Radiation effects on the behavior of carbon and oxygen impurities and the role of Ge in Czochralski grown Si upon annealing

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The annealing behavior of the oxygen and carbon impurities in Czochralski grown silicon (Cz-Si) was investigated in electron- and neutron-irradiated materials. The irradiated samples were subjected to isochronal anneals of up to $\sim 1000\ ^\circ$C, and the evolution of oxygen and carbon concentrations was monitored by means of infrared spectroscopy from the amplitudes of the 1106 and 605 cm^{-1} bands of the two impurities correspondingly. It was found that the electron irradiation does not affect the temperature of annealing of oxygen, although in the neutron-irradiated samples the oxygen band begins to decay in the spectra at a lower temperature than that in the nonirradiated samples. This behavior could be determined by supersaturation of vacancies mainly liberated from disordered regions in the latter material. This assists the oxygen aggregation process. Regarding carbon evolution, it was found that in the irradiated samples the annealing out of the 605 cm^{-1} band occurs at a lower temperature than that of the nonirradiated samples. Prior to the onset of decay of the 605 cm^{-1} band an inverse annealing stage was observed in the irradiated samples, indicating partial restoration of substitutional carbon. The general behavior was discussed with respect to the supersaturation of intrinsic defects, mainly self-interstitials. As a result, large $C_N(Si_I)_M$ complexes are formed. There are two processes running in parallel: the recovery of substitutional carbon from carbon-related defects and $C_N(Si_I)_M$ complexes and the transformation of $C_N(Si_I)_M$ complexes to SiC-based precipitates. Noticeably, in electron-irradiated Ge-doped Si the inverse annealing stage of substitutional carbon is suppressed. Furthermore, our results showed that the Ge doping of Cz-Si of up to $2 \times 10^{20}\ \text{cm}^{-3}$ does not practically affect the temperature at which oxygen and carbon are completely lost in irradiated Cz-Si:Ge. © *2009 American Institute of Physics*.
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I. INTRODUCTION

Oxygen is a key impurity in silicon crystals grown by the Czochralski technique (Cz-Si). Isolated oxygen atoms are incorporated at interstitial sites in the crystal lattice being electrically inactive. They form supersaturated solid solutions. As a consequence, oxygen atoms are prone to precipitate upon annealing,[1–3] giving various SiO_x particles with pertinent volume dilatation. Noteworthy, such oxygen precipitates occur in the temperature range used for the fabrication of large-scale/ultra-large-scale integrated devices. Oxygen precipitates exert both beneficial and detrimental effects on electrical properties of Cz-Si materials.[2–5] First of all, they are effective internal getters for unwanted metallic impurities (the so-called lifetime killers). On the other hand, special heat treatment regimes are applied, preventing their formation in the active regions of devices. Oxygen precipitation processes are known to be sensitive to the presence of other impurities, especially carbon[6,7] as well as radiation-produced defects.[8,9]

Besides oxygen, carbon is another important impurity being sometimes present in Cz-Si crystals in substantial concentrations. Normally, carbon atoms are substitutional in the Si lattice and they are electrically inactive.[10] Carbon tends also to precipitate in Si upon annealing if its concentration exceeds the solubility limit. As a result, SiC-like particles with corresponding volume diminution are formed. Apparently, coprecipitation of oxygen and carbon is energetically favorable because of compensation of unlike volume changes.[3] Carbon precipitates can also strongly affect electrical properties of Cz-Si. It is clear that a fundamental understanding of oxygen and carbon precipitation processes in Si crystals is essential in improving the device performance.

For Cz-Si materials, irradiation and implantation are also widely used in technological processing. Among primary intrinsic defects produced by irradiation of Si with various atomic particles (fast electrons, neutrons, α-particles, ions, etc.), Frenkel pairs, i.e., vacancies V bound to their parent self-interstitials Si_I, are most important. A portion of Frenkel pairs dependent on irradiation conditions is annihilated during irradiation ($V + Si_I \rightarrow Si_S$). Frenkel pairs escaping annihilation are separated into isolated vacancies and self-interstitials mobile at room temperature. While migrating in the crystal lattice they interact with impurity atoms such as oxygen and carbon producing various complexes. Vacancies are mainly trapped by oxygen atoms forming V_O centers. Self-interstitials are predominantly captured by carbon atoms, leading to the formation of interstitial carbon atoms.

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TABLE I. The initial oxygen, carbon, and germanium concentrations of the samples used and the conditions of their irradiations.

Sample name	$[O_i]_0$ (10^{17} cm^{-3})	$[C_s]_0$ (10^{16} cm^{-3})	[Ge] (10^{20} cm^{-3})	Irradiations
Cz-Si 0	10.0	14.8	⋯	⋯
Cz-Si 1	7.0	7.1	⋯	⋯
Cz-Si 2	10.0	16.0	⋯	2 MeV electron irrad. (fluence=5×10^{17} cm^{-2})
Cz-Si 3	10.0	15.0	⋯	5 MeV fast neutron irrad. (fluence=1×10^{17} cm^{-2})
Cz-Si:Ge 0	6.8	9.1	2.0	⋯
Cz-Si:Ge 1	5.5	9.1	0.04	2 MeV electron irrad. (fluence=5×10^{17} cm^{-2})
Cz-Si:Ge 2	7.7	20	2.0	2 MeV electron irrad. (fluence=5×10^{17} cm^{-2})

The latter ones also being mobile at room temperature interact with the same impurities C_s and O_i in Cz-Si. As a result, the appearance of C_iC_s and C_iO_i pairs is observed. Together with this, mobile vacancies and self-interstitials if present in large concentrations can pair with one another, giving rise to formation of more complex defects such as di-vacancies and di-interstitials. These reactions are very much more pronounced in neutron-irradiated crystals where the formation of multivacancies and large self-interstitial clusters as well as disordered regions takes place.[11–15] With increasing temperature of annealing, VO centers are transformed into large V_mO_n clusters seen in IR spectra up to 750 °C.[16] Concurrently, small interstitial clusters are also growing to extended interstitial-type defects, e.g., rodlike defects stable in the same temperature range.[3,17,18]

Intrinsic point defects play an important role in growth and evolution of oxygen precipitates.[2,3] To take one example, the critical radius for the growing precipitates depends strongly on concentration of intrinsic defects.[3] It is thus expected that the presence of radiation defects will affect precipitation processes of both oxygen and carbon impurities in Cz-Si. Actually, such phenomena have been described in literature. By way of illustration, in neutron-irradiated carbon-lean Cz-Si oxygen precipitation is markedly enhanced[9] upon thermal annealing in a temperature range from 1050 to 1150 °C. In addition, an enhanced oxygen precipitation at 900 °C is also observed[8] in carbon-lean materials irradiated with fast electrons and then annealed at 350 °C in order to create VO_2 complexes. It is worth noting that even an early work on this issue has demonstrated[19] that the precipitation of oxygen and carbon in silicon fails to appear without proper nuclei and one of the ways that can be initiated is by electron irradiation. Given the tendency of the carbon and oxygen impurities to interact presently[3,10,20] between themselves and with primary defects, it will be very interesting to investigate the effect of radiation defects on their thermal behavior.

In the present work we studied in a systematic way the behavior of carbon and oxygen impurities in carbon-rich Cz-Si subjected to irradiation with fast neutrons and electrons and subsequently annealed from room temperature to ~1000 °C. A faster disappearance of isolated interstitial oxygen atoms was evidenced in neutron-irradiated materials. On the other hand, the complete loss of isolated substitutional carbon atoms in both electron- and neutron-irradiated Cz-Si was observed at markedly lower temperatures as compared to that in nonirradiated crystals. Additionally, the behavior of substitutional carbon atoms displays an inverse annealing stage prior to their complete disappearance in irradiated Cz-Si. These observations are discussed and plausible explanations are offered. Taking into account the importance of an isoelectronic impurity of Ge in Cz-Si materials widely used in modern technical applications, we carried out some preliminary experiments on such materials. Some interesting results of the effects of germanium doping on the behavior of oxygen and carbon impurities in irradiated and annealed Cz-Si are also presented mainly for comparison purposes.

II. EXPERIMENTAL

Samples used in this work were cut from Cz-Si wafers. The dimensions of optically polished samples were $20\times10\times2$ mm^3. There are several groups of materials with various concentrations of oxygen, carbon, and germanium impurities. Their initial concentrations are given in Table I. Samples Cz-Si 2, Cz-Si:Ge 1, and Cz-Si:Ge 2 were irradiated with 2 MeV electrons at a fluence of 5×10^{17} cm^{-2} using the Dynamitron accelerator at Takasaki-JAERI (Japan) at $T<95$ °C. Samples Cz-Si 3 were irradiated with 5 MeV fast neutrons at a fluence of 1×10^{17} cm^{-2} using the pool water reactor in Demokritos (Greece) at $T\leq50$ °C. Samples Cz-Si 0, Cz-Si 1, and Cz-Si:Ge 0 were not irradiated. After irradiations all the samples were subjected to isochronal annealing in steps of $\Delta T\approx10$ K and $\Delta t=20$ min, starting from 50 up to ~1000 °C. The annealing procedure was carried out as follows. The samples were put inside a high-purity quartz tube, which was inserted in the furnace whose starting temperature was 50 °C. They were annealed for 20 min and then the quartz tube with the samples was removed from the furnace. Then IR spectra of the samples were recorded at room temperature by means of a Fourier Transform Infrared (FTIR) spectrometer with a resolution of 1 cm^{-1}. The intrinsic two-phonon absorption was always subtracted using a float-zone Si sample of equal thickness. Next, the temperature of the furnace was increased to 60 °C. The samples were put in the quartz tube and into the furnace where they were annealed again for 20 min. Afterward, they were removed from the furnace and IR spectra of the samples were recorded at room temperature, as above. The procedure was repeated up to ~1000 °C in steps of 10 K. Oxygen and carbon concentrations were estimated from the intensities of

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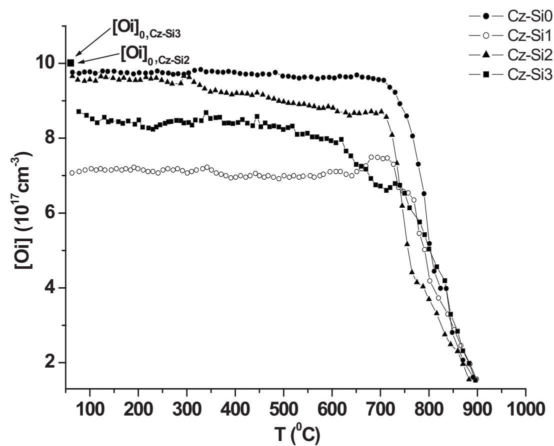

FIG. 1. Behavior of isolated oxygen impurity (IR band at 1106 cm^{-1}) in the Cz-Si 0 Cz-Si 1, Cz-Si 2, and Cz-Si 3 samples upon isochronal annealing.

the bands at 1106 cm^{-1} for O_i and 605 cm^{-1} for C_s using calibration coefficients[3,10] of 3.14×10^{17} and 0.94×10^{17} cm^{-2}, respectively.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Cz-Si

1. Behavior of oxygen

Figure 1 displays the behavior of oxygen impurity atoms in samples Cz-Si 0, Cz-Si 1, Cz-Si 2, and Cz-Si 3. As is seen, the oxygen concentration in the Cz-Si 0 and Cz-Si 1 (nonirradiated samples) remains practically unaltered upon annealing to ≈700 °C. In the case of the Cz-Si 1 sample the oxygen concentration shows a small increase in the temperature range from 650 to 700 °C. After that point a sharp drop in the oxygen concentration is observed. In the case of irradiation it is expected that the damage caused in the Si lattice by fast neutrons is much larger than that caused by fast electrons at the doses used, and hence, the loss of isolated interstitial oxygen due to formation of vacancy-oxygen complexes should be significantly higher for the neutron-irradiated material. Actually, the relative oxygen loss $\Delta[O_i]/[O_i]_0$ due to the irradiation is ≈16% and ≈4% in the neutron- and electron-irradiated Cz-Si samples, respectively.

As seen from Fig. 1, in both irradiated samples the oxygen concentration shows a small gradual decrease starting from ≈350 °C. This may be related to the participation of oxygen atoms in the formation of various V_mO_n defects.[21] In the electron-irradiated Cz-Si the isolated oxygen atoms begin to disappear from their interstitial sites at $T\approx700$ °C, such as in the nonirradiated material. In contrast, in the neutron-irradiated samples the onset of oxygen loss, i.e., the onset of decay of the oxygen band in the course of the isochronal anneals sequence, is observed at markedly lower temperatures of around $T\approx600$ °C.

The disappearance of interstitial oxygen upon annealing is accompanied by formation of oxygen precipitates. These precipitates give rise to IR bands close to the characteristic peak at 1106 cm^{-1} associated with isolated interstitial oxygen.[2,3] Figures 2 and 3 display several distorted bands recorded for the Cz-Si samples neutron- and electron-

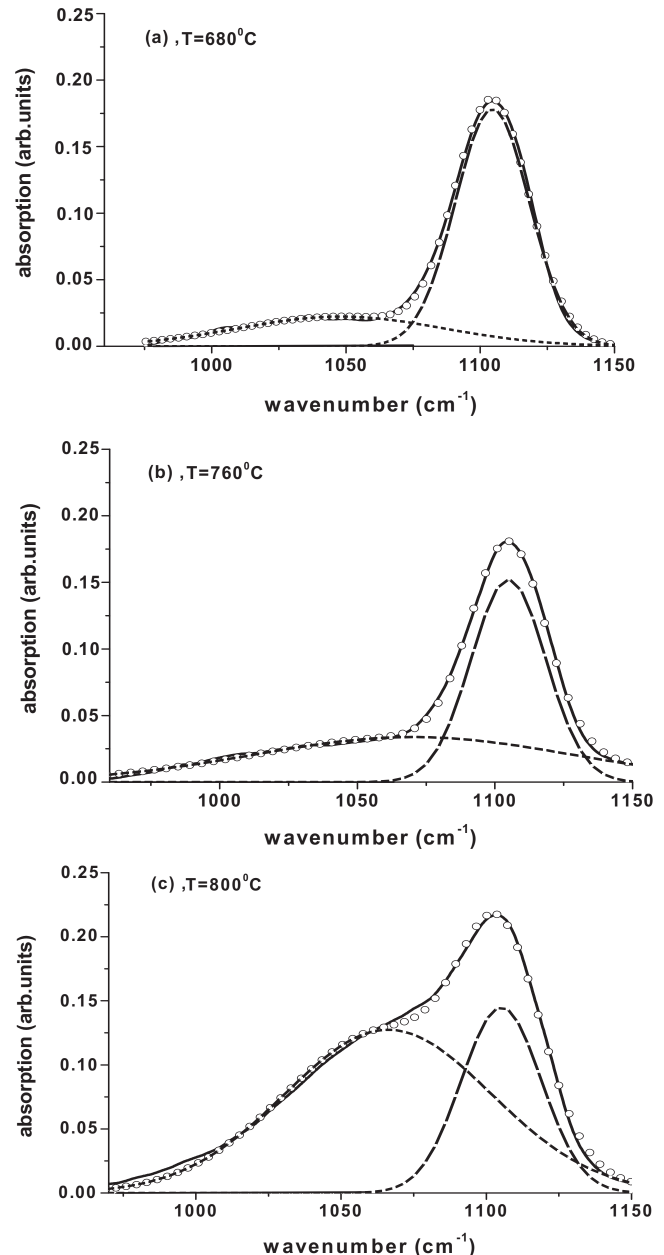

FIG. 2. Deconvolution of the IR band around 1106 cm^{-1} (isolated interstitial oxygen) into Lorentzian-shaped constituents recorded for the Cz-Si 3 sample irradiated with fast neutrons and subsequently annealed at several selected temperatures [(a) $T=680$ °C, (b) $T=760$ °C, and (c) $T=800$ °C]. Solid lines represent the experimental results; dashed lines represent Lorentzian profiles; and dotted lines represent the best fitting curves.

irradiated and then annealed in the temperature range where the oxygen loss is setting in. The relevant deconvolution of these bands by Lorentzian-shaped constituents is presented in the same figures. It is apparent that there is a broadband around 1060 cm^{-1} attributed to oxygen precipitates. Again, the oxygen precipitation process occurs earlier in neutron-irradiated Cz-Si, and this effect is clearly seen in Fig. 4 where the onset of decay of the oxygen band is well correlated with the onset of growth of the precipitate band. The behavior of the oxygen band in nonirradiated materials is much the same as in electron-irradiated Cz-Si.

According to the classical nucleation theory,[3] the onset of oxygen precipitation requires the formation of precipitate

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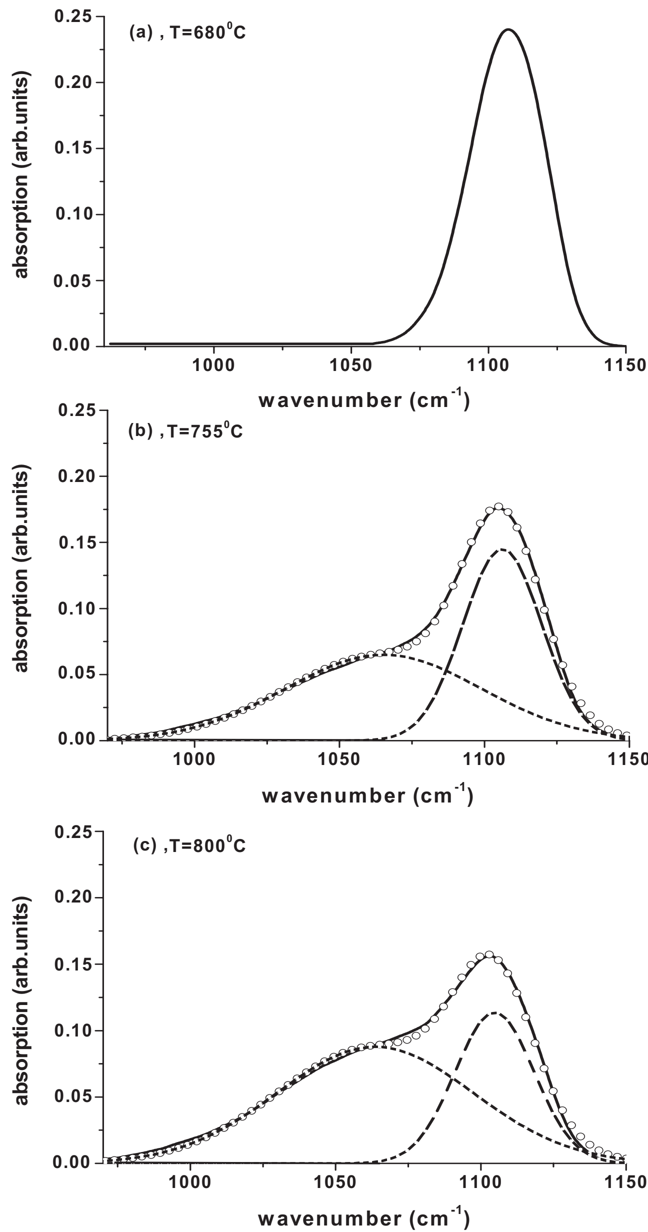

FIG. 3. The same as Fig. 2 for the electron-irradiated Cz-Si 2 sample [(a) $T=680$ °C, (b) $T=755$ °C, and (c) $T=800$ °C].

nuclei when the diffusing oxygen atoms begin to aggregate upon annealing. The formation of these nuclei occurs when the radius of growing aggregates exceeds a critical size. The formation of SiO_x precipitates is known to be accompanied by injection of self-interstitials. In the presence of self-interstitials, vacancies, and oxygen precipitation particles, the critical radius r_{c,SiO_x} is given by the equation[3]

$$r_{c,\mathrm{SiO}_x}=2\sigma\left\{\frac{ExkT}{\Omega_P}\ln\left[\frac{C_\mathrm{O}}{C_\mathrm{O}^*}\left(\frac{C_V}{C_V^*}\right)^\beta\left(\frac{C_I^*}{C_I}\right)^\gamma\right]-6\mu\delta\varepsilon\right\}^{-1}. \quad (1)$$

Here σ is the interface energy per unit area; C_O, C_V, C_I and $C_\mathrm{O}^*, C_V^*, C_I^*$ are the concentrations of interstitial oxygen, vacancies, and self-interstitials in the matrix and those under thermal equilibrium, respectively; Ω_P is the SiO_x molecular volume; β and γ represent the number of absorbed vacancies and the number of emitted self-interstitials for the release of the strain per precipitated oxygen atom, respectively; and x is the number of oxygen atoms per silicon atom, k the Boltzmann constant, δ is the linear misfit, ε is the constrained strain, and μ is the shear modulus of the matrix M and $E=(1+\delta-\varepsilon)$.[3] The concentrations of interstitial oxygen atoms C_O^*, vacancies C_V^*, and self-interstitials C_I^* under intrinsic thermal equilibrium conditions are approximately equal[22] to their solubilities $C_\mathrm{O}^{\mathrm{eq}}$, C_V^{eq}, and C_I^{eq} correspondingly. Therefore, Eq. (1) gives

$$r_{c,\mathrm{SiO}_x}=2\sigma\left\{\frac{ExkT}{\Omega_P}\ln\left[\frac{C_\mathrm{O}}{C_\mathrm{O}^{\mathrm{eq}}}\left(\frac{C_V}{C_V^{\mathrm{eq}}}\right)^\beta\left(\frac{C_I^{\mathrm{eq}}}{C_I}\right)^\gamma\right]-6\mu\delta\varepsilon\right\}^{-1}. \quad (2)$$

In the case of strain-free precipitate growth under intrinsic thermal equilibrium conditions, one can set[22] $\delta=0$ and $E=1$. Therefore, Eq. (2) can be written as

$$r_{c,\mathrm{SiO}_x}=2\sigma\left\{\frac{xkT}{\Omega_P}\ln\left[\frac{C_\mathrm{O}}{C_\mathrm{O}^{\mathrm{eq}}}\left(\frac{C_V}{C_V^{\mathrm{eq}}}\right)^\beta\left(\frac{C_I^{\mathrm{eq}}}{C_I}\right)^\gamma\right]\right\}^{-1}. \quad (3)$$

It is obvious from the foregoing equation that under supersaturation of intrinsic defects, the oxygen precipitation can be affected in two ways: excess vacancies decrease r_{c,SiO_x}, and thus, they enhance the nucleation process, whereas excess self-interstitials produce an opposite effect.

On the other hand, the free energy for addition of an oxygen atom ($x=1$) to a precipitate nucleus is obtained from the critical radius of the precipitate[23] by using the formula

$$\Delta G=-\frac{2\sigma\Omega_P}{r_{c,\mathrm{SiO}_x}}. \quad (4)$$

Combining Eqs. (3) and (4) one gets

$$\Delta G=-kT\ln\frac{C_\mathrm{O}}{C_\mathrm{O}^{\mathrm{eq}}}\left(\frac{C_V}{C_V^{\mathrm{eq}}}\right)^\beta\left(\frac{C_I^{\mathrm{eq}}}{C_I}\right)^\gamma. \quad (5)$$

If the self-interstitial emission ratio is not taken into account ($\gamma=0$), Eq. (5) leads to a more simple formula,[24]

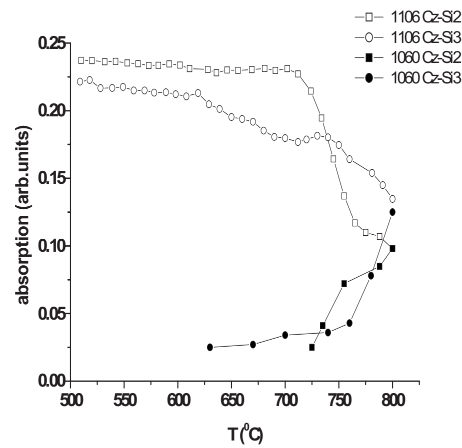

FIG. 4. Evolution of the IR bands of isolated interstitial oxygen (1160 cm^{-1}) and oxygen precipitates (1060 cm^{-1}) in the neutron-irradiated Cz-Si 3 and electron-irradiated Cz-Si 2 samples upon isochronal annealing.

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$$\Delta G = -kT\left[\ln\frac{C_{\mathrm{O}}}{C_{\mathrm{O}}^{\mathrm{eq}}} + \beta\ln\left(\frac{C_V}{C_V^{\mathrm{eq}}}\right)\right]. \tag{6}$$

Obviously, excess vacancies contribute to lower ΔG, thus making the oxygen nucleation process energetically more favorable. Therefore, it is expected that precipitation processes should be enhanced under this condition.

Along with the production of isolated Frenkel pairs in Cz-Si during neutron irradiation, there are also disordered regions as an additional source of vacancies and self-interstitials upon annealing. Mobile self-interstitials are trapped by carbon atoms forming various carbon-related complexes in carbon-rich materials, but they are also prone to form larger aggregates. With increasing temperature of annealing the latter ones are transformed into extended structural defects such as dislocation loops[3] and rodlike defects.[17] Because of this, an effect of self-interstitials on the loss of isolated interstitial oxygen after each annealing step in the course of the isochronal anneals sequence is relatively less important than that of vacancies. Therefore, the supersaturation of vacancies in neutron-irradiated Cz-Si plays a key role in enhanced precipitation processes of oxygen. This is reflected in the observed changes in the IR spectra displaying a marked decay of the oxygen band at lower temperatures in the case of neutron irradiation. Besides, it might also be well to point out that the influence of self-interstitials on oxygen precipitation processes in heat-treated Cz-Si was found to be rather small.[25]

Earlier it has been suggested that oxygen diffusion can be enhanced in the presence of VO complexes.[26] In the temperature range where oxygen precipitation takes place, such defects are known to be very unstable. However, in the presence of large excess of vacancies in neutron-irradiated Cz-Si, they, as temporary traps of oxygen atoms, can be of considerable significance for enhanced diffusion of oxygen. Because of a much smaller damaging factor for electron irradiation, such effects may play a subsidiary role in the latter case.

Additionally, there is evidence that for oxygen precipitates carbon impurity atoms can act as effective heterogeneous nucleation sites[27] particularly in the form of various perturbed O_i-C_i complexes[28] at $\sim 750\ ^\circ\mathrm{C}$. Therefore, an effect of enhanced oxygen precipitation can also be observed in carbon-rich Cz-Si irradiated with fast neutrons. Moreover, it has been argued[29] that similar effects of effective heterogeneous nucleation sites upon enhanced oxygen precipitation can be produced by large vacancy-oxygen complexes. Actually, such complexes V_mO_n exist in neutron-irradiated materials in appreciable concentrations.[16] Finally, in the temperature range of about $700\ ^\circ\mathrm{C}$ both vacancy- and interstitial-type large complexes coexist in neutron-irradiated Cz-Si. However, such interstitial-type complexes are believed to be more stable[30] because of their shorter distorted bonds, in contrast to multivacancy complexes. As a result, the latter defects should be annealed out at lower temperatures, retaining large excess of vacancies for enhanced oxygen precipitation.

No significant restoration of isolated interstitial oxygen is observed at any stage of isochronal annealing. This means that some oxygen-related complexes, most likely being IR inactive, are very stable even at high temperatures.

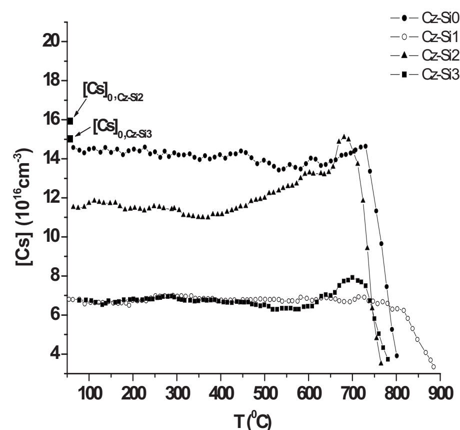

FIG. 5. Behavior of isolated substitutional carbon (IR band at 605 cm^{-1}) in the Cz-Si 0, Cz-Si 1, Cz-Si 2, and Cz-Si 3 samples upon isochronal annealing.

2. Behavior of carbon

Figure 5 displays the behavior of carbon impurity atoms in the Cz-Si 0, Cz-Si 1, Cz-Si 2, and Cz-Si 3. The relative loss of isolated substitutional carbon C_s due to the irradiation in the neutron-irradiated Cz-Si was found to be much larger than that in the electron-irradiated material, $\Delta[C_s]/[C_s]_0 \approx 55\%$ and 28%, respectively. The reason for this is a significant difference in the damaging factors for irradiation with fast neutrons and electrons, as pointed out above in this section. It is well known[10] that self-interstitials in irradiated Cz-Si are selectively trapped by C_s. As a result, interstitial carbon atoms C_i are created. They are mobile around room temperature leading to formation of C_iC_s and C_iO_i pairs as well as large complexes.[10]

In contrast to the behavior of oxygen upon annealing at higher temperatures, there is a well defined annealing stage in both the electron- and neutron-irradiated samples, leading to a partial restoration of isolated substitutional carbon. As is seen from Fig. 5, this stage begins to develop around $500\ ^\circ\mathrm{C}$ in the electron-irradiated Cz-Si, and it becomes much more pronounced around $600\ ^\circ\mathrm{C}$ where a similar stage also appears in the neutron-irradiated material. The restoration of carbon impurity atoms at lattice sites continues up to the onset of their disappearance from the IR spectra around $700\ ^\circ\mathrm{C}$. It is interesting that $\approx 94\%$ of substitutional carbon is recovered in the electron-irradiated Cz-Si at this annealing stage, whereas only $\approx 53\%$ in the neutron-irradiated material (see Fig. 5). Remarkably, the complete loss of isolated substitutional carbon in the course of the isochronal anneals sequence occurs at lower temperatures in irradiated Cz-Si than in nonirradiated materials, $T \approx 800\ ^\circ\mathrm{C}$ and $T \approx 900\ ^\circ\mathrm{C}$, respectively.

The restoration of isolated substitutional carbon in irradiated Cz-Si upon annealing is apparently a combination of reactions that result in recovery of interstitial carbon atoms at lattice sites. The general picture appears to be more sophisticated than it could be envisioned at first sight. It is possibly related to the nucleation process and growth of immobile

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atomic clusters, thus providing the driving force for precipitation processes of carbon upon annealing. With the increasing temperature of annealing the reactions involving vacancies, self-interstitials, and impurity atoms C_s and C_i give rise to the formation of $C_N(Si_I)_M$ complexes.[31] The latter ones can serve as nuclei for carbon precipitation. By this way of arguing, we think that with increasing annealing temperature a fraction of $C_N(Si_I)_M$ defects trapping extra self-interstitials can be transformed to SiC-based precipitates. Concurrently, vacancies V and self-interstitials Si_I can also react with $C_N(Si_I)_M$ complexes, leading to the recovery of substitutional carbon. Thus, there are two processes running in parallel: the recovery of substitutional carbon from carbon-related defects and $C_N(Si_I)_M$ complexes and the transformation of $C_N(Si_I)_M$ complexes to SiC-based precipitates. Upon annealing the latter process is much more pronounced in irradiated Cz-Si materials than in nonirradiated Cz-Si because of large excess of vacancies and self-interstitial available after irradiation. This is why carbon precipitation processes take place at lower temperature in irradiated Cz-Si (see Fig. 5).

It would be instructive to compare the oxygen and carbon precipitation processes in terms of the classical nucleation theory. As mentioned above, oxygen in Si is an interstitial impurity, and its precipitation is a diffusion-limited process with random jumps of an oxygen atom from one interstitial site to another. It is well known that the growth of oxygen precipitates in the form of silicon dioxide is accompanied by a dilatation of volume. Carbon in Si, however, is a substitutional impurity and its diffusion requires the presence of point defects.[32] Carbon diffusion is assisted by mobile carbon interstitials C_i (in reality C_i is a complex defect $[CSi]_I$ in a dumbbell configuration due to trapping of a self-interstitial by a substitutional carbon atom). However, an accurate description of experimental diffusion data suggests[32,33] that the Frank–Turnbull mechanism ($C_s \rightarrow C_i + V$) should also be taken into account. Furthermore, the carbon precipitation processes necessitate a nucleation stage, which, in turn, involves either formation of small SiC particles or loose C–Si agglomerates.[4,32,33] Both processes result in a diminution of volume. This is accompanied by absorption of self-interstitials or emission of vacancies. It should be noticed that the exact reverse is needed for formation of oxide precipitates. The critical radius $r_{c,\mathrm{SiC}}$ for carbon precipitates is given by the equation[32]

$$r_{c,\mathrm{SiC}} \approx \sigma_c \left\{ \frac{kT}{\Omega} \ln\left[\frac{C_\mathrm{C}}{C_\mathrm{C}^*} \left(\frac{C_I}{C_I^*} \right) \right] \right\}^{-1}. \tag{7}$$

Here σ_c is the interface energy per unit area, C_C, C_I, C_C^*, and C_I^* are the concentrations of carbon and self-interstitials in the matrix and those under thermal equilibrium, respectively, and Ω is the SiC molecular volume. Obviously, the critical radius $r_{c,\mathrm{SiC}}$ depends on excess concentration of self-interstitials, contrary to the case of oxide precipitates where the critical radius r_{c,SiO_x} depends on excess concentration of vacancies.

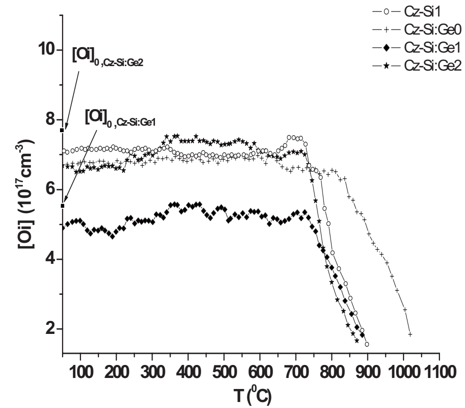

FIG. 6. Behavior of isolated interstitial oxygen (IR band at 1160 cm^{-1}) in the Cz-Si 1 Cz-Si:Ge 0, Cz-Si:Ge 1, and Cz-Si:Ge 2 samples upon isochronal annealing.

3. Ge-doped Cz-Si

This section contains preliminary results on the behavior of carbon and oxygen impurities in Ge-doped irradiated and nonirradiated samples. In the Si crystal lattice Ge impurity atoms assume substitutional sites. Being isoelectronic to host atoms they are electrically inactive. However, their tetrahedral covalent radius is larger than that of Si atoms. Because of this, the Ge doping of Si leads to the appearance of internal strains. As a consequence, the Ge atoms trap selectively free vacancies produced by irradiation with fast electrons, and in this way they can serve as temporary traps for vacancies at room temperature. These impurity atoms are expected to strongly affect formation processes between other impurities such as C and O and intrinsic point defects. The main purpose of this section is to study the behavior of carbon and oxygen impurities in Ge-doped Cz-Si and compare them in relation to Ge-free materials.

4. Behavior of oxygen

Figure 6 displays the oxygen behavior upon annealing in the Cz-Si:Ge materials. For reference, in the same figure we also show the oxygen behavior in the nonirradiated Cz-Si 1 without Ge, having similar oxygen concentration.

It is clearly seen that the Ge doping does not markedly affect the temperature of the complete loss of isolated interstitial oxygen in the irradiated samples upon annealing, cf. samples Cz-Si:Ge 1 and Cz-Si:Ge 2 in Fig. 6 with samples Cz-Si 2 and Cz-Si 3 in Fig. 1. In all these samples, no matter if irradiated or not, the oxygen disappears around 900 °C. Surprisingly, in the nonirradiated Ge-doped sample Cz-Si:Ge 0 the disappearance stage of interstitial oxygen spans a temperature interval from ~840 to ~1020 °C. We observed that the complete disappearance of oxygen in the Cz-Si:Ge 0 sample occurs at about 120 °C higher temperature than that of the sample Cz-Si 1, which has nearly the same initial oxygen concentration. We notice that in the both samples the initial oxygen concentration is below 9×10^{17} cm^{-3} previously suggested[4] as a threshold for effective oxygen precipitation. On the other hand, it is well-known from the literature[2,3] that the oxygen in Si begins to precipitate at much lower initial oxygen concentrations. Together with this,

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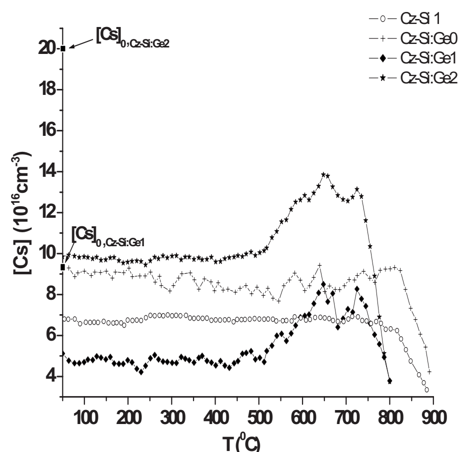

FIG. 7. Behavior of isolated substitutional carbon (IR band at 605 cm^{-1}) in the Cz-Si 1, Cz-Si:Ge 0, Cz-Si:Ge 1, and Cz-Si:Ge 2 samples upon isochronal annealing.

it should be noted that electron irradiation of samples with similar initial concentrations of oxygen below the threshold value does not exhibit such effects (see Fig. 6). Earlier it has been reported[34] that the oxygen precipitation is enhanced in Ge-doped Cz-Si. However, in Cz-Si:Ge samples pretreated at 650 or 750 °C for 64 h, the oxygen precipitation is retarded[35] upon annealing at 1050 °C. We think that the role of Ge in oxygen precipitation in Si cannot be extracted from these preliminary results, and further investigations are needed to gain a deeper insight into this problem.

5. Behavior of carbon

Figure 7 displays the carbon behavior in the Cz-Si:Ge materials as well as the reference nonirradiated Cz-Si 1 sample. It is seen that the Ge doping does not markedly affect the temperature of the complete loss of isolated substitutional carbon in the irradiated samples, cf. samples Cz-Si:Ge 1 and Cz-Si:Ge 2 in Fig. 7 and samples Cz-Si 2 and Cz-Si 3 in Fig. 5. In all these samples the substitutional carbon disappears around 800 °C. However, the recovery stage of substitutional carbon over a temperature range from 500 to 700 °C is substantially suppressed in the electron-irradiated Cz-Si:Ge 1 and Cz-Si:Ge 2 as compared to the Cz-Si 2 also subjected to electron irradiation. Most likely, the Ge atoms serving as temporary traps for vacancies inhibit the recovery reaction of substitutional carbon atoms from $C_N(Si_I)_M$ complexes. It is also possible that in the strained lattice of Cz-Si:Ge carbon atoms are not easily released from the same complexes. It should be noted that this effect in Ge-doped Cz-Si can be practically important for internal gettering of unwanted contaminants. It is also seen that in the nonirradiated samples Cz-Si 1 and Cz-Si:Ge 0, the carbon evolution is practically unaffected by the Ge doping, with the complete loss of carbon at ~900 °C, whereas following electron irradiation the complete loss in the Cz-Si:Ge 1 and Cz-Si:Ge 2 is observed at ~800 °C.

It might be well to point out that the higher concentration of Ge in electron-irradiated Cz-Si, the higher rates of carbon (Fig. 7), and oxygen losses (Fig. 6) are due to irradiation. This is also true for the production of the VO and the C_iO_i defects.[36]

IV. CONCLUSIONS

This work is further documentation of the notion that radiation defects in Si can strongly affect the annealing behavior of practically important impurities such as oxygen and carbon impurities. Especially neutron irradiation with a massive damage factor contributes to a marked lowering of the temperature where the signals from the relevant impurities begin to decay in IR spectra. In this case isolated interstitial oxygen atoms in Cz-Si start to disappear around 600 °C, where the onset of loss of isolated oxygen in the course of isochronal anneals sequence in electron-irradiated and nonirradiated Cz-Si is observed to 700 °C. The effect is attributed to large excess of vacancies in the case of neutron irradiation due to the presence of disordered regions, providing an additional source of vacancies upon annealing. On the other hand, neutron and electron irradiations affect the disappearance of isolated substitutional carbon in Cz-Si, as compared to nonirradiated materials. The phenomenon is attributed mainly to excess self-interstitials, which are present in irradiated materials. The behavior of substitutional carbon in irradiated Cz-Si appears to be complicated, showing partial recovery prior to its complete disappearance. Interestingly, this stage of partial recovery is suppressed in Ge doped Cz-Si. The role of Ge atoms as temporary traps for vacancies in irradiated materials, thus inhibiting one of the ways of carbon restoration, is thought to offer a plausible explanation. In nonirradiated Cz-Si:Ge the temperature of complete loss of isolated interstitial oxygen atoms was found to be higher as compared to that of Cz-Si without Ge. In irradiated Cz-Si:Ge with Ge concentrations of up to 2×10^{20} cm^{-3}, a similar effect is lacking.

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