CALCULATION OF D IN THE CASE OF DIFFUSION FROM THE VAPOR PHASE

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A method is proposed for determining the diffusion coefficient in cases when data on the surface concentration of the diffusing substance are lacking.

The determination of the diffusion coefficients D of easily vaporized metals such as zinc, tellurium, cadmium, etc. is associated with a number of difficulties [1]. The method usually employed is that of depositing a thin film of radioactive material on the surface of the specimen. The solution of the problem then has the form

$$N(x, t) = \frac{Q}{\sqrt{\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right).$$

In this case the value of D is easily determined from the concentration curve of the radioactive substance in the specimen (a knowledge of Q is not required). This method is very convenient when the diffusing substance does not evaporate during annealing. However, when the diffusing substance evaporates readily, the condition Q = const is not satisfied and the above solution becomes unsuitable for calculation. Experience shows [2] that the evaporation of metals varies little even in an inert gas medium. Moreover, joining specimens with their working surfaces face to face does not completely eliminate evaporation. In our opinion, one of the principal reasons for the considerable scatter of the experimental data on the self-diffusion of chromium [3] is the high vapor pressure of chromium vapor at the experimental temperatures.

It is more convenient to investigate the diffusion of easily vaporized metals by another method based on saturation of the specimen from the vapor phase.

In this case the high vapor pressure of the diffusing substance is a necessary condition of application of the method. This problem is characterized in that a constant concentration of the radioactive substance N_0 must be maintained at the surface of the specimen throughout the annealing time. As is known [1], the solution of the diffusion problem for this process has the form

$$N(x, t) = N_0\left\{1 - \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)\right\} \equiv$$

$$\equiv N_0 \operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right). \qquad (1)$$

As follows from Eq. (1), to determine D by this method it is necessary to know the distribution curve of the radioactive substance in the diffusion zone and its concentration at the surface of the specimen N_0. However, the direct application of this method involves considerable difficulties, since the experimental determination of N_0 with sufficient accuracy is almost impossible for various reasons, one of the most important being the sharp change in the concentration of the diffusing substance at the surface of the specimen. Moreover, after diffusion annealing a certain amount of radioactive substance may be present on the surface of the specimen itself. If the solubility of the diffusing element is limited, new phases may be formed. In the latter case N_0 can be estimated on the basis of the corresponding phase diagram; however, the accuracy of this estimate is not sufficient for determining D.

These difficulties in the experimental determination of N_0 have prompted the development of indirect methods of determining that quantity. For example, in [4] N_0 was determined by extrapolation of the experimental curve in J, log x coordinates, where J is the intensity of the radioactive emission, which is proportional to the concentration of the diffusing substance N, and x is the distance from the surface of the specimen. When reliable experimental data are available on the N corresponding to values of x close to zero (of the order of a few microns), this method permits the accurate calculation of N_0. It is usually possible to obtain reliable experimental data at distances of 10–15 μ or more from the surface of the specimen. In these cases of practical importance extrapolation becomes indeterminate, since on this scale the form of the N(x) relation is not previously known. In [5] an attempt was made to avoid this difficulty by constructing a theoretical curve and comparing it with the experimental curve on a logarithmic graph. However, the application of this laborious method of trial and error is complicated by the fact that in constructing the theoretical curve it is necessary to carry out a variation with respect to two unknowns, N_0 and D. Accordingly, this method has no advantages over that used in [4] and is useful only as a check on the correctness of calculation of N_0 and D by the method proposed in [4].

We have worked out a method of determining N_0 and D using a probability diagram. This is a linear network in the coordinates u and x, where x, as in Eq. (1), is the distance from the surface, and u is related with the concentration N by the expression

$$N = N_0 (1 - \operatorname{erf} u). \qquad (2)$$

Comparing (1) and (2), we find that $u = x/2(Dt)^{1/2}$. This means that the relation between u and x is expressed

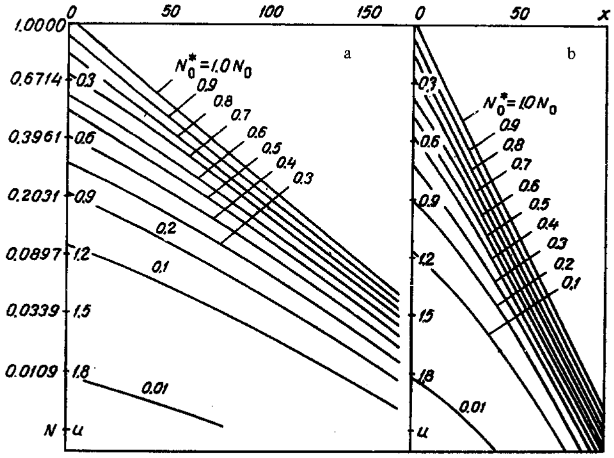

Fig. 1. Values of the concentration of the diffusing substance N as a function of the distance from the surface x (μ) in probability coordinates for various values of N_0: a) $D = 10^{-9}$ cm²/sec, t = 10 hr; b) $D = 4 \cdot 10^{-12}$ cm²/sec, t = 40 hr.

by a straight line through the point x = 0 ($N/N_0 = 1$). The slope of this line will obviously be equal to

$$\frac{\partial u}{\partial x} = \frac{1}{2\sqrt{Dt}}. \tag{3}$$

If instead of the true value of N_0 in Eq. (1) we take a certain value $N_0^* \neq N_0$ (naturally, it may be both greater and less than N_0), then on the probability diagram, as follows from Eq. (1), the dependence of N/N_0^* on x will not be linear. Consequently, the dependence of N on x will likewise not be linear. It is easy to see that the function N(x) has as its asymptote the straight line $N(x)/N_0$ at large values of x.

From the standpoint of the problem posed it was necessary to investigate the dependence of N/N_0^* on x at different degrees of deviation of N_0^* from the true value N_0. In order to obtain practical recommendations it was important to carry out the analysis in the range of real values of D and the duration of the diffusion process (annealing time) t. For this purpose we calculated the dependence of N on x on the probability diagram for $N_0^* = 1.0N_0$, $0.9N_0$, $0.8N_0$, ..., $0.1N_0$, $0.01N_0$. The case $N_0^* > N_0$ did not introduce anything essentially new. In these calculations the quantity D was varied in the range 10^{-9}–10^{-11} cm²/sec, and t = 10–40 hr.

As may be seen from Fig. 1, which shows the calculated dependence of N on x for a number of values of N_0^*, the graph of this function is quite smooth and the closer to a straight line, the less N_0^* deviates from N_0. From this there follows the possibility of determining N_0 by means of extrapolation of the experimental N = N(x) curve on such a coordinate network. In fact, if we plot the experimental data on a probability diagram and carry out extrapolation to x = 0 by means of a straight line (bearing in mind the smooth dependence), we obtain a value that should be close to N_0 (see Eq. (1)). We note that in these calculations the quantity N can be expressed in arbitrary units. If the value of N_0 calculated from this extrapolation proves sufficiently accurate, then, having constructed on the same graph the dependence of N/N_0 on x, we should obtain a straight line. D is easily calculated from the slope of this line $\partial u/\partial x$ (Eq. (3)).

When $N_0^{(1)}$ (this is our notation for the first approximation) differs from N_0, the graph of $N/N_0^{(1)}$ as a function of x will not be a straight line. As follows from the behavior of the concentration curves on the probability diagram close to x = 0 (see Fig. 1), $N_0^{(1)} \geq N_0$ is most probable (although, naturally, the possibility of $N_0^{(1)} < N_0$ is not excluded). To be specific, we assume that $N_0^{(1)} > N_0$. In this case the graph of $N/N_0^{(1)}$ vs. x proves to be below the true straight line $N(x)/N_0$. Repeating the linear extrapolation to obtain a more accurate value, this time for the curve $N(x)/N_0^{(1)}$, we obtain at x = 0 a certain new value $N_0^{(2)}$. We will assume that in this case also the result can only be too high, i.e., $N_0^{(2)} \geq N_0/N_0^{(1)}$. Consequently, now dividing N(x) by $N_0^{(1)}N_0^{(2)}$, we have a new curve closer to the straight line $N(x)/N_0$. This method of successive approximations obviously converges and leads to the value

$$N_0 = N_0^{(1)} N_0^{(2)} N_0^{(3)} \ldots. \tag{4}$$

Obviously, the form of (4) will not change if we consider the sequence

$$N_0^{(1)} < N_0, \quad N_0^{(2)} < N_0/N_0^{(1)}, \ldots \text{etc.}$$

Repeating the approximation until $N_0^{(k)}$ becomes equal to 1, we can thus obtain the true value N_0.

The method described was applied to the case of diffusion of Cd into GaAs in accordance with the data of [5], which are presented in Fig. 2. The calculation of the diffusion coefficient (Fig. 3) proved to be very simple and even in the first approximation led to a result very close to that obtained in [5].

When the value of the diffusion coefficient is approximately known, it is possible to determine N_0 by varying D. This possibility is examined in Fig. 4. From (1) we can derive

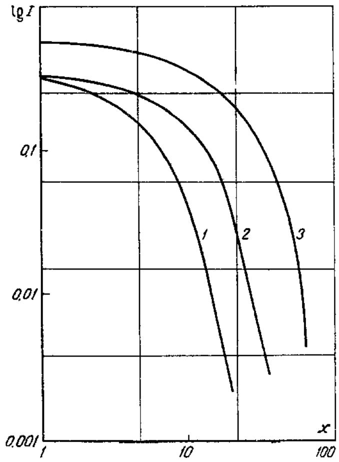

Fig. 2. Concentration curves for the diffusion of cadmium into GaAs according to the data of [5]: 1) T = 868° C, $t = 2.5 \cdot 10^5$ sec; 2) T = 993° C, $t = 6.55 \cdot 10^4$ sec; 3) T = 1149° C, $t = 1.54 \cdot 10^4$ sec, x in μ.

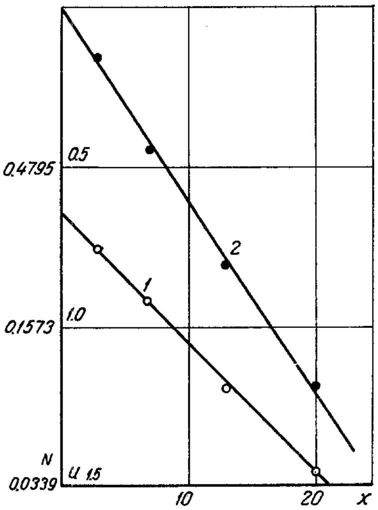

Fig. 3. Calculation of the diffusion coefficient from curve 2 of Fig. 2 in probability coordinates 1. The value of D is determined from the slope of the straight line 2 obtained from 1. x in μ.

$$\frac{dN}{d\left[\operatorname{erfc}\left(\frac{x}{2\sqrt{Dt}}\right)\right]} = N_0. \tag{5}$$

Hence it follows that the graphical dependence of N on erfc $(x/2(Dt)^{1/2})$ should be a straight line with slope N_0 in accordance with (5) (see Fig. 4). If, however, $D \neq D_{\text{true}}$, then on the graph we obtain a curve, as shown in Fig. 4 for the cases $D = 5 \cdot 10^{-11}$ cm²/sec and $D = 5 \cdot 10^{-12}$ cm²/sec (true value $D_{\text{true}} = 1.06 \cdot 10^{-11}$ cm²/sec). Consequently, if the order of magnitude of D is known, it is possible by varying D to determine the value that gives a straight line on the graph. The latter is a criterion showing whether the value of D obtained is the true one, since only in this case is Eq. (5) satisfied. However, as may be seen from the calculation presented (Fig. 4), the accuracy is not high, since the slope of the straight line representing N as a function of erfc $(x/2(Dt)^{1/2})$ is insensitive to variation of the diffusion coefficient.

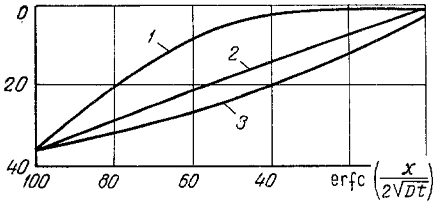

Fig. 4. Calculation of the diffusion coefficient for curve 2 (Fig. 2) by variation of D. Curve 1) $D = 5 \cdot 10^{-11}$, 2) $1 \cdot 10^{-11}$, and 3) $5 \cdot 10^{-12}$ cm²/sec.

The above analysis of the variation of the concentration curves on the probability diagram enables us to state that the corresponding method of linear extrapolation combined with the method of successive approximations makes it possible to determine reliable values of N_0 and D for diffusion from the vapor phase, which is confirmed by direct computations. The calculation of N_0 or D by varying the diffusion coefficient may also prove useful when the approximate value of the diffusion coefficient is known beforehand.

An estimate of the accuracy of the determination of D by the method of successive approximations using linear extrapolation, when the depth of the diffusion zone is not less than 50 μ and the accuracy of determination of the concentration of diffusing substance in the layer removed ±2%, showed that the error in calculating D does not exceed 15 rel.%. When D is varied, the error increases to 30–40%.

NOTATION

Q is the amount of radioactive substance deposited; t is the annealing time; x is the distance from the surface; erf is the error function; N is the concentration of radioactive substance at a distance x from the surface of the specimen; N_0 is the concentration of the diffusing substance at the surface of the specimen.

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