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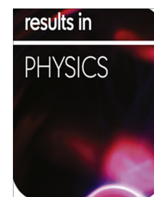

Kinetics of growth of thin-films of Co_2Si, Ni_2Si, WSi_2 and VSi_2 during a reactive diffusion process

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A theoretical approach is developed which describes the growth kinetics of thin films of near noble metal silicide (especially of cobalt silicide (Co_2Si) and nickel silicide (Ni_2Si)) and refractory metal silicide (particularly of tungsten disilicide (WSi_2) and vanadium disilicide (VSi_2)) at the interfaces of *metal–silicon* system. In this approach, metal species are presented as *A*-atoms, silicon as *B*-atoms, and silicide as *AB*-compound. The *AB*-compound is formed as a result of chemical transformation between *A*- and *B*-atoms at the reaction interfaces *A*/*AB* and *AB*/*B*. The growth of *AB*-compound at the interfaces occurs in two stages. The first growth stage is reaction controlled stage which takes place at the interface with excess *A* or *B*-atoms and the second stage is diffusion limited stage which occurs at both interfaces. The critical thickness of *AB*-compound and the corresponding time is determined at the transition point between the two growth stages. The result that follows from this approach shows that the growth kinetics of any growing silicides depends on the number of kinds of dominant diffusing species in the silicide layer and also on their number densities at the reaction interface. This result shows a linear-parabolic growth kinetics for WSi_2, VSi_2, Co_2Si, and Ni_2Si and it is in good agreement with experiment.

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Introduction

The thin film of near noble and refractory metal silicides gained wide attention in solid state reaction because of their applicability as low resistance contacts, gate electrodes, and interconnect materials in integrated circuit technology [1–3].

A number of works in the literature report the formation and growth kinetics of these silicides [4–7]. Silicide formation can be explained from two approaches: diffusion approach (which is considered as the conventional approach) and physicochemical approach (alternative approach to the former). From diffusion approach silicides are formed as a result of intermixing of silicon with metal species after the diffusion of either silicon atoms into the metal layer or metal atoms into the silicon layer. This intermixing is initiated by heat treatment process. Diffusion approach usually leads to loss of reaction controlled stage [8] due to lack of consideration for chemical reaction between metal and silicon species.

Unlike diffusion approach, physicochemical approach incorporates two processes: diffusion and chemical reaction. It describes metal and silicon layers as two immiscible layers with interface (s) separating them. Chemical reaction takes place between silicon and metal atoms at the interface(s). The metal atoms or silicon atoms or both are brought to the interface(s) by means of diffusion. This approach creates room for the possibility of accounting for chemical reaction contributions to the silicide growth during reaction controlled stage.

It is shown that the growth kinetics of silicides of near noble metals (for example, palladium, platinum, and cobalt) obey parabolic law [4–6] and the dominant atomic species in the first silicide phase (such as Ni_2Si, Pt_2Si, and Co_2Si) are unanimously identified as metal [2,7]. Metal species are reported as dominant species because the silicide is a metal rich silicide. However, there are different viewpoints on dominant species in the Pd_2Si phase [9–13].

In refractory metal silicides (such as molybdenum disilicide ($MoSi_2$), titanium disilicide ($TiSi_2$), tungsten disilicide (WSi_2), and vanadium disilicide (VSi_2)) the dominant diffusing species is reported as silicon [2–7]. This is due to the richness of this silicide phase in silicon. There are different growth kinetics exhibited by silicide in this phase [2,6–7]. For instance, in VSi_2 and WSi_2 growth kinetics are described as linear and parabolic, in $TiSi_2$ it's delineated as parabolic, and in $MoSi_2$ and $CrSi_2$ it is shown to be linear.

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In this paper, we present a model that describes the growth kinetics of the AB-compound layer based on the first approximation of reaction rate as product of reactant number densities. This approximation is in accord with mass action law. The speed of growth is proportional to reaction rate during the reaction controlled and diffusion limited stages. The AB-compound layer growth kinetics that follow from this approach show that the growth behavior of the growing layer can be explained from the viewpoint of the number of kinds of atomic species actively diffusing into the AB-layer during their formation process.

Model and result

Suppose that the A-layer occupies space $x < 0$ and the B-layer occupies space $x > 0$ in A–B system.

At time $t > 0$ heat treatment process commences in A- and B-layers. The interfaces A/AB and AB/B spatially separates A- and B-layers. A-atoms diffuse from the A-layer via AB-layer into interface AB/B and B-atoms diffuse from the B-layer via AB-layer into interface A/AB. At interface AB/B, diffuse A-atoms chemically react with surface B-atom to form AB-compound. Likewise, at interface A/AB, diffuse B-atoms interact chemically with surface A-atoms to form additional AB-compound. The AB-layer occupies space from $x = -h_a$ to $x = h_b$. The thickness of the compound layer formed at interface A/AB is denoted by $h_a(t)$ and at interface AB/B by $h_b(t)$. The total thickness of the AB-compound layer formed between A- and B-layers is designated by $h(t)$; $h(t) = h_a(t) + h_b(t)$ where h_a, h_b, and h are function of time t.

The rate of chemical transformation at interfaces of solid layers depends on number densities of A and B atoms. If there are excess A- or B-atoms at the interface, the rate of reaction remains the same with change of number density of A-or B-atoms [14]. On the other hand if number densities of A- and B-atoms are approximately equal ($\upsilon_a n_a \approx \upsilon_b n_b{}^0$ or $\upsilon_b n_b \approx \upsilon_a n_a{}^0$), then the rate of AB-compound formation can be represented in the first approximation as product of A- and B-atomic number densities. Where $n_a{}^0$ and $n_b{}^0$ are number densities of A- and B-atoms in A- and B-layers respectively, n_a and n_b are number densities of A- and B-atoms inside the AB-layer, υ_a and υ_b are stoichiometric coefficients of A- and B-atoms.

Thus the rate of chemical reaction between A- and B-atoms, at reaction interfaces A/AB and AB/B can be approximately expressed in two stages as follows:

$$R_a = \begin{cases} \gamma (n_a^0)^2 = const & \upsilon_b n_b(-h_a(t)) \geqslant \upsilon_a n_a^0 \\ \gamma n_a^0 n_b(-h_a(t)) & \upsilon_b n_b(-h_a(t)) \leqslant \upsilon_a n_a^0 \end{cases}$$
$$R_b = \begin{cases} \gamma (n_b^0)^2 = const & \upsilon_a n_a(h_b(t)) \geqslant \upsilon_b n_b^0 \\ \gamma n_b^0 n_a(h_b(t)) & \upsilon_a n_a(h_b(t)) \leqslant \upsilon_b n_b^0 \end{cases} \tag{1}$$

where $n_b(-h_a(t))$ and $n_a(h_b(t))$ are the number densities of B- and A-atoms which diffuse into reaction interfaces A/AB and AB/B, γ is the reaction rate constant, R_a and R_b are the reaction rates at interfaces A/AB and AB/B.

Due to this approximation, the growth of the AB layer can be described in two stages. The first growth stage occurs when there are excess of one kind of diffusing atoms, for example, excess A-atoms at interface AB/B or excess B-atoms at interface A/AB and the second growth stage takes place when there are no excesses of any kind of atoms at the corresponding interfaces.

The growth rate of the AB-layer is determined by both diffusion of A- and B-atoms inside the AB-layer and rate of reaction at interfaces:

$$\frac{dh}{dt} = \frac{dh_a}{dt} + \frac{dh_b}{dt} = V_{ab}\left(\gamma n_a^0 n_b(-h_a(t)) + \gamma (n_b^0)^2\right). \tag{2a}$$

Eq. (2a) holds only if A-atoms are in excess at interface AB/B or

$$\frac{dh}{dt} = \frac{dh_a}{dt} + \frac{dh_b}{dt} = V_{ab}\left(\gamma (n_a^0)^2 + \gamma n_b^0 n_a(h_b(t))\right). \tag{2b}$$

Eq. (2b) holds only if B-atoms are in excess at interface A/AB, where V_{ab} is the volume of one molecule of AB-compound.

Suppose that all A-atoms at AB/B interface and all B-atoms at A/AB interface reacted at once. Therefore the growth of the AB-compound layer is determined by flux of A-atom toward the B-layer and flux of B-atom toward the A-layer. Thus we consider the diffusion of A- and B-atoms inside the AB-compound layer.

Diffusion of A- and B-atoms inside the AB-layer is described by Fick's second law under a stationary condition thus:

$$D_{a(b)} \frac{\partial^2 n_{a(b)}(x)}{\partial x^2} = 0. \tag{3}$$

With corresponding boundary conditions:

$$J_a(h_b(t)) = -D_a \nabla n_a(x) = \upsilon_a \gamma n_b^0 n_a(h_b(t)); \quad J_b(-h_a(t)) = -D_b \nabla n_b(x) = \upsilon_b \gamma n_a^0 n_b(-h_a(t));$$

$$n_a(-h_a(t)) = n_a^0; \quad n_b(h_b(t)) = n_b^0.$$

where J_a and J_b are fluxes of A- and B-atoms, D_a and D_b are diffusivities of A- and B-atoms.

Solving Eq. (3) with boundary conditions for the first stage of layer growth (before critical time), we obtain an expression for the distribution of A- and B-atoms inside the AB-compound layer when A-atom is in excess at AB/B interface:

$$n_a(x) = -\frac{\gamma (n_b^0)^2}{D_a}(x + h_a) + n_a^0 \quad \text{and}$$
$$n_b(x,t) = \frac{\gamma n_a^0 n_b^0 \upsilon_b}{D_b + \gamma n_a^0 \upsilon_b h(t)}(x - h_b) + n_b^0 \tag{4a}$$

And for excess B-atoms at A/AB interface, the distribution of A- and B-atoms in the AB-layer is described by:

$$n_a(x,t) = \frac{\gamma n_a^0 n_b^0 \upsilon_a}{D_a + \gamma n_b^0 \upsilon_a h(t)}(x + h_a) + n_a^0 \quad \text{and}$$
$$n_b(x) = -\frac{\gamma (n_a^0)^2}{D_b}(x - h_b) + n_b^0. \tag{4b}$$

Number densities of A-atoms at interface AB/B and B-atoms at interface A/AB during the second growth stage are:

$$n_a(h_b(t)) = \frac{D_a n_a^0}{D_a + \gamma n_b^0 \upsilon_a h(t)} \quad \text{and}$$
$$n_b(-h_a(t)) = \frac{D_b n_b^0}{D_b + \gamma n_a^0 \upsilon_b h(t)}. \tag{5}$$

If there are excess A-atoms at reaction interface AB/B at time $\boldsymbol{t < t_c}$, ($\boldsymbol{t_c}$, is the critical time), the AB-layer at this interface grows under reaction controlled process and at A/AB interface the growth is diffusion limited and vice versa for excess B-atoms at interface A/AB; therefore, the relationship between time and layer thickness can be found by solving either Eq. (2a) or (2b)

$$t = \frac{h(t)}{\gamma V_{ab} (n_b^0)^2} - \frac{D_b \upsilon_a^2}{\gamma^2 \upsilon_b^3 V_{ab} (n_b^0)^3} \ln\left[\frac{\gamma n_a^0 n_b^0 \upsilon_b^2 h(t)}{D_b (n_a^0 \upsilon_a + n_b^0 \upsilon_b)} + 1\right] \tag{6a}$$

or

$$t = \frac{h(t)}{\gamma V_{ab} (n_a^0)^2} - \frac{D_a \upsilon_b^2}{\gamma^2 \upsilon_a^3 V_{ab} (n_a^0)^3} \ln\left[\frac{\gamma n_a^0 n_b^0 \upsilon_a^2 h(t)}{D_a (n_a^0 \upsilon_a + n_b^0 \upsilon_b)} + 1\right]. \tag{6b}$$

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