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On the impact of germanium doping on the vacancy formation energy in Czochralski-grown silicon

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The formation energy and thermal equilibrium concentration of vacancies in Ge doped Czochralski-grown Si are studied by quenching of samples annealed at temperatures between 1200 and 1350 °C for 1 h under hydrogen atmosphere. After quenching, the majority of the formed vacancy and hydrogen containing point defect clusters are transformed into VH_4 defects by a 1 h anneal at 450 °C. Measuring the amplitude of the vibrational band of VH_4 at 2223 cm^{-1} as function of the quenching temperature allows estimating the vacancy formation energy. An apparent formation energy of about 2 eV is obtained for Ge doping between 7×10^{17} and $6.5 \times 10^{20}\text{ cm}^{-3}$ which is significantly lower than the 4 eV obtained for high purity Si. In the whole quenching temperature window, the vacancy thermal equilibrium concentration is significantly higher than in Si without Ge doping. It is shown that this lower apparent formation energy can be explained by the presence of vacancy traps. © 2010 American Institute of Physics.
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Intrinsic point defects in semiconductors play an important role in a wide range of processes ranging from Czochralski (Cz) crystal growth to device processing. In order to control and to optimize these processes, it is crucial to have a quantitative knowledge of the intrinsic point defect properties.

In the early days already quenching from high temperatures has been explored to study the intrinsic point defects in Si. It was indeed observed that by quenching from high temperatures, donors are formed which change the resistivity of the Si material and can easily be detected using resistivity and Hall measurements. Unfortunately, it soon turned out that in most cases these donors were due to iron contamination either grown-in during crystal growth and activated by the quenching treatment or diffusing in from the surface of the samples during the high temperature treatment.¹ Often the concentration of iron was so high that it was the main cause of the observed resistivity changes. Only in few careful studies also donors were observed that could not be related to metallic impurities^{2,3} but even in these cases the relation with the intrinsic point defects was not clear.

For those reasons, beginning of the 1990s a new quenching technique was developed at Tohoku University which is based on performing the high temperature anneal and the quenching step itself with the sample kept under hydrogen ambient.⁴⁻⁷ The originality of this approach is to detect vacancies as vacancy-hydrogen complexes. Isolated vacancies can indeed not exist after quenching because of the very small vacancy migration energy. Further more, *ab initio* calculations reveal that the binding energy of the various vacancy-hydrogen complexes that can be formed is larger than that of vacancy-only clusters with a similar number of

vacancies.⁸ Due to this, vacancies will preferentially cluster with hydrogen atoms/molecules during the quench and during subsequent low temperature anneals. After the quench from high temperature, an anneal at 450 °C is indeed performed to stabilize the quenched-in vacancy-hydrogen complexes by the formation of VH_4 that has a well-known infrared absorption band^{4,9} at 2223 cm^{-1} .

Doping during Si crystal growth with a Ge concentration in the range between 10^{16} and 10^{20} cm^{-3} is actively investigated due to the expected beneficial influence on the Si crystal and wafer quality.¹⁰⁻¹⁴ Some of the main advantages of Ge doping on Si crystal quality are an enhancement of oxygen precipitation—important for large diameter wafers which have typically a low oxygen content—a reduced crystal originated particle (COP) size and flow pattern defect (FPD) density, see e.g., Ref. 10, and references therein. As it can be assumed that this improvement of material properties is related to the interaction of Ge doping with Si vacancies, the impact of Ge on vacancy behavior has been studied extensively both experimentally and theoretically, see e.g., Refs. 15–17, and references therein.

In the present communication, first results are presented of a study of the impact of Ge doping of conventional B doped Cz-grown Si on the vacancy formation energy and thermal equilibrium concentration as determined from quenching experiments.

10^{15} cm^{-3} B doped, Cz-grown Si samples doped with 7×10^{17} , 6.5×10^{18} , 5.9×10^{19} , and $6.5 \times 10^{20}\text{ cm}^{-3}$ Ge were used in the present study. Samples with dimensions of $6 \times 6 \times 11\text{ mm}^3$ were prepared from a 4 in. diameter crystal and were sealed in a quartz capsule that was filled with H_2 gas at a pressure of 160 mm Hg. After a 1 h anneal at the quench temperature that is varied between 1200 and 1350 °C, the capsules were quenched in water at room temperature and a 1 h anneal was performed at 450 °C in order to transform most of the V_mH_n complexes in VH_4 . The VH_4

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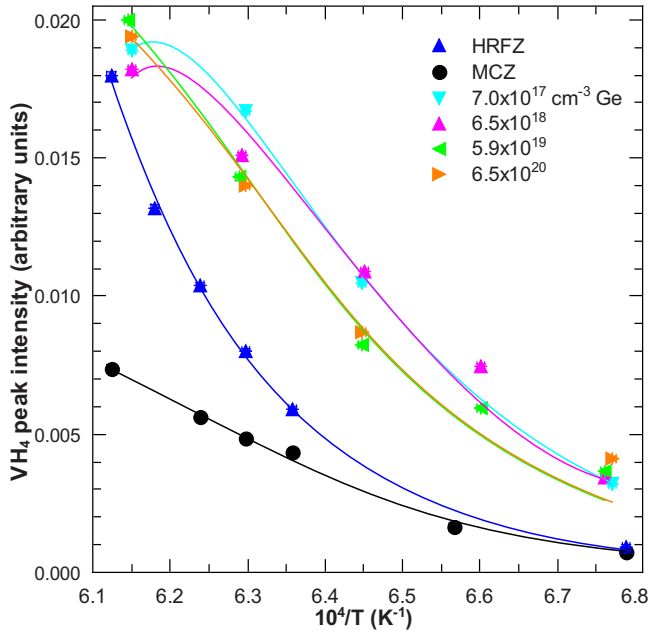


FIG. 1. (Color online) Quenching temperature dependence of the peak intensity of the 2223 cm^{-1} absorption band after the $450 \text{ }^\circ\text{C}$ anneal for the four Ge concentrations of the present study. Results for HRFZ and MCZ Si (Ref. 6) are also shown as a reference. The lines are best fits using Eq. (2) as listed in Table II.

concentration was determined by performing FTIR measurements along the 11 mm axis of the samples. The concentration of VH_4 defects is hereby assumed to be proportional to the vacancy concentration at the temperature before quenching.

The quenching temperature dependence of the intensity of the 2223 cm^{-1} peak for high resistivity floating zone-grown (HRFZ) and magnetic field assisted Cz-grown (MCZ) Si (Ref. 6) and for the Ge doped material of the present study is shown in Fig. 1, revealing for HRFZ an Arrhenius type dependence of the peak intensity I_{VH_4} on temperature T , that can be described by

$$I_{\text{VH}_4} = I_{\text{VH}_4}^0 e^{-E_V^F/kT}, \quad (1)$$

with E_V^F the apparent vacancy formation energy and k the Boltzmann constant. The prefactor $I_{\text{VH}_4}^0$ includes both the formation entropy and the infrared calibration coefficient. The extracted vacancy formation energies and prefactors us-

TABLE I. Vacancy formation energies E_V^F and prefactors $I_{\text{VH}_4}^0$ extracted from Fig. 1 using Eq. (1).

C_{Ge} (cm^{-3})	E_V^F (eV)	$I_{\text{VH}_4}^0$ (arbitrary units)	R-Square
0 (HRFZ)	4.06 ± 0.12	$(6.2 \pm 5.2) \times 10^{10}$	0.999
0 (MCZ)	2.51 ± 0.27	$(4 \pm 9) \times 10^5$	0.976
0 (MCZ, $T < 1300 \text{ }^\circ\text{C}$)	3.83 ± 0.22	$(8 \pm 13) \times 10^9$	0.998
0 (MCZ, $T > 1300 \text{ }^\circ\text{C}$)	1.99 ± 0.07	$(1.01 \pm 0.50) \times 10^4$	0.998
7.0×10^{17}	1.95 ± 0.49	$(2.2 \pm 7.9) \times 10^4$	0.935
6.5×10^{18}	1.84 ± 0.26	$(10 \pm 18) \times 10^3$	0.959
5.9×10^{19}	2.37 ± 0.12	$(4.5 \pm 3.8) \times 10^5$	0.995
6.5×10^{20}	2.20 ± 0.13	$(1.3 \pm 1.2) \times 10^5$	0.996

ing Eq. (1) are listed in Table I. The Ge doped samples reveal an apparent vacancy formation energy of about 2 eV and a vacancy concentration that varies only slightly with the Ge concentration for the studied concentration range varying over three orders of magnitude. In previous work⁶ a similar reduction in vacancy formation energy was observed for MCZ material. For quenching temperatures above $1300 \text{ }^\circ\text{C}$, a reduced apparent formation energy of about 2 eV was indeed obtained while below that temperature the formation energy was close to that in HRFZ as illustrated in Table I. This suggests that the main reason for the apparent vacancy formation energy of 2 eV in the Ge doped samples, is probably not the Ge doping but the high concentration of interstitial oxygen in Cz material.

If Ge acts as a trap for vacancies at higher temperatures (well above $1000 \text{ }^\circ\text{C}$) it will retard the formation of vacancy clusters during crystal pulling leading to a higher concentration of smaller voids and thus also COP's. At the same time, more free vacancies are available at temperatures below $1000 \text{ }^\circ\text{C}$ thereby enhancing the formation of oxide precipitate nuclei in the crystal cooling. At the same time the thermal equilibrium concentration of vacancies increases in the presence of Ge atoms. As the covalent tetrahedral radius of the Ge atom (1.22 \AA) is about 4.3% larger than that of the Si atom (1.17 \AA), replacing a Si atom by a Ge atom is with respect to strain roughly equivalent with the introduction of 0.04 Si self-interstitials. This strain can be reduced by the formation of additional vacancies thus leading to a higher vacancy concentration.

The reduced free vacancy concentration and apparent vacancy formation energy in MCZ Si for quenching temperatures above $1300 \text{ }^\circ\text{C}$ can be explained by the formation of VO in a concentration comparable to that of vacancies at high temperatures.^{18,19} This population of VO that coexists with the thermal vacancies, represents an effective sink for vacancies lowering the number of vacancies that can be captured by hydrogen to form VH_4 . The apparent vacancy formation energy derived from the quenching experiments is thus strongly influenced by the formation of VO. At temperatures below $1100 \text{ }^\circ\text{C}$ the VO_2 concentration is higher than that of VO and VO_2 thus becomes the dominant sink for vacancies. The formation energies of VO and of VO_2 are 1.85 eV and 0.3 eV, respectively.¹⁸

When a vacancy trapping species exists with a formation energy E_T , Eq. (1) can in first order approximation be rewritten as

$$I_{\text{VH}_4} \approx (1 - A e^{-E_T/kT}) I_{\text{VH}_4}^0 e^{-E_V^F/kT}. \quad (2)$$

Using Eq. (2) to fit the MCZ data shown in Fig. 1 assuming that $E_V^F = 3.85 \text{ eV}$ and $E_T = E_{\text{VO}} = 1.85 \text{ eV}$, reproduces well the observed dependence of the vacancy concentration on the quenching temperature. When applying Eq. (2) to the HRFZ data, an excellent fit is also obtained and one should note that the resulting value A is about one order of magnitude smaller than that for the MCZ and Ge doped Cz materials, in agreement with the oxygen content which is also one order of magnitude lower. It is also interesting to note that the prefactor $I_{\text{VH}_4}^0$ for HRFZ and MCZ is nearly the

TABLE II. Prefactors $I_{\text{VH}_4}^0$ and A , extracted from Fig. 1 using Eq. (2) and assuming $E_V^0=3.85$ eV and $E_T=E_{\text{VO}}=1.85$ eV.

C_{Ge} (cm^{-3})	$I_{\text{VH}_4}^0$ (a.u. $\times 10^{10}$)	A (a.u. $\times 10^5$)	R-Square
0 (HRFZ)	1.16 ± 0.09	0.88 ± 0.49	0.999
0 (MCZ)	1.35 ± 0.07	3.00 ± 0.15	0.994
7.0×10^{17}	5.61 ± 0.17	3.85 ± 0.06	0.998
6.5×10^{18}	5.61 ± 0.39	3.94 ± 0.15	0.982
5.9×10^{19}	4.18 ± 0.38	3.22 ± 0.24	0.987
6.5×10^{20}	4.27 ± 0.52	3.32 ± 0.32	0.982

same, suggesting that the observed apparent vacancy formation energy in MCZ is fully due to the trapping of vacancies by oxygen.

When besides oxygen an additional (weaker) vacancy trap is present like Ge which influences the concentration of VO, Eq. (2) can still be used in first order approximation but with different prefactors. As Ge will compete with V to pair with O and also strongly enhances oxygen precipitation, besides the strain effect which also increases the number of vacancies, the number of vacancies available for VH_4 formation will increase leading to an increase in $I_{\text{VH}_4}^0$, as illustrated in Table II. The major effect of the Ge doping seems thus to be an increase in the prefactor $I_{\text{VH}_4}^0$.

Also in Ge doped Cz Si, the apparent vacancy formation energy in the studied temperature window is thus considerably lower than for HRFZ material but at the same time the amplitude of the VH_4 related absorption line is increased with respect to MCZ and HRFZ suggesting that Ge doping leads to a higher thermal equilibrium concentration of vacancies in Cz Si.

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