Ge Self-Diffusion in Epitaxial $Si_{1-x}Ge_x$ Layers

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Diffusion coefficients and activation energies have been determined for Ge diffusion in strain-relaxed $Si_{1-x}Ge_x$ with $x = 0.00$, 0.10, 0.20, 0.30, 0.40, and 0.50. The activation energy drops from 4.7 eV in Si and $Si_{0.90}Ge_{0.10}$ to 3.2 eV at $x = 0.50$. This value compares with the literature value for Ge self-diffusion in Ge, suggesting Ge-like diffusion already at $x \approx 0.5$. The effect of strain on the diffusion was also studied showing a decrease in diffusion coefficient and an increase in activation energy upon going from compressive over relaxed to tensile strain.

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Silicon germanium is an exciting material from both technological and physical viewpoints. The two elements crystallize in the diamond lattice structure and are fully miscible since their lattice constants differ by only 4%. The SiGe matrix is ideal for gaining an understanding of self-diffusion in unordered alloys and, furthermore, the kinematics of dopants in many cases calls for an understanding of self-diffusion. The layers of SiGe have proved their worth in the silicon-based technology as, e.g., heterojunction bipolar transistor base material. Despite the employment of the material in microtechnological contexts, self-diffusion of neither Si nor Ge in SiGe is well studied.

Fahey *et al.* have shown [1] that, in pure Si, Ge diffuses both by a vacancy and an interstitial-related mechanism. The diffusion coefficient can thus be described as two terms with separate prefactors and activation energies [2]:

$$D_{\mathrm{Ge}} = D_0^I \exp(-E_a^I/kT) + D_0^V \exp(-E_a^V/kT). \quad (1)$$

These are the two basic mechanisms of diffusion and it is not expected that other mechanisms will contribute significantly to the process. Ge self-diffusion in Ge is satisfactorily accounted for by assuming only a contribution from vacancies [3]. The activation energy for self-diffusion via the X defect (vacancies, V, or interstitials, I) is composed of an energy of formation and an energy of migration:

$$E_a^X = H_f^X + H_m^X. \quad (2)$$

The effect of changing the composition or applying biaxial strain on these fundamental parameters is basically unknown. Calculations show [4] that biaxial tensile strain in Si will have no effect on the energy of formation of vacancies but decreases that of interstitials.

Several experiments (see Ref. [1], and references therein) have been made on Ge diffusion in Si and have given comparable diffusion coefficients. On the activation energies and prefactors, however, consensus is far from obtained, and activation energies of 4.1–5.4 eV are extracted from measurements in overlapping temperature regions [1].

It has been suggested that Si and Ge exhibit the same diffusional behavior in Si owing to their comparable covalent bonding radii [1]. Sn is isovalent with Si and Ge and dissolves substitutionally in the Si lattice. However, it has a larger bonding radius, and similar diffusional behavior is not expected. The fractional vacancy contributions to the diffusion are found to vary from 0.4–0.5 for Si [5] (800–1100 °C) to 0.6–0.7 for Ge [1] (1050 °C) and 1 for Sn [6], i.e., it increases with the size of the diffuser.

Recently, activation energies were measured to be 4.75(4) eV [7] (measured in the temperature range 855–1388 °C) and 4.76 eV [5] for Si self-diffusion and 4.91(9) eV [8] and 4.8(3) [6] for Sn diffusion. Turning to diffusion in Ge, Sn [8], Si [9], and Ge are found to have similar activation energies of ~3.1 eV supporting that all three elements diffuse via vacancies in Ge. Extracted activation energies of the V-mediated diffusion of Sn diffusion [6,10] in $Si_{1-x}Ge_x$, $0 \leq x \leq 1$, show a linear decrease with Ge content [8]. No data for diffusion of Si in SiGe could be found.

Theoretical treatments of self-diffusion in SiGe are uncharted areas — and the effect of strain even more so. Turning to experiments, McVay and DuCharme [11] studied indiffusion of Ge into polycrystalline $Si_{1-x}Ge_x$ with $x = 0$ up to 0.77 and found a decreasing activation energy for $0 \leq x \leq 0.3$. The diffusion coefficient increases with increasing Ge content but the activation energy remains constant for $0.3 \leq x \leq 0.77$ at 3.1 eV which is also the literature value for Ge self-diffusion in Ge [3,12].

In this Letter, epitaxial layers grown with molecular-beam epitaxy were used to study the self-diffusion of Ge in relaxed $Si_{1-x}Ge_x$ with x ranging from 0 to 0.5 in steps of 0.1. In the case of $Si_{0.90}Ge_{0.10}$, samples with compressive and tensile strains have also been produced.

Our key to the study of Ge self-diffusion in SiGe is ^{72}Ge isotopically enriched Ge. A thin layer of natural Ge is sandwiched between ^{72}Ge layers, as shown in Fig. 1. In pure Si, a spike of ^{72}Ge is grown with a peak concentration of 2×10^{20} cm^{-3}.

The layers were grown on (100)-Czochralski Si wafers and the desired Ge concentrations were reached by using the stepwise equilibration technique described in Ref. [13] and confirmed by Rutherford backscattering spectrometry to an absolute accuracy of 1% Ge. Transmission electron

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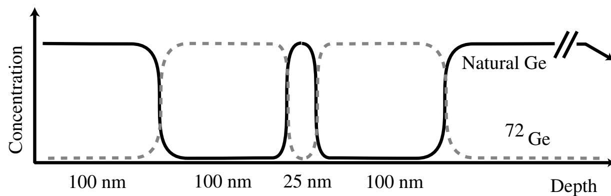

FIG. 1. Schematic profile of a relaxed SiGe sample.

microscopy (TEM) showed in all cases that the density of threading dislocations was below 10^6 cm^{-2}.

To create strained layers, the spike and the two surrounding layers were grown with a Ge concentration of 10%. The surface and substrate layers were made with 5% or 15% Ge to produce tensile or compressive strain, respectively. The step in Ge content of 5% introduces a strain $s = -0.042(x - y) = 0.21\%$ [14], where x and y are the Ge contents in the diffusion and sandwiching layers, respectively. This corresponds to an in-plane stress of 0.4 GPa [15]. Strain relaxation by creation of misfit dislocations was proven negligible with TEM.

Annealings were performed in an open furnace on samples protected by layers of 100-nm Si_2N_3, working as a barrier against surface injection of point defects, on top of 100-nm SiO_2 that prevents surface strain effects from the nitride layer. Layers deposited by chemical vapor deposition ensures diffusion in an inert ambience [16,17]. Although our capping layers were deposited by sputtering at room temperature, inert annealing is confirmed by the fact that our tests gave the same diffusion coefficients in different annealing atmospheres (argon, nitrogen, and air). The annealing times were chosen from 20 minutes to 20 hours (not only for the different temperatures but also for different Ge-content samples at the same temperature) to ensure that the spikes were broadened comparably.

The profiles were measured with secondary-ion-mass spectrometry (SIMS) on an Atomika 4000 apparatus using a 3.5 keV beam of O_2^+ at an angle of 20° off-normal. The SIMS signal from $^{70}Ge^{16}O^-$ ions was found to give the highest signal-to-background ratio. For the samples with ^{72}Ge in Si an 8.0 keV Cs^+ beam was used to prevent interference of ^{72}Ge with the combinations of silicon and oxygen atoms. The crater depths for calibrations were measured on a Dektak stylus positioning apparatus, to an accuracy of ~50 Å. A software program was used for extracting the diffusion coefficients by minimizing the χ^2 deviations of the calculated from the measured diffused profile by simulating Fickian diffusion.

In the strained samples, interdiffusion will cause the region over which the strain is built up to extend over more atomic layers. It will not, however, alter the numerical value of the strain in the region around the peak.

Figure 2 shows a typical measured profile after background subtraction and concentration normalization. Also included in the plot is the fitted curve.

The diffusion coefficients for each sample can be fitted perfectly with a single exponential of the form $D = D_0 \exp(-E_a/kT)$. This does not prove that only one term from Eq. (1) is dominant since, within the narrow temperature interval, two mechanisms can give the impression of a straight line in the Arrhenius plots. The parameters obtained in the fit (D_0 and E_a) will in that case lie between D_0^i and D_0^v and E_a^i and E_a^v.

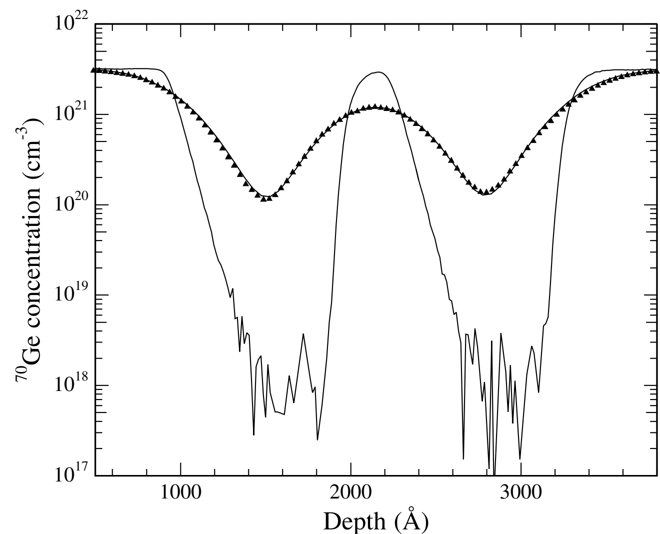

FIG. 2. Example of measured profile after normalization and depth calibration (relaxed $Si_{0.70}Ge_{0.30}$ annealed 1 hour at 950 °C). The solid ragged line is the SIMS-measured as-grown profile while (▲) show the diffused profile. Also included is the solid line of the simulated curve to the diffused profile.

The Arrhenius curves are shown in Fig. 3 (relaxed materials) and Fig. 4 (strained $Si_{0.90}Ge_{0.10}$). A summary of the obtained parameters and the temperature ranges used for the different samples is given in Table I.

A significant increase in the Ge diffusion coefficient with increasing Ge content is seen at all temperatures. The relaxed samples with 0% and 10% germanium give

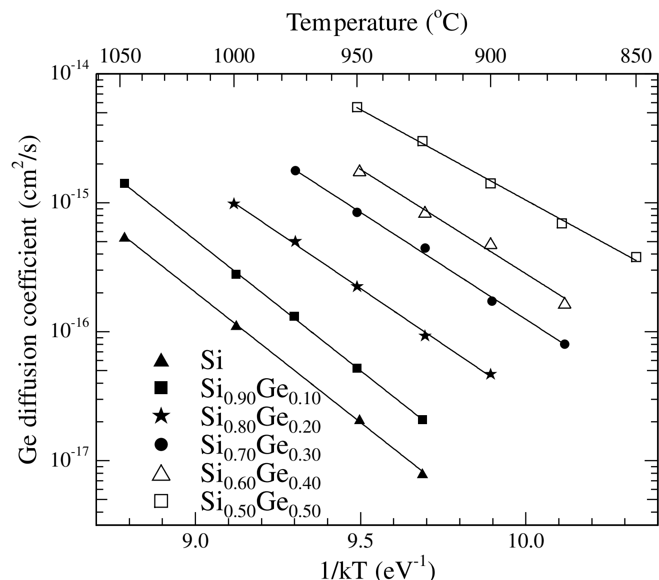

FIG. 3. Arrhenius plots of Ge diffusion in relaxed materials.

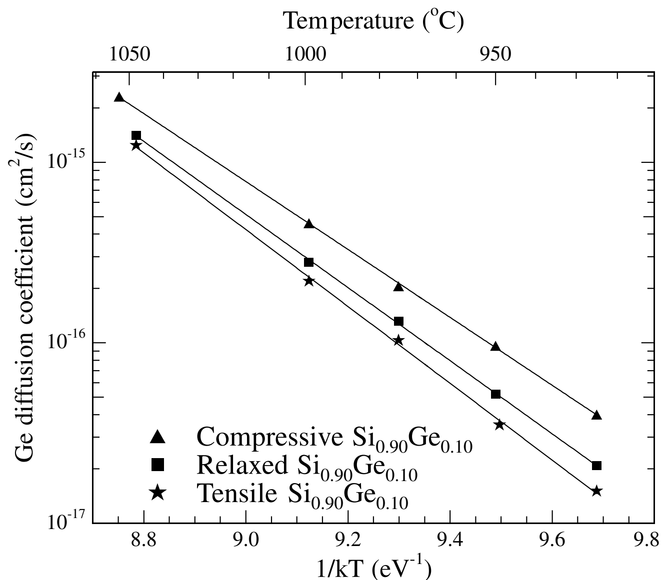

FIG. 4. Arrhenius plot of Ge diffusion in compressive, relaxed, and strained $Si_{0.90}Ge_{0.10}$.

activation energies of 4.7 eV. From 20% to 40% Ge, the activation energy decreases from 4.0 to 3.7 eV before it reaches a value of 3.2 eV at $x = 0.50$. Despite the large statistical uncertainty in the prefactors, they show a tendency to decrease with increasing Ge content over 4 orders of magnitude from Si to $Si_{0.50}Ge_{0.50}$.

The diffusion coefficients of the strained samples also make perfect Arrhenius lines, as seen in Fig. 4. If the isolated effect of strain, s, is approximated to be linear, $E_a = E_a^x(x) + E_a^s s$, where $E_a^x(x)$ is the separate effect of the Ge content [14], it is found that $E_a^s = 1.6(4)$ eV/% strain for compressive strain while $E_a^s = 1.1(5)$ eV/% for tensile strain. Within the uncertainties these numbers are identical for the two types of strain.

The influence of strain on Si/Ge interdiffusion has been described in the literature by Cowern *et al.* [14]. They attribute the increase in the diffusion coefficient when adding Ge to come purely from strain which is seen not to be true from our investigation.

The effect of strain on the Ge diffusion coefficients is similar to that found by Kringhøj *et al.* [18] for the diffusion of Sb in strained SiGe. Sb diffuses via vacancies in Si and, presumably, also in $Si_{0.90}Ge_{0.10}$ and, thus, a similar reaction to strain is indeed expected for Sb and Ge. The activation energies, however, are not found to vary with strain by Kringhøj *et al.* which we suggest is an effect of the negligible I component for Sb diffusion as compared to Ge diffusion. Hence, the activation energy for vacancy diffusion is apparently not strongly influenced by the strain (unlike that of interstitialcies) as is also indicated from the formation energy calculations of Ref. [4].

The obtained activation energies are presented in Fig. 5, where the value for Ge diffusion in Ge from Werner *et al.* [12] of 3.09 eV is included.

For diffusion in Si, the activation energy of 4.65(6) eV lies within the previously reported values [1] and agrees with the values for Si self-diffusion in Si underlining the resemblance of Si and Ge diffusers. It is also, within the uncertainties, the same as the activation energy for Sn diffusion in Si of 4.8(3) eV [6] despite the fact that Sn diffusion is purely vacancy mediated. The diffusion of Sn and Ge does not, however, appear to evolve analogously in SiGe, where $E_a(\text{Sn}) \geq E_a(\text{Ge})$. The reason for this high activation energy is not understood, not even in Si, where $E_a(\text{Sn}) > E_a^V(\text{Ge})$.

The dashed line in Fig. 5 is the modeled line for the diffusion of Sb in SiGe from Nylandsted Larsen and Kringhøj [19]. Sb diffusion is expected to be vacancy driven all the way from Si to Ge [19]. According to Hu [20], the activation energy for Sb diffusion via vacancies should be lower than self-diffusion via vacancies due to the attraction (binding energy) between the diffuser and a vacancy. This is indeed seen for the diffusion of Sb and Ge in pure Ge, where the difference is 0.5 eV. For Sb diffusion in Si, the activation energy is 4.08 eV [19], whereas the activation energy for the vacancy part of the Si self-diffusion is suggested to be between 4.14 [7] and 4.68 eV [5]. These values must also be close to the ones for Ge diffusion in Si since the effective activation energies are the same and the vacancy contribution is only slightly higher for Ge, as stated earlier. For $Si_{0.50}Ge_{0.50}$ our data show that the difference in activation energy between Sb and Ge is 0.25 eV but it is inverted as compared to the diffusion in Si and Ge. This is not compatible with the Hu picture mentioned above and for the time being we offer no explanation for this.

TABLE I. Parameters obtained from the Arrhenius plots. The uncertainties given are statistical from the fits to the data points.

Ge content [%]	Strain state	Temp. range [°C]	D_0 [cm²/s]	E_a [eV]
0	relaxed	925–1050	$3.1(1.7) \times 10^2$	4.65(6)
10	relaxed	925–1050	$8.7(3.3) \times 10^2$	4.66(4)
20	relaxed	900–1000	$6.6(5.8) \times 10^0$	4.00(9)
30	relaxed	875–975	$4.7(5.3) \times 10^0$	3.82(12)
40	relaxed	875–950	$4.2(10.7) \times 10^0$	3.72(27)
50	relaxed	850–950	$1.1(1.1) \times 10^{-1}$	3.23(10)
10	compressive	925–1050	$6.7(2.4) \times 10^1$	4.33(4)
10	tensile	925–1050	$6.1(6.7) \times 10^3$	4.90(8)

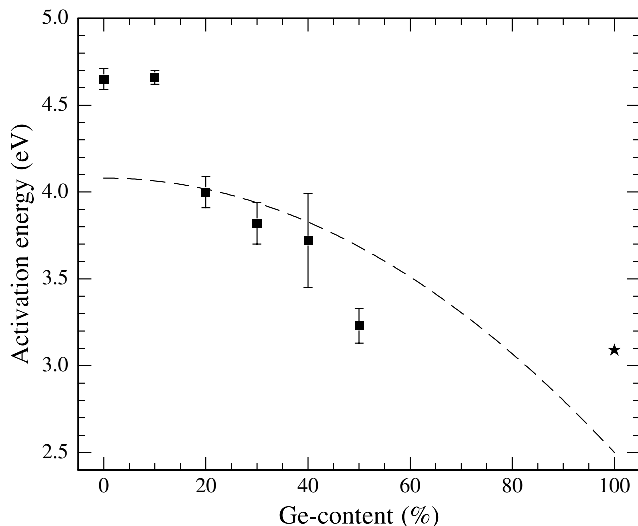

FIG. 5. Obtained activation energies (■) with statistical uncertainties. Also included is the value for the Ge diffusion in Ge (★) [12] and the modeled Sb diffusion from Ref. [19] (- -).

The drop in activation energy from 4.7 eV in $Si_{0.90}Ge_{0.10}$ to 4.0 eV at $Si_{0.80}Ge_{0.20}$ (identical to the activation energy of the vacancy-assisted Sb diffusion in $Si_{0.80}Ge_{0.20}$) suggests that from this point the interstitial path for diffusion with a high activation energy is no longer favorable, as compared to vacancy diffusion in the SiGe matrix. The continuing decrease of the activation energy for $0.2 \leq x \leq 0.5$ presumably results from a decrease of the vacancy formation energy which in Si is calculated to be 3.5–4.0 eV [21,22] and in Ge, experimentally and theoretically, is found to be 1.7–2.3 eV [23]. From Eq. (2) we note that a contribution from H_m^V should also be expected.

Surprisingly, already at $x \approx 0.5$ the activation energy for Ge diffusion in Ge is attained. Thus, for $x \geq 0.5$ the formation energy of vacancies must be constant and, as the activation energy is determined by the energy barrier, it demonstrates that those diffusion paths which the Ge atoms choose are predominantly Ge-like already at $x \approx 0.5$. The preexponential factor, however, continues to increase from $x \approx 0.5$ to 1 which could be due to an increase in the number of possible jump directions. The theory of diffusion in unordered alloys is very limited and much work is needed in this area to turn speculations into facts.

Ge diffusion coefficients in SiGe from the work of McVay and DuCharme [11] extrapolated to temperatures used in the present investigation are found to be much higher than the ones we have obtained. An explanation can be grain boundary diffusion in the polycrystalline material. McVay and DuCharme find that the activation energy already reaches the pure Ge value at $x = 0.30$, while our results from Fig. 5 qualitatively agree but instead reach this value at about $x = 0.50$.

In summary, these are, to our knowledge, the first measurements of self-diffusion performed on strain-relaxed crystalline $Si_{1-x}Ge_x$. The activation energies of diffusion have been accurately determined for $x = 0$, 0.10, 0.20, 0.30, 0.40, and 0.50. For $x = 0$ and 0.10 the activation energy is found to be 4.7 eV, while concentrations between 0.20 and 0.40 give activation energies of 3.7–4.0 eV, indicating the absence of diffusion via intersitials. Surprisingly, for $Si_{0.50}Ge_{0.50}$ the activation energy has dropped to 3.2 eV which, in contradiction with the Hu picture [20], is smaller than that of Sb diffusion, and close to the value found in Ge.

The separate effect on Ge self-diffusion of strain was measured in SiGe. The diffusion coefficient decreases from compressive to tensile strain for temperatures between 925 and 1050 °C. Also, from compressive to tensile strain, the activation energy increases significantly although the strain is only 0.21%.

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