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Defect engineering of the oxygen-vacancy clusters formation in electron irradiated silicon by isovalent doping: An infrared perspective

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Infrared spectroscopy was used to study the production and evolution of oxygen–vacancy (VO_n for n = 1, 2, 3 and V_mO for m = 1, 2, 3) clusters, in electron-irradiated Czochralski silicon (Cz-Si) samples, doped with isovalent dopants. It was determined that the production of the VO pair is enhanced in Ge-doped Si but is suppressed in Sn and Pb-doped Si. The phenomenon is discussed in terms of the competition between isovalent dopants and oxygen atoms in capturing vacancies in the course of irradiation. In the case of Ge, only transient GeV pairs form, leading finally to an increase of the VO production. Conversely, for Sn and Pb the corresponding pairs with vacancies are stable, having an opposite impact on the formation of VO pairs. Regarding V_2O and V_3O clusters, our measurements indicate that Ge doping enhances their formation, although Sn and Pb dopants suppress it. Similar arguments as those for the VO pair could be put forward, based on the effect of isovalent impurities on the availability of vacancies. Additionally, it was found that the conversion ratio of VO to VO_2 decreases as the covalent radius of the isovalent dopant increases. These results are discussed in terms of the local strains introduced by the isovalent dopants in the Si lattice. These local strains affect the balance of the intrinsic defects created as a result of irradiation, as well as the balance between the two main reactions ($VO + O_i \rightarrow VO_2$ and $VO + Si_I \rightarrow O_i$) participating in the VO annealing, leading finally to a decrease of the VO_2 production. The larger the covalent radius of the isovalent dopant ($r_{Ge} < r_{Sn} < r_{Pb}$), the larger the introduced strains in the lattice and then the less the VO_2 formation in accordance with our experimental results. Interestingly, an opposite trend was observed for the conversion ratio of VO_2 to VO_3. The phenomenon is attributed to the enhanced diffusivity of oxygen impurity as a result of the presence of isovalent dopants, leading to an enhanced formation of the VO_3 cluster. The results indicate that isovalent doping of Si is an effective way to control the formation of the deleterious oxygen-vacancy clustering that can affect Si-based devices.
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I. INTRODUCTION

Electron irradiation is an important tool to investigate the production and the interactions between point defects in Si. The defect processes of the oxygen-vacancy related clusters (VO_n and V_mO clusters) have attracted particular attention due to their scientific and technological importance.[1,2] A lot of information has been accumulated from results collected by means of various experimental techniques including electrical (for example, deep level transient spectroscopy, DLTS), magnetic (for instance, electron paramagnetic resonance, EPR), optical (infrared absorption, IR), structural (X-rays), and theoretical techniques.[3–11] In spite of the data collected, there are still a lot of unclear points related with the production and with the mechanisms that govern the interactions of VO_n and V_mO clusters with dopants and intrinsic defects. These are important as they will impact technological applications.

The VO pair is the first and most important member of the oxygen-vacancy families (VO_n and V_mO clusters). It is one of the most intensively studied defects in semiconductors in the last 50 years and a lot of information has been gathered concerning its electrical, electronic, optical and structural properties, as well as its thermal stability and the reactions with other defects.[1–11] The VO pair introduces an acceptor level (E_c−0.17 eV) in the energy gap of Si, has a well-known IR band (830 cm^{-1}, in the neutral charge state) and a characteristic EPR signal. It is an important recombination center[12] playing a critical role in lifetime control of relative electronic devices. Upon thermal anneals it converts to the VO_2 cluster (885 cm^{-1}). Although VO_2 does not introduce[6] electrical levels in the gap, it has been suggested[13] that it may act as a nucleation center for oxygen aggregation processes and therefore its role is significant for the development of oxygen precipitates. Finally, to the best of our knowledge, there is not any definite report in the literature about electrical levels related with the VO_3 cluster, which is therefore considered as electrically inactive.

Additionally, V_mO clusters can also form[14–17] in the course of irradiation or/and annealing process. On heavy doses a VO pair can trap a V to form V_2O. Alternatively, V_2O can form by the reaction $V_2 + O_i \rightarrow V_2O$. The V_3O cluster can form via a number of processes described by the reactions $V_2O + V \rightarrow V_3O$; $V_2 + VO \rightarrow V_3O$ and $V_3 + O_i \rightarrow V_3O$. The V_2O cluster introduces[15] two levels in the energy gap of Si at E_c−0.23 eV and at E_c−0.47 eV. The V_3O cluster introduces[18]

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four levels in the gap at $E_c-0.34$ eV and at $E_c-0.456$ eV as well as at $E_v+0.235$ eV and at $E_v+0.12$ eV. Due to their electrical activity, V_2O and V_3O clusters (as well as VO) were found[12,19–22] to be effective recombination centers affecting minority carrier life time, and being the origin of leakage currents. These should therefore be avoided, for instance, in the case of reverse biased p-n junctions and in Si-based radiation detectors. Leakage currents have a negative effect on the characteristics of power devices.[22] Defect engineering strategies demand the full knowledge of the properties and behavior of clusters in order to improve the output of the relative devices and therefore a clear picture of these clusters is required. Although the electrical activity of the V_2O and V_3O clusters is more or less known the optical picture is less clear. Both clusters contain[16] a Si-O-Si bonding structure as the case of the VO pair and therefore their vibrational frequencies are very close to the VO pair at 830 cm^{-1}. At room temperature, the separation of the bands is usually made by Lorentzian profiling[23,24] and two bands at ∼825 and ∼839 cm^{-1} have been definitely correlated[23] with the V_2O and the V_3O clusters, respectively.

The isovalent doping of Si is an established way to improve the yield and output of devices by controlling the properties of deleterious defects such as the vacancy-oxygen clusters. In particular, Ge-doping,[25–30] Sn-doping,[31–33] and Pb-doping[33–36] affect the formation, the thermal stability, the mechanisms that govern the reactions and the kinetics of the VO pair indicating that isovalent doping is a valuable technique to optimize devices. In the present paper we investigate the impact of Ge, Sn, and Pb doping on the formation of the VO, V_2O, and V_3O, as well as on the conversion of VO to the VO_2 cluster.

II. EXPERIMENTAL METHODOLOGY

We studied radiation defects in Cz-Si doped with isovalent impurities (Ge, Sn, and Pb) by means of IR spectroscopy. We used five groups of samples: one Cz-Si doped with Ge labelled (Cz-Si:Ge), one Cz-Si doped with Sn (Cz-Si:Sn), and one Cz-Si doped with Pb (Cz-Si:Pb). These three groups of samples contain also carbon and thus we used another two groups of Cz-Si samples: one with low carbon content (Cz-Si:C_L) and another one with high carbon content (Cz-Si:C_H), for the sake of completeness. Hereafter, we shall use short names for the samples, for instance, (Ge) instead of Cz-Si:Ge and so on, that is (Sn), (Pb), (C_L) and (C_H). The Ge, Sn, and Pb concentrations of the samples were measured by secondary ion mass spectroscopy (SIMS). The oxygen and carbon concentrations of the samples were calculated from the 1106 cm^{-1} oxygen IR band and the 606 cm^{-1} carbon IR band, using calibration coefficients of 3.14×10^{17} cm^{-2} for oxygen and 1×10^{17} cm^{-2} for carbon, respectively.[37,38] Details of the samples used in this work are given in Table I.

The samples were irradiated with 2 MeV electrons at ∼80 °C, with a fluence of 1×10^{18} cm^{-2}. After the irradiation the samples were subjected to 20 min isochronal anneals, at temperatures up to 600 °C. The annealing temperatures were accurate within ∼ ±2 °C. After each annealing step, the infrared measurements were carried out at room temperature by using a Fourier transform IR (FTIR) spectrometer operating at a resolution of 1 cm^{-1}. The contribution in the spectra of the two phonon intrinsic absorption was always removed by subtracting the spectrum of a pure float zone Si (Fz-Si) sample of equal thickness.

III. RESULTS AND DISCUSSION

Figures 1(a) and 1(b) show segments of the IR spectra of the (C_L) and (Ge), after irradiation and at characteristic temperatures in the course of the isochronal anneals. The corresponding figures for the Sn and Pb-doped samples were recently reported.[36] IR bands of the VO (830 cm^{-1}), VO_2 (888 cm^{-1}), and VO_3 (904, 968, 1000 cm^{-1}) are clearly seen in the spectra. The well-known 862 cm^{-1} band of C_iO_i pair is also shown. It has been reported that carbon affects[39] the formation of VO pairs although other reports[40] consider this effect to be negligible. In the discussion below, the effect of carbon on the production and evolution of oxygen-vacancy clusters will not be considered. Nevertheless, measurements from a low carbon concentration and a high carbon concentration Cz-Si sample are given for the sake of completeness.

Figure 2 shows the production of VO pair as a function of the covalent radius of the isovalent dopant. It is observed that although VO concentration increases when Si is doped with Ge it decreases when doped with Sn and Pb. In our previous work,[25] we have suggested that in the case of Ge doping the latter impurities act as temporary trapping sites for vacancies in the course of irradiation preventing the direct annihilation of these vacancies by self-interstitials. This in essence is equivalent with an increased availability of vacancies in the course of irradiation which is reflected in the spectra by the enhanced formation of VO pairs. The association of Ge atoms with vacancies leads to GeV pairs which dissociate[41] below room temperature and therefore they cannot survive to be detected at these experiments. On the other hand, for Sn-doped Si the formation of SnV pairs,[32,42] which are stable at room temperature, results in the suppression of

TABLE I. The concentrations of Ge, Sn, and Pb and the concentrations of O_i and C_s before and after irradiation, as well as the absorption coefficient a_{VO}, a_{VO2}, and a_{VO3} and the ratio a_{VO2}/a_{VO}, a_{VO3}/a_{VO2} for the used samples irradiated with 2 MeV electrons at a dose of 1×10^{18} cm^{-2}.

Sample	Dopant [cm^{-3}]	$[C_s]_o$ 10^{16} (cm^{-3})	$[C_s]_{a.i.}$ 10^{16} (cm^{-3})	$[O_i]_o 10^{17}$ (cm^{-3})	$[O_i]_{a.i.} 10^{17}$ (cm^{-3})	a_{VO} (cm^{-1})	a_{VO2} (cm^{-1})	a_{VO3} (cm^{-1})	a_{VO2}/a_{VO}	a_{VO3}/a_{VO2}
(C_L)	…	5	<2	9.5	9.07	0.94	0.43	0.18	0.46	0.43
(C_H)		22	13.2	9.3	9	0.97	0.39	0.18	0.40	0.46
(Ge)	2×10^{20}	8.6	2.3	6.5	5.5	1.06	0.24	0.12	0.23	0.5
(Sn)	9×10^{18}	20	25.2	9.2	10.1	0.79	0.12	0.11	0.15	0.92
(Pb)	1×10^{18}	19	…	2.1	1.5	0.53	0.07	…	0.13	…

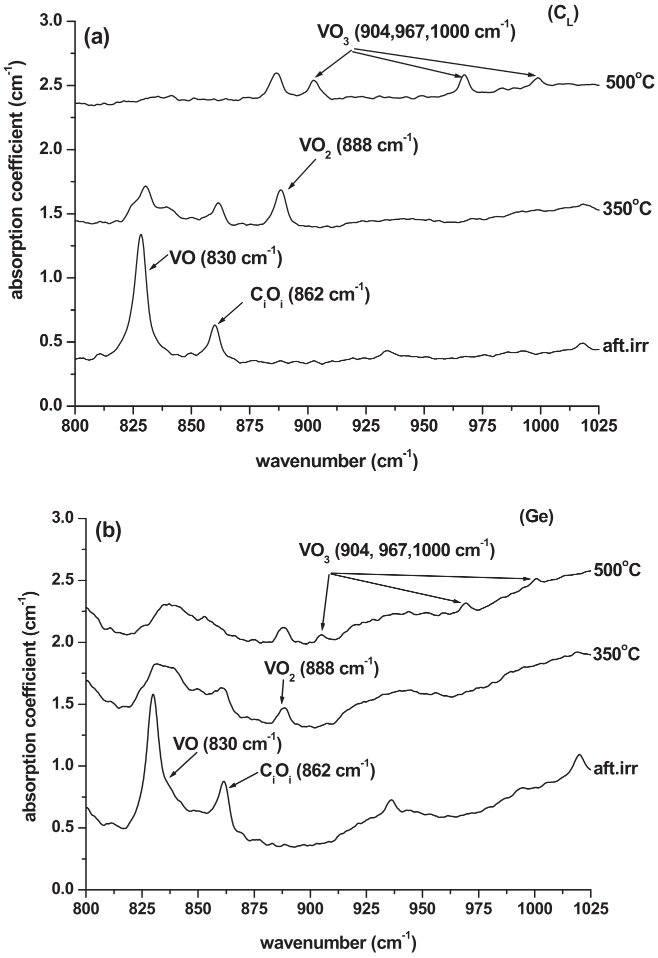

FIG. 1. Segments of the IR spectra of the (C$_L$) (a) and (Ge) (b) samples after irradiation and at 350 °C and 500 °C, in the course of the 20-min isochronal anneals sequence.

the production of *V*O pairs. In room temperature irradiations, Sn compete with interstitial O impurities in capturing vacancies, which results in the suppression of *V*O, as opposed to Ge, which assists indirectly O interstitial atoms in capturing more vacancies, leading to the increase of the *V*O production.

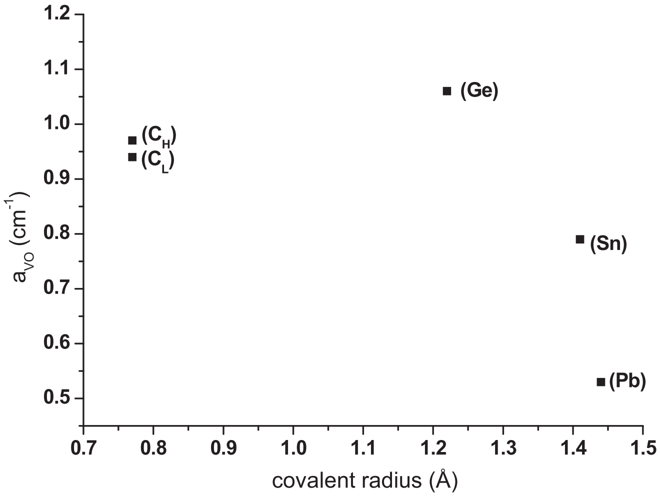

FIG. 2. The production of *V*O defect as a function of the isovalent dopant covalent radius.

Regarding Pb doping, a similar situation could be envisaged as that of Sn doping. The formation of stable Pb*V* pairs suppresses the formation of *V*O pairs. Pb competes with interstitial O impurities in capturing vacancies and this suppresses *V*O production. Although any direct experimental evidence for the Pb*V* pair has not been reported so far there are a lot of indirect indications[34,36] for the existence of stable Pb*V* pairs in irradiated Pb-doped Si.

From a theoretical perspective, previous density functional theory (DFT) calculations report that the Pb*V* pair has a significant binding energy (-1.37 eV), which is higher than Ge*V* pairs (-0.27 eV) and Sn*V* (-1.17 eV) but lower compared to *V*O (-1.53 eV).[31] The binding energy is defined here as the energy difference between the pair and its constituent isolated defects, with the more negative binding energies reflecting the stronger association between the defects. As these calculations consider neutral pairs, the binding energies in effect represent the relaxation of the lattice when a vacancy relieves the strain from the oversized dopant. This is in turn reflected by the binding energy of the dopant-vacancy pair (for example for the Sn$V = -1.17$ eV) over the difference in atomic radius between the Si atom and the isovalent atom (for Sn: $r_{Si} - r_{Sn} = -0.24$ Å), which is around 5 eV/Å (for Sn: 4.9 eV/Å) for all the dopants considered here. There is generally good correspondence between the calculated (via DFT) and experimentally determined parameters (for example activation energies of diffusion) in group IV semiconductors.[43]

Figure 3 shows the evolution with temperature of the *V*O, *V*O$_2$, *V*O$_3$ clusters and O$_i$ for the (C$_L$), (Ge), and (Pb) samples. The corresponding figures for the Sn and Pb-doped samples were recently reported.[36] Figure 4 shows the conversion ratio (a_{VO2}/a_{VO}) as a function of the covalent radius of the isovalent dopant. Obviously, the formation of *V*O$_2$ cluster is suppressed by the isovalent dopant and most importantly the larger the covalent radius the smaller the corresponding ratio. In the elimination of the *V*O pair upon annealing there are two reactions that take place in parallel: $VO + O_i \rightarrow VO_2$ and $VO + Si_I \rightarrow O_i$. The latter reaction is enhanced in the case of isovalent doping. Additionally, the larger the dopant the more efficient the second reaction involving self-interstitials. As a result, the formation of the *V*O$_2$ cluster is suppressed. In a previous study[28] regarding Ge-doped Si, we have argued that the emission of self-interstitials participating in the second reaction is sensitive to the presence of Ge. More specifically, in heavily irradiated material large self-interstitial clusters are formed.[44] The binding of these self-interstitials to these clusters is affected by the strain fields introduced in the Si lattice due to the substitutional incorporation of the larger Ge isovalent impurity ($r_{Ge} = 1.22$ Å, $r_{Si} = 1.17$ Å). It was argued that the binding energy decreases as a result of the Ge presence, which leads to an enhanced emission of self-interstitials changing the balance between the two reactions that govern the annealing of *V*O pair in favor of the $VO + Si_I \rightarrow O_i$ reaction over the $VO + O_i \rightarrow VO_2$ reaction. This is translated to a suppressed formation of *V*O$_2$ clusters. The observed increase of the O$_i$ concentration in the case of the Ge and Pb doped samples (Figs. 3(b) and 3(c), respectively), in the temperature range where *V*O pair anneals out,

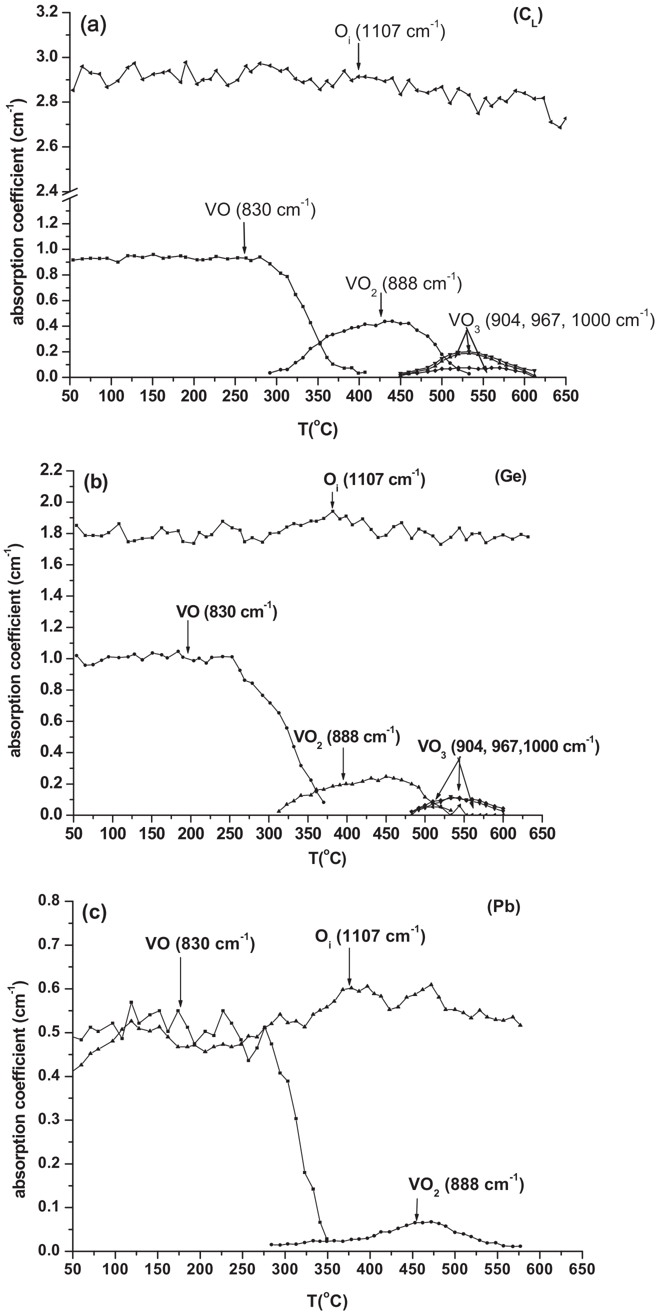

FIG. 3. The evolution with temperature of the *VO*, *VO*$_2$, *VO*$_3$ and the O$_i$ IR bands for the (C$_L$) (a), (Ge) (b), and (Pb) (c) samples.

support our argument. In contrast, the concentration of the O$_i$ impurity in the case of the (C$_L$) sample, which is not doped with isovalent impurities, does not show this increase (Fig. 3(a)). Extending the idea of the enhancement of the *VO* + Si$_I$ → O$_i$ reaction for the case of the Sn and Pb impurities in Si, which are larger than that of Ge ($r_{Sn} = 1.41$ Å, $r_{Pb} = 1.44$ Å) one would expect a further suppression of the *VO*$_2$ clusters formation in agreement with our results (refer to Fig. 4).

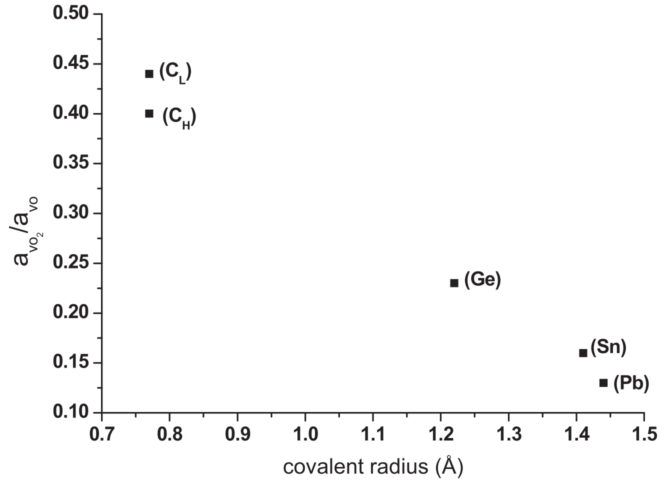

FIG. 4. The conversion ratio (a_{VO2}/a_{VO}) of the *VO* to the *VO*$_2$ cluster as a function of the covalent radius of the isovalent impurities; data for the Sn and Pb *points* are from Ref. 36.

Figure 5 shows the conversion ratio (a_{VO_3}/a_{VO2}) of the *VO*$_2$ to *VO*$_3$ cluster as a function of the covalent radius of the isovalent dopant. An increase is observed in this ratio as a function of the covalent radius at least for the Ge and Sn doped samples since in the (Pb) sample the *VO*$_3$ cluster cannot be detected. Thus, this ratio shows an opposite tendency in its behaviour in comparison with that of the (a_{VO2}/a_{VO}) ratio. We notice, however, that in the case of formation of the *VO*$_3$ cluster the diffusing species is the O interstitial atom, although in the case of the formation of the *VO*$_2$ cluster the moving species is the *VO* pair. It has been reported that, for instance, the Ge dopant enhances[45] the diffusivity of the oxygen interstitial atom. In that case the formation reaction is expected to be enhanced leading to an increase of the concentration of the *VO*$_3$ cluster. This argument could be extended in the case of Sn, since it has been reported[46] that the latter impurity enhances the oxygen precipitation process in Cz-Si. Regarding Pb doping in our samples the *VO*$_2$ concentration was quite low and any IR bands originated from the *VO*$_3$ cluster could not be detected.

Figures 6(a)–6(d) represent the Lorentzian analysis of the *VO* frequency range for the (C$_L$), (Ge), (Sn) and (Pb) samples, correspondingly. Besides the 830 cm^{-1} band of the *VO* pair, bands at ∼826 cm^{-1} and ∼839 cm^{-1} related[23] with the *V*$_2$O and *V*$_3$O clusters, respectively, could be separated in

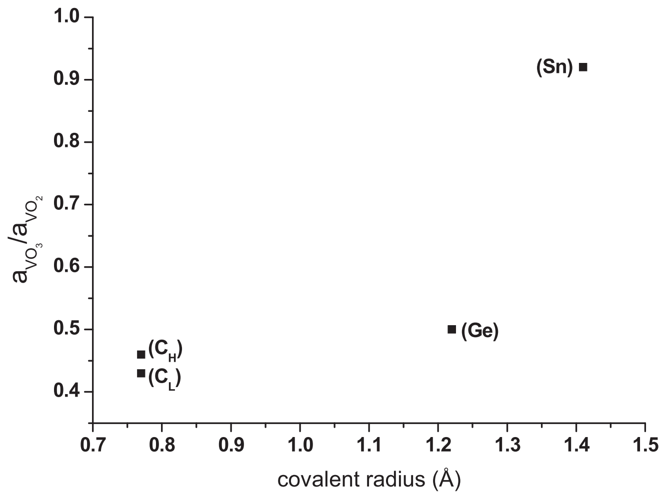

FIG. 5. The conversion ratio (a_{VO3}/a_{VO2}) of the *VO*$_2$ to the *VO*$_2$ cluster as a function of the covalent radius of the isovalent impurities; data for the Sn and Pb *points* are from Ref. 36.

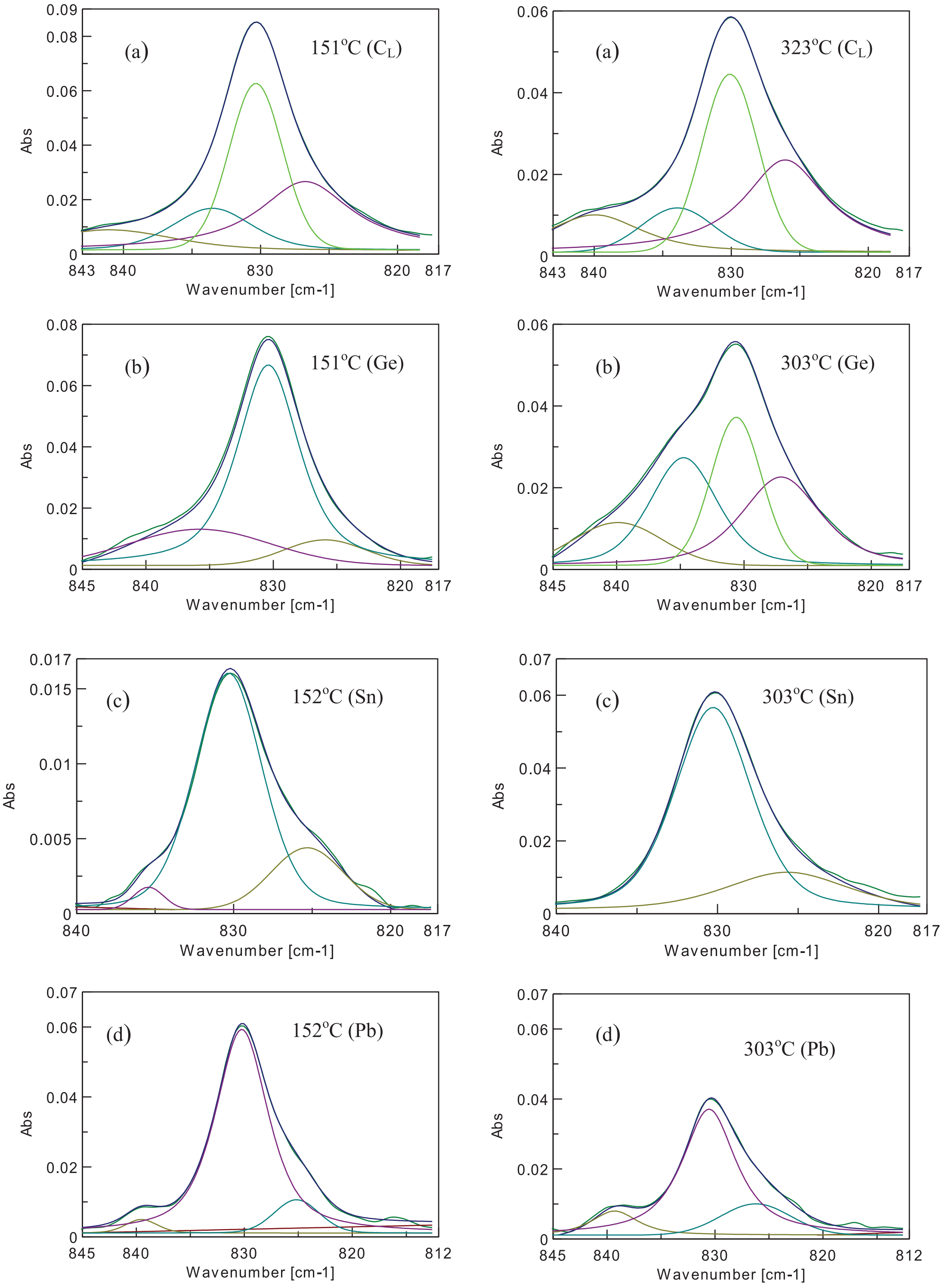

FIG. 6. Deconvolution of the *V*O defect region infrared bands into Lorentzian profiles for the (C_L) (a), (Ge) (b), (Sn) (c), and (Pb) (d) samples.

the profiles together with another band at ~835 cm^{-1} most probably related with a V_mO_n structure but its exact identity is not certain.

Figures 7(a)–7(d) show the evolution with temperature of the 826, 839, and 835 cm^{-1} bands for the (C_L), (Ge), and (Pb) samples. Figure 8 shows the amplitudes of the V_2O (a) and the V_3O (b) clusters as a function of the covalent radius. It is clearly seen that the formation of the V_2O and the V_3O clusters is enhanced in Ge doped samples and suppressed in the Sn and Pb doped samples. Notably the V_3O band is missed from the spectra of the Sn-doped sample. This behaviour is similar to that depicted in Fig. 2 for the dependence of the *V*O formation as a function of the covalent radius of the isovalent impurities. The observed enhancement of V_2O cluster in the Ge-doped samples is attributed (for the same reasons as that of the *V*O pair) to the enhancement of the availability of vacancies as the result of the formation of transient Ge*V* pairs. This could lead to an enhancement of

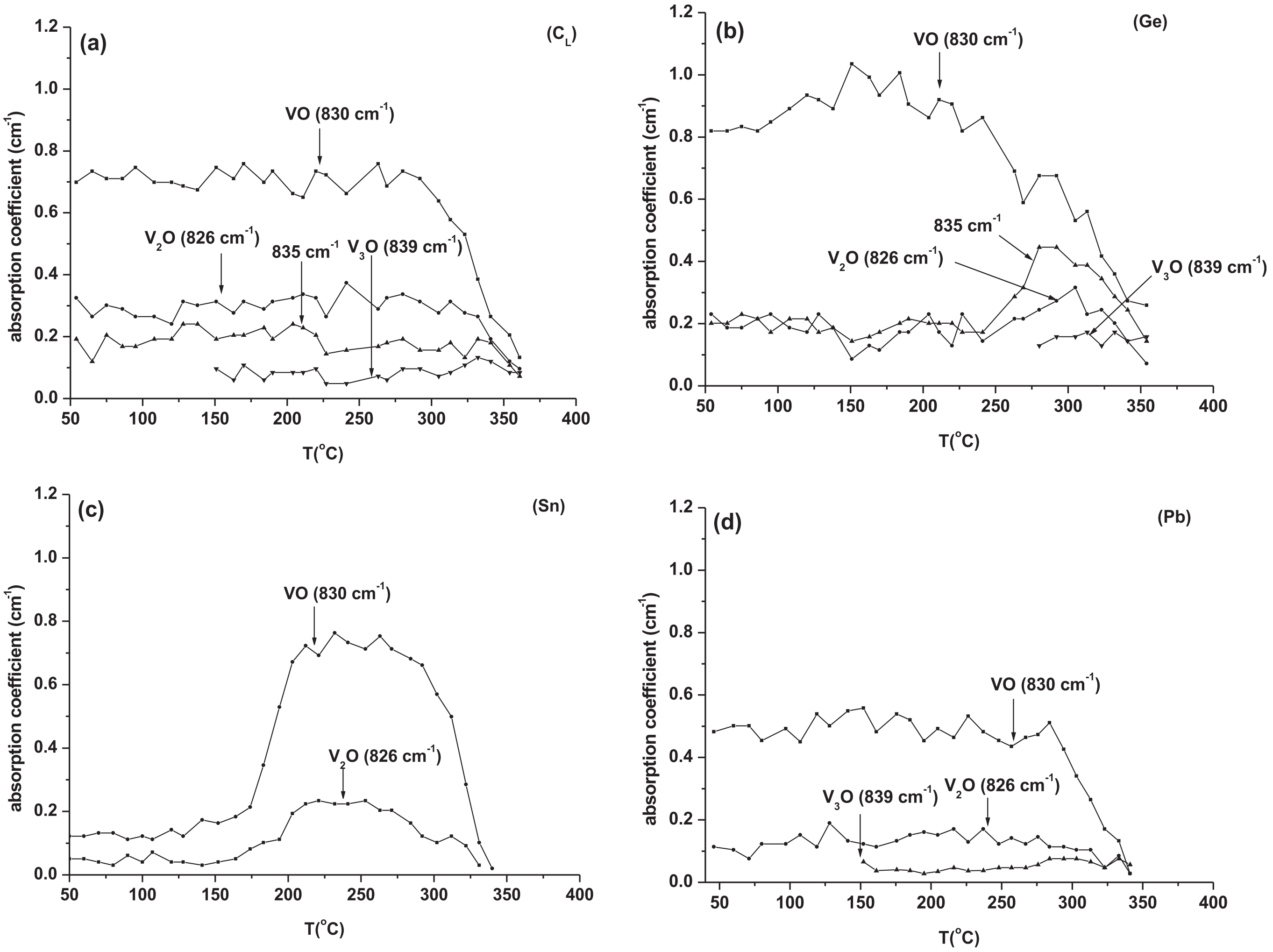

FIG. 7. The evolution with temperature of the V_2O and the V_3O clusters for the (C$_L$) (a), (Ge) (b), (Sn) (c), and (Pb) (d) samples.

the formation reaction $VO + V \rightarrow V_2O$. Similarly, the suppression of the V_2O cluster in Sn and Pb doped Si is attributed to the decrease of the availability of vacancies in the course of irradiation due to the formation of stable SnV and PbV pairs. This in turn leads to a suppression of the formation reaction $VO + V \rightarrow V_2O$. Regarding V_3O clusters (refer to Fig. 8(b)) we observe that as it is shown by the Lorentzian analysis of the spectra (Figs. 6 and 7), they do not appear immediately after irradiation but during annealing at elevated temperatures. The V_3O cluster forms possibly by the reactions $V_2 + VO \rightarrow V_3O$, or/and $V_2O + V \rightarrow V_3O$. In any case, similar statements as those for the V_2O cluster could be made regarding its dependence on the Ge, Pb, and Sn isovalent dopants. For instance, if the concentration of V_2 or V_2O is enhanced in Ge-doped Si this is reflected in the enhanced formation of the V_3O cluster. On the other hand the formation of the V_3O defect is expected to be suppressed in the Sn and Pb-doped Si due to the suppressed availability of vacancies.

Intrinsic defects play a critical role in most of the processes related with the growth of Si and the fabrication of Si-based devices. Central to this, is the role of intrinsic defects on the mechanisms that govern the formation of various clusters and the reactions between them. More specifically, they are critical for the formation of oxygen-vacancy clusters and their evolution on annealing as they convert from one member of the family to the next. Therefore, any information regarding the properties and behaviour of intrinsic defects is valuable for the better understanding of their behaviour and mainly the optimization of the Si-based devices. In the present study, the impact of isovalent dopants on the formation of the VO, the V_2O and the V_3O clusters is important with respect to their influence on the association of oxygen atoms with vacancies. Additionally, the effect of the isovalent dopants on the conversion of the VO to the VO_2 cluster is also very important regarding their influence on the association of self-interstitials with the VO which affects the formation of the VO_2 cluster. The latter phenomenon was discussed here in terms of the local strains introduced in the lattice by the isovalent dopants and how in turn these strains affect the formation of the VO_2 cluster. As mentioned above the VO_2 clusters are significant as their formation has been correlated with the nucleation of oxide precipitates. Oxygen aggregation processes in Si are technologically important. For example, precipitates in Si can help to suppress metallic contamination of integrating circuits as well as to enhance the mechanical strength of the wafers.[47] Notably, measurements on Ge-doped Si have shown[48] that as a result of the

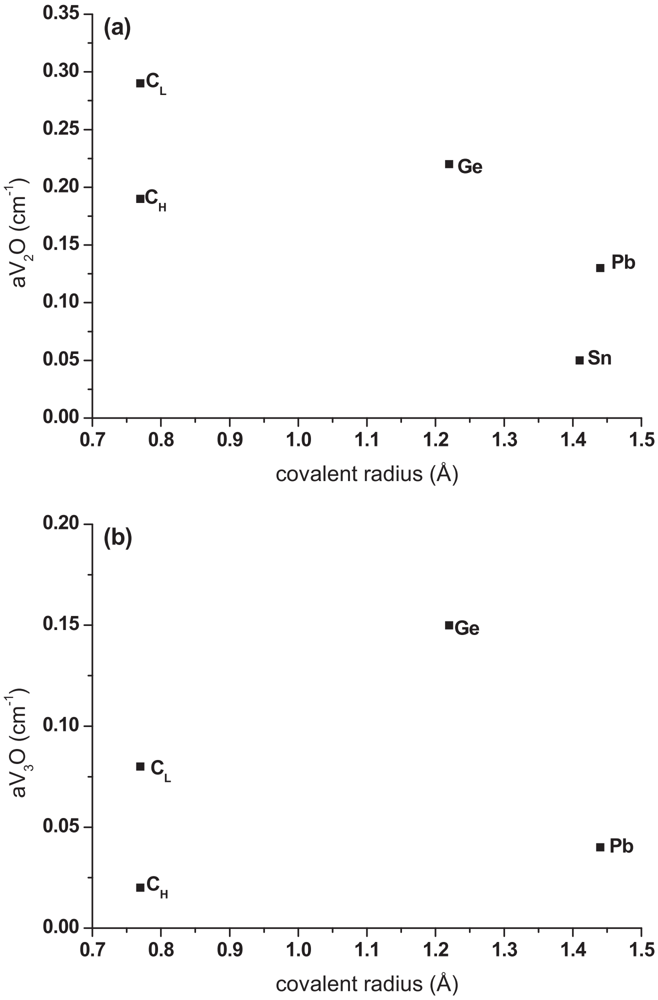

FIG. 8. The production of the V_2O (a) and the V_3O (b) clusters as a function of the isovalent dopants covalent radius.

introduced local strains, the equilibrium concentrations of vacancies and self-interstitials increase. The application of external hydrostatic pressure also increases the equilibrium concentrations and diffusion of vacancies and self-interstitials. Given that hydrostatic pressure affects[49,50] oxygen agglomeration processes in Si, it will be mutually beneficial to compare results from oxygen aggregation processes in isovalent doped Si with corresponding results where hydrostatic pressure is applied.

IV. CONCLUSIONS

Investigations of the properties and the behavior of radiation defects in Cz-Si doped with isovalent dopants aim to enhance the radiation hardness of Si-based devices. The present work was focused on oxygen-vacancy clusters and in particular on the VO, V_2O, and the V_3O clusters, which are effective recombination centers that are detrimental for devices.

Regarding the VO pair, we determined that its formation is enhanced by Ge but suppressed by the Sn and Pb. The phenomenon was attributed to the ability of the isovalent dopants to compete with oxygen in trapping vacancies. In the case of Ge, any GeV pairs formed in the course of the room temperature irradiation dissociate, increasing in essence the availability of vacancies and therefore the production of VO pairs. Conversely, the corresponding SnV and PbV pairs are stable at room temperatures thus decreasing the availability of vacancies, which results in the suppression of the VO production. The conversion of the VO to the VO_2 cluster is also suppressed by the isovalent dopants and in particular, the larger the covalent radius of the isovalent dopant the smaller the conversion ratio (a_{VO2}/a_{VO}). The phenomenon was discussed in terms of the local strains introduced by the larger isovalent impurities in the lattice, which affect the balance between the two main reactions that govern the VO annealing, that is $VO + O_i \rightarrow VO_2$ and $VO + Si_I \rightarrow O_i$. In the case of isovalent dopants the second reaction prevails over the first leading to a suppression of the VO_2 formation. Consistently, a decrease of the (a_{VO2}/ a_{VO}) ratio is observed as the isovalent radius increases from Ge to Sn to Pb. The larger strains are induced in the case of Pb were the smaller conversion ratio is observed. Additionally, the conversion ratio (a_{VO3}/ a_{VO2}) was found to increase as the covalent radius of the isovalent dopant increases. This behavior may be attributed to the enhanced diffusivity of oxygen atoms due to the presence of isovalent dopants. Finally, it is determined that the formation of the V_2O and the V_3O clusters shows a similar dependence on the covalent radius of the isovalent dopants as that of the VO pair. In essence the present study unambiguously proves the potential of isovalent doping on the oxygen-vacancy defects engineering for the improvement of the Si-based devices.

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