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# The effect of germanium doping on the evolution of defects in silicon

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ABSTRACT

In the present work infrared (IR) spectroscopy measurements are taken on Ge-doped silicon samples irradiated by 2 MeV electrons to study the thermal evolution of VO defects and $VO_2$ complexes upon annealing. The annealing behavior of these radiation defects was found to be complicated in the presence of Ge. The main reaction $VO + O_i \rightarrow VO_2$ leading to annealing of VO defects and formation of $VO_2$ complexes turned out to be sensitive to concentrations of Ge impurity atoms in Czochralski grown silicon. These processes are discussed in some detail. Moreover, the rates of annealing reactions associated with self-interstitials can also be enhanced in silicon materials doped with Ge. The effects observed are most likely related to elastic strains due to Ge impurity atoms in the silicon lattice.

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## 1. Introduction

At present silicon is most extensively employed in a wide variety of electronic devices. However, modern electronics and microelectronics based on Si materials face up some problems in the field of high speed operation and low noise levels as well as the steadily increasing demand for higher radiation hardness and thermal stability. All these problems, coupled with great request for lower production costs, generate a pressing need for creating new materials. In this respect, doping of silicon with isovalent impurities, first of all, substitutional C and Ge, attract considerable interest. These impurities are electrically inactive in the silicon lattice and, hence, they have no significant influence on electrical parameters of materials. However, they can strongly interact with intrinsic point defects, i.e. vacancies and self-interstitials, because of elastic strains in the crystal lattice related to the mismatch of their atomic size as compared to that of host atoms. This property of isovalent impurities can be used to affect and somehow modify interactions of point defects during crystal growth as well as under irradiation and annealing.

Oxygen is another important impurity in silicon, inadvertably added in crystals during growth from the melt in quartz crucibles, i e by the Czochralski technique (Cz-Si). These impurity atoms are electically inactive. However, they can form a variety of complexes in Si while aggregating upon annealing or interacting with intrinsic point defects under irradiation conditions. In radiation experiments on Cz-Si at room temperature the interstitial oxygen atoms $O_i$ are most effective trapping sites for vacancies giving rise to the appearance of oxygen-vacancy complexes, labelled the A-centers [1]. It is known that at low-temperature irradiation oxygen atoms also trap self-interstitials forming O-$Si_I$ pairs [2]. However, these pairs dissociate slightly above room temperature, so their influence is believed to be subsidiary at $T \geq 300$ K. In contrast, the A-centers are stable at room temperature and they are annealed out around $T \approx 300\,^{\circ}$C. Their annealing behaviour is rather complicated, since there is not a unique reaction path of disappearance of VO defects [3]. Actually, mobile VO pairs can be captured by isolated oxygen atoms, in accordance with the reaction $VO + O_i \rightarrow VO_2$. The local vibrational modes of the VO and $VO_2$ defects are well-known, in particular bands at 830 and 887 $cm^{-1}$ for the neutral VO defect and the $VO_2$ defect, respectively. Along with this way of defect annealing, the disappearance of A-centers can also take place when a mobile self-interstitial $Si_i$ encounters a VO defect $VO + Si_i \rightarrow O_i$ [3].

On the other hand, it is common knowledge that the introduction of isovalent Ge atoms into the silicon lattice gives rise to local compressive strains at Ge sites because of their larger tetrahedral covalent radii. This, in turn, results in the emergence of additional effective traps for mobile vacancies [4]. Taking the both factors into consideration one can expect that the formation and annealing processes of oxygen-vacancy complexes should be sensitive to the Ge presence, though the Ge-vacancy complex is not so stable as the A-center. In the development of our earlier paper [5] the aim of this work is to investigate in detail the annealing behaviour of VO and $VO_2$ defects in Ge-doped Cz-Si with various Ge concentrations.

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## 2. Experimental

There are three groups of samples. As a reference the first group without Ge contained samples of Cz-Si whose oxygen and carbon concentrations before irradiation were $[O_i]_o = 9.45 \times 10^{17}\,cm^{-3}$ and $[C_s]_o < 2 \times 10^{16}\,cm^{-3}$, respectively. Other two groups of Ge-doped Cz-Si labelled Cz-Si:Ge-1 ($[O_i]_o = 6.5 \times 10^{17}\,cm^{-3}$, $[C_s]_o < 2 \times 10^{16}\,cm^{-3}$, and $[Ge] = 7 \times 10^{17}\,cm^{-3}$) and Cz-Si:Ge-2 ($[O_i]_o = 7.7 \times 10^{17}\,cm^{-3}$, $[C_s]_o = 1.2 \times 10^{17}\,cm^{-3}$, and $[Ge] = 2 \times 10^{20}\,cm^{-3}$) consisted of samples with the increasing concentration of Ge. The samples of 2 mm thick were mechanically polished. They were irradiated with 2 MeV electrons at a dose of $5 \times 10^{17}\,cm^{-2}$ using the Dynamitron at Takasaki-JAERI. The irradiation temperature did not exceed 95 °C. Afterwards, the samples were subjected to isochronal annealing up to $T = 650\,°C$, in steps of $\Delta T \approx 10\,°C$ and $\Delta t = 20$ min. After each annealing step IR spectra were recorded by means of FTIR spectroscopy at room temperature, the resolution being of $1\,cm^{-1}$. The two-phonon absorption was always subtracted by using a reference float-zone sample of the same thickness.

## 3. Experimental results and discussion

In the current work we intended to study the effect of Ge doping in silicon on the thermal evolution of the VO and $VO_2$ defects. To this end we used samples with relatively low Ge content, with high Ge content, as well as samples without Ge, for comparison purposes. The used samples had different initial oxygen $[O_i]$, and carbon $[C_s]$ concentrations. These differences are expected to affect the concentration of the VO and $VO_2$ defects but not, to the best of our knowledge, the annealing temperature of the VO defect and the growth temperature of the $VO_2$ defect, which was the main objective of this work.

Fig. 1a and b displays the IR spectra at several selected temperatures over a region of 800–900 $cm^{-1}$ for the reference Cz-Si and Cz-Si:Ge-2, respectively. In this spectral region there are the both bands of interest, at 830 $cm^{-1}$ for the VO defect and at 888 $cm^{-1}$ for the $VO_2$ complex. Going from Fig. 2a–c one can see the thermal evolution of the VO, $VO_2$ and $O_i$ bands for the reference Cz-Si, Cz-Si:Ge-1, and Cz-Si:Ge-2, respectively. Prior to proceed with the discussion of the results, some information concerning the depicted curves should be given. The experimental errors in the IR spectroscopy measurements are of the dimensions of the points of the depicted curves. Since the oxygen concentration is more than one order of magnitude larger than those of the VO and $VO_2$ defects, in order to show their thermal evolution on the same figure, the vertical axis in Fig. 2 were broken and two arbitrary units were chosen. One for the VO and $VO_2$ defects and one for the $O_i$ defect. The latter was about one order of magnitude larger than the former. It is also important to note at this point that, as the temperature was raised in the course of the isochronal anneal sequence, the shape of the 830 $cm^{-1}$ band of the VO defect was distorted at elevated temperatures by the emergence of sidebands of various $V_mO_n$ defects: $V_2O_2$ (824 $cm^{-1}$), $V_3O_2$ (833 $cm^{-1}$) and $V_2O$ (839 $cm^{-1}$) [6]. The contribution of each one of the above bands was recorded by doing computer deconvolution using Lorenztian profiles as described previously [6]. The presented data in Fig. 2 for the evolution of the VO defect represent the net contribution of the 830 $cm^{-1}$ band

As is clearly seen from Fig. 2c, the emergence of the 887 $cm^{-1}$ band occurs at markedly lower temperatures in the Cz-Si:Ge-2 sample than that in the reference one without Ge. In actual fact, this band begins to appear at $T \approx 290\,°C$ for the reference Cz-Si, at $T \approx 280\,°C$ for the Cz-Si:Ge-1, and at $T \approx 250\,°C$ for the Cz-Si:Ge-2. In our previous paper [5], we have preliminary stated that the growth of the $VO_2$ band takes place nearly at the same temperature, both in lightly and heavily Ge-doped Cz-Si. However, the detailed IR measurements in the present work revealed that this temperature decreases with the increasing Ge concentration. From this, it follows that Ge impurity atoms being present in high concentrations in Cz-Si can significantly enhance the formation rate of $VO_2$ complexes upon annealing. It is well known [7,8] that the formation of the $VO_2$ complexes results from the capture of diffusing VO defects by isolated oxygen atoms, in accordance with the reaction $VO + O_i \rightarrow VO_2$ where a vacancy-oxygen pair diffuses as an entity in the crystal lattice until it encounters any oxygen atom being immobile at temperatures around $T \approx 290\,°C$. The enhanced rate of this reaction in Cz-Si:Ge is thought to be due to compressive strains in the Si lattice induced by Ge impurity atoms. Actually, theoretical calculations suggest that the energy barrier for diffusion of vacancy-impurity pairs in Si under compressive stresses is reduced and, as a result, the diffusivity of vacancy-type defects is expected to be increased [9]. Thus, the reaction $VO + O_i \rightarrow VO_2$ occurs at lower temperatures and the growth of the $VO_2$ band makes itself evident in IR spectra. Preliminary measurements showed that even for Cz-Si with lower Ge concentrations of about $1 \times 10^{18}\,cm^{-3}$ this effect is still detectable.

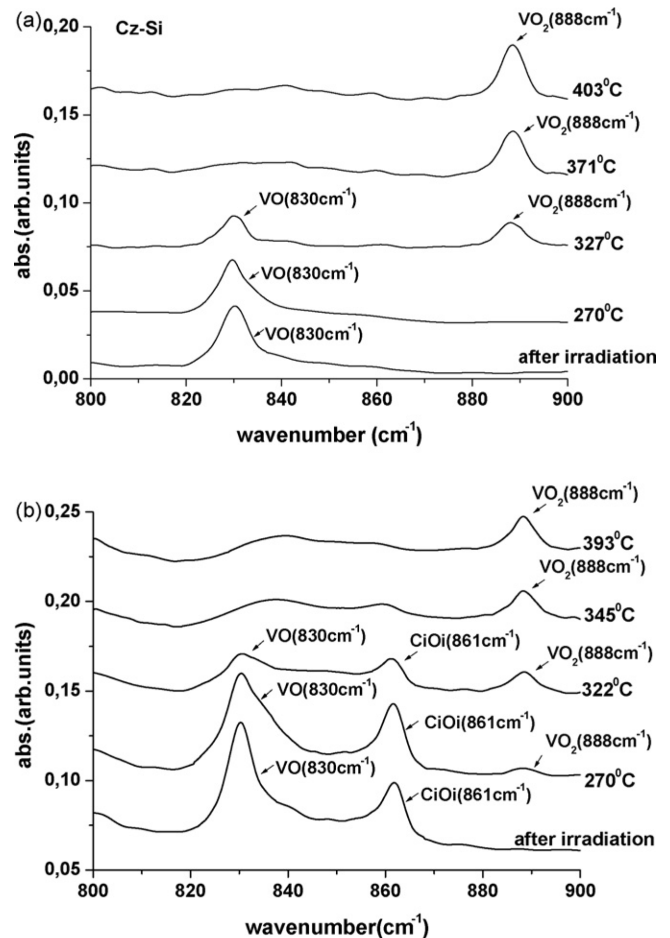


**Fig. 1.** Infrared absorption spectra in the spectral range of VO defects and $VO_2$ complexes for the reference Cz-Si sample without Ge (a) and the heavily Ge-doped Cz-Si:Ge-2 sample (b). Irradiation dose of 2 MeV electrons, $\Phi = 5 \times 10^{17}\,cm^{-2}$. The temperatures of spectra recording are indicated.

Further inspection of Fig. 2c reveals that in Cz-Si with high concentrations of Ge impurity atoms VO defects start to decay before the appearance of $VO_2$ complexes becomes much more pronounced. We suggest that this decay is most likely associated

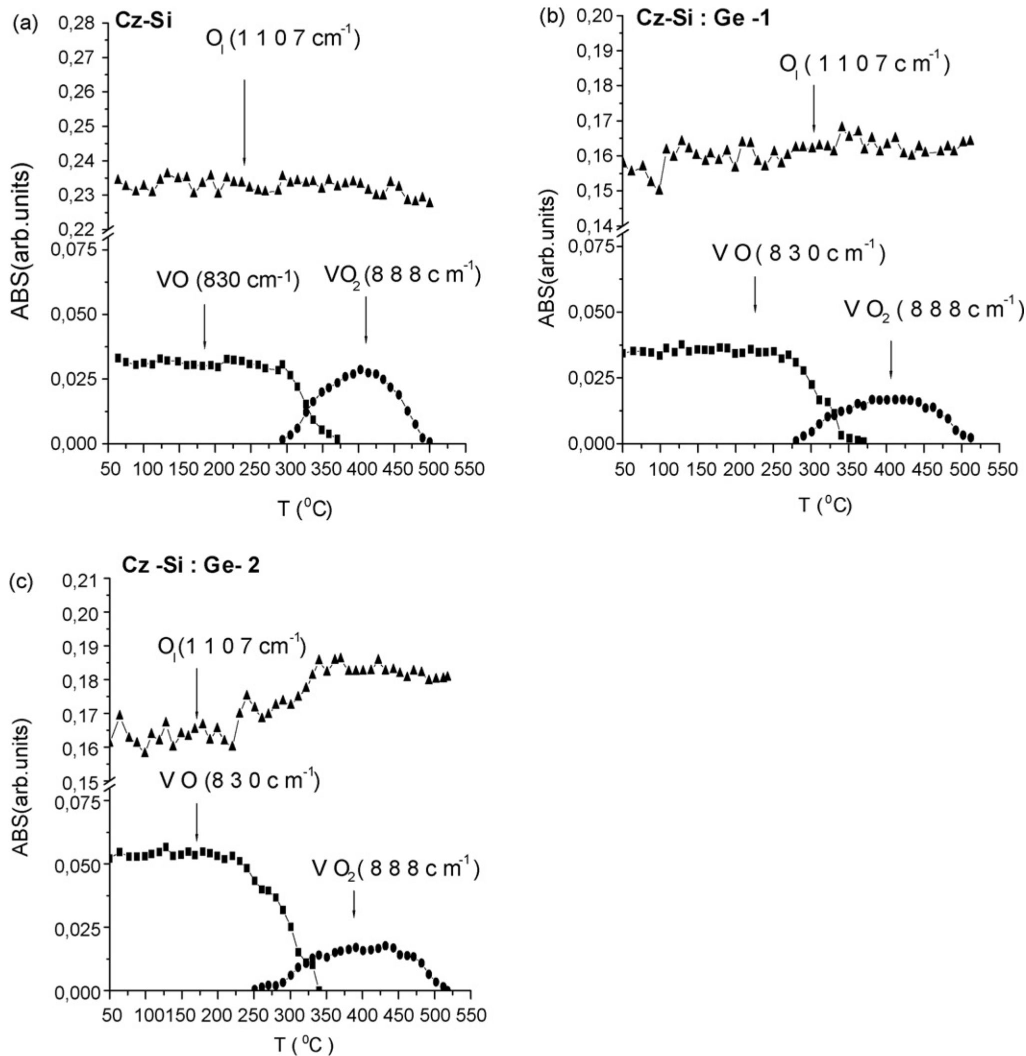


**Fig. 2.** Thermal evolution of $O_i$, VO and $VO_2$ defects in the Cz-Si (a), Cz-Si:Ge-1 (b), and Cz-Si:Ge-2 (c) over the temperature range of $T$ = 50–550 °C.

with the reaction $VO + Si_i \rightarrow O_i$. At these temperatures the self-interstitials can be emitted from small clusters of interstitial type formed during electron irradiation of Cz-Si [10]. Again, such an effect is believed to be enhanced in the presence of Ge atoms in high concentrations. They induce compressive strains in the crystal lattice and, as result, the release of self-interstitials in Cz-Si:Ge should start at lower temperatures as is observed in Cz-Si. What is more, Ge atoms act as effective temporary traps of vacancies during electron irradiation, thus reducing the rate of indirect annihilation of primary defects. Therefore, the concentrations of interstitial-type complexes and clusters in irradiated Cz-Si:Ge is expected to be larger as compared to those in Cz-Si under similar irradiation conditions. The fact that a noticeable increase in the concentration of $O_i$ is seen in IR spectra over the temperature range discussed is also consistent with this way of arguing, see Fig. 2c.

Of course, one should take into consideration that the VO centers diffusing through the lattice can also be captured by Ge atoms, especially in the Cz-Si:Ge-2 where the Ge concentration is about two orders-of-magnitude higher than that of oxygen. Based on the data published in literature [11], the sidebands at 834.6 and 839.2 $cm^{-1}$ attributed to such perturbed VO centers are very close to the main VO band at 830 $cm^{-1}$, so it was impossible for us to separate their contributions. This may be done only for Cz-Si:Ge with Ge concentrations in mid $10^{20}$ $cm^{-3}$.

The thermal evolution of VO defects and $VO_2$ complexes in irradiated Cz-Si:Ge has revealed another important feature of the defect annealing. Upon further heating up to $T$ = 410 °C, the concentration of $VO_2$ complexes is still increasing, even after the complete disappearance of VO defects in IR spectra at $T \approx 375$ °C. This effect is much more pronounced in CZ-Si:Ge with large concentrations of Ge; see for instance Fig. 2c. Apparently, another production reaction of $VO_2$ complexes takes place at these temperatures. It is highly plausible that an additional increase in the concentration of $VO_2$ complexes is caused by formation of oxygen dimers at the temperatures under consideration. As a result, another reaction path $(O_i)_2 + V \rightarrow VO_2$ becomes efficient [12]. Below some arguments in favor of this modeling are given.

It is well known that the diffusivity of isolated oxygen atoms in Si is characterized by an activation energy of 2.5 eV. However, the formation of oxygen-related thermal donor defects in Cz-Si as a result of oxygen aggregation at $T \approx 450$ °C [10] is governed by a substantially lower activation energy of about 1.8 eV. It has been established [9] that this process of oxygen aggregation is mostly associated with diffusion of oxygen dimers formed over a temperature range of $T \approx 350$–470 °C [13,14]. In contrast to isolated oxygen atoms, the dimers turned out to be much faster diffusing species and their diffusivity is characterized by an activation energy slightly less than 1.5 eV [13]. Moreover, it has also been found that the

diffusivity of oxygen atoms in Cz-Si in the temperature range discussed can be greatly enhanced under compressive stresses [15]. A similar effect is also expected for Ge-doped Cz-Si because of isoelectronic Ge atoms having a larger tetrahedral covalent radius than that of host atoms. As a consequence, an additional formation of $VO_2$ complexes can take place with the involvement of divacancies at temperatures around $T \approx 350\,^{\circ}C$ via the following reaction paths $V_2 + O_2 \rightarrow V_2O_2 + Si_I \rightarrow VO_2$ and $V_2 + Si_I \rightarrow V + O_2 \rightarrow VO_2$. These new ways of formation of $VO_2$ defects is marked off by a change in the slope of the evolution curve; see for instance Fig. 2c.

## 4. Conclusions

We have studied the influence of Ge doping on the thermal evolution of VO defects and $VO_2$ complexes in electron-irradiated Cz-Si. It has been found that the reaction $VO + O_i \rightarrow VO_2$ leading to formation of $VO_2$ complexes runs at markedly lower temperatures in Ge-doped materials, so the higher is the Ge concentration, the lower is the temperature at which their formation occurs. Moreover, in Cz-Si:Ge with large Ge concentrations the decay of the VO band is observed at even lower temperatures, before the growth of the $VO_2$ band becomes noticeable. This annealing stage of VO defects is attributed to the reaction $VO + Si_I \rightarrow O_i$. In addition, the concentration of $VO_2$ complexes is still increasing even after the complete disappearance of VO defects. Such additional formation of $VO_2$ complexes is ascribed to the reactions $V_2 + O_2 \rightarrow V_2O_2 + Si_I \rightarrow VO_2$ and $V_2 + Si_I \rightarrow V + O_2 \rightarrow VO_2$. All the above-mentioned reactions that govern the thermal evolution of VO defects and $VO_2$ complexes are influenced by the presence of Ge in Cz-Si. The reaction rates can be enhanced because of compressive strains in the crystal lattice due to Ge impurity atoms.

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## References

[1] G.D. Watkins, J.W. Corbett, Phys. Rev. 121 (1961) 1001.
[2] A. Brelot, J. Charlemagne, in: J.W. Corbett, G.D. Watkins (Eds.), Radiation Effects in Semiconductors, Gordon and Breach, London, 1971, p. 161.
[3] C.A. Londos, N.V. Sarlis, L.G. Fytros, Phys. Stat. Sol. (a) 163 (1997) 325.
[4] V.V. Emtsev, P.M. Klinger, V.I. Fistul, Yu.V. Shmartsev, Sov. Phys. Semicond. 25 (1991) 602.
[5] C.A. Londos, A. Andrianakis, D. Aliprantis, H. Ohyama, V.V. Emtsev, G.A. Oganesyan, Physica B 401–402 (2007) 487.
[6] N.V. Sarlis, C.A. Londos, L.G. Fytros, J. Appl. Phys. 81 (1997) 1645.
[7] J.W. Corbett, G.D. Watkins, R.S. McDonald, Phys. Rev. 135 (1964) A1381.
[8] J.L. Lindström, B.G. Svenson, Mater. Res. Soc. Symp. Proc. 59 (1986) 45.
[9] H. Park, K.S. Jones, J.A. Sinkman, M.E. Law, J. Appl. Phys. 78 (1995) 3664.
[10] R.C. Newman, R. Jones, in: F. Shimura (Ed.), Semiconductor and Semimetals, vol. 42, Academic, New York, 1994, p. 289.
[11] Yu.V. Pomozov, M.G. Sosnin, L.I. Khirunenko, V.I. Yashnik, N.V. Abrosimov, W. Schroder, M. Hohne, Semiconductors 34 (2000) 989.
[12] B.G. Svenson, J.L. Lindström, J.W. Corbett, Appl. Phys. Lett. 47 (1981) 841.
[13] T. Hallberg, J.L. Lindström, Mater. Sci. Eng. B36 (1996) 13.
[14] C.A. Londos, M.J. Binns, A.R. Brown, S.A. McQuaid, R.C. Newman, Appl. Phys. Lett. 62 (1993) 1525.
[15] L.I. Murin, J.L. Lindström, A. Misiuk, Physica B 340–342 (2003) 565.