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Diffusion of Ge in SiGe alloys*

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Germanium diffusion was measured in SiGe alloys of 100/0, 77.6/22.4, 69.2/30.8, 44.6/55.4, and 22.3/77.7 silicon to germanium atomic-percent ratios by the use of the radioisotope ^{71}Ge and a thin-sectioning technique. As expected from the calculated, small, strain-energy contributions from the ^{71}Ge impurities, the diffusion is similar to silicon self-diffusion for the silicon end member. Since the results fit an Arrhenius plot for the compositions and temperature ranges studied, activation energies and pre-exponentials were determined. These diffusion parameters indicate that the ^{71}Ge diffusion is compatible with the monovacancy mechanism up to 70-at.% silicon in the SiGe alloys. For more silicon-rich material, the diffusion is quite analogous to the extended-defect mechanism previously suggested for high-temperature silicon self-diffusion.

I. INTRODUCTION

Despite numerous studies of self- and impurity diffusion in silicon and germanium extending over the past twenty years, specification of diffusion mechanisms remains to be demonstrated for many systems involving these elements. In particular, the defect associated with self-diffusion in silicon is still the subject of considerable controversy.[1–4]

Early models[5,6] for diffusion in silicon and germanium were based on the monovacancy from analogy to the established mechanism for self-diffusion in close-packed metals. The observed self-diffusion in germanium[7] is in general agreement with the monovacancy mechanism, although at least one author[1,3] contends that the large pre-exponential factors and activation energies observed for self-diffusion in both germanium and silicon as compared to metals warrant consideration of more extended defects.

It is likely, however, that self-diffusion in silicon is considerably different from that in germanium. The monovacancy mechanism seems incompatible[1,2] with the data available for self-diffusion in silicon. Two alternative defect models which are in better agreement with the silicon self-diffusion observations are (i) the extended interstitial[1,3] and (ii) the divacancy.[2,8]

Since the mechanisms for slow impurity diffusion may be expected to be related to those for self-diffusion in silicon or germanium,[1,9] impurity diffusion of this type should exemplify self-diffusion towards each end of the SiGe composition range. It has in fact been shown[9] that ^{71}Ge diffuses in single-crystal silicon in like manner to silicon self-diffusion. This similarity is to be expected from the constitution of SiGe alloys, where ion-valence differences are absent and size differences between component ions are small.

The study of ^{71}Ge diffusion in SiGe alloys of various compositions serves not only to investigate the self-diffusion differences between Ge and Si but also to study impurity diffusion in high-concentration binary alloys of considerable homogeneity. Although a few measurements are available[10] for metal alloys, more data are required before any theory for impurity diffusion in nondilute alloys can be adequately tested.

Tracer-diffusion experiments in silicon-rich materials are more difficult to perform than corresponding studies in pure germanium or in most metals owing to the slow diffusion rates observed for certain tracers and the high working temperatures typically involved. Since the most easily obtained silicon tracer (^{31}Si) has a half-life of only 2.6 h, we have used ^{71}Ge ($T_{1/2}$= 11.4 days) as an indicator of silicon diffusion behavior at the silicon-rich end of alloy compositions.

II. EXPERIMENTAL TECHNIQUE

Since it was impossible to obtain single crystals of SiGe alloys suitable for this experiment, the samples used were prepared by zone leveling.[11] This technique leads to polycrystalline alloys of large-grain size (approximately 10 grains/cm^2). Semiconductor grade Si and Ge with a purity in excess of 99.999% were melted in a fused-silica crucible in the proper ratios, stirred, and cast into a water-cooled Rh-plated Cu mold. Both melting and casting were done under an Ar atmosphere. The chill-cast material was then placed in a fused-silica boat which had been pyrolytically coated with carbon by the high-temperature decomposition of methane. This boat was then placed in the zone-leveling apparatus which was set to pass a 1-in. molten zone along the boat at the rate of approximately 0.04 in/h. The advantage of zone leveling chill-cast material is that it is already somewhat homogeneous and therefore greater homogeneity of the zone-leveled material is normally obtained. It was observed that if SiGe alloys were zone leveled in an uncoated fused-silica boat,

cracking of the boat occurred as the molten zone progressed. However, coating the boat with carbon eliminated the problem. Impurity analysis of the zone-leveled ingots showed that although some SiC formed at the melt-boat interface, no carbon was detected in the interior of the ingots. Total impurities, both electrically active and inactive, were determined by electrical and various analytical means to be typically less than 1 ppm. Compositional variation across the diffusion samples ($\sim 1\ cm^2$) was less than $\frac{1}{2}$ at.% as determined by a scanning electron microprobe.

Germanium diffusion was measured by use of the radioisotope ^{71}Ge and a thin-sectioning technique. Samples approximately 1 cm^2 in area were polished and the isotope (in the form of sodium germanate) was immediately placed on the sample surface as a thin film and allowed to dry. The samples were then placed active-surface down on a fused-silica plate and sealed under vacuum in a fused-silica tube. Samples were annealed in an electric furnace, capable of holding temperatures to $\pm 2\ ^\circ C$, from 1 to 24 days depending upon composition and temperature. Temperatures were measured with a Pt vs Pt + 10-at.% Rh thermocouple in contact with the fused-silica tube. The edges were then ground from each sample to remove the effects of surface diffusion. The samples were sectioned by a previously described sectioning apparatus[12] which utilizes abrasive paper and allows the sample to be removed for weighing while assuring that all sections are kept parallel. Sections were 2–5 μm thick, and the total thickness removed was 30–40 μm. Section thicknesses were determined from the density, cross-sectional area of the sample, and the weight of each section. After a section was taken, the sample was wiped with a small piece of lint-free paper to remove any particles adhering to the sample; this paper was then folded inside the abrasive paper. The activity of each section was determined by use of a scintillation counter containing a thallium-activated NaI crystal with Be end window.

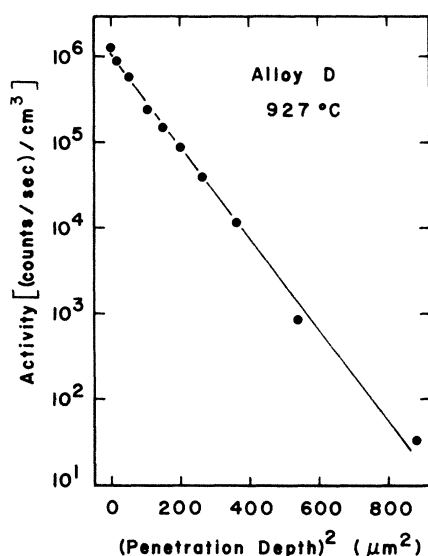

FIG. 1. Typical data showing the activity as a function of diffusion distance squared for alloy D (See Table I) at 927 °C. Sectioned depth was 29 μm.

In an effort to determine the effects of Na in the sodium germanate source, an experiment was performed in which a substantial amount of ^{22}Na radioisotope was exchanged with the nonradioactive ^{23}Na found in sodium germanate. This material was placed on a SiGe sample and annealed in the same manner as all the other SiGe samples. No ^{22}Na was detected in the sample sections while a standard ^{71}Ge profile was present.

The diffusion observed in this study is described by the thin-film solution to Fick's second law,

$$A_i = [A_0/(\pi D t)^{1/2}]\, e^{-X_i^2/4Dt}, \qquad (1)$$

where X_i is the distance from the sample isotope interface, A_i is the activity concentration at distance X_i from the surface, t is the time of diffusion, A_0 is the original activity at $X_i = 0$ and $t = 0$, and D is the diffusion coefficient.

III. RESULTS

Figure 1 illustrates typical experimental data in the form of log activity as a function of the square of penetration depth for ^{71}Ge diffusion in a given SiGe alloy. Diffusion coefficients were determined by a least-squares fit of Eq. (1) to the data. It is observed that although the penetration depth is usually quite small compared to metallic diffusion on the same time scale, the data provide a good fit to Eq. (1). No evidence of grain-boundary diffusion was detected over the temperature ranges studied on any of the compositions.

The temperature dependence of the ^{71}Ge diffusion coefficients obtained for the alloy compositions investigated are shown in Fig. 2. It is clear that the diffusion coefficients satisfy the Arrhenius equation

$$D = D_0\, e^{-E_A/kT} \qquad (2)$$

for all alloy compositions and temperature ranges studied. The values determined from a least-squares fit to Eq. (2) for the pre-exponential D_0 and the activation energy E_A are reported in Table I for ^{71}Ge diffusion in single-crystal Si and the four zone-leveled binary-alloy compositions measured.

Table I illustrates that the diffusion parameters for composition E are quite similar to previous single-crystal germanium results (labeled F).[13] It has been shown previously[14] that diffusion in

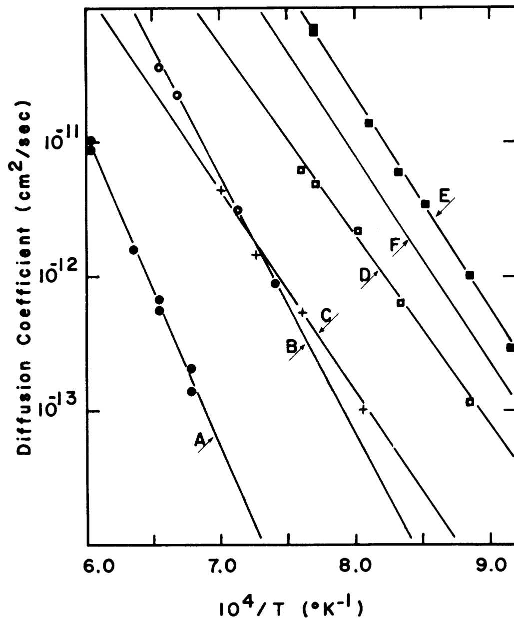

FIG. 2. Temperature dependence of the diffusion coefficients for the alloys A-F as designated in Table I.

polycrystalline samples closely approximates diffusion in single crystals if the temperatures are near the melting point and the tracer diffusion is directionally independent. We make use of this fact later to compare the diffusion results of the intermediate alloy compositions with the results found for the single-crystal end members.

IV. DISCUSSION

The measured activation energies for the diffusion of ^{71}Ge in SiGe alloys are plotted in Fig. 3 as a function of alloy composition. It is observed that the activation energies remain close to 3 eV from pure germanium to nearly 70-at.% silicon content in the SiGe alloy. At higher silicon compositions, the activation energy rises precipitously, until, for nearly pure silicon, it closely approximates the values of ~5 eV measured previously for silicon self-diffusion.[15-17]

It is possible within experimental error to assign a linear dependence to the activation energy as a function of composition for both branches of the data. If the linear portion of the activation energy originating from the germanium-rich end of alloy composition is extrapolated to pure silicon, a value of ~3.1 eV is obtained. This value is reasonably close to that calculated by Swalin[6] (3.38 eV) for the activation energy for self-diffusion in silicon assuming a monovacancy mechanism. More recently, Watkins's[18] measurement of only 0.33 eV for the migration energy of a monovacancy in silicon indicates that Swalin's calculation may include an overestimate of that term.

The diffusion of ^{71}Ge in the silicon-rich end of alloy composition constitutes a case of impurity diffusion in a binary alloy. Since a germanium impurity ion has the same valence as the silicon solvent ions, no relative-charge effects on impurity diffusion are expected such as are found to occur for group-III and group-V dopants in semiconductors.[5] The principal effect expected then between the activation energies for self-diffusion in silicon and impurity diffusion in SiGe alloys is the strain energy E_S related to the difference in formation energy of the defect associated with the diffusion. That is,

$$(E_A)_{\text{imp}} = (E_A)_{\text{self}} \pm E_S \, . \qquad (3)$$

TABLE I. Diffusion data for the compositions studied.

Alloy	Composition at.% Si/at.% Ge	D_0[a] (cm^2/sec)	E_a[b] (eV)	Temperature range (°C)
A	100/0	1.5×10^{3}	4.7 ± 0.15	1381–1200
B	77.6/22.4	1.1×10^{2}	3.8 ± 0.15	1252–1077
C	69.2/30.8	4.3×10^{-1}	3.1 ± 0.15	1151–968
D	44.6/55.4	1.0×10^{0}	2.9 ± 0.15	1040–856
E	22.3/77.7	3.3×10^{1}	3.0 ± 0.10	1024–820
F[c]	0/100	1.1×10^{1}	3.0 ± 0.10	916–731

[a]The pre-exponential factor should be considered as an order of magnitude estimate.

[b]Errors were determined from standard deviations from a linear least-squares analysis.

[c]Reference 13.

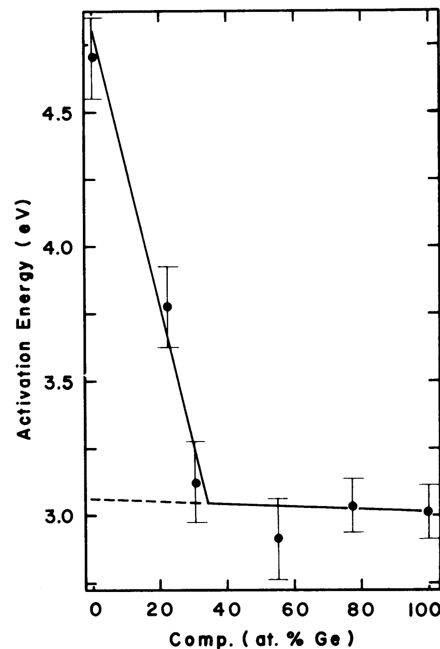

FIG. 3. Compositional dependence of the activation energy for ^{71}Ge diffusion in SiGe alloys.

A reasonable estimate for E_S in dilute alloys can be made using Friedel's[19] solution for the strain-energy contribution to the heat of solution of a wrong-sized impurity atom. For an extended defect this strain energy is approximately given by

$$E_S = \frac{6\pi(r_s - r_s')^2 r_s'}{(1+\alpha)\chi'} , \tag{4}$$

where

$$\alpha = \frac{(1+p)\chi r_s'}{2(1-2p)\chi' r_s} . \tag{5}$$

The covalent radius r_s, the compressibility[20] χ, and Poisson's ratio[21] p are for silicon; the primed quantities are for germanium. In the case of impurity diffusion via monovacancies, Eq. (4) should be divided by the coordination number (4) appropriate to the diamond structure. For higher-concentration alloys containing solute of c at.%, solute-solute interactions modify Eq. (4) to give

$$E_S(c) = \frac{6\pi(r_s - r_s')^2 \bar{r}_s}{(1+\alpha)\chi'} \left(1 - 2\frac{\chi'}{\chi} c\right) , \tag{6}$$

where $\bar{r}_s$ is the average covalent radius. Numerically, Eq. (4) gives $E_S \leq 0.013$ eV for the difference between ^{71}Ge diffusion in nearly pure silicon and silicon self-diffusion. Similarly, a small magnitude is given for the coefficient of c in Eq. (6) since the covalent radii and compressibilities of germanium and silicon do not differ appreciably.

The small "size effect" found for germanium diffusion in SiGe alloys predicts that ^{71}Ge will diffuse in like manner to silicon at the silicon-rich end of alloy composition. If the vacancy-related mechanism associated with germanium self-diffusion were valid in silicon, we would expect a nearly linear dependence of the ^{71}Ge activation energy as a function of composition in close agreement with the dashed line shown in Fig. 3. The strain-energy effects are expected to be even smaller for the germanium-rich end of the alloy, where silicon atoms act as impurities and we observe their influence on germanium self-diffusion. In view of our calculation for impurity diffusion and since silicon atoms do not have to be in close proximity to the defect associated with germanium diffusion toward the germanium-rich end of composition, the strain-energy effects for that composition region should be quite small.

An activation energy of ~ 3 eV for ^{71}Ge diffusion over a large composition region extending from pure germanium seems reasonable if the defect related to the diffusion remains the same. The nature of the defect may change, however, as evidenced by the observed rise in activation energy at the silicon end of composition in Fig. 3.

A change-over in entropy behavior may also be noted in the 70/30 alloy region in Fig. 4, where the log of the pre-exponential factor is plotted as a function of alloy composition. Although the experimental error is generally quite large for this quantity, the behavior noted implies that the entropy associated with the defect first decreases and then rises as the alloy becomes more silicon-like in composition. The initial decrease in D_0 as the alloy moves from pure germanium and towards alloys with higher melting points is similar to the entropy behavior predicted by the Zener[22] theory as applied to diffusion by monovacancies.[23] Above 70-at.% silicon, the entropy rises rapidly, again indicating a change-over in the nature of the defect associated with the diffusion.

This change-over in diffusion mechanism in the SiGe alloy is comparable to that predicted by Seeger and Chik[1] and Seeger[3] for self-diffusion in silicon. They predict that diffusion will change over from a monovacancy to an extended interstitialcy mechanism in silicon between 800–900 °C. They argue that extended defects are preferred at high temperatures due to their large entropy of formation which gives them a lower free energy of formation. Their suggestion would lead to larger activation energies and entropies of diffusion with increasing temperature over the region where the extended defects prevail. This prediction is in accord with the observed rise in both diffusion parameters seen in Figs. 3 and 4 for the silicon-rich end of alloy composition.

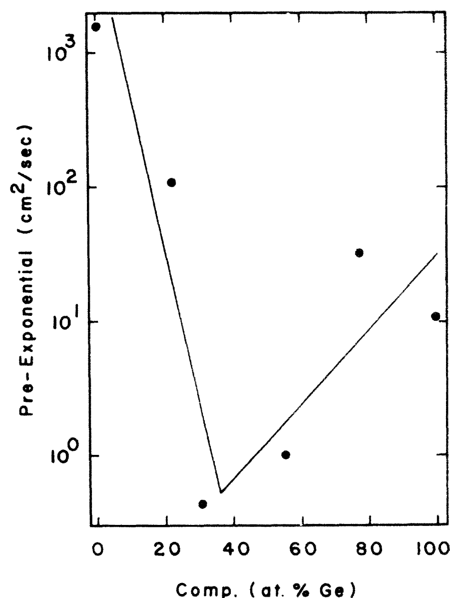

FIG. 4. Compositional dependence of the pre-exponential for ^{71}Ge diffusion in SiGe alloys. Solid lines only illustrate trends.

V. CONCLUSION

It has recently been observed that self-diffusion in silicon may be considerably different than in germanium despite the known similarity of these elements with respect to many chemical and physical properties. Properties which could affect mass transport in these materials are the much higher melting point of silicon (1410 °C) compared to germanium (938 °C) and the slightly larger ratio of interatomic distance to atom radius for Si.[1,3] One way of varying these factors simultaneously is to study the diffusion of ^{71}Ge tracer in SiGe alloys of varying composition.

As expected from calculated, small, impurity-size effects, the tracer ^{71}Ge is found to display diffusion behavior similar to previously observed self-diffusion at both ends of alloy composition. The diffusion at the germanium-rich end is in accord with the monovacancy mechanism up to approximately 70-at.% silicon. For the ^{71}Ge diffusion in alloys containing more silicon, the mechanism may change over in accord with the extended-defect mechanism suggested by Seeger and Chik[1] for higher-temperature silicon self-diffusion. It is likely from our data that the size and configuration of this defect increases with silicon concentration.

Despite the small number of compositions which were feasible to prepare and study for this system, an abrupt difference was noted between diffusion in germanium-rich and silicon-rich SiGe alloys. More study is certainly necessary, however, to delineate on an atomic scale the nature of the defect associated with silicon self-diffusion and slow impurity diffusion in silicon-based alloys.

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