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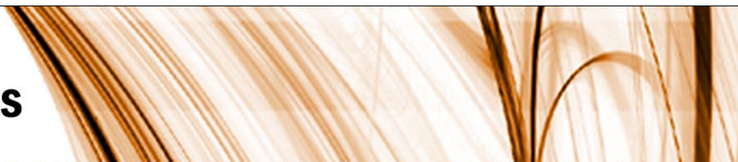

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Impact of isovalent doping on radiation defects in silicon

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Isovalent doping is an important process for the control of point defects in Si. Here, by means of infrared spectroscopy, we investigated the properties of the two main radiation-induced defects in Czochralski-Si (Cz-Si) the oxygen-vacancy (VO) and the carbon-oxygen (C_iO_i) centres. In particular, we investigated the effect of isovalent doping on the production, the thermal evolution, and the thermal stability of the VO and the C_iO_i defects. Additionally, we studied the reactions that participate upon annealing and the defects formed as a result of these reactions. Upon annealing VO is converted to VO_2 defect although part of the C_iO_i is converted to C_sO_{2i} complexes. Thus, we studied the conversion ratios $[VO_2]/[VO]$ and $[C_sO_{2i}]/[C_iO_i]$ with respect to the isovalent dopant. Additionally, the role of carbon in the above processes was discussed. A delay between the temperature characterizing the onset of the VO decay and the temperature characterizing the VO_2 growth as well the further growth of VO_2 after the complete disappearance of VO indicate that the VO to VO_2 conversion is a complex phenomenon with many reaction processes involved. Differences exhibited between the effects of the various dopants on the properties of the two defects were highlighted. The results are discussed in view of density functional theory calculations involving the interaction of isovalent dopants with intrinsic defects, the oxygen and carbon impurities in Si. © 2013 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4821116]

I. INTRODUCTION

There are many reasons for studying radiation defects in semiconductors: First, the need for manufacturing devices with certain characteristics for instance fast response devices, such as Si diodes and transistors. In these, the decrease of the lifetime of non-equilibrium charge carriers requires the introduction of defects on purpose and under control with electron irradiation, implantation, and other techniques; Second, the need for devices to operate under special conditions. Due to the operational environment of semiconductor devices, when used for example for docimetry, particle detection, aerospace applications, and nuclear medicine, the material is exposed to charged particles. In these cases, the introduction of defects can cause changes in the electrical and optical parameters of the material leading to deterioration of the yield and the quality of the corresponding devices. Third, various defects formed in the course of material growth and processing can be introduced by irradiation in a controllable way. This allows their investigation under laboratory conditions with many experimental techniques. A fourth reason is related with the vacancies and self-interstitials, which are the primary radiation defects in any semiconductor. The two defects play an important role in silicon both in processes related with material growth but with device manufacturing as well. They interact promptly with other impurities and defects in the course of irradiation and therefore by studying radiation defects crucial details regarding their properties and behaviour can be obtained.

Czochralski-Si as a result of the growth procedure incorporates oxygen and carbon impurities in the crystal lattice. Oxygen is positioned at interstitial sites (O_i) and carbon at substitutional sites (C_s). Upon irradiation, the two main defects formed are the vacancy-oxygen pair, the well-known A-center (VO) and the carbon-oxygen center (C_iO_i). The first is formed directly in the course of irradiation through the capture of mobile vacancies by oxygen intertitial atoms ($V + O_i \rightarrow VO$). The second is formed indirectly through the conversion of substitutional carbon atoms to carbon interstitials by the capture of self-interstitials ($C_s + Si_I \rightarrow C_i$). The C_i's are mobile at room temperature and can be subsequently trapped by oxygen atoms in Cz-Si ($C_i + O_i \rightarrow C_iO_i$). Another potential trap for the migrating C_i atoms is C_s leading to the formation of the C_iC_s pair. In the case of Cz-Si with the oxygen content about one order of magnitude larger than that of carbon the main carbon-related defect formed is the C_iO_i. VO and the C_iO_i defects have been previously studied and a more or less complete picture has been established for the formation mechanism, their structure, properties, and behaviour.[1–8] Importantly, both defects introduce intermediate states inside the forbidden energy gap. As a result, they act as recombination centers having adverse effects on the performance of the Si-based devices.[9,10]

Isovalent doping is an important strategy to control the properties of defects in Si. Previous reports demonstrate the potential of Ge, Sn, and Pb isovalent dopants to enhance

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the radiation tolerance of Si.[11–20] In the present study, we systematically investigate the effect of isovalent doping on the production of the VO and the C_iO_i defects and their evolution with temperature. In particular, we compare the influence of each dopant (Ge, Sn, Pb) on the production and thermal stability of VO and C_iO_i defects discussing the observed differences.

II. METHOD

A. Experimental methodology

A large number of pre-polished Cz-Si samples doped with Ge, Sn, and Pb were used. Their isovalent dopant concentrations given by the supplier are reported in Table I. Their oxygen and carbon content are also cited, as well as the concentrations of the VO and C_iO_i defects. The calibration coefficients used were $3.14 \times 10^{17}\,\mathrm{cm}^{-2}$ for the $1107\,\mathrm{cm}^{-1}$ band of oxygen, $1.0 \times 10^{17}\,\mathrm{cm}^{-2}$ for the $605\,\mathrm{cm}^{-1}$ band of carbon, $6.25 \times 10^{16}\,\mathrm{cm}^{-2}$ for the $830\,\mathrm{cm}^{-1}$ band of VO, and $1.1 \times 10^{17}\,\mathrm{cm}^{-2}$ for the $862\,\mathrm{cm}^{-1}$ band of C_iO_i. The samples were irradiated with 2 MeV electrons using the Dynamitron accelerator at Takasaki-JAERI (Japan). The irradiation dose was $1 \times 10^{18}\,\mathrm{cm}^{-2}$. One additional sample irradiated with $5 \times 10^{17}\,\mathrm{cm}^{-2}$ was used to facilitate comparisons. After the irradiation, all the samples were subjected to a sequence of isochronal anneals up to 600 °C, in steps of $\Delta T \approx 10\,°C$ with 20 min duration. After each annealing step, the infrared (IR) spectra were recorded at room temperature by means of a Fourier Transform IR (FTIR) spectrometer (JASCO-470 plus) with a resolution of $1\,\mathrm{cm}^{-1}$. The two phonon intrinsic absorption was always subtracted by using a float-zone Si sample of equal thickness.

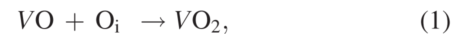
B. Theoretical methodology

The BigDFT[21] code was used to perform DFT calculations within the Generalized Gradient Approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional.[22] This code is using a wavelet basis-set and is very attractive for dealing with complex and inhomogeneous systems due to the adaptivity of the basis-set. Moreover, the basis-set has high convergence properties and the code can run on massively parallel or hybrid architectures.[21,23] A cubic supercell of 216 atoms was used to construct the defected structures with periodic boundary conditions (PBCs). The calculation parameters were chosen in accordance to those reported previously since they have proven to give converged results for vacancy diffusion in similar Si supercells.[24] Core electrons were treated within the norm-conserving pseudo-potential approximation using the *Hartwigsen-Goedeker-Hutter* family.[25] The wavelet basis-set accuracy in PBC is given by the grid step size, which has been chosen to be 0.4423 Bohr in the three space directions. This value provides variations in formation energies of oxygen related defects in silicon within 20 meV, while the oxygen pseudopotential is harder than all other dopants we introduced (C, Si, Ge, and Pb). Finally, Γ-point alone was used for Brillouin zone integration since the size of the supercell ensures enough convergence for formation and migration energies of defects in Si.[26] For this work, we have calculated the binding energies of the defects of interest as $E_b = E_A + E_B - E_{A+B}$ with E_A and E_B being the formation energy of the former isolated defects A and B, E_{A+B} the energy of defect complex. Energies already present in references have also been recalculated here for consistency and comparison of obtained results.

III. RESULTS AND DISCUSSION

Figure 1 presents segments of the IR spectra of some representative samples among those used in this work, as Ge_H (a), Sn_H (b), and SnPb (c), after irradiation to show the VO ($830\,\mathrm{cm}^{-1}$), the C_iO_i ($862\,\mathrm{cm}^{-1}$) and at 400 °C in the course of the isochronal anneals sequence the VO_2 ($888\,\mathrm{cm}^{-1}$) and the C_sO_{2i} bands. The bands at 936 and $1020\,\mathrm{cm}^{-1}$ originate from the $C_iO_iSi_I$ complex. Notably, a band at $806\,\mathrm{cm}^{-1}$ related with the SnVO complex[17,27] is also shown in Fig. 1(b), regarding a sample with high Sn content sample Sn_H (see Table I). Notably, the latter defect does not appear in the spectra of the low Sn content sample Sn_L, an indication that when [Sn] is substantially lower than $[O_i]$ the percentage of VO pairs trapped by Sn is negligible. In this context, the Sn_L sample will be further considered as a Cz-Si sample with a very high carbon concentration (see Table I).

Figure 2 presents the thermal evolution of the VO defect as well as that of the VO_2 defect, for representative samples selected from Table I. The annealing of VO defect is governed mainly by the reactions



$$VO + O_i \rightarrow VO_2, \quad (1)$$

$$VO + Si_I \rightarrow O_i. \quad (2)$$

The first reaction leads to the formation of the VO_2 defect. The binding energy of the VO_2 complex is calculated to be

TABLE I. Information on the samples used in this work. a_{CsO2i}/a_{CiOi} is the ratio of the absorption coefficients of the C_sO_{2i} and C_iO_i defects.

Sample	Dopant (cm^{-3})	$[C_s]_o$ 10^{16} (cm^{-3})	$[O_i]_o$ 10^{17} (cm^{-3})	Fluence (e cm^2)	[VO] 10^{16} (cm^{-3})	$[VO_2]/[VO]$	$[C_iO_i]$ 10^{16} (cm^{-3})	a_{CsO2i}/a_{CiOi}
Cz-Si		<1	9.6	5×10^{17}	2.3	0.46		
Cz-Si:C_L		5	9.5	1×10^{18}	5.9	0.22	2.9	0.11
Cz-Si:C_H		22	9.3	1×10^{18}	6.1	0.2	5.6	0.10
Cz-Si:Ge_L	4×10^{18}	4.4	5.2	1×10^{18}	4.9	0.11	2.9	0.15
Cz-Si:Ge_H	2×10^{20}	8.6	6.5	1×10^{18}	6.6	0.12	4.2	0.13
Cz-Si:Sn_L	3×10^{17}	47	9.6	1×10^{18}	7.4	0.18	6.9	0.09
Cz-Si:Sn_H	9×10^{18}	20	9.2	1×10^{18}	4.9	0.08	5.8	0.08
Cz-Si:SnPb	2×10^{17}, 1×10^{18}	40	6.2	1×10^{18}	5.3	0.09	5.7	0.10
Cz-Si:Pb	1×10^{18}	19	2.1	1×10^{18}	3.3	0.07	2	0.11

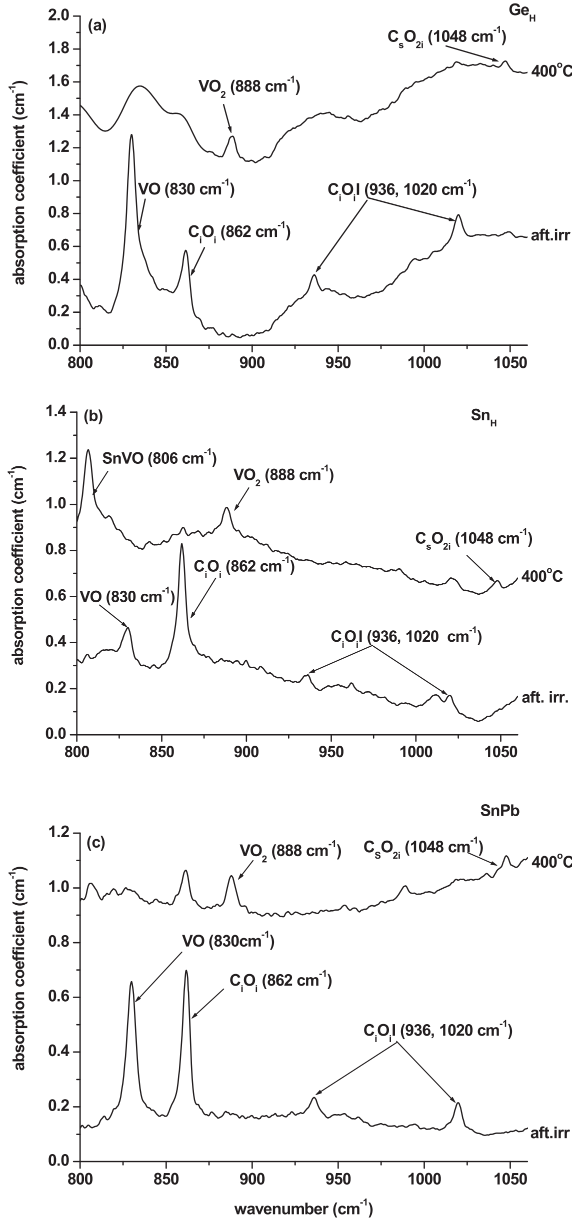
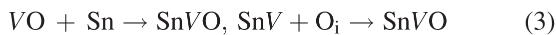


FIG. 1. Fragments of the IR spectra for the samples Ge_H (a), Sn_H (b), and SnPb (c).

2.71 eV. This value is higher by near 1.2 eV compared to the binding energy of VO (1.53 eV).[11] Therefore, it is possible to convert easily the VO to VO_2. However, such transformation is constrained by the migration energies of VO as well as by the associated reactions in the case of isovalent doped silicon. Additionally, the evolution of the 806 cm^{-1} of the SnVO complex, formed by the reactions



$$VO + \mathrm{Sn} \rightarrow \mathrm{Sn}VO,\ \mathrm{Sn}V + \mathrm{O_i} \rightarrow \mathrm{Sn}VO \tag{3}$$

is also shown in Fig. 2.

Figure 3 shows the production of the VO defect as a function of the dopant covalent radius. For the case of the SnPb codoped sample, the average value of the covalent radius of the two corresponding dopants was taken as the covalent radius of the codoped sample. It is observed that Ge enhances VO production, although Sn and Pb reduce it. In the latter case, the tendency of Sn and Pb to compete with O in capturing vacancies to form SnV and PbV pairs[17] has led to a reduction of the VO pairs. In the former case, there is also a competition between Ge and O in capturing vacancies but at room temperature irradiation the formed GeV pairs are thermally unstable leading to the liberation of the trapped vacancies. The higher propensity of the larger dopants to attract V in Si is reflected on the binding energy of the pairs that have been previously calculated using DFT.[11] The physical reason is the relaxation of the oversized dopant atoms in the vacant space. This effect is also important for other group IV compounds and alloys, such as Ge or $Si_{1-x}Ge_x$ alloys. Moreover, due to the temporal trapping of vacancies by Ge, the annihilation ratio with self-interstitials decreases. Thus, in the case of Ge, the availability of vacancies increases substantially leading to an enhanced production[15] of VO pairs, quite larger than that in the samples without isovalent dopant.

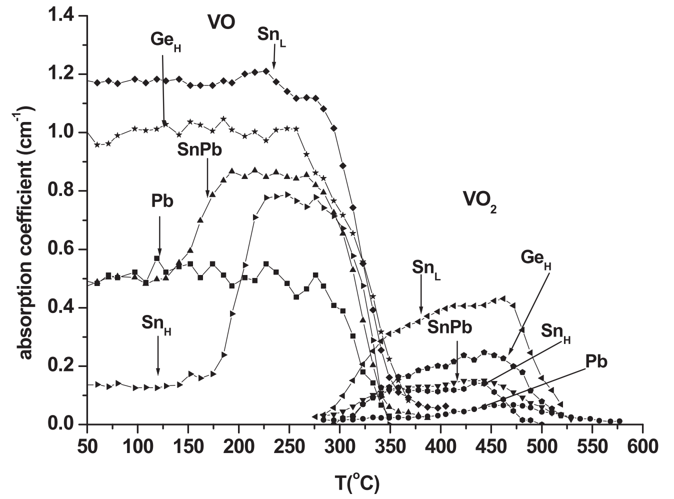


FIG. 2. The evolution with temperature of the VO and VO_2 defects for various representative samples from the list of Table I.

Of course one should take into account the differences in the carbon concentration among the samples. It is generally expected that carbon has an enhancing effect[28,29] in the VO production. In the course of irradiation, the vacancies that escape dissociation with self-interstitials react with

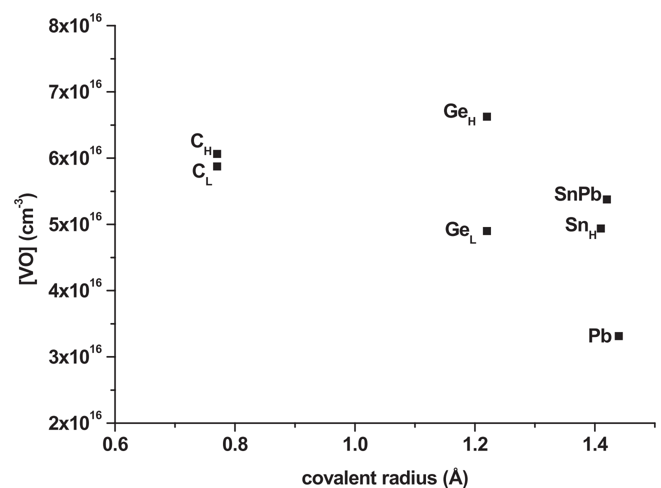


FIG. 3. The production of the VO defect as a function of the covalent radius of the isovalent dopants.

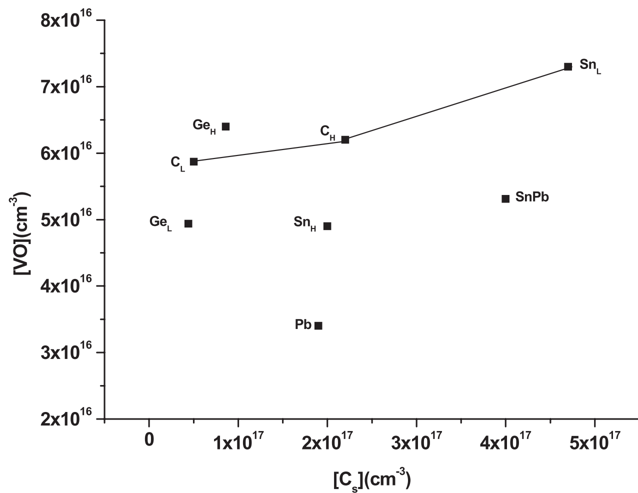


FIG. 4. The production of the VO defect as a function of the carbon concentration of the various isovalent dopants.

oxygen to produce VO pairs. Reasonably, some of the produced VOs are simultaneously destroyed by self-interstitials. Apparently, in the presence of carbon, which readily traps self-interstitials[2], the second process is largely suppressed. This leads to an enhancement of the VO production. In this respect, it is important to study the impact of carbon on the VO production. Figure 4 shows that VO is an increasing function with the carbon content (compare samples C_L, C_H, and Sn_L). Nevertheless, for samples with about the same concentration of carbon, the production of VO is reduced when larger isovalent dopants are present in the lattice (compare samples C_H, Sn_H, and Pb) in accordance with the aforementioned argumentation in relation with the effect of the isovalent dopant. In essence, Fig. 4 shows on one hand the enhancing effect of C in the production of VO; and on the other hand, the reducing effect of isovalent dopants, in particular Sn and Pb in the VO production. The latter case becomes clear by comparing samples as C_H, Sn_H, and Pb, with about the same amount of carbon.

Figure 5 displays the ratio $[VO_2]/[VO]$ versus the covalent radius of the isovalent dopants for various representative samples from Table I. Obviously, the larger the covalent radius, the smaller the percentage of VO defects converted to VO_2 defects. We have argued previously[30] that this is a manifestation of the effect of internal strains introduced in the Si lattice due to the presence of the larger isovalent dopants. In this case, reaction $VO + Si_I \rightarrow O_i$ is enhanced, due to the increased availability of self-interstitials. As a result, the balance between the reactions $VO + O_i \rightarrow VO_2$, $VO + Si_I \rightarrow O_i$ is shifted towards the second one, and this is revealed in the spectra by the reduction of the VO production.

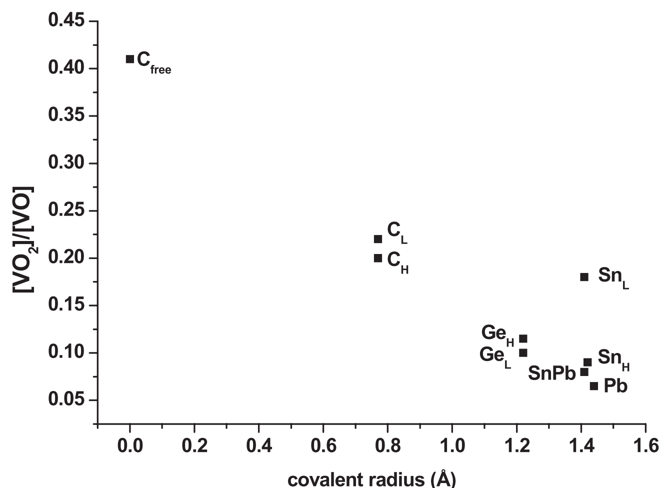


FIG. 5. The conversion ratio $[VO_2]/[VO]$ as a function of the covalent radius isovalent dopants for some representative samples from the list of Table I.

Figure 6 shows that the $[VO_2]/[VO]$ ratio is affected by the carbon content of Si in particular is a decreasing function of carbon (compare samples C_L, C_H, and Sn_L). For samples with about the same concentration of carbon, the conversion $[VO_2]/[VO]$ ratio is reduced with the increase of the isovalent radius (compare samples C_H, Sn_H, and Pb) in accordance with the above mentioned discussion (the larger the covalent radius of the dopant, the larger the induced strains in the lattice).

While examining the $[VO_2]/[VO]$ ratio (see Table I), one can also distinguish a difference between solely carbon doped and co-doped samples. These values are of the range of 0.18–0.22 for the carbon doped samples, whereas they are approximately two times lower for the co-doped samples. This suggests that the radius of isovalent dopant has a strong impact on the $VO \rightarrow VO_2$ conversion. Notably, the Sn_L sample clearly behaves as the first group, i.e., it is essentially a Cz-Si sample with high carbon content.

Furthermore, the effect of $[C_s]$ on the $[VO_2]/[VO]$ ratio must be commented. It has been reported[31] previously that the $[VO_2]/[VO]$ ratio becomes smaller as the carbon concentration of Si material increases. As a possible explanation, it was suggested that VO defect, besides reacting with O_i, participates to another competing reaction with another defect, which was unidentified but possibly of carbon- related origin. Alternatively, it was suggested that the other defect may be self-interstitial. The latter idea can be elaborated a bit further here. As we mentioned above, carbon can increase the

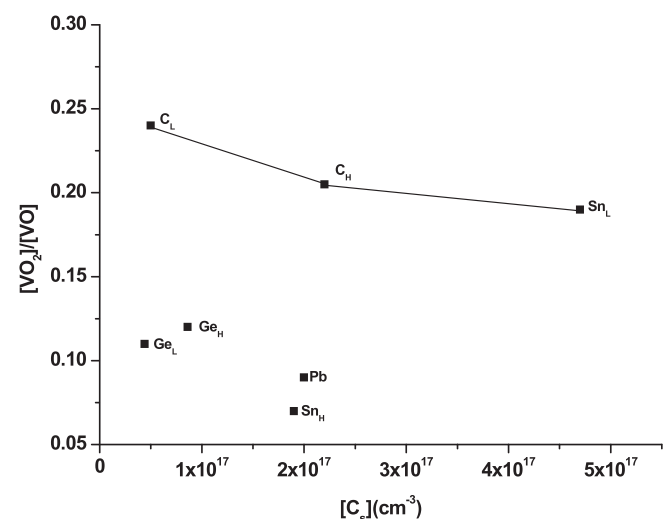


FIG. 6. The conversion ratio $[VO_2]/[VO]$ as a function of the carbon concentration of the various isovalent dopants for some representative samples from the list of Table I.

production of VO in the course of irradiation due to the trapping of self-interstitials which in turn increase the availability of vacancies and therefore the produced VO. In the course of annealing carbon may affect in a different way, the balance between the reactions $VO + O_i \rightarrow VO_2$, $VO + Si_I \rightarrow O_i$ that mainly govern the annealing of VO. In the case of the latter reaction, due to the presence of carbon, some of the self-interstitials released from relative sources may be trapped by carbon atoms to convert them to carbon interstitials

$$C_s + Si_I \rightarrow C_i. \quad (4)$$

At these temperatures, some of these C_i which possibly escape the capture by oxygen atoms to form C_iO_i or other carbon atoms to form C_iC_s are converted again to carbon substitutional atoms

$$C_i \rightarrow C_s + Si_I. \quad (5)$$

In that case, the released self-interstitials can react with VO pairs leading essentially to a reduction of the VO available to convert to VO_2. Therefore, the final number VO_2 defects formed is reduced and the conversion ratio $[VO_2]/[VO]$ is reduced as well. It is reasonable to consider that a percentage of VO may dissociate in the course of annealing.[32] The produced vacancies may react with another VO pair to form V_2O defects that in turn react with self-interstitials to produce VO. The envisaged reaction scheme is the following:

$$VO \rightarrow V + O_i, \quad (6)$$

$$VO + V \rightarrow V_2O, \quad (7)$$

$$V_2O + Si_I \rightarrow VO, \quad (8)$$

and as a whole describes an indirect dissociation of VO defects where two VO defects participate leading finally to one VO defect. This process essentially reduce the final number of VO that are converted to VO_2 and therefore to a reduced formation of the latter defect. This is reflected as a reduction of the $[VO_2]/[VO]$ conversion ratio.

Another issue is the effect of isovalent dopant on the annealing temperature of the VO defect and the growth temperature of the VO_2 defect. Regarding the thermal stability of VO, it has been reported[19] that it is reduced in the case of Ge-doped Si. Using a series of samples with various Ge concentrations, it was determined[19] that the larger the Ge concentration the lower the annealing temperature of VO. On the other hand, the corresponding growth temperature of VO_2 defect that is the temperature that the defect arises in the spectra is also reduced with the increase of the Ge concentration (refer to Figs. 3 and 4 in Ref. 19). A similar behaviour is observed in the case of Sn and Pb-doped Si (refer to Fig. 2). Since we do not possess samples with various Sn and Pb concentrations, it is not possible in this investigation to present a systematic study as in Ref. 19 for Ge-doped Si. For Ge-doped Si samples, the phenomenon was attributed to loosely bound self-interstitials around Ge atoms. In the case of high Ge content, it is suggested that there is an enhancement of the induced strain fields, which may facilitate the liberation of these self-interstitials at a lower temperature in the course of annealing. This equivalently activates the reaction $VO + Si_I \rightarrow O_i$ at a lower temperature, leading in essence to a reduction of the temperature that VO begins to disappear from the spectra. The produced O_i atoms as a result of the reaction above may capture vacancies liberated from other sources, for instance due to the dissociation of V_2. This could lead to a reformation of VO pairs which being mobile at these temperatures they are trapped by oxygen atoms leading to the formation of VO_2 defects. This mechanism[19] was deemed to account for the earlier growth in the spectra of the VO_2 defect in Ge-doped Si and can be applied for the case of Sn and Pb-doped Si. The argumentation is also consistent with the observation that the temperature T_{VO} marking the onset of the disappearance from the spectra of the VO defect does not coincide with the temperature T_{VO2} of the emergence of the $VO2$ defect in the spectra. Indeed there is a shift $\Delta T = T_{VO}\text{-}T_{VO2}$ between the two temperatures which is shown in Fig. 7, where we have used the results previously presented in Ref. 19 for Ge-doped Si. In essence, Fig. 7 manifests that the temperature of the onset that characterizes the annealing of the VO defect due to the reaction $VO + Si_I \rightarrow O_i$ occurs at a different temperature from that characterising the onset of the growth of the VO_2 defect due to the reaction $VO + O_i \rightarrow VO_2$. This is simply because different reactions govern the disappearance of VO and the emergence of VO_2. VO has two activation energies, E_1 and E_2 related with reactions (1) and (2), correspondingly. Evidently, the activation energy E_2 for the decay of VO as described by the reaction ($VO + Si_I \rightarrow O_i$) is smaller than the activation energy E_3 characterizing the emergence of VO_2 described by the reaction ($VO + O_i \rightarrow VO_2$). Even more the activation energy E_1 for the migration of the VO (left part of reaction (1)) is different than the activation energy E_3 characterizing the growth of VO_2 (right part of reaction (1)). Indeed an additional energy term ΔE is required to associate VO and O_i to form the VO_2 defect, that is $E_3 = E_1 + \Delta E$. Understandably a delay is observed between the onset of the VO_2 growth and the decay of the

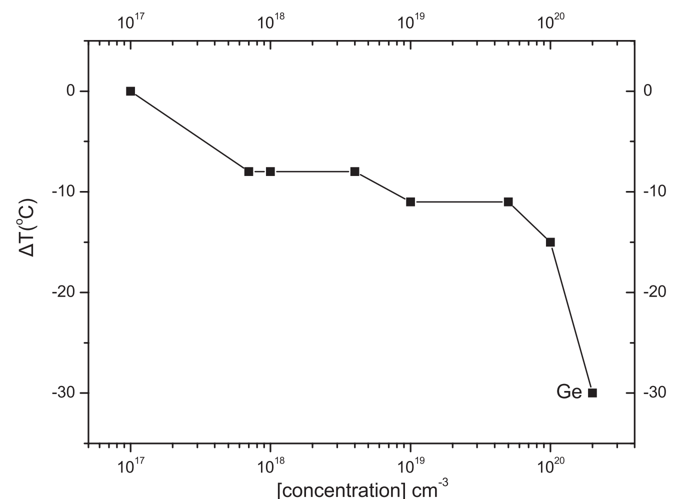


FIG. 7. The difference $\Delta T = T_{VO}\text{-}T_{VO2}$ between T_{VO} that characterizes the onset of the decay of the VO defect in the spectra and T_{VO2} that characterizes the onset of the growth of the VO_2 defect in the spectra versus the isovalent dopant concentration (Data from Ref. 19).

*V*O and this delay characterizes the complexity of the phenomenon given the numerous reactions that participate in it at the various stages of the process. Alternatively, the observed delay is a manifestation of the additional processes involved in the phenomenon. Notice that in the case of samples with Ge content higher than 3×10^{19} cm^{-3}, the shift between the above two temperatures increases indicating a stronger effect of the isovalent dopant on the involved reaction processes. This complexity makes a DFT[33] approach not sufficient to capture the possible mechanisms. Monte Carlo simulations would be required to disentangle the complexity of effective mechanisms.[34] This will be considered in a future study.

The existence of various reactions taking place in this temperature regime can also explain that the observed maximum of the VO_2 concentration occurs at a larger temperature than that marked the total disappearance of *V*O from the IR spectra as exhibited in Fig. 2. Although *V*O disappears around 350 °C, VO_2 continues to grow up to 450 °C (Fig. 2). Clearly, the VO_2 growth is not related only with the reaction $VO + O_i \rightarrow VO_2$, but other reactions also contribute.[30] One reaction scheme is related to the dissociation of larger vacancy complexes as V_2 and V_3. For instance in the case of V_2 part of the dissociated vacancies

$$V_2 \rightarrow V + V \qquad (9)$$

are *trapped* by oxygen atoms to form *V*O pairs

$$V + O_i \rightarrow VO. \qquad (10)$$

These A-centers are mobile at these temperatures and can be captured by other oxygen atoms and converted to VO_2 defects, according to reaction (1). Furthermore, at around 450 °C, oxygen atoms begin to diffuse in the Si lattice and in the first step of oxygen aggregation process oxygen dimers are formed.[35] Thus, an alternative reaction channel for the formation of the VO_2 defect involving the association of vacancies encountering oxygen dimers has been also proposed[36] in the literature

$$O_i + O_i \rightarrow O_{2i}, \qquad (11)$$

$$O_{2i} + V \rightarrow VO_2. \qquad (12)$$

Interestingly, other reaction schemes as for instance

$$V_2 + O_{2i} \rightarrow V_2O_2 \qquad (13)$$

then

$$V_2O_2 \rightarrow VO_2 + V \qquad (14)$$

could also been considered. The whole phenomenon of the continuing growth of the VO_2 defect even after the complete disappearance of the *V*O defect is reflected in the thermal evolution curves of the two defects exhibited in Fig. 2. Importantly, the conversion ratio $[VO_2]/[VO]$ does not represent exactly the percentage of *V*O pairs produced by irradiation that are converted to VO_2 defects, since with the increase of temperature in the course of the isochronal anneals new *V*O are formed as a result of intermediate reactions and new VO_2 are finally produced. However, the general trend indicated in Fig. 5 describing the effect of isovalent doping on the conversion ratio is representative of the phenomenon.

Figure 8 shows the production of the C_iO_i defect as a function of the covalent radius of the dopant. Although it is difficult to extract any particular trend from the present results by comparing the effect of the different isovalent dopants, it is clearly seen that the defect concentration is largely suppressed in the case of Pb. A possible explanation may be related to the tendency of Pb to react with C to form related defects. It could be envisaged that C_i defects formed in the course of irradiation are readily captured by Pb to form PbC_i defects. These defects in turn may trap vacancies leading to the formation of PbC_s defects. The existence of lead-carbon clusters has been discussed previously[33,37] but there are no reports for any particular IR signal related for instance with the PbC_i and the PbC_s complexes. To the best of our knowledge, no electrical levels have been connected with the above defects. Interestingly, in the case of Sn-doped Si bands attributed to SnC defects has been reported.[38,39] These complexes are not stable at room temperature and therefore at first sight, one may not expect a significant effect on the formation of the C_iO_i defect. However, in previous work, we have suggested[40] that the coexistence of C and Sn could lead to a reduction of the C_iO_i production when Sn concentration increases. Regarding GeC complexes, our previous calculations have shown that Ge will tend to interact with interstitial carbon with the binding energy of 0.27 eV.[33] This could be a transient complex existing during the irradiation flow, but to the best of our knowledge, there is no experimental report for their existence. Notably, in a previous investigation,[41] using a number of samples with various Ge contents, it was found that the C_iO_i production depends on the coexistence of C and Ge and it tends to increase as a function of the Ge content. Interestingly, for high Ge content for instance 2×10^{20} cm^{-3} as in our case, it tends to decrease. We note by comparing C_H, Sn_H, and Pb samples with about the same C content that the production of the C_iO_i defect is rather

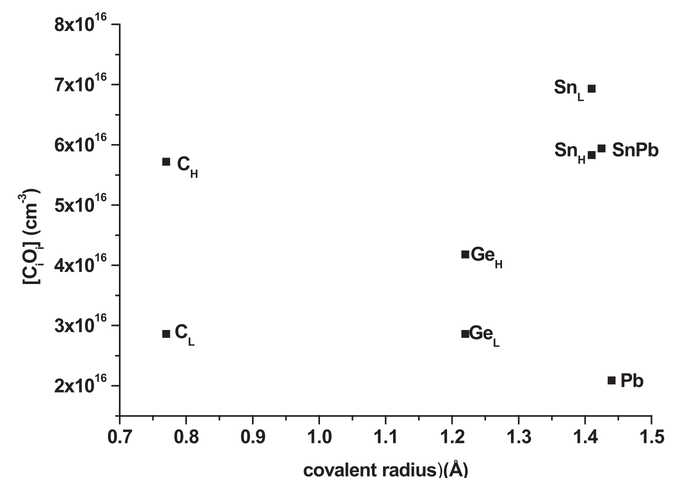


FIG. 8. The production of the C_iO_i defect as a function of the covalent radius of the isovalent dopants for some representative samples.

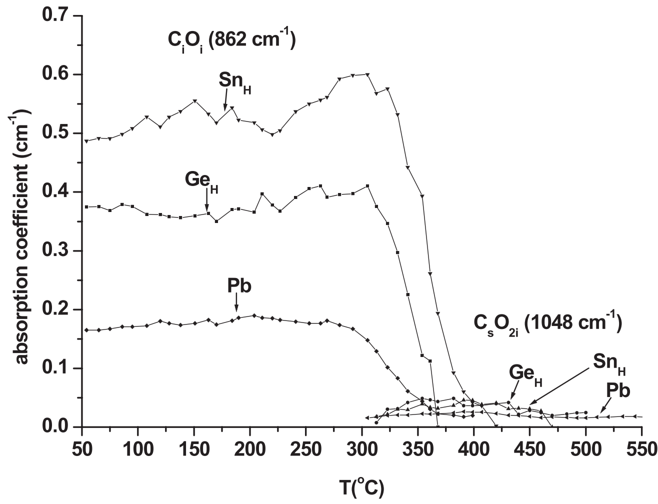
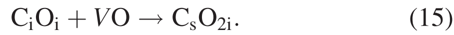


FIG. 9. The evolution with temperature of the C_iO_i and the C_sO_{2i} defects for the samples Ge_H (a), Sn_H (b), and Pb (c).

slightly increased in the Sn_H sample although is substantially decreased in the Pb sample.

Figure 9 presents the thermal evolution of the C_iO_i defect as well as that of the C_sO_{2i} defect, for the samples of Fig. 1, correspondingly. It is well-known that the C_iO_i defect anneals out mainly by dissociation.[2] Apparently, this does not prohibit the defect upon annealing to participate to other reaction channels. Notably, both C_iO_i and *V*O defects anneal out at about the same temperature around 300 °C (compare Figures 2 and 9). It has been suggested[42] that part of the migrating *V*O pairs encounter C_iO_i defects to form the C_sO_{2i} complex



$$C_iO_i + VO \rightarrow C_sO_{2i}. \qquad (15)$$

Also it is possible that upon C_iO_i dissociation, some of the liberated interstitial carbon atoms to interact with VO_2 centers to form C_sO_{2i} defects according to the reaction

$$C_i + VO_2 \rightarrow C_sO_{2i}. \qquad (16)$$

Fig. 10 presents the conversion ratio a_{CsO2i}/a_{CiOi} as a function of the covalent radius of the isovalent dopants. Although the effect of isovalent doping seems marginal, at least for the samples used in this study, it should be noted that the conversion ratio appears to be slightly increased in the case of Ge and Pb. However, it shows an opposite behaviour in the case of Sn dopant, where the ratio is slightly decreased. Comparing the ratio for the Sn_H and Pb samples which have about the same C content, we see that it is smaller in the case of the Sn_H sample. Further experiments are necessary to study these differences in the influence of the Sn dopant on the C_iO_i defect (as compared to Ge and Pb dopants), employing a number of samples with various concentrations of the isovalent dopants.

Figure 11 presents the variation ΔT in the annealing temperature of the C_iO_i defect as a function of the covalent radius of the dopant (as a reference, annealing temperature was taken that of the C_L sample). The present results are in agreement with a recent work[19,43] that there is a relative small shift of the annealing temperature of the C_iO_i defect towards smaller temperature values. Isovalent doping affects differently the annealing temperature of the *V*O and C_iO_i defects. In the case of *V*O, the influence is profound although in the case of C_iO_i is negligible. This maybe related with the structure as well as with the reactions that participate in the annealing of the two defects. It has been reported[19] that in the case of *V*O defect the initial annealing is governed by the reaction (2). Thus, since the induced strain by the larger isovalent dopants affect in one hand the availability of self-interstitials and on the other hand the temperature of their liberation in order to participate in reaction (2) it is reasonable to expect a strong effect of the annealing temperature of *V*O. On the other hand, these strains have a negligible effect on the annealing of the C_iO_i defect since self-interstitials do not participate in its annealing. Indeed besides dissociation C_iO_i defect reacts directly with the *V*O defect to form C_sO_{2i} (via reaction (15)) and this reaction is apparently not substantially affected by the presence of larger isovalent dopants in the lattice. Notably, the effect of strain is a universal issue in semiconductors, affecting defect process and merits further investigation.[44]

Thus, in order to enhance device performance (for example for devices operating as particle detectors), it is crucial to

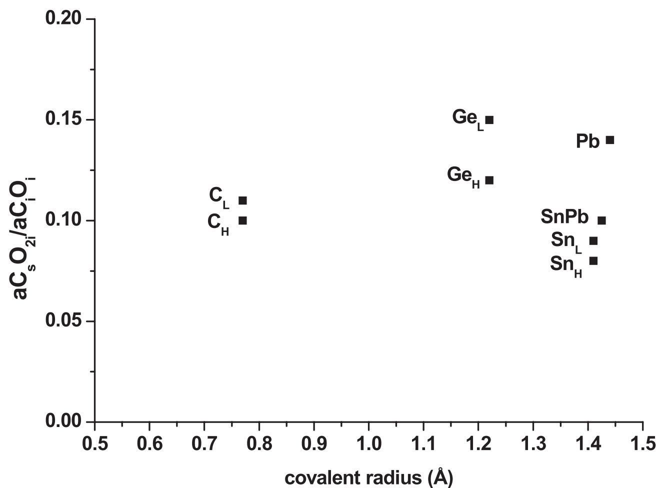


FIG. 10. The conversion ratio aC_sO_{2i}/aC_iO_i as a function of the covalent radius isovalent dopants.

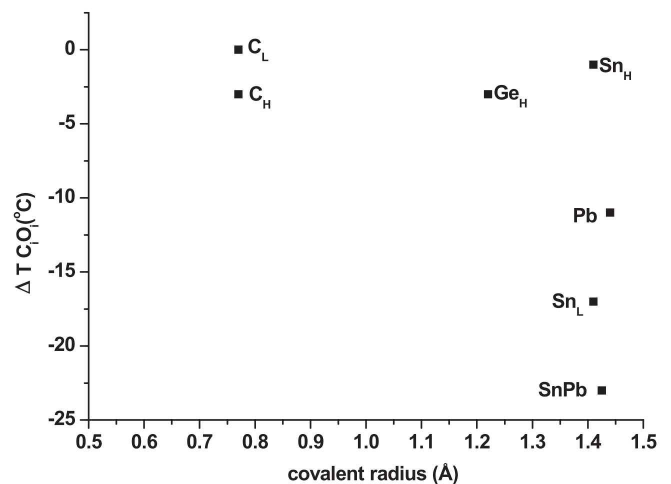


FIG. 11. The difference ΔT of the C_iO_i defect as a function of the covalent radius of the dopants.

control radiation defects as the VO and C_iO_i pairs, which are the most common defects in irradiated Cz-Si containing carbon. In this respect, isovalent doping of Si is a promising technique and it is the focus of relative research in order to exploit all the potential, it can be provided for the benefit of the electronic industry. In particular, the present results indicate that codoping of Si with carbon and one of the Ge, or Sn or Pb impurities is a practical and non-expensive way to improve the radiation hardness of the material.

IV. CONCLUSIONS

We have investigated the effect of thermal doping on the properties and behaviour of the VO and the C_iO_i defects in electron-irradiated Si. Regarding VO, it was found that its production is enhanced with the presence of Ge, although it is suppressed with Sn and Pb. Its thermal stability is reduced due to the presence of isovalent dopants. Furthermore, the percentage of VO pairs that are converted to the VO_2 defects is affected. More specifically, it was determined that the larger the covalent radius of the dopant the less the VO_2 defects formed. It was determined that the conversion of VO to VO_2 is a complicated phenomenon due to the participation of a number of reactions. Isovalent dopants affect the number of the self-interstitials participating in the processes and this characterizes their role in this phenomenon. Regarding C_iO_i, it was found that its production is reduced substantially in Pb-doped Si. The respective effect of Sn and Ge depends on their concentration as well as on the carbon content of the material. The conversion ratio of the C_iO_i pair to the C_sO_{2i} complex does not show significant changes with respect to isovalent dopant in species Si. However, it appears that Ge and Pb enhances it slightly although Sn reduces it slightly. Its thermal stability seems to be less affected by isovalent dopants in comparison with the same effect on the VO pair. Importantly, it was verified that carbon has a significant effect on the above processes regarding the VO and the C_iO_i defects and this role is mainly related with the tendency of carbon to trap self-interstitials and therefore to affect the balance of the reactions when intrinsic defects are involved.

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