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IR studies of oxygen–vacancy defects in electron-irradiated Ge-doped Si

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Abstract

The thermal evolution of multioxygen–vacancy (VO_n) centers produced in electron-irradiated Czochralski-grown Ge-doped Si was studied by means of IR spectroscopy. Two groups of samples with low $[Ge] \leqslant 1 \times 10^{17}\,cm^{-3}$ and high $[Ge] = 2 \times 10^{20}\,cm^{-3}$ were used. We found that the annealing temperature of vacancy–oxygen complexes (A-centers) produced in the course of irradiation at room temperature is substantially decreased in the samples with high [Ge]. This effect is explained taking into account an influence of the elastic stresses due to Ge atoms in the Si lattice on the migration barrier of A-centers as well as the rate of oxygen-related reactions, i.e. $VO + O_i \rightarrow VO_2$, $VO + Si_I \rightarrow O_i$, etc. We also found that the ratio of A-centers converted to VO_2 defects is smaller in the material with high [Ge]. The same is also true for the conversion reaction $VO_2 + O_i \rightarrow VO_3$. Contrary, the next reaction $VO_3 + O_i \rightarrow VO_4$ shows a markedly enhanced rate if the Ge content is high. This observation can be explained considering the effects of Ge-induced stresses in the Si lattice on the successive trapping of oxygen atoms by A-centers and other VO_n complexes as well as on the enhanced diffusivity of oxygen.

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1. Introduction

Irradiation of Czochralski-grown silicon (Cz-Si) leads to the formation of oxygen–vacancy complexes, so-called A-centers, where a single oxygen atom occupies a vacant site, with a slight off-center displacement. The A-center has been studied extensively by many experimental techniques [1]. Upon thermal annealing these defects are transformed into V_mO_n complexes by successive trapping of oxygen and vacancies [2]. An important class of such complexes represents a family of VO_n defects [2,3] which forms in the course of coalescence of oxygen atoms to the initial VO cores. There is keen interest in understanding their electrical and optical properties for engineering purposes in the fabrication of Si-based electronic devices.

The characteristics of Si-based devices, e.g. their resistance to radiation damage, are also sensitive to the presence of such isovalent impurities as C and Ge. Actually, carbon and germanium impurity atoms in Si are effective sinks for intrinsic defects (self-interstitials and vacancies, respectively) and, therefore, they can be practically important in radiation and heat treatment processes. The presence of substitutional Ge atoms gives rise to compressive elastic strains in the Si lattice due to a sizeable difference in their covalent tetrahedral radii ($r_{Ge} = 1.22$ Å, $r_{Si} = 1.17$ Å). These strains can be relieved by the capture of vacancies and it is expected that Ge impurity atoms act as effective trapping sites for vacancies. In actual fact, the germanium–vacancy complex in Si irradiated at low temperatures was reliably identified by EPR a long time ago [4]. This complex was found to be unstable in the temperature range of 220–280 K. Studies of the annealing behavior of these defects revealed a

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pronounced tendency for the Ge atoms to form complexes with oxygen and carbon, too [5]. The picture of the annealing processes observed is yet incomplete.

There are many steps in processing of Si materials, among them implantation and thermal treatment. The formation of many complex defects in the processing depends on the concentration and properties of intrinsic defects produced. Certainly, the presence of Ge atoms prone to associate with vacancies in Si affects the balance of intrinsic defects in technological processes. By way of example, these isovalent impurity atoms can exert a significant influence on the formation and annealing kinetics of secondary radiation defects in Si [6–8]. The observed reduction in the formation rate of radiation defects in Ge-doped Si is satisfactorily explained taking into account that Ge atoms can also act as indirect annihilation centers for vacancies and self-interstitials [7]. However, this model was subjected to question in Ref. [9] where heavily Ge-doped materials were used. Thus, the role of Ge doping in radiation-produced defects in Si needs further investigation. The purpose of this paper is to study the effect of low and high Ge doping levels on the thermal evolution of VO_n defects in irradiated Si.

2. Experimental

Two groups of Cz-Si samples doped with phosphorus in concentrations $[P] = (1–2) \times 10^{14}\,cm^{-3}$ were used. The first group was strongly doped with Ge in concentrations of about $2 \times 10^{20}\,cm^{-3}$ and the second one contains Ge impurity atoms in concentrations $\leqslant 10^{17}\,cm^{-3}$ as a background impurity. The oxygen and carbon contents were $[O_i] = 9.3 \times 10^{17}\,cm^{-3}$ and $[C_s] = 2 \times 10^{16}\,cm^{-3}$ in the lightly Ge-doped samples and $[O_i] = 7.7 \times 10^{17}\,cm^{-3}$ and $[C_s] = 2 \times 10^{17}\,cm^{-3}$ in the strongly Ge-doped samples. The thickness of samples was about 2 mm and they were mechanically prepolished. Irradiations with 2 MeV electrons were carried out using the Dynamitron accelerator at Takasaki-JAERI. The irradiation temperature was 95 °C. The typical fluence of fast electrons was $5 \times 10^{17}\,e^-/cm^2$. After the irradiation, the samples were subjected to isochronal annealing up to 650 °C, in steps of $\Delta T = 10\,°C$ and $\Delta t = 20\,min$. After each annealing step, the IR absorption spectra were recorded by means of a FTIR spectrometer with a resolution of $1\,cm^{-1}$. The two-phonon absorption was always subtracted using a reference float-zone Si sample of the same thickness.

3. Experimental results and discussion

Fig. 1a and b displays the IR spectra in the region of $800–1050\,cm^{-1}$ at several selected temperatures of annealing. There are many peaks in the spectra, among them the VO band ($830\,cm^{-1}$), VO_2 band ($888\,cm^{-1}$), VO_3 band (904, 968, $1000\,cm^{-1}$) and VO_4 band (985, $1010\,cm^{-1}$) [2,10] for the lightly (Fig. 1a) and heavily (Fig. 1b) Ge-doped samples. Fig. 2a and b shows the thermal evolution

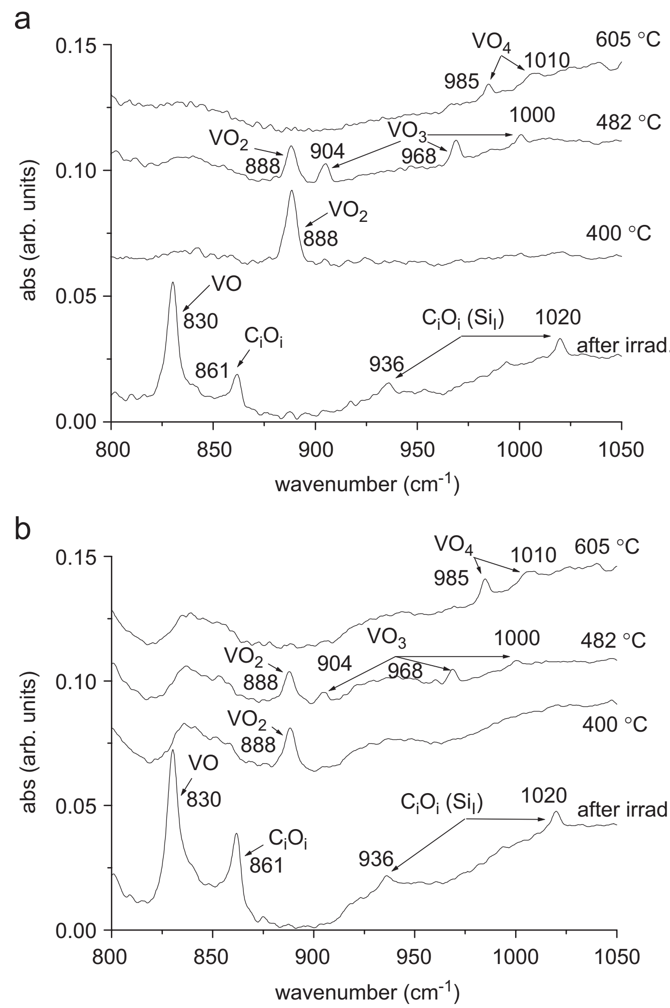

Fig. 1. Fragments of IR absorption spectra for the lightly (a) and heavily (b) Ge-doped Cz-Si subjected to fast electron irradiation and subsequent annealing at selected temperatures.

of the VO, VO_2 and VO_3 bands for the lightly and heavily Ge-doped samples, respectively. As is clearly seen from these figures, the annealing temperature of VO defects in the heavily Ge-doped sample is much lower (~220 °C) than that in the lightly Ge-doped sample (~290 °C). In the following, two explanations are possible:

(1) A significant fraction of VO defects can be localized near Ge impurity atoms, especially in the heavily Ge-doped Si where the inter-impurity distance of Ge is about 20 Å. Earlier in Ref. [8] it has been concluded that similar defects in the vicinity of a source of elastic strains due to Ge atoms are characterized by a reduced energy barrier for migration. In this line of thinking, one can expect a noticeable decrease in the annealing temperature of VO complexes.
(2) Studies of Cz-Si irradiated with 2 MeV electrons, especially at large doses, have led to the conclusion [11] that, along with the reaction $VO + O_i \rightarrow VO_2$, the VO defects also participate in the reaction with self-interstitials $VO + Si_I \rightarrow O_i$ during the annealing.

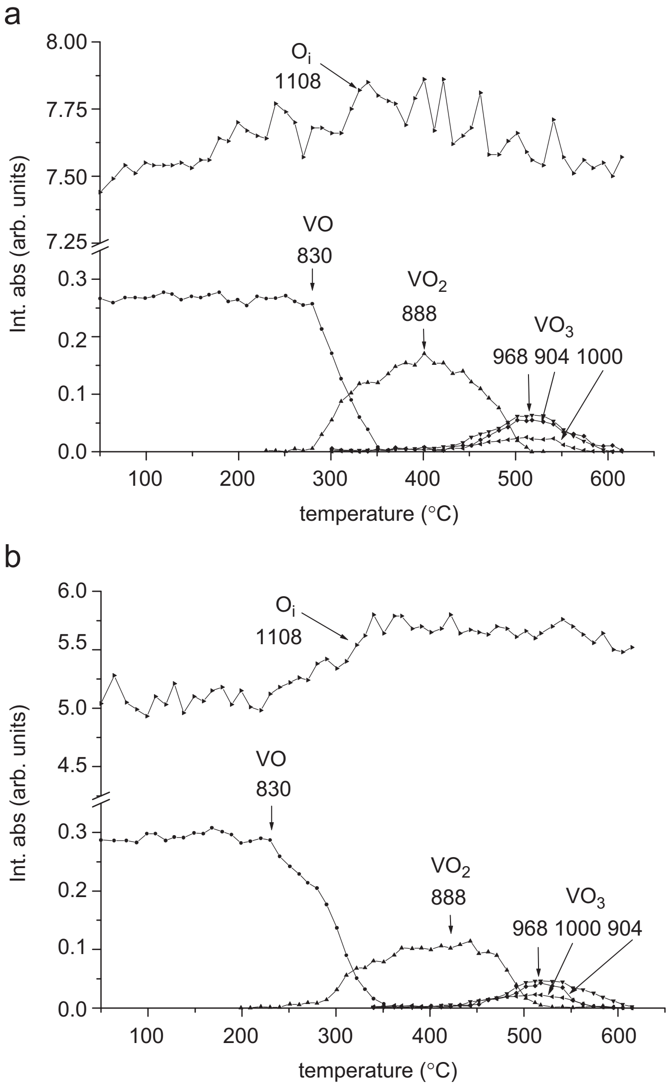

Fig. 2. Thermal evolution of the VO (830 cm^{-1}), VO_2 (888 cm^{-1}) and VO_3 (904, 968 and 1000 cm^{-1}) IR bands in the lightly (a) and heavily (b) Ge-doped Cz-Si subjected to fast electron irradiation with subsequent annealing.

The sources of self-interstitials upon heating are their large clusters formed in the course of heavy irradiation. The binding energy of self-interstitials at these clusters is also thought to be sensitive to the strains induced by Ge impurity atoms. As a result, the liberation of self-interstitials from these clusters leading to the above-mentioned annealing reaction should take place at lower temperatures. This suggestion is strongly supported by the fact that the oxygen concentration increases in parallel with a faster annealing of VO defects in the heavily Ge-doped material (Fig. 2b), in agreement with the reaction $VO+Si_I \rightarrow O_i$. However, the real picture appears to be more complicated. In actual fact, a similar tendency for an increase in the oxygen concentration is observed in the lightly Ge-doped Si as well, though to a lesser extent; see Fig. 2a. It may be that in this temperature range additional oxygen atoms are also released from other sources which are inactive in IR absorption, both in the lightly and heavily Ge-doped materials. An increase in the concentration of oxygen seen after the annealing at 300 °C can be related to the dissociation reaction $VO \rightarrow V+O_i$ [12] running together with the reaction $VO+Si_I \rightarrow O_i$.

As is evident from Fig. 2a and b, the concentration of VO_2 defects is markedly decreased with increasing concentration of Ge in Cz-Si. It means that the conversion of VO complexes into VO_2 defects is retarded in heavily Ge-doped materials. This observation is consistent with the model of the increasing efficiency of the $VO+Si_I \rightarrow O_i$ reaction in materials with high concentration of Ge, indicating that a larger fraction of VO defects are destroyed by trapping of self-interstitials. Interestingly, in the lightly and heavily Ge-doped samples the growth of the VO_2 band occurs in the same temperature range around 290 °C (Fig. 2a and b), indicating that the reaction $VO+O_i \rightarrow VO_2$

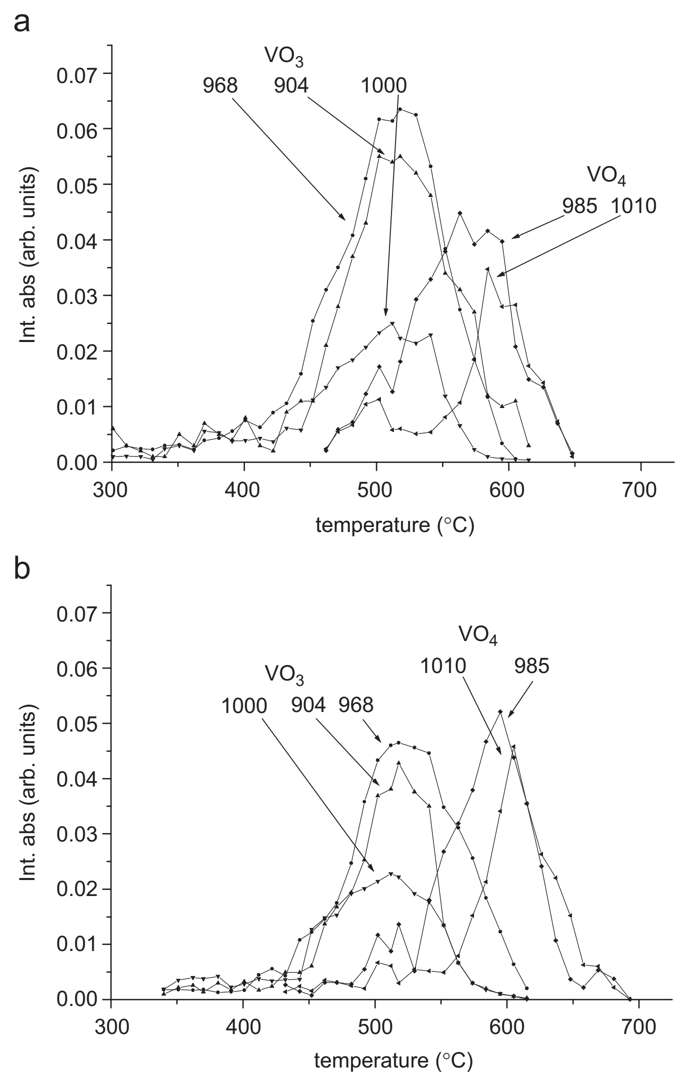

Fig. 3. Thermal evolution of the VO_3 (904, 968 and 1000 cm^{-1}) and VO_4 (985 and 1010 cm^{-1}) IR bands in the lightly (a) and heavily (b) Ge-doped Cz-Si subjected to fast electron irradiation with subsequent annealing.

takes place at this temperature, whereas the annealing reaction $VO+Si_I \rightarrow O_i$ is activated at lower temperatures around 220 °C. As a consequence, the formation of VO_3 defects due to the reaction $VO_2+O_i \rightarrow VO_3$ in the heavily Ge-doped material is slow down, too. In the foregoing, we take into account that variations in the carbon concentration of samples should appreciably affect neither the formation rate of VO complexes [13] nor the formation of VO_n defects. Accordingly, we believe that the observed changes are mostly related to the presence of Ge impurity atoms in Cz-Si.

Fig. 3a and b displays the evolution of VO_3 and VO_4 defects in the lightly and heavily Ge-doped samples, respectively. Evidently, the conversion of VO_3 into VO_4 complexes running at temperatures above 500 °C is markedly enhanced in the heavily Ge-doped material. At these temperatures oxygen impurity atoms in Si diffuse rapidly [14], so the formation of VO_4 defect takes place via the direct reaction $VO_3+O_i \rightarrow VO_4$. The oxygen diffusivity is reportedly enhanced in Ge-doped Cz-Si [15]. Consequently, the trapping rate of oxygen atoms in the latter reaction should also increase with increasing concentration of Ge.

4. Conclusions

We have studied the evolution of a sequence of VO_n defects in Ge-doped Czochralski-grown Si subjected to fast electron irradiation and subsequent annealing. It is demonstrated that the annealing processes of VO defects as well as such related VO_2, VO_3 and VO_4 complexes formed in the consecutive reactions $VO \rightarrow VO_2 \rightarrow VO_3 \rightarrow VO_4$ are markedly sensitive to the presence of germanium. The effects observed are attributed to the strains induced in the Si crystal lattice by Ge impurity atoms. As a result, the concentrations of these defects and their annealing characteristics can be distinctly changed with increasing Ge concentration.

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