Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

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Reports supporting requests for additional beam time

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Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

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All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** XRD of modified Ge-nanocrystals	**Experiment number**: Si 851
Beamline: BM 20	**Date of experiment**: from: 01/09/2002 to: 06/09/2002	**Date of report**: 06/11/2002
Shifts: 12	**Local contact(s)**: Andreas Bauer	*Received at ESRF:* **06/11/2002**

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Report: The aim of the experiment has been to characterize very small Ge-nanocrystals by mean of high resolution x-ray diffraction methods (HRXRD). The Ge-nanocrystals forming in 4H-SiC(0001) substrates wafer after implantation and annealing with sizes under 5 nm are from specially interest. The current nanocrystals forming process has been advanced by supplementary implantation of Xe ions. For this, the former successful methods of the crystal characterization used, in recent periods of HRXRD measurements [June 2001/ February 2002] at the CRG-beamline ROBL BM 20, shall be applied once more.
Additional investigations are required to clear up the recently observed angle shift of the Ge-reflections. Is this caused by any impurities with Si or by hydrostatic strain inside of the Ge-nanocrystals. Therefore the stoichiometric composition of Ge-nanocrystals should be determined with measurements at different wavelengths apart and in the vicinity of the Ge-K-absorption-edge. This allows an distinction between Ge respectively Si contribution in the diffractograms in consequence of the changing the x-ray atomic scattering factor *f* of Ge.

Samples

Ge^+ ions with an energy of 250keV were implanted into 4H–SiC(0001) crystal wafers produced and supplied by Cree Research Inc. The implantation temperature was kept at 700°C. The ion current density was less than 1 µAcm^{-2}. Samples were tilted about 6°–8° to the ion beam to avoid channeling effects during implantation. The ion fluency of $1*10^{16}$cm^{-2} we used causes a Ge peak concentration of approximately 1 at.% in the deepness of 105nm below the surface. Thermal annealing was carried out at temperatures up to 1600°C in Ar-atmosphere (pressure 20kPa) using a rapid thermal annealing machine. The samples were placed between two electrically heated graphite stripes. To prevent significant decomposition, the annealing process was done with a sample arrangement face-to-face to an unimplanted SiC piece [1]. Ge-nanocrystals in 4H-SiC with sizes under 5 nm are most interesting for applications. Up to our knowledge these nanocrystals have not yet been realized. A new procedure of preparation has been applied to our samples. Xe ions with a very high energy of 390 MeV at 20°C and a dose of $1*10^{14}$ cm^{-2} have been implanted in the samples after theirs

primarily implantation and annealing process of Ge^+ ions as described above. This procedure should activate the Ge-nanocrystals formation inside of the crystalline SiC matrix.

Characterization

The x-ray diffraction experiments carried out at ROBL can be separated in two parts.

- **Firstly, characterization of Ge-nanocrystals formed in SiC samples after implantation with Xe ions**

Samples which was implanted with Ge^+ ions and annealed at 1600°C have been shown a significant 111-Ge diffraction peak. The occurrence of 111-Ge diffraction peaks in the XRD pattern of the annealed samples indicate the formation of Ge crystallized inside the SiC samples. After the added implantation of Xe the 111-Ge diffraction peak was not more observed.
Obviously, the Ge-nanocrystals disappear in samples which have been implanted with Xe ions after the implantation and annealing process of Ge^+ ions. Furthermore, the upper layer of the substrate was strong destroyed because of the implantation of Xe ions with a very high energy of 390 MeV. The reflections of substrate were split up in many peaks. Therefore a determination of the inherent strain in the crystalline substrate was very difficult.

- **Secondly, investigations to clear up the observed angle shift of the Ge-reflections**

It is obvious that the measured maximum of the 111-Ge diffraction peak is located at $2\theta=28.2°$. Compared to the theoretical value for crystalline Ge ($2\theta=27.3°$) this means a significant shift of the Bragg angle toward the value for crystalline Si ($2\theta=28.4°$). We can discuss two possible reasons for this behavior. The Ge-nano-crystals could be added impurities of Si atoms. On the one hand, the XRD measurements cover a sample area of nearly 1 mm^2 and for that a large volume of implanted SiC. The measurement represents an average of all crystallites in that area, including crystallites with different chemical composition. On the other hand, the shift of the Bragg angle can be caused by strain in the crystallites. The observed shift corresponds to a change of the lattice constant of $\Delta a/a=3.1*10^{-2}$.
Therefore, the stoichiometric composition of Ge-nanocrystals should be determined with measurements at different wavelengths apart and in the vicinity of the Ge-K-absorption-edge. This allows an distinction between Ge respectively Si contribution in the diffractograms in consequence of the changing the x-ray atomic scattering factor f of Ge. Because the size of the nanocrystals are smaller as the extinction distance therefore we can use the kinematical approximation. The reflected intensity I is proportional to $|F_{hkl}|^2$ in the case of the kinematical approximation. For Ge in the diamond structure we have following terms:

$$\left|F_{hkl}\left(\frac{\sin\theta}{\lambda}\right)\right|^2 = 32\left[(f_0+f_1)^2+(f_2)^2\right] \quad \textit{für} \quad h+k+l=4n\pm1$$

f_0 – atomic scattering factor of Ge
f_1 – real part of the dispersion correction of the atomic scattering factor of Ge
f_2 – imaginary part of the dispersion correction of the atomic scattering factor of Ge

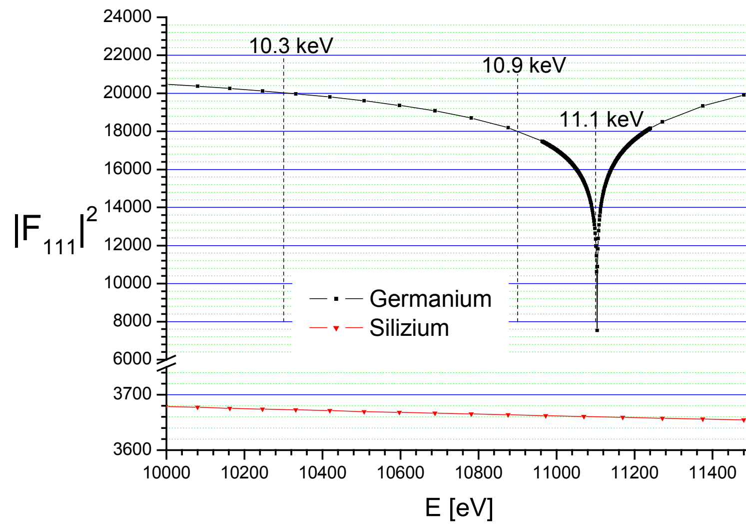

Fig. 1 shows the absolute value of the quadratic x-ray scattering factor F_{111} for Ge and Si in the vicinity of the Ge-K-absorption-edge (E = 11,103keV).

Considering the wavelengths and the anomalous dispersions corrections of the structure factor (Fig. 1), the ratio of the integrated reflectivity between a Ge-reflection at 10.3 keV and a Ge-reflection at 11.1 keV for a pure Ge-crystal (in the case of the kinematical approximation) is 1to1.631. The fitted peak areas can be used to calculate the ratio of the integrated reflectivity between the Ge-nanocrystals peak at 10.3 keV and the peak at 11.1 keV.

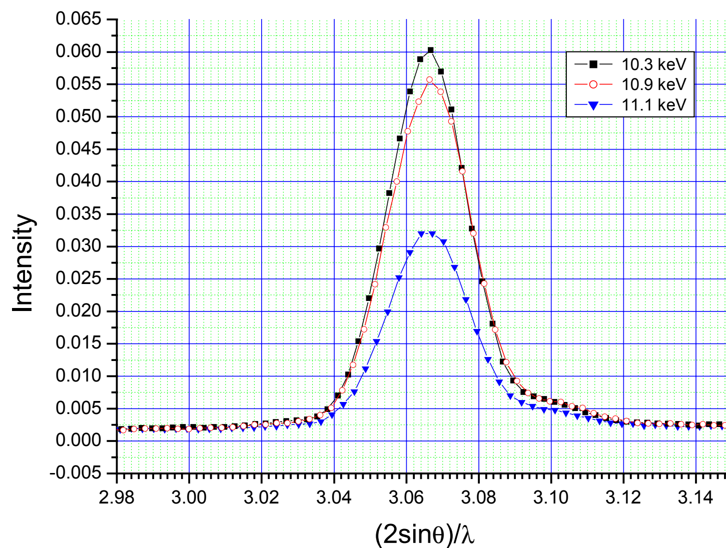

Fig. 2 shows the measured X-ray diffractograms (θ/2θ−scans) of Ge-nanocrystals grown on 6H-SiC(0001) at three different wavelengths in the vicinity of the Ge-K-absorption-edge, represented in terms of the reciprocal lattices vector (2sinθ)/λ. (a) 10.3 keV λ= 0.12039nm (b) 10.9 keV λ= 0.11374nm (c) 11.1 keV λ= 0.11169nm (measured in recent period of HRXRD measurements [June 2001] at the CRG-beamline ROBL BM 20)

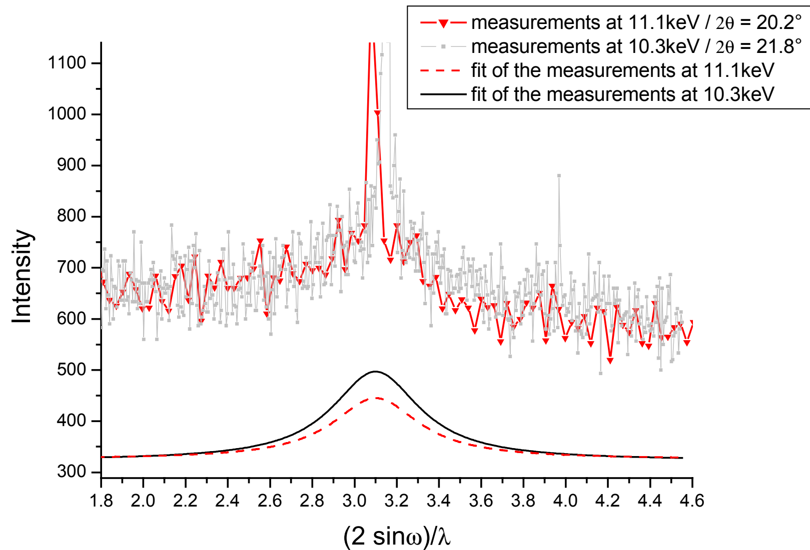

Fig. 3 shows the X-ray diffractograms (ω–scans) of Ge-nanocrystals has been produced in 4H-SiC by implantation of Ge^+-ions and subsequent rapid thermal annealing at two different wavelengths apart and in the vicinity of the Ge-K-absorption-edge, represented in terms of the reciprocal lattices vector (2sinθ)/λ. (a) 10.3 keV λ= 0.12039nm (b) 11.1 keV λ= 0.11169nm (measured in the last period of HRXRD measurements [September 2002] at the CRG-beamline ROBL BM 20)

The evaluation of the x-ray diffraction measurements (Fig. 2) obtained by Ge-nanocrystals grown on 6H-SiC(0001) results a ratio of 1 to 1.594±0,026. Hence, these Ge-nanocrystals consists in 84%±10% of Germanium.

The assessment of the Ge-nanocrystals produced in 4H-SiC by implantation of Ge^+-ions and subsequent rapid thermal annealing is more difficult because the reflected intensity of the 111-Ge diffraction peak is very low and the thus ratio of the line – underground is dramatically decreases. (Fig. 3)

This investigation has shown that the stoichiometric composition of Ge-nanocrystals can be determined with measurements at different wavelengths apart and in the vicinity of the Ge-K-absorption-edge. But for the determination of the stoichiometric composition of Ge-nanocrystals has been produced in 4H-SiC by implantation of Ge^+-ions and subsequent rapid thermal annealing the method have to advance to the limit of the resolution.

We thank all members of the ROBL beamline team, especially Dr. N. Schell and A. Bauer for the helpful support at the time of execution on this experiment.

[1] Ch. Schubert, U. Kaiser, A. Hedler, and W. Wesch, T. Gorelik, and U. Glatzel, J. Kräußlich, B. Wunderlich, G. Heß, and K. Goetz; Journal of Applied Physics, Vol. 91 No. 3 (2002), pp.1520-1524