Development of quenching technique to study intrinsic point defects in germanium and germanium doped silicon

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1. Background and purpose of proposed research period

The goal of the research stay at IMR was twofold. In the first place quenching experiments will be performed on a selection of Ge and Ge doped Si samples using the technique and set-up that was developed at Tohoku university by the host group during the last decade. The novel quenching technique has not yet been applied for Ge and Ge doped Si and could yield very valuable new information on intrinsic point defect properties in both types of materials that is not available at the moment. The second goal was to get acquainted with the experimental set-up at IMR so that afterwards the existing basic quenching set-up at Ghent university can be improved.

During the stay also two lectures were given dealing with properties and impact of intrinsic point defects in Si and Ge.

2. Proposed plan

2.1. Planned quenching experiments

It was planned to investigate the formation energy and thermal equilibrium concentration of vacancies in Ge and in Si doped with different concentrations of Ge. For Ge the quenching technique itself had first to be adapted especially with respect to the low temperature treatment to transform all vacancy containing point defect clusters into VH4 after the quenching step.

2.2 Quenching set-up and characterization of samples

Special about the quenching technique developed at IMR is that the samples are heated in hydrogen atmosphere that reduces out-diffusion of vacancies during quenching. The concentration of the vacancies in silicon is measured indirectly after quenching by measuring the concentration of vacancy-hydrogen complexes (VH_4) using FTIR. Similar defects have been reported to be formed in Ge heated in hydrogen atmosphere. It can therefore be expected that the quenching technique developed at IMR can also be used with success for Ge.

3. Results and discussions

3.1 Quenching experiments on Ge

Initial quenching experiments on Ge were performed at Ghent university revealing that vacancy related defects are created in similar concentrations as in Si [1]. As the experiments were not performed under hydrogen atmosphere and as the defect characterization was based on electrical measurements, the results were however prone to suffer from metal contamination. Quenching under hydrogen atmosphere using the technique developed at Tohoku university could be an alternative approach to study vacancy properties in Ge.

During the stay, quenching experiments under hydrogen atmosphere were performed on high purity Ge material supplied by IMR. After quenching from high temperatures several low temperature anneals were performed in order to create VH_4 defects that can be detected by FTIR. Unfortunately no absorption bands could be detected even after using a higher hydrogen pressure in the sealed capsules containing the Ge samples and despite quenching from temperatures close to the melting temperature. To increase to a maximum the sensitivity of the FTIR measurements also the standard sample length was increased to the maximum size accepted by the FTIR holder. Afterwards it was realized that the starting Ge material was dislocated and that these dislocations probably act as sink for vacancies during the quench explaining why no vacancy related infra red absorption bands could be detected after the quenching and the low temperature anneals.

3.2 Quenching experiments on Ge-doped Si

10^{15} cm^{-3} B doped, Cz-grown silicon samples doped with 7×10^{17}, 6.5×10^{18}, 5.9×10^{19} and 6.5×10^{20} cm^{-3} Ge were used. Samples with dimensions of 6×6×11 mm^3 were prepared from a 4 inch diameter crystal and sealed in a quartz capsule that is filled with H_2 gas at a pressure of 160 mm Hg. After a 1h anneal at the quench temperature, 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 concentration is determined by performing FTIR measurements along the 11 mm axis of the samples. The concentration of VH_4 defects is 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 undoped FZ-grown (HRFZ) and magnetic field assisted Cz -grown (MCZ) silicon and for the Ge doped material of the present study all reveal an Arrhenius type dependency of the peak intensity I_{VH4} on temperature T, described by $I_{VH4} = I^0_{VH4}$ exp[-E_V^F/kT], with E_V^F the apparent vacancy formation energy and k the Boltzmann constant. The pre-factor I^0_{VH4} includes both the formation entropy and the infra red calibration coefficient.

The extracted effective vacancy formation energies and pre-factors are listed in Table I.

The Ge doped samples reveal a lower apparent vacancy formation energy that depends only slightly on the Ge concentration for the studied concentration range varying over three orders of magnitude. This suggests that the main reason for the lowering of the vacancy formation energy from about 3.85 eV to about 2.2 eV is probably not the Ge doping but the presence of a high concentration of interstitial oxygen present in Cz material. This is in agreement with the observations on the MCZ material where for quenching temperatures above 1300°C a strongly reduced apparent formation energy of about 2eV was also obtained while below that temperature the formation energy is close to that in HRFZ.

4. Summary and perspective

Unfortunately the quenching of Ge specimens under hydrogen atmosphere experiments have been unsuccessful so far probably due to the use of dislocated material. New quenching experiments are scheduled using state of the art dislocation-free Ge samples supplied by Ghent university. First experiments will be performed during Spring 2010.

With respect to the Ge doped Si material a journal paper has been submitted for publication [2] and first results were also presented at the Spring Meeting of The Japan Society of Applied Physics [3].

The experimental data for the Ge doped Si might also be fitted with two vacancy formation energies like is the case for MCZ, i.e. a formation energy around 2 eV at high temperatures and around 3.85 eV below a critical transition temperature. More experimental data will be collected in the course of 2010 in order to establish this unambiguously and to estimate the transition temperature and its dependence on Ge concentration.

References

[1] J. Vanhellemont, J. Lauwaert , A. Witecka, P. Spiewak, I. Romandic and P. Clauws, “Experimental and theoretical study of the thermal solubility of the vacancy in germanium”, Physica B 404 (2009) 4529–4532.

[2] Jan Vanhellemont, Masashi Suezawa, and Ichiro Yonenaga, “On the impact of germanium doping on the vacancy formation energy in Czochralski-grown silicon”, submitted for publication in Journal of Applied Physics.

[3] Masashi Suezawa, Jan Vanhellemont, Ichiro Yonenaga, “Vacancy formation energy in Ge-doped Si crystals”, presented at the Spring Meeting of The Japan Society of Applied Physics, March 17-20, Tokai University (2010).

Table 1. Vacancy formation energies E^F_V and pre-factors I^0_{VH4} determined from the quenching experiments.

Ge concentration (cm^{-3})	E^F_V **(eV)**	I^0_{VH4} **(arbitrary units)**	***RSQ***
0 (HRFZ)	4.065 ± 0.058	$(6.2 \pm 5.2)\times10^{10}$	0.999
0 (MCZ, T<1300°C)	3.83 ± 0.11	$(8.2 \pm 6.7)\times10^{9}$	0.998
0 (MCZ, T>1300°C)	1.989 ± 0.034	$(1.01 \pm 0.25)\times10^{4}$	0.998
$7\text{x}10^{17}$	1.95 ± 0.24	$(2.2 \pm 4.0)\times10^{4}$	0.935
$6.5\text{x}10^{18}$	1.84 ± 0.13	$(9.6 \pm 9.1)\times10^{3}$	0.959
$5.9\text{x}10^{19}$	2.372 ± 0.058	$(4.5 \pm 1.9)\times10^{5}$	0.995
$6.5\text{x}10^{20}$	2.196 ± 0.067	$(1.25 \pm 0.61)\times10^{5}$	0.996