SURFACE IMPURITY DIFFUSION FOR AN INITIAL DISTRIBUTION GIVEN BY THE SEGREGATION COEFFICIENT IN ALKALI HALIDES

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ABSTRACT: The concentration profile of impurities in alkali halide crystals is calculated from Fick's second law for the case where the initial distribution is given by the segregation coefficient. Computer-obtained graphs are presented for the concentration profile as a function of $\frac{1}{2}\sqrt{Dt}$.

In the study of surface impurity diffusion frequently an initial uniform distribution is assumed.[1] The constant value used, is an average value obtained from the experimental measurements. Another method which is commonly followed consists in thermal annealing of the sample in order to obtain a uniform impurity distribution. Afterwards the diffusion to the surface is investigated.[2] The aim of this paper is to give the concentration distribution of impurities as a function of distance and time for the case where the initial distribution is given by the segregation coefficient.

A. In order to establish the basis of the procedure employed, we attack first a well-known problem: the solution for a pair of semi-infinite cylinders of unit cross section, where the boundary conditions are given by

$$C(x,t) = 0 \quad \text{for } x < 0, \quad \text{at } t = 0$$
$$C(x,t) = C_0 \quad \text{for } x > 0, \quad \text{at } t = 0 \tag{1}$$

where $C(x,t)$ is the concentration.

The solution to Fick's second law of diffusion

$$\partial C(x,t)/\partial t = D\,\partial^2 C(x,t)/\partial x^2 \tag{2}$$

for the thin-film case is given by[3]:

$$C(x,t) = (\sigma/2\sqrt{\pi D t})\exp(-x^2/4Dt) \tag{3}$$

where D is the diffusion coefficient, σ is the quantity of solute plated as a thin film and x is the distance in either direction normal to the initial solute film.

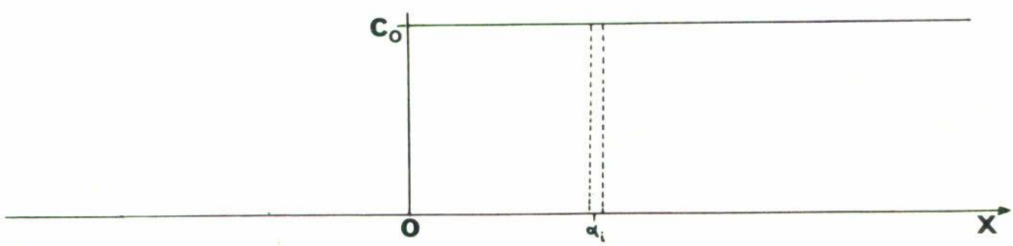

Figure 1a. The initial condition for a pair of semi-infinite cylinders.

This solution can be used in the case of a pair of semi-infinite cylinders if we imagine that the region of $x>0$ consists of n slices, each of thickness $\Delta\alpha_i$. Each slice will contain initially $(t=0)$ $\sigma_i = C_0\Delta\alpha_i$ of solute, where C_0 is the initial concentration of impurities. If α_i is the distance from the centre of the i^{th} slice to $x=0$ (Fig. 1a), the concentration at any given value of x after a time t will be

$$C(x,t) = (C_0/2\sqrt{\pi D t})\sum_{i=1}^{n}\Delta\alpha_i \exp[-(x-\alpha_i)^2/4Dt]\ . \tag{4}$$

In the limit of n going to infinity, the sum is replaced by the integral:

$$C(x,t) = (C_0/2\sqrt{\pi D t})\int_0^{\infty}\exp[-(x-\alpha)^2/4Dt]\,d\alpha\ . \tag{5}$$

Substituting

$$(x - \alpha)/2\sqrt{Dt} = \eta$$

we can rewrite the solution

$$C(x,t) = (C_0/\pi^{\frac{1}{2}})\int_{-\infty}^{x/(2\sqrt{Dt})} \exp(-\eta^2)\,d\eta$$

and finally

$$C(x,t) = \tfrac{1}{2} C_0 [1 + \operatorname{erf}(x/2\sqrt{Dt})] \quad . \tag{6}$$

The computer-obtained graphs of Eq. 6 are given in Fig. 1b.

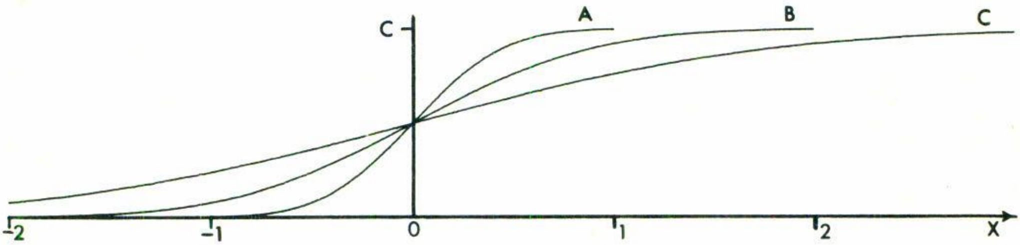

Figure 1b. $C(x,t)$ as the sum of the exponential curves which represents the solute diffusing out of each slab $\Delta\alpha_i$ thick. (A) for $(2\sqrt{Dt})^{-1} = 2$, (B) for $(2\sqrt{Dt})^{-1} = 1$ and (C) for $(2\sqrt{Dt})^{-1} = 0.5$.

B. In reality, the dimension of the crystal is finite, and Eq. 5 can thus be rewritten as

$$C(x,t) = (C_0/2\sqrt{\pi D t}) \int_0^b \exp[-(x-\alpha)^2/4Dt]\,d\alpha, \tag{7}$$

where b is the thickness of the crystal; so the concentration will then be:

$$C(x,t) = \tfrac{1}{2} C_0 [\operatorname{erf}(x/2\sqrt{Dt}) - \operatorname{erf}((x-b)/2\sqrt{Dt})] \quad . \tag{8}$$

The concentration profile in this case (Eq. 8) has already been plotted in Fig. 2.

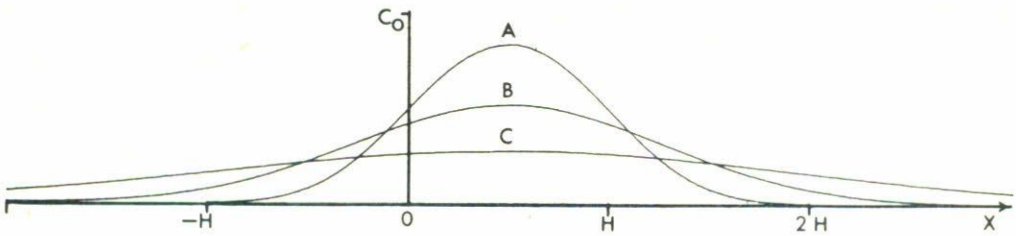

Figure 2. The concentration profile for a finite crystal with constant initial concentration. (A) for $(2\sqrt{Dt})^{-1} = 2$, (B) for $(2\sqrt{Dt})^{-1} = 1$ and (C) for $(2\sqrt{Dt})^{-1} = 0.5$.

C. In the case of interest, the initial condition for the concentration of impurities in the bulk of the crystal is given by

$$C(x,t) = -K_s \alpha, \quad \text{at} \quad t = 0 \tag{9}$$

where K_s is the segregation coefficient,[4] α is the distance from the plane $x = 0$, and $\alpha \leqslant b$, with b the thickness of the crystal.

Under such conditions, applying the same procedure as in A and B we have

$$C(x,t) = -(K_s/2\sqrt{\pi D t}) \int_0^b \alpha \exp[-(x-\alpha)^2/4Dt]\, d\alpha \tag{10}$$

and

$$C(x,t) = (K_s/\pi^{\frac{1}{2}}) \int_{x/2\sqrt{Dt}}^{(x-b)/2\sqrt{Dt}} (x - 2\eta\sqrt{Dt}) \exp(-\eta^2)\, d\eta \;; \tag{11}$$

so finally the concentration will be given by:

$$C(x,t) = \tfrac{1}{2} K_s x \,\{\mathrm{erf}([x-b]/2\sqrt{Dt}) - \mathrm{erf}(x/2\sqrt{Dt})\} + \tag{12}$$

$$+ (K_s\sqrt{Dt}/\pi^{\frac{1}{2}})\{\exp[-(x-b)^2/(4Dt)] - \exp[-x^2/(4Dt)]\}\;, \tag{12}$$

which satisfies Fick's second law (Eq. 2) and the boundary conditions

$$\begin{aligned} &C(x,0) = 0 \quad \text{for} \quad x < 0, \quad \text{at} \quad t = 0 \\ &C(x,0) = 0 \quad \text{for} \quad x > b, \quad \text{at} \quad t = 0 \\ &C(x,0) = -K_s x \;\text{ for } \; 0 \leqslant x \leqslant b, \quad \text{at} \quad t = 0\,. \end{aligned} \tag{13}$$

The computer-obtained graphs for the concentration profile according to Eq. 12 are shown in Fig. 3.

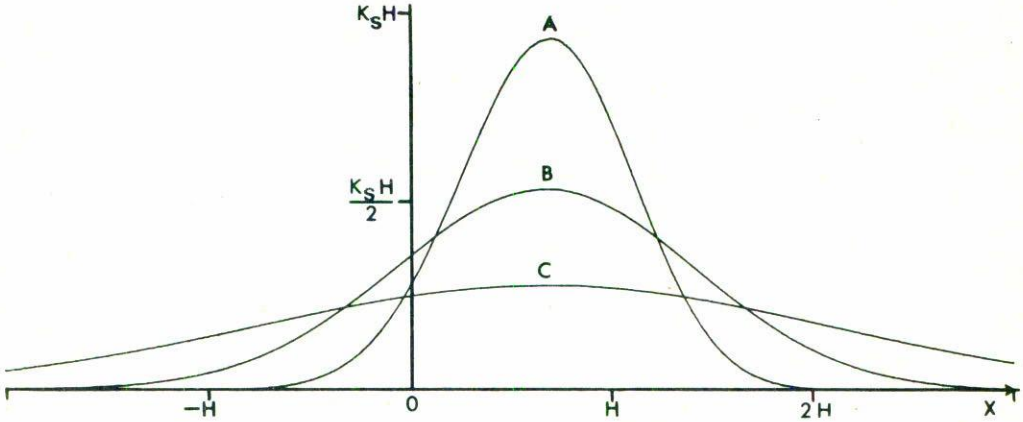

Figure 3. The solution of Fick's second law when the initial condition was given by the segregation coefficient. (A) for $(2\sqrt{Dt})^{-1} = 2$, (B) for $(2\sqrt{Dt})^{-1} = 1$ and (C) for $(2\sqrt{Dt})^{-1} = 0.5$.

CONCLUSIONS

The solution we have found is good only for a finite crystal of thickness h, with an initial concentration distribution given by the segregation coefficient (8). From it, at some time t, we can obtain the amount of impurities diffused to the surface just integrating $C(x,t)$ (Eq. 13) from h to infinity. However, this is true only for low concentrations of impurities on the surface, i.e., for small t; otherwise a sufficiently high concentration of impurities is built up on the surface, so that diffusion back to the volume of the crystal can occur. Such a restriction is avoided if the surface acts as a drain for impurities (for example when they become oxidized). One of the experimental points of interest, suggested by this equation is the determination of the limiting time at which there is no appreciable diffusion to the volume.

Finally, this calculation can be useful in experimental studies of diffusion of impurities to the surface.

REFERENCES

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2. E. Cabrera and H. Riveros. To be published.
3. P.G. Shewmon, *Diffusion in Solids*. (McGraw-Hill Book Co., New York, 1963).
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RESUMEN

Se calcula el perfil de concentración de impurezas en cristales de alogenuros alcalinos a partir de la segunda ley de Fick en el caso en que la concentración esté dada por el coeficiente de segregación. Se presentan las gráficas obtenidas por computadora del perfil de concentración en función del parámetro $\frac{1}{2}\sqrt{Dt}$.