EUROPEAN ORGANIZATION FOR NUCLEAR RESEARCH

Proposal P115 to the ISOLDE Scientific Committee (ISTC)

Diffusion Mechanisms and Lattice Locations of Thermal-Equilibrium Defects in Si–Ge Alloys


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1. Introduction

Si–Ge alloys are of great importance in semiconductor device technology because of the following reasons: (i) Their charge carrier mobility and band structure can be altered by changing the alloy composition. (ii) In contrast to compound semiconductors, their device integration may be done by means of the conventional and thus inexpensive silicon technology. (iii) Additions of gold permit to control the minority-carrier lifetime.

Concerning the technological side, investigations of the diffusion in Si–Ge play a great rôle for doping with elements that determine the electric properties as well as for avoiding the penetration of unwanted impurities. From the scientific point of view, Si–Ge alloys are unique for testing and improving our understanding of diffusion in its components Si and Ge, as will be shown in what follows.

It is generally accepted that Ge and Si differ considerably with respect to intrinsic-point-defect-mediated diffusion [1]. In Ge, the native point defects dominating under thermal-equilibrium conditions at all solid-state temperatures accessible in diffusion experiments are vacancies, and therefore Ge self-diffusion is vacancy-controlled. The same holds for the diffusion of substitutional solutes in Ge, particularly for dopants of the groups III and V of the periodic table. In Si, by contrast, self-interstitials and vacancies coexist in thermal equilibrium. Whereas in the most thoroughly investigated temperature regime above about 1000 °C Si self-diffusion is self-interstitial-controlled, it is vacancy-controlled at lower temperatures. Under these circumstances it is not surprising that the diffusion behaviour of group-III and group-V dopants in Si is quite sophisticated due to the different electrostatic and elastic interactions of these atoms with self-interstitials and vacancies.

The scenario displayed above prompts us to perform self-diffusion experiments on Si$_{1-y}$Ge$_y$ as a function of composition $y$, which aim at revealing the transition from the interstitialcy mechanism on the Si side ($y = 0$) to the vacancy mechanism on the Ge side ($y = 1$). This appears to be doable: (a) Irrespective of composition, Si–Ge is a solid solution that does not decompose. (b) As shown by McVay and DuCharme [2], Ge diffuses in Si almost like Si. Therefore, Ge may be used as a probe for monitoring self-diffusion in Si–Ge over the entire range of composition. (c) The radioisotope $^{71}$Ge possesses a half-life of 11.2 days, which is very convenient for diffusion studies by means of a radiotracer technique.

Additional information on the equilibrium defects mediating self-diffusion in Si$_{1-y}$Ge$_y$ may be obtained from measurements of the diffusion of Au as a function of the Ge content $y$. This is possible because of the hydridic nature of Au in Si, Ge, and its alloys. Whereas the overwhelming fraction of Au is incorporated on regular lattice sites (substitutional configuration Au$_s$) and thus immobile, the diffusive Au transport occurs via a small fraction of Au atoms rapidly hopping from interstitial site to interstitial site (interstitial configuration Au$_i$).
Obviously this interstitial–substitutional diffusion mechanism requires an exchange of Au atoms between substitutional and interstitial sites, which is mediated either by self-interstitials (I),

\[ \text{Au}_s + \text{I} \leftrightarrow \text{Au}_i \]  \hspace{1cm} \text{(kick-out mechanism [3]),} \hspace{1cm} (1)

and/or vacancies (V),

\[ \text{Au}_s \leftrightarrow \text{Au}_i + \text{V} \]  \hspace{1cm} \text{(dissociative mechanism [4]).} \hspace{1cm} (2)

Under favourable circumstances, the reactions (1) and (2) lead to diffusion profiles of different shape. In this way, it is possible to discriminate between self-interstitial-mediated and vacancy-mediated diffusion, and to calculate the self-interstitial and vacancy components of the self-diffusion coefficient from measured Au diffusion data, respectively. Therefore, we plan to study the diffusion of Au in Si–Ge, since, via this route, conclusions concerning the diffusion mechanisms in Si–Ge, which are based on $^{71}$Ge diffusion studies, may be cross-checked. In particular, it is intended to study the diffusion of $^{195}$Au radiotracers in Si–Ge as a function of composition.

In the above procedure it is attempted to deduce atomistic models from macroscopic data. Therefore, it is desirable that the results arrived at are confirmed by experiments directly yielding microscopic information. To this end, the lattice location of Ge will be determined with the aid of emission channelling experiments. For this purpose, implantations of $^{69}$Ge radiotracers will be conducted. From the channelling and blocking behaviour of the positrons emitted by $^{69}$Ge one can determine its lattice site and the degree of damage of the crystal lattice caused by the implantation. By following the damage recovery as a function of temperature, it is possible to obtain information on the mechanisms involved. The knowledge of the Ge location as well as the implantation-induced damage and its recovery may also be helpful in designing technical applications.

2. Experimental Techniques and Experience

2.1. Diffusion Experiments

The most convenient experimental method for carrying out the planned studies of diffusion in Si–Ge is a modified radiotracer technique, in which the radioactive atoms are implanted into the specimens to depths ranging from 20 nm to 100 nm. In this way, the radioisotopes are deposited beyond unwanted diffusion barriers at the specimen surface (e.g., oxides) [5]. The mother isotopes of the radioactive ions $^{71}$Ge and $^{195}$Au to be implanted are available at ISOLDE. As will be reported in Sect. 3.1, first investigations of the diffusion of
$^{195}$Au in Si–Ge have been done.

After implantation, the specimens are sealed in quartz ampoules evacuated to $10^{-5}$ mbar. The diffusion anneals are carried out in conventional resistance furnaces for annealing durations $\Delta t > 30$ min or in a rapid-thermal-annealing furnace for $10 \text{ s} < \Delta t < 30$ min, depending on the diffusivities of the tracers. The serial sectioning required for the determination of the diffusion profiles is performed by high-precision grinding for penetration depths $\Delta$ between 10 and 100 $\mu$m or by Ar$^+$-ion-beam sputtering for $\Delta < 500$ nm. Sputtering facilities are available in Stuttgart and Jyväskylä. In the case of ion-beam sputtering the removed material is collected on a foil which is wound up segment by segment like a film in a camera. Then the specific radioactivities of the foil segments, which correspond to different penetration depths, are measured. For this purpose, a Ge(Li) $\gamma$-spectrometer and a liquid-scintillation $\beta$-spectrometer are used. By fitting the appropriate solutions of the diffusion equation to the penetration profiles of the tracer atoms obtained in this way, the diffusion coefficients may be deduced.

The know-how in diffusion studies required for the performance of the experiments described above is guaranteed by the fact that the Stuttgart group possesses a long-lasting experience in radiotracer experiments on a large variety of (crystalline [6], amorphous [7, 8, 9], and quasicrystalline [5]) solid materials. While at Jyväskylä the radiotracer technique has just been established, this group has extended experience with studies of foreign-atom diffusion by other techniques (RBS, SIMS, NRA) in Si and Ge [10] as well as in compound semiconductors [11, 12]. Moreover, the Jyväskylä researchers are experts in implantation-induced damage and its investigation by ion-beam techniques and positron spectroscopy [13], and in conventional channelling techniques [14].

2.2. Emission Channelling Studies

Emission channelling offers an alternative to ion-beam lattice-location techniques [15]. These conventional techniques are limited to rather high impurity concentrations and therefore suffer from high implantation doses. Emission channelling is based on the fact that charged particles emitted in nuclear decays experience channelling and blocking effects in major crystallographic directions and planes. This results in an anisotropic emission yield, which depends on the lattice sites occupied by the radiotracers during their decay.

In the emission channelling experiments, implantations of $^{69}$Ge radiotracers are required. The half-life of $^{69}$Ge is 39 h. 36% of the $^{69}$Ge atoms decay by emitting positrons with end point energies of 0.6 and 1.2 MeV. The blocking experiments will be carried out preferentially at CERN, where position-sensitive detectors for electron emission channelling are in routine use within experiments IS360 and IS368 [15, 16, 17]. In Jyväskylä, a facility comprising a position-sensitive detector for emission channelling studies will be completed by the end of 1999.
3. Previous Results

3.1. Measurements of $^{195}$Au Diffusion in Si–Ge

Using the modified radiotracer technique described in Sect. 2.1, a researcher of the Stuttgart group [18] has recently studied the $^{195}$Au diffusion in relaxed, low-dislocation-density, 5 to 10 μm thick Si$_{1-x}$Ge$_x$ layers grown epitaxially on Si substrates in the temperature regime 700–950 °C as a function of the Ge content up to $y \approx 0.24$. A selection of diffusion profiles from these investigations is shown in Fig. 1. From computer fits of such profiles (solid curves in Fig. 1) it was concluded that in the entire composition range investigated the diffusion of Au occurs via the kick-out mechanism (1). More specifically, in the regime $0 \leq y \leq 0.09$, the kick-out mechanism is self-interstitial-controlled by the effective diffusion coefficient

$$D_i^* = D_i C_i^{eq}/C_s^{eq},$$

(3)

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Fig. 1: $^{195}$Au diffusion profiles $C(x)$ in Si$_{1-x}$Ge$_x$ epi-layers for 240 s anneals at 800 °C ( ▲ $y = 0.013$, ● $y = 0.239$) and a 60 s anneal at 950 °C ( ■ $y = 0.24$). The data points on the right-hand sides of the dashed vertical lines refer to the Si substrates.
which is obviously related to the self-interstitial component $D_i C_i^{eq}$ of the Si–Ge self-diffusion coefficient ($D_i =$ self-interstitial diffusivity, $C_i^{eq} =$ equilibrium concentration of self-interstitials, $C_s^{eq} =$ substitutional Au solubility). For $0.09 < y \leq 0.24$, the kick-out mechanism is Au-interstitial-controlled by the effective Au diffusivity

$$D_i^* = D_i C_i^{eq} / C_s^{eq} ,$$

($D_i$ and $C_i^{eq} =$ Au diffusivity and solubility, respectively), which is shown in Fig. 2 as a function of $y$ for 900 °C.

Fig. 2: Dependence of the effective diffusion coefficient $D_i^*$ [Eq. (4)] of $^{195}$Au at 900 °C on the Ge content $y$ for Si$_{1-y}$Ge$_y$ epi-layers in the regime $0.09 < y \leq 0.24$ (○). For $y \leq 0.09$, where the Au diffusion is self-interstitial-controlled, the $D_i^*$ (900 °C) values could not be determined. However, these must lie in the interval marked by the arrows. Also included are the $D_i^*$ (900 °C) values for dislocated bulk Si [19] (▲) and dislocation-free bulk Ge [20] (■).
4. Proposed Experiments

4.1. Material

In both the diffusion studies and the positron channelling experiments to be proposed, two kinds of Si–Ge specimens will be used: (i) 5 to 10 μm thick, low-dislocation-density Si<sub>1−y</sub>Ge<sub>y</sub> layers of the compositions 0 ≤ y ≤ 0.24, which were grown epitaxially on 440 μm thick silicon substrates by means of CVD at the Institute of Electronics of the Academy of Sciences of Uzbekistan in Tashkent. (ii) High-Ge-content specimens, which will be CVD-produced by Okmetic Ltd., Vantaa, Finland. The impurity content of this material is lower than 10<sup>18</sup> m<sup>−3</sup>; the accuracy of the wafer thicknesses is better than 2%.

4.2. Diffusion Experiments

It is proposed to do both <sup>195</sup>Au and <sup>71</sup>Ge diffusion measurements in Si<sub>1−y</sub>Ge<sub>y</sub> alloys by means of the modified radiotracer technique described in Sect. 2.1. In particular, the Au diffusivity will be determined in the composition regime 0.24 < y < 1 not covered in our previous investigations (Sect. 3.1). Moreover, it is intended to measure the <sup>71</sup>Ge self-diffusion coefficient in Si–Ge at compositions ranging from y = 0 (Si) to y = 1 (Ge).

As pointed out in Sect. 1, for the clarification of the diffusion mechanisms operating in Si–Ge a comparison of the diffusion coefficients of <sup>195</sup>Au and <sup>71</sup>Ge is of great importance. At alloy compositions and diffusion temperatures at which Au diffuses either via the self-interstitial-controlled kick-out mechanism or the vacancy-controlled dissociative mechanism, a comparison of the Au diffusivity with the self-diffusion coefficient permits a quantitative cross-check. At any rate, this will be the case for 0 ≤ y ≤ 0.09, where we already have shown that Au undergoes self-interstitial-controlled kick-out diffusion [Eq. (3)].

4.3. Emission Channelling Experiments

It is intended to study the lattice sites of <sup>69</sup>Ge in Si<sub>1−y</sub>Ge<sub>y</sub> samples of different Ge content (0 ≤ y ≤ 1) in the as-implanted state and as a function of the annealing temperature up to 900°C. We expect that the implanted <sup>69</sup>Ge is finally incorporated on substitutional sites. The emission channelling experiments will give direct information on how this process proceeds, when it will be completed, and when most of the lattice damage resulting from the implantation will be annealed out. This information will be required in order to characterize the proper starting conditions for the diffusion experiments.
5. Technical Requirements

An advantage of the experiments proposed above is that they exclusively require facilities and services available at ISOLDE and our own equipment. For instance, the standard targets and ion sources yield a sufficient flux of the radioisotopes required, and the implantation can be done in a chamber owned by the Max-Planck-Institut für Metallforschung.

5.1. $^{71}\text{Ge}$ Diffusion

The $^{71}\text{Ge}$ isotopes needed in the studies of self-diffusion in Si–Ge (Sect. 1) can be obtained via the chain of rapid radioactive decays

$$^{71}\text{Br} \ (t_{1/2} = 21.4 \text{ s}) \rightarrow ^{71}\text{Se} \ (t_{1/2} = 4.7 \text{ min}) \rightarrow ^{71}\text{As} \ (t_{1/2} = 65.3 \text{ h}) \rightarrow ^{71}\text{Ge} \ (t_{1/2} = 11.2 \text{ h}). \quad (5)$$

Thus at ISOLDE $^{71}\text{Ge}$ may be produced in the following ways: (i) 1 GeV-proton bombardment of a Nb foil generates all isotopes of mass 71 in chain (5) preceding $^{71}\text{Ge}$, where the yield of $^{71}\text{As}$ is largest $(9.7 \times 10^8 \text{ ions/s/\mu A})$. (ii) Using a Zr-oxide target, again $^{71}\text{As}$ is produced at the highest rate $(5.6 \times 10^8 \text{ ions/s/\mu A})$, while there is an additional minor yield of $^{71}\text{Se}$.

The $^{71}\text{Ge}$ radioactivity per specimen required in our experiments is about $1 \times 10^5 \text{ Bq}$. This corresponds to an implantation of $2 \times 10^{11} \ ^{71}\text{Ge}$ atoms, which is achieved within 3 min. The number of specimens $^{71}\text{Ge}$-implanted in one run should not exceed 25, since more specimens cannot be examined within about 1 month, after which the radioactive signal has dropped below the detectability limit. As a consequence, a first series of $^{71}\text{Ge}$ diffusion experiments with about 150 specimens may be carried out within a reasonable time, if two implantation runs a year with a minimum interruption of 1 month can be performed.

5.2. $^{195}\text{Au}$ Diffusion

The radioisotope $^{195}\text{Au} \ (t_{1/2} = 186 \text{ d})$ is obtained as a daughter of $^{195}\text{Hg} \ (t_{1/2} = 9.5 \text{ h})$, which can be produced at ISOLDE by proton bombardment of a molten Pb target. The wanted $^{195}\text{Au}$ radioactivity per sample is $3.7 \times 10^4 \text{ Bq}$, which corresponds to an implantation of $8 \times 10^{11} \ ^{195}\text{Hg}$ ions. At a yield of $6.3 \times 10^9 \text{ ions/s/\mu A}$, this is achieved within 2 min. In a first series about 150 Si–Ge specimens of various compositions are to be $^{195}\text{Hg}$-implanted. For practical reasons, the number of specimens implanted in one run should not exceed about 40.
5.3. Emission Channelling Experiments

The $^{69}$Ge radioisotope to be used in the positron channelling experiments may be obtained either from a Nb-foil ($9.1 \times 10^7$ ions/s/$\mu$A) or a Zr-oxide ($1 \times 10^9$ ions/s/$\mu$A) target. Recent tests have shown that the Nb-foil hot-plasma target also shows high yields of $^{69m}$Zn, roughly equal to the yield of $^{69}$Ge. $^{69m}$Zn has a half-life (14 h) similar to that of $^{69}$Ge (39 h) and decays, by internal transition, into $^{69}$Zn, which is a $\beta^-$-emitter with an endpoint energy of 0.90 MeV. Since the energy spectra of the $\beta^+$ from $^{69}$Zn and the $\beta^+$ from $^{69}$Ge overlap, immediately after implantation meaningful emission-channelling lattice-location experiments are impossible with a sample containing both isotopes in similar amounts. Hence, the samples would first have to be stored for three days, so that $^{69m}$Zn would have decayed before the channelling experiments begin. However, according to the SC-yield database and discussions with the ISOLDE technical-group leader, the Zn contamination is much lower for ZrO hot-plasma targets ($2 \times 10^5$ ions/s/$\mu$A). Therefore, ZrO targets would be preferred. However, we should like to point out that the measurements are also feasible with Nb-foil targets if ZrO targets are not available. The implantation duration per sample would be about 30 min; three specimens would be $^{69}$Ge-implanted per beam time. The determination of the lattice location of the implanted $^{69}$Ge atoms would be done by means of the three existing emission channelling set-ups of the Leuven and Lisboa groups available at ISOLDE. All set-ups are equipped with position-sensitive detectors and in-situ annealing facilities, thus allowing for most efficient measurements.

The optimum implantation energy for all isotopes is 60 keV. The ion beams can be shared with other users, namely in the case of the Pb target with IS302, IS314, IS348, IS357, IS360, and in the case of the Nb target with IS362, IS328, IS325, IS375. Very likely, the Zr-oxide target needed for the $^{69}$Ge production may also be used by the present users of the Nb-HP targets. We intend to contact these users in order to check this possibility.
6. Target Requirements

The following beam time is requested:

<table>
<thead>
<tr>
<th>Beam</th>
<th>Min. Intensity</th>
<th>Target Material</th>
<th>Ion Source</th>
<th>Shifts</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{71}$As</td>
<td>$5.0 \cdot 10^8$ ions/s/µA</td>
<td>Nb foil</td>
<td>hot-plasma ion source (FEBIAD)</td>
<td>6</td>
</tr>
<tr>
<td>or</td>
<td>Zr oxide</td>
<td></td>
<td>hot-plasma source at 2000°C</td>
<td>(6)</td>
</tr>
<tr>
<td>$^{69}$Ge</td>
<td>$9.0 \cdot 10^7$ ions/s/µA</td>
<td>Nb foil</td>
<td>hot-plasma ion source (FEBIAD)</td>
<td>2</td>
</tr>
<tr>
<td>or</td>
<td>Zr oxide</td>
<td></td>
<td>hot-plasma source at 2000°C</td>
<td>(2)</td>
</tr>
<tr>
<td>$^{192}$Hg</td>
<td>$6.3 \cdot 10^9$ ions/s/µA</td>
<td>molten Pb</td>
<td>plasma-heated line</td>
<td>4</td>
</tr>
</tbody>
</table>

- stable beam time for setting up the beamline and the experiment: 1 shift per beam time
- mass resolution: 2400 (GPS)
- hall space: 10 m²
- first possible date for data taking: January 1999

All data are taken from the ISOLDE SC-yield database and ISOLDE users' guide.

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References

Diffusion Mechanisms and Lattice Locations of Thermal-Equilibrium Defects in Si-Ge Alloys


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Summary

This proposal aims at a systematic investigation of the diffusion of implanted $^{71}$Ge and $^{195}$Au in Si-Ge alloys over the entire regime of compositions. Diffusion in Si-Ge alloys, which are of great practical importance (e.g., because of their integrability in conventional silicon device technology and the possibility to tailor their band structure and charge carrier mobility via composition), plays an important rôle in their doping and contamination. Concerning the scientific aspect of diffusion, Si-Ge is an extraordinary solid, since there is strong evidence that self-diffusion undergoes a transition from an interstitialcy mechanism on the Si side to a vacancy mechanism on the Ge side, while Au diffusion changes over from a kick-out mechanism to a dissociative mechanism with increasing Ge content. Therefore, measuring the diffusivities of both Ge and Au in Si-Ge as functions of the alloy composition is not only invaluable for technical purposes, but may also allow us to cross-check quantitatively the current models of diffusive transport in Si, Ge, and their alloys.

The diffusion of Ge and Au in Si-Ge will be measured by means of the radiotracer technique, because this is the most reliable method for determining diffusivities in solids. The introduction of the radiotracer atoms $^{71}$Ge and $^{195}$Au will be done by implantation, since in this way unwanted diffusion barriers at the specimen surfaces (e.g., oxide layers) are elegantly overcome. The price to be paid for is the crystal lattice damage unavoidably generated by the implants. In order to judge the influence of this damage on diffusion, it is intended to investigate the lattice location of implanted $^{69}$Ge in Si-Ge and the recovery of the correlated damage by means of positron emission channelling experiments.

Because of the need of radioactive $^{69}$Ge and $^{195}$Au ions, the package of experiments described above can exclusively be done at ISOLDE. The $^{195}$Au may be obtained as a daughter of $^{195}$Hg, which can be produced by proton bombardment of molten Pb, whereas $^{71}$Ge is created in the decay of $^{71}$As which may be obtained from either a Nb-foil or a Zr-oxide target. The latter target would also be most suitable for the production of $^{69}$Ge needed for the emission channelling experiments, though these may also be done with Nb-foil-target-produced $^{69}$Ge ions.