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Self-diffusion in germanium isotope multilayers at low temperatures

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Self-diffusion in intrinsic single crystalline germanium was investigated between 429 °C and 596 °C using ^{70}Ge/$^{\mathrm{nat}}$Ge isotope multilayer structures. The diffusivities were determined by neutron reflectometry from the decay of the first and third order Bragg peak. At high temperatures the diffusivities are in excellent agreement with literature data obtained by ion beam sputtering techniques, while considerably smaller diffusion lengths between 0.6 and 4.1 nm were measured. At lower temperatures the accessible range of diffusivities could be expanded to D $\approx 1 \times 10^{-25}$ m^{2}s^{-1} which is three orders of magnitude lower than the values measured by sputtering techniques. Taking into account available data on Ge self-diffusion, the temperature dependence is accurately described over nine orders of magnitude by a single Arrhenius equation. A diffusion activation enthalpy of (3.13 ± 0.03) eV and a pre-exponential factor of 2.54×10^{-3} m^{2}s^{-1} for temperatures between 429 °C and 904 °C are obtained. Single vacancies are considered to prevail self-diffusion in Ge over the whole temperature range.

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Diffusion is a fundamental process of matter transport in solids, important for preparation, processing and heat treatment of materials [1]. The field of modern semiconductor science and technology and the generation of ultra shallow junctions during fabrication of electronic devices are typical examples [2–5]. The motion of native point defects (vacancies and self-interstitials) as well as defect reactions control the kinetic behaviour of dopants [6]. A fundamental quantity is the self-diffusivity of the host atom in crystalline materials. From self-diffusion experiments with isotopically enriched heterostructures important information on the properties of native point defects in Si [7], SiGe [8], GaP [9], GaAs [10], GaSb [11], SiC [12], SiN [13], and TiB_2 [14] were obtained. The isotope heterostructures are chemically homogeneous solids which are composed of a stack of isotope enriched layers (e.g. ^{28}Si/^{30}Si) grown by suitable deposition techniques. The interdiffusion of stable isotopes during diffusion annealing takes place at the isotope interface(s) inside the crystal, unaffected by possible surface effects. Beside self-diffusion experiments, isotopically controlled heterostructures enable even more advanced diffusion studies such as investigations of radiation enhanced self-diffusion [15, 16] and the impact of dopant diffusion on self-diffusion [17, 18]. Such kinds of diffusion studies are difficult to realize with radiotracer techniques since radioactive elements possess limited half-lifes and are usually deposited on the sample surface or implanted with a low dose to minimize radiation damage.

Irrespective of the use of stable or radioactive isotopes commonly ion beam sputtering techniques [1] are applied for measuring diffusion profiles after annealing. This technique is applicable to mean penetration depths of a few tens of nanometer, corresponding to diffusivities of about 10^{-22} m^{2}s^{-1} (see e.g. [19]). This limitation is caused by intrumental broadening of the profiles associated with the ion beam sputtering process. To detect even lower diffusion coefficients or to extend diffusion experiments to lower temperatures other intrumental methods needs to be applied. In this respect, it has recently been demonstrated that isotopically enriched superlattice structures in conjunction with Raman scattering are

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suitable to detect the thermal broadening of ^{70}Ge/^{74}Ge [20] and ^{28}Si/^{30}Si [21] superlattices. Diffusion coefficients of the order of 10^{-25} m^{2}s^{-1} could be measured. An other approach has recently been demonstrated by Schmidt et al. [22, 23]. By means of neutron reflectometry (NR) diffusion lengths down to 0.6 nm could be measured in Si^{14}N$_x$/Si^{15}N$_x$ isotope multilayers resulting in self-diffusion coefficients as low as 10^{-25} m^2s^{-1}.

In order to test the capability of the method, NR is applied to measure self-diffusion in single crystalline Ge. Ge is an important semiconductor with a high potential for future commercial fabrication of field effect transistors [3, 5]. At the same time information about fundamental properties of native point defects in Ge are required since all technological important dopant atoms utilize native point defects as diffusion vehicle. Self-diffusion in Ge is considered to be mainly mediated by vacancies [24–27], i.e., the contribution of self-interstitials is assumed to be negligible. This result stems from the temperature and pressure dependence of self-diffusion in Ge. The former experiments of Werner et al. [24] were performed at temperatures between 535 and 904 °C. In this temperature range Ge self-diffusion is accurately described with a single diffusion activation enthalpy of 3.09 eV. With the NR measurements we have extended the self-diffusion experiments to temperatures as low as 429°C to investigate whether or not the activation enthalpy of self-diffusion changes at these low temperatures. A change in enthalpy would indicate an additional process governing self-diffusion.

The NR experiments were performed at the Geesthacht Neutron Facility (GeNF) at the reflectometer PNR using cold neutrons at incoming wavelength of 0.64 nm. The measurements were carried out on single crystalline isotope multilayers containing 10 bilayers of the form [^{nat}Ge/^{70}Ge] which were deposited on a (001) oriented ^{nat}Ge substrate by molecular beam epitaxy at 250 °C. The samples were annealed inside a vacuum chamber at a pressure below 10^{-7} mbar at temperatures between 596 °C and 429 °C for times between 20 min and 39 days.

The NR measurements revealed a thickness of 14.1 nm for both the ^{nat}Ge and ^{70}Ge layers. For Ge, there exists a difference in the bound neutron scattering lengths of ^{70}Ge (10.0 fm) and ^{nat}Ge (8.19 fm). Bragg peaks due to isotopic periodicity are measured in the neutron reflectivity pattern, as presented in Fig.1. Peaks of first and third order can clearly be distinguished. When the isotope multilayer is isothermally annealed, the Bragg peak intensity decays with increasing annealing time (Fig.1b). The diffusivity can be calculated using

$$D(T) = \frac{l^2}{8\pi^2 n^2 t} ln\left(\frac{I_o}{I(t)}\right) \quad (1)$$

where I_o is the intensity of the nth order Bragg peak at time $t = 0$, D is the diffusivity, l is the bilayer periodicity and t is the annealing time [23].

Figure 2 presents the self-diffusivities between 429 °C and 596 °C as obtained by NR. At temperatures between 525 and 600 °C our data are in excellent agreement with literature data measured by ion beam sputtering techniques [24, 28]. The data point for 500 °C measured by Raman scattering [20] is also in agreement with our experimental results. Our diffusion study expands the range of experimental data by three orders of magnitude compared to results obtained with the sputtering techniques. At 429 °C a self-diffusion coefficient of as low as D = $(9.7 \pm 3.7) \times 10^{-26}$ m^{2}s^{-1} was measured. At 596 °C diffusion anneals for 20 min (D = $(1.50 \pm 0.32) \times 10^{-21}$ m^{2}s^{-1}) and 68 min (D = $(1.63 \pm 0.35) \times 10^{-21}$ m^{2}s^{-1}) were performed. The corresponding diffusion values agree within experimental accuracy (see Fig. 2) indicating that the diffusion is not time dependent. A possible time dependence might be expected as a result of frozen in defects. Depending on the nature of these defects, i.e, vacancy- or

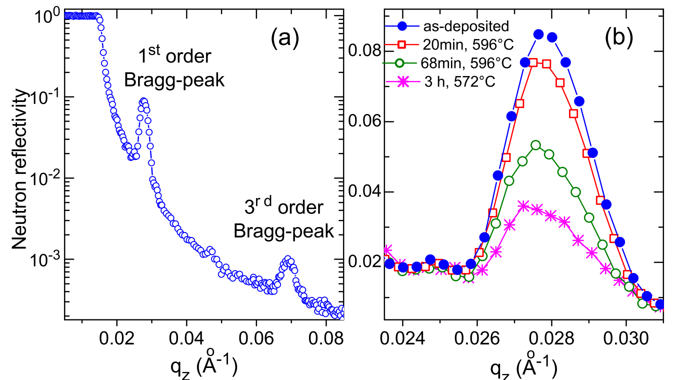

FIG. 1: (a) NR of an as-deposited Ge isotope multilayer. (b) Decrease of first order Bragg peak after annealing the Ge isotope multilayer.

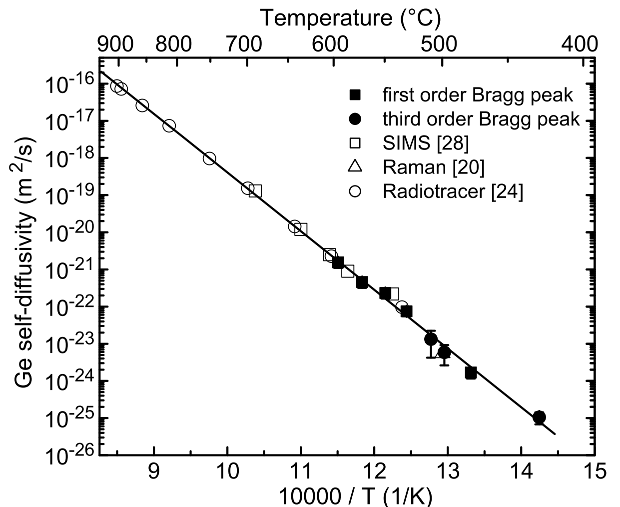

FIG. 2: Arrhenius plots of Ge self-diffusivities obtained by NR (filled circles and filled squares) in comparison to literature data from SIMS [28], Raman spectroscopy [20] and radiotracer sputter sectioning [24]. The continuous line represents a fit to the Arrhenius equation of all diffusivities displayed.

interstitial-like, they could give rise to transient enhanced or retarded self-diffusion.

An important quantity is the diffusion length d. In one dimension it is defined as $d = \sqrt{2Dt}$. The diffusion lengths determined by NR are in the range between 0.6 and 4.1 nm and significantly smaller than the diffusion lengths measured with conventional ion beam sputtering techniques. This means, that also diffusion lengths of the order of 1 nm correctly characterize long range diffusion processes. According to Eq. (1) the diffusivity and diffusion length scale as $\mathrm{D_n = D_1/n^2}$ and $\mathrm{d_n = d_1/n}$, respectively. $\mathrm{D_1}$ ($\mathrm{d_1}$) and $\mathrm{D_n}$ ($\mathrm{d_n}$) are the diffusivity (diffusion length) of the first order and n^{th} order Bragg peak. From this relationship it becomes evident that Bragg peaks of higher order have to be measured to detect diffusion lengths of the order of atomic jump distances. Such measurements are in progress.

As shown in Fig. 2 the diffusivities obtained by NR can be very well described by an Arrhenius equation $\mathrm{D = D_0 \exp[-Q/(kT)]}$ with a single diffusion activation enthalpy $Q = (3.13 \pm 0.12)$ eV and a pre-exponential factor $D_0 = 2.35 \times 10^{-3}$ $\mathrm{m^2s^{-1}}$ (relative error of $ln(D_0)$: 29 %). Taking into account all data between 429 °C and 904 °C, the Arrhenius parameters $Q = (3.13 \pm 0.03)$ eV and $D_0 = 2.54 \times 10^{-3}$ $\mathrm{m^2s^{-1}}$ are obtained. The parameters only slightly differ from $Q = 3.09$ eV and $D_0 = 1.3 \times 10^{-3}$ $\mathrm{m^2s^{-1}}$ reported by Werner et al. [24]. The strict Arrhenius behavior demonstrates that the vacancy mechanism, where the diffusing atom and a vacancy exchange sites during atomic motion, controls self-diffusion over the whole temperature range.

Summarizing, we have measured self-diffusion in single crystalline germanium isotope multilayers at temperatures between 429 °C and 596 °C using neutron reflectometry. By means of this method the experimental data of Ge self-diffusion could be expanded over three orders of magnitude to diffusivities down to $\mathrm{D} \approx 1 \times 10^{-25}$ $\mathrm{m^2s^{-1}}$. Such low diffusion coefficients result in diffusion lenghts below 1 nm for practical diffusion times that are hardly accessible by ion beam sputtering techniques. The Ge self-diffusion data given in the literature and in this work are accurately described with a single activation enthalpy $Q = 3.13$ eV and a pre-exponential factor $D_0 = 2.54 \times 10^{-3}$ $\mathrm{m^2s^{-1}}$ for temperatures between 429 °C and 904 °C. Single vacancies control self-diffusion in Ge over the whole temperature range.

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