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AKAPIT

COMPUTER METHODS IN MATERIALS SCIENCE
Informatyka w Technologii Materiałów

Vol. 15, 2015, No. 1

COMPETITION BETWEEN KIRKENDALL SHIFT AND FRENKEL EFFECT DURING 2D DIFFUSION PROCESS

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Abstract

In this paper numerical description of the interdiffusion process where the competition between the Kirkendall shift and Frenkel effect is showed. The vacancy generation and voids evolution (Frenkel effect) is discussed in terms of numerical simulations in 2 dimensional space. The proposed approach based on the generalized Darken approach where the volume velocity is essential in defining the local material velocity at non-equilibrium.

Key words: Kirkendall shift, Frenkel effect, vacancy distribution, void formation

1. INTRODUCTION

The Kirkendall experiment (Smigelskas & Kirkendall, 1947) has focused new attention on the mechanism of diffusion in metallic systems. After his experiment there is no longer doubt that a marker shift occurs in diffusion couples and indicate the vacancy mechanism of the diffusion (Seitz, 1953).

The first experimental evidence that the holes form from a supersaturated solution by a process of heterogeneous nucleation was presented by Balluffi (Balluffi, 1954). He showed, that required relative excess vacancy concentration for hole formation in most specimens is probably <0.01. Balluffi suggested that the holes will form in all systems when vacancies are pumped into any small region of the diffusion zone at the rate of about 10^{16} / sec/cc.

Control of voiding in alloys is an important practical problem of materials science. As a rule, the voiding should be suppressed since they lead to failure of microelectronic circuits (Tu, 2007; Tu, 2011). Voiding is a result of relaxation of pure material or alloy supersaturated with vacancies. The relaxation of vacancy subsystem can proceed by joining of vacancies into voids.

In this paper the method for the voids grow during diffusion in 2 dimensional space is presented. The method allows for the estimation of the radius of the voids during mass transfer.

2. MODEL

The model was developed by Wierzba, 2014. The bi-velocity method is based on the Darken model for interdiffusion. The main law is the mass conservation law for each component. This law in 2D can be written as:

$$\frac{\partial N_i}{\partial t} + \nabla \cdot \left(-D_i \nabla N_i + N_i \upsilon^{drift} \right) = 0 \qquad (1)$$

where: N_i denote the molar fraction of the component, D_i is the intrinsic diffusion coefficient and υ^{drift} denote the drift velocity. The drift velocity, after Darken, is defined from known diffusional fluxes of the components:

 ISSN 1641-8581

$$\nabla \cdot \left(-\sum_{i=1}^{r} D_i \nabla N_i + \upsilon^{drift} \right) = 0 \qquad (2)$$

Above equation is called the Poisson equation and can be solved by iteration methods. The model take into account the vacancy conservation law:

$$\frac{\partial N_v}{\partial t} + \nabla \cdot j_v + \frac{N_v - N_v^{eq}}{\tau_v} = 0 \qquad (3)$$

Where N_v is the vacancy molar fraction, j_v is the vacancy flux. The N_v^{eq} and τ_v denote the vacancy equilibrium molar fraction and relaxation time, respectively. The vacancy flux is a sum of the fluxes of the components, mainly:

$$\sum_{i=1}^{r} j_i + j_v = 0 \quad \Rightarrow \quad j_v = \sum_{i=1}^{r} D_i^I \nabla N_i \qquad (4)$$

Above equations should be supplemented by boundary conditions. The concentration of the vacancies growth around the initially inserted void(s) ($|\Omega_V|$). This growth is due to the drift velocity. The following boundary condition should be implemented around the void(s):

$$\frac{\partial N_i}{\partial t} = \frac{\partial N_V}{\partial t} = 0 \qquad i = 1,...,r, \text{ on } |\Omega_V| \qquad (5)$$

The void radius can be approximated from the analytical expression:

$$R = D_V \left(N_V - N_V^{eq} \right) \frac{1}{L_V} t + R^{\min} \qquad (6)$$

where: $R^{\min}$ denote the minimal void radius ($R^{\min}$ = 10^{-8} m) and t is the experimental time in seconds. L_V denote the mean vacancy migration length ($L_V \approx \sqrt{D_V \tau_V}$).

Finally for the binary A-B system the following set of the equations should be solved:

1. The components conservation law, Equation (1) describes the redistribution of components with account of lattice drift. This equation for A component can be rewritten in the following form:

$$\frac{\partial N_A}{\partial t} - \nabla \cdot \left(D_A^I \nabla N_A \right) + \nabla \cdot \left(N_A \upsilon^{drift} \right) = 0 \qquad (7)$$

2. The redistribution of vacancies, Equation (3), taking the sinks and sources of vacancies into account in relaxation approximation (for simplicity we assumed that the vacancy fraction is small and does not influence the drift velocity):

$$\frac{\partial N_v}{\partial t} + \nabla \cdot \left(\sum_{i=1}^{r} D_i^I \nabla N_i \right) + \frac{N_v - N_v^{eq}}{\tau_v} = 0 \qquad (8)$$

3. The drift velocity, Eq. (2) - the Poisson equation - should be solved by e.g. iterative numerical schema. For the binary A-B system this equation reduces to the following form:

$$\nabla \cdot \upsilon^{drift} = \nabla \cdot \left(\nabla u^{drift} \right) = \nabla \cdot \left[\left(D_A^I - D_B^I \right) \nabla N_A \right] \qquad (9)$$

where u^{drift} is the drift potential.

4. The radius of the void, Equation, (6), in the system:

$$R = D_V \left(N_V - N_V^{eq} \right) \frac{1}{L_V} t + R^{\min} \qquad (10)$$

3. RESULTS

In this section the voids formation in binary diffusion couple will be simulated. We have introduced 5 voids into the simulation as the initial conditions. During the process these voids are growing. We assume that the mean migration length for vacancy was $L_V = 10^{-8}$ m and the diffusion coefficients $D_A = 10^{-9}$ and $D_B = 10^{-10}$ cm^{2}s^{-1}. Figures 1 - 4 show the two dimensional diffusion profiles over the time. Figure 1 presents the initial conditions (initial distribution over the components and initial void radius). Figures 2, 3 and 4 present the evolution of the components and voids. It is presented that during the time the diffusion flow from the faster to the slower diffusion part of the diffusion couple. From the figures the voids radius can be estimated. It is presented that the voids grow during the diffusion.

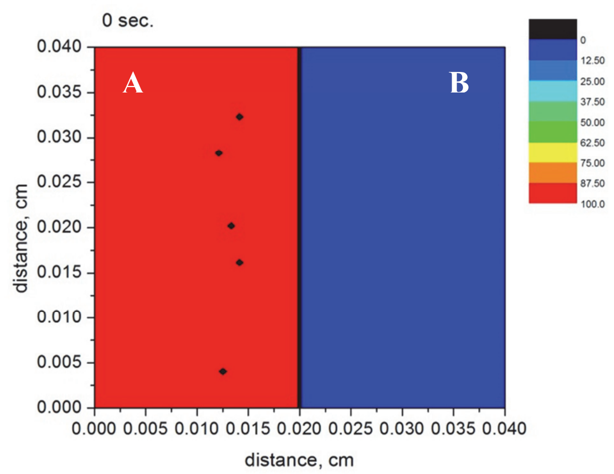

Fig. 1. The simulation results of the concentration profile in binary A-B diffusion couple after 0 s of annealing.

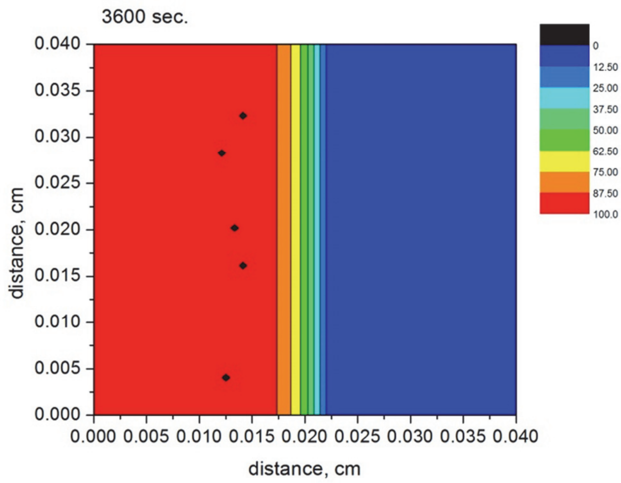

Fig. 2. The simulation results of the concentration profile in binary A-B diffusion couple after 3600 s of annealing.

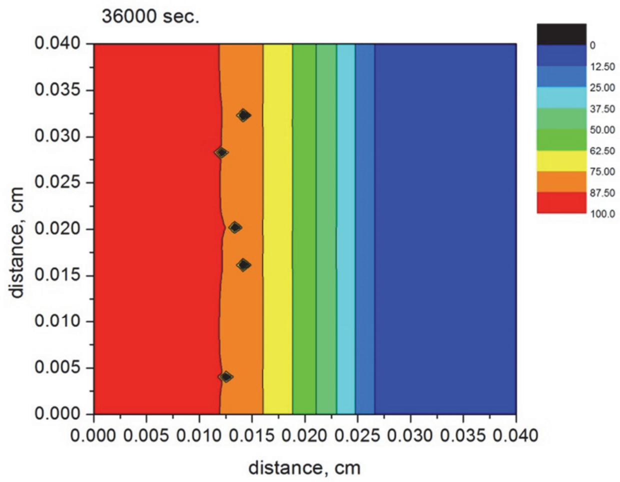

Fig. 3. The simulation results of the concentration profile in binary A-B diffusion couple after 36000 s of annealing.

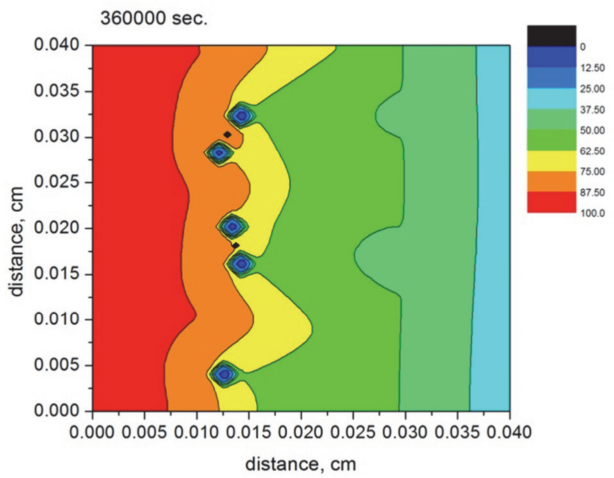

Fig. 4. The simulation results of the concentration profile in binary A-B diffusion couple after 360000 s of annealing.

4. CONCLUSIONS

The analysis of the voids formation was presented and discussed. The two dimensional calculations for interdiffusion and voids formation processes was presented. It was showed that the voids grow during the diffusion process. The voids are formed on the faster diffusion side of the diffusion couple. The method can be extended to calculate the void grow during the diffusion and electric field in solder joints.

ACKNOWLEDGEMENTS

This work has been supported by the National Science Centre (NCN) in Poland, decision number 2013/09/B/ST8/00150.

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WPŁYW POŁOŻENIA PŁASZCZYZNY KIRKENDALLA ORAZ EFEKTU FRENKLA PODCZAS PROCESU DYFUZJI WZAJEMNEJ

Streszczenie

W artykule zaprezentowana została metoda pozwalająca na wykonanie obliczeń oraz pokazanie wpływu efektów Kirkendalla oraz Frenkla podczas procesu dyfuzji wzajemnej. Metoda dwu-prędkości jest uogólnieniem metody Darkena. Pokazano, że metoda pozwala na poprawne wyznaczenie położenia płaszczyzny Kirkendalla jak również określenie promienia pustki powstającej podczas procesu transportu masy.

Received: August 7, 2014
Received in a revised form: December 5, 2014
Accepted: December 11, 2014