

IR Studies on VO_n , C_iO_i , and C_iC_s Defects in Ge-doped Cz-Si

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Abstract. This paper reports experimental results on the production and annealing of oxygen-vacancy related (VO_n , $1 < n < 5$) and carbon-related (C_iO_i , C_iO_iI , and C_iC_s) defects in Ge-doped Czochralski-grown silicon (Cz-Si) materials containing carbon. The samples were irradiated by 2 MeV fast electrons and the behavior of radiation-produced defects is studied by means of infrared (IR) spectroscopy, monitoring the relevant bands in spectra. Regarding the VO_n family, it was found that the presence of Ge affects the annealing temperature of VO defects as well as their fraction that is converted to VO_2 defects. Both effects are discussed in relation with an impact of Ge on the concentration of self-interstitials that take part in the annealing of VO defects via two reaction paths $VO + I \rightarrow O_i$ and $VO + O_i \rightarrow VO_2$. Furthermore, two bands at 1037 and 1051 cm^{-1} are attributed to the VO_5 defect, although three other bands at 762, 967 and 1005 cm^{-1} are believed to be associated with V_nO_m clusters containing carbon, most likely having a VO_nC_s structure. Regarding carbon-related complexes, it has been established that the annealing of the 862 cm^{-1} band belonging to the C_iO_i defect is accompanied by the emergence of the 1048 cm^{-1} band previously assigned to the C_sO_{2i} center. The evolution of the C_iC_s and the C_iO_iI bands is monitored and the identification of bands at 947, 967 and 1020 cm^{-1} making their appearance in IR spectra over the temperature range where C_iC_s and C_iO_iI defects are annealed out is discussed.

Introduction

The performance of Si-based devices is influenced by the presence of various impurities in materials. Most important among them are interstitial oxygen (O_i) and substitutional carbon (C_s), both of which are inevitably added to crystals grown by the Czochralski (Cz) technique. Oxygen and carbon impurity atoms are effective traps for vacancies and self-interstitials, respectively. As a result of irradiation of Si with MeV electrons, oxygen atoms pair with mobile vacancies, giving rise to VO centers [1, 2]. These defects have been studied extensively by various experimental techniques for a long time, and a lot of information has been gathered so far [1-5].

On the other hand, substitutional carbon atoms in irradiated materials are partly turned to carbon interstitials (C_i). The latter ones are mobile at room temperature and they can be trapped by O_i and C_s atoms, forming C_iO_i and C_iC_s complexes, respectively [6]. Moreover, with increasing dose of irradiation C_iO_i , C_iC_s and C_i defects act as traps for self-interstitials (I) giving rise to larger clusters, such as C_iO_iI , C_iC_sI and C_iI complexes. The behavior and properties of carbon-related defects, especially those mentioned above, have also been extensively studied, but the whole picture of defect reactions is not complete. Particularly, the identification of defects formed in the course of annealing is not well understood yet [6-12]. Some important points need further investigations.

It is apparent that the doping of Si crystals with isoelectronic impurities is a convenient way to affect some important properties of materials. In particular, it was found that the Ge dopant can be widely used for defect engineering in Cz-Si [13]. Because the tetrahedral covalent radius of a Ge impurity atom in the Si lattice is larger than that of a host atom, the Ge atoms give rise to local

elastic strains which, in turn, affect quasi-equilibrium concentrations of vacancies and self-interstitials upon irradiation and annealing. Reasonably, one can expect that secondary defect reactions would be affected, too. Hence, it is instructive to study an impact of the Ge dopant on the behavior and properties of oxygen-vacancy and carbon-related defects in Si.

Upon annealing at about 300°C, mobile VO defects (830 cm⁻¹) are transformed to VO₂ complexes (888 cm⁻¹) by trapping one additional oxygen atom. At elevated temperatures progressive agglomeration of oxygen takes place, giving rise to VO₃ (904, 967, and 1000 cm⁻¹) and VO₄ defects (985 and 1010 cm⁻¹), and then to VO₅ and VO₆ complexes [14-17]. A number of IR bands have been generally attributed to the VO₅ or VO₆ structures [18-21] but a reliable assignment to the VO₅ and VO₆ defects has not been made. The picture of defect formation processes is still incomplete mainly because of weak intensities of the relevant bands. No identification have been made so far for the VO_n (n>6) bands, even though theoretical predictions for the VO₇ complex are already available in the literature [22].

The main aim of the present work is to study the thermal stability and transformation processes of VO_n (n<6) defects as well as carbon-related C_iO_i, C_iC_s and C_iO_iI complexes in Ge-doped Cz-Si. In this way we are broadening investigations carried out in the last years [23-27], regarding some important effects of the Ge presence in Cz-Si on the behavior and properties of radiation-produced defects.

Experimental

In this experiment we studied two groups of Cz-Si samples with 15·10·1.8 mm³ dimensions. One group of Ge-free samples with initial concentrations of oxygen and carbon [O_i]_o=9.56·10¹⁷ cm⁻³ and [C_s]_o < 2·10¹⁶ cm⁻³, respectively, is labeled E4 and another group of Ge-doped samples with initial impurity concentrations [Ge]_o=2·10²⁰ cm⁻³, [O_i]_o=7.7·10¹⁷ cm⁻³ and [C_s]_o=1.8·10¹⁷ cm⁻³ is designated Ge8. Several samples from the two groups were irradiated with 2 MeV electrons at ~80°C using the Dynamitron accelerator at Takasaki-JAERI (Japan). The irradiation dose was 5·10¹⁷ cm⁻². After the irradiation, they were subjected to 20 min isochronal anneals. After each annealing step, IR spectra were recorded at room temperature by means of a Fourier Transform Infrared (FTIR) spectrometer, of type JASCO-470 plus, operated with a resolution of 1 cm⁻¹. The intrinsic two-phonon absorption was always subtracted making use of a float-zone sample of equal thickness.

Experimental results and discussion

Fig.1a and Fig. 1b show some fragments of the IR spectra of the E4 and Ge8 samples, respectively, just after the irradiation and in the course of isochronal annealing at two characteristic temperatures of 250°C and 300°C. Fig.2 is complementary to Fig.1, displaying the spectra at higher annealing temperatures, i.e. between 400°C and 670°C. In doing so, some weak IR bands appearing at elevated temperatures could be depicted more clearly.

VO_n defects Fig.3a and Fig.3b show the evolution of the VO_n bands for the E4 and the Ge8 samples, respectively. Upon annealing, VO is converted to VO₂ at about 300°C and successively to VO₃, VO₄ and generally to VO_n defects at higher temperatures. In this experiment, we studied the transformations of VO_n to VO_{n+1} defects, tracing the members of this family up to n=5. It was found that some characteristic features of these complexes are greatly affected by the Ge presence. As an example, the annealing temperature of VO defects shifts at lower temperatures in the Ge-doped samples compared to that in the Ge-free samples, T~220°C and 290°C, respectively. Together with this, the fraction of VO defects converted to VO₂ complexes is greatly reduced in the Ge-doped Cz-Si. These effects were investigated earlier [25-27]. There is a certain correlation with elastic strains introduced by Ge isoelectronic impurity atoms in the Si lattice. As a result, the fraction of self-interstitials taking part in the annealing of VO defects is turned out to be sensitive to the presence of Ge. Actually, this annealing is mainly governed by two reactions: VO + O_i → VO₂ and VO + I → O_i. Sources of self-interstitials are large defect clusters formed in irradiated materials [28]. It is

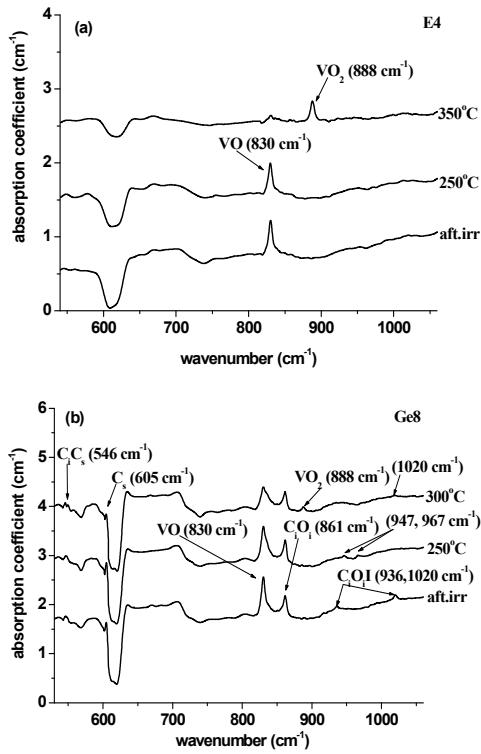


Fig.1 IR spectra of the E4 (a) and Ge8 (b) samples, after irradiation and at selective temperatures below 400°C.

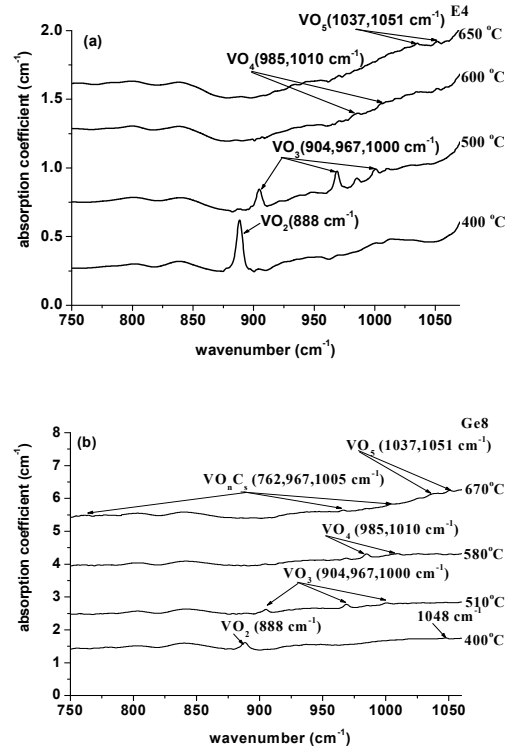


Fig.2 IR spectra of the E4 (a) and Ge8 (b) samples, at selective temperatures in the range 400-700°C.

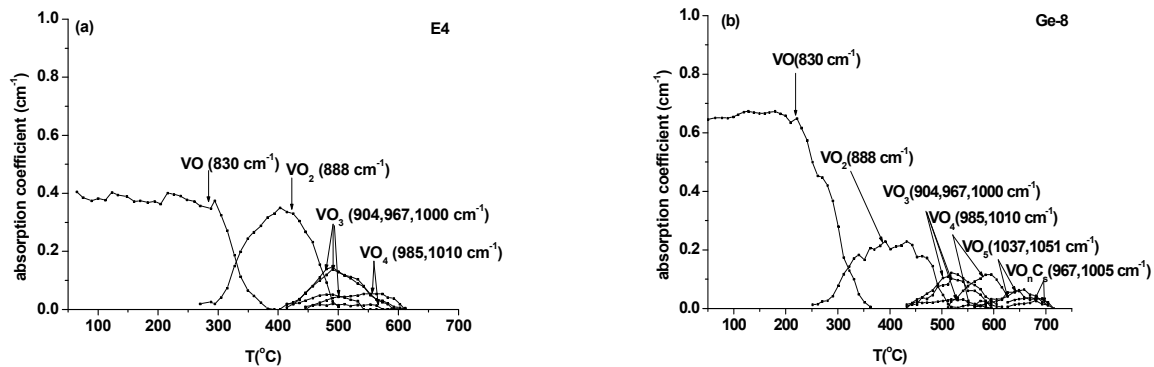


Fig.3 Thermal evolution of VO_n related bands for the E4 (a) and Ge8 (b) samples.

argued that the presence of Ge impurity atoms due to their elastic strains enhance the release of self-interstitials from such clusters by reducing their binding energy [26-27]. In other words, the reaction $VO + I \rightarrow O_i$ could start at lower temperatures, in accordance with our observations. In the same way of arguing, the enhancement of the $VO + I \rightarrow O_i$ reaction relative to the reaction $VO + O_i \rightarrow VO_2$ leads to reduced concentration of VO defects available for the transformation into VO_2 complexes, as the [Ge] content increases, in agreement with our experimental findings.

At higher annealing temperatures, above 550°C, two bands at 1037 and 1051 cm^{-1} are emerging in IR spectra in both groups of samples, simultaneously with the disappearance of the 985 and 1010 cm^{-1} bands related to VO_4 defects; see Fig.2. These bands could be positively attributed to the VO_5 defect [27, 29], the next member of the VO_n family. Their thermal evolution depicted in Fig.3,

however only for the Ge-8 sample. For the E4 sample the bands are very weak and therefore their evolution is not presentable. At elevated temperatures above 620°C, three bands at 762, 967 and 1005 cm^{-1} are developed in IR spectra in the carbon-rich Ge8 samples only. The 762 cm^{-1} band is very weak, slightly above the detection limit of our equipment. However, it features the same thermal stability as the other two bands, so all the three bands are thought to stem from the same complex. Their identification is not completely positive, since they could be related either to the VO_6 defect or, in general terms, to higher-numbered V_nO_m complexes [18-22, 27, 29]. Taking into account that they appear only in carbon-rich materials [27, 29] we should tentatively attribute them to V_nO_m complexes, also incorporating carbon impurity atoms in their atomic structures. Interestingly, a simple candidate of a VO_nC_s complex was suggested previously [27].

Carbon-related defects It was found that the annealing of C_iO_i (862 cm^{-1}) defects is accompanied

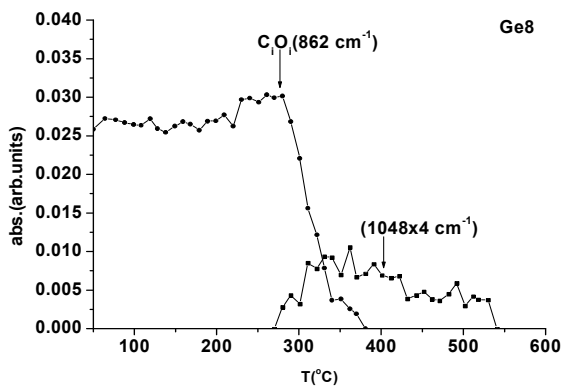


Fig.4 Thermal evolution of the C_iO_i and the 1048 cm^{-1} bands.

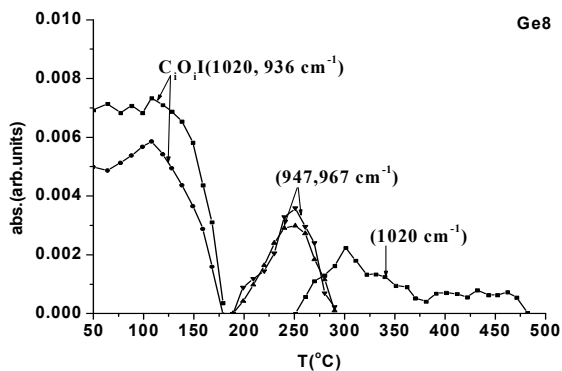


Fig.5 Thermal evolution of the $\text{C}_i\text{O}_i\text{I}$, the 947, 967 cm^{-1} pair and the 1020 cm^{-1} bands.

belonging to $\text{C}_i\text{O}_i\text{I}$ defects are transformed into three bands at 724, 952 and 973 cm^{-1} in the course of annealing around 200°C. At higher temperatures of 250° to 275°C, these three bands are, in turn, transformed into other three bands at 969, 951 and 977 cm^{-1} . In optical measurements taken at room temperatures, the intermediate group of bands is missed and only two bands at 947 and 966 cm^{-1} from the third group are detected. Apparently, these two bands correlate well with a pair of bands at 947 and 967 cm^{-1} observed in our IR measurements. Murin et al [32] have proposed that the three groups of the bands under discussion correspond to different atomic configurations of $\text{C}_i\text{O}_i\text{I}$ defects. However, this seems to be in conflict with theoretical calculations which predicted that the two latter groups may originate from $\text{C}_i\text{O}_i\text{I}_n$ complexes with $n>1$ [33]. Additionally, it should be noted

with the emergence of another weak band at 1048 cm^{-1} (Fig.4) in IR spectra, earlier attributed to $\text{C}_s\text{O}_2\text{i}$ defects [30]. Accordingly, the following formation reaction was proposed: $\text{C}_i\text{O}_i + \text{VO} \rightarrow \text{C}_s\text{O}_2\text{i}$. It should be noticed that two bands at 1052 and 1099 cm^{-1} , detected with IR measurements taken at cryogenic temperatures, are reportedly associated with $\text{C}_s\text{O}_2\text{i}$ defects [31]. These bands are observed after irradiation at temperatures over the range of 400° to 600°C. Another formation reaction was suggested: $\text{VO}_2 + \text{C}_i \rightarrow \text{C}_s\text{O}_2\text{i}$. The 1052 cm^{-1} band seen in the optical measurements at cryogenic temperatures may likely correspond to the 1048 cm^{-1} band recorded in our measurements at room temperature. Any signal corresponding to the 1099 cm^{-1} band was not detected in our studies, possibly because it is very weak. Besides, it may be masked by a strong O_i band at 1106 cm^{-1} in this spectral range.

Fig.5 shows the evolution of the 1020 and 936 cm^{-1} bands previously assigned to $\text{C}_i\text{O}_i\text{I}$ complexes [6, 11, 32]. In the annealing experiments the bands begin to decay at $\sim 120^\circ\text{C}$ and they disappear completely in IR spectra at $\sim 180^\circ\text{C}$. At elevated temperatures, two other bands at 947 and 967 cm^{-1} make their appearance in the IR spectra. Their intensities reach a maximum around 250°C and after that point they disappear at $\sim 300^\circ\text{C}$. From this picture, any apparent connection between the two pairs of bands could not be drawn. However, IR measurements carried out at cryogenic temperatures [32] revealed that two bands at 940 and 1024 cm^{-1}

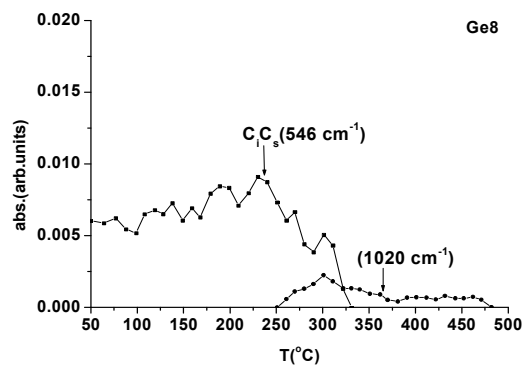


Fig.6 Thermal evolution of the C_1C_s and the 1020 cm^{-1} bands.

that two bands at 965 and 944 cm^{-1} in neutron-irradiated silicon have been previously attributed to $C_1C_sI_2$ defects [34]. This assignment was based on the fact that the two latter bands appear in IR spectra simultaneously with the disappearance of another pair of bands at 987 and 993 cm^{-1} ascribed to C_1C_sI defects. However, the 987 and 993 cm^{-1} bands were not detected in the present study and, therefore, any assignment of these bands to a next member of this family, i.e. the $C_1C_sI_2$ complex, cannot receive support. In any case, further experiments are required in order to establish the nature of the 947 and 967 cm^{-1} bands. Interestingly, the thermal stability of the carbon-related bands is not affected by the Ge presence, at least in concentration up to $[Ge]=2\cdot 10^{20}\text{ cm}^{-3}$ [26].

Finally, it is worthwhile to comment on the following observation. The decay of the 947 and 967 cm^{-1} bands is accompanied by the emergence of another band at 1020 cm^{-1} (Fig.5). It is hardly conceived that C_1O_iI defects could be restored to their original form. Reasonably, one should suggest that the new 1020 cm^{-1} band stems from different complexes, so there is a mere coincidence of frequencies. Fig.6 indicates that the 1020 cm^{-1} band may correlate with the decay of the 546 cm^{-1} band belonging to C_1C_s defects. Future experiments will settle this issue.

Summary

Effects of Ge doping on the evolution of oxygen-vacancy defects in Cz-Si were studied. It was found that the conversion of VO defects to VO_2 complexes is sensitive to the Ge presence, both in lowering the temperature of the VO annealing and $[VO_2]/[VO]$ ratios. The effects of Ge are explained by enhanced releasing of self-interstitials from clusters, affecting the balance between the reactions $VO + O_i \rightarrow VO_2$ and $VO + I \rightarrow O_i$. Regarding carbon-related defects, the effects of Ge doping is not clearly defined. The identity of defects associated with IR bands at 947 and 967 cm^{-1} emerged upon annealing of C_1O_iI defects is discussed. Another band at 1020 cm^{-1} was found to be related to carbon impurity atoms. The positive identification of these bands needs further investigation.

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