

## CRYSTAL-LATTICE DEFECTS

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### Method of Dislocation and Bulk Diffusion Parameters Determination

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A method of dislocation pipe diffusion parameters determination during the type *B* diffusion kinetics is suggested. Proposed method involves diffusion dislocation pipe kinetics for two different annealing times at the same temperature during the type *B* kinetics and dislocation pipe kinetics for one annealing time at other (lower) temperature during the type *C* kinetics. Transition time for type *B* kinetics to type *A* kinetics (volume diffusion) and kinetics law  $t^{1/6}$  for cone top rate are used in this method. Literature experimental data are used for separate determination of the volume diffusion activation energy and the dislocation pipe diffusion activation energy.

**Key words:** diffusion, dislocations, diffusion laws, activation energy, mathematical modelling.

Запропоновано метод визначення параметрів дифузійних процесів уздовж дислокацій, використовуючи кінетику типу *B*. У методі використовується дифузійна кінетика типу *B* вздовж дислокацій для двох різних часів відпалу при одній і тій самій температурі та дифузійна кінетика типу *C* вздовж дислокацій для одного часу відпалу за іншої (нижчої) температури; застосовується перехідний час від *B*-режиму до *A*-режиму (об'ємна дифузія) і кінетичний закон  $t^{1/6}$  для швидкості руху вершини конуса. Літературні експериментальні дані використовуються для визначення енергії активації дифузії окремо в об'ємі та вздовж дислокацій.

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**Ключові слова:** дифузія, дислокації, дифузійні закони, енергія активації, математичне моделювання.

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## 1. INTRODUCTION

To predict the behaviour of microelectronic components at working temperature we need to know the dislocation pipe diffusion activation energy and the volume diffusion activation energy. Dislocation pipe diffusion becomes a major contribution to device failure in microelectronic components at working temperatures. A model to describe analytically the diffusion phase ball growth kinetics from point source inside polycrystal grains was presented in [1]. It was shown that phase ball growth law from point source is  $t^{1/3}$ . It was proved mathematically in [2] that phase cone growth law  $t^{1/6}$  is valid during the type B kinetics of dislocation pipe diffusion and it is possible to calculate dislocation pipe diffusion coefficients not only for the phase cone formation, but for migration of atoms along dislocations and self diffusion along dislocation pipes too. Even well annealed single grain metallic films contain dislocations densities of about  $10^{14} \text{ m}^{-2}$  [3], so average distance between dislocations is about 100 nm. An experimental determination of dislocation pipe diffusion parameters would require a large set of data points as function of time. Proposed method involves dislocation pipe kinetics for two different annealing times at the same temperature during the type B kinetics and dislocation pipe kinetics for one annealing time at other temperature during the type C kinetics.

## 2. MODEL

Physical model of dislocation-pipe diffusion involving outflow is as follows (Fig. 1).

Diffusion flux,  $j_d$ , flows along dislocation pipe with diffusion coefficient  $D_d$  and, simultaneously, outflows into volume from each point,  $dy$ , with bulk diffusion coefficient  $D \ll D_d$  in 2D space to be perpendicular to the dislocation pipe (Eq. (1)).

$$\pi R_d^2 C_1 \frac{dy}{dt} = \pi R_d^2 j_d - 2\pi R_d \int_0^{y(t)} j_1 dy, \quad (1)$$

where  $R_d$  is the radius of dislocation pipe.

Here

$$j_d(t) = D_d \Delta C_1 / y(t)$$

and

$$j_1(t) = D \frac{\partial C}{\partial R} = \frac{D\Delta C_1}{R(t,0)} = \frac{D\Delta C(R(t,y))}{R(t,y)}. \tag{2}$$

Diffusion flux is uniform from dislocation line and concentration profiles are approximately linear [4] along dislocation line and along the phase cone radii.

Correlative differential diffusion equation is as follows:

$$\frac{dy}{dt} = \frac{D_d\Delta C_1}{C_1 y(t)} - \frac{2D\Delta C_1 y(t)}{C_1 R(t,0)R_d}. \tag{3}$$

Analytical solution of Eq. (3) was presented in [2].

### 3. METHOD

Lattice diffusion is negligible in the type C kinetics and it is possible to calculate dislocation diffusion coefficient  $D_d$  itself using random walk law  $t^{1/2}$ :

$$y^2(t_c) = 2D_d t_c \text{ and } D_d = \frac{y^2(t_c)}{2t_c}, \tag{4}$$

where  $y(t_c)$  is average diffusion length along dislocation pipe,  $t_c$  is annealing time.

Intermediate phase length  $y(t_c)$  along dislocation pipe can be found [2]:

$$y^2(t_c) = \frac{2D_d\Delta C_1}{C_1} t_c, \tag{5}$$

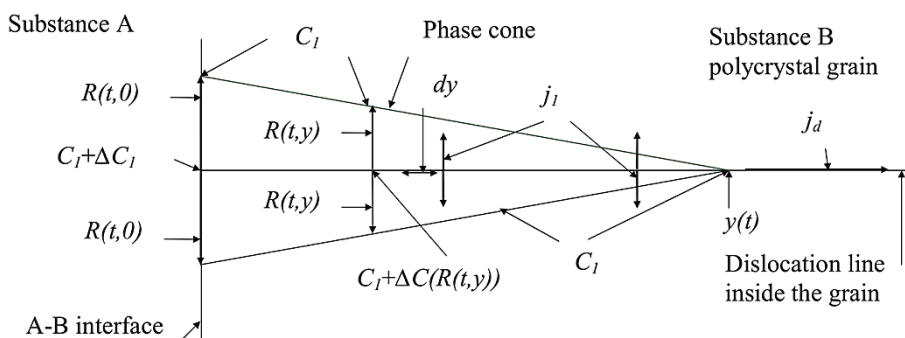


Fig. 1. Model of the intermediate phase cone formation during A-atoms diffusion along dislocation line involving outflow from the dislocation pipe.

where  $\Delta C_1$  is the concentration range of phase homogeneity,  $C_1$  is the concentration of the component  $B$  on the side of phase 1 boundary between the broadening phase 1 and the matrix  $A$  [4]. One can find transition time from type  $C$  to type  $B$  kinetics [1]

$$R^3 = \left(\frac{\delta}{2}\right)^3 = \frac{3D\Delta C_1\delta}{2C_1} t_{C \rightarrow B} \text{ or } t_{C \rightarrow B} = \frac{C_1\delta^2}{12D\Delta C_1}, \quad (6)$$

and the average diffusion length along dislocation pipe

$$y(t_{C \rightarrow B}) = \sqrt{\frac{D_d}{6D}} \delta, \text{ where } \delta = 1 \text{ nm}. \quad (7)$$

Attention is drawn to the result, that  $C_1$  and  $\Delta C_1$  are absent in equation (7), so it is possible to calculate dislocation diffusion coefficients not only for the phase cone formation, but for migration of atoms along dislocations and self-diffusion along dislocation pipes too.

Dislocation pipe diffusion is negligible in the type  $A$  kinetics, lattice diffusion distance is much longer than an average distance between dislocations, and it is possible to calculate bulk diffusion coefficient  $D$  itself:

$$y^2(t_A) = x^2(t_A) = 2Dt_A \text{ and } D = \frac{y^2(t_A)}{2t_A} = \frac{x^2(t_A)}{2t_A}. \quad (8)$$

Intermediate phase lattice length  $y(t_A)$  can be found [5]:

$$y^2(t_A) = x^2(t_A) = \frac{2D\Delta C_1}{C_1} t_A. \quad (9)$$

One can find transition time from type  $B$  to type  $A$  kinetics [2]

$$y^2(t_{B \rightarrow A}) = \left(\frac{D_d}{D}\right)^{2/3} D_d^{1/3} \left(\frac{\Delta C_1}{C_1}\right)^{1/3} \frac{3^{1/3}\delta^{4/3}}{2^{7/3}} t_{B \rightarrow A}^{1/3} = \frac{2D\Delta C_1}{C_1} t_{B \rightarrow A}$$

or

$$t_{B \rightarrow A} = \frac{D_d^{3/2}}{D^{5/2}} \frac{3^{1/2}\delta^2 C_1}{2^5 \Delta C_1}, \quad (10)$$

and the average intermediate phase lattice length

$$y(t_{B \rightarrow A}) = \left(\frac{D_d}{D}\right)^{3/4} \frac{3^{1/4}}{4} \delta. \quad (11)$$

Cone radius is equal

$$R(t_{B \rightarrow A}) = \frac{3^{1/2}}{2^2} \left( \frac{D_d}{D} \right)^{1/2} \delta. \quad (12)$$

Attention is drawn to the result, that  $C_1$  and  $\Delta C_1$  are absent in equations (11) and (12) too.

So, the type  $B$  kinetics is valid for

$$\left( \frac{D_d}{6D} \right)^{1/2} \delta < y(t_B) < \left( \frac{D_d}{D} \right)^{3/4} \frac{3^{1/4}}{4} \delta. \quad (13)$$

For comparison, the grain boundary Fisher diffusion regime is valid [4] for

$$\sqrt{\frac{D_b}{2D}} \delta < y(t) < \frac{D_b}{2D} \delta. \quad (14)$$

The Arrhenius law is valid for dislocation pipe diffusion and volume diffusion in ultra high purity samples:

$$D_d = D_{0d} e^{-\frac{E_d}{k_B T}} \quad \text{and} \quad D_V = D_{0V} e^{-\frac{E_V}{k_B T}}. \quad (15)$$

Here  $k_B$  is the Boltzmann constant,  $E_d$  is the dislocation pipe diffusion activation energy,  $E_V$  is the volume diffusion activation energy,  $D_{0d}$  and  $D_{0V}$  are the pre-exponential factors,  $T$  is absolute temperature. Highly segregated state requires higher activation energy for self-diffusion along dislocations, so downward curvature of the Arrhenius plot was observed in [6]. The pre-exponential factors are diffusion coefficients at  $T \rightarrow \infty$  or  $T_m/T \rightarrow 0$ , where  $T_m$  is melting point, so assumption  $D_{0V} = D_{0d} = D_0$  is reasonable and has experimental evidence [7], [10].

Equations (15) yield for two different temperatures:

$$\ln \left( \frac{D_d(T_1)}{D_d(T_2)} \right) = \frac{E_d}{k_B} \frac{T_1 - T_2}{T_1 T_2}, \quad T_1 > T_2 \quad \text{and} \quad E_d = \ln \left( \frac{D_d(T_1)}{D_d(T_2)} \right) k_B \frac{T_1 T_2}{T_1 - T_2}. \quad (16)$$

The pre-exponential factor is equal:

$$D_0 = D_d(T_1) \exp \left( \frac{E_d}{k_B T_1} \right). \quad (17)$$

The volume diffusion activation energy  $E_V$  is calculated:

$$E_V = \ln \left( \frac{D_0}{D_V(T_1)} \right) k_B T_1. \quad (18)$$

#### 4. ANALYSIS

It was proved in [8] that perpendicular grain boundaries do not influence diffusion kinetics in *B*-regime. This result allows us to use the well-known model of a polycrystal as a 3D array of grain boundaries to be perpendicular to the interface for describing the phase growth. One can assume the same for dislocation pipe diffusion [9], [10]. We can analyse experimental results, obtained in [6]. Bulk diffusion coefficients for the diffusion of  $^{59}\text{Fe}$  in the high purity iron were calculated in [6] using type *B*  $\rightarrow$  *A* kinetics and the methods, described in [15]:  $D_V = 1.5 \cdot 10^{-18} \text{ m}^2 \cdot \text{s}^{-1}$  at  $T_1 = 973 \text{ K}$  for  $t_{B \rightarrow A} = 67.5 \text{ ks}$  ( $T_m/T = 1.86$ ). The average diffusion length is equal  $y(t_{B \rightarrow A}) = \sqrt{D_V t_{B \rightarrow A}} = 318 \text{ nm}$ .

Equations (11) and (12) give  $\frac{D_d}{D_V} = \sqrt[3]{\frac{4^4}{3\delta^4} y^4(t_{B \rightarrow A})} = 9.55 \times 10^3 \approx 10^4$ ,

$D_d = 1.4 \cdot 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ , and  $R = 43 \text{ nm}$ .

Only one experiment was carried at the same temperature for two annealing times  $t_1$  and  $t_2$  ( $t_1 \ll t_2$ ,  $t_2 = 40t_1$ ). The average diffusion length at the same temperature  $T_1 = 973 \text{ K}$  for  $t_B = 1.68 \text{ ks}$  is equal [2]

$$y(t_B) = y(t_{B \rightarrow A}) \left( \frac{t_B}{t_{B \rightarrow A}} \right)^{1/6} = 172 \text{ nm}.$$

Cone radius is equal [1]

$$R(t_B) = R(t_{B \rightarrow A}) \left( \frac{t_B}{t_{B \rightarrow A}} \right)^{1/3} = 13 \text{ nm}.$$

Figures 2 and 3 can demonstrate such results.

Dislocation diffusion coefficients for the diffusion of  $^{59}\text{Fe}$  in the iron were calculated in [6] using type *C* kinetics:  $D_d = 3 \times 10^{-16} \text{ m}^2 \cdot \text{s}^{-1}$  at  $T_2 = 753 \text{ K}$  for  $t_C = 2.4 \text{ ks}$  ( $T_m/T = 2.4$ ). One can find ratio  $D_d/D$  using equation (7):  $y^2(t_{C \rightarrow B}) = D_d t = \frac{D_d}{6D} \delta^2$  and  $\frac{D_d}{D} = 4.3 \times 10^6$ . Ratio  $D_d/D$  increases remarkably for lower temperature [4].

Dislocation pipe and volume diffusion activation energies and pre-exponential factors did not calculate in [6]. It is possible to calculate  $E_d$  and  $D_0$  using equations (16) and (17):  $E_d = 1.1 \text{ eV}$ ,  $D_0 = 6.85 \times 10^{-9} \text{ m}^2 \cdot \text{s}^{-1}$ . One can calculate dislocation pipe diffusion coefficient for temperature 973 K directly, using Eqs. (16) and (17) ( $T_1 = 753 \text{ K}$  and  $T_2 = 693 \text{ K}$  (type *C* kinetics)):  $D_d \approx 10^{-14} \text{ m}^2 \cdot \text{s}^{-1}$ . Such value corresponds to value calculated using proposed method. Fisher law ( $t^{1/4}$ ) gives:  $D_d \approx 10^{-16} - 10^{-15} \text{ m}^2 \cdot \text{s}^{-1}$ . Such value is in two orders lower than experimentally ob-

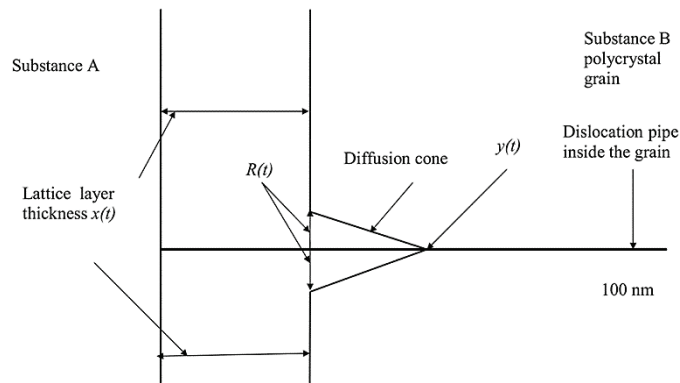


Fig. 2. Early type B diffusion kinetics for  $t = t_{C \rightarrow B}$ .

tained in [6]. The volume diffusion activation energy  $E_V$  is calculated using Eq. (18):  $E_V = 1.85$  eV. Ratio  $E_d/E_V = 0.6$ , as described in [9], [10].

It was found in [11] that dislocations can accelerate diffusion of Si from precipitate  $P_1$  to precipitate  $P_2$  in an Al grain at 623 K ( $T_m/T = 1.5$ ,  $\Delta l = 100$  nm,  $\Delta l$  is the dislocation length) by three orders of magnitude as compared with bulk diffusion ( $D_d = 8.2 \times 10^{-13} \text{ m}^2 \cdot \text{s}^{-1}$ ). Moreover, precipitate volume decreasing is linear as a function of time from  $t_0 = 0$  s to  $t_1 = 900$  s and up to  $t_2 = 2640$  s (at  $t_3 = 2880$  s the precipitate  $P_1$  has completely dissolved by diffusion through dislocation end point):

$$V_p \approx 2 \cdot 10^4 \text{ nm}^3 = \frac{4}{3} \pi R_p^3 = \frac{4}{3} \pi R_{0p}^3 - \frac{4}{3} \pi \alpha t \approx 19 \cdot 10^4 \text{ nm}^3 - \frac{4}{3} \pi \alpha t. \quad (19)$$

Here  $V_p$  is the precipitate  $P_1$  volume,  $R_p$  and  $R_{0p}$  are the precipitate ra-

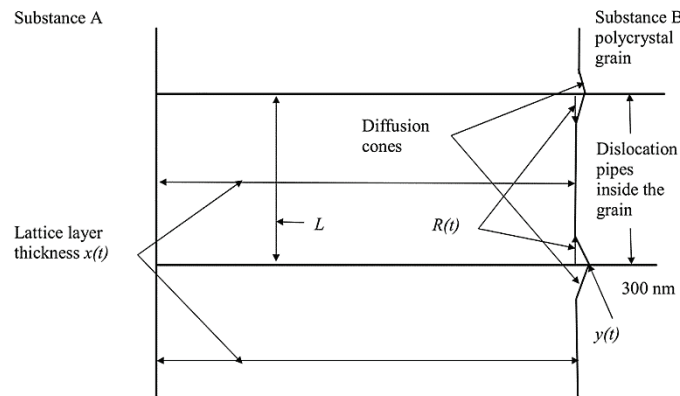


Fig. 3. Late type B diffusion kinetics for  $t = t_{B \rightarrow A}$ ,  $L$  is an average distance between dislocations.

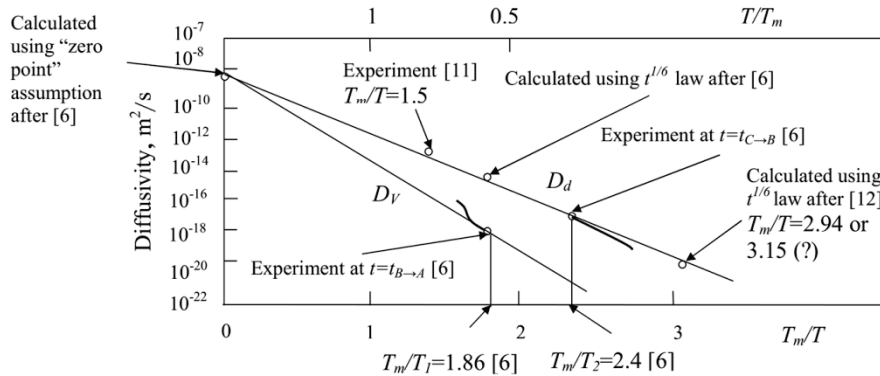
dii at  $t = t_2$  and  $t = 0$ , correspondingly. Calculations using Eq. (19) give:  $\alpha = 15.4 \text{ nm}^3 \cdot \text{s}^{-1}$ ,  $R_{0p} = 36 \text{ nm}$  and  $R_p(t_2) = (R_{0p}^3 - \alpha t)^{1/3} \approx 17 \text{ nm}$ . It agrees with *in situ* TEM observation of Si precipitate dissolution through a dislocation in an aluminium grain at 623 K [11]. So, the diffusion law  $R = (\alpha t)^{1/3}$  from point source (practically, through dislocation end point) obtained mathematically in [1] was proved experimentally in [10]. Dislocation diffusion energy for the diffusion of Si in an Al grain were calculated in [11]:  $E_d = 1.12 \text{ eV}$ . Such value is the same as calculated using Eq. (16).

The diffusion penetration lengths of Hf into the HfN/ScN superlattice sample were directly measured and an average value was calculated in [3] at 950°C ( $T_m/T = 2.94$ ) for  $t_1 = 24 \text{ h}$  and  $t_2 = 48 \text{ h} = t_{B \rightarrow A}$ :  $y(t_1) = 4.5 \text{ nm}$ ,  $y(t_2) = 5 \text{ nm}$ ,  $D_V^{\text{Hf}} = 2.34 \cdot 10^{-22} \text{ m}^2 / \text{s}$ . Authors noted that their scientific interests are far from diffusion problems, so they choose simple random walk law ( $t^{1/2}$ ) to calculate dislocation pipe diffusion coefficient. This is not correct. Figure 3 in [3] shows that Hf diffusion occurs along semi-plane of edge dislocation between HfN layer and ScN layer with simultaneous outflow into volume (Fisher law ( $t^{1/4}$ )). It gives:  $D_d \approx (y/\delta)^2 y^2 / t \approx 4.75 \cdot 10^{-21} \text{ m}^2 \cdot \text{s}^{-1}$ . Such value is in order higher than calculated in [3]. One can find using Eq. (11):

$$\frac{D_d}{D_V} = \sqrt[3]{\frac{4^4}{3\delta^4} y^4(t_{B \rightarrow A})} = 38 \text{ and } D_d^{\text{Hf}} = 8.9 \cdot 10^{-21} \text{ m}^2 / \text{s}. \text{ Such value exact-}$$

ly corresponds to the Arrhenius law presented in Fig. 4 [3].

General result is shown in Fig. 4.



**Fig. 4.** Averaged diffusion spectrum in metals after [10]. Downward curvature of the  $D_d$  Arrhenius plot (solid curve) was observed in [6] and [9] because highly segregated state requires higher activation energy for self-diffusion along dislocations. Upward curvature of the  $D_V$  Arrhenius plot (solid curve) was observed in [6] because of structure changes in Fe near the Curie temperature (1043 K) and  $\alpha \rightarrow \gamma$  transition (1183 K).



Monte Carlo modelling is an additional method to mathematical modelling [12], [13].

By the way, melting point of HfN [14, page 535] is  $T_{m,\text{HfN}} = 3580^\circ\text{C} = 3853\text{ K}$ , no  $3573\text{ K}$  as pointed in [3], so  $T_m/T = 3.15$ , no  $2.94$ ; and Hf diffusion occur into ScN (not in HfN), so we need to know melting point of ScN (not HfN).

## 5. SUMMARY

A method to determine separately of the volume diffusion activation energy and the dislocation pipe diffusion activation energy during the type  $B$  diffusion kinetics is suggested. Proposed method involves dislocation pipe kinetics for two different annealing times at the same temperature during the type  $B$  kinetics and dislocation pipe kinetics for one annealing time at other temperature during the type  $C$  kinetics. An experimental determination of  $D_d$  and  $D_v$  require only two data points: one is  $(t_{B \rightarrow A}, y(t_{B \rightarrow A}))$  measured at temperature  $T_1$  and another is  $(t_c, y(t_c))$  measured at temperature  $T_2 < T_1$ .  $D_v$  is calculated using equation

$D_v = \frac{y^2(t_{B \rightarrow A})}{2t_{B \rightarrow A}}$ ,  $D_d$  is calculated using equation

$\frac{D_d}{D_v} = \sqrt[3]{\frac{4^4}{3\delta^4} y^4(t_{B \rightarrow A})}$  at temperature  $T_1$ ,  $D_d$  is calculated using equation

$D_d = \frac{y^2(t_c)}{2t_c}$  at temperature  $T_2$ , the volume diffusion activation energy

is calculated using equation  $E_d = \ln\left(\frac{D_d(T_1)}{D_d(T_2)}\right) k_B \frac{T_1 T_2}{T_1 - T_2}$ , and the pre-exponential factor is calculated using equation:

$$D_0 = D_d(T_1) \exp\left(\frac{E_d}{k_B T_1}\right).$$

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