

Formation of Chemical Compound Layer at the Interface of Initial Substances A and B with Dominance of Diffusion of the A Atoms

Pavlo Selyshchev, Samuel Akintunde

Abstract—A theoretical approach to consider formation of chemical compound layer at the interface between initial substances *A* and *B* due to the interfacial interaction and diffusion is developed. It is considered situation when speed of interfacial interaction is large enough and diffusion of *A*-atoms through *AB*-layer is much more than diffusion of *B*-atoms. Atoms from *A*-layer diffuse toward *B*-atoms and form *AB*-atoms on the surface of *B*-layer. *B*-atoms are assumed to be immobile. The growth kinetics of the *AB*-layer is described by two differential equations with non-linear coupling, producing a good fit to the experimental data. It is shown that growth of the thickness of the *AB*-layer determines by dependence of chemical reaction rate on reactants concentration. In special case the thickness of the *AB*-layer can grow linearly or parabolically depending on that which of processes (interaction or the diffusion) controls the growth. The thickness of *AB*-layer as function of time is obtained. The moment of time (transition point) at which the linear growth are changed by parabolic is found.

Keywords—Phase formation, Binary systems, Interfacial Reaction, Diffusion, Compound layers, Growth kinetics.

I. INTRODUCTION

DIFFUSION of *A* and *B*-atoms and interaction between them results in the formation of a continuous solid compound layer $A_{va}B_{vb}$ at the interface of two mutually immiscible phases *A* and *B* [1]. The *AB*-layer growth is due to two processes: (1) diffusion of atoms (ions) of the reactants across the layer bulk and (2) subsequent chemical transformations (chemical reaction) taking place at the layer interfaces with the participation of diffusing atoms of one of two components and the surface atoms of another component. The compound layer formed is single-phase. Let us consider the main features of layer-growth kinetics, which are the same for compounds of whatever chemical nature (oxides, intermetallics, silicides, salts, etc.).

Usually in the early stage of the reaction-diffusion process, the layer growth kinetic is governed by linear law and the final stage is controlled by parabolic law [1], [2]. In each case, the layer growth is related to reaction time. The parabolic law relates the square of layer growth to the reaction time. The layer growth during the diffusion process is in the range of few tens of micrometers while that of chemical controlled

process is in few hundred of nanometers [2].

Theoretical description of a chemical reaction in the contact area between two solids, must take into account both the kinetics of chemical reaction and diffusion of reagents [1], [3]. This is due to the fact that chemical reactions occur in the interface solid phase (reactants and products) are characterized by enhanced reactivity. The feature of the process is the relationship of the diffusion fluxes and rates of chemical reactions.

Indeed, the rate of chemical transformation is supported by the diffusion of reactants through the layer of reaction product. The diffusion rate is inversely proportional to the layer thickness, and the layer growth rate is proportional to the quantity of material penetrating there through reagents. The calculation of diffusion, which is well described by Fick's law, does not cause difficulties, but the rate of chemical reactions are complex functions of reactant concentrations.

An exhaustive description of the growth of the product layer holds for simple dependencies of the reaction rate on the concentration of the reactants [1], [3]. If, by analogy with the gas mixture, it is assumed that the reaction rate is proportional to the product of the reactant concentrations, the growth layer described quadratic dependence of time. In this case, the resulting quadratic dependence is close to linear only for short times. This does not agree with the experimental data.

Unlike the motion of atoms in gas, the motion of atoms in a solid are strongly correlated; chemical transformation is accompanied by the formation of the crystal lattice of the reaction product. Therefore, the rate of chemical transformation does not equal to the product of the concentrations (the probability of independent events). The reaction rate depends not only on the concentration of reagents, but also the ratio between them.

In this paper, we approximate the complex dependence of the reaction rate on the concentrations as follows. In the case of an excess of one of the reactants, the reaction rate does not depend on its concentration. Otherwise, it is proportional to the product of the reactant concentrations.

As example of using of our model we consider the interfacial reaction and diffusion in binary *Si-Pd* system and estimate the size of the grown layer and the corresponding reaction time taking into account the experimental data of some investigators on *Si-Pd* systems [4]-[7]. The estimates obtained are compared with the experimental results. The model developed here can be also applied in any binary systems, to find the layer thickness and the corresponding

P. Selyshchev is with the Department of Physics University of Pretoria Private bag X20 Hatfield 0028 South Africa (phone: 012-420-6641; fax: 012-362-5288; e-mail: pavel.selyshchev@up.ac.za).

S. Akintunde is a PhD student of Physics, at University of Pretoria Private bag X20 Hatfield 0028 South Africa (e-mail: jesutofunmi123@yahoo.com).

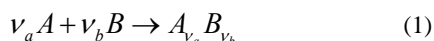
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reaction time at the transition point, in which the linear growth law is changed by parabolic one.

II. MODEL AND BASIC EQUATIONS

Let us consider layer of A -atoms with concentration n_a^0 and layer of B -atoms with concentration n_b^0 which have general surface. Axis Ox is perpendicularly to the surface and point O corresponds to the surface. A -atoms occupy space $x < 0$ and B -atoms occupy space $x > 0$.

There is chemical reaction between A and B atoms



The layer of AB compound is formed as result of this reaction. The thickness of the AB -layer is h . The h is a function of time $h=h(t)$; at initial moment the thickness of AB -layer is equal to zero, $h(0)=0$. Let A -atoms be the dominant diffusing species and B -atoms be practically immobile. In this case the chemical reaction occurs on surface between AB and B -layers and AB -layer is formed in region $0 < x < h(t)$. A -atoms diffuse from A -layer to surface of B -atoms through the AB -layer. Change of concentration of A -atoms (n_a) in AB -layer ($0 < x < h(t)$) is described by equation

$$\frac{\partial n_a}{\partial t} = D_a \frac{\partial^2 n_a}{\partial x^2} \quad (2)$$

Equation is valid for $0 < x < h(t)$ with boundary conditions $n_a(0) = n_a^0$ and flux of A atoms at $x=h(t)$ is equal to speed of reaction $J_a \equiv -D_a \nabla n_a = v_a \varphi(n_a(h))$ taking into account that $n_b(h) = n_b^0 = \text{const}$. At initial time ($t=0$) the AB -layer is absent and $h(t=0)=0$.

Since v_a of A -atoms are needed to form one AB -compound the growth of AB -layer is described by equation

$$\frac{dh(t)}{dt} = V_{ab} \varphi(n_a(h(t))) \quad (3)$$

Here V_{ab} is volume a molecule (structural component) of AB -compound. For stationary diffusion

$$n_a(x) = Cx + n_a^0 \quad (4)$$

where according the second boundary condition C satisfies equation

$$-D_a C = v_a \varphi(C h(t) + n_a^0) \quad (5)$$

Since $h(t)$ is a function on time the C is function of time too, ($C=C(t)$). Equation (5) allows obtaining C and together with (3) to obtain closed equation for growth of AB -layer. It is clear now the speed of chemical reaction (function φ) drives speed of AB -layer growth. For example when the speed of a reaction is proportional to product of reagent concentrations like for

reaction of gases, parabolic law takes place. When the speed of a reaction is constant, linear law takes place.

Experimental results show that at the beginning AB -layer grows as linear function and then as parabolic one. To obtain needed dependence we must assume that at the beginning the speed of reaction does not depend on concentration of A -atoms. It can be connected with excess of A -atoms or with nondiffusive flux of A -atoms. Let at the initial time concentration of A -atoms in A -layer be much more concentration of B -atoms ($v_a n_a^0 \gg v_b n_b^0$). Then AB -layer grows and concentration of A -atoms near surface between AB and B -layers decreases. Thus the speed of the reaction is $\varphi = \gamma n_b^0$ when $v_a n_a^0 > v_b n_b^0$ and $\varphi = \gamma n_b^0 n_a(h(t))$ when $v_a n_a^0 < v_b n_b^0$. As result the growth of AB -layer has two stages and the formation of AB -layer has also two stages. At the moment $t=t_c$ the first stage is changed by the second one. Let $h(t_c)=h_c$.

III. RESULTS AND DISCUSSION

To find t_c and h_c consider kinetic of the first stage of the AB -layer formation. For this stage $t < t_c$ and $h < h(t_c)=h_c$. The boundary conditions for the first stage are $n_a(0) = n_a^0$ and $J_a|_{x=h} \equiv -D_a \nabla n_a = v_a \gamma n_b^0$.

Concentration of A atoms inside the AB -layer is

$$n_a(x) = -\frac{v_a \gamma n_b^0}{D_a} x + n_a^0 \quad (6)$$

The AB -layer formation occurs as result of chemical reaction near surface between AB and B -layers and change of its thickness is equals to volume of produced AB -compound per surface unit. Than the equation for change of AB -layer's thickness is

$$\frac{dh(t)}{dt} = \gamma V_{ab} n_b^0 \quad (7)$$

Thus there is linear growth

$$h(t) = \gamma V_{ab} n_b^0 t \quad (8)$$

Let us define t_c as the moment of time at which $n_a(h_c) = v_b n_b^0 / v_a$. Then

$$h_c = h(t_c) = \gamma n_b^0 V_{ab} t_c = \frac{D_a (v_a n_a^0 - v_b n_b^0)}{v_a^2 \gamma n_b^0} \quad (9)$$

and

$$t_c = \frac{D_a (v_a n_a^0 - v_b n_b^0)}{v_a^2 \gamma^2 V_{ab} (n_b^0)^2} \quad (10)$$

For the second stage $t > t_c$ and $h > h(t_c) = h_c$. The boundary conditions are $n_a(0) = n_a^0$ and $J_a|_{x=h} \equiv -D_a \nabla n_a = v_a \gamma n_b^0 n_a(h)$. Concentration of A -atoms inside the AB -layer is

$$n_a(x) = -\frac{v_a \gamma n_a^0 n_b^0 x}{D_a + v_a \gamma n_b^0 h(t)} + n_a^0 \quad (11)$$

The growth of the AB -layer is now described by the nonlinear equation

$$\frac{dh(t)}{dt} = \frac{v_a \gamma V_{ab} n_a^0 n_b^0}{1 + v_a \gamma n_b^0 h(t) / D_a} \quad (12)$$

Taking into account that $h = h(t_c) = h_c$ when $t = t_c$ we obtain the thickness of the AB -layer grows as square of time.

$$h(t) = A \left[-1 + \left((1+B)^2 + BB(t-t_c) \right)^{\frac{1}{2}} \right] \quad (13)$$

where

$$A = \frac{D_a}{v_a \gamma n_b^0}$$

$$B = \frac{v_a \gamma n_b^0 h_c}{D_a}$$

$$BB = \frac{2V_{ab} n_a^0 (v_a \gamma n_b^0)^2}{D_a}$$

The formation of AB -layer at the interface of initial substances A and B was obtained with assumption about dominance of diffusion of the A -atoms. Its generalization to the case of diffusion of two (A and B) of the reagents is not difficult.

In framework of our model the AB -layer grows at the beginning as linear function of time (first stage) and then as of parabolic one (second stage). During the first stage concentration of A -inside AB -layer decreases vs. depth with constant rate starting from n_a^0 . This distribution does not change with time. During second diffusion-controlled stage the distribution of A -atoms becomes no stationary. Distribution of A -atoms is described by linear function of thickness that becomes more and more sloping with time and the concentration grows to n_a^0 .

The critical time t_c increases together with an increase of the diffusion coefficient, the excess of A -atoms, and with a decrease of rate of chemical reaction. The critical thickness grows proportional to the critical time with the rate of the growth that is equal to reaction rate.

As example let us estimate parameters of silicide layer formation in the binary $Si-Pd$ system. The growth of silicide layer at annealing temperature of 523K until critical thickness (263nm) lasts 439 s. When temperature grows up to 573K the

silicide thickness at transition point is 350nm at a corresponding critical reaction time of 1750 s. These results agree fairly well with the experimental values obtained in [8].

IV. CONCLUSION

The model presented here allows explaining peculiarity of formation of AB chemical compound layer at the interface of initial substances A and B .

It is shown that growth of the thickness of the AB -layer determines by dependence of chemical reaction rate on reactants concentration. In special case the thickness of the AB -layer can grow linearly or parabolically depending on that which of processes (interaction or the diffusion) controls the growth. It is obtained a value of critical time when linear dependence is changed by parabolic one. The critical thickness of AB -layer which corresponds critical time is determined too.

Obtained results can be used for any binary systems with chemical interaction and diffusion. They can address any problem that has to do with the growth of layer at the boundary between interfacial reaction and diffusion process in any binary system.

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