

Time-of-Flight Secondary Mass Spectrometry Analysis of Isotope Composition for Measurement of Self-Diffusion Coefficient

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The analysis of isotope ratio in a material consisting of a single element was developed as a fundamental technique to determine a self-diffusion coefficient in a melt based on time-of-flight secondary mass spectrometry (TOF-SIMS). The self-diffusion coefficient for a pure Ge melt was measured using the stable isotope ⁷³Ge as a tracer under a homogeneous static magnetic field in order to evaluate the influence of thermal convection upon isotope distribution. The results obtained showed that the magnetohydrodynamic effect in the melt obviously damped the convection, but it was not strong enough for the self-diffusion measurement. [DOI: 10.1143/JJAP.45.5274]

KEYWORDS: time-of-flight secondary mass spectrometry, isotope, self-diffusion coefficient, germanium, convection, static magnetic field

A semiconductor melt is attractive from the viewpoint of both fundamental physics and applied physics. Itami *et al.* pointed out the possibility that covalent bonds are still present in the melt and have an effect on the physicochemical properties,¹⁾ although these covalent bonds are usually broken on melting. In order to investigate the complex structure of the melt, the self-diffusion coefficient in a high-purity melt is usually determined with a stable isotope as a tracer. However, in spite of the importance of diffusion, the diffusion coefficient in a melt obtained in a terrestrial environment is thought to be less accurate than one obtained in microgravity because of the disturbance by convection in the melt. Some self-diffusion experiments in metals and semiconductors were performed in space to confirm the difference in diffusion coefficients obtained in microgravity from those obtained in the terrestrial environment.^{1–4)}

A dynamic secondary mass spectrometry (dynamic-SIMS) analysis has been used to determine isotope ratios in specimens obtained from the experiments in space, because this analysis yields quantitative information about the material. However, the primary ion beam sputters the sample surface deeply, and thus it is difficult to simultaneously count the secondary ions with different mass numbers in the analysis. In contrast, time-of-flight secondary mass spectrometry (TOF-SIMS) is capable of analyzing all the elements with isotopes on the surface simultaneously due to its shallow detection depth, and it has good sensitivity for a small amount of the elements on the sample surface with high resolution in mass number, although it is difficult to deduce the absolute quantities from its output alone compared with dynamic-SIMS. Isotope separation, purification, and crystal growth are work of the greatest difficulty to accomplish,^{5,6)} and a specimen consisting of an enriched isotope should be nondestructively analyzed to pick up as much information as possible after completion of the microgravity experiment. In this research, the secondary ions from more than one Ge stable isotope on the specimen's surface were counted by TOF-SIMS and then the isotope ratio was determined from the count considering the binding fraction of each isotope to hydrogen atoms.

Applying a static magnetic field to the metallic melt may be a good method for accurate measurement of diffusion coefficients to substitute for microgravity. When a uniform static magnetic field is applied to an electrically conducting fluid, fluid motion is reduced because of the interaction between the imposed magnetic field and the electric current induced by the field.^{7,8)} The damping effect of Lorentz force on convection is evident when the vector of the magnetic flux density is perpendicular to gravity.⁹⁾ Mathiak *et al.*¹⁰⁾ and Miyake *et al.*¹¹⁾ have performed interdiffusion experiments for an In–Sn melt with the same composition as that used in Froberg's experiment in space²⁾ by applying a static magnetic field. Since the inter-diffusion coefficient obtained by Miyake agreed well with that from the experiment in space, it was expected that convection in other metallic melts could be damped as in a diffusion-dominated condition by the same technique. In this study purified Ge was selected as a target material for the self-diffusion coefficient measurement for the following reasons: 1) interest in its complex liquid structure, 2) relative ease of running the diffusion experiment because of the low melting point, and 3) the availability of excellent reference data.¹⁾

A capillary method¹²⁾ was adopted for the diffusion process because of its simple specimen structure. A cylindrical diffusion couple 2 mm in diameter was made from two Ge rods of 5 N purity: 95 at. % ⁷³Ge of length 1 mm, and naturally available Ge (^{nat}Ge) of length 14 mm. Each Ge rod was made by casting in a graphite mold due to its poor machinability. The diffusion couple was placed in a boron nitride crucible 4 mm in diameter and 40 mm long, because the material is chemically stable in the Ge melt and electrically insulating over 1000 K. The 95 at. % ⁷³Ge rod was set in the bottom of the crucible. The open end of the crucible was sealed with a lid and graphite paste to prevent Marangoni convection. The experimental setup for the diffusion was described in a previous paper from this laboratory.¹¹⁾ The output of the heating lamps in the furnace was controlled by a proportional-integral-differential temperature control system with a precision of ±0.1 K using a Pt/Pt–Rh type thermocouple, the tip of which was glued to the top of the lid. The driving force of thermal convection was strongly suppressed because of temperature inhomoge-

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neity of less than 1 K on the crucible surface. The crucible was heated at a rate of 50 K/s, and the diffusion process was subsequently carried out for a holding time of 180 s at 1273 K. The melt specimen was quenched to room temperature by a gas flow of dry nitrogen after the diffusion. The solidified Ge rods were then cut into two semi-cylinders along the specimen's z -axis direction with a diamond wire saw after quenching, and the cut surface was subsequently polished and etched by hydrofluoric acid to remove the mechanically damaged layer. The same heat treatment was applied to several of the specimens under 0 T and under a homogeneous static magnetic flux density of 1 T in a horizontal direction. The magnetic flux density was produced by a superconducting magnet, and the furnace was mounted at the center of the bore.¹¹⁾ To avoid deformation of filaments in the heating lamps by Lorentz forces, the maximum magnetic flux density was limited to 1 T at a diffusion temperature of 1273 K.

Composition profiles of stable isotopes of Ge, ⁷⁰Ge, ⁷²Ge, ⁷³Ge, ⁷⁴Ge, and ⁷⁶Ge, on the specimen surface were measured along the specimen's z -axis using a TOF-SIMS (ULVAC-PHI: PHI TRIFT III). The measurement conditions were as follows: the ionization source, ¹⁹⁷Au⁺; the ion accelerating voltage, 22 keV; the current, 2 nA; the area analyzed, 100 μm²; and the integrating time, 180 s. Ge atoms on the specimen surface are usually bound to hydrogen atoms after etching. The composition distribution of the isotopes was determined by solving the following simultaneous eqs. (1)–(3) based on the assumption that a binding fraction of the atoms of each Ge isotope to hydrogen atoms, α , is constant regardless of the atomic mass of the isotope:

$$C_m = k\{(1 - \alpha)X_m + \alpha X_{m-1}\} \quad \text{for } 70 \leq m \leq 76, \quad (1)$$

$$X_{69} = X_{71} = X_{75} = 0, \quad (2)$$

$$X_{70} + X_{72} + X_{73} + X_{74} + X_{76} = 1, \quad (3)$$

where m is the mass number; C_m , the count of the secondary ions of mass m ; X_m , the composition of ^{m} Ge; and k , the constant coefficient depending on the surface conditions of the specimen and on the measurement setup. A cubic equation with α was derived from eqs. (1)–(3) for $72 \leq m \leq 76$ taking into account the large ratio of ⁷³Ge in the specimen, and subsequently the other variables k and X_m were calculated by substituting α into the above equations. The purified ^{nat}Ge and ⁷³Ge rods were analyzed using dynamic-SIMS (ATOMIKA: 6500) and TOF-SIMS prior to the diffusion experiment. Table I shows ratios of the stable isotopes on the rod surfaces, and the fact that the values obtained by TOF-SIMS agreed well with those from dynamic-SIMS within an accuracy of 1 at. % shows the usefulness of the quantitative analysis with TOF-SIMS. The

calculated α s of each measurement point were in the range of 20 to 30 at. %.

Mass transport in the isotope melt without convection in a one-dimensional system is described by the following equation:

$$\partial C(z, t) / \partial t = D \partial^2 C(z, t) / \partial z^2, \quad (4)$$

where $C(z, t)$ is the isotope composition in the melt; t , the time; D , the self-diffusion coefficient of the isotope in the melt; and z , the position along the specimen axis. For the capillary method, $C(z, t)$ is obtained using a Fourier series as in the following equation by solving eq. (4) with the boundary condition $(\partial C / \partial z)_{z=0} = (\partial C / \partial z)_{z=L_1+L_2} = 0$ and with the initial conditions $C(z, 0) = C_1$ for $0 \leq z < L_1$, $C(L_1, 0) = (C_1 + C_2) / 2$, and $C(z, 0) = C_2$ for $L_1 < z \leq L_1 + L_2$:

$$C(z, t) = C_1 + (C_2 - C_1) \left[\frac{L_1}{L_1 + L_2} + \frac{2}{\pi} \sum_{n=1}^{\infty} \frac{1}{n} \times \exp \left\{ - \frac{n^2 \pi^2 D t}{(L_1 + L_2)^2} \right\} \sin \frac{n \pi L_1}{L_1 + L_2} \cos \frac{n \pi z}{L_1 + L_2} \right], \quad (5)$$

where L_1 and L_2 are the initial lengths of the ⁷³Ge and ^{nat}Ge melts, respectively. The self-diffusion coefficient of ⁷³Ge for the measured composition profile along the specimen axis was determined with eq. (5) by a nonlinear least squares curve-fitting method based on the Levenberg–Marquardt algorithm.¹³⁾ The numerical value of eq. (5) was approximated by summation with a maximum number of terms, namely $n = 100$. The measurement position on the specimen axis was calibrated by considering the volume expansion due to a phase change at the melting point and the temperature change¹⁴⁾ during the quench.

Figure 1 shows the isotope profiles along the specimen axes experimentally obtained at 1273 K under 0 and 1 T, respectively. The profiles in Fig. 1(b) show that Lorentz force induced by the magnetic field obviously damped convection in the melt, and therefore the composition gradient in the vicinity of the junction between the ^{nat}Ge and the enriched isotope under 1 T was steeper than that under 0 T. The profile obtained for ⁷³Ge under 1 T from 0.5 to 5.5 mm was roughly same as the computed profile with a self-diffusion coefficient of 2.5×10^{-8} m²/s, which was about three times larger than that of ⁷⁶Ge determined in the microgravity experiment,¹⁾ 7.8×10^{-9} m²/s at 1243 K and 8.8×10^{-9} m²/s at 1313 K. In addition there was a large discrepancy between the measured profile and the computed one over 5.5 mm, and thus isotope transport in the melt was not dominated by diffusion due to residual convection even under 1 T.

The influence of thermal convection on the composition profile was evaluated using nondimensional numbers, the Grashof number $Gr = \beta_T g_0 \Delta T r^3 / \nu^2$ and the Hartmann number $Ha = Br(\sigma_e / \rho \nu)^{1/2}$, where β_T is the thermal volume expansion coefficient of melt; g_0 , the gravitational acceleration; ΔT , the temperature difference between the maximum and minimum values; r , the radius of the melt; ν , the kinematic viscosity of the melt; B , the magnetic flux density; σ_e , the electrical conductivity of the melt; and ρ , the density of melt. The two nondimensional numbers correspond to the driving force of thermal convection and the damping force

Table I. Ratio of stable isotopes in purified ^{nat}Ge and ⁷³Ge rods.

	Purified ^{nat} Ge (at. %)		Purified ⁷³ Ge (at. %)	
	ref. 15	TOF-SIMS	Dynamic-SIMS	TOF-SIMS
⁷⁰ Ge	20.84	20.8	0.3	0.3
⁷² Ge	27.54	28.1	2.1	2.1
⁷³ Ge	7.73	7.8	95.0	94.5
⁷⁴ Ge	36.28	35.2	2.5	2.8
⁷⁶ Ge	7.61	8.0	0.1	0.3

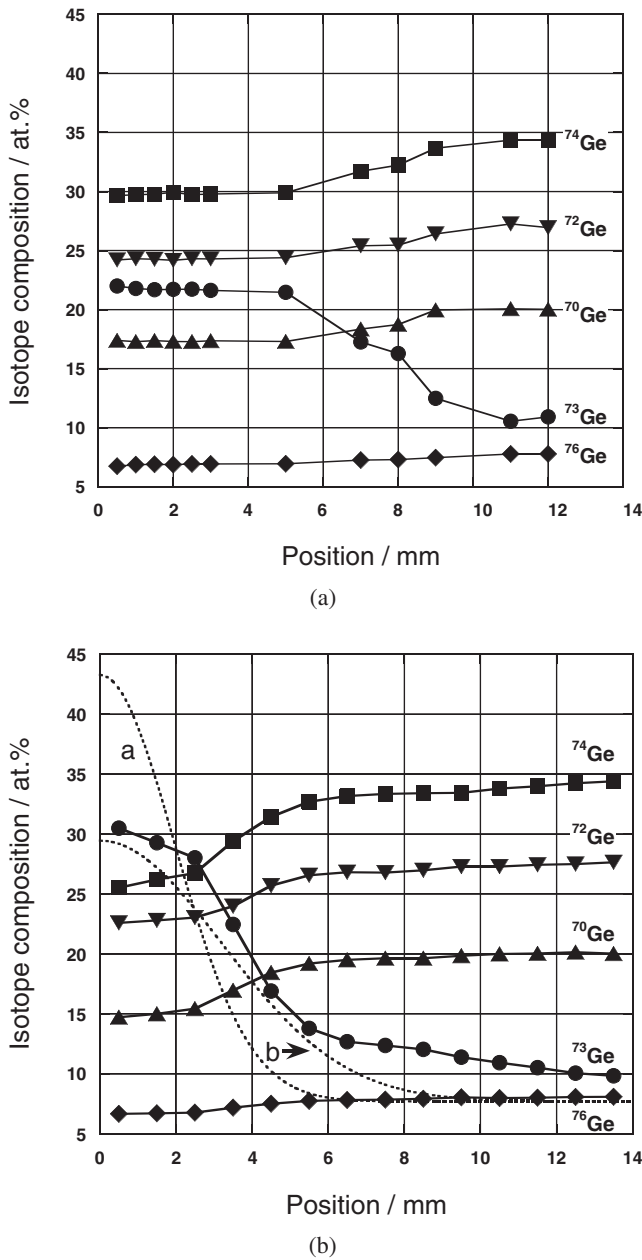


Fig. 1. Composition profile of stable isotopes in the solidified diffusion couple along the specimen axis at 1273 K: (a) under 0 T, and (b) under 1 T. The dashed lines a and b in (b) are values computed by substituting self-diffusion coefficients of 8.8×10^{-9} and 2.5×10^{-8} m²/s into eq. (5).

of a magnetic field on the convection, respectively. The Reynolds number Re is roughly estimated as Gr/Ha^2 for low Gr .¹⁶⁾ Gr and Ha for the pure Ge melt at the melting point under 1 T are calculated as 64 and 30, respectively, with the assumptions that $\beta_T = 1.1 \times 10^{-4}$ K⁻¹, $\Delta T = 1$ K, $r = 10^{-3}$ m, $\nu = 1.3 \times 10^{-7}$ m²/s, $B = 1$ T, $\sigma_e = 6.7 \times 10^5$ Ω^{-1} m⁻¹, and $\rho = 5.6 \times 10^3$ kg/m³.¹⁴⁾ On the other hand, Gr and Ha for the pure In melt with 0.5 mm radius are calculated as 1.6 and 21 respectively in a manner similar to

the Ge melt. Since Re 's for Ge and In are obtained as 0.07 and 0.004 respectively based on the above values, the influence of convection in the Ge melt upon the composition distribution is obviously larger than that in the In melt. In the case of the experiment with 20 at. % Sn-In,¹¹⁾ the alloy with higher density was set in the lower half of the diffusion couple in order to depress an influence of convection on mass transport. The steep positive concentration gradient in the vicinity of the melt junction of the diffusion couple affects the convection as a stagnant layer, and thus it weakens the driving force for convection. The concentration gradient decreases to zero with time, and the maximum flow velocity increases as the width of the stagnant layer decreases. Finally, thermal convection becomes a dominant flow as a steady state condition. The computed results for this prediction will appear elsewhere.¹⁷⁾ Since the composition gradient for isotopes in a pure melt has no effect on convection, a stronger magnet field is required to damp thermal convection for the measurement of purified Ge in the terrestrial condition.

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- 1) T. Itami, M. Kaneko, M. Uchida, S. Yoda and T. Masaki: J. Jpn. Soc. Microgravity Appl. **14** (1997) 323 [in Japanese].
- 2) G. Frohberg, K. H. Kraatz and H. Weber: Proc. 6th European Symp. Material Sciences under Microgravity Conditions, Bordeaux, 1986, ESA SP-256, 1987, p. 585.
- 3) T. Itami, H. Aoki, M. Kaneko, M. Uchida, A. Sisa, S. Amano, O. Odawara, T. Masaki, H. Oda, T. Ooida and S. Yoda: J. Jpn. Soc. Microgravity Appl. **15** (1998) 225.
- 4) T. Itami *et al.*: J. Jpn. Soc. Microgravity Appl. **16** (1999) 198.
- 5) K. Itoh, W. L. Hansen, E. E. Haller, J. W. Farmer, V. I. Ozogin, A. Rudnev and A. Tikhomirov: J. Mater. Res. **8** (1993) 1341.
- 6) K. M. Itoh, J. Kato, F. Uemura, A. K. Kaliteyevskii, O. N. Godisov, G. G. Devyatych, A. D. Bulanov, A. V. Gusev, I. D. Kovalev, P. G. Sennikov, H.-J. Pohl, N. V. Abrosimov and H. Riemann: Jpn. J. Appl. Phys. **42** (2003) 6248.
- 7) D. T. J. Hurle, E. Jakeman and C. P. Johnson: J. Fluid Mech. **64** (1974) 565.
- 8) R. W. Series and D. T. J. Hurle: J. Cryst. Growth **113** (1991) 305.
- 9) Y. Inatomi, T. Miyake and K. Kuribayashi: J. Jpn. Soc. Microgravity Appl. **20** (2003) 160 [in Japanese].
- 10) G. Mathiak and G. Frohberg: Cryst. Res. Technol. **34** (1999) 181.
- 11) T. Miyake, Y. Inatomi and K. Kuribayashi: Jpn. J. Appl. Phys. **41** (2002) L811.
- 12) T. S. Lakshmanan and D. A. Rigney: Mater. Sci. Eng. **12** (1973) 285.
- 13) S. A. Teukolsky, W. H. Press and W. T. Vetterling: *Numerical Recipes in C: The Art of Scientific Computing* (Cambridge Univ. Press, New York, 1992) 2nd ed., Chap. 15, p. 683.
- 14) *Smithells Metals Reference Book*, ed. E. A. Brandes and G. B. Brook (Butterworth-Heinemann, Oxford, 1992) 7th ed., Chap. 14.
- 15) C. M. Lederer and V. S. Shirley: *Table of Isotope* (Wiley, New York, 1978) 7th ed.
- 16) Y. Inatomi, A. Kato, K. Horiuchi, A. Takada and K. Kuribayashi: Mater. Trans., JIM **41** (2000) 1026.
- 17) Y. Inatomi: to be published in Int. J. Heat Mass Transfer.