

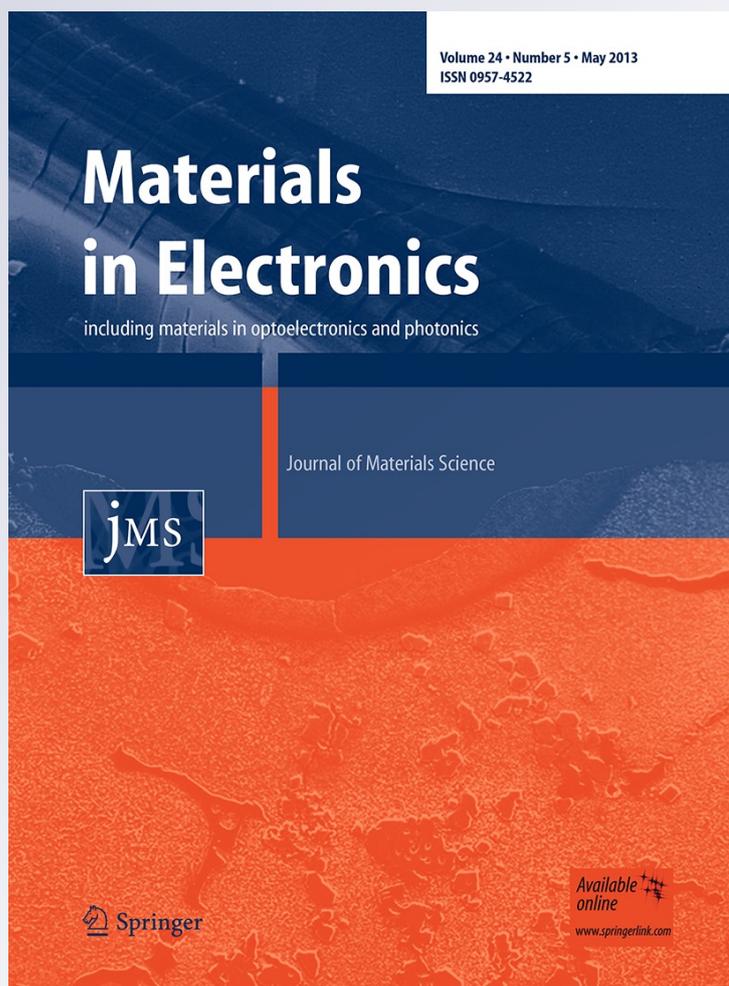
Impact of isovalent defect engineering strategies on carbon-related clusters in silicon

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Impact of isovalent defect engineering strategies on carbon-related clusters in silicon

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Abstract In electron-irradiated silicon (Si) the formation of oxygen-vacancy pairs (VO or A-centers) is deleterious and for this reason isovalent defect engineering strategies have been proposed to suppress their concentration. Carbon-related clusters such as C_iO_i and C_iC_s are also important as they are electrically active and their properties need to be determined. The present study has two aims. The first aim is to review the impact of isovalent doping [germanium (Ge), tin (Sn) and lead (Pb)] on the thermal stability of the C_iO_i and C_iC_s pairs in Si by means of infrared (IR) spectroscopy. The second aim is to analyze these results and show that the presence of isovalent dopants in Si reduces the temperature of annealing (T_{ann}) of the C_iO_i pairs and increases the temperature of annealing of the C_iC_s pairs. The results are discussed in view of recent experimental and theoretical studies. It is suggested that the change in the thermal stability of the C-related defects is due to the local strains induced in the lattice by the oversized isovalent dopants. It is surmised that these strains have an opposite impact on the T_{ann} of the C_iO_i and C_iC_s pairs as a result of their different structures.

1 Introduction

The properties of semiconductors are affected and can be tuned by the control of defects and doping [1–4]. In recent studies defect engineering strategies involving oversized isovalent dopants (Ge, Sn, Pb) were employed to suppress the formation of A-centers in Si [5]. In essence the oversized isovalent dopants trap vacancies limiting their availability for VO formation [5].

There are strong indications that Ge doping can enhance the radiation hardness of Si [6–12]. The potential of radiation hardness has also been demonstrated for Sn [13, 14] and Pb [15, 16] dopants in Si. The introduction of these oversized isovalent impurities in the Si lattice gives rise to local strain fields [17] affecting the properties of the intrinsic point defects (i.e. vacancies and self-interstitials). Consequently, the formation of radiation defects is expected to be affected and this is verified experimentally, both by electrical and optical techniques [6–16].

The efficacy of the defect engineering strategy will depend upon the impact it will have on the defect processes of all the impurities in the material. In Czochralski-grown Si (Cz-Si) carbon is unintentionally added in the lattice during crystal growth. C is isovalent to Si and is electrically inactive, however, upon irradiation it forms clusters such as C_iO_i and C_iC_s [18–22]. Both pairs are electrically active introducing levels in the energy gap, thus affecting the operation of Si-based electronic and optoelectronic devices. A comprehensive knowledge of the fundamental processes related with these pairs is required to control their formation, thermal stability and the mechanisms involved in their destruction. In previous studies [12, 14] we have reported that Ge and Sn affect the thermal stability of the C_iO_i and C_iC_s pairs. In the present work we

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Table 1 The O_i , C_s , C_iO_i and C_iC_s concentrations of the used samples

Sample	(Dopant) (cm^{-3})	Fluence (e cm^{-2})	$(C_s)_o$ 10^{16} (cm^{-3})	$(O_i)_o$ 10^{17} (cm^{-3})	(C_iO_i) 10^{16} (cm^{-3})	(C_iC_s) 10^{15} (cm^{-3})
Cz-Si	–	5×10^{17}	16	10	3.7	0.15
Sn _L	3×10^{17}	1×10^{18}	47	9.6	6.9	0.36
Sn _H	9×10^{18}	1×10^{18}	20	9.2	5.5	0.29
Pb	1×10^{18}	1×10^{18}	19	2.1	2	0.17
SnPb	$2 \times 10^{17}, 1 \times 10^{18}$	1×10^{18}	40	6.2	5.8	0.29
Ge _L	1×10^{18}	5×10^{17}	3	10	2	0.13
Ge _H	1×10^{19}	5×10^{17}	20	6.74	4.3	0.13

systematically study the effect of Ge, Sn and Pb doping on the thermal stability of C_iO_i and C_iC_s .

2 Experimental methodology

Four groups of Cz-Si samples of ~ 2 mm thickness, doped with Ge, Sn, Pb and (Pb/Sn) were used. In particular: (a) was Ge-doped with $[Ge] = 1 \times 10^{18} \text{ cm}^{-3}$ (Cz-Si:Ge_L) and $[Ge] = 1 \times 10^{19} \text{ cm}^{-3}$ (Cz-Si:Ge_H) (b) Sn-doped with $[Sn] = 3 \times 10^{17} \text{ cm}^{-3}$ (Cz-Si:Sn_L) and $[Sn] = 9 \times 10^{18} \text{ cm}^{-3}$ (Cz-Si:Sn_H), (c) was Pb-doped with $[Pb] = 1 \times 10^{18} \text{ cm}^{-3}$ (Cz-Si:Pb) and (d) codoped with Pb and Sn with $[Pb] = 1 \times 10^{18} \text{ cm}^{-3}$ and $[Sn] = 2 \times 10^{17} \text{ cm}^{-3}$ (Cz-Si:SnPb). Hereafter, for the sake of simplicity, the above samples will be named by the last part of their label, for instance Ge_L instead of Cz-Si:Ge_L and so on. An undoped Cz-Si sample was also used for comparison purposes. The Ge, Pb and Sn concentrations were determined by Secondary Ion Mass Spectrometry (SIMS). The oxygen and carbon concentrations were calculated by using calibration coefficients respectively $3.14 \times 10^{17} \text{ cm}^{-2}$ for the $1,107 \text{ cm}^{-1}$ oxygen band and $1.0 \times 10^{17} \text{ cm}^{-2}$ for the 605 cm^{-1} carbon band. The samples were irradiated with 2 MeV fast electrons at $\sim 80^\circ\text{C}$, using the Dynamitron accelerator at Takasaki-Jaeri (Japan). The irradiation fluence was $5 \times 10^{17} \text{ cm}^{-2}$ for the Ge-doped samples and $1 \times 10^{18} \text{ cm}^{-2}$ for the Sn and Pb doped samples. The initial concentrations of the C_s and O_i impurities and the concentrations of the C_iO_i and C_iC_s pairs of all the samples are given in Table 1. The C_iO_i and C_iC_s pairs concentrations were calculated by using calibration coefficients [23, 24] $1.1 \times 10^{17} \text{ cm}^{-2}$ for the 860 cm^{-1} carbon–oxygen band and $1.5 \times 10^{15} \text{ cm}^{-2}$ for the 546 cm^{-1} di-carbon band respectively. After the irradiations the samples were subjected to 20 min isochronal anneals in open furnaces in $\sim 10^\circ\text{C}$ steps, from room temperature up to 400°C . After each annealing step, the IR spectra were recorded with a Fourier Transform IR (FTIR) spectrometer (Jasco-470 plus), with a resolution of 1 cm^{-1} .

3 Results and discussion

Figure 1 presents the IR spectra after irradiation of some representative samples among those used in this study (Cz-Si, Ge_H, Sn_H and Pb samples). The well known bands of the carbon-related clusters C_iO_i (860 cm^{-1}) and C_iC_s (546 cm^{-1}), together with that of the VO (830 cm^{-1}) pair are clearly seen.

Figure 2 represents the evolution of the C_iO_i pair as a function of temperature for all the samples. It is observed that the annealing temperature (T_{ann}) of the C_iO_i cluster is always smaller in the isovalent doped material. Any other trend (i.e. a relation of the covalent radius with respect to the T_{ann}) cannot be deduced from the present results.

Figure 3 demonstrates the evolution of the C_iC_s pair as a function of temperature for all the samples considered. The annealing temperature of the C_iC_s pair is always higher in the isovalent doped Si than that in the undoped Si. From the present results, it can be tentatively established that T_{ann} increases with the increase of the covalent radius (r).

Figure 4 represents the annealing temperature T_{ann} of the (a) C_iO_i and the (b) C_iC_s pairs with respect to the

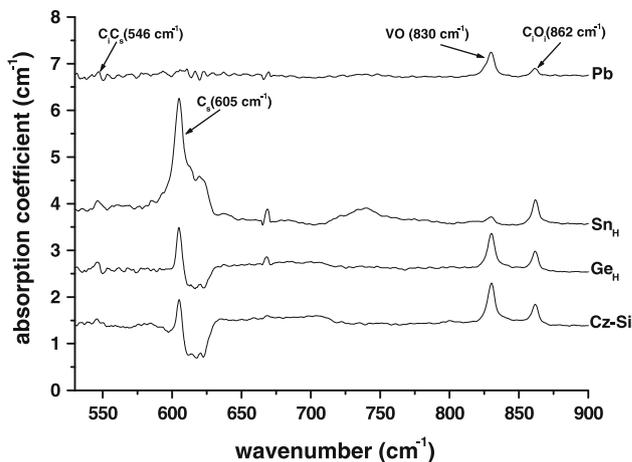


Fig. 1 Fragments of IR absorption spectra after irradiation for some representative samples used in this experiment (Cz-Si, Ge_H, Sn_H, Pb)

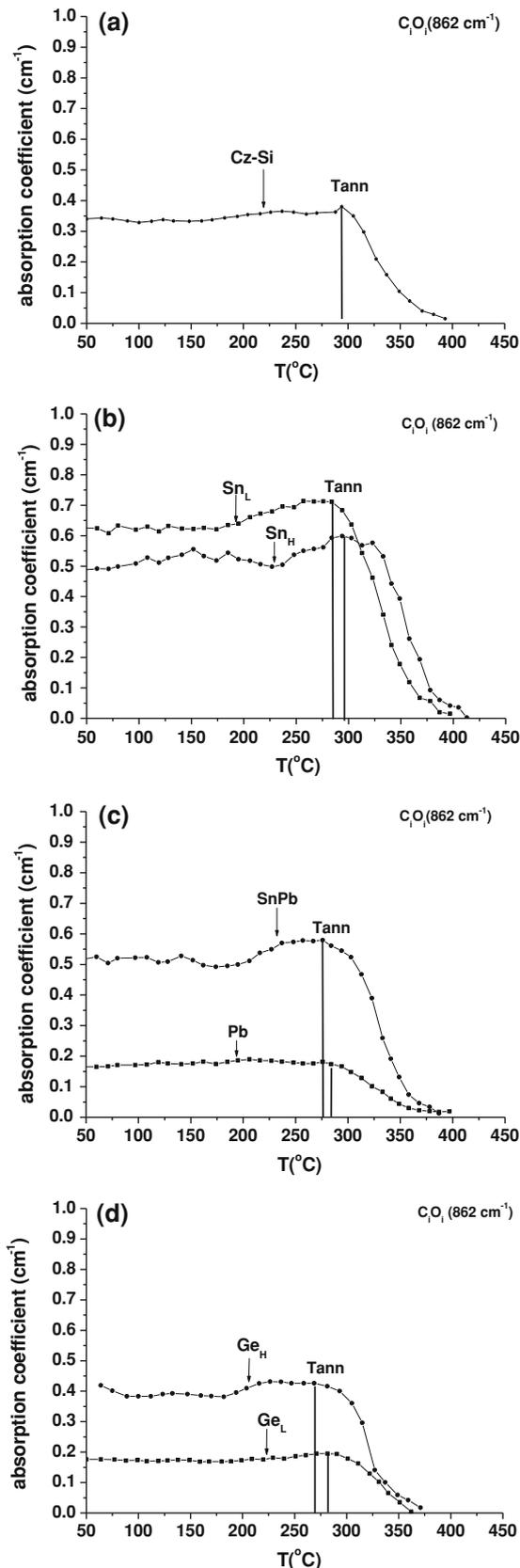


Fig. 2 The evolution with temperature of the C_iO_i 862 cm^{-1} band for the **a** Cz-Si, **b** Sn_L and Sn_H , **c** Pb and SnPb, **d** Ge_L and Ge_H

concentration of the isovalent dopants for all the samples considered. From Fig. 4 it becomes clear that isovalent dopants in Si reduce the temperature of annealing of the C_iO_i pairs and increase the temperature of annealing of the C_iC_s pairs. Although for the C_iO_i there is no clear relation of the T_{ann} with respect to the covalent radius of the isovalent dopants, for the C_iC_s pairs the T_{ann} increases for the oversized dopants (Sn, Pb and Sn + Pb) when the dopant concentration is $1 \times 10^{18}\text{ cm}^{-3}$ or more (refer to Fig. 5). Furthermore, the magnitude of the increase of the T_{ann} for the C_iC_s pair is substantially larger than the corresponding decrease of the T_{ann} for the C_iO_i pair. This is an indication that the effect of the induced strains by the oversized dopants on the thermal stability of the C-related defects is related with the particular geometry of the pairs, as it is mentioned below.

Importantly, C_iO_i and C_iC_s pairs introduce deep levels in the energy gap of Si and therefore can affect its electrical properties. In particular, C_iO_i complexes are thought to act as recombination centers [25, 26] which may lead to a severe degradation of Si devices. Interestingly, for C_iC_s recent research on Si lasers has demonstrated that its introduction can be used to obtain optical gain and stimulated emission that in turn enhances the performance of Si-based devices [27]. In previous FTIR studies it was determined that the concentration of C_iO_i and C_iC_s pairs is suppressed in the Sn-doped Si and Pb-doped Si as compared with Ge-doped Si or undoped Si [14, 15]. The introduction of the oversized Sn or Pb in the lattice is bound to affect the concentration of the carbon-related clusters as they will associate with the substitutional carbon atoms to relieve the strains around them (therefore there will be less unbound C_s atoms ready to associate and form C-related clusters) [28]. On the contrary, oversized dopants repel the O_i at nearest neighbor positions [28]. Reverting back to the issue of the temperature of annealing the question is why do the two pairs behave differently? The reduction of the T_{ann} of C_iO_i implies that this pair is less bound in doped Si, whereas the increase of the T_{ann} of C_iC_s implies that this pair is more bound in doped Si. One way to explain the increase in binding energy of C_iC_s would be to propose the formation of dopant- C_iC_s clusters. There is no experimental evidence, however, to support such a scenario. Another way to explain the different behavior of the C_iO_i and C_iC_s pairs is to consider the induced strain fields in the lattice due to the incorporation of the oversized isovalent dopants (note in Fig. 4 (b) only the high content Sn has a significant impact as opposed to the low content Sn). These strains certainly affect the mechanisms of diffusion of the various impurities and defects, which in turn have an impact on the thermal stability of radiation induced defects.

Further to this discussion we notice that both C_iO_i and C_iC_s pairs anneal out by dissociation [18] ($C_iO_i \rightarrow C_i + O_i$)

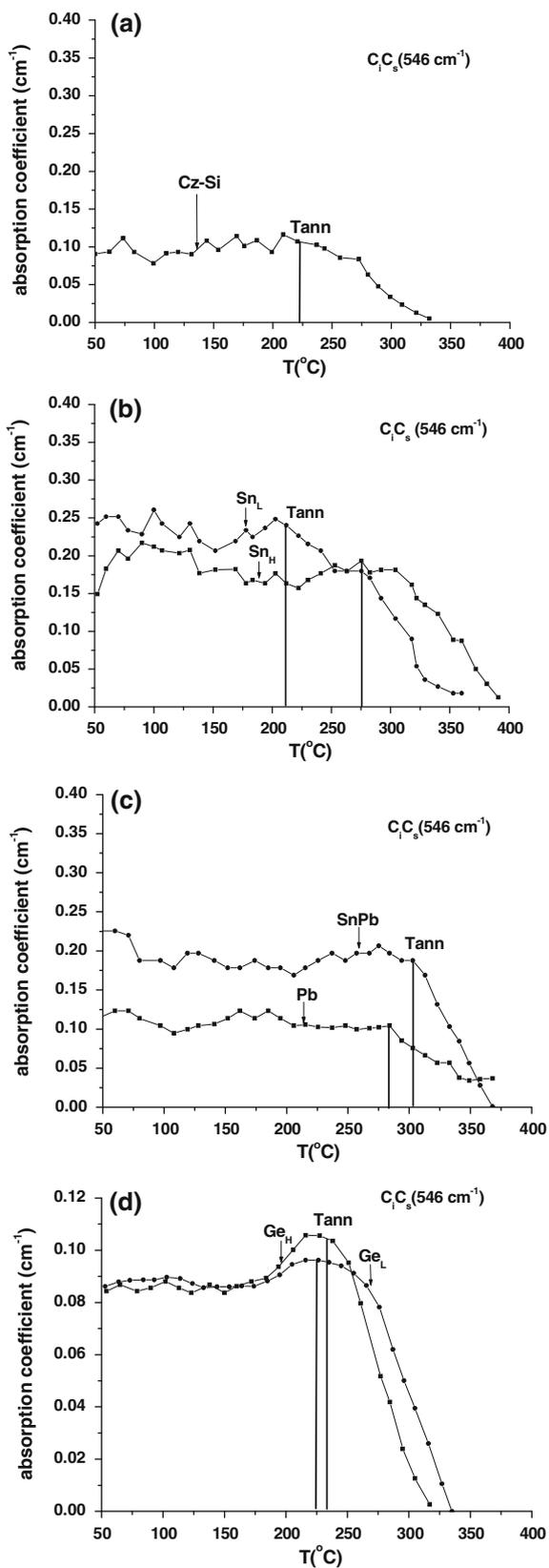


Fig. 3 The evolution with temperature of the C_iC_s 546 cm⁻¹ band for the **a** Cz-Si, **b** Sn_L and Sn_H, **c** Pb and SnPb, **d** Ge_L and Ge_H

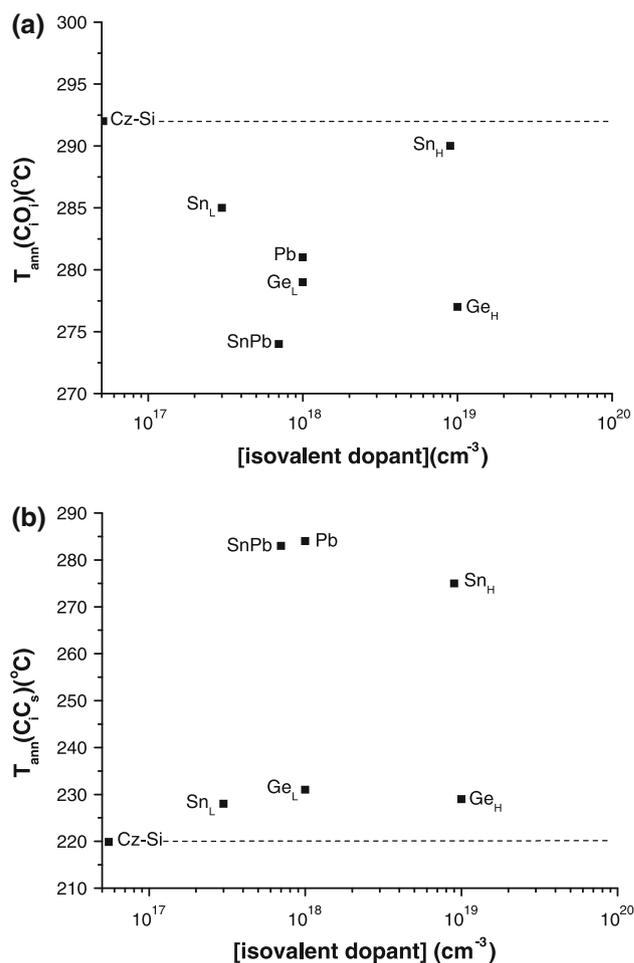


Fig. 4 Annealing temperatures of the **a** C_iO_i and **b** C_iC_s pairs versus isovalent dopant concentrations

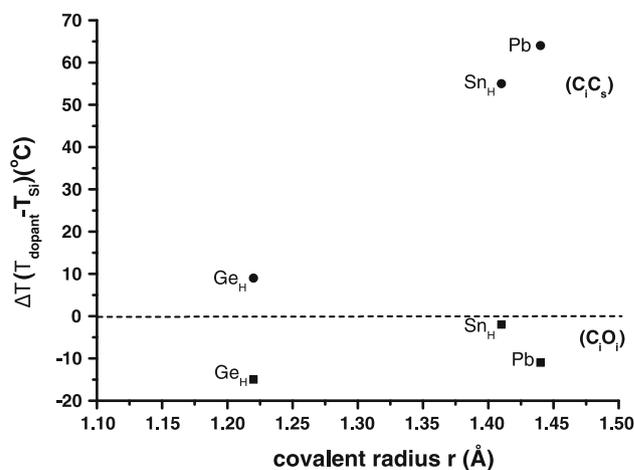


Fig. 5 The variation of the T_{ann} of the **a** C_iO_i and **b** C_iC_s pairs versus the covalent radius of the isovalent dopants

and (C_iC_s → C_i + C_s). Thus the annealing temperature of the two complexes represents the temperature of their breaking up. Due to the fact that the dopants considered here

are isovalent, it is reasonable to conclude that the effect of doping on the annealing temperature of the two defects is in essence the effect of the local strains. These are induced in the lattice by the larger isovalent dopants, and it is believed that they have a significant impact on the strength of the bonds in the C_iO_i and C_iC_s structures. In the case of C_iO_i [29] the structure comprises a carbon interstitial atom slightly disturbed from its isolated configuration, pairing with an interstitial oxygen atom. The C_iC_s pair on the other hand can exist in two configurations A and B [24, 30]. In heavily electron irradiated Si, C_iC_s is expected to be in the neutral charge state, which corresponds to the B configuration where a bond-centered Si atom is lying between two substitutional carbon atoms. Recent theoretical studies have calculated a binding energy E_b for the C_iC_s defect in the B configuration as 1.28 eV ($C_i^\circ + C_s^\circ \rightarrow C_iC_s^\circ + E_b$) [31], and a binding energy for the neutral charge state of the C_iO_i defect as 1.63 eV ($C_i + O_i \rightarrow C_iO_i + E_b$) [32]. Our experimental results indicate that the energy required to dissociate the C_iO_i pair is smaller in the presence of isovalent dopants, although it is larger for the C_iC_s pair. It is surmised that, the effect of local strains may have a different impact on the strength of bonds of the two structures. In essence, the potential barrier for the dissociation is affected differently by the presence of isovalent dopants. In particular, in the case of the C_iO_i pair the barrier decreases, although the opposite is observed for the C_iC_s pair. The constant k of the reaction that describes the dissociation of the pairs can be expressed by the following relation: $k = k_0 e^{-(E_a/KT)}$, where K is Boltzmann's constant. The activation energy E_a characterizes the dissociation of the pairs upon annealing. We consider that the two main contributions of E_a are the formation energy E_f of the pair and its binding energy E_b , ($E_a \approx E_f + E_b$). It can be argued that the binding energy E_b is affected by the strain, which introduces another energy term E_s . In other words, when oversized isovalent dopants are introduced in the lattice the binding energy becomes $E_b^* = E_b + E_s$. In the case of C_iO_i , the E_s is presumably negative reducing the binding energy and actually the activation energy E_a of the dissociation of the pair. Conversely, in the case of the C_iC_s pair E_s is positive leading to an opposite result.

4 Conclusions

Isovalent defect engineering strategies will influence the thermal stability, that is the T_{ann} of the C_iO_i and C_iC_s pairs differently. It is determined that the T_{ann} for C_iO_i pairs will be reduced, whereas for C_iC_s pairs T_{ann} will increase. The phenomenon is discussed in terms of the local strains introduced in the lattice by the isovalent dopants and the effect of these strains on the T_{ann} of the C_iO_i and C_iC_s pairs. It is argued that the magnitude and the size of the

change of the T_{ann} is related with the particular structure of each one of these defects. To conclude, isovalent defect engineering strategies aiming to reduce the concentration of A-centers (will also reduce the concentration of C_iO_i and C_iC_s) will constitute C_iC_s pairs more thermally stable and C_iO_i pairs less thermally stable. This is in turn beneficial as C_iO_i pairs are deleterious, whereas C_iC_s pairs can be utilized in certain devices.

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