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Abstract

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DETERMINATION OF THE DIFFUSION COEFFICIENT BY AN ABSORPTION METHOD FROM THE MEAN DISPLACEMENT

Known absorption methods for determining the diffusion coefficient that are associated with the use of the absorption coefficient μ of a diffusing radioisotope (^{1,2}) have limited applicability, since for β-emitters with a complex β- (or β, γ-) spectrum μ is not a constant and depends on the depth of penetration into the material under study. The variant of the absorption method proposed below makes it possible to use, for the investigation of diffusion, practically any β-emitter with a sufficiently long half-life.

The process of change in radiation intensity is easily modeled by placing, on the surface of a source with a diffusing radioisotope, plates made of the material in which diffusion is being studied. Using a series of plates of different thicknesses, one can construct a plot of the dependence of the change in radiation intensity on the thickness of the absorbing layer (or on the magnitude of the mean displacement). With the aid of such a plot one can also solve the inverse problem, namely: from the change in the radiation intensity of the diffusing isotope, determine the magnitude of its mean displacement $\overline{X}$. The diffusion coefficient D is calculated from the relation

$$D = \text{const}\, \overline{X}^2 / t, \tag{1}$$

where t is the time of diffusion annealing.

Use of the proposed method in a number of cases makes it possible to increase the sensitivity of the absorption method that uses the absorption coefficient. As is known, for most β-emitters, in the regions of small and very large values of $\overline{X}$, a noticeable deviation from the exponential law is observed. Therefore the absorption coefficient has a constant value only for intermediate values of $\overline{X}$, the lower limit of which also determines the sensitivity of the method. The mean-displacement method makes it possible to obtain reliable data over practically the entire range of the working plot. Since in this case the sensitivity is determined by the accessible minimum thickness of the plates used in constructing the working plot, the proposed method is most expediently applied to the study of diffusion processes in metals and certain semiconductors.

The method was tested using the example of the diffusion of antimony, labeled with Sb^{124}, into single-crystal germanium. Sb^{124} ($T_{1/2} = 53.7$ days) is an isotope with a complex spectrum of β- and γ-radiation. The specimens, which were plane-parallel plates $7 \times 5 \times 2.5$ mm in size, were prepared from an ingot of single-crystal germanium of grade GDL-05/05. After mechanical grinding with M5 corundum abrasive, the specimens were treated in polishing etchant SR-4. Antimony was deposited on the surface of the specimens electrolytically from citric-acid solutions containing thiourea and bismuth salts, according to the procedure described in ([3]), with some modifications. The coating thickness amounted to fractions of a micron.

Taking into account the possibility of a decrease in the intensity of β-radiation due to radioactive decay and due to losses during the diffusion anneal—

burn-in (mechanical losses, evaporation, etc.), we used the "witness" method ([4]), i.e., before and after diffusion annealing we recorded the ratio of the intensity of the β-radiation to the intensity of the γ-radiation. Since the relative intensity of the γ-radiation is practically independent of diffusion, the change in the value of this ratio characterizes the change in the intensity of the β-radiation. As the "witness" we used not only the γ-radiation of Sb^{124}, but also its hard β-radiation, passing through an aluminum filter 2 mm thick. Taking into account the complete analogy existing between these variants, below we consider only the case in which γ-radiation acts as the "witness."

For simultaneous recording of the β- and γ-radiation, the sample, in a special Teflon holder ensuring strictly identical orientation, was placed between two scintillation detectors. Above the sample was placed a β-detector—an anthracene crystal (diameter 20 mm and $h = 10$ mm), coupled to an FEU-29; below, under the sample, was located a γ-detector—a NaJ(Tl) crystal (diameter 40 mm and $h = 40$ mm) with an FEU-13. In both cases recording was carried out on instruments of the PS-10 000 ("Floks") type.

Before the radiometric measurements before and after diffusion annealing, the activity was completely removed from the lateral surface of the sample.

First the integral intensity of the β- and γ-radiation of the sample turned toward the β-detector with side A was measured; then the same quantities were measured for the opposite side B, after which the ratio was calculated

$$K_0 = (N_{0A} + N_{0B} + N_{0a} + N_{0b})/N_{0\gamma}, \tag{2}$$

where N_{0A} and N_{0B} are the radiations arriving at the detector from surfaces A and B, respectively, in the case when the sample is turned toward the β-detector with side A; N_{0b} and N_{0a} are the β-activities reaching the detector from surfaces B and A, respectively, in the case when the sample is turned toward the β-radiation detector with side B; $N_{0\gamma}$ is the intensity of the γ-radiation.

Since the lateral surface of the sample is free of activity, it is obvious that, for a given sample thickness, the value K_0 does not depend on its shape or dimensions.

Substituting into (2) the value N_{0b} obtained from the obvious equality

$$N_{0a}/N_{0A} = N_{0b}/N_{0B}, \tag{3}$$

we obtain

$$K_0 = \frac{N_{0A} + N_{0B}}{N_{0\gamma}} F, \tag{4}$$

where $F = N_{0a}/N_{0A} + 1$ is a constant for samples of the given thickness h.

The quantity

$$(N_{0A} + N_{0B})/N_{0\gamma} = K_0/F = N_0/N_{0\gamma} \tag{4a}$$

is that part of the total β-activity of the sample, taken relative to its γ-activity, which reaches the detector without being absorbed in the sample. Therefore it also does not depend on the thickness of the sample. The change in precisely this quantity serves as the true criterion for estimating the depth of diffusion.

After diffusion annealing, the value K was determined experimentally; by analogy with (2), it is expressed by the equality

$$K = (N_A + N_B + N_a + N_b)/N_\gamma. \tag{5}$$

If the magnitude of the mean displacement $\overline{X}$ is small compared with the sample thickness h, then the relative intensity of the β-radiation reaching the

the detector from the reverse side of the specimen before and after diffusion is practically the same, i.e.,

$$(N_\mathrm{a} + N_\mathrm{b})/N_\gamma = (N_\mathrm{0a} + N_\mathrm{0b})/N_{0\gamma}. \tag{16}$$

Substituting into (6) the value of N_0b from (3), and into (7) the value of $(N_\mathrm{a} + N_\mathrm{b})/N_\gamma$ from (6), we obtain:

$$K = \frac{N_\mathrm{A} + N_\mathrm{B}}{N_\gamma} + \frac{N_\mathrm{0A} + N_\mathrm{0B}}{N_{0\gamma}} \frac{N_\mathrm{0a}}{N_\mathrm{0A}}. \tag{7}$$

After substituting into (7) the value $(N_\mathrm{0A} + N_\mathrm{0B})/N_{0\gamma}$ from (4a), we find N/N_γ:

Fig. 1. Working graph constructed according to relation (8), using as a "monitor" the γ-radiation (1) and hard β-radiation (2) of the isotope Sb^{124}

Figure 1: Fig. 1. Working graph constructed according to relation (8), using as a "monitor" the γ-radiation (1) and hard β-radiation (2) of the isotope Sb^{124}

$$\frac{N}{N_\gamma} = \frac{N_\mathrm{A} + N_\mathrm{B}}{N_\gamma} = K - \frac{K_0}{F}(F-1). \tag{7a}$$

Dividing (7a) term by term by (4a), we finally obtain

$$\frac{N}{N_0} = \frac{N}{N_\gamma} : \frac{N_0}{N_{0\gamma}} = \left(\frac{K}{K_0} - 1\right) F + 1. \tag{8}$$

Fig. 1. Working graph constructed according to relation (8), using as a "monitor" the γ-radiation (1) and hard β-radiation (2) of the isotope Sb^{124}.

We experimentally established the dependence of the quantity F on the specimen thickness h. For this purpose, Ge specimens of various thicknesses were prepared with radioactive antimony concentrated only on one of the working surfaces (A). Having measured the β-activity of side A ($N_{0\mathrm{A}}$) and side B ($N_{0\mathrm{a}}$), we calculated $N_{0\mathrm{a}}/N_{0\mathrm{A}} = F-1$. As is seen from the data in Table 1, in the thickness interval studied the quantity F is practically constant and is 1.13 ± 0.01.

Table 1

h, mm	1.34	1.64	2.11	2.34	2.47	2.62
$F-1$	0.135	0.130	0.130	0.127	0.117	0.126
Mean				0.127$±$0.016		

To construct the working graph we used a series of plane-parallel germanium plates with thicknesses from 9 to 106 μ, which were brought to the required thickness by mechanical grinding and polishing followed by treatment in a polishing etchant. One of the specimens under study was used as the radiation source. Having measured K_0, by successively placing on the radiation source plates of thickness $\bar{X}$ we measured the corresponding values $K_{\bar{X}}$. Substituting the values K_0 and $K_{\bar{X}}$ into formula (8), we obtained the values N/N_0, from which working graph 1 was constructed (Fig. 1)*.

To determine the quantity const we used the fact that in the interval $\bar{X} \simeq 40 \div 95\,\mu$ the absorption of β-radiation from Sb^{124} practically obeys an exponential law, which permits the use of

* In constructing the working graph for copper (the minimum thickness of the copper plates was $5\,\mu$), in the region $5 < \bar{X} < 10\,\mu$ an increase in the intensity of

the β-radiation of Sb^{124} was observed, i.e., $N/N_0 > 1$. This phenomenon may be connected with the formation of secondary electrons in the thin absorbing layer. As the plate thickness increases, the effect ceases to appear owing to a more intense absorption process. It is clear that in the region $0 < \bar{X} < 10\,\mu$ the graph passes through a maximum, i.e., in this region one value of $\bar{X}$ corresponds to two values of N/N_0 (with the exception of the maximum point). In essence, this means a decrease in the sensitivity of the method, since unambiguous results can be obtained only in the case $N/N_0 < 1$, and this is satisfied when $\bar{X} > 10\,\mu$.

in this range of the absorption method using the absorption coefficient. Assigning arbitrary values of $\overline{X}$, from graph 1 (Fig. 1) we find the corresponding values N'/N_0. Knowing N'/N_0 and μ (μ proved to be equal to 67.4 cm^{-1}), by the absorption procedure described in (2), we calculate Dt. Substituting the values of $\overline{X}$ and Dt into formula (1), we determine const. The values of const calculated in this way are given in Table 2.

Table 2

$\overline{X}$, μ	30	40	45	50	60	70	80	90	95	100	105
const	0,199	0,237	0,248	0,261	0,274	0,274	0,268	0,262	0,258	0,255	0,250

In the interval $\overline{X} = 45 \div 105\ \mu$ the values of const average 0.262 ± 0.012.

Diffusion annealing of the specimens was carried out in quartz ampoules in an argon atmosphere at temperatures of 700–850° (see Table 3).

Table 3

Temp., °C	700	750	800	825	850
$D \cdot 10^{-11}$, $\frac{\mathrm{cm}^2}{\mathrm{sec}}$	0,195	1,09	2,85	4,50	7,20

The temperature was maintained, on average, with an accuracy of 3–4°. With the minimum error of the radiometric measurements, the scatter of the results of individual determinations from the mean value is on the order of ±10–15%.

Having determined graphically the values of the activation energy Q and the factor D_0, we compared our data with the results of other investigators (see Table 4).

Table 4

	Literature source (5)	Literature source (6)	Literature source (7)	Literature source (8)	Literature source (9)	Literature source (10)	Our results
D_0, $\frac{\text{cm}^2}{\text{sec}}$	0,71	0,7–10	6,9	1,2	4,0	1,3	0,65
Q, $\frac{\text{kcal}}{\text{g} \cdot \text{mol}}$	51	51,8–57,5	57	53	55,6	52	51,3
$D \cdot 10^{-11}$, $\frac{\text{cm}^2}{\text{sec}}$ at 850° C	7,3	6,6–8,2	6,4	7,0	7,3	9,5	7,2

The values we obtained are in satisfactory agreement with the values published earlier.

The use of the proposed method is especially expedient in studying the kinetics of diffusion processes and in carrying out work connected with establishing the influence of various physicochemical factors on diffusion in solids.

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Note: Figure translations are in progress. See original paper for figures.

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