IR studies of the impact of Ge doping on the successive conversion of VO_n defects in Czochralski-Si containing carbon

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We report infrared absorption studies of oxygen-related defects in electron-irradiated Ge-doped Czochralski-Si. Our investigation was mainly focused on the reaction channel leading to the formation of VO_n ($1 \leq n \leq 6$) defects. The VO_n defects form mainly upon annealing, as a result of the successive aggregation of oxygen atoms in the initial VO defect produced by the irradiation: $(VO+O_i \rightarrow VO_2+O_i \rightarrow VO_3+O_i \rightarrow VO_4, \ldots)$. It was found that the ratio of the conversion of VO_n to VO_{n+1} defects is sensitive to the Ge content of the material. In particular, the ratio of the conversion of the VO to the VO_2 defects was found to decrease with the increase in Ge concentration of the samples, although the opposite trend was observed for the VO_3 to VO_4 conversion. However, the VO_2 to VO_3 conversion changes only slightly with Ge content, being practically unaffected for Ge concentrations up to 2×10^{20} cm^{-3}. In the case of VO_2 formation, the phenomenon was attributed to the elastic strains induced in the lattice due to the Ge presence which affects the balance between the reactions $VO+O_i \rightarrow VO_2$, $VO+Si_I \rightarrow O_i$, mainly involved in the decay of the VO and the growth of the VO_2 defects. In the case of VO_4 formation, the phenomenon was discussed by taking into account the enhancement of the diffusivity of the O_i atoms in the Ge-doped Si, which could lead to an enhancement of the rate of the reaction $VO_3+O_i \rightarrow VO_4$. For the VO_3 formation this effect is practically negligible due to the fact that at the temperatures of VO_2 to VO_3 conversion oxygen diffusivity is quite small. The exhibited behavior in the conversion of the VO_n to VO_{n+1} defects ($n=1,2,3$) was similar in Ge-doped samples with low carbon content ($[C_s] < 2 \times 10^{16}$ cm^{-3}) and in Ge-doped samples with high carbon content ($[C_s] \geq 1 \times 10^{17}$ cm^{-3}). The impact of C as well as its role in the conversion efficiency of VO to VO_2 was studied by comparing the spectra in low carbon and high carbon Ge free Si material. Furthermore, a pair of bands at $(1037, 1051$ cm$^{-1})$ was attributed to the VO_5 defect. The origin of another pair of bands $(967, 1005$ cm$^{-1})$ was discussed and tentatively correlated with a VO_nC_s structure. The role of Ge and C in the formation of the latter two pairs of bands was discussed. © *2011 American Institute of Physics*. [doi:10.1063/1.3544040]

I. INTRODUCTION

Oxygen atoms are the main impurities incorporated in the Si lattice during growth by the Czochralski technique, most of them at interstitial sites. Oxygen interstitials are major traps for vacancies and upon irradiation the produced vacancies are readily captured by them to form VO pairs, well-known as A-centers. The A-center is one of the most studied defects in Si. It has been studied extensively and intensively by many experimental techniques and its electrical, electronic, and optical properties as well as its structure are well understood.[1–6]

VO center is an acceptorlike defect which introduces a level at $E_c - 0.17$ eV in the energy gap of silicon. It is considered as a very important trap for electrical-hole recombination, affecting for instance the electrical properties of power devices under high-injection conditions. On thermal anneals VO transforms to various V_mO_n defects[7–10] by the capture of additional oxygen atoms and vacancies. Among the V_mO_n defects an important class is that of VO_n defects

which form upon thermal anneals by the successive aggregation of O_i atoms in the initial VO defect, as the temperature increases. The sequence of defects VO, VO_2, VO_3, and VO_4, have been studied in detail and certain localized vibrational mode (LVM) bands were attributed to their structures.[7,8,11–13] Important among them is VO_2. It has been found that VO_2 exhibits metastable properties.[14,15] Although the center is considered electrically inactive,[11] an acceptor level at $E_c - 0.06$ eV was recently attributed to its metastable configuration.[16] Furthermore, theoretical studies have indicated that VO_2 may act as nucleation center for oxygen precipitates.[17] Thus any knowledge acquired for this defect is valuable both for scientific and technological purposes. Also VO_3 and VO_4 defects attract the interest of researchers because they appear in the spectra in the temperature range of 450–600 °C which is a usual range of thermal treatments for material processing. Additionally, there are also reports both theoretical and experimental about the VO_n ($n > 4$) defects and LVMs bands were generally attributed[18–22] to VO_5/VO_6 structures, although any definite assignments are still lacking for each one of the VO_5 and VO_6 defects.

The use of Si-based microelectronics for certain applica-

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TABLE I. The Ge, O_i, and C_s concentration before and after irradiation, and the VO concentration of the used samples.

Sample name	d (mm)	[Ge] cm^{-3}	$[O_i]_o \times 10^{17}$ cm^{-3}	$[O_i]_{af.irr} \times 10^{17}$ cm^{-3}	$[C_s]_o \times 10^{16}$ cm^{-3}	$[C_s]_{af.irr} \times 10^{16}$ cm^{-3}	$[VO] \times 10^{16}$ cm^{-3}	Remarks
Cz-Si0	1.88	$\cdots$	9.56	9.30	<2.0	a	2.35	LC
Cz-Si1	1.91	$\cdots$	10.00	9.89	16.0	9.92	3.76	HC
Ge-2	2.0	7×10^{17}	6.50	5.68	<2.0	a	2.50	LC
Ge-4	1.92	4×10^{18}	5.55	5.33	10.0	4.9	3.60	HC
Ge-6	2.13	5×10^{19}	7.60	7.22	<2.0	a	3.10	LC
Ge-8	1.78	2×10^{20}	7.70	6.53	18.0	10	4.25	HC

[a]Below detection limit.

tions makes it necessary to modify the properties of silicon material. One way in doing that is by isovalent impurity doping and more specifically with Ge atoms. It has been found for instance, that the presence of Ge in the Si lattice increases the mechanical strength of the material by retarding dislocation movement.[23] It also enhances the radiation hardness of the material.[24–26] Generally, Ge incorporation into the Si lattice has been proven a very successful application for "impurity engineering."[27] Due to the fact that Ge has a larger covalent radius than that of Si ($r_{Ge}=1.22$ Å, $r_{Si}=1.17$ Å) its incorporation in the Si lattice induces elastic strains which are relieved by the capture of vacancies.[24] Ge presence is expected to have a profound impact on the various reactions where vacancies, self-interstitials and impurities are involved. Reasonably, the general behavior of the VO_n defects should also be influenced by the incorporation of Ge impurity in the Si lattice.

Besides oxygen, carbon is another important impurity in Si, unintentionally added in the lattice during growth. Most of the carbon atoms occupy substitutional sites (C_s). Carbon is an isovalent impurity in Si. Due to the fact of having a smaller covalent radius than that of Si ($r_c=0.77$ Å) it acts as effective trap for self-interstitials.[28] During irradiation the carbon atoms C_s are kicked out at interstitial sites C_i ($C_s + Si_I \rightarrow C_i$). C_i atoms are unstable around room temperature participating in a large number of reactions as experiments by electrical and optical techniques have shown.[28–34] Thus, in a material containing Ge, O, and C, where the first two impurities act mainly as traps for vacancies as opposed to the third impurity which acts as trap for self-interstitials, it will be interesting to study their effect on the behavior of VO_n defects.

It should be further noticed that the application of external pressure both hydrostatic and uniaxial is used extensively in investigating various phenomena in solids.[35–37] In the case of Si, it has been found, for example, that hydrostatic pressure enhances thermal donor formation and oxygen aggregation processes.[38,39] On the other hand Ge, which induces compressive strains in the Si lattice, suppresses thermal donor formation and enhances oxygen precipitation.[40,41] Apparently, the full understanding of both phenomena would certainly improve our understanding of Si material and its behavior under various circumstances. In this sense, any information on the impact of Ge presence in Si is considered valuable.

The main aim of this paper is to study the effect of Ge-doping on the evolution of VO_n defects in Si and their successive conversion from one species to the next. Besides the qualitative picture of these defects, a quantitative description of their successive conversion upon thermal anneals is quite an interesting issue. The present work is a continuation of recent studies by our group[25,26,42–45] on the behavior of defects in Ge-doped Si.

II. EXPERIMENTAL DETAILS

The samples used in this study were cut from prepolished Czochralski-grown Si (Cz-Si) wafers. Their thickness was 2 mm. Their initial oxygen, carbon, and Ge concentrations are given in Table I. The oxygen concentration was calculated by using a value of the calibration coefficient[46] of 3.14×10^{17} cm^{-2}. The calibration coefficient[47] for carbon was 1×10^{17} cm^{-2}. The Ge concentration of the samples was estimated from the mass ratio of Si and Ge in the melt and the values were given by the supplier's certificate. The samples were irradiated with 2 MeV electrons at a fluence of 5×10^{17} cm^{-2}, using the Dynamitron accelerator at Takasaki-JAERI (Japan). After the irradiation, the samples were subjected to isochronal anneals up to 750 °C, in steps of $\Delta T \approx 10$ °C and $\Delta t=20$ min. After each annealing step, the IR spectra were recorded at room temperature by means of a Fourier transform infrared spectrometer (JASCO-470 plus) operated with a resolution of 1 cm^{-1}. The intrinsic two-phonon absorption was always subtracted by using a float-zone sample of equal thickness.

III. EXPERIMENTAL RESULTS AND DISCUSSION

Figure 1 shows the IR spectra at various characteristic temperatures of the isochronal anneal sequence for the samples Cz-Si0, Cz-Si1, and Cz-Ge-8. The latter sample was labeled as Ge-8; all the Ge-doped samples used in this work are labeled in the same way (Table I). To facilitate the discussion of the results, the samples used in these experiments were classified in two groups: those of low carbon content LC (Cz-Si0, Ge-2, and Ge-6) and those of high carbon content HC (Cz-Si1, Ge-4, and Ge-8). Well-known LVM bands of VO (830 cm^{-1}), VO_2 (888 cm^{-1}), VO_3 (904, 968, 1000 cm^{-1}), and VO_4 (985, 1010 cm^{-1}) (Refs. 2, 7, 11, and 12) are depicted in Fig. 1 together with another four bands at 1037, 1051, 967, and 1005 cm^{-1}. We notice that the latter four bands have also been detected in neutron irradiated silicon[22] and in a first assessment were generally
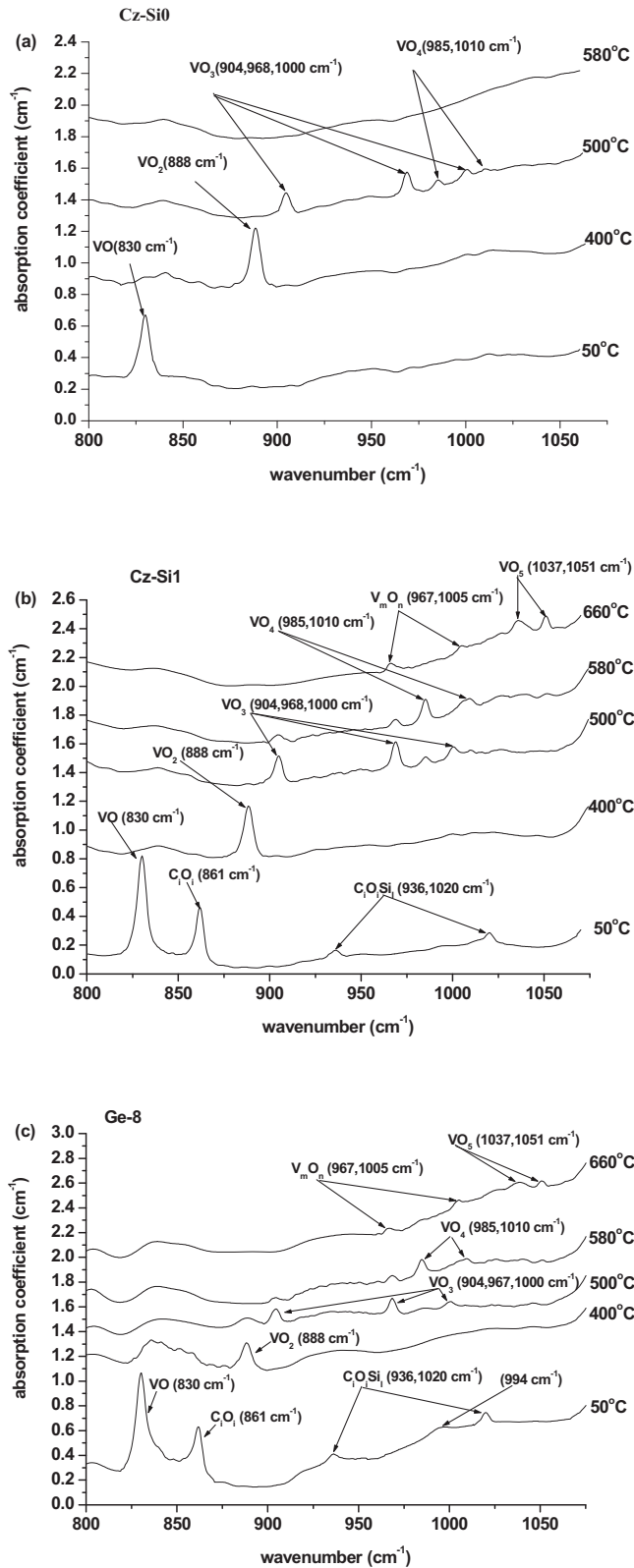
FIG. 1. IR spectra of the Cz-Si0 (a), the Cz-Si1 (b), and Ge-8 (c) samples after irradiation and at various selective temperatures.

FIG. 2. Thermal evolution of the VO_n defects and O_i impurity for the LC samples Cz-Si0 (a), Ge-2 (b), and Ge-6 (c).

correlated with V_mO_n defects. We shall deal first with these bands in an attempt to make a more definitive assignment of the particular structures that give rise to them.

Figures 2 and 3 show the evolution of all the bands appearing in the spectra of the samples used in this experiment. Concernin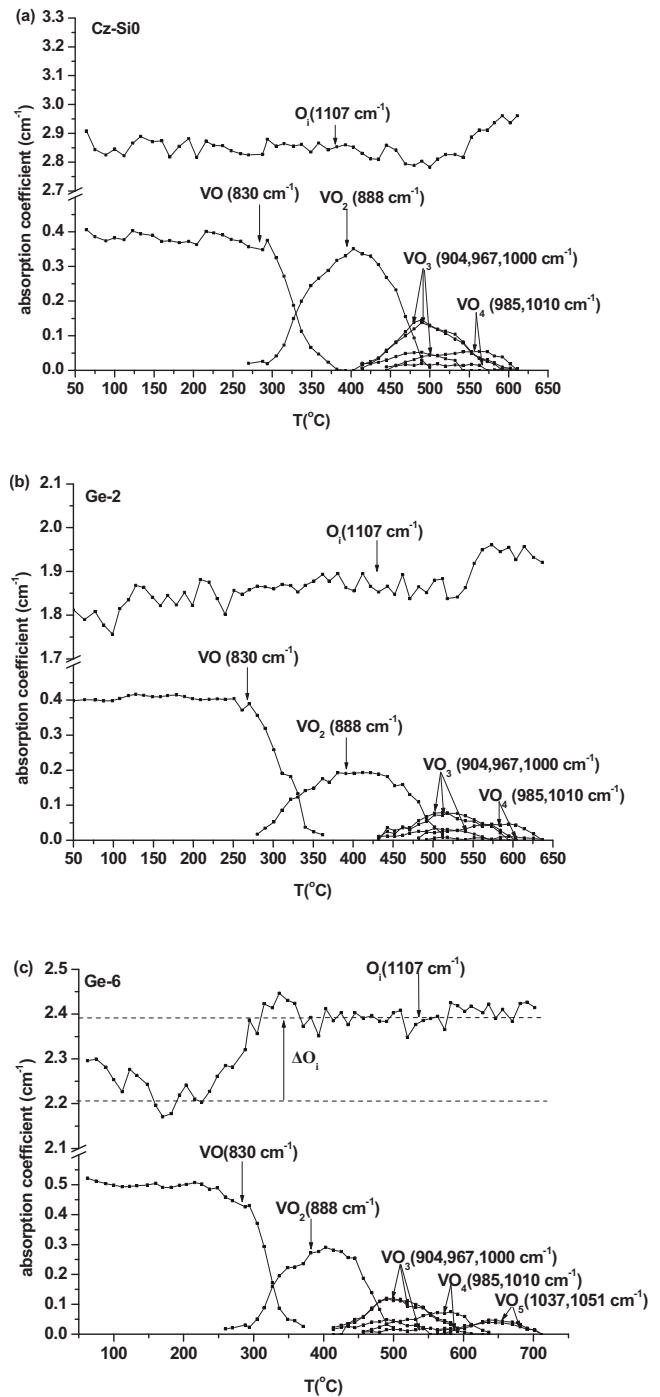g the four bands 1037, 1051, 967, and 1005 cm^{-1} the following observations and comments could be made: (i) they do not appear in the spectra of all the samples. However, where they appear, they emerge in the spectra when the two bands (985, 1010 cm^{-1}) of the VO_4 defect decay out. But, although the pair (1037, 1051 cm^{-1}) appears in the spectra around 550 °C, the other pair (967, 1005 cm^{-1}) appears at a higher temperature around 620 °C (Fig. 3). All these bands disappear from the spectra almost together just above 700 °C. (ii) In the LC material the two pair of bands are missed in the Ge free sample Cz-Si0 as well as in the low Ge-doped sample Ge-2, although only the pair (1037, 1051 cm^{-1}) appears in the high Ge-
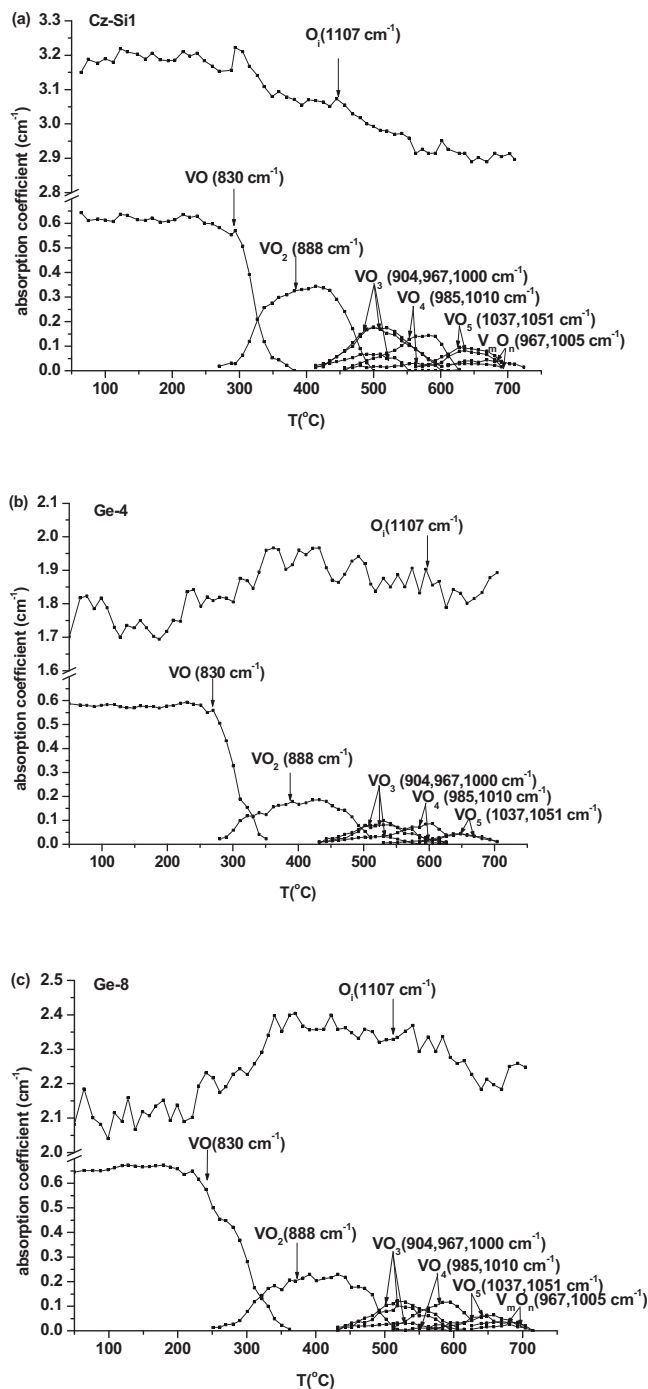
FIG. 3. Thermal evolution of the VO_n defects and O_i impurity for the HC samples Cz-Si1 (a), Ge-4 (b), and Ge-8 (c).

doped sample Ge-6 (Fig. 2). On the other hand, both pairs appear in the HC samples Cz-Si1 and Ge-8 although only the first pair appears discretely in the Ge-4 sample, which however has a lower carbon content than that of Cz-Si1 and Ge-8 samples [Figs. 3(a) and 3(c)]. Traces of the second pair appear in the IR spectra of the Ge-4 sample but they are too weak making impossible the presentation of their evolution [Fig. 3(b)]. (iii) One expects that the LVM frequencies of the VO_n bands would increase as n increases since the available room for vibrations of the oxygen atoms becomes less, as the number of the oxygen atoms of the VO_n structures increases. This is actually the case for the VO_n ($1 < n < 4$) defects. In

this sense it is reasonable to attribute the first pair of bands ($1037, 1051$ cm^{-1}) to the VO_5 defect. Importantly, the two bands emerge in the spectra in the temperature range where VO_3 decays out and subsequently their intensity is enhanced when VO_4 decays out. Thus, one could suggest[21,22] the following possible formation reactions for VO_5 defect: ($VO_3 + O_i \rightarrow VO_4$ then $VO_4 + O_i \rightarrow VO_5$) or directly $VO_4 + O_i \rightarrow VO_5$. It is worth noting that these bands have also been reported previously in room-temperature measurements of electron irradiated Si.[20,21] Furthermore, these experimental values are consistent with the results of theoretical calculation about the LVM frequencies of the VO_5 defect. Of course there were expected[18] more than two bands to be related with the VO_5 defect. The two observed bands in our studies are most possibly the stronger ones allowing for their detection at room temperature measurements.

On the basis of the above criterion the second pair of bands ($967, 1005$ cm^{-1}) cannot be correlated with the VO_6 structure. The frequencies of VO_6 defect are generally expected to have higher values[18] than those of VO_5 defect ($1037, 1051$ cm^{-1}) and apparently the pair of bands at ($967, 1005$ cm^{-1}) does not fulfill this criterion. Furthermore, the latter two bands start to emerge in the spectra at a higher temperature than that of VO_5 defect indicating that they may be the product of other reactions, as for example $V_2O_3 + O_i \rightarrow V_2O_4$, $V_2O_3 + 2O_i \rightarrow V_2O_5$, $V_3O_2 + O_i \rightarrow V_3O_3$, etc.,[22] leading generally to the formation of V_mO_n defects with more than one vacancy in their structure. Thus, with the available information so far, we can at first sight correlate the origin of the $967, 1005$ cm^{-1} pair of bands with a multivacancy-multioxygen V_mO_n complex and more generally with V_mO_n complexes having some impurity attached. The latter issue is discussed below in relation with the C impurity.

Finally, the role of Ge and C in relation with the appearance of the above two pairs of bands should be discussed. We observe that in the LC material the first pair of bands attributed to VO_5 defect appears clearly only in the high Ge-doped (Ge-8) sample. It is well known that above 450 °C the oxygen atoms begin to diffuse in the Si lattice. Oxygen dimers O_{2i} are also formed which are very mobile.[48,49] It has also been found that the diffusivity of oxygen is enhanced in Ge-doped Si.[50] As a consequence, the formation reactions $VO_4 + O_i \rightarrow VO_5$ and ($VO_3 + O_i \rightarrow VO_4$ then $VO_4 + O_i \rightarrow VO_5$), as well as $VO_3 + O_{2i} \rightarrow VO_5$ of the VO_5 defect are enhanced which is manifested in the spectra by the emergence of the two bands at $1037, 1051$ cm^{-1}. Reasonably, VO_5 defect should also form in the Cz-Si and in the low Ge-doped Si samples but their concentration is very low to be detected in the IR spectra recorded at room temperature. On the other hand, in the HC samples the two bands $1037, 1051$ cm^{-1} appear even if the material is Ge free (for instance the Cz-Si1 sample). Since the $1037, 1051$ cm^{-1} bands appear[20,21] also in a material with low carbon concentration, reasonably carbon is not incorporated in their structure. Carbon most possibly plays an indirect role enhancing the formation of the VO_5 defects. It has been found[51] that the diffusion coefficient of oxygen at 750 °C in carbon-rich Si is higher by a factor of 3 than its normal value. Thus, in our HC
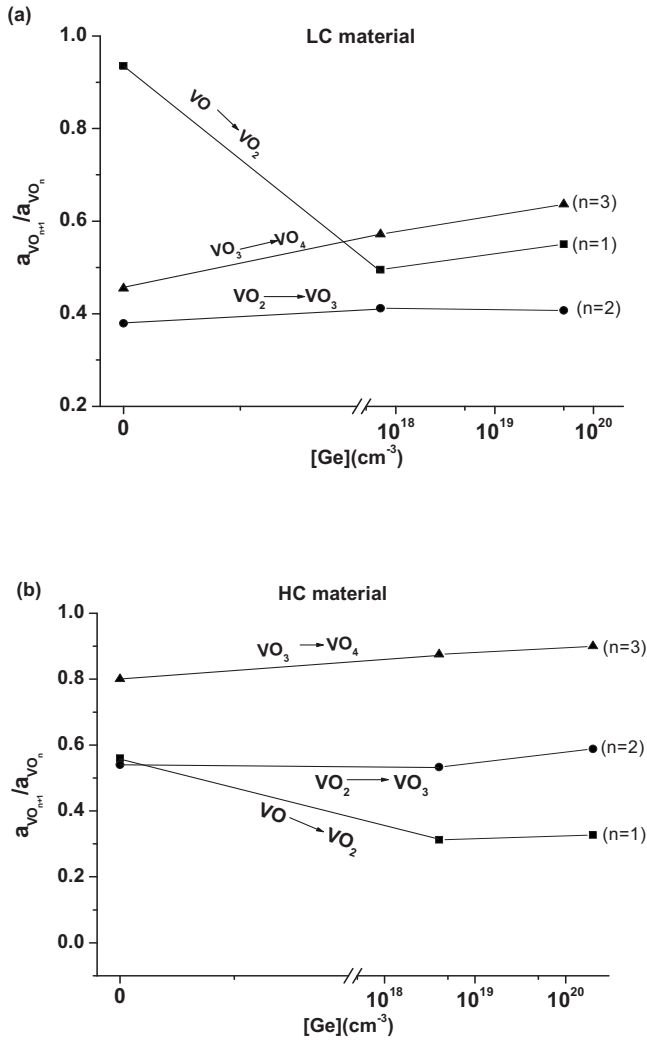
FIG. 4. The absorption coefficient ratio of the conversion of the VO_n to the VO_{n+1} defects for $n=1,2,3$ for the LC Cz-Si0, Ge-2, and Ge-6 samples (a) and for the HC Cz-Si1, Ge-4, and Ge-8 samples (b).

material, one would expect that the diffusivity of oxygen is larger than the usual value in the temperature range of the VO_5 defects formation. However, since at these temperatures the normal oxygen diffusivity is very low, the induced enhancement is not expected to lead to diffusivity values high enough to explain the phenomenon. The exact role of carbon is not clear at this stage and more work needs to be done in this field. On the other hand, the pair of bands at $967, 1005$ cm^{-1} appears in the HC samples Cz-Si1 and Ge-8, a strong indication that carbon plays an essential role in their formation incorporated in their structure. One may assume that the two bands result from attaching of some V_mO_n to a C_s impurity with a potential candidate a VO_nC_s structure.

Figure 4 exhibits the variation in the ratio $a_{VO_{n+1}}/a_{VO_n}$ ($n=1,2,3$) of the absorption coefficient a of the VO_n bands as a function of the Ge content of the material for the LC [Fig. 4(a)] and HC [Fig. 4(b)] samples. At a first sight, one observes that the ratio a_{VO_2}/a_{VO} is substantially lower in the Ge-doped samples in comparison with the Ge free sample, the ratio a_{VO_3}/a_{VO_2} is practically unaffected by the Ge presence, although the ratio a_{VO_4}/a_{VO_3} shows a slight but clear tendency to increase with the Ge content of the material. Let

us first focus on the a_{VO_2}/a_{VO} ratio. Its decrease versus Ge content shows that less VO_2 defects are formed when Ge is present, indicating a strong influence of Ge in the VO to VO_2 conversion. Notably, a multitude of reaction channels that VO defect could participate upon annealing have been cited[5,8,52–55] in the literature;

$$VO + O_i \rightarrow VO_2, \tag{1}$$

$$VO + Si_I \rightarrow O_i, \tag{2}$$

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

$$VO + V \rightarrow V_2O, \tag{4}$$

$$VO + VO \rightarrow V_2O_2. \tag{5}$$

In the latter reaction, more than one pathways have been suggested[5,53] for the dissociation of the V_2O_2 defect as follows:

$$V_2O_2 \rightarrow VO_2 + V \tag{6}$$

or

$$V_2O_2 \rightarrow V_2O + O_i \rightarrow V_2 + 2O_i. \tag{7}$$

For Cz-Si material irradiated with 2 MeV electrons at high fluencies as in our case it has been found[52] that the first two reactions are mainly involved in the annealing of the VO defect. Sources of the Si_I's participating in the reaction $VO + Si_I \rightarrow O_i$ are self-interstitial clusters formed in the course of the heavy irradiation of the Cz-Si.[52] We argue that the emission of the Si_I's is sensitive to the presence of Ge atoms in the Si material and in particular to the strains induced in the lattice due to the fact that Ge atoms are larger than the Si atoms which they substitute. Thus, the binding energy of the Si_I's at these clusters is affected and most probably decreases. In other words, we argue that the liberation of the Si_I's is facilitated as a result of the Ge presence, leading to an enhancement of the reaction $VO + Si_I \rightarrow O_i$. Another important point, in the high oxygen samples (Cz-Si) the conversion reaction $VO + O_i \rightarrow VO_2$ is enhanced in comparison with the competing reaction $VO + Si_I \rightarrow O_i$. Indeed, since the oxygen concentration is much higher than VO_2 the rate of the constant of the VO the VO_2 reaction is strictly proportional to the oxygen concentration. In other words the higher the oxygen concentration in a sample the stronger the reaction $VO + O_i \rightarrow VO_2$. It means that the conversion degree should be lower in the samples with lower oxygen content (Ge-2 and Ge-6) in comparison with that of the high oxygen samples (Cz-Si). In our opinion it is both the Ge and the oxygen content of the material responsible for the behavior of the conversion ratio of the VO to VO_2, as depicted in Fig. 4.

Additionally, Ge can affect the reaction $VO + Si_I \rightarrow O_i$ in another way. In the course of the irradiation event the rate of annihilation between vacancies and self-interstitials is expected to be reduced[26] due to the temporary trapping of vacancies by the Ge atoms. In this sense, more Si_I's survive the annihilation process leading to an increase in the concentration of the self-interstitial clusters, in comparison with those in Cz-Si material irradiated under the same conditions. This

increase of course is quite small. Actually, the total amount of Si_I's, both clustered and trapped, is precisely equal to the concentration of VO since V and Si_I are produced and annihilated in pair. Since VO is slightly increased with Ge presence (Table I), one would expect that the amount of clustered Si_I's is also slightly increased.

The increase in the O_i concentration in the temperature range where VO anneals out, depicted in the evolution curves of the highly Ge-doped samples Ge-6 [Fig. 2(c)] and Ge-4 [Fig. 3(b)] and Ge-8 [Fig. 3(c)] is a strong supporting element of the above argumentation concerning the contribution of the reaction $VO+Si_I \rightarrow O_i$. Actually, in the Ge doped Si samples, especially in the samples Ge-4, Ge-6, and Ge-8 with relative high Ge content a substantial increase in the O_i concentration is observed in the temperature range where VO anneals out. Although this increase in O_i is a corroborating evidence of the dominant role of the reaction $VO+Si_I \rightarrow O_i$ in the VO anneal in Ge-doped Si, the phenomenon is more complicated than one could consider in the face of it. Indeed we notice that, the increase in the oxygen concentration in the temperature window where VO anneals out, is larger than the concentration of VO defect. Thus, in the case for instance of the Ge-6 sample, VO concentration is about 3.1×10^{16} cm^{-3}, taking a calibration coefficient[56] of 6.25×10^{16} cm^{-2}, although the oxygen increase ΔO_i is about 6×10^{16} cm^{-3} [Fig. 2(c)]. It means that even if all the VO centers were dissociated, that is, without any conversion of VO to VO_2, their concentration would not be adequate for the produced O_i atoms. This suggests the existence of additional sources of interstitial oxygen atoms. The phenomenon needs further investigation.

Importantly, not all of the VO pairs convert to the VO_2 centers. Taking into account that the calibration factor of the VO_2 defect is only half that of the VO defect[11,57] we can estimate that in the LC Cz-Si0 sample [Fig. 2(a)] about 50% of the VO defect converts to VO_2 defect. The fact that VO is partially transformed to VO_2 is mainly due to the competing reaction of VO with self-interstitials.

A final comment: admittedly, the formation and diffusion mechanisms of the VO defect in Si is a much discussed point in the literature (see for instance Refs. 58–61). Two atomic mechanisms of the VO diffusion have been recently[61] discussed, depending either on the migration of the oxygen atom or on the migration of the vacancy in the VO structure. One can think that in the atomistic level, the presence of Ge in the Si lattice may have an impact on the migration mechanisms, which in turn could affect the annealing behavior and more specifically the kinetics and the degree of contribution of each one of the reactions participating in the annealing of the VO defect. And this is finally reflected in the concentration of the successively formed VO_n defects.

Finally, the role of C in the VO annealing should be discussed. Comparing Figs. 2(a) and 3(a), a decrease in the VO to VO_2 conversion efficiency is observed between the LC and HC Ge free samples. Remarkably, there is no increase in oxygen concentration in the corresponding temperature range. Actually, a lower conversion efficiency of VO to VO_2 in Si material with high carbon content has been previously reported.[11,62] The exact role of carbon in the

whole process was not clear. A competing reaction in the VO annealing has been suggested,[53] that is, $Z+VO \rightarrow Z'+O_i$, where Z represents a radiation-induced carbon related defect and Z' the reaction product. In any case, we know that carbon substitutional (C_s) is an effective trap for self-interstitials ($C_I+Si_I \rightarrow C_i$). At about 300 °C where VO begins to migrate, the C_i defect is not stable participating in various reactions. It is probable that some of the C_i's may return at substitutional sites. It has been proposed[58] that the subsequent release of the self-interstitials ($C_i \rightarrow C_s+Si_I$) can lead to a vacancy-interstitial recombination at VO sites in the course of the annealing process. Thus, less VO centers are available to form VO_2 defects, and therefore the corresponding conversion efficiency is reduced. In this sense, a number of the self-interstitials present at this temperature are temporarily trapped by carbon and then released to contribute to the destruction of VO centers.

However, as we mentioned above no increase in the oxygen concentration was observed in the HC Cz-Si1 sample [Fig. 3(a)]. Instead, a gradual decrease in O_i is observed from about 300 °C onwards. Within the lines of the above argumentation, one can try to explain these observations in the following way. The release of self-interstitials in a HC material triggers the reaction $VO+Si_I \rightarrow O_i$, but also in parallel the reaction $C_s+Si_I \rightarrow C_i$. Some of the temporarily formed C_i defects may be captured by O_i atoms to form stable C_iO_i centers.[28] Figure 5(a) exhibits the evolution of C_iO_i in the Cz-Si1 sample. Actually there is a slight increase in the C_iO_i concentration but this is not adequate to account for the expected increase in O_i. Similar trends in the C_iO_i behavior are also observed in the HC Ge-doped samples [Figs. 5(b) and 5(c)]. The formation of C_sO_i (Ref. 28) complexes ($C_s+O_i \rightarrow C_sO_i$) is also expected to occur. In our case the C_sO_i signals in the spectra are very weak and any substantial increase in their intensities in the temperature above 300 °C cannot be definitely verified. The formation of VO_3 and VO_4 defect is not adequate to account for the loss of oxygen in the temperature range where the bands related to these defects appear in the spectra. Since the diffusivity of oxygen is low at these temperatures, even at 600 °C, Dox$=3.3 \times 10^{-16}$ cm^2/s, the rate of oxygen attachment to any defect is negligible. On the other hand the attachment of other defects to oxygen atoms is not verified by any new IR bands in the spectra. The oxygen loss in the HC sample Cz-Si1 may be due to a strongly enhanced oxygen precipitation where the vehicles for oxygen are C_iO_i complexes. Of course the concentration of the C_iO_i is low (judging from the spectral signals) but it may be quite sufficient for transportation of oxygen to some oxygen clusters of a high density. Once C_iO_i reaches a cluster, it passes O_i to the cluster, and a liberated C_i is ready again to be used as a vehicle for oxygen transportation.

Concerning now the conversion of the VO_2 to the VO_3 defect which seems practically unaffected by the Ge presence, we can argue in the line of the argumentation presented above, that the sources of Si_I's are practically not available in the temperature range where the conversion of the VO_2 to the VO_3 occurs and therefore any destruction of VO_2 by Si_I's is negligible. Thus the reaction $VO_2+O_i \rightarrow VO_3$ appears

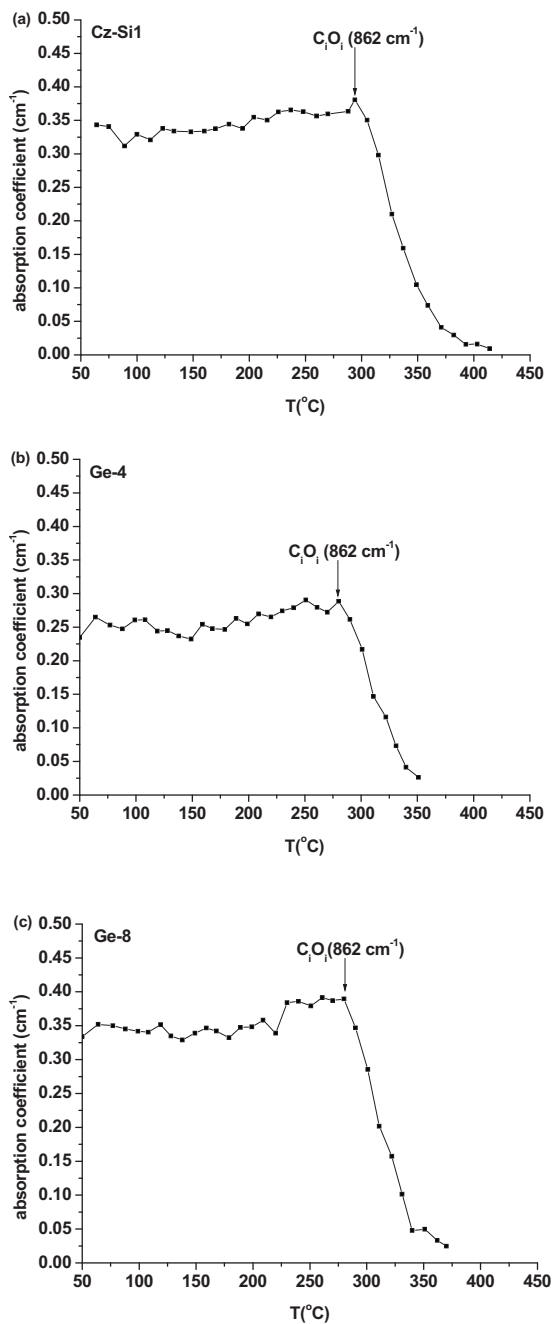FIG. 5. Thermal evolution of the C_iO_i defect in the HC samples Cz-Si1 (a), Ge-4 (b), and Ge-8 (c).

duced in Ge-doped material. The phenomenon was attributed to the contribution of Ge on the release of self-interstitials which enhances the effect of the reaction $VO + Si_I \rightarrow O_i$ over the reaction $VO + O_i \rightarrow VO_2$ on the annealing of the VO defect. This effect of Ge on self-interstitials is practically negligible in the temperature range of VO_2 to VO_3 conversion and the a_{VO_3}/a_{VO_2} ratio essentially does not change. However, the ratio a_{VO_4}/a_{VO_3} increases with Ge content. Behind this observation lies the increase in the oxygen diffusivity due to the presence of Ge. In Ge free material the a_{VO_2}/a_{VO} ratio also decreases when carbon is present in high concentration. The role of carbon could be related to its ability to attract and release self-interstitials at temperatures above 300 °C ($C_s + Si_I \leftrightarrow C_i$) leading to vacancy—self-interstitials recombination at VO sites.

(ii) Two bands at $(1037, 1051\ \text{cm}^{-1})$ appearing in Ge-doped Si have been attributed to the VO_5 defect. Another pair of bands at $967, 1005\ \text{cm}^{-1}$ appearing only in HC material was attributed to a VO_nC_s structure. It was found that Ge and C enhance the formation of the VO_5 defect. Furthermore, our results suggest that C plays an important role in the formation of the $967, 1005\ \text{cm}^{-1}$ clusters.

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practically unaffected by the Ge presence and this is reflected in the corresponding curves of Fig. 4 both for the LC and HC material. This is not the case however for the VO_3 to the VO_4 conversion. However, the degree of conversion of the VO_3 to VO_4 defects is slightly increased versus Ge content. Since there is not any competing reaction at this temperature range, affected by the Ge presence, it is not prudent to speculate at the present stage about the possible reason.

IV. CONCLUSIONS

We have studied the effect of Ge doping on the successive conversion of VO_n to VO_{n+1} ($1 < n < 3$) defects in Si containing carbon. Our results allow the following conclusions to be drawn: (i) the conversion of VO to VO_2 is re-

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