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Effect of germanium doping on the annealing characteristics of oxygen and carbon-related defects in Czochralski silicon

C. A. Londos,[1,a)] A. Andrianakis,[1] E. N. Sgourou,[1] V. Emtsev,[2] and H. Ohyama[3]
[1]*Solid State Physics Section, University of Athens, Panepistimiopolis Zografos, Athens 157 84, Greece*
[2]*Ioffe Physicotechnical Institute of the Russian Academy of Sciences, Politeknicheskaya ul. 26, 194021 St. Petersburg, Russia*
[3]*Kumamoto National College of Technology, 26592, Nishigoshi, Kumamoto 861-1102, Japan*

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This paper is devoted to the annealing studies of defects produced in carbon-rich Ge-doped Czochralski-grown Si (Cz-Si) by 2 MeV electron irradiation. The annealing temperature of vacancy-oxygen (VO) complexes, carbon interstitial-oxygen interstitial (C_iO_i), and carbon interstitial-carbon substitutional (C_iC_s) pairs as well as the formation temperature of vacancy-two oxygen (VO_2) complexes are monitored as a function of Ge concentration. It has been established that the annealing of C_iO_i and C_iC_s defects remains practically unaffected by the Ge presence, whereas the annealing temperature of VO defects and the formation temperature of VO_2 complexes are substantially lowered at Ge concentrations larger than 1×10^{19} cm^{-3}. The hydrostatic component of elastic strains introduced by Ge atoms in the Si crystal lattice was calculated. It appears to be very small, at least insufficient to exert a pronounced effect upon the annealing behavior of radiation-produced defects. This conclusion is in line with what is observed for the C_iO_i and C_iC_s species. In the case of VO, whose annealing process in Cz-Si is concurrently conducted by two reaction paths $VO+O_i\rightarrow VO_2$ and $VO+Si_I\rightarrow O_i$, we suggest that the latter reaction in Ge-doped Cz-Si is enhanced by emitting self-interstitials (Si_I) from loosely bound self-interstitial clusters predominantly formed around Ge impurity atoms. As a result, the liberation of self-interstitials at lower annealing temperatures leads to an enhanced annealing of VO defects. An enhanced formation of VO_2 complexes at lower temperatures is also discussed in terms of other reactions running in parallel with the reaction $VO+Si_I\rightarrow O_i$. *© 2010 American Institute of Physics.*
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I. INTRODUCTION

It is well known that the routine processing Si materials for device applications is always tied with structural defects produced during etching, heat treatment, oxidation, etc. Therefore, the understanding of how structural defects and their interactions with impurities can affect electrical and optical properties of materials to be processed is vital both from the practical and scientific point of view. However, detailed studies of processing-induced defects is hardly realized, so a convenient way of defect investigations is usually provided by fast electron irradiation. This technique allows one to produce intrinsic point defects in a controllable manner. The primary radiation defects are Frenkel pairs unstable at room temperature. Their fate during irradiation is to annihilate or separate into isolated vacancies V and self-interstitials Si_I.[1] These intrinsic defects being mobile at room temperature make it possible to investigate any defect-impurity reactions under favorable conditions.

The two electrically inactive impurities unintentionally added in Si crystals grown by the Czochralski technique (Cz-Si) are oxygen and carbon, both being present in appreciable concentrations. Oxygen atoms are known to be effective traps for mobile vacancies in both n-type and p-type silicon giving rise to the formation of vacancy-oxygen (VO) complexes via the well-known reaction path $V+O_i\rightarrow VO$. These defects called the A-centers are electrically active, having an acceptor level at 0.17 eV below the conduction band.[2–4] They are also optically active, with infrared (IR) bands at 830 cm^{-1} and 885 cm^{-1} in the neutral and negative charge states, respectively.[5,6] The A-centers are annealed out around 300 °C and their annealing proceeds mainly through two reactions: $VO+O_i\rightarrow VO_2$ and $VO+Si_I\rightarrow O_i$.[7,8] The vacancy-two oxygen (VO_2) defect in n-type material is electrically neutral[9] but optically active, with an IR band at 888 cm^{-1}.[5,10]

On other hand, carbon atoms in Si are effective traps for mobile self-interstitials leading to the formation of interstitial carbon-related defects via the reaction $C_s+Si_I\rightarrow C_i$. These interstitial carbon atoms disappear just above room temperature, being involved in many quasichemical reactions with intrinsic point defects as well as other impurities present in silicon crystals.[11–13] Mobile C_i defects can be trapped by O_i atoms giving rise to the formation of C_iO_i complexes by the reaction $C_i+O_i\rightarrow C_iO_i$ or by C_s atoms leading to the appearance of C_iC_s pairs by the reaction $C_i+C_s\rightarrow C_iC_s$. The C_iO_i defect having an energy level at 0.36 eV above the valence band[14] is electrically active. It is also optically active giving rise to a number of local vibrational bands, among them the most intense band is at 862 cm^{-1}.[13,15] The C_iO_i defects can be annealed out at around 300 °C.[13] The C_iC_s pair is bistable and amphoteric, with energy levels at $E_c-0.17$ eV and E_v

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[a)]Electronic mail: hlontos@phys.uoa.gr.

+0.09 eV in one configuration and at $E_c-0.11$ eV in the other.[16] It is also optically active giving rise[17] to a number of local vibrational modes mainly detected only at cryogenic temperatures. Among them, a band at around 544 cm^{-1} is detected by IR measurements[18] at room temperature, too. The C_iC_s pairs are disappeared at around 250 °C.[18]

The demand for improvements of Si based devices (higher operation speed and radiation hardness, lower noise level, and chip size) requires close control over defect reactions in Si. The presence of structural defects in material is usually a limiting factor in the device operation. The understanding of their behavior is very important for rapid progress in device technology.[19] In this context, the doping of Si with isovalent impurities has gained considerable interest. Germanium in Si is an isovalent impurity. Being electrically inactive in Si, the presence of this impurity does not affect electrical properties of materials. These impurity atoms assume normally lattice sites and because of their bigger atomic size as compared to that of host atoms (cf. relevant covalent radii $\alpha_{Si}=1.17$ Å and $\alpha_{Ge}=1.22$ Å) they induce noticeable elastic strains in the lattice. Because of this Ge impurity atoms can affect defect-impurity interactions, first of all producing marked effects upon quasichemical reactions with vacancies and self-interstitials. Such changes are easily observed in Ge-doped silicon under irradiation.

The application of stress on materials and/or the appearance of internal stress during processing is another important technological issue. Depending on the case, stresses in Si may have beneficial or detrimental effects on the fabrication of devices. Any relevant information on their effects in Si is of high interest. It is worth noting that the application of external pressures, either uniaxial or hydrostatic, is a common technique to investigate stress-related phenomena not only in semiconductors but generally in solids.[20–24] On the other hand, it is known that internal stress in the Si crystal lattice due to the Ge presence affects the defect behavior as well.[25–27] Thus, the use of external or internal stresses in Si materials may be beneficial for device manufacture.

In this paper that broadens our study[28–31] of the defect behavior in Ge-doped Cz-Si new light is shed on the role of Ge impurity atoms in the annealing processes of oxygen-related and carbon-related defects such as VO, C_iO_i, and C_iC_s and also in the formation of VO_2 complexes.

II. EXPERIMENTAL

Samples used in this work were cut from prepolished Cz-Si wafers. Their dimensions were $20\times10\times2$ mm^3. The initial germanium, carbon, and oxygen concentrations in those samples are given in Table I. The concentrations of Ge impurity were estimated from the mass ratio of Si and Ge in the melt provided by the supplier's certificate. It is known that Raman spectroscopy is an effective tool for determining Ge concentrations in SiGe crystals.[30] Unfortunately, in our case of Ge-doped Si crystals with Ge concentrations of about one atomic per cent or less this technique can be used only for a qualitative comparison of Raman spectra, since the relations between the frequencies of optical phonons and Ge content in this concentration range is unknown. Because of this the mass ratio of Si and Ge in the melt appears to be an only appropriate guide to the scale of Ge content. The samples were irradiated with 2 MeV electrons using the Dynamitron accelerator at Takasaki-JAERI (Japan). The irradiation dose was 5×10^{17} cm^{-2}. After the irradiation, all the samples were subjected to isochronal anneal up to 600 °C, in steps of $\Delta T\approx10$ °C and $\Delta t=20$ min. After each annealing step, IR spectra were recorded at room temperature by means of a Fourier transform IR spectrometer with a resolution of 1 cm^{-1}. The two phonon intrinsic absorption was always subtracted by using a float-zone sample of equal thickness.

TABLE I. Initial concentrations of Ge, O, and C in the Cz-Si:Ge samples used.

Sample	[Ge] (cm^{-3})	$[O_i]_0$ (10^{17} cm^{-3})	$[C_s]_0$ (10^{16} cm^{-3})
Cz-Si	⋯	9.56	<2.0
Ge-1	1×10^{17}	9.60	2.0
Ge-2	7×10^{17}	6.50	<2.0
Ge-3	1×10^{18}	10.00	3.0
Ge-4	4×10^{18}	5.55	10.0
Ge-5	1×10^{19}	6.74	20.0
Ge-6	5×10^{19}	7.60	<2.0
Ge-7	1×10^{20}	8.77	3.7
Ge-8	2×10^{20}	7.70	18.0

III. RESULTS AND DISCUSSION

Figure 1 shows some IR spectra of the Cz-SiGe-7 sample (shortly Ge-7; hereafter all the Ge-doped Cz-Si samples are labeled in the similar way) before and after the irradiation, as well as after an annealing step at 350 °C. In the irradiated sample the bands of VO defects (830 cm^{-1}), C_iO_i defects (862 cm^{-1}), C_iC_s defects (544 cm^{-1}), as well as $C_iO_i(Si)_I$ complexes (936, 1020 cm^{-1}) are observed. After an annealing step at 350 °C the 888 cm^{-1} band of VO_2 defects can also been seen in the spectra.

Figure 2 displays the thermal evolution of VO and VO_2 defects in the Cz-Si, Ge-3, Ge-6, and Ge-8 samples. Appar-

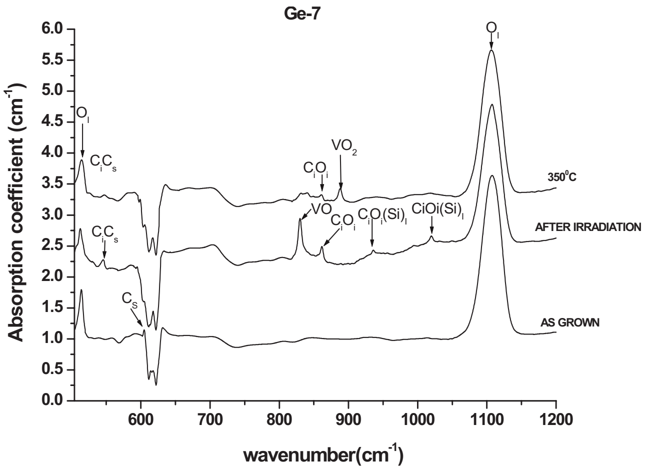

FIG. 1. IR spectra of the Ge-7 sample (a) before, (b) after irradiation, and (c) after annealing at 350 °C.

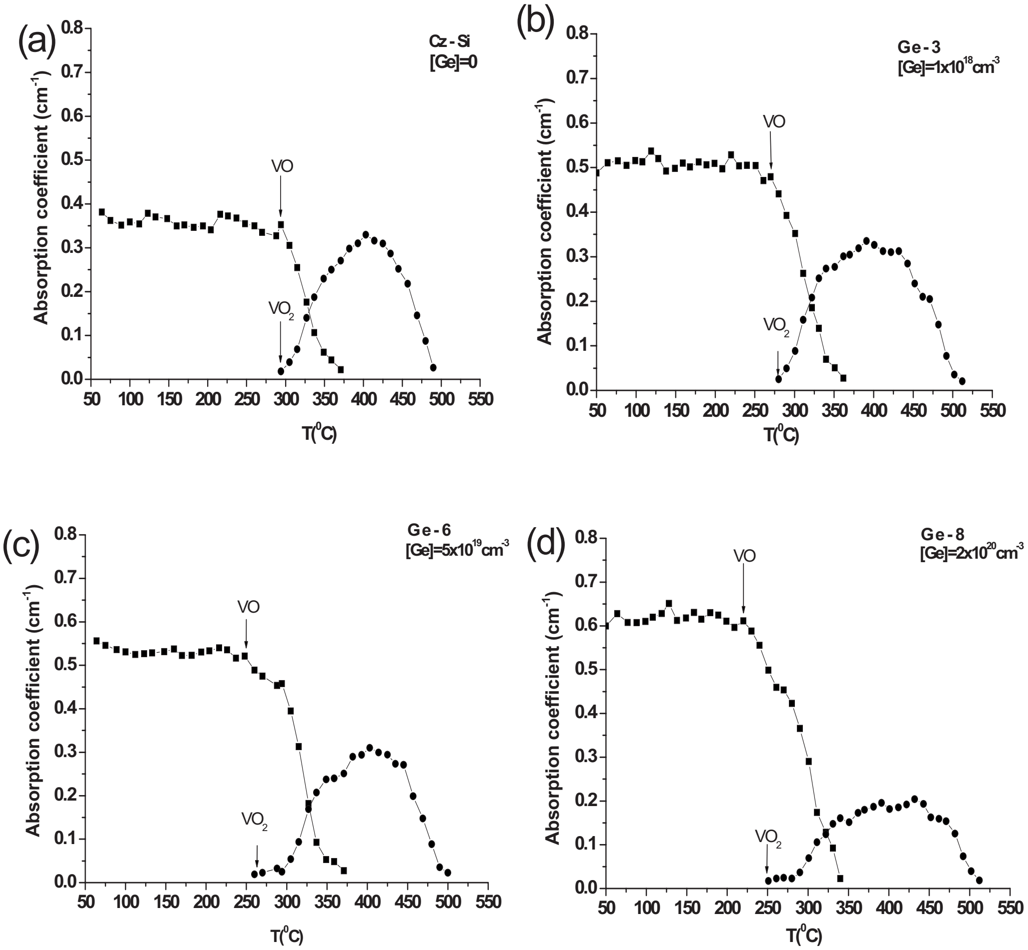

FIG. 2. Thermal evolution of VO and VO_2 defects in samples (a) Cz-Si, (b) Ge-3, (c) Ge-6, and (d) Ge-8.

ently, the annealing temperature of VO complexes ($T_{ann\ VO}$), i.e., the temperature at which the defects begin to disappear in the IR spectra, decreases as the concentration of Ge impurity increases. As a consequence, the formation temperature of VO_2 defects ($T_{form\ VO2}$), i.e., the temperature at which these defects start to appear in the spectra, decreases, too. Moreover, at large Ge concentrations the annealing temperature of VO defects turned out to be even lower than the formation temperature of VO_2 complexes; cf. the evolution curves of VO and VO_2 defects in the Ge-8 sample in Fig. 2. These observations will be discussed below.

Figures 3 and 4 depict the characteristic temperatures $T_{ann\ VO}$ and $T_{form\ VO2}$ as a function of Ge concentration for all the samples studied. As is seen, the $T_{ann\ VO}$ decreases slightly at [Ge] up to $4\times10^{18}\ cm^{-3}$ as compared to the Ge-undoped Cz-Si sample but at larger [Ge] the decrease in $T_{ann\ VO}$ becomes much more pronounced. Actually, in the Ge-8 sample with $[Ge]=2\times10^{20}\ cm^{-3}$ the $T_{ann\ VO}$ was found to be ~220 °C, which one should compare to 290 °C characteristic for the Ge-undoped Cz-Si sample. In other words, a shift in about 70 °C in the annealing temperature is clearly defined. A similar behavior of the formation temperature of VO_2 complexes, $T_{form\ VO2}$, is also evident. In actual fact, in the Ge-8 sample the $T_{form\ VO2}$ is about 250 °C, displaying a shift of 40 °C as compared to the Ge-undoped Cz-Si sample. At $[Ge]<4\times10^{18}\ cm^{-3}$ the both $T_{ann\ VO}$ and $T_{form\ VO2}$ are nearly the same, although at $[Ge]>4\times10^{18}\ cm^{-3}$ a marked difference between them is observed, being ~30 °C at $[Ge]=2\times10^{20}\ cm^{-3}$.

To explain the thermal behavior shown in Figs. 3 and 4 one should consider the basic defect reactions underlying the annealing of VO defects and formation of VO_2 complexes. These reactions are $VO+O_i\rightarrow VO_2$ and $VO+Si_I\rightarrow O_i$.[8] It would be reasonable to believe that clusters of self-interstitials formed during irradiation serve as a source of isolated self-interstitials upon annealing.[7] First, it is worth

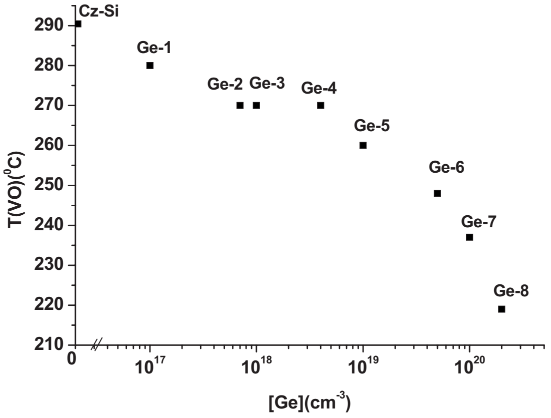

FIG. 3. Annealing temperature of VO defects vs Ge concentration.

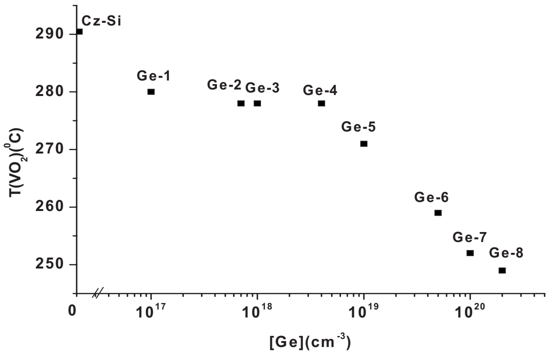

FIG. 4. Formation temperature of VO_2 defects vs Ge concentration.

noting that the carbon presence in Cz-Si materials does not produce any pronounced effect upon the $T_{\text{ann VO}}$. On the other hand, it has been suggested[32,33] that Ge impurity atoms are effective traps for mobile VO defects. In actual fact, in SiGe materials two peaks at 834.6 and 839.2 cm^{-1} are thought to be associated with the VO–Ge complexes. However, in our investigation of electron-irradiated Ge-doped Cz-Si these bands were not observed. Generally speaking, they might exist but their intensity could be below the detection limit of our optical equipment. What is more, any reliable report on such bands in Ge-doped materials is lacking in the literature. Because of this one should think of a stress-related enhanced annealing of VO complexes in Cz-SiGe taking into account that compressive hydrostatic pressures increase the diffusivity of vacancy-impurity atom complexes in Si.[34] Furthermore, we note that in the course of isothermal annealing the annealing rate of VO defects, α, as a function of pressure, adheres[35,36] the expression

$$\left.\frac{\partial \ln a}{\partial P}\right|_T = -\frac{\Delta V_{\text{act}}}{K\text{T}}, \tag{1}$$

where $\Delta V_{\text{act}}=-4.5$ Å^3/defect is the corresponding activation volume. Therefore, the $\vartheta \ln a/\vartheta P$ is positive, indicating that the annealing rate of VO defects is enhanced under pressure. Really, at pressures around 5 kbar the annealing rate of these defects can be markedly increased; see Fig. 5 of Ref. 35. In addition, it should be noted that inhomogeneous distributions of Ge impurity atoms in Cz-Si at [Ge] around 10^{20} cm^{-3} lead to the appearance of large clusters of Ge atoms which are associated with considerable strain fields in the crystal lattice.[37] This, in turn, can also enhance the annealing rate of VO complexes. Because of this it will be interesting to assess the stress induced by Ge impurity atoms in Si.

Let us roughly estimate the stress related to the presence of Ge impurity atoms in the Si lattice. The application of external hydrostatic pressure P on Si crystal leads to a change in the unit cell volume. It has been found that at pressures up to 45 kbar the relative change in the volume of an undoped Si crystal can be derived from the empirical equation[38]

$$\frac{\Delta V}{V_0} = \alpha_0 + \alpha P + bP^2 + cP^3, \tag{2}$$

where $\Delta V = V_0 - V$; V_0 and V are the unit cell volume under normal conditions and applied pressure, respectively. In the case of silicon the coefficients in the equation are[38] $\alpha_0=0$, $\alpha=10.211\times10^{-4}$ kbar^{-1}, $b=-2.9614\times10^{-6}$ kbar^{-2}, and $c=0$ kbar^{-3}. Owing to their bigger atomic size than that of host atoms the presence of Ge atoms in the Si lattice induces strains because of the increasing volume of the unit cell. Defining the "defect volume" υ^d as an increase in the volume if one Si atom is replaced by a Ge atom, the volume V_{N+n} of a crystal containing N atoms of Si and n atoms of Ge is given by [see p. 326 of Ref. 39]

$$V_{N+n} = V_1 + \frac{n}{N}(N\upsilon^d + V_1), \tag{3}$$

where V_1 stands for the volume of a crystal containing only N atoms of Si. Equation (3) has been obtained from the general thermodynamical concepts provided that the concentration of an impurity is small enough to produce a linear relationship between the volume V_{N+n} and impurity concentration. With the aid of Eq. (3) the relative increase in the unit cell volume can be expressed by (see p. 328 of Ref. 39)

$$\frac{\Delta V}{V_1} = \frac{n}{N}\left(\frac{\upsilon^d}{\upsilon^{\text{Si}}}\right), \tag{4}$$

where $N=5\times10^{22}$ cm^{-3} is the number of host atoms in Si and υ^{Si} is the volume per one atom in undoped Si. The experimental value of the linear expansion coefficient for one Ge atom in Si has been found[40] to be 6.2×10^{-25} cm^3 and hence the volume coefficient υ^d, which is thrice as large, would be 1.86×10^{-24} cm^3. Thus the relative volume expansion of the unit cell in Ge-doped Si at [Ge] of about 10^{20} cm^{-3} is approximately 1.86×10^{-4}. Upon differentiating Eq. (3) in respect to pressure, it follows that the compressibility κ of a Si crystal containing n atoms of Ge differs from the compressibility κ^{Si} of a "pure" Si crystal by (see p. 33 of Ref. 39)

$$\kappa - \kappa^{\text{Si}} = \frac{n}{N}\frac{\upsilon^d}{\upsilon^{\text{Si}}}(\kappa^d - \kappa^{\text{Si}}),$$

where κ^d is the compressibility of the volume υ^d defined as $\kappa^d = (-1/\upsilon^d)\cdot(d\upsilon^d/dP)_{\text{T}}$ or in a similar way due to relation (4) by

$$\kappa - \kappa^{\text{Si}} = \frac{\Delta V}{V_1}(\kappa^d - \kappa^{\text{Si}}). \tag{5}$$

Thus, to see how the compressibility of a pure Si crystal is affected by the presence of Ge atoms one must know an order-of-magnitude value of κ^d. Unfortunately, the experimental value of κ^d is not available in the literature. In the absence of a better approximation, we rely on a thermodynamical model[41,42] (for a review see Ref. 43), giving

$$\frac{\kappa^d}{\kappa^{\text{Si}}} = 1 - \frac{B_T B_T''}{B_T' - 1}, \tag{6}$$

where B_T $(=1/\kappa^{\text{Si}})$ is the isothermal bulk modulus and B_T', B_T'' designate the first and second derivatives of B_T in respect to the stress for undoped Si crystal. Taking into account that $B_T B_T'' \approx -B_T'$ (see p. 206 of Ref. 39) and inserting[44] $B_T'=3.20$ it can be found that $\kappa^d/\kappa^{\text{Si}} \approx 2.5$. Thus, setting κ^d

$\approx 2.5\kappa^{\mathrm{Si}}$, and $\Delta V/V_1$ is 1.86×10^{-4} in Eq. (5) one can conclude that, to a first approximation, κ and κ^{Si} differ only slightly. In other words, an addition of a small amount of Ge into Si crystals does not significantly affect its compressibility κ^{Si}. Therefore, it makes possible using the same coefficients a, b, and c as those determined in Ref. 38 for a pure Si crystal. These coefficients show that at pressures up to 45 kbar Eq. (2) is simplified to $\Delta V/V_0 \approx aP$ giving $P \approx 0.2$ kbar. Hence, the hydrostatic component of internal stress due to the presence of Ge atoms at $[\mathrm{Ge}]\approx 10^{20}\ \mathrm{cm}^{-3}$ is very small to be insufficient to exert a noticeable effect on the annealing behavior of radiation-produced defects.

Actually, this is the case for the $\mathrm{C_iO_i}$ and $\mathrm{C_iC_s}$ species. Figure 5 displays the thermal evolution of $\mathrm{C_iO_i}$ defects in the Ge-3, Ge-5, and Ge-8 samples. Figure 6 depicts the annealing temperature $\mathrm{T_{ann\ CiOi}}$ of $\mathrm{C_iO_i}$ defects against Ge concentration. The $\mathrm{T_{ann\ CiOi}}$ is apparently the same for all the Ge-doped samples and it turned out to be lower by ~10 °C as compared to that for Ge-undoped Cz-Si. The thermal evolution of $\mathrm{C_iC_s}$ pairs in the Ge-3, Ge-5, and Ge-8 samples is given in Fig. 7. Figure 8 shows how the annealing temperature $\mathrm{T_{ann\ CiCs}}$ of $\mathrm{C_iC_s}$ pairs varies with Ge concentration. The $\mathrm{T_{ann\ CiCs}}$ is obviously the same for all the Ge-doped samples and it displays a slight increase of ~10 °C as compared to that for Ge-undoped Cz-Si. It appears that the annealing mechanisms governing the disappearance of carbon-related defects in IR spectra are not affected by the Ge presence at least at $[\mathrm{Ge}]$ up to $2\times 10^{20}\ \mathrm{cm}^{-3}$. In any case, the behavior of such interstitial defects is expected to be little influenced[35] by high hydrostatic stresses, in contrast to those of vacancy type; cf. a shift of ~10 °C in the annealing temperatures $\mathrm{T_{ann\ CiOi}}$ and $\mathrm{T_{ann\ CiCs}}$, though different in sign.

A peculiar annealing behavior of VO defects should be stemmed from other reasons. Importantly, deep level transient spectroscopy (DLTS) measurements on $\mathrm{Si}_{1-x}\mathrm{Ge}_x$ materials with $x=0.015$ have shown that upon isochronal annealing the peak associated with VO defects starts to decrease at temperatures around 200 °C as contrasted to about 300 °C in Ge-free Cz-Si; see Fig. 4 of Ref. 32). This decrease in the annealing temperature of VO complexes is accompanied by the appearance of another DLTS peak reportedly related to VO–Ge complexes, with an Ge atom in the first nearest neighbor surrounding. This tentative identification was connected with earlier data[33] on two IR bands at 834.6 and 839.2 cm^{-1} attributed to a VO structure perturbed by a nearby Ge atom. As was already mentioned above, these bands if exist are very weak and in our Ge-doped materials with Ge concentrations less than 1 at. % they may be undetectable. On the other hand, the formation of VO–Ge defects cannot account for an enhanced formation of $\mathrm{VO_2}$ complexes. Therefore, other reasons for a plausible explanation of our data should be suggested. In Ge-doped Cz-Si it is possible that a fraction of self-interstitials may be responsible for formation of loosely bound $\mathrm{Si_I}$ clusters around Ge atoms. Upon annealing below 300 °C, they can be emitted from these clusters leading to the enhanced disappearance of VO defects via the reaction $\mathrm{VO}+\mathrm{Si_I}\rightarrow \mathrm{O_i}$. As a result, the annealing of VO complexes takes place at temperatures lower than that observed in irradiated Cz-Si without Ge.

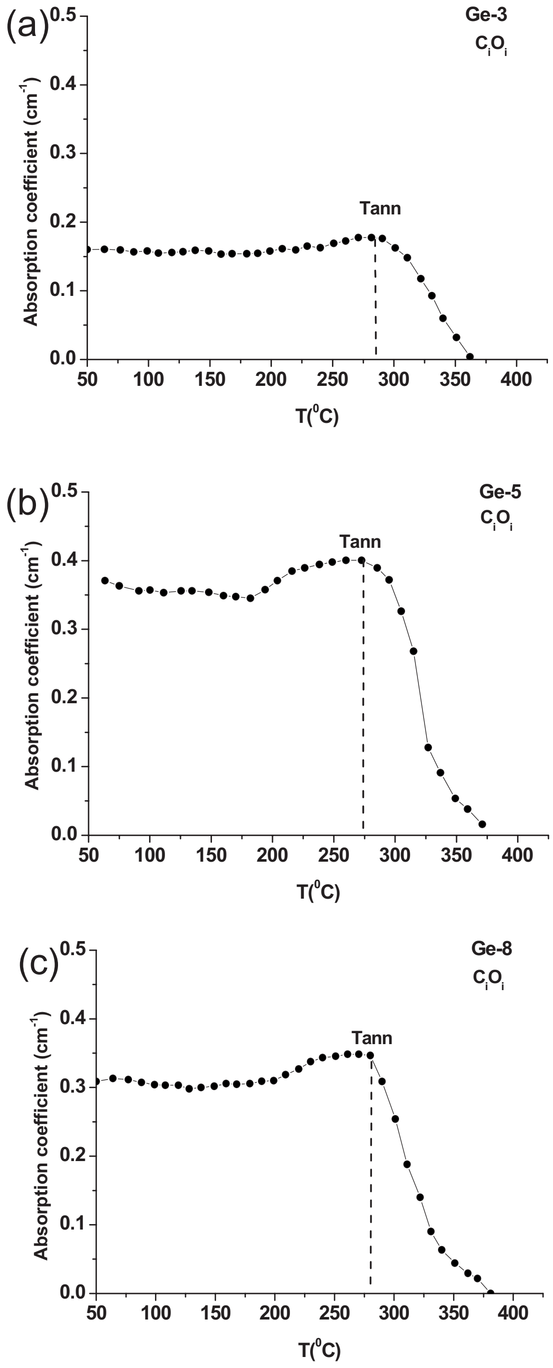

FIG. 5. Thermal evolution of $\mathrm{C_iO_i}$ complexes in samples (a) Ge-3, (b) Ge-5, and (c) Ge-8.

For an enhanced formation of $\mathrm{VO_2}$ complexes in Ge-doped Cz-Si one can propose another way of explanation. It is known that in the temperature range of 250–300 °C divacancies can be annealed out partly by their dissociation[45,46] ($\mathrm{V_2}\rightarrow \mathrm{V}+\mathrm{V}$) releasing isolated vacancies. It may be possible that a fraction of these mobile vacancies encounters $\mathrm{O_i}$ atoms liberated via the reaction $\mathrm{VO}+\mathrm{Si_I}\rightarrow \mathrm{O_i}$. This restoration of VO complexes ($\mathrm{V}+\mathrm{O_i}\rightarrow \mathrm{VO}$), in turn, may be responsible for an enhanced formation of $\mathrm{VO_2}$ defects when the mobile VO complexes are captured by isolated oxygen atoms. It is argued that in Ge-doped Cz-Si a fraction of vacancies is temporarily trapped by Ge atoms.[30] In this way they survive from capturing by other defects, therefore, increasing their

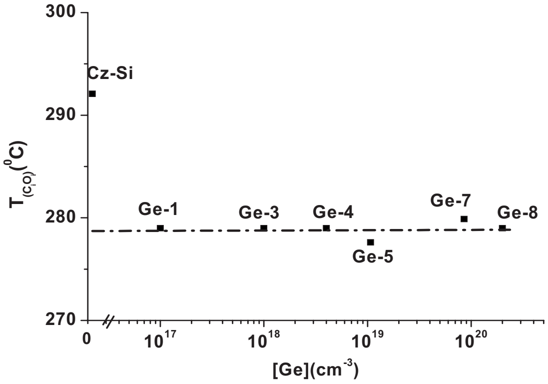

FIG. 6. Annealing temperatures of C_iO_i complexes vs Ge concentration.

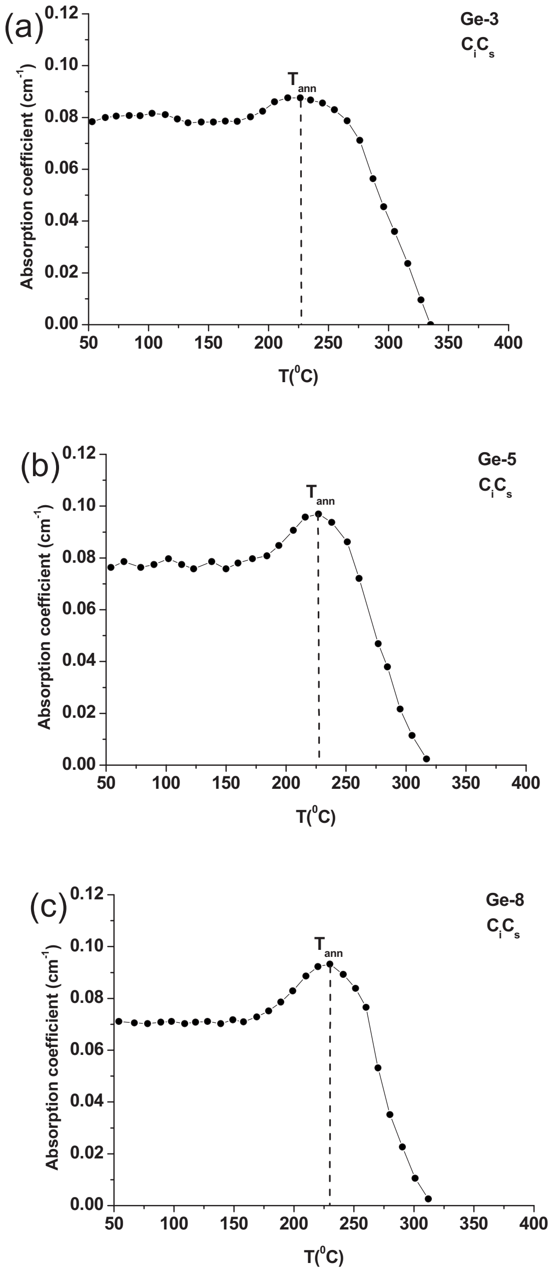

FIG. 7. Thermal evolution of C_iC_s complexes in samples (a) Ge-3, (b) Ge-5, and (c) Ge-8.

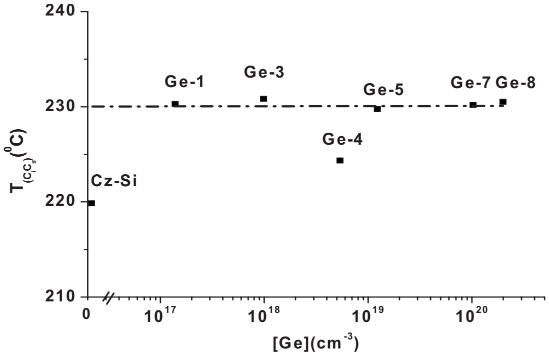

FIG. 8. Annealing temperatures of C_iC_s complexes vs Ge concentration.

possibility to be finally trapped by oxygen atoms. The fraction of VO_2 complexes formed in the indicated way is expected to be small. Nevertheless, it can be detected in the evolution curves of VO_2 defects; see for instance Figs. 2(c) and 2(d). Actually, in the temperature range of 250 to 290 °C the VO_2 signal is small, although above 290 °C it begins to increase, indicating the direct formation of VO_2 defects ($VO+O_i \rightarrow VO_2$) again.

IV. CONCLUSIONS

The annealing processes of oxygen-related and carbon-related defects in Ge-doped Cz-Si have been investigated. Although the annealing temperatures of C_iO_i and C_iC_s pairs are not affected by the Ge presence, the annealing of VO defects as well as the formation of VO_2 complexes starts at lower temperatures as compared to those observed in Ge-undoped Cz-Si. Assuming that these phenomena could be related to the stress induced by Ge impurity atoms in the Si lattice we have tried to assess this stress. Estimations have been made, which demonstrated that at impurity concentrations around one atomic per cent the hydrostatic component of induced internal stresses is very small. This conclusion is in line with the observed annealing behavior of interstitial-related C_iO_i and C_iC_s defects. It indicates, however, that internal strains cannot offer a plausible explanation for the observed annealing behavior of VO and VO_2 defects in Cz-SiGe. It has been suggested that a fraction of self-interstitials Si_I formed loosely bound clusters around Ge atoms can be responsible for the enhanced reaction $VO+Si_I \rightarrow O_i$ by emitting Si_I upon annealing. A decrease in the formation temperature of VO_2 defects is discussed in terms of the reactions running in parallel with $VO+Si_I \rightarrow O_i$.

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