

CONCENTRATION PHASE TRANSITIONS DURING DIFFUSION ALONG PHASE AND GRAIN BOUNDARIES*

L. M. KLINGER, I. R. KOGAY and B. B. STRAUMAL

Institute of Solid State Physics, Academy of Sciences U.S.S.R.

(Received 12 May 1981)

The problem of describing how an intermediate phase grows by diffusion as a wedge in a boundary region is solved, and the parameters of boundary and volume diffusion during development of a γ phase wedge when indium is diffusing along a single $\langle 001 \rangle$ tin-germanium twist boundary with misalignment $\varphi = 3$ have been determined.

It is well known that if intermediate phases are present on the constitution diagram of two elements layers of those intermediate phases can develop and grow in the diffusion pair formed of those elements. The problem of such concentration phase transitions was originally examined by Wagner [1, 2], but more details are given in [3].

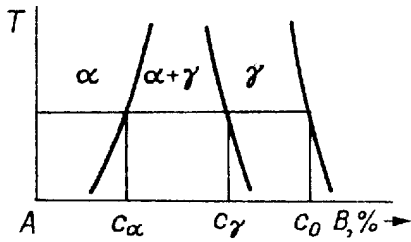


FIG. 1

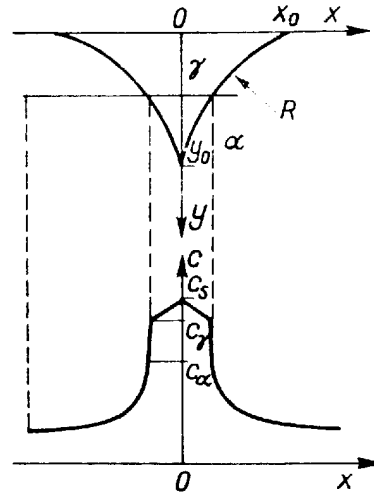


FIG. 2

FIG. 1. Constitution diagram of a system AB with intermediate phase γ .

FIG. 2. Wedge of intermediate γ phase formed during diffusion along interface $x=0$ (above) and shape of cross concentration profile (below).

On the other hand, the boundaries of grains and phases are known to be diffusion paths [4, 5], in which case the diffusion profiles in pairs with intermediate phases will be "pooled" to form a "wedge" of intermediate phase in the boundary region.

In this study we examine and solve the diffusion problem which describes this phenomenon and give the results of experiments in which it is observed for the first time. When atoms of element B are diffused from a layer with concentration c_0 along a grain boundary a wedge of intermediate γ phase is formed (Fig. 1 and 2).

As in Fisher's model [6] the boundary shall be a homogeneous layer with high diffusion permeability; and there shall be no diffusion flux from surface to volume and no diffusion inside. The shape of the interface is described by $x=\xi(y, t)$. Then the volume diffusion of atoms B in the γ region is described by

$$\frac{\partial c_1}{\partial x} = D_\gamma \frac{\partial^2 c_1}{\partial x^2}, \quad (1)$$

t is time, c the concentration of B in the volume, D_γ the coefficient of volume diffusion in the γ phase. Diffusion along the grain boundary in the γ phase is described by

$$\frac{\partial^2 c_{sy}}{\partial y^2} + \frac{2D_\gamma}{D_{sy} \delta} \frac{\partial c_1}{\partial x} \Big|_{x=0} = 0; \quad (2)$$

c_{sy} is the concentration on the boundary, D_{sy} —the coefficient of grain boundary diffusion in the γ phase, δ the width of the boundary. The boundary conditions for (1) have the form

$$c_1 \Big|_{x=0} = 0; \quad (3)$$

$$c_1|_{x=0} = c_{s\gamma}; \quad (4)$$

$$c_1|_{x=\xi} = c_\gamma; \quad (5)$$

c_γ is the solubility limit in the γ phase (see Fig. 1).

The boundary conditions for equation (2) are given as

$$c_{s\gamma}|_{y=0} = c_0; \quad (6)$$

$$c_{s\gamma}|_{y=y_0} = c_\gamma. \quad (7)$$

By analogy, in the α region

$$\frac{\partial c_2}{\partial t} = D_\alpha \frac{\partial^2 c_2}{\partial x^2}; \quad (8)$$

$$\frac{\partial^2 c_{s\alpha}}{\partial y^2} + \frac{2D_\alpha}{D_{s\alpha}} \frac{\partial c_2}{\partial x} \Big|_{x=0} = 0; \quad (9)$$

$$c_2|_{t=0} = 0; \quad (10)$$

$$c_2 \Big|_{\substack{x=\xi \\ y < y_0}} = c_\alpha; \quad (11)$$

$$c_2 \Big|_{\substack{x=0 \\ (y > y_0)}} = c_{s\alpha}; \quad (12)$$

$$c_2|_{x=\infty} = 0; \quad (13)$$

$$c_{s\alpha}|_{y=y_0} = c_2; \quad (14)$$

$$c_{s\alpha}|_{y=n} = 0, \quad (15)$$

where D_α is the coefficient of volume diffusion, $D_{s\alpha}$ —of boundary diffusion in the α phase, c_2 —the concentration in the α phase, c_α —the solubility limit in the α phase (see Fig. 1). We are ignoring diffusion fluxes on the α — γ interface and also parasitic grain boundaries in the γ phase. The solution of the problem is in the form

$$c_1 = c_{s\gamma} - \frac{c_{s\gamma} - c_\gamma}{\operatorname{erf} b} \operatorname{erf} \left(\frac{x}{2\sqrt{D_\gamma t}} \right), \quad \text{where } 0 < x \leq 2b\sqrt{D_\gamma t}; \quad (16a)$$

$$c_2 = \frac{c_\alpha}{\operatorname{erfc}(b\sqrt{D_\gamma/D_\alpha})} \operatorname{erfc} \left(\frac{x}{2\sqrt{D_\alpha t}} \right), \quad \text{where } x \geq 2b\sqrt{D_\gamma t}. \quad (16b)$$

Equation (13b) holds when $y < \varphi_0$ (Fig. 2). If $y > y_0$ then

$$c_2 = c_{s\alpha} \operatorname{erfc} \left(\frac{x}{2\sqrt{D_\alpha t}} \right) \quad (17)$$

as in Fisher's model. The unknown parameter is found from the condition of material balance at a point on the boundary α — γ ($x = \xi = 2b\sqrt{D_\gamma t}$)

$$(c_\gamma - c_\alpha) \frac{d\xi}{dt} = -D_\gamma \left(\frac{\partial c}{\partial x} \right)_{x=2b\sqrt{D_\gamma t}} + D_\alpha \left(\frac{\partial c}{\partial x} \right)_{x=2b\sqrt{D_\gamma t}} \quad (18)$$

After substituting (16) we get

$$c_\gamma - c_\alpha = \frac{c_s - c_\gamma}{\sqrt{\pi} b e^{b^2} \operatorname{erf} b} - \frac{c_\alpha}{\sqrt{\pi} b \varphi^{-1} e^{b^2} \varphi^{-2} \operatorname{erfc}(b\sqrt{\varphi})}, \quad (19)$$

where $\varphi = \sqrt{D_\alpha/D_\gamma}$.

After this we only examine cases of small b . Then, from (19) we get

$$b = \frac{c_s - c_\gamma}{c_\alpha} \frac{\sqrt{\pi}}{2} \sqrt{D_\gamma/D_\alpha}. \quad (20)$$

Essentially, this approximation means a linear fall of concentration with increasing x in the γ range

$$c = c_\gamma = \frac{c_s - c_\gamma}{2b\sqrt{D_\gamma t}} \cdot x \approx c_s - \frac{c_\alpha \sqrt{D_\alpha}}{\sqrt{\pi t} D_\gamma} \cdot x. \quad (21)$$

The diffusion "withdrawal" from the boundary

$$\frac{2}{\delta} D_\gamma \left(\frac{\partial c}{\partial x} \right)_{x=0} = - \frac{2\sqrt{D_\alpha}}{\sqrt{\pi t} \delta} \cdot c_\alpha \quad (22)$$

being independent of y , so within the γ range the dependence $c_s(y)$ defined by

$$D_{s\gamma} \frac{\partial^2 c_s}{\partial y^2} + \frac{2}{\delta} D_\gamma \left(\frac{\partial c}{\partial x} \right)_{x=0} = 0, \quad (23)$$

is in the shape of a parabola

$$c_s = c_0 - \frac{c_0 - c_\gamma}{y_0} y - \frac{c_\alpha}{2L_1^2} (yy_0 - y^2), \quad (24)$$

where

$$L_1 = \left\{ \frac{\sqrt{\pi t} D_{s\gamma} \delta}{2\sqrt{D_\alpha}} \right\}^{\frac{1}{2}}, \quad (25)$$

and y_0 is the maximum depth of the γ region, which is found from condition

$$c_s|_{y=y_0} = c_\gamma.$$

With (24) we can now find the shape of the γ phase wedge

$$\xi(y) = 2b\sqrt{D_\gamma t} = \frac{c_s - c_\gamma}{c_\alpha} \sqrt{\pi t} \frac{D_\alpha}{D_\gamma} = \left[\frac{c_0 - c_\gamma}{c_\alpha} - \frac{c_0 - c_\gamma}{c_\alpha y_0} y - \frac{Y y_0 - y^2}{2L_1^2} \right] \frac{\sqrt{\pi} + D_\gamma}{D_\alpha}. \quad (26)$$

This is a parabola with "width" x_0 along the base (see Fig. 2)

$$x_0 = \frac{c_0 - c_\gamma}{c_\alpha} \frac{\sqrt{\pi t} D_\gamma}{\sqrt{D_\alpha}} \quad (27)$$

and curvature

$$\xi''(y) = \frac{\sqrt{\pi t} D_\gamma}{L_1^2 \sqrt{D_\alpha}} = \frac{2D_\gamma}{D_{s\gamma} - \delta}. \quad (28)$$

If $\frac{D_\gamma}{D_{\gamma\delta}} \gg (y_0, x_0)$ we can neglect the curvature of the parabola

$$\zeta(y) = x_0(t) - \frac{x_0(t)}{y_0(t)} y.$$

But if condition

$$\left(\frac{y_0}{L_1}\right)^2 \ll \frac{c_0 - c_\gamma}{c_\alpha}, \quad (30)$$

is satisfied as well we can assume that within the γ region distribution $c_s(Y)$ is non-linear

$$c_s(Y) = c_\gamma + (c_0 - c_\gamma) \left(1 - \frac{y}{y_0}\right). \quad (31)$$

To determine $y_0(t)$ we have to join solution (16) for the region with solution (32) for the α region

$$c_s(Y) = c_\alpha \exp\left(-\frac{y - y_0}{L_2}\right); \quad (32a)$$

$$c = c_s \operatorname{erfc}\left(\frac{x}{2\sqrt{D_\alpha t}}\right), \quad (32b)$$

where

$$L_2 = \sqrt{\frac{D_{\alpha\alpha}}{D_{\gamma\gamma}}} L_1. \quad (33)$$

That is done with condition

$$(c_\gamma - c_\alpha) \frac{dy_0}{dt} = -D_{\gamma\gamma} \left(\frac{\partial c}{\partial y}\right)_{x=y_0^-} + D_{\alpha\alpha} \left(\frac{\partial c}{\partial y}\right)_{y=y_0^+}. \quad (34)$$

Putting (16) and (32) into that condition we find

$$(c_\gamma - c_\alpha) \frac{dy_0}{dt} = D_{\gamma\gamma} \frac{c_0 - c_\gamma}{y_0} - D_{\gamma\gamma} \frac{c_\alpha}{2L_1^2} y_0 - \frac{c_\alpha}{L_2} D_{\alpha\alpha}. \quad (35)$$

In equation (35) the lefthand part is much less than the term in the righthand part. In fact

$$(c_\gamma - c_\alpha) \frac{dy_0}{dt} \sim (c_\gamma - c_\alpha) \frac{y_0}{t} \quad (36)$$

and the ratio of those terms

$$\frac{c_\gamma - c_\alpha}{c_\alpha} \frac{2L_1^2}{D_{\gamma\gamma} t} \sim \frac{c_\gamma - c_\alpha}{c_\alpha} \frac{\delta}{\sqrt{D_\alpha t}} \ll 1. \quad (37)$$

We therefore neglect the second part and for y_0 obtain a quadratic equation

$$\left(\frac{y_0}{L_1}\right)^2 + 2\varphi_S \left(\frac{y_0}{L_1}\right) - 2\frac{c_0 - c_\gamma}{c_\alpha} = 0, \quad (38)$$

where $\varphi_S = \sqrt{\frac{D_{\alpha\alpha}}{D_{\gamma\gamma}}}$.

From (38) follows

$$\frac{y_0}{L_1} = -\varphi_S + \sqrt{\varphi_S^2 + 2 \frac{c_0 - c_\gamma}{c_\alpha}}; \quad (39)$$

$$\frac{y_0}{L_2} = -1 \sqrt{1 + 2 \frac{c_0 - c_\gamma}{c_\alpha} \varphi_S^{-1}}. \quad (40)$$

A diagram of relation $\ln c_s - y$ is given in Fig. 3.

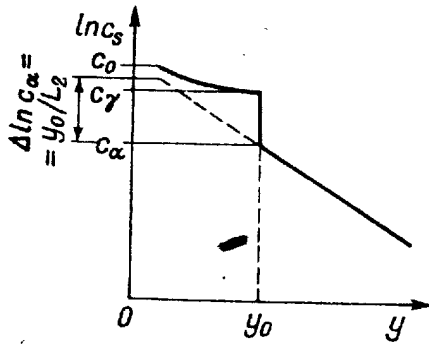


FIG. 3

FIG. 3. Dependence of concentration c_s near boundary on depth y .

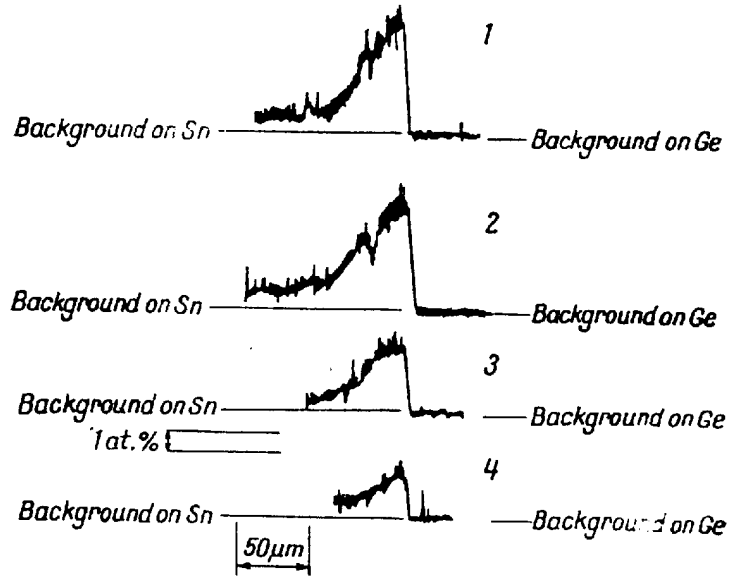


FIG. 4

FIG. 4. Cross concentration profiles of indium diffusion along a $\langle 001 \rangle$ Sn-Ge twist boundary interface ($\varphi = 3^\circ$); 1,2 - in region of γ phase wedge ($y < y_0$); 3,4 - where $y > y_0$.

Thus, having found the experimental dependence $\ln c_s(y)$ and values of y_0 and x_0 , with known D_α we can now calculate D_γ , $D_{s\gamma}$ and the value of $\alpha - \gamma$ boundary curvature on the basis of equations (27), (40), (33) and (28). We must first determine the boundary diffusion coefficient for the α phase. Knowing the slope of line $\ln c_{s\alpha} - y$ it can be calculated from (36) and (37) as usual:

$$D_{s\alpha} \delta = - \left(\frac{4D_\alpha}{\pi t} \right)^{\frac{1}{2}} \left(\frac{y}{\ln c/c_0} \right)^2. \quad (41)$$

The solution of problem (1) to (12) is readily generalized to the case of diffusion along an interface, with volume diffusion in only one of the phases, making the substitution

$$\frac{\delta}{2} \rightarrow \delta. \quad (42)$$

Our approximate solution to the problem is valid when the wedge of second phase is much less in width than the diffusion wedge

$$x_0 \ll \sqrt{D_\alpha t}. \quad (43)$$

But the depth must be comparable

$$y_0 \sim L. \quad (44)$$

We are the first to study the diffusion of indium along a single interface in Sn-Ge bicrystals when formation of an intermediate γ phase has been observed. The experiment was performed as follows. An indium film was electrolytically deposited on the surface of a bicrystal, perpendicular to the interface. A γ phase with variable composition (with homogeneity range from 11 to 25 at.% In) [7, 8] was formed by concentration phase transition during annealing.

The process was studied on a single interface with given crystallographic parameters, produced in the process we developed in [8]. Diffusion treatments were given for 5×10^5 sec at 161°C . After annealing the specimens were kept at 77 K until measurements were started.

We obtained diffusion profiles like those in the diagrams of Fig. 2 by means of X-ray microanalysis on the JXA-5. For the photography high-purity indium (99.995 at.% In) was used as standard with accelerating voltage 20 kV. The typical intensity ratio of the L_{α_1} In line on standard to specimen background was 300-350. So the radiation intensity of the indium could be measured up to values corresponding to its concentration in the specimen, i.e. 0.8-1.0 at.%. With the given voltage the analysis could be localized to a region of $2.7 \mu\text{m}$ [10]. The corrections for absorption, electron back scattering and breaking were calculated at around 0.1%, a low value, because the properties of diffusant and matrix were so similar, (for Sn and In the $\Delta Z/Z$ is 0.02 in value). The possibility of fluorescence due to the continuous spectrum and characteristic Ge radiation makes it difficult to measure the In concentration near the interface. But calculations with the methods of [10] did not allow for small values, their maximum contributions being 0.1 and 0.2%.

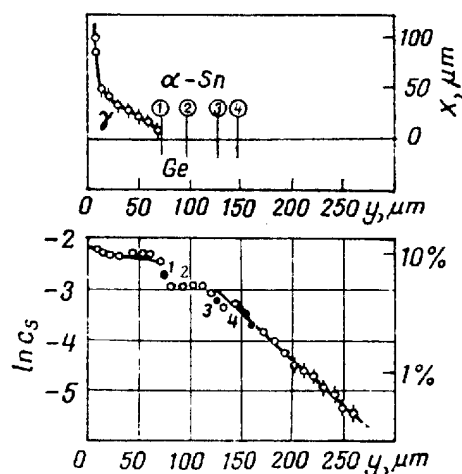


FIG. 5

FIG. 5. Dependence of c_s on depth y and profile of γ phase wedge during diffusion of indium along $\langle 001 \rangle$ Sn-Ge twist interface, $\varphi = 3^\circ$. The numbers give the points from which the diffusion profiles have been taken and are given in Fig. 4.

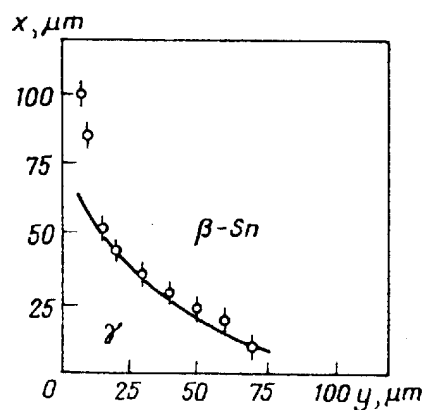


FIG. 6

FIG. 6. Theoretical (solid line) and experimental (points) shape of γ phase wedge during diffusion of indium along $\langle 001 \rangle$ Sn-Ge twist interphase boundary, $\varphi = 3^\circ$.

When concentration c_s is determined from the peak of a diffusion profile it is usually necessary to allow for dilution because the total intensity includes a fraction from regions next to the boundary, where the concentration is lower. Moreover, in Fisher's model we are measuring \bar{c} averaged over a region of width $L = 28 \mu\text{m}$; $\bar{c}/c \approx 1$ if $2\sqrt{D_{\text{vol}}t} \gg L$. In our experiment $\sqrt{D_{\text{vol}}t} = 28 \mu\text{m}$. So dilution can be neglected.

Now we give the results obtained in the study of heterodiffusion of In along the Sn-Ge interface with simultaneous formation of a wedge of γ phase for one of the boundaries (twist boundary with common axis $\langle 001 \rangle$ in Sn and Ge and angle of rotation 3°). Figure 4 shows the In diffusion profiles taken perpendicular to the interface. It is easy to see they are asymmetrical because there is no diffusion withdrawal into the Ge (the diffusion coefficient of In in Ge is 10^{-33} cm²/sec at this temperature). The peak intensity is less further from the surface. The first two curves describe a region of γ phase contracting as γ grows, which is entirely absent from curves 3 and 4. We can see that the profiles are consistent with theoretical predictions (see Fig. 2). The same numbers 1-4 are used in Fig. 5 to denote the lines along which the profiles have been taken and the points with corresponding c_i values. In Fig. 5 we give a diagram of a specimen with a boundary $(\beta\text{-Sn})-\gamma$. That profile was also obtained with X-ray spectral microanalysis. The profile corresponds to the theoretical prediction (see Fig. 2). The experimental dependence $\ln c-y$ is given in the bottom half of Fig. 5. The points correspond to maxima on the diffusion profiles (see Fig. 4). That dependence also differs very little from the relation given in the first part of this article (see Fig. 3). The horizontal intercept with concentration c_0 is probably related with diffusion along $(\beta\text{-Sn})-\gamma$, which the calculation does not allow for.

The straightening out of intercept $\ln c-y$ below c_0 shows that Fisher's model can be used to calculate $D_{\alpha\alpha}$. The value was found as $D_{\alpha\alpha}\delta = 7.27 \times 10^{-13}$ cm²/sec. The volume diffusion coefficient D_α we determined experimentally from the diffusion profile taken perpendicular to the Sn surface a long way from the boundary, and it agrees with published data [11]. Then, knowing $x_0 = 4.8 \times 10^{-5}$ m and $y_0 = 7.0 \times 10^{-5}$ m, with formulae (27), (40), (33) and (28) we calculate D_γ as 3×10^{-14} cm/sec, $D_{S\gamma}\delta = 5 \times 10^{-15}$ cm/sec, $1/R = 0.25$ cm⁻¹, and we have used the concentration values found from Fig. 5: $c_0 = 0.105$; $c_\gamma = 0.083$; $c_\alpha = 0.052$.

The points on Fig. 6 describe the experimental shape of the $\beta\text{-Sn}-\gamma$ interface, while the continuous line is that predicted by formula (29). The agreement theory and experiment is evidently good.

REFERENCES

1. C. Wagner, *Zs. Phys. Chem. (B)*, **23**, 25 (1933).
2. C. Wagner, *Zs. Phys. Chem. (B)*, **32**, 447 (1936).
3. Ya. Ye. Geguzin, *Diffuzionnaya zona (The Diffusion Zone)* Moscow, Nauka (1979).
4. A. N. Aleshin, B. S. Bokshiteyn, A. L. Petelin and L. S. Shvindlerman, *Metallofizika*, **2**, 83 (1980).
5. D. Juvè-Duc, D. Ireheux and P. Guiraldenor, *Acta Met.*, **27**, 1487 (1979).
6. J. C. Fisher, *J. Appl. Phys.*, **22**, 74 (1951).
7. C. W. Goulding and G. V. Raynor, *J. Inst. Metals*, **85**, 535 (1956-57).
8. C. V. Raynor and T. Graham, *Research*, **10**, 369 (1957).
9. B. S. Bokshiteyn, L. M. Klinger, B. B. Strauman and L. Shvindlerman, *Fiz. tverd. tel*, **23**, 202 (1981).
10. S. J. B. Read, *Electron Probe Microanalysis*, Mir, Moscow (1979).
11. A. J. Sawatsky, *J. Appl. Phys.*, **19**, 1303 (1958).