Atomic transport during solid-phase epitaxial recrystallization of amorphous germanium

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The atomic mixing of matrix atoms during solid-phase epitaxy (SPE) is studied by means of isotopically enriched germanium (Ge) multilayer structures that were amorphized by Ge ion implantation up to a depth of 1.5 μm . Recrystallization of the amorphous structure is performed at temperatures between 350 °C and 450 °C. Secondary-ion-mass-spectrometry (SIMS) is used to determine the concentration-depth profiles of the Ge isotope before and after SPE. An upper limit of 0.5 nm is deduced for the displacement length of the Ge matrix atoms by the SPE process. This small displacement length is consistent with theoretical models and atomistic simulations of SPE indicating that the SPE mechanism consists of bond-switching with nearest-neighbours across the amorphous-crystalline (a/c) interface.

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Ion implantation and subsequent recrystallization are common device processing steps used to achieve high dopant activation in semiconductors such as silicon (Si) and germanium (Ge). In the presence of a crystalline substrate seed, the recrystallization occurs via solid phase epitaxy (SPE) and is characterized by a single activation energy of 2.70 eV for Si [1–4] and 2.15 eV for Ge [5–7]. The atomistic process associated with these energies has never been definitively identified. SPE growth is presently thought to occur by the lateral spread of {111} terraces at a fully coordinated amorphous-crystal (a/c) interface [8, 9]. So-called kinks at $\langle 110 \rangle$ ledges on {111} terraces have been proposed as favourable sites for bond rearrangement. The long held assumption here is that for an atom to be attached to the crystalline phase it must have two nearest neighbours already in the crystalline phase at the interface. Alternatively, long range transport of defects to the a/c interface has also been proposed where the SPE activation energy is determined by the defect’s diffusion coefficient [10–12]. However, differences between activation volumes found in pressure dependent diffusion and SPE studies largely discount these processes [6], although there has not yet been any direct evidence. The characterization of atomic mixing during SPE would provide support to one model over another.

The development of highly enriched stable isotopes of Si and Ge has enabled the preparation of isotopically controlled semiconductor nano structures. Using such

layers atomic mixing can be investigated [13–15]. Furthermore, fundamental studies on important technological processes such as self-diffusion [16–23] and self- and dopant diffusion interactions [24–27] can be investigated. These processes have a significant impact on device fabrication and performance and, with the growing technological importance of Ge, such studies provide timely insight into atomic transport. In this work we utilize isotopically controlled heterostructures to provide fundamental insight into atomic transport processes during SPE including the possibility of long range defect diffusion, structural relaxation and dopant-defect interactions in Ge.

The atomic mixing of matrix atoms during SPE was determined by means of amorphous Ge (a-Ge) isotope multilayer structures at different recrystallization temperatures. For this purpose, a mono crystalline structure consisting of 20 $^{nat}\text{Ge}/^{70}\text{Ge}$ isotopically enriched bilayers was first grown by means of molecular beam epitaxy (MBE). The epitaxial growth was performed with a VG Semicon V80 MBE system equipped with electron guns to evaporate the Ge. The growth temperature was kept at 500 °C and the thickness of each natural and isotopically enriched ^{70}Ge layer is about 10 nm. The structure was deposited on a (100)-oriented n-type Ge wafer with a specific resistivity of 40 Ωcm . After the MBE growth, the crystalline multilayer structure was amorphized by Ge ion implantation. Four sequential implants were performed at 77 K with ion energies and fluences of 2 MeV with $1.1 \times 10^{14} \text{ cm}^{-2}$, 1 MeV with $2.5 \times 10^{13} \text{ cm}^{-2}$, 310 keV with $3.0 \times 10^{13} \text{ cm}^{-2}$, and 50 keV with $3.0 \times 10^{13} \text{ cm}^{-2}$ to achieve a homogeneous energy deposition

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within the isotope layers. The thickness of the resulting amorphous layer is about $1.5\ \mu\text{m}$ was estimated by SRIM calculations and confirmed by Rutherford Backscattering (RBS) and cross-section Transmission Electron Microscopy (X-TEM) measurements of samples prepared under similar experimental conditions. The distribution of matrix-atoms before and after SPE annealing was measured by means of time-of-flight secondary-ion-mass-spectrometry (TOF-SIMS). Oxygen ions with an energy of 1 keV were used for sputtering and 25 keV bismuth ions served as an analysis beam. A sample area of $100\ \mu\text{m} \times 100\ \mu\text{m}$ was analyzed with SIMS. Figure 1 shows concentration profiles of ^{74}Ge derived from the SIMS analyses of the crystalline (green) and amorphized (blue) Ge isotope multilayer structure. The concentration profiles are accurately reproduced by

$$C_{\text{Ge}}(x) = C_1 + \frac{C_2 - C_1}{2} \sum_{i=1}^{20} (-1)^{i+1} \text{erfc} \left(\frac{x - x_i}{r_i} \right) \quad (1)$$

where x is the depth, C_1 and C_2 the minimum and maximum concentrations of the ^{74}Ge isotope, and $\text{erfc}(x)$ the complementary error function. The position of the i th isotope interface is represented by x_i . r_i is a measure of the steepness in the Ge concentration (broadening) at the i th interface between the natural and isotopically enriched Ge layers. The broadening at each interface can be obtained by fitting Eq. 1 to the experimental data using a least-squares algorithm. The associated relative error of the broadening at each interface was found to be approximately 3%.

The SPE rate was monitored during annealing with time-resolved reflectivity (TRR) at three different temperatures, 350°C , 400°C , and 450°C . The error associated with the temperature reading was found to be $\pm 1^\circ\text{C}$. Further details on the experimental apparatus are presented elsewhere [4].

Because the TRR technique allowed us to monitor the recrystallization process, the annealing of the samples was stopped before full recrystallization of the amorphous structure occurred. In this way it was possible to analyze with SIMS the broadening both in the amorphized and recrystallized part of the same Ge sample. The annealing times at the respective temperatures were chosen to retain a 150 nm thick surface a-Ge layer. The surface roughness of the sample before and after annealing was checked by means of atomic force microscope (AFM) measurements. A surface roughness of about 1.5 nm was detected before and after annealing at all temperatures, that is, no significant change in the roughness upon annealing was found, which may have resulted from surface oxidation. Accordingly, we can exclude that the broadening of the Ge isotope structure measured with SIMS after annealing is affected by a lower depth resolution associated with an increased surface roughness [28, 29].

In order to detect possible non-equilibrium diffusion phenomena in the crystalline part of the SPE-samples

that could be induced by surface reactions, a crystalline reference (as-grown) sample was annealed at each temperature contemporaneously under the same experimental conditions. No difference in the broadening of this annealed reference samples compared to the crystalline as-grown sample was observed. This demonstrates that a contribution of self-diffusion to the overall broadening in the crystalline structure can be neglected for the temperatures considered in our experiments. Additionally we performed experiments to investigate the influence of end-of-range defects on the overall broadening of the amorphized samples. For this reason a Ge sample containing six boron (B) delta spikes with a peak concentration of $3 \times 10^{19}\ \text{cm}^{-2}$ was grown by MBE and amorphized under the same experimental conditions as the multilayer structures. B diffusion in Ge is highly sensitive to the presence of self-interstitials [30–33] that can be formed by the dissolution of end-of-range defects during annealing [34]. No broadening is observed after recrystallization at a temperature of 450°C for 40 seconds. Therefore, an influence of end-of-range defects can be neglected at all temperatures and times employed in our experiments.

Figure 2 shows the ^{74}Ge concentration profile of the amorphized Ge isotope multilayer structure before SPE (blue line) and after recrystallization at 400°C (red line). The position of the a/c interface after SPE is indicated by the vertical black-dotted line. The blue and red dotted lines show the broadening of the premorphized reference and partly recrystallized sample, respectively. Compared to the broadening of the amorphized reference sample (blue dotted line), the annealed sample reveals a slightly higher broadening both within the recrystallized (red dotted line for $x > 150\ \text{nm}$) and amorphous region (red dotted line for $x < 150\ \text{nm}$). It is noticeable that for both regions of the annealed sample the change in the broadening compared to the amorphized reference sample is identical, that is, about 0.5 nm. The lack of a depth-dependent broadening indicates, that no significant self-diffusion in the amorphous region occurs. Otherwise a decreasing broadening with increasing depth should be observable since the isotope layers close to the surface are longer in the amorphous state than the layers close to the crystalline substrate. Samples recrystallized at 350°C (7595 seconds) and 450°C (40 seconds) reveal the same homogeneously increased broadening compared to the reference sample. This demonstrates that a transient relaxation in the amorphous phase rather than the SPE process itself causes this increased broadening. On the other hand, the same broadening observed within the recrystallized and amorphous region of the isotope structure reveals that the broadening due to SPE must be smaller than 0.5 nm. Accordingly, the SPE experiments with the isotope multilayer structures provide strong evidence that recrystallization of a-Ge is a process based on local bond-switching mechanisms without long-range atomic transport.

In order to verify the experimental results we performed molecular dynamics (MD) simulations on SPE

recrystallization of a-Ge at different temperatures. The impact of the moving a/c interface on the redistribution of the matrix atoms was extracted from the simulation results. Details of the SPE simulations in Ge are described in a previous paper [35]. In the present work the simulation cell was a cuboid with a size of $12a \times 12a \times 72a$ (representing 82944 atoms) where $a = 5.657 \text{ \AA}$ is the lattice parameter of crystalline Ge (c-Ge). Periodic boundary conditions were applied in three dimensions and an isobaric-isothermal ensemble (NPT with $P = 0$) was considered.

During the simulation the atoms are continuously classified depending on their coordination number and crystal structure of their nearest neighbours. To visualize the mixing caused by the moving a/c interface atoms on the crystalline side of the a/c interface (atoms in c-Ge with at least one neighbour in a-Ge) are compared to atoms that change from the amorphous to the crystalline side. For the different classes of atoms the mean square displacement

$$\text{msd}(t) = \frac{1}{N} \sum_i^N (x_i(t) - x_i(t - \Delta t))^2 \quad (2)$$

was calculated for periods of $\Delta t = 50 \text{ ps}$. The results are shown in Fig. 3 for 800 K, 850 K, and 900 K. The mean square displacements of atoms on the crystalline side of the a/c interface and of those switching from the amorphous to the crystalline phase are very small. As expected, in the case of the change from the amorphous to the crystalline side the value is slightly higher. On the other hand, thermal vibrations lead to a small increase with temperature. This result together with the fact, that no temperature dependent mixing is observed experimentally indicates that SPE does not cause any significant atomic mixing of the host atoms at the moving a/c-interface.

The equal and temperature independent broadening within the amorphous and recrystallized regions of the Ge isotope structure observed after the SPE process reveals that the broadening must be due to structural relaxations within the amorphous structure, that, beforehand, was formed by ion implantation. Relaxations of implantation induced amorphous structures are confirmed by calorimetric measurements [36] but have not yet been visualized by means of self-atom mixing until now. The structural relaxation of the amorphous material is accompanied by a reduction in the free energy of the material [36] and has been linked to short-range ordering and annihilation of defects in the amorphous structure [37, 38]. The process of relaxation is completed before the a/c interface reaches the region of interest, i.e., the isotope multilayer structure. This leads to a transient contribution in atomic mixing of the entire amorphous isotope structure. The lack of any additional self-atom mixing during SPE indicates that no long-range atomic transport process during crystallization takes place. This is in full accord with atomistic models which describe the

crystallization process with bond-switching mechanisms at the a/c interface [8, 9, 39].

In conclusion, solid phase epitaxial recrystallization in amorphized, isotopically enriched germanium multilayer structures was investigated at three different temperatures. With the exception of transient structural relaxations within the amorphized Ge layer that lead to an intermixing of the isotope structure, no significant displacement of matrix atoms is caused by SPE. Accordingly, the displacement length of the matrix atoms during SPE must lower than 0.5 nm. Molecular dynamics simulations of SPE recrystallization in germanium fully confirm the small atomic displacements observed experimentally. Overall the present work clearly reveals that recrystallization of Ge is mediated by bond-switching with minimal local rearrangements of the matrix atoms at the a/c interface.

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Figure 1: ^{74}Ge concentration-depth profile of the crystalline as-grown (green) $(^{nat}\text{Ge}/^{70}\text{Ge})_{20}$ isotope multilayer structure in comparison to the amorphous Ge isotope structure (blue) obtained by Ge implantation of the crystalline structure. The broadening of the profiles is derived from Eq. 1. The broadening parameter r_i at the i th $^{nat}\text{Ge}/^{70}\text{Ge}$ interface is given by the dotted lines that refer to the right y-axis.

Figure 2: ^{74}Ge concentration-depth profile of the amorphized sample (blue) in comparison to the sample after SPE (red) at 400°C for 569 seconds. The broadening of the profiles is described with Eq. 1. Within experimental accuracy a homogenous broadening is detected for both the amorphized (blue dotted line) and the annealed sample (red dotted lines). The annealed sample (red) reveals a clearly higher broadening than the amorphized sample (blue). This increased broadening is homogeneous across the whole Ge isotope superlattice structure with recrystallized and still amorphous regions. The vertical black dotted line shows the final position of the amorphous/crystalline interface after annealing.

Figure 3: Calculated mean square atomic displacements within 50 ps as function of time for different annealing temperatures: 800 K, 850 K, and 900 K. The green line shows the mean square displacement of atoms in c-Ge with at least one neighbour in a-Ge and the black line shows atoms that change their state from a-Ge to c-Ge within 50 ps.

Figure1

Figure2

Figure3

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