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The effect of germanium doping on the production of carbon–related defects in electron-irradiated Czochralski silicon

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Abstract. We present infrared (IR) spectroscopy measurements on carbon-rich, germanium-doped Czochralski-grown (Cz-Si) subjected to irradiation with 2 MeV electrons. The study is focused on the effect of germanium doping on the production of carbon-related defects C_iC_s, C_iO_i and $C_iO_i(Si_I)$. For carbon concentrations $[C_s]$ up to $1\cdot10^{17}$ cm^{-3} the production of the defects increases with the increase of Ge content, for [Ge] up to $1\cdot10^{20}$ cm^{-3}. However, for carbon concentrations around $2\cdot10^{17}$ cm^{-3} the production of these defects shows a decrease for samples with $[Ge]=2\cdot10^{20}$ cm^{-3} in comparison with those of $[Ge]=2\cdot10^{19}$ cm^{-3}. The results are discussed taking into account the effect of germanium on the annihilation of vacancies and self-interstitials in the course of irradiations. In the first case, due to the temporary trapping of vacancies by Ge atoms in the course of irradiation, more self-interstitials are available for the production of carbon interstitials (C_s+ $Si_I \rightarrow C_i$), leading finally to an increase of the carbon-related defects. In the second case, and for [Ge] of the order of $\sim10^{20}$ cm^{-3} or higher, Ge atoms tend to form large clusters. These clusters attract primary defects facilitating their annihilation on them. As a result, the availability of self-interstitials decreases, which finally leads to a decrease of the carbon-related defects.

Introduction

Carbon, besides oxygen, is the most common impurity in silicon introduced during crystal growth. It belongs to the IV group of the periodic system. It is an isovalent impurity in the Si lattice incorporated at substitutional sites (C_s). Because of the fact that its tetrahedral covalent radius (r_{cs} = 0.77 Å) is smaller than that of Si (r_{si} = 1.17 Å), its addition to the lattice induces strains. As a result the impurity reacts promptly with self-interstitials.

Germanium, is another isovalent impurity in Si. Its importance for the silicon-based technology has been increased in the late years. For instance, due to its presence in the Si lattice the density of microdefects, the formation of thermal donors and oxygen precipitates as well is affected [1]. Additionally, the mechanical strength of the material increases. Moreover, Ge-doped Si appears suitable for certain applications of the ULSI technology. Because Ge has a tetrahedral covalent radius larger than that of Si (r_{Ge} =1.22 Å), it introduces compressive strains in the lattice. These strains are relieved by the capture of vacancies.

Miniaturization is inevitable in modern electronic technology both for increasing the packing density of various circuits but also for improving the efficiency of devices, decreasing simultaneously the energy consumption. The diminution of the dimensions introduces stresses which affect the formation and the properties of various defects. It is important therefore to study the impact of pressure in silicon. Additionally, since Ge introduces internal mechanical stresses in the material, it would be reasonable to investigate their effect. Any acquired knowledge would be beneficial by analogy to corresponding issues related with pressure in the framework of device design and fabrication for microelectronics. For instance in Cz-Si, germanium dopant suppresses the formation of thermal donors although it enhances oxygen precipitation [1]. On the other hand external hydrostatic pressure has a different effect. It enhances TDs formation and oxygen precipitation as well [2,3]. Thus, understanding the mechanisms that govern the influence of germanium doping on oxygen aggregation processes in silicon we expect to shed light on the corresponding mechanisms of the application of hydrostatic pressure on these phenomena and vice versa. Notice in addition that pressure, either uniaxial or hydrostatic, is used widely as a probe to investigate various phenomena, processes and mechanisms in solids [4,5,6,7,8]. It provides an additional channel for getting insight on the properties of materials. Therefore the study of Ge induced internal local strains in the Si lattice and the influence on the behavior of the material is important from this point of view as well, in order to draw relative conclusions, and apply the acquired experience.

During irradiation substitutional carbon atoms are displaced to interstitial positions by the capture of self-interstitials: $C_s + Si_I \rightarrow C_i$ (Watkins replacement reaction). These carbon interstitials are very mobile at room temperature and react readily with oxygen interstitials to form the C_iO_i center ($C_i + O_i \rightarrow C_iO_i$) and with carbon substitutional to form the C_iC_s center ($C_i + C_s \rightarrow C_iC_s$) [9]. On high radiation doses the C_i, C_iO_i and C_iC_s defect act as additional sinks for self-interstitials leading to the formation of $C_i(Si_I)$, $C_iC_s(Si_I)$ and $C_iO_i(Si_I)$ complexes [9,10]. Spectroscopic techniques as Electron Paramagnetic Resonance (EPR), Infrared Spectroscopy (IR), Deep Level Transient Spectroscopy (DLTS), Photoluminescence (PL), and others has shown [9,11-14] that carbon in Si participate in a large number of reactions giving a large variety of carbon-related complexes. Most of the carbon-related defects introduce levels in the gap, affecting the electrical properties of Si. This issue is very important for the electronic technology. The major scope of this paper is to investigate the effect of germanium doping on the concentrations of carbon-related defects in Si.

Experimental details

Czochralski grown germanium-doped silicon (Cz-Si:Ge) samples with dimensions of 20x10x2 mm^3 were used in this work. Their initial germanium, carbon, and oxygen concentrations are cited in table 1. The samples were irradiated with 2MeV electrons, at a dose of $5{\cdot}10^{17}$ cm^{-2}, using the Dynamitron accelerator at Takasaki-JAERI (Japan). After the irradiation all the samples were subjected to 20min isochronal anneals up to 800^{o}C, in steps of $\Delta T \approx 10^o$C. After each annealing step, the IR spectra were recorded at room temperature, by means of a FT-IR spectrometer with a resolution of 1cm^{-1}. The two phonon intrinsic absorption was always subtracted by using a float-zone sample of equal thickness.

Experimental results and discussion

Fig.1 shows the IR spectra of sample Cz-Si:Ge-4 prior and after irradiation. In the following we shall omit the part Cz-Si from the name of the samples: for instance Cz-Si:Ge-4 will appear as Ge-4. Prior to irradiation only the usual bands of the O_i (1107 cm^{-1}, 515 cm^{-1}) and the C_s (604 cm^{-1}) impurities are present. After the irradiation a number of bands appear in the spectra. The most prominent of them are those of the VO defect at 830 cm^{-1} and the C_iO_i defect at 861 cm^{-1}. Another pair of bands at 936 and 1020 cm^{-1} originate from the $C_iO_i(Si_I)$ complex [9,10].The band at 546 cm^{-1} has been previously correlated with the C_iC_s pair [15], although the band at 526 cm^{-1} with the C_sC_s pair [16].The initial concentrations of the oxygen, carbon and Ge impurities are cited in table 1. The oxygen concentration of the samples was found by measurements of the 1107 cm^{-1} absorption band using a calibration coefficient of $3.14{\cdot}10^{17}$ cm^{-2} [17]. The concentration of carbon was found by measurements of the 605 cm^{-1} absorption band using a calibration coefficient of $3.14{\cdot}10^{17}$ cm^{-2} [18]. The concentrations of the C_iO_i, C_iC_s and $C_iO_i(Si_I)$ defects are also cited in table 1. The calibration

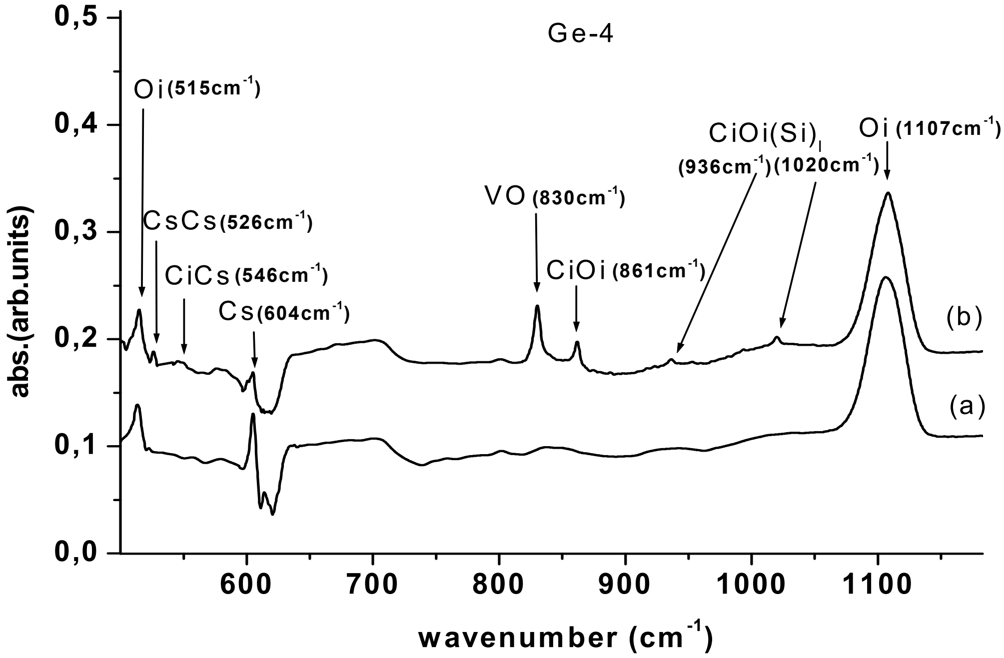

Fig.1. Fragments of the IR spectra of Ge-4 sample before (a) and after irradiation (b).

coefficients for the C_iO_i (861 cm^{-1}) band was taken $1.1\cdot10^{17}$ cm^{-2} [19], for the $C_iO_i(Si_I)$ (1020cm^{-1}) band $3.8\cdot10^{16}$ cm^{-2} [19], and for the C_iC_s (546 cm^{-1}) band $1.5\cdot10^{15}$ cm^{-2} [15].

As we can see from the data in table 1, the samples used contain carbon with concentrations in the range of $2\cdot10^{16}$-$2\cdot10^{17}$ cm^{-3} and Ge with concentrations in the range $1\cdot10^{17}$-$2\cdot10^{20}$ cm^{-3}. Although the results could be presented by ordering the samples based on carbon content we decided to order them based on Ge content for two reasons. Firstly, because Ge concentrations in the samples span over three orders of magnitude in comparison with the concentrations of carbon which spans over one order. Secondly, because the effect of Ge isovalent impurity on carbon-related defects has not been discussed as extensively in the literature as has been done with carbon.

Figs 3, 4 and 5 show the concentration of the C_iO_i, C_iC_s and $C_iO_i(Si_I)$ defects versus [Ge],correspondingly. In order to describe the effect of Ge content on the production of the carbon-related defects, we have divided the samples in two groups. Group I contains the samples Ge-1, Ge-3, Ge-4, Ge-7 with initial carbon concentration up to $1\cdot10^{17}$ cm^{-3}. Group II contains the samples Ge-5 and Ge-8 with initial carbon concentration around $2\cdot10^{17}$ cm^{-3}. We notice at first that in all the used samples the Ge concentrations was less than one atomic per cent. We have no reason to believe that such low Ge concentrations could noticeably affect the threshold energy of elastic displacement of the host Si atoms as well as the fraction of Frenkel pairs as primary defects separated into isolated vacancies and self-interstitials [20]. However, the indirect annihilation rate of the primary defects is expected to be dependent on the Ge concentration. In this line of argumentation, the results presented in Figs 3-5 and table 1 can be understood as follows.

Sample name	[Ge] (cm^{-3})	$[O_i]_o$ 10^{17}(cm^{-3})	$[C_S]_o$ 10^{16}(cm^{-3})	$[C_iO_i]$ 10^{16}(cm^{-3})	$[C_iC_s]$ 10^{14} (cm^{-3}	$[C_iO_i(Si)_I]$ 10^{15}(cm^{-3})
Ge-1	$1\cdot10^{17}$	9.60	2.0	1.55	1.25	2.96
Ge-3	$1\cdot10^{18}$	10.00	3.0	1.96	1.30	3.20
Ge-4	$4\cdot10^{18}$	5.55	10.0	2.55	1.31	3.29
Ge-5	$1\cdot10^{19}$	6.74	20.0	4.21	1.30	3.34
Ge-7	$1\cdot10^{20}$	8.77	3.7	2.31	1.35	3.81
Ge-8	$2\cdot10^{20}$	7.70	18.0	3.91	1.20	3.16

Table 1. The initial oxygen, carbon and Ge concentrations as well as the concentrations of the C_iO_i , C_iC_s and $C_iO_i(Si)_I$ defects of the electron-irradiated Ge-doped Si samples used. The irradiation dose is $5\cdot10^{17}$ cm^{-2}.

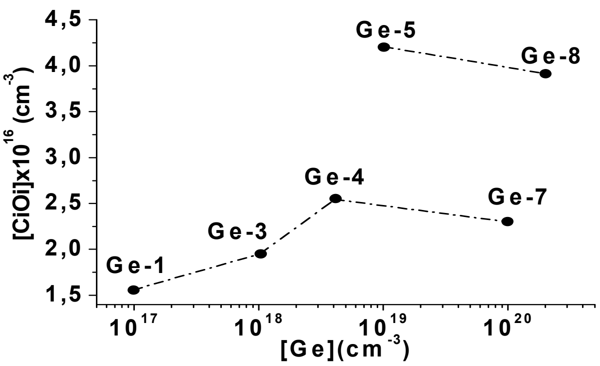

Fig.3 C_iO_i concentration versus Ge content in Si

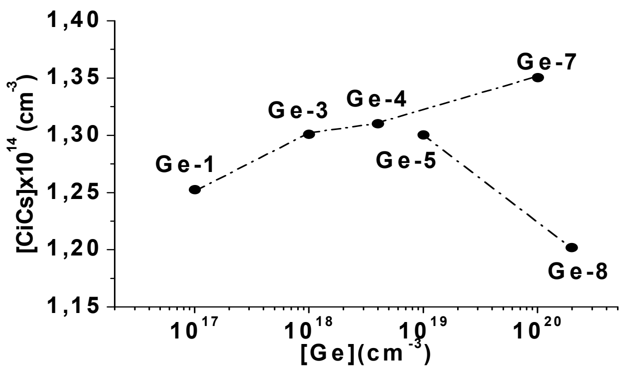

Fig.4 C_iC_s concentration versus Ge content in Si

Concerning group I samples we observe immediately that the concentrations of the C_iO_i, CiC_s and $C_iO_i(Si_I)$ defects increase with the increase of Ge concentration. It is well-known that Ge atoms can efficiently compete with oxygen in silicon in trapping the vacancies [21,22]. Thus during low temperature irradiation Ge-V pairs are formed which are stable [21] up to 200K. At higher temperatures, the Ge-V centers dissociate releasing vacancies. At room temperature irradiation, Ge atoms act as temporary traps for vacancies. These temporary trapped vacancies are preventing from direct annihilation with self-interstitials allowing for more self-interstitials to participate in alternative reaction channels. In other words the annihilation ratio of vacancies and self-interstitials is reduced due to the Ge presence. As a result, more self-interstitials are available for reaction with C_s atoms (C_s+Si_I $\rightarrow C_i$). Therefore, more C_iO_i, C_iC_s and $C_iO_i(Si_I)$ defects are produced in agreement with our observations. Concerning group II samples we observe that the concentrations of the C_iO_i, C_iC_s and $C_iO_i(Si_I)$ defects of

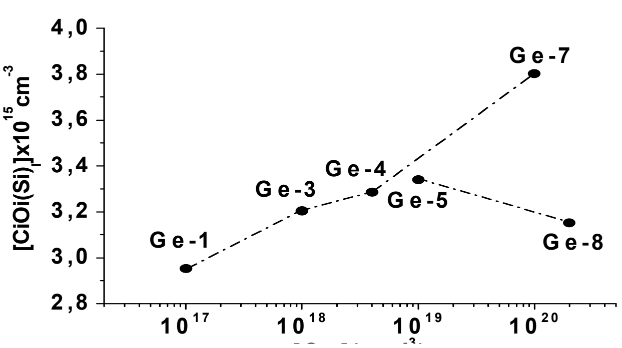

Fig.5 $C_iO_i(Si_I)$ concentration versus Ge content in Si.

samples with [Ge]=$1\cdot10^{19}$ cm^{-3} are larger than those of samples with [Ge]=$2\cdot10^{20}$ cm^{-3}. Noticeably, the photoluminescence spectra of irradiated Ge-doped samples exhibit [23] significant differences between Ge concentrations of $1\cdot10^{19}$ cm^{-3}and $2\cdot10^{20}$ cm^{-3}. It was found that when Ge atoms are present at concentrations of the order of 10^{20}cm^{-3} they become the main sinks for Frenkel pairs components. At these concentrations, Ge atoms induce high compressive strains in the Si lattice and they tend to form clusters. A percentage of the primary defects produced by the irradiation are forced to migrate along the gradient of the strain fields and annihilate at the sites of these clusters. As a result, the annihilation rate of the primary defects is enhanced. Therefore,the availability of self-interstitials is reduced which leads to lesser production of the C_iO_i, C_iC_s and $C_iO_i(Si_I)$ defects at samples with [Ge]=$2\cdot10^{20}$ cm^{-3}.

Summary

The effect of Ge doping on the production of the irradiation-induced defects C_iO_i, C_iC_s and $C_iO_i(Si_I)$ in Cz-Si crystals containing various carbon concentrations was investigated. For samples with [Cs]≤$1\cdot10^{17}$ cm^{-3} the production of the radiation defects show an increase with the Ge content. It is argued that the ability of Ge atoms to act as temporary traps for vacancies reduce the annihilation rate ($V+ Si_I\rightarrow\varnothing$) of the primary defects, thus increasing the availability of self-interstitials to react with carbon substitutional atoms. As a result, the concentrations of the carbon-related defects is increased. For [Cs]≈ $2\cdot10^{17}$ cm^{-3} the concentrations of the radiation defects is higher for samples with [Ge]= $1\cdot10^{19}$ cm^{-3} than those with [Ge]= $2\cdot10^{20}$ cm^{-3}. These results are explained by taking into account the tendency of Ge atoms at [Ge] of the order 10^{20} cm^{-3} to form clusters. The strain fields of these clusters force a percentage of the primary defects to be trapped by them. As a result, the annihilation rate of the primary defects is increased. Therefore the availability of self-interstitial is reduced. This finally leads to a reduction of the concentration of the carbon-related radiation-induced defects.

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