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SECONDARY ION MASS SPECTROMETRY STUDIES OF  
ISOTOPE EFFECT IN DIFFUSION

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Abstract

The mass effect of diffusion is of interest in connection with interactions between defects and impurities and with the mechanisms of atomic displacements in the condensed states. The delineation entails the precise measurement of the isotope ratio as function of tracer concentration, varying within several orders of magnitude along the diffusion profile. The measurement by SIMS (secondary ion mass spectrometry), using stable isotopes, has proved to possess advantages compared to familiar techniques with radiotracers. However, the aims require the utmost counting economy and optimal precision available in SIMS, including the control of the mass fractionation and of some features peculiar to cyclic profiling. Very good results have been obtained for the isotope effect at relatively deep profiling, where step scan analysis can be effected. For more shallow profiles, requiring head-on sputtering, more serious artifacts are encountered and the error margins have hitherto been relatively high. The paper discusses salient experimental points of the determination by SIMS of the isotope effect at different diffusion geometry, and briefly reviews the hitherto obtained results.

**KEY WORDS:** Secondary ion mass spectrometry; depth profiling by secondary ion mass spectrometry; diffusion; isotope effect; mass fractionation; stable tracer analysis.

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Introduction

The technique of secondary ion mass spectrometry has for more than a decade been recognized as an attractive tool for studying atomic transport phenomena, and particularly tracer diffusion /19/. The attraction is partly based on the avoidance of radioactive tracers and on the wide choice of available stable isotopes. Principally, however, SIMS is found suitable for diffusion study because the technique combines a quantitative detection sensitivity for trace concentrations with an excellent in-depth resolution in analysis.

The sensitivity of SIMS has been adequate for measuring diffusion coefficients in systems with very low tracer solubility, i.e., to obtain accurate determinations of D at concentrations between ppm and ppb /9, 16/. The depth resolution of SIMS has made it possible to measure as low diffusion coefficients as  $10^{-19} \text{ cm}^2/\text{s}$  and to span, by a single technique for a given tracer-matrix system, a dynamic range of some 10 orders of magnitude in D /4, 5, 10, 17, 35/. Provided the detectability of the tracer (i.e., in SIMS, its ionizability) is relatively high, and the specimen surface sufficiently smooth, great accuracy of measurement is available (see e.g. fig.1).

A particularly exacting experimental task in the study of atom transport is the measurement of the isotope effect of diffusion, entailing the relative differences in the diffusivities of two or several isotopes of a given element. Such difference is never greater than ca 5%; in many cases, differences  $\Delta D (= D_2 - D_1$ ; the subscripts referring to two isotopes of masses  $M_1$  and  $M_2$ ) of the order of 0.02 % are of interest to determine quantitatively. This requires the measurement of isotope ratios ( $c_1/c_2$ ) along a diffusion profile with a dynamic range of at least two orders of magnitude in tracer concentration  $c$ , with an accuracy of the order of 0.5 % or better. Although difficulties and special artifacts have had to be recognized in connection with these requirements /26/, it has in recent years proved possible to perform reliable measurements by SIMS of the isotope effect in both solid state /13, 21, 33, 35/ and liquid state /8, 34/ diffusion.

This paper is intended to survey recent SIMS work on the isotope effect of diffusion, and to discuss some topical experimental points.

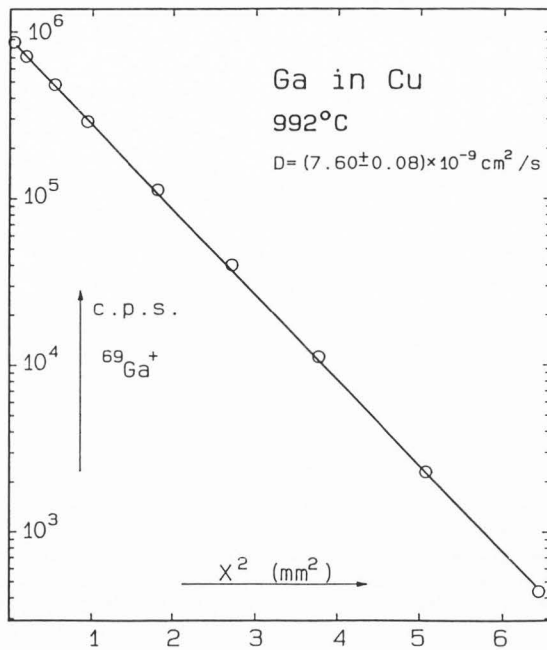


Fig. 1. Diffusion penetration of  $^{69}\text{Ga}$  in Cu single crystal. Thin film geometry. The slope is obtained with an accuracy better than 1%; additional error in  $D$  is due to measurement of  $x$ -coordinate.

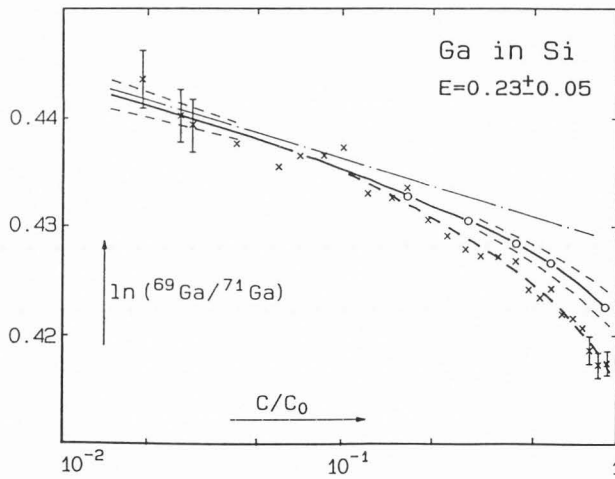


Fig. 2. Logarithmic plot of the  $^{69,71}\text{Ga}$  isotope ratio as function of Ga concentration after diffusion into single-crystal Si from saturated Ga vapor /21/. The raw data represented by heavily dashed curve. Staples: counting error margins. The whole-drawn curve obtained by correction for counting deadtime (see eqs. 8a,b). Light dashed lines are margins of error, combined from count statistics and deadtime uncertainty. The isotope effect  $E$  is derived via eq. 3 from the gradient of the broken line, corresponding to the whole-drawn curve after correction for the factor  $A$  (see fig. 3; surface-saturation, constant  $c_0$  diffusion geometry).

Ideal tracer diffusion profiles  
Isotope fractionation effects

"Gaussian" type of tracer penetration profile is expected as solution of Fick's 2nd law /1/ when the tracer isotope has been applied on a flat specimen surface as a thin film, which yields

$$c/c_0 = \exp(-x^2/4Dt) \quad (1)$$

where  $c_0$  is the surface concentration of tracer,  $x$  is the coordinate perpendicular to the surface,  $D$  the diffusion coefficient (assumed independent of concentration  $c$ ), and  $t$  the anneal time. The diffusivity is thus obtained, in the thin-film geometry, from the gradient of the  $\ln c$  vs.  $x^2$  plot (see fig. 1).

"Error-function" type profile is obtained, on the other hand, if the surface concentration is

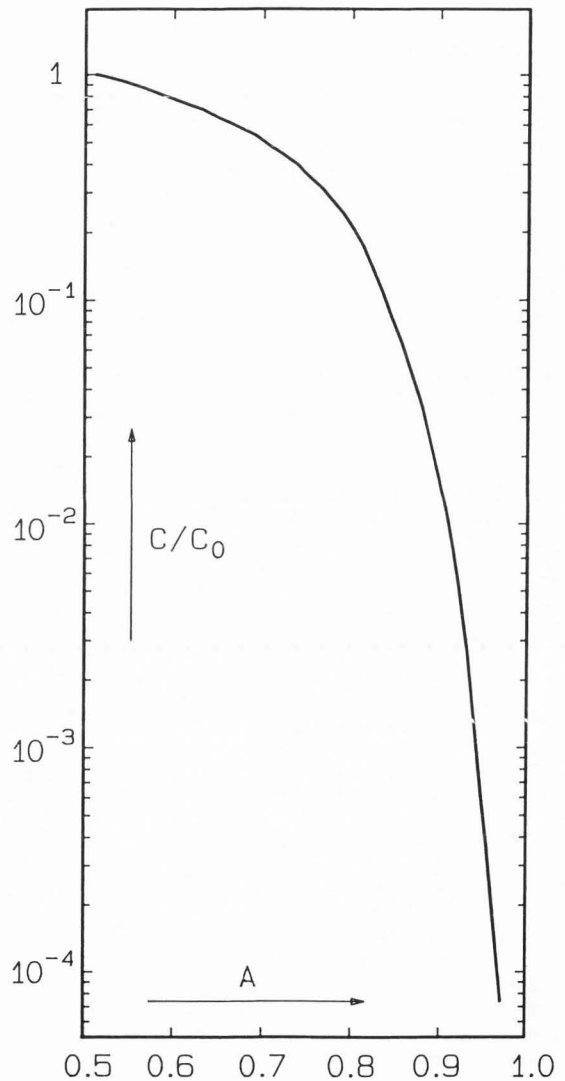


Fig. 3. Calculated correction factor for diffusion couple or surface-saturation type diffusion geometry /26/. At low values of  $c/c_0$ ,  $A$  approaches unity, and the gradient in a semi-logarithmic plot of  $c_2/c_1$  vs.  $c$  becomes independent of geometry.

constant ("diffusion couple" or "surface saturation" geometry) which yields

$$c/c_0 = \text{erfc}(x/2\sqrt{Dt}) \quad (2)$$

The diffusion coefficient can here be obtained from the slope of the  $c$  plot in a probability diagram.

For the mass effect of diffusion one may deduce /1, 36, 37/

$$\Delta D/D = A \cdot d \ln(c_2/c_1) / d \ln c \quad (3)$$

where  $D$  is the mean diffusion coefficient of the isotopes 1 and 2,  $\Delta D = D_1 - D_2$ , and  $c$  is the (total) tracer concentration. The factor  $A$  is unity for the thin film geometry, while for the error-function type profile  $A$  has been shown to vary from 0.5 at  $c=c_0$  to unity at  $c \rightarrow 0$  (U. Södervall, diploma work, CTH Gothenburg, 1979; to be published).

The definition of the isotope effect of diffusion may be written as

$$E = -2 \frac{\Delta D/D}{\Delta M/M} \quad (4)$$

where  $\Delta M = M_2 - M_1$  and  $M$  is the mean isotope mass of the tracer. The entity  $E$  can thus, via eq.3, be derived from the slope of the log-log diagram of  $c_2/c_1$  versus  $c$ , for the gaussian type profile directly, for the error-function geometry after correction with the factor  $A$  (see figs. 2,3).

Diffusion theory /1, 24/ expects

$$E = f \Delta K \quad (5)$$

where  $f$  is the Bardeen-Herring correlation factor, expressing the departure of tracer diffusion from ideal random walk and relating to defect-impurity binding;  $\Delta K$  is the energy sharing factor, expressing the diffusing atom's own share of the total kinetic energy at the saddle-point of displacement. Both factors (each between unity and zero) are of considerable interest in the study of diffusion mechanisms and point defects. For a discussion of their physical significance one may refer to standard literature on atomic transport /1, 20, 24/, but a few features may be mentioned here for non-specialist orientation. Thus, for self-diffusion in given lattice geometry the value of  $f$  is uniquely indicative of the diffusion mechanism (e.g., for self-transport via monovacancies in a fcc lattice  $f=0.78$ ; for diffusion by non-dissociative divacancies  $f=0.475$ ). In impurity diffusion  $f$  is given by the relative atomic jump frequencies in the neighborhood of a defect; for the motion of purely interstitial impurity  $f=1$  applies; impurity-defect repulsion yields  $f$  values above that of self-diffusion; strong impurity-defect binding gives low  $f$ . The  $\Delta K$  factor is about 0.8 - 0.9 in the fcc lattice, where a diffusion jump causes only slight relaxation of neighbor atom positions; but in more open lattices lower  $\Delta K$  is found. Simultaneous position adjustments of several atoms are characterized by low  $\Delta K$ ; e.g., for self-diffusion by the two-atom interstitial mechanism one may expect  $\Delta K \leq \frac{1}{2}$ .

Of experimental relevance in all isotope studies by SIMS is the mass fractionation introduced by the analytical technique itself, due to, e.g., the sputtering mechanism and the transmission of the mass spectrometer /30, 31, 36/. The isotopic

fractionation may be expressed by the "isotope factor" defined as

$$\alpha = \Delta \ln(c^*/c')_{1,2} / \Delta \ln M \quad (6a)$$

at constant  $c'$ . Here  $c_{1,2}^*$  are the "apparent" concentrations of the two isotopes as observed experimentally by SIMS. The factor  $\alpha$  is derived when comparing the  $c^*$  values with the "true" isotope concentrations,  $c'$ , say, listed in accepted tables of elemental isotopic abundances (such as /3/). At a given tracer concentration  $c$

$$\alpha_c = \left( \frac{(c_2^*/c_1^*)_c}{(c_2/c_1)^c} - 1 \right) (M/\Delta M) \quad (6b)$$

When the isotope ratio of the penetrating tracer varies with concentration, as in the case of diffusion, a variable factor  $\alpha$  is measured, which is related to both instrumental and diffusive isotope effects. From eq.6b it can be deduced that

$$E = -2A \cdot (d\alpha/d \ln c) \quad (7)$$

provided the instrumental fractionation is independent of tracer concentration. This expression may be used as an alternative to eqs.3 and 4 for the evaluation of  $E$ , viz., from the gradient of the plot of  $\alpha$  versus  $\ln c$  (see fig.4).

#### Experimental Aspects

With respect to the capacity of SIMS for reliable measurements of the isotope effect  $E$ , numerous experimental factors are of special relevance.

At the high concentration end of the tracer profile, account must be taken of:

- a) the limited dynamic range of the collector and amplifier; counting deadtime; b) collector discrimination; c) departure from ideal gaussian diffusion geometry; d) surface chemical ion emis-

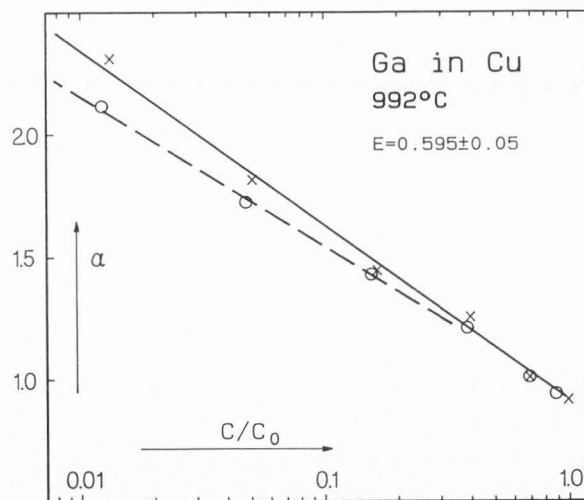


Fig.4. Plot of the (combined diffusive and instrumental) isotope factor  $\alpha$  vs. logarithm of tracer concentration for the Ga isotopes along the diffusion profile of Ga in Cu (ref./37/). Isotope effect  $E$  obtained from slope via eq.7. Solid line, crosses: profiling from low to high  $c$ . Dashed line, rings: from high to low; showing effect of memory.

sion effects; e) uncertainty in assumed  $x=0$  position in the concentration plot.

At the low concentration end of the profile, severe limitations are set by

f) tracer ionizability and isotopic abundance; detection sensitivity; g) spectral background.

When profiling is effected by head-on ion bombardment (sputter front parallel to the diffusion front), additional problems arise from

h) interdependence between available signal intensity and the speed of sputtering; i) time variable memory; crater wall effects; neutral beam contamination; j) mass-number cycling; switching and counting time algorithm; k) (in very shallow profiles) sputter implantation effects; atomic mixing.

Some of these factors (such as d, f, i, k) have been adequately discussed in recent review publications on SIMS /2, 22, 23/, and are here only mentioned in passing. Others are to be discussed below in connection with particular profiling modes for evaluating the isotope effect of diffusion.

Profiling by step-scan.

If the diffusion penetration is relatively deep, and consequently no extreme in-depth resolution is required, it is of multiple advantage to study the diffusion profile by a step-scan along a line in the  $x$  direction. The lateral resolution of a modern commercial SIMS-instrument (such as Cameca IMS-3F, used in most of the examples to follow) is in the order of  $1 \mu\text{m}$ , but reasonable counting speed in isotope measurements usually requires an analyzed area at least  $10 \mu\text{m}$  in diameter. Accordingly the applicability of the step-scan profiling mode is relatively good where the tracer concentration falls by 3 powers of ten from  $c_0$  within ca  $0.2 \text{ mm}$  or more.

The most obvious advantage of the step-scan mode lies in the fact that unlimited time is, in principle, available for the collection of statistically ample ion counts at each point of the profile, including the low concentration end. As implied in the introduction above, typically an accuracy of the order of 0.5 % may be needed for the  $c_2/c_1$  ratio. This entails the accumulation of at least some  $10^5$  counts for each isotope. Considering that the isotope concentration may be in the order of 10 ppm at the "useful end" of the profile, and that a reasonably easily ionized element may, under the prevailing analytical conditions, yield about one count/sec at 0.1 ppm, a counting time of the order of 20 minutes will be required for each isotope at the low concentration end. A complete profile may under such circumstances take more than half a working day.

To reduce the need of time it may be advisable to exploit relatively large analyzed areas at each point, at the cost of in-depth resolution. For this reason the step-scan mode has hitherto been successfully applied only to profiles with relatively deep penetration, i.e. where the tracer concentration decreases to  $0.001 c_0$  at depths of at least ca  $1 \text{ mm}$ .

The need of great dynamic range in  $c$  for the determination of the isotope effect entails that the counting intensity at the high concentration end may be very high. In practice at least ca  $10^4$

counts/sec are needed at the surface; good measurements often require up to  $10^6$  counts/sec for the tracer isotopes. While the total counting time at the near-surface points may now be kept conveniently short, special care must be exercised in relation to the abovementioned experimental factors.

The dynamic range (factor  $a$  above) is mainly restricted by the effective counting lifetime  $\tau_{\text{eff}}$ , a function of the instrumental lifetime  $\tau_0$  and of the size and raster of the primary ion beam. As discussed in ref./26/, if the true secondary ion current is  $I_0$  when the beam is stationary, and  $I_R$  when rastered, and if  $I_0 = g \cdot I_R$ , then the instrument will register only an apparent current  $I'_R$ , such that

$$I'_R = I_R(1 - gI'_R \cdot \tau_0) \quad (8a)$$

Thus the effective lifetime is

$$\tau_{\text{eff}} = g\tau_0 \quad (8b)$$

The factor  $g$  is of the order of 1 to 10 in practical profiling, and  $\tau_{\text{eff}}$  may vary between ca 15 and 250 ns. In many published reports the effect of rastering has been neglected, and hence the effective lifetime is assessed too low. The effect of such underestimate of the determination of  $E$  is illustrated in fig.5.

In successful measurements of  $E$ ,  $\tau_{\text{eff}}$  is frequently checked and a correction routine is incorporated in the evaluation program. However, at intensities above ca  $5 \times 10^6$  counts/sec the uncertainty in lifetime may introduce too great error margins in the measurement of  $c_2/c_1$ .

Because of the factor  $g$ , to increase the raster is obviously not a solution of the lifetime problem when the signal at the specimen surface is found excessive. Alternative recourses would seem to be either to analyze a smaller area via a gating aperture, or to use a higher energy offset for the secondary ions at the high concentration part

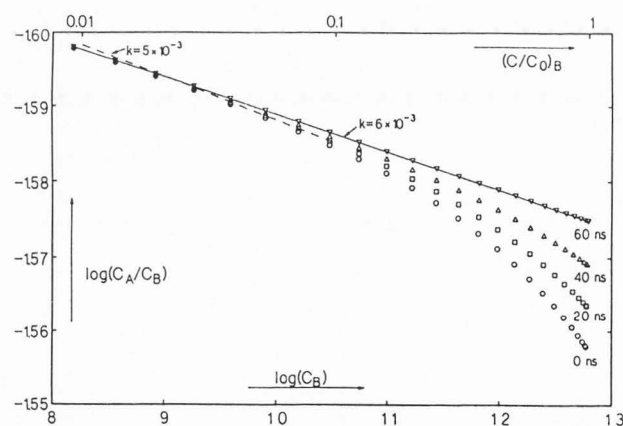


Fig.5. Effect of incorrect assignment of counting lifetime on the apparent gradient in the log-log plot of isotope ratio vs. tracer concentration. Computed for  $(c_A/c_B)_0 = 5$ ,  $\tau_{\text{eff}} = 60 \text{ ns}$ ,  $\tau_0 = 20 \text{ ns}$ . If rastering is disregarded (see eqs. 8a,b), the resultant error in gradient  $k$  is seen to be ca 20 % even at relatively low concentrations /26/.  $g \approx 3$  is found normal in most recent studies of  $E$ .

of the profile. However, the instrumental contribution to  $\alpha$  has often been found to be sensitive both to the kinetic energy of the secondary ions and to their exit angle /7, 31, 36/; hence, such measures would necessitate very careful calibration of instrumental mass fractionation effects.

The fractionation in collector output (point b above) is usually small /36, 39/ and, as other instrumental effects, does not normally affect the measurement of E. However, in aged or intensively used electron multipliers it has been noted that local discrimination in sensitivity may develop on the collector plate, especially at high densities of impinging ion currents. This would make the instrumental mass effect concentration dependent, and affect the apparent  $c_2/c_1$  ratios. Mass effect studies thus require a careful check of the collector function.

Near the surface of the specimen the profile may be affected either by excessive thickness of the tracer coating or by insufficient thickness of the partners in a diffusion couple. This would cause departures from the ideal values of A (see eq.3, fig.3). Such consequences of specimen preparation may necessitate that the profile be pursued to greater depths, where the effect of A becomes negligible.

Similar problems may ensue if the surface of the specimen, on which the step-scan is undertaken, is not in good contact with the specimen holder. A gap at the surface may cause enhanced incidence of primary ions at the edge, which would affect not only the apparent concentrations but also, via shifts in the energy distribution and the exit angle of the ions, the observed  $c_2/c_1$  ratio. The edge effect would also introduce an uncertainty in the position of  $x=0$  in the diffusion column; however, as discussed in ref./26/, although this sensitively influences the measurement of the diffusion coefficient, it does not normally affect the measured isotope effect E.

At the low-signal end of the profile, the problem of insufficient count accumulation may be aggravated by background pick-up (point g above). If the intrinsic spectrum of the matrix contains peaks at the same mass number(s) as the tracer isotope(s), the evaluation may require high resolution or high offset in secondary ion energy. Both measures may jeopardize the minimum required counting rate. The former recourse (high resolution) may also make it difficult to achieve flat-topped peak shape, a practical need for exact isotope work. As an alternative, in a homogeneous matrix one may obtain the background from the signal measured at depths far beyond the effective tracer profile. However, this is efficient only if the background is less than some 20 % of the tracer signal at the low concentration end of the measured profile. A complication occasionally occurs if the background signal varies with depth (inhomogeneous matrix; signal enhancement by presence of tracer; surface memory; etc.). To counter memory effects, stepscan is preferably performed in the direction from the low concentration towards the surface (see fig.4).

The background assumes a particularly important role in the case of self-diffusion measurement. The isotope effect is here determined in using two or several enriched stable isotopes of the matrix. Hence, in the above equations,  $c_1$  and  $c_2$  have to

be replaced by  $(c-c_0)_1$  and  $(c-c_0)_2$ , the subscript zero denoting the respective isotope concentration in the original, non-enriched, matrix. To maintain a dynamic range of 3 powers of ten may require an accuracy in the order of 0.5 % in the difference between two near-equal concentrations. Extreme care is then needed particularly in the determination of the isotope counts from the undiffused matrix. Because of the sensitivity of the factor  $\alpha$  to small instrumental changes, the matrix measurement is to be performed under nearly the same experimental conditions as the step-scan /34/.

#### Head-on profiling.

When the profile is shallow, i.e., when the concentration decreases to  $10^{-3}c_0$  in less than ca 0.2 mm, the step-scan type measurement may be difficult unless a low-angle bevel (see, e.g., ref. /11/) can be made. The alternative is profiling by head-on bombardment of specimen, and successive erosion from  $x=0$  inwards. This procedure involves many more disturbing artifacts than the step-scan mode. The influence, in head-on profiling, of crater wall memory, neutral beam contamination, residues in imperfect vacuum, atomic mixing, etc., has frequently been discussed in literature /2, 22/. In general such effects are countered by good vacuum, high primary ion density, wide rastered area and relatively small analyzed (gated) area.

For the exceptional accuracy needed in the work on isotope effects, counting economy is a primary factor. As mentioned above, an isotope ion current of the order of  $10^6$  counts/sec is desired at the specimen surface. However, it is not practical to sputter very fast; for reasons of counting economy as well as several factors to be mentioned below, one normally wishes to register as many cycles as possible before the profile intensity drops too much. This is certainly a realistic wish in the normal peak switching mode of SIMS, i.e. magnetic, therefore time-consuming, mass cycling. The wide raster may therefore have to be combined with relatively wide analyzed area, even at the expense of depth resolution. At the same time, the requirement of flat crater bottom, throughout the profile, is not to be disregarded; increasingly slanting bottom might induce a variation in the instrumental part of the  $\alpha$  factor. The setting of the primary beam must therefore be a judicious compromise.

The problem becomes easier, and higher sputter rates may be allowed, if peak cycling can be made rapidly, and time between successive effective counting periods can be eliminated. This is achieved in the electrostatic peak switching mode. A recent modification in the Cameca ion probe instrumentation /32/ rapidly cycles a mass range up to  $\pm 6\%$  from a preset mass number; switching time between successive masses is ca 1 ms, and counting time per peak is in the order of 20 ms. This is to be compared with the usual magnetic switching mode, where one cycle of, say, three mass numbers may take something like 10 seconds in switching and peak-finding time only.

The importance of the fast electrostatic switching device in regard of the feasibility of isotope effect measurements is far-reaching. Not least, it allows the accumulation of counts from many successive cycles at the low-intensity end of

the profile, without introducing, in the apparent  $c_2/c_1$  ratio, the artifact of pseudo-simultaneous counting time. This is illustrated in figs. 6, 7 and 8 (from ref./26/). In normal "slow" cycling with time  $T$ , say, per cycle, the isotope 2 is counted at a certain internal time, say  $t_c$  (where  $0 < t_c < T$ ) between two successive count periods of isotope 1. The diffusion profile is curved according to a more or less gaussian behavior. Nevertheless the usual way of comparing  $c_1$  and  $c_2$  is by linearly interpolating between  $A_1$  and  $A_2$  (see fig. 6) and taking the ratio of  $c_2$  to a value of  $c_1$  interpolated to the inner time  $t_c$  within the cycle. Similar interpolation may then be made between  $B_{1+t_c}$  and  $B_{2+t_c}$ , and divided with the counts at  $A_2$ . Such a procedure introduces considerable errors in the log-log plot if the apparent  $c_2/c_1$  vs.  $c_1$ , from the gradient of which the isotope effect  $E$  is obtained. It is seen in fig.7 that the plot remains linear, but the slope receives a decrement, i.e. a negative contribution to  $E$ , without any relevance at all to the true isotope effect. It is seen that the error is aggravated if relatively few cycles are covered within the counted length of the profile. Where the cycle time is as long as  $1/30$  of the total profiling time, the error due to linear interpolation is seen to be as high as ca 40%. If, on the other hand, the cycling is performed at a trebled frequency, the error is decreased to only 5%. Fast electrostatic switching of course reduces the error practically to zero.

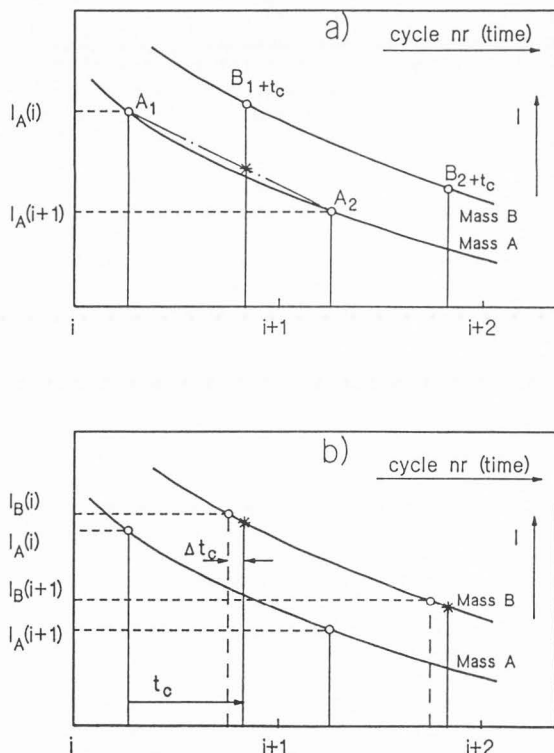


Fig.6. Time scale of cyclical head-on recording of two isotope concentrations along a diffusion profile /26/. a) Interpolation of the recorded ion current of isotope A for comparison with isotope B. b) Faulty assignment of internal time  $t_c$  within a switching cycle.

If the mathematical shape of the diffusion curve can be reasonably predicted, the interpolation error may be reduced even in "slow" cycling. However the wrong assessment of the internal time  $t_c$  in the cycling algorithm may lead to another serious error. Fig.8 illustrates that an error of  $T/10$  in the assessment of the exact time of a counting period introduces an erroneous increment to  $E$  of ca 30% when 45 cycles are counted along the profile, and 15% error when 90 cycles are counted. Again, the use of electrostatic switching, with some  $10^4$  cycles in the profile, would eliminate the error.

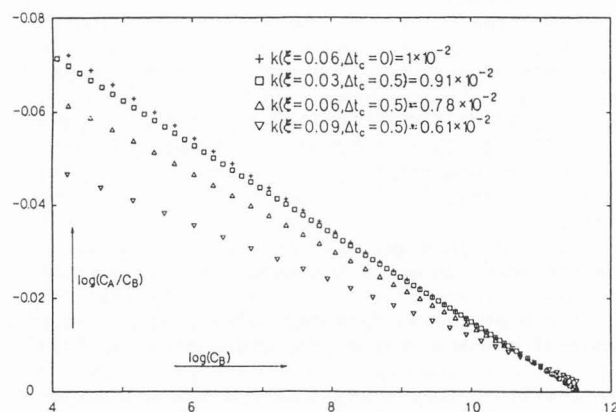


Fig.7. Effect of linear interpolation of successive isotope counts within a switching cycle in head-on profiling /26/. Computed for thin-film geometry; "correct" gradient  $k = 1 \cdot 10^{-2}$ . The three values of  $\xi$  correspond, respectively, to 90, 45, and 30 measuring points along the profile.

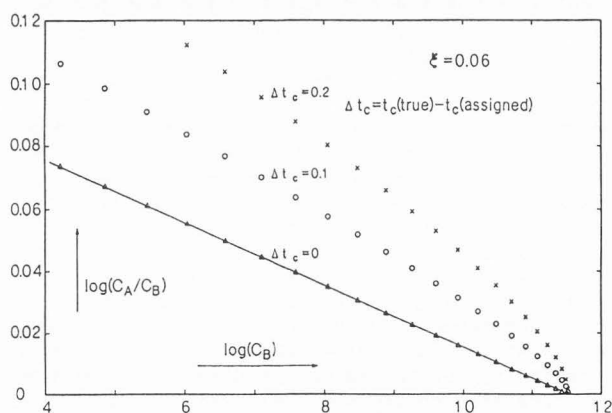


Fig.8. Effect of faulty assignment of internal time within a switching cycle in head-on profiling /26/. Computed for thin-film geometry; 45 measuring points along the profile.

## Isotope Diffusion Study by SIMS

In the few laboratories where a fast electrostatic peak-switching device has been installed, time has not yet permitted any completed application of isotope-effect study in shallow diffusion. For this reason the hitherto obtained data on  $E$  as measured by head-on profiling all have much wider uncertainty margins than those measured by step-scan profiling (see Table 1; also cf. fig.9 with fig.4 or fig.11).

### Results and Discussion

In Table 1 are seen the hitherto reported measurements by SIMS of the isotope effect in diffusion. The listed results represent, with one exception, the only values of  $E$  determined so far in the respective systems, and so cannot be compared with results obtained with radiotracer techniques. The exception is the Cu-Ge system; a determination was made /12/ with the  $^{68,77}\text{Ge}$  isotopes at 1239 K, yielding  $E = 0.45 \pm 0.03$ , which may be seen from Table 1 to be in excellent agreement with the SIMS results.

An early study on Ni in copper /29/, performed with a relatively primitive SIMS facility and yielding  $E \approx 0.78$ , may be regarded mainly as a pioneer effort and is not listed in Table 1. As for the listed results, their margins of error, at least where the work was done by step-scan profiling, are in class with, or better than those of the best radiotracer measurements reported for other systems /6, 12, 14, 15, 24, 25, 27, 28/. The good reproducibility is also seen when comparing the present results on Ge in Cu with work done several years earlier /13/ on the same system, using different SIMS equipment. Another illustration of the principles and accuracy of the present technique may be seen in figs. 10 and 11.

The narrow margins of error obtained for  $E$  by the step-scan technique, as well as the wide range of stable isotopes available for such studies, should be conducive to further precise investiga-

tions of the isotope effect, to be performed on numerous matrix systems and at wide ranges of temperature and pressure. It may also be expected that, once the recently recognized artifacts, as discussed above, are mastered, the accuracy of  $E$  as measured in shallow diffusion layers by head-on profiling will approach that of the step-scan technique, at least for relatively easily ionized tracers. Such studies are of particular interest, e.g. in Si, Ge and the III-V type semiconductors, in view of the complicated and contested defect mechanisms in these systems.

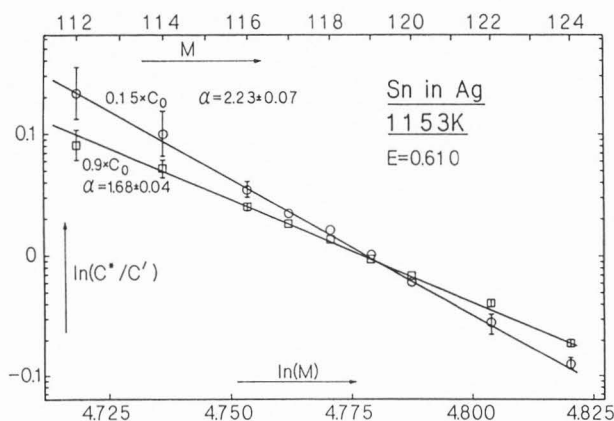


Fig.10. Log-log plot of  $c^*/c'$  (see eq.6:  $c'$  from ref./37/) vs. mass for the Sn isotopes at two concentrations along the diffusion profile of Sn in single-crystal silver /37/. Surface concentration of Sn: ca 0.1 at.%. Staples: standard deviations. Slopes yield  $\alpha$  values for evaluation of  $E$  by eq.7.

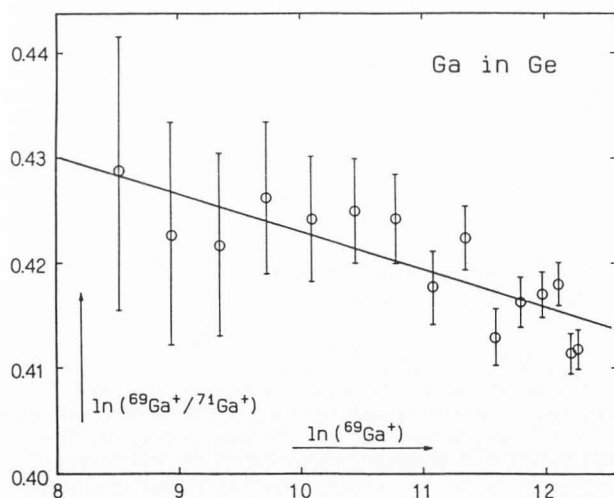


Fig.9. Logarithmic plot of the isotope ratio vs. tracer concentration for Ga diffusing into single-crystal germanium /35/. Thin film geometry, head-on profiling. Gradient yields  $E = 0.24 \pm 0.07$ .

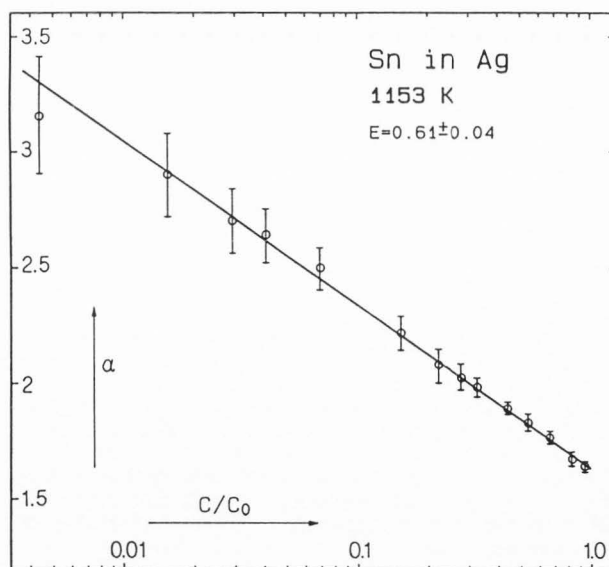


Fig.11. Isotope factor  $\alpha$  vs.  $\log c_{\text{Sn}}$  for Sn diffusion in single-crystal silver. Via eq.7, the gradient yields  $E = 0.61 \pm 0.04$  /37/.



Table 1. SIMS measurements of the isotope effect in tracer diffusion; results. Abbreviations: SC, single crystals; PC, polycrystalline; LM, liquid metal; TF, thin-film geometry; EF, error-function geometry; HDO, head-on profiling; STS; step-scan profiling.

Matrix	Tracer	Temp. (K)	E	Remark	Reference
Si (SC)	Ga	1372	0.31 ± 0.07	EF (from Ga vapor); HDO	/21/
		1473	0.27 ± 0.06		
Si (SC)	Ge	(1370 - 1475)	0.24 ± 0.05	TF; HDO	/33/
		1262	0.28 ± 0.10		
		1323	0.32 ± 0.08		
		1422	0.33 ± 0.14		
		1498	0.23 ± 0.06		
Ge (SC)	Ga	(1260 - 1500)	(0.27 ± 0.03)	TF; HDO	/35/
		1040	0.24 ± 0.05		
Al (PC)	Li	1097	0.25 ± 0.06	EF (diffusion couple); STS	/38/
		728 - 795	0.74 ± 0.10		
W (SC)	Cr	705 - 813	0.57 ± 0.21	EF (diffusion couple); STS	/18/
		2249	0.18 ± 0.02		
Sn (LM)	Sn	543	0.46 ± 0.13	TF; enriched <sup>112,124</sup> Sn; STS	/8, 34/
		601	0.39 ± 0.06		
		661	0.50 ± 0.10		
		764	0.51 ± 0.06		
		1048	0.59 ± 0.14		
		(540 - 1050)	(0.49 ± 0.05)		
Cu (SC)	Ga	1228	0.535 ± 0.03	TF; STS	/37/
		1229	0.555 ± 0.035		
		1230	0.595 ± 0.035		
		1233	0.525 ± 0.03		
		1265	0.575 ± 0.03		
Cu (SC)	Ge	(1228 - 1265)	(0.57 ± 0.015)	TF; STS	/This work/ /13/ /This work/ / " " / / " " /
		1023	0.44 ± 0.04		
		1135	0.465 ± 0.02		
		1198	0.445 ± 0.02		
		1223	0.47 ± 0.03		
Cu	Sn	1273	0.51 ± 0.03	TF; STS	/This work/
		1223	0.48 ± 0.04		
Ag	Ga	1223	0.45 ± 0.04	TF; STS	/This work/
Ag	Sn	1119	0.45 ± 0.02	TF; STS	/37/
		1120	0.46 ± 0.03		
		1130	0.49 ± 0.05		
		1153	0.575 ± 0.02		
		1178	0.635 ± 0.02		

Of great potential value are also the measurements of E in low-temperature atomic transport, such as surface and grain-boundary diffusion /11/.

The work on liquid diffusion, where large amounts of specimen and tracer material are handled, is also conveniently performed by stable isotopes, i.e., by SIMS. The measurements of tin self-diffusion /34, 8/, performed at g(0) conditions in a Spacelab satellite, represent the only precise results hitherto available on the isotope effect of liquid diffusion.

The ever increasing experience in quantitative SIMS and the steadily improving ion probe instrumentation will no doubt result in expanding applications of SIMS to solid and liquid state dif-

fusion, and yield valuable and unique new information on the mechanisms of atomic transport.

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This work has been supported by the Swedish Natural Science Research Council. We are indebted to Prof. Th. Hehenkamp (Göttingen), Drs. W. Gust and U. Roll (Stuttgart) and Dr. V. Schlett (Bremen) for valuable discussions, specimen preparation, and part of the experimental work in diffusion anneals. Mr. E.U. Engström has contributed to the experimental work on the intrinsic isotope fractionation effect of SIMS.

## Isotope Diffusion Study by SIMS

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may also be due to differences between tracer and matrix atoms in respect of binding and/or mass. Such an effect should, however, only be noted in the first atomic layers at the surface and, anyway, recent theory /P. Sigmund, Nucl. Instr. and Meth. B18, 375 (1987)/ expects the isotope effect of sputtering (as distinct from that of ionization) to be quite small. As regards ion beam mixing, it does affect very shallow diffusion profiles, but normally only by a certain loss of depth resolution, rather than an error in the determined diffusion coefficient. In principle the extent of mixing may be expected to be, to some extent, dependent on isotope mass; but I doubt that this would be very relevant to diffusion measurements, unless one has the ambition to utilize concentration profiles less than, say, ca 50 nm in depth.

#### Discussion with Reviewers

R. Gijbels: Could the author comment on the availability of data on diffusion (self-diffusion) coefficients and isotope effects in insulating materials, e.g. glasses or ceramics, obtained by SIMS or other methods?

Authors: Such material is regularly and thoroughly compiled in the periodical Diffusion and Defect Data - Solid State Data, ISSN 0377-6883, hitherto published by Trans Tech Publications, Aedermannsdorf (CH). As of 1988, the publisher will be Sci-Tech Publications, Vaduz, Liechtenstein. Reliable data on the isotope effect of diffusion in insulators are, however, as yet quite few.

J.D. Brown: In head-on sputtering, selective sputtering and ion beam mixing may limit the accuracy in determining diffusion coefficients. Do you consider that an isotope effect exists in these phenomena and is there any published work which demonstrates that it does exist?

Authors: To my knowledge, apart from considerations of isotope effects in the sputter yield (see, e.g., refs. /7/ and /36/ above), no such work relevant to the phenomena you mention has been published. In a chemically homogeneous matrix, selective sputtering is usually given by crystallographic effects (faceting, channeling). Faceting may be encountered even in single crystals. Different crystal facets might conceivably exhibit some differences in the parameters of instrumental mass fractionation. However, in good diffusion experiments faceting is avoided. Selective sputtering