

The Effect Of Germanium Doping On The Annealing Characteristics Of The VO And VO₂ Defects In Silicon

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Nowadays, silicon is the most important material in electronic industry. It is employed in a wide variety of applications. However, modern electronics and microelectronics face problems with corresponding Si-based devices especially concerning high speed operation, low noise level, high operating frequencies, as well as the increased demand for higher radiation hardness and thermal resistance. All these problems, coupled with the need of low manufacturing costs, pose the necessity of creating new materials. In this context, doping of silicon with isovalent impurities attract considerable interest. These impurities are electrically inactive and they do not exert strong influence on initial parameters of materials. However, the elastic strains introduced in materials due to their different atomic size than that of regular atoms can effectively change interactions of impurities with intrinsic defects such as vacancies and self-interstitials. This property of isovalent impurities can be used to affect and somehow control interactions between point defects during crystal growth as well as under irradiation and annealing.

Oxygen is the most important impurity in commercial Czochralski grown silicon. It is electrically inactive. However, during irradiation or/and heat treatment various oxygen-related defects, especially multioxygen-multivacancy complexes V_nO_m, are formed. The majority of these defects are electrically active, exerting strong effects on electrical properties of Si materials. On the other hand, it is known that the introduction of Ge into silicon gives rise to compressive strains in the lattice, since the isovalent Ge atoms are larger in atomic size. As a result, they are effective traps for vacancies. Therefore, the formation and annealing of V_nO_m defects is expected to be influenced by the Ge presence. The aim of this work is to investigate these effects.

To this goal, Ge-doped Si samples (table 1) with various Ge concentrations up to 2×10²⁰ cm⁻³ were used. They were irradiated with 2 MeV electrons at a dose of 5×10¹⁷ e/cm². The irradiation temperature was 95°C. After the irradiation, the samples were subjected to isochronal annealing up to 650°C, in steps of ΔT= 10°C and Δt= 20 min. After each annealing step, IR absorption spectra were recorded by means of a FTIR spectrometer.

Sample name	[Ge] cm ⁻³	[O _i] 10 ¹⁷ cm ⁻³	[C _i] 10 ¹⁶ cm ⁻³	[VO] 10 ¹⁶ cm ⁻³
Cz-Si	0	9.56	<2.0	2.35
Ge-1	1·10 ¹⁷	9.60	2.0	3.40
Ge-2	7·10 ¹⁷	6.50	<2.0	2.50
Ge-3	1·10 ¹⁸	10.00	3.0	3.50
Ge-4	4·10 ¹⁸	5.55	10.0	3.60
Ge-5	1·10 ¹⁹	6.74	20.0	5.00
Ge-6	5·10 ¹⁹	7.60	<2.0	3.10
Ge-7	1·10 ²⁰	8.77	3.7	3.75
Ge-8	2·10 ²⁰	7.70	18.0	4.25

Table 1 The initial germanium oxygen and carbon concentrations as well as the VO defects concentration in the Ge-doped Si samples used.

As can be seen from table 1, the used samples can be separated into three groups. Group 1 contains samples with initial carbon concentration below the detection limit namely Cz-Si, Ge-2 and Ge-6. Group 2 contains samples with low initial carbon concentration up to 1·10¹⁷ cm⁻³ including the samples Ge-1, Ge-3, Ge-4 and Ge-7. Group 3 contains samples with high initial carbon concentration up to 2·10¹⁷ cm⁻³ including the samples Ge-5 and Ge-8. As a result of irradiation, vacancy-oxygen (VO) pairs are formed. Their presence in the spectra is verified by the 830 cm⁻¹ IR band. The VO defect concentration versus Ge content in the used samples is shown in Fig.1. It is clearly seen

from this figure that in group 1 samples VO concentration is slightly increased versus Ge content for Ge up to 5·10¹⁹ cm⁻³. This can be explained by the fact that Ge atoms in the temperature of irradiation act as temporary traps for vacancies reducing thus the annihilation rate with self-interstitials (V + (Si)_i → (Si)_i). As a consequence, more vacancies are available to be captured by O_i atoms to form VO defects. In group 2 samples, VO concentration also increases versus Ge content for Ge up to 1·10²⁰ cm⁻³ being sufficiently higher from the values of group 1. The observed increase can be explained taking into account that during irradiation carbon atoms captures self-interstitials while Ge atoms act as temporary traps for vacancies. Both carbon and germanium impurities result in a reduction of the annihilation rate of vacancies and self-interstitials, leading more vacancies to be captured by O_i atoms. In group 3 samples, VO concentration is enhanced in comparison

with the samples of group 2, but for $[Ge]=2 \cdot 10^{20} \text{ cm}^{-3}$ a decrease is observed in relation with the corresponding

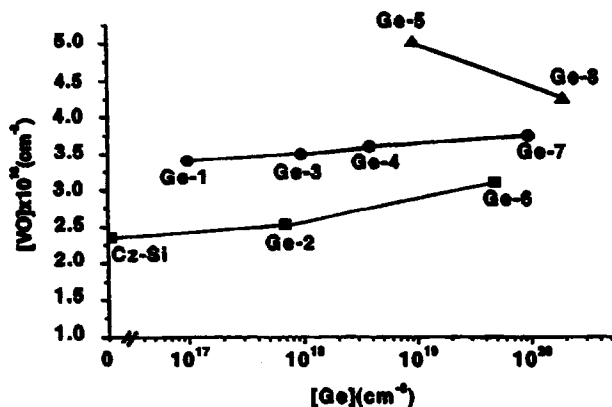


Fig.1 The VO defect concentration versus Ge content in the Ge-doped Si samples used.

value for $[Ge]=1 \cdot 10^{19} \text{ cm}^{-3}$. The enhancement in the VO concentration can be explained by the presence of carbon in high concentration that results in a suppress of the annihilation rate of vacancies and self-interstitials although Ge impurity in high concentration ($2 \cdot 10^{20} \text{ cm}^{-3}$) seem to enhance this rate due to the clusters of Ge atoms formed, which act as sites for annihilation of primary defects [1].

Upon annealing this band begins to decay and another band at 888 cm^{-1} , attributed to the VO_2 defect, begins to grow in. The relevant reaction is $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$. It has been established that the temperature of the VO_2 defect formation is markedly reduced due to the presence of Ge atoms [2]. This reduction is relatively small for $[Ge]$ up to $\sim 4 \cdot 10^{18} \text{ cm}^{-3}$, and more pronounced for higher; (Fig. 2.(a))

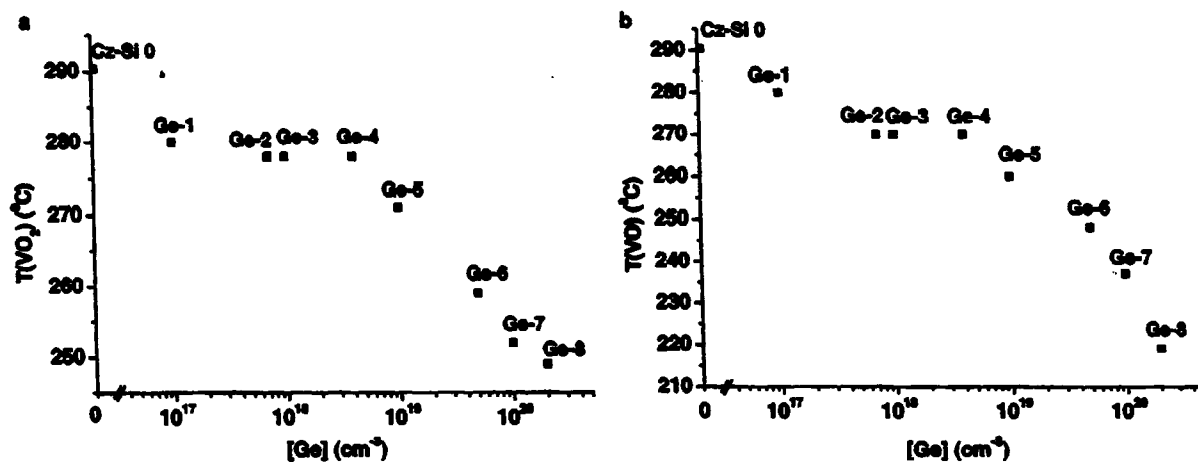


Fig.2. The annealing temperature of VO defect (a) and the formation temperature of the VO_2 defect (b) versus $[Ge]$.

On the other hand, the annealing temperature of VO defects, especially in materials with high $[Ge]$, it was found to be even lower than the corresponding temperature of the VO_2 defect formation (Fig. 1(b)), indicating that another defect reaction ($\text{VO} + (\text{Si})_i \rightarrow \text{O}_i$) is also running in the annealing processes of VO complexes. These phenomena could be reasonably explained if one takes into account an influence of elastic strains due to Ge atoms in the Si lattice on the rates of both principal reactions, i.e. $\text{VO} + \text{O}_i \rightarrow \text{VO}_2$ and $\text{VO} + \text{Si}_i \rightarrow \text{O}$ which govern the annealing of the VO defects. The migration energy of VO defects in the first reaction and the binding energy of self-interstitials at large agglomerates in the second reaction are believed to be sensitive to the Ge concentration in Si [2,3]. More specifically, they are reduced as $[Ge]$ increases, leading the above reactions to occur at lower temperatures.

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