup> that  $VO_2$  plays a key role in oxygen precipitation processes.

The need of radiation hard Si led to various strategies for defect engineering. In particular, isovalent doping in Si has been proven very important especially for the control and manipulation of oxygen-vacancy defects and oxygen aggregation processes. For example, germanium (Ge) affects<sup>24–26</sup> the formation and the thermal stability of the VO pair and also its conversion to  $VO_2$ . Sn has been determined<sup>27–29</sup> to substantially reduce the formation of VO and its conversion to  $VO_2$  defect. Due to the larger covalent radius than that of Si, both Ge and Sn have the tendency to capture vacancies and the formation of GeV and SnV pairs has been reported.<sup>24,27</sup> Both GeV and SnV are optically inactive not giving bands in the IR spectra. At least four electrical levels are related<sup>30</sup> to the SnV pair. Pb another isovalent dopant in Si with covalent radius ( $r_{\text{Pb}} = 1.44 \text{ \AA}$ ) even larger than that of Sn ( $r_{\text{Sn}} = 1.41 \text{ \AA}$ ) is expected to form PbV pairs and affect the behavior of oxygen-vacancy defects. There is no indication<sup>31,32</sup> of any electrical levels associated with Pb-related defects in Si. More specifically, there is no indication<sup>32</sup> of any PbV related electrical levels in Si. Also, any optical signals related to the Pb presence in the Si lattice have not been reported so far, to the best of our knowledge. The Pb properties and behavior in Si are far from being complete, and the effect of its presence in the lattice on radiation-induced defects has not been fully investigated. Notably, the Pb introduction in the Si lattice is usually accompanied by the introduction of C. The reason is that Pb has a larger covalent radius than that of Si ( $r_{\text{Si}} = 1.17 \text{ \AA}$ ), whereas the covalent radius of C is smaller ( $r_{\text{C}} = 0.77 \text{ \AA}$ ). Their simultaneous introduction leads to a strain

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TABLE I. The concentrations of Sn and Pb ([Sn] and [Pb]) and the concentrations of O<sub>i</sub> and C<sub>s</sub> before irradiation ([O<sub>i</sub>]<sub>0</sub> and [C<sub>s</sub>]<sub>0</sub>). a<sub>VO</sub> and a<sub>VO<sub>2</sub></sub> are the absorption coefficients of VO and VO<sub>2</sub>, respectively, and a<sub>VO<sub>2</sub></sub>/a<sub>VO</sub> their ratio.

Sample name	[Sn] × 10 <sup>17</sup> cm <sup>-3</sup>	[Pb] × 10 <sup>17</sup> cm <sup>-3</sup>	[O <sub>i</sub> ] <sub>0</sub> × 10 <sup>17</sup> cm <sup>-3</sup>	[C <sub>s</sub> ] <sub>0</sub> × 10 <sup>17</sup> cm <sup>-3</sup>	a <sub>VO</sub> cm <sup>-1</sup>	a <sub>VO<sub>2</sub></sub> cm <sup>-1</sup>	a <sub>VO<sub>2</sub></sub> /a <sub>VO</sub>
Cz-Si:Pb		10	2.1	1.9	0.50	0.07	0.14
Cz-Si:Sn <sub>L</sub>	3		9.6	4.7	1.20	0.43	0.36
Cz-Si:Sn <sub>H</sub>	90		9.2	2	0.80	0.12	0.15
Cz-Si:SnPb	2	10	6.2	4.0	0.88	0.15	0.17

compensation stabilizing the Pb atoms at substitutional sites, thus preventing their precipitation.<sup>33–35</sup> In that respect, codoping of Cz-Si with C and Sn has been suggested<sup>36,37</sup> as a promising defect engineering strategy for improving the radiation hardness of Si. Similarly, it is interesting to investigate (C, Pb) codoped Si. Apparently, due to the ability of C to associate readily with various impurities and defects in Si,<sup>38–40</sup> its presence in the lattice should be considered when investigating radiation-induced defects.

Strain engineering is an important strategy to improve the quality of semiconductor devices.<sup>41</sup> The use of strained Si is accompanied with various challenges and its behavior is different compared to unstrained Si. For example, diffusion in strained Si is quite different<sup>5,42</sup> than that in the unstrained material. The change in diffusion of intrinsic defects and impurities affects in turn reactions between radiation defects and the aggregation processes in Si. The substitutional introduction of isovalent impurities such as Sn and Pb in Si influences<sup>43,44</sup> the aggregation processes of oxygen, as a result of the local strains introduced in the lattice. Since oxygen migration is affected by Sn,<sup>43</sup> Pb,<sup>44</sup> and C,<sup>45</sup> one expects that the formation of VO<sub>n</sub> clusters would also be affected. Interestingly, the application of high hydrostatic pressure has been determined to exhibit a significant effect on radiation defects<sup>46</sup> in Si and on oxygen aggregation.<sup>47,48</sup> In previous studies, pressure has been used to investigate and tune the properties of semiconductors.<sup>49,50</sup> The similarities and the differences in the behavior of strained Si material (or material subjected to external pressure or having local strains due to isovalent doping) is expected to enhance the understanding of the behavior of Si and improve the yield of relative devices.

The aim of this study is to investigate the impact of Sn and Pb doping in Cz-Si on radiation induced defects and especially oxygen-vacancy complexes. A more specific target is to reach to an assessment of the Sn and Pb hardening potential in the Si material, by making comparisons between the two isovalent dopants.

## II. EXPERIMENTAL METHODOLOGY

We used four groups of mechanically polished Cz-Si samples of ~2 mm thickness doped with Pb and/or Sn. In particular: (a) was Pb-doped with [Pb] = 1 × 10<sup>18</sup> cm<sup>-3</sup>, (b) Sn-doped with [Sn] = 3 × 10<sup>17</sup> cm<sup>-3</sup>, (c) Sn-doped with [Sn] = 9 × 10<sup>18</sup> cm<sup>-3</sup>, and (d) codoped with Pb and Sn with [Pb] = 1 × 10<sup>18</sup> cm<sup>-3</sup> and [Sn] = 2 × 10<sup>17</sup> cm<sup>-3</sup>. Hereafter, these samples will be labeled as Cz-Si:Pb, Cz-Si:Sn<sub>L</sub>, Cz-Si:Sn<sub>H</sub>, and Cz-Si:SnPb, respectively. The Pb and Sn concentrations were determined by secondary ion mass spectrometry (SIMS). The oxygen and carbon concentrations of

the samples are cited in Table I. The oxygen and carbon calibration coefficients were, respectively, 3.14 × 10<sup>17</sup> cm<sup>-2</sup> for the 1107 cm<sup>-1</sup> oxygen band and 1.0 × 10<sup>17</sup> cm<sup>-2</sup> for the 605 cm<sup>-1</sup> carbon band. The samples were irradiated with 2 MeV fast electrons at ~80 °C, using the Dynamitron accelerator at Takasaki-Jaeri (Japan). The irradiation fluence was 1 × 10<sup>18</sup> cm<sup>-2</sup>. After the irradiations, the samples were subjected to 20 min isochronal anneals in open furnaces in ~10 °C steps, from room temperature up to 900 °C. After each annealing step, the IR spectra were recorded with a FTIR spectrometer (Jasco-470 plus), with a resolution of 1 cm<sup>-1</sup>. The phonon contribution in the spectra was always removed by using a reference very pure float zone Si (Fz-Si) sample of equal thickness.

## III. RESULTS AND DISCUSSION

Fig. 1 presents the IR spectra of the Cz-Si:Pb (a), the Cz-Si:Sn<sub>L</sub> (b), Cz-Si:Sn<sub>H</sub> (c), and the Cz-Si:SnPb (d) samples, at a range of temperatures in the course of the isochronal anneal sequence. Well-known bands of defects as those of VO (830 cm<sup>-1</sup>), C<sub>i</sub>O<sub>i</sub> (862 cm<sup>-1</sup>), C<sub>i</sub>O<sub>i</sub>C<sub>i</sub>C<sub>s</sub> (546 cm<sup>-1</sup>), C<sub>i</sub>O<sub>i</sub>(Si<sub>i</sub>) (936, 1020 cm<sup>-1</sup>), C<sub>s</sub>O<sub>i</sub> (585, 637, 684 cm<sup>-1</sup>), C<sub>s</sub>O<sub>2i</sub> (1048 cm<sup>-1</sup>), VO<sub>2</sub> (888 cm<sup>-1</sup>), and C<sub>i</sub>O<sub>i</sub>(Si<sub>i</sub>)<sub>n</sub> (n > 1) (947, 967 cm<sup>-1</sup>) appear in the IR spectra of the samples (Ref. 29 and references therein). Additionally, above 400 °C bands from the VO<sub>3</sub> (904, 968, 1000 cm<sup>-1</sup>),<sup>18,19</sup> VO<sub>4</sub> (985, 1010 cm<sup>-1</sup>),<sup>18,19</sup> VO<sub>5</sub> (1037, 1051 cm<sup>-1</sup>),<sup>51,52</sup> as well as the VO<sub>n</sub>C<sub>s</sub> (967, 1005 cm<sup>-1</sup>) (Ref. 52) clusters are present. Interestingly, bands from the latter two clusters do not appear in the spectra of the Pb-doped Si samples. Even the bands from the VO<sub>3</sub> and VO<sub>4</sub> defects are very weak. In particular, from the three bands of the VO<sub>3</sub> cluster only that of 904 cm<sup>-1</sup> is clearly observed, whereas only traces from the other two are present. Similarly, from the two bands of VO<sub>4</sub> cluster only the 985 cm<sup>-1</sup> is clearly detected. The band at 762 cm<sup>-1</sup> belongs to the VO<sub>n</sub>C<sub>s</sub> family.

Fig. 2 presents the evolution of the VO, VO<sub>2</sub>, and VO<sub>3</sub> clusters in the Cz-Si:Pb (a), the Cz-Si:Sn<sub>L</sub> (b), the Cz-Si:Sn<sub>H</sub> (c), and the Cz-Si:SnPb (d) samples. Notably, the 904 cm<sup>-1</sup> band of VO<sub>3</sub> in Pb-doped sample is very weak to be depicted properly in Fig. 2(a) and it is, therefore, omitted. Fig. 3 presents the evolution of the VO<sub>3</sub>, VO<sub>4</sub>, VO<sub>5</sub>, and VO<sub>n</sub>C<sub>s</sub> clusters in the Cz-Si:Sn<sub>L</sub>(a), the Cz-Si:Sn<sub>H</sub>(b), and the Cz-Si:SnPb (c) samples. The evolution of the VO<sub>3</sub> cluster is depicted both in Figs. 2 and 3 in order to appreciate the relative amplitudes of the various VO<sub>n</sub> clusters.

In the Cz-Si:Sn<sub>H</sub> sample, SnV pairs are formed at the expense of VO centres and analogously one may consider the formation of PbV pairs. Since r<sub>Pb</sub> > r<sub>Sn</sub> a larger number

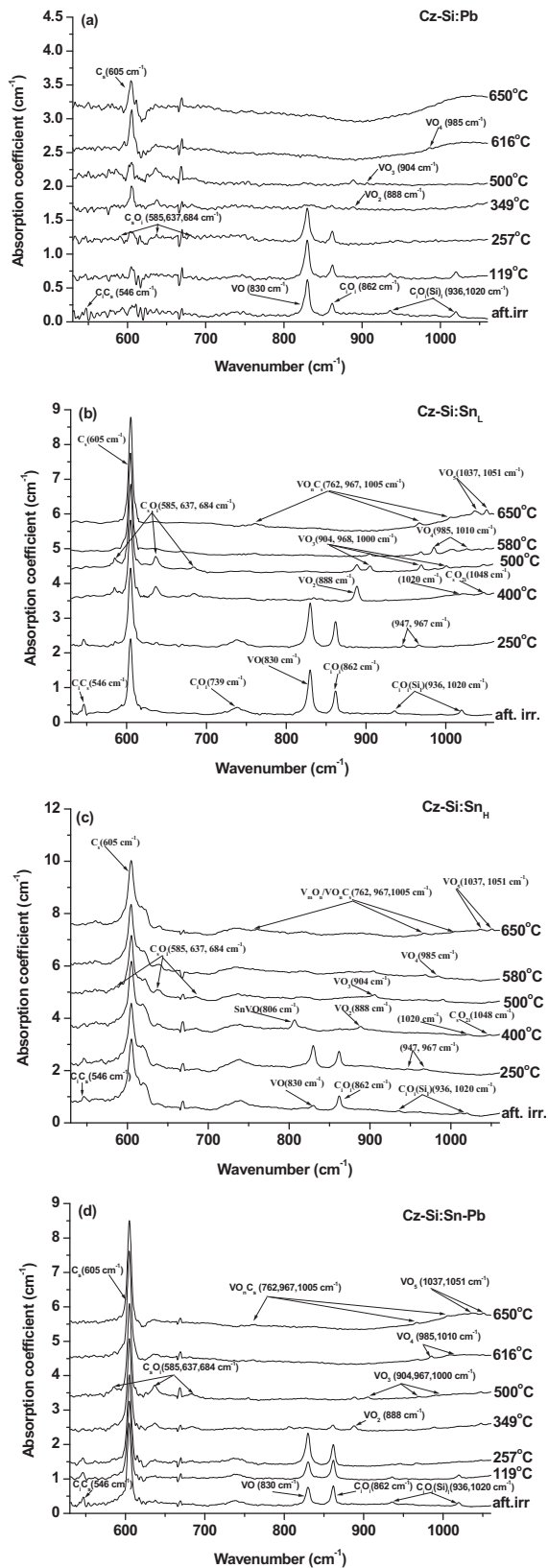


FIG. 1. Segments of the IR spectra of the (a) Cz-Si:Pb, (b) Cz-Si:Sn<sub>L</sub>, (c) Cz-Si:Sn<sub>H</sub>, and (d) Cz-Si:SnPb (d) samples, at characteristic temperatures of the isochronal anneals sequence.

of vacancies are expected to be trapped by Pb than by Sn (i.e., to relieve the local strains induced by the introduction of the larger isovalent dopant) and therefore less VO centres would form in the Pb-doped Si, in agreement with the

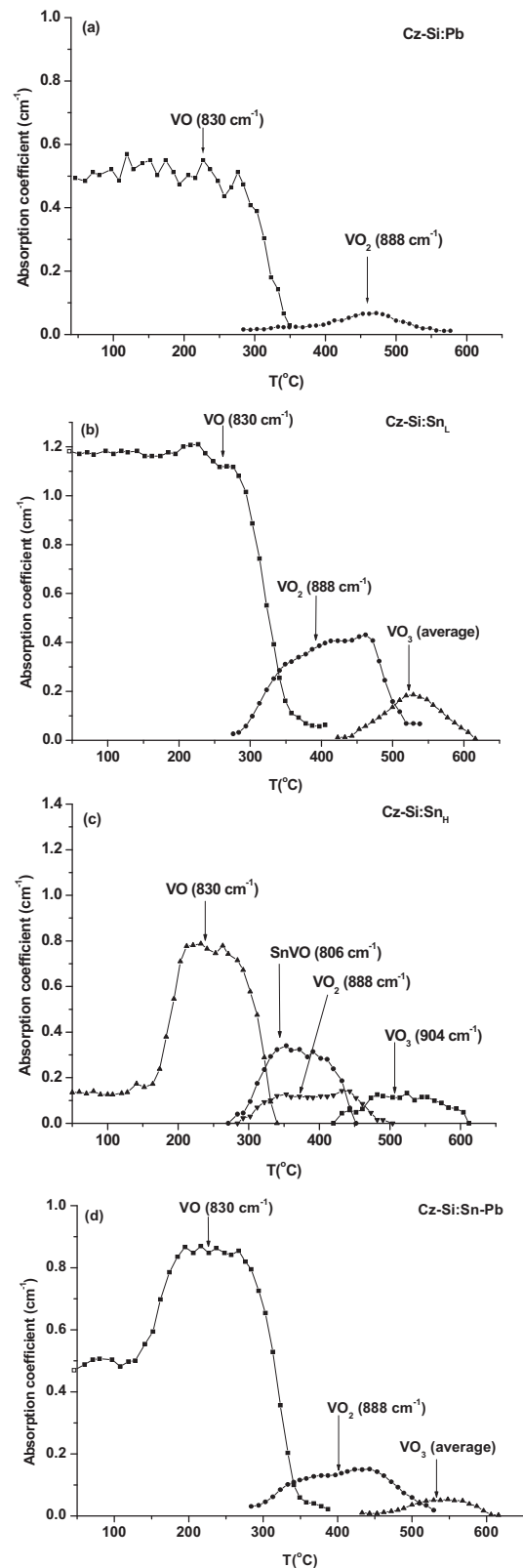


FIG. 2. The evolution with temperature of the VO, VO<sub>2</sub>, and the VO<sub>3</sub> IR related bands of the (a) Cz-Si:Pb, (b) Cz-Si:Sn<sub>L</sub>, (c) Cz-Si:Sn<sub>H</sub>, and (d) Cz-Si:SnPb samples. The complete figure with all the contributions to the absorption coefficient for VO<sub>3</sub> (denoted here “average”) is given in Ref. 58.

observations of Figs. 2(a) and 2(b). Although, there are strong indications about the existence of the SnV pairs,<sup>36,53,54</sup> there are no experimental indications<sup>32</sup> for the existence of PbV pairs. From a theoretical perspective, previous density

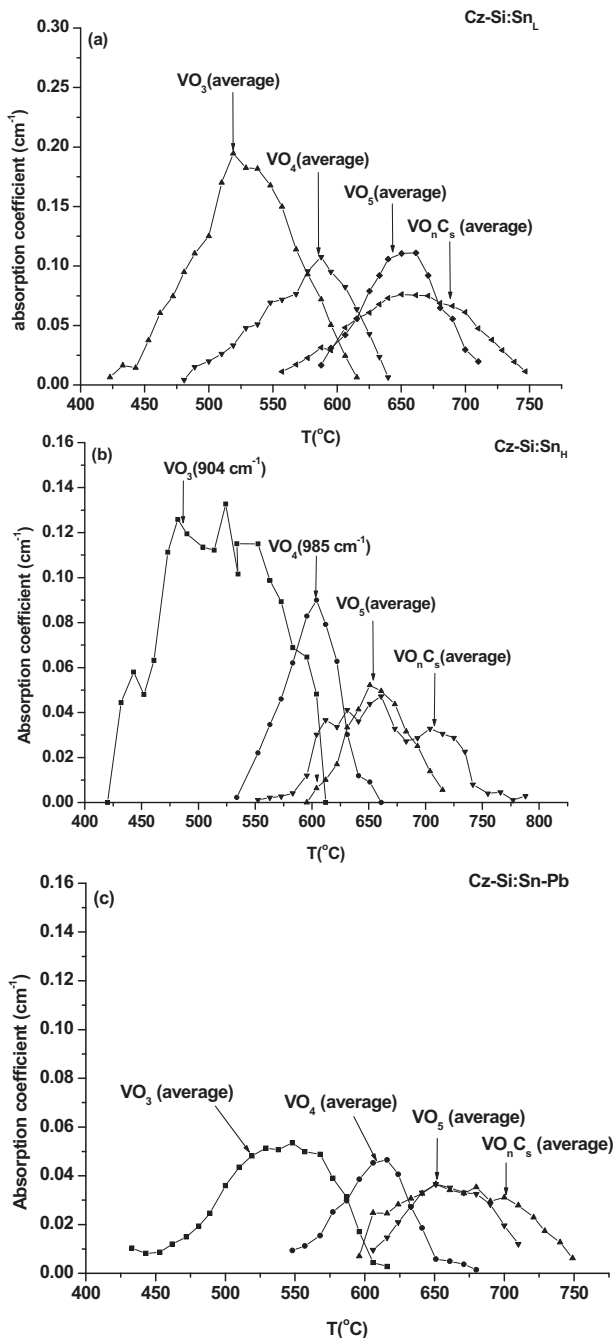


FIG. 3. The evolution with temperature of the  $VO_3$ ,  $VO_4$ ,  $VO_5$ , and  $VO_nC_s$  IR related bands of the (a) Cz-Si:Sn<sub>L</sub>, (b) Cz-Si:Sn<sub>H</sub>, and (c) Cz-Si:SnPb samples. The complete figure with all the contributions to the absorption coefficients for all clusters (denoted here “average”) is given in Ref. 58.

functional theory calculations revealed that the PbV pair is strongly bound.<sup>55</sup> In fact its binding energy (energy of pair minus isolated defects) is found to be more negative ( $-1.37$  eV) compared to the SnV pair ( $-1.17$  eV) but still less negative compared to the A-center ( $-1.53$  eV).<sup>55</sup> These binding energies strongly indicate the stability and thus the existence of PbV pairs. These pairs should also be more stable than the corresponding SnV pairs.

In Figure 2, we observe that the production of the VO defect after irradiation is substantially reduced in the Cz-Si:Pb sample (Fig. 2(a)) in comparison with Cz-Si:Sn<sub>L</sub> sample (Fig. 2(b)). Moreover, the reduction is lower than the one observed

in the Cz-Si:Sn<sub>H</sub> sample (Fig. 2(c), considering the [VO] at 250 °C). Following our previous analysis on Sn doped samples,<sup>55</sup> this reduction is attributed to the oversized-dopant-induced recombination of Frenkel pairs during irradiation. Notably, the Pb concentration in Cz-Si:Pb sample is 3 times bigger than the Sn concentration in Cz-Si:Sn<sub>L</sub> and almost one order of magnitude smaller than in Cz-Si:Sn<sub>H</sub>. Interestingly, the same Pb concentration in Cz-Si:Pb and Cz-Si:SnPb lead to the same reduction of VO after irradiation also in line with the oversized-dopant-induced recombination mechanism.

At this point, it is reasonable to focus on the thermal evolution of VO defect and especially on the presence of an inverse annealing stage in the VO defect at  $\sim 170$  °C in the (Pb, Sn)-doped Si sample (Cz-Si:SnPb), although this stage is absent in both the Pb and the Sn<sub>L</sub> doped samples. Interestingly, the inverse annealing stage also appears in the case of the Sn<sub>H</sub> sample.<sup>29</sup> In the Sn<sub>H</sub> sample, this stage is attributed to the release of V through the dissociation of the SnV pair leading to an increase of the VO concentration at a threshold temperature labeled  $T_{za}$  in Ref. 55.

The absence of an inverse annealing stage in the Cz-Si:Pb sample can be rationalized, in the view of the DFT results, by an increase of  $T_{za}$  above the  $T_{ab}$  temperature<sup>55</sup> where the VO signal starts to vanish (280 °C). However, it is notable that for almost the same Sn concentration, the inverse annealing stage is present in Cz-Si:SnPb and not present in the Cz-Si:Sn<sub>L</sub> sample. This is puzzling as the Pb concentration in the Cz-Si:Pb sample and in the Cz-Si:SnPb sample are the same.

This apparent discrepancy only underlines the limitation of our previous analysis<sup>55</sup> only based on thermodynamics arguments (binding energy). Indeed starting from isolated dopants and vacancies, to reach the 2NN position, a vacancy first needs to diffuse in the lattice around the corresponding impurity. Here, the diffusion barrier should be similar to that in pure silicon. However, the strain field induced by the neighbouring impurity will always retard the diffusion. In particular, the diffusion can be either retarded or enhanced depending on the type (tensile or compressive) of an externally applied strain.<sup>5</sup> More interestingly, the higher the compressive strain, the higher the diffusion barrier (see Fig. 17 of Ref. 56). In the case of oversized-dopant, the surrounding lattice is compressively strained and obviously more strained around Pb atoms than around Sn atoms. This effect should then favour the diffusion of V in the direction of Sn atoms rather than in the direction of Pb atoms when both atoms compete as V traps. The relative concentration of each trap is also important. In the Cz-Si:SnPb sample, the Pb concentration is 5 times higher than the Sn concentration. Thus preferred formation of SnV as compared to PbV will be only partial. The observed reverse annealing stage in Cz-Si:SnPb would then correspond to a distribution (such as 10% of Sn atoms are close enough to Pb) favouring the formation of SnV as opposed to PbV.

The lower production of VO pairs in Pb-doped Si and the absence of any increase of [VO] upon annealing clearly indicates a potential of radiation hardening of Si, at least regarding vacancy-oxygen defects. This is further supported by the fact that no Pb-related electrical levels have been

reported in Pb-doped Si. Conversely, for Sn-doped Si, the SnV pairs are electrically active.<sup>30</sup>

Regarding the conversion of the VO to the VO<sub>2</sub> defect, it is observed that the ratio  $a_{VO_2}/a_{VO}$  is substantially reduced in the Cz-Si:Pb sample than in the Cz-Si:Sn<sub>L</sub> sample [compare Figs. 2(a) and 2(b)]. The main reactions participating in the disappearance of the VO defect are  $VO + O_i \rightarrow VO_2$  (1) and  $VO + Si_i \rightarrow O_i$  (2). In a previous work,<sup>52</sup> the influence of Ge on the VO to the VO<sub>2</sub> conversion in Ge-doped Si was discussed. The reduction of the corresponding ratio in the Cz-Si:Ge sample in comparison with Ge free material was attributed to the local strains induced in the Si lattice by the presence of the larger Ge atoms. It was argued that these strains have a profound effect on the balance between the above two reactions of VO. The presence of Ge can facilitate the release of self-interstitials, which increase the contribution of reaction (2) over reaction (1), thus resulting in a reduction of the VO<sub>2</sub> defects. A similar argument could be put forward here, and since Pb has a larger covalent radius than that of Sn, one expects a larger reduction in the Pb samples than the Sn samples, in agreement with our results. Note that in the case of the Cz-Si:Sn<sub>H</sub> sample, the ratio  $a_{VO_2}/a_{VO}$  is largely reduced in comparison to that of the Cz-Si:Sn<sub>L</sub> sample. However, in the Cz-Si:Sn<sub>H</sub> sample many VO pairs (upon annealing) are trapped by Sn atoms to form SnVO clusters.

By inspection of Fig. 2 and in particular Fig. 2(a), it is immediately observed that the VO<sub>2</sub> cluster continues to grow in the spectra even after the disappearance of VO pair. This implies the existence of another mechanism operating in parallel with the usual ( $VO + O_i \rightarrow VO_2$ ) for the VO<sub>2</sub> formation. Similar observations have been made previously<sup>57</sup> in Ge-doped Si where we suggested that oxygen dimmers, divacancies, and self-interstitials are possibly involved in an alternative reaction scheme leading to the VO<sub>2</sub> formation.

Importantly, the VO<sub>2</sub> clusters formed are quite low in concentration in the Pb-doped Si sample. Consequently, the next members of the VO<sub>n</sub> family that is the VO<sub>3</sub> and the VO<sub>4</sub> clusters have very weak signals and only traces of some of the related bands could be seen (Fig. 1(a)), and therefore, their evolution could not be depicted (Fig. 2(a)). Traces from other members of the VO<sub>n</sub> with  $n > 4$  are not detected in the spectra of the Cz-Si:Pb sample. For the case of the Cz-Si:(Pb, Sn) sample, where the inverse annealing stage leads to a larger concentration of VO pairs, resulting to a larger concentration of VO<sub>2</sub> clusters. Thus, signals from the VO<sub>n</sub> clusters with  $n = 5$  are clearly detected in the spectra (Fig. 1(d)), and their evolution is depicted (Fig. 3(c)). Two bands at 1037 and 1051 cm<sup>-1</sup> and another two bands at 967 and 1005 cm<sup>-1</sup> have been previously attributed<sup>52</sup> to the VO<sub>5</sub> and VO<sub>n</sub>C<sub>s</sub> structures, respectively. In our case, both in the Sn-doped (Sn<sub>L</sub>, Sn<sub>H</sub>) and the (Sn, Pb) codoped Si material, another band at 762 cm<sup>-1</sup> showing the same annealing behavior with that of the 967 and 1005 cm<sup>-1</sup> bands is tentatively attributed to the VO<sub>n</sub>C<sub>s</sub> cluster as well.

#### IV. CONCLUSIONS

Using IR spectroscopy, we present a systematic study of the effect of the Sn and Pb doping, as well as the (Sn, Pb)

codoping on the production and evolution of the VO<sub>n</sub> ( $n \leq 5$ ) defects in Cz-Si. The main aim was to make an assessment on the hardening potential of both isovalent impurities regarding oxygen-vacancy clusters in Si. First, it is determined that the production of the VO pair is smaller in the Pb than in the Sn-doped Si. The phenomenon was attributed to the larger tendency of Pb in comparison with Sn to pair with V at the expense of VO centers and form PbV and SnV pairs, respectively. The PbV pairs are more stable as they do not dissociate below 280 °C while SnV pairs dissociate at 170 °C. The partial capture of vacancies by Sn in co-doped samples is rationalized through the higher compressive strain around Pb atoms that leads to a retardation of vacancy diffusion. The presence of PbV pairs cannot be experimentally confirmed. Second, we discussed the absence of an inverse annealing stage in the evolution of VO pair around 170 °C in the Sn<sub>L</sub> and Pb-doped Si, although the stage is present in the Pb,Sn-doped Si. The SnV pairs, upon dissociation at 170 °C release vacancies leading to the increase of the VO. The lower production of VO in the Cz-Si:Pb sample clearly indicates the perspectives of Si radiation hardening by Pb doping. Third, the evolution curves of VO and VO<sub>2</sub> clusters clearly demonstrate the existence of additional mechanisms involved in the formation of the VO<sub>2</sub> cluster besides  $VO + O_i \rightarrow VO_2$ . Finally, we verified the detection of two bands at 1037 and 1051 cm<sup>-1</sup> of the VO<sub>5</sub> defect, as well as of three bands at 762, 967, and 1005 cm<sup>-1</sup> attributed to VO<sub>n</sub>C<sub>s</sub> clusters. The results provide a promising perspective regarding radiation hardening by Sn, Pb, and (Sn,Pb) codoping of Si and motivate the study of Sn containing group IV alloys.<sup>59</sup>

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