The Influence of Grain Boundary Migration on the Diffusion Behaviour of Thin Films

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Simultaneous grain boundary-, surface- and lattice diffusion in hypothetical thin film couples of miscible components was computer simulated. On this basis the diffusion into fixed and moving grain boundaries is discussed with respect to the determination of diffusivities by depth profiling methods. The data evaluated from the synthesised depth profiles according to Whipple-Le Claire as well as to Gilmer and Farrell were compared with the diffusivities used for the computation. Agreement was found for systems with a fixed grain boundary network. Moving grain boundaries, however, may cause errors of an order of magnitude towards lower grain boundary diffusivities.

1. Introduction

The diffusional mixing process in thin laminated structures consisting of polycrystalline layers is commonly dominated by fast grain boundary diffusion. Hence, many of the recently published papers concerning thin film diffusion deal with the quantitative determination of grain boundary diffusion parameters (see e. g. Refs. [1 – 5]). The usual procedure is the analysis of the penetration profiles according to Whipple-Le Claire [6 – 8]. An alternate method using the amount of diffusant transported through the grain boundary to the surface was reported by Gilmer and Farrell [9, 10].

The shape of the depth profiles as well as the surface concentration rarely exhibit any significant criterion for the satisfaction of the basic conditions permitting these treatments. Thus, one has always to be concious that results may contain non-detectable errors. Some of their possible origins are:

> The damming of atoms within the grain boundary network.
> The limited amount of diffusant.
> The movement of grain boundaries during recrystallisation taking place simultaneously with diffusion.

Some aspects of the latter influence have already been briefly reported in a foregoing paper [11]. Further results as well as a discussion of additional causes are presented in the following.

2. Analytical and Numerical Treatment of the Grain Boundary Diffusion Problem

The basic papers of Fisher [12] and Whipple [6] deal with diffusion from a constant concentration source into an infinite half space of lattice diffusivity D split perpendicularly to the surface by a narrow slab of the much higher grain boundary diffusivity D'. Denoting the lateral coordinate x, the depth coordinate y and the grain boundary width $\delta \ll (D_0\,t)^{1/2}$ the problem in miscible systems is described by

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2}\right), \quad |x| > \frac{\delta}{2} \qquad (1)$$

and

$$\frac{\partial c}{\partial t} = \frac{2\,D}{\delta} \times \frac{\partial c}{\partial x} + D'\,\frac{\partial^2 c}{\partial y^2}, \quad |x| = \frac{\delta}{2}. \qquad (2)$$

Suzuoka [13 – 15] generalized these treatments to finite sources and a network of many grain boundaries. Comparison reviews of these theories were given by Young and Funderlic [16], LeClaire [8] and Canon and Stark [17]. Levine and MacCallum [7], Suzuoka [13, 14] and Le Claire [8] also dealt with the separation of bulk and grain boundary diffusion coefficients from measured depth profiles to be discussed later. Mimkes and Wuttig [18 – 20] treated the case of finite media with perpendicular grain boundaries. Gilmer and Farrell [9, 10] examined the influence of finite diffusion spaces on the Whipple-Le Claire analysis in papers concerning simultaneous lattice, grain boundary and surface diffusion in thin films.

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An alternate conception of solving the grain boundary diffusion problem in connection with surface diffusion is the application of numerical methods, the finite element method [10, 21], the Monte Carlo simulation [22], and the discretisation of the diffusion law [23 – 25].

Since the latter method is also applied in this work we first give a short description:

The two-dimensional diffusion Eq. (1) is written in terms of finite differences in time (Δt) and space ($\Delta x, \Delta y$)

$$\frac{\Delta_t c}{\Delta t} = \frac{\Delta_x (D\,\Delta_x c)}{(\Delta x)^2} + \frac{\Delta_y (D\,\Delta_y c)}{(\Delta y)^2}\,. \tag{3}$$

The spatial differences form an orthogonal grid intersecting the system. In the middle point of each grid mesh, the concentration at the time $t + \Delta t$ is evaluated from the concentration difference and the diffusivity to the adjoining meshes at the time t. Starting from any element and scanning the sample from mesh to mesh we obtain the distribution of the concentration at a particular time. The progress of diffusion is obtained by repeating this treatment in successive time steps.

Spatial and temporary steps may not be chosen independently. The maximum time step $\Delta t_{\max}$ up to which this method converges, is given by the diffusivity D, and the grid size Δx and Δy

$$\frac{1}{\Delta t_{\max}} = \frac{2D}{(\Delta x)^2} + \frac{2D}{(\Delta y)^2}\,. \tag{4}$$

In our problem the diffusivities extend over several orders of magnitude ($D'/D \leqq 10^7$). Thus, one would have to confine the whole treatment to the smallest time step even for those parts of the system where a small diffusivity would permit a much higher value. It is thus economical to run several scans only in the high diffusivity regions before the much slower material flux into the interior of the low diffusivity region is calculated. Since we can change the position of the grain boundary only by discrete steps from mesh-point to mesh-point, the element containing the grain boundary is subdivided in order to obtain a better approximation to the real continuous migration.

3. Results

3.1. Parameters used for the simulation

We used input data within a range which is characteristic of thin film diffusion systems. The layer thickness was chosen from 45 nm to 500 nm, the ratio of diffusivities D'/D ranged from 10^2 to 10^7. Such a ratio is representative of most metallic systems at temperatures of several hundred degrees [5]. The values D and D' themselves are not explicitely relevant for the stage of diffusion since only the products $D\,t$ and $D'\,t$ appear in the relevant equations. Therefore a change of D and D' means a changed time scale and migration velocity. Intermediate stages of diffusion are characterized by $D\,t < Y_0^2$ where Y_0 is the layer thickness. The speed of grain boundary migration v_{gb} was assumed to be $0.25\ \mathrm{nm\,s^{-1}}$ which was reported for Al layers by Severdenko, Trocickij and Milasevskaja [26]. Similar results were found by Hillert and Purdy [27].

3.2. Distribution of concentration

The spatial distribution of the diffusant in hypothetical diffusion couples is first discussed by pointing out qualitatively the influence of grain boundary motion on the diffusional mixing process. In order to given a vivid impression of the spatial distribution of the concentration we have used quasi three dimensional plots.

Examples are given in Fig. 1 and Fig. 2 for a 110 nm long cut out piece* of a 45 nm/45 nm couple containing just one grain boundary. The

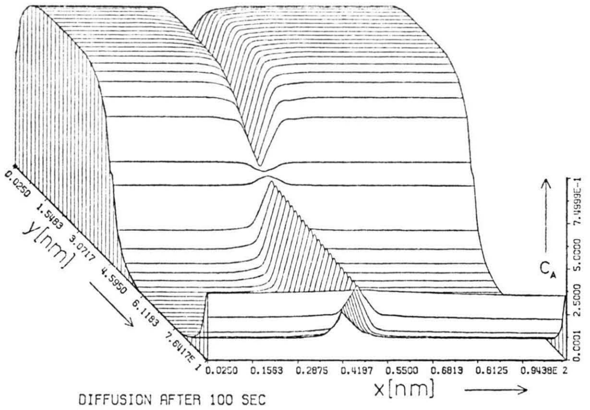

Fig. 1. Spatial distribution of the concentration in a thin film diffusion couple containing one fixed grain boundary in each layer. Data of the model: layer thickness $d_{\mathrm{A}} = d_{\mathrm{B}} (= Y_0) = 45$ nm, $D = 10^{-15}\ \mathrm{cm^2\,s^{-1}}$, $D' = D'_{\mathrm{surface}} = 10^{-11}\ \mathrm{cm^2\,s^{-1}}$, $t = 100$ s.

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* To obtain the whole sample we have to imagine this piece to be periodically replicated at the cut planes since the flux through them was set equal zero in the calculation.

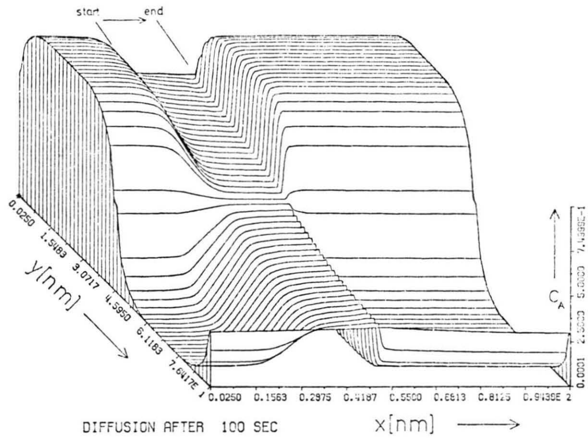

Fig. 2. Spatial distribution of the concentration in a thin film diffusion couple containing one moved grain boundary in each layer, same data as Fig. 1 and $v_{\mathrm{gb}} = 0.25\ \mathrm{nm\ s^{-1}}$.

diffusion time t was 200 sec. In the couple considered in Fig. 2 the grain boundary moved 50 nm during the diffusion period.

The enhanced total atomic transport by the moving grain boundary is evident as clearly indicated by the trace of diffusant along the part crossed by the grain boundary (Figure 2). Indeed the total amount of material transport into layer B is 20.1% with respect to 8.1% for fixed grain boundaries. Moving grain boundaries thus increase the total diffusivity in thin films. Experimental evidence of this effect was given by Cook and Hillard [28] who found abnormally high diffusion coefficients in modulated Ag – Au film structures during an initial grain growth.

3.3. *Influence of moving grain boundaries on diffusion data obtained from depth profiles*

Modern micro-sectioning techniques provide the average concentration c in the depth y of thin film couples. Such depth profiles can be directly used for a Whipple-Le Claire analysis. According to this treatment the product of the grain boundary width δ (commonly $\delta = 0.5$ nm) and the grain boundary diffusivity D' can be written as [8]

$$\delta D' = \left(\frac{4\,D}{t}\right)^{1/2} \left(\frac{\partial \ln(\overline{c})}{\partial y^{6/5}}\right)^{-5/3} (0.78)^{5/3} . \quad (5)$$

The slope $\partial \ln(\overline{c})\, y^{6/5}$ of the depth profile in a $y^{6/5}$ scale (Whipple plot) has to be taken in a region sufficiently far from the interface where diffusion via interface does not interfere with grain boundary diffusion. In thin films the boundary conditions for Whipple's model can be satisfied approximately by confining the treatment to early diffusion stages where the grain boundaries are not yet traversed (semi-infinite grain) and by a sufficient supply of diffusant. In a thin film couple a constant concentration source can be approximated by a symmetrical setup with respect to the interface, as used below. This condition need not be observed strictly since the finite source solution of Suzuoka [13, 14] leads to almost the same results

$$\delta D' = \left(\frac{4\,D}{t}\right)^{1/2} \left(\frac{\partial \ln(\overline{c})}{\partial y^{6/5}}\right)^{-5/3} (0.72\,\beta^{0.008})^{5/3} \quad (6)$$

with β denoting $(D'/D - 1) \times \delta \times (4\,D\,t)^{-1/2}$.

Gilmer and Farrel [9] have already pointed out that a saturation effect in grain boundaries simulates higher grain boundary diffusivity. Saturation occurs when the diffusant arrives at the surface before being absorbed by the lattice. It is obviously more significant for later diffusion stages. The concentration slope in the depth profile then becomes flatter thus simulating the higher diffusivity D'. Since migration along the grain boundary competes with the leaking into the grain this effect is more pronounced for larger ratios D'/D. Hence, the latter authors suggested a method for the evaluation of grain boundary diffusivity just in the special case of saturated grain boundaries. The information is taken from the concentration at the surface. Its normalized value $L\,\overline{c}(Y_0, t) \times (D\,t)^{-1/2}$ was fround to depend only upon

$$\beta\,\eta_0^{-2} = \left(\frac{D'}{D} - 1\right) \frac{\delta}{2} \frac{(D\,t)^{1/2}}{Y_0^2} , \quad (7)$$

when $2\,L$ is written for the average grain boundary spacing (Figure 3).

An infinite source of diffusant is required. The known values L, D, t and the amount of diffusant at the surface $(\overline{c}(Y_0, t))$ allow the determination of the quantity $\beta\,\eta_0^{-2}$ from the universal dependence Fig. 3 and $\beta\,\eta_0^{-2}$ leads to the grain boundary diffusivity (Equation (7)).

3.4. *Grain boundary diffusion parameters evaluated from Whipple-Le Claire and from Gilmer-Farrell analysis*

The following results were obtained by means of the usual graphical procedure applied to Whipple plots which were directly calculated from the spatial

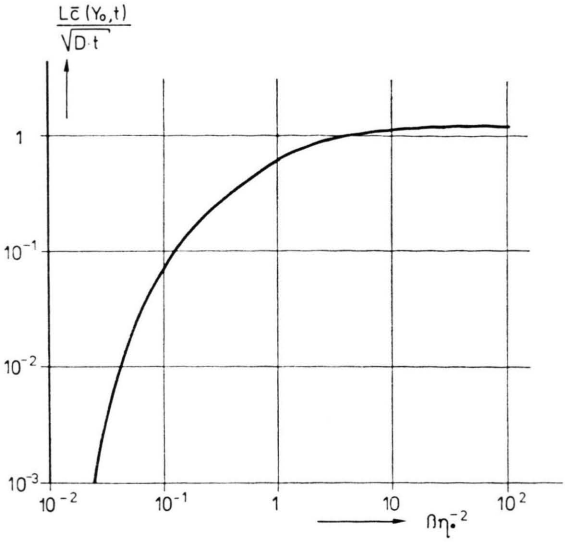

Fig. 3. Universal dependence of the normalized surface concentration according to Gilmer and Farrell [9].

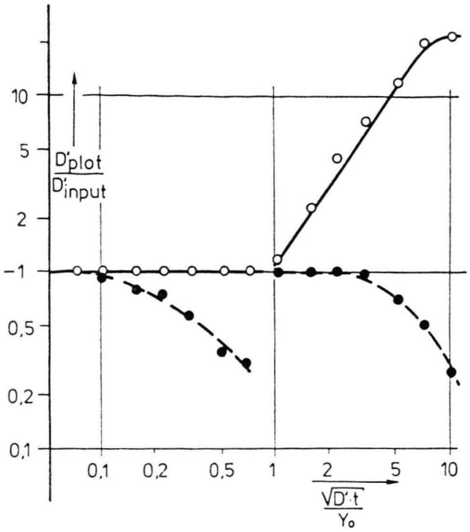

Fig. 4. Results of the Whipple plots of synthesised diffusion couples. Data of the model: layer thickness $d_A = d_B (= Y_0) = 55$ nm, $D = 10^{-15}$ cm^2 s^{-1} for $(D' t)^{1/2}/Y_0\, 1$, $D' = 5.6 \times 10^{-14}$ cm^2 s^{-1}, for $(D' t)^{1/2}/Y_0\, 1$, $D' = 5.5 \times 10^{-12}$ cm^2 s^{-1}. Open circles: fixed grain boundaries, full circles: moved grain boundaries ($v_{gb} = 0.25$ nm s^{-1}).

atomic distribution. For the lattice diffusivity D, which is necessary for the evaluation of D', the input value for the simulation D_{input} was used.

The examples discussed here were chosen such that the influence of moved grain boundaries and the saturation effect in the grain boundaries can be clearly demonstrated. The damming of diffusant is shown in a sample where penetration distances into grain boundaries (estimated by $(D' t)^{1/2}$) strongly exceed the film thickness. In the other sample, saturation in the grain boundaries is suppressed by a drastic reduction of its diffusivity os that $(D' t)^{1/2} < Y_0$. Both samples are considered with fixed and moving grain boundaries.

In order to point out the deviations from the input data, we express them in terms of $D'_{\text{plot}}/D'_{\text{input}}$ (D'_{plot} = value of grain boundary diffusivity obtained from Whipple plots).

Figure 4 shows that the influence of the saturation appears in fact at the diffusion state given by $(D' t)^{1/2}/Y_0 = 1$. Up to this state the Whipple treatment gives excellent results whereas deviations rise quickly with proceeding $(D' t)^{1/2}$.

The dashed curves obtained for the case of moved grain boundaries reveal deviations of D'_{plot} towards smaller values. The discrepancies increase with the migration distance. Evidently the moving grain boundary crosses regions where the diffusant is not yet significantly present. The grain boundary depleted in this way has to be replenished again in each new position, thus distributing the diffusant in the interface region rather than deep into the film. Hence, the evaluated grain boundary diffusivity is too small. In the present example the resulting effect is dominated by the influence of grain boundary motion, whereas slower grain boundary migration and/or higher values of D' would lead to a more pronounced saturation effect.

For the same diffusion system the Gilmer-Farrell method was applied. According to this treatment the concentration at the surface was taken as the amount of diffusant in the grain boundary surface junction averaged over the total surface. It must be remarked that this is obviously no realistic assumption, since surface diffusion is generally of similar speed to that of grain boundary diffusion and the diffusant spreads rapidly over the surface as shown in the concentration landscape Fig. 1 and Figure 2. For this case Gilmer and Farrell propose to take the minimum value of the concentration in the depth profile rather than the value of the surface concentration. More accurate results could possibly be achieved by an extrapolation of the linear part of the concentration profile to the surface. However, the intended advantage of the method, the avoidance of experimental depth profile analysis, is then lost.

In the following we want to apply the method in its original version. We investigate its consistency and the influence of grain boundary motion. Observing that the concentration in the couple interface is $C = 0.5$ instead of 1 as was assumed in the derivation of the curve shown in Fig. 3, we have to take the doubled values of the surface concentration. As can be seen in Fig. 5, for systems with fixed grain boundaries this method gives proper results even for those diffusion stages where Whipple's method is not suitable any more.

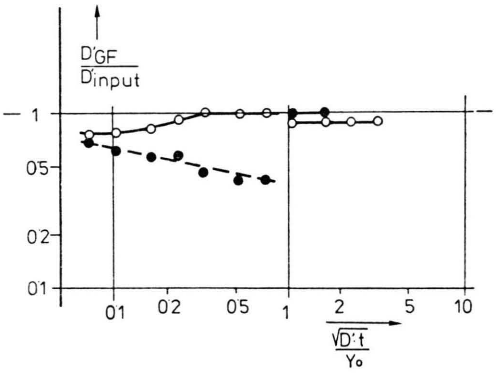

Fig. 5. Results of the Gilmer Farrell treatment, same data as Figure 4.

For large ratios D'/D and long diffusion times the method fails completely since the normalized surface concentration $L\,\overline{c}(Y_0, t)\,(D\,t)^{-1/2}$ may be out of the range of the curve of Figure 3.

When grain boundaries move, two different cases can be distinguished. If the saturation effect is absent already in the sample with fixed grain boundaries, the moving grain boundary supplies even less diffusant to the surface. Too small values for D' are obtained. If, on the other hand, the grain boundary diffusion is so fast that the grain boundary can be penetrated in each position, then a trace of diffusant exists on the surface too. In this case the amount of diffusant at the surface can be larger than it would be for a fixed grain boundary, where the damming at the grain boundary surface junction inhibits a further atomic transport along the grain boundary.

3.5. *Effect of grain boundary motion on the evaluation of the bulk diffusivity*

In general bulk diffusivities in thin films may not be deduced from an extrapolation of values measured on bulk samples at high temperatures. Very often the quenched-in defect structure inside the crystallites leads to enhanced values. The knowledge of the correct value of D, however, is necessary for the evaluation of grain boundary diffusivities, as mentioned before. Therefore D should be measured in each particular case.

The interface region of the depth profile contains information about the bulk diffusivity and permits an estimation of bulk diffusivity [3]. Systems with moving grain boundaries show a higher amount of diffusant near the interface. We wish to discuss this case in the following for different lattice diffusivities in systems with identical geometry ($Y_0 \gg (D'\,t)^{1/2}$), diffusion time, migration distance and grain boundary diffusivity. Figure 6 shows the bulk diffusivity D_{plot} estimated according to Hall et al. [3] from the slope of the concentration profile at the interface. The deviations caused by the moving grain boundary after traversing 1/4 of the grain may reach several orders of magnitude. These errors towards higher values increase with the ratio of D'/D which can be explained as follows: The mean concentration in layers near the interface is dominated by lattice diffusion as well as by the trace of the diffusant left by the moved grain boundary. When bulk diffusivity is

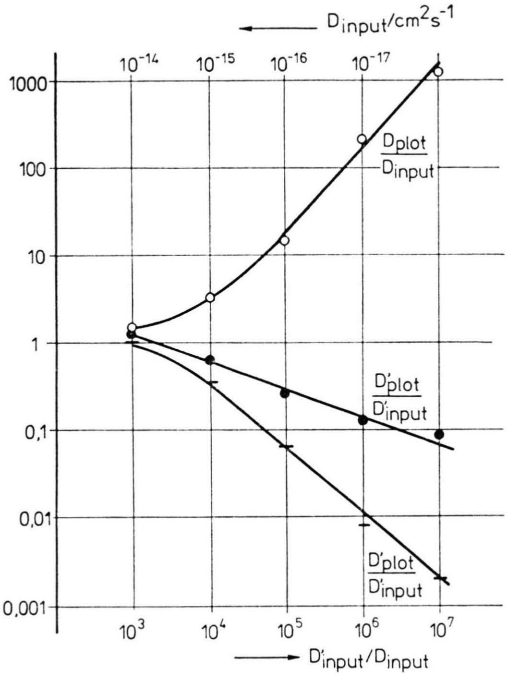

Fig. 6. Dependence of evaluated diffusion data upon D'/D. Data of the models: $d_{\mathrm{A}} = 250$ nm, $d_{\mathrm{B}} (= Y_0) = 680$ nm, $D'_{\mathrm{input}} = 10^{-11}\ \mathrm{cm^2\,s^{-1}}$, $t = 200$ s, $v_{\mathrm{gb}} = 0.25\ \mathrm{nm\,s^{-1}}$, $D_{\mathrm{input}} = 10^{-14}, 10^{-15}, 10^{-16}, 10^{-17}, 10^{-18}\ \mathrm{cm^2\,s^{-1}}$.

very small compared to the grain boundary diffusivity ($D < 10^5 D'$) then the slope of the depth profile near the interface is mainly given by the concentration gradient in the grain boundary and is fairly independent of the buld diffusivity. Hence, the lower the value of D_{input} the larger is the deviation of D_{plot}.

On the other hand the less extended penetration of diffusant in moving grain boundaries gives the impression of a smaller grain boundary diffusivity as discussed before. This effect depends also upon the ratio D'/D: The concentration gradient sufficiently far from the interface determines D'. It is almost independent of the bulk diffusivity and is thus mainly defined by the trace of diffusant. Since the slope of the Whipple plot contains the factor $D^{1/2}$ the evaluated value D'_{plot} directly corresponds to this factor although D has in fact no influence upon the slope.

In Fig. 6 we have also plotted the grain bondary diffusivities evaluated from Whipple plots using the real bulk diffusivity D_{input} and the value D extimated as before. The deviations may extend over several orders of magnitude, if D' were calculated on the basis of the real bulk diffusivity. If we use the incorrect value of the diffusion coefficient in bulk for a subsequent calculation of the grain boundary diffusivity then we obtain a better agreement between D'_{plot} and the true value D'_{input}. Nevertheless, in the case of moving grain boundaries diffusion data evaluated in this way must be considered with great reservation.

4. Conclusion

As a consequence of columnar film growth the grain boundary network generally intersects a thin film perpendicularly to the surface. The lateral crystallite diameter may be increased during recrystallization by orders of magnitude. Diffusion into such recrystallizing thin films differs very much from the diffusion process usually considered in systems with fixed grain boundaries: The distribution of atoms into the interior of the crystallites is a result of the replenishing of the grain boundaries in each new position rather than leaking out of the grain boundary by lattice diffusion. Diffusant is therefore mainly distributed near to that interface directed towards the source of diffusant where the grain boundary is rapidly charged. Less material is brought deep into the film. Such a process seems to be the result of increased bulk- and decreased grain boundary diffusivity. On the other hand the limited length of the grain boundaries causes a quick saturation with diffusant. Methods using the slope of the concentration profile for the calculation of the grain boundary diffusivity lead to values which are too large. The extent of possible errors was estimated in this paper, which shows the necessity for particularly careful analysis of the behaviour of the systems to be investigated.

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