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The influence of surface defects on the pinhole formation in silicide thin film

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Abstract. The growth of the CoSi layer was considered within the framework of the grain boundary diffusion model. The time dependences of the temperature due to the exothermic reaction of silicide formation as well as the dependences of the CoSi layer thickness were calculated for various values of the reaction activation energy. It was shown that the heat release at high reaction velocities can lead to the considerable increase of the temperature up to melting of the silicide and covering Co layers. The model of pinhole formation in cobalt silicide films was proposed on the basis of local melting in the reaction area at crystal defects of the silicon surface.

Keywords: formation of silicide, activation energy, zone of reacting, local melting, defects on surface.

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1. Introduction

Thin films of CoSi₂ have a wide application both in the semiconductor technology and for buffer layers to grow new materials such as high-temperature superconductors due to their good epitaxial and electrical properties [1-8]. However, the principal difficulty in obtaining films with needed properties remains the problem of film roughness (formation of pinholes) [2]. To solve this problem, considerable efforts were applied but the reason of origin of this pinhole formation has not been found till now. It was shown that pinhole formation was promoted by decreasing the surface and interface energies [3]. On the other hand, experimental investigations show that the kinetic processes are important in this case [2]. The supposition was made that some diffusion channels are activated in the film, permitting a significant mass transport to the surface during the rapid thermal process [2]. Moreover, the density of pinholes correlates with the density of structural defects on the Si surface [1]. These experimental data allow to suppose that structural defects play a considerable role in the pinhole formation. Due to the high diffusion coefficient inside the defect and the high reaction ability of atoms on the walls, a considerable increase of the layer growth velocity can be expected. Besides, increasing the temperature owing to exothermic reactions of silicide formation have to be taken into account. Investigations show that Co₂Si, CoSi and CoSi₂ layers can be formed in silicide [4]. Formation of these chemical compositions is an exothermic reaction with a considerable heat effect [5]. At high diffusion coefficients and velocities of the chemical

reaction, this heat release can result in increase of the temperature in the silicide layer.

In this work, we describe the formation of the silicide layer in a two-dimensional structural defect such as a boundary of a grain or a dislocation. We show that Co diffusion into the defect leads to growing the heat release and to melting both the silicide and Co layers due to the low activation energy for the silicide formation reaction. The melted alloy is extracted by capillary forces of spills onto the surface of the Co film and crystallizes creating CoSi₂. This process of the pinhole formation can exist when the thickness of the Co layer reaches up to 10 nm.

2. The model

The investigation of nucleation stage of the cobalt silicide phases revealed the local formation of the crystallites of the silicide phase surrounded by the unreacted Co film (Fig. 1a, b, d, e). The local origin of the Co silicide phases was found in structural defects on the silicon surface at the initial stage of the Co-Si interaction [1]. The coalescence of the lateral cobalt silicide crystallites is supposed to be the preferable mode of the growth during the silicide layer formation on the Si surface with high density of structural defects (Fig. 1d, e). Therefore, account must be taken of the diffusion processes into the crystal defects at the Co/Si interface for the adequate description of the silicide phase growth. The Fisher model [9-11] allows to describe a diffusion process in two-dimensional defects such as the grain boundaries or dislocations. In the

frames of this model, the defect is considered as the plate with high diffusion coefficient which is implanted between boundaries of the bulk Si material (Fig. 2). The Co atoms penetrate into the defect (plate) from the top thin Co film on the silicon and forming the Co-Si mixture. For simplicity, suppose that the chemical reaction $\text{Co} + \text{Si} = \text{CoSi}$ occurs only at the interface between Co-Si mixture and silicon inside the plate; the opposite Si atom flux in the top Co film is neglected. In the present model, the system is instantly heated from the room temperature up to $T_0 = 1000$ K when the Co + Si chemical reaction begins.

According to the Fisher model, for the diffusion of Co atoms into the dislocation the displacement of atoms x (Fig. 2) is proportional to the fourth root of time t :

$$x = At^{1/4},$$

$$A = \sqrt{\frac{\delta D' \sqrt{\pi}}{2\sqrt{D}}}, \quad (1)$$

where δ is the thickness of the plate, D is the Co diffusion coefficient in the bulk material (Si). D' is the diffusion coefficient of Co atoms into the plate as well as into the Co-Si mixture formed into the plate. As the silicide is formed between grains it is assumed that $D'/D \sim 10^4 \dots 10^5$ [11].

The diffusion time of Co atoms between the Co/Co-Si and Co-Si/Si interfaces in Fisher's model is determined from Eq. (1). The full time of the layer growth is the sum of the time of diffusion and the time of the chemical reaction:

$$t = \frac{x^4}{A^4} + \frac{x}{v'}, \quad (2)$$

where v' is the velocity of the chemical reaction Co + Si after Co atom crossed the boundary between Co-Si mixture and Si. The thickness of the layer after the arbitrary time t can be found as the root of the fourth degree from Eq. (2):

$$x^4 + \frac{A^4}{v'} x - A^4 t = 0. \quad (3)$$

The velocity of the layer growth V is also found from equation (2) by differentiation:

$$V = \frac{dx}{dt} = \left(\frac{4x^3}{A^4} + \frac{1}{v'} \right)^{-1}. \quad (4)$$

The limiting cases of (4) are $V = v'$ if $4x^3 v' \ll A^4$ and $V = \frac{a^4}{4x^3}$ at $4x^3 v' \gg A^4$. The change of these cases

occurs when $x' \approx \sqrt[3]{\frac{A^4}{4v'}}$. Comparing this expression with the characteristic thickness x_1 of changing the growth

mechanisms, which follows from the usual diffusion [12-15] $x_1 \approx \frac{D}{v}$ (v is the constant of layer growth in the kinetic regime for the homogeneous layer), we can see that at large v and v' the first expression allows to get much more thickness than in the usual case. For example, at $D \approx 10^{-14} \text{ m}^2/\text{s}$, $\delta \approx 10^{-8} \text{ m}$ and $D' \approx 10^{-10} \text{ m}^2/\text{s}$ we obtain $A \approx 3 \cdot 10^{-6}$ that at $v' \approx 10^{-2} \text{ m/s}$ gives $x' \approx 1.3 \cdot 10^{-7} \text{ m}$ instead of $x_1 \approx 1 \cdot 10^{-12} \text{ m}$ at the same value of v . The high velocities of the chemical reaction can exist due to the dependence of the activation energy on the density of the surface charge [12] which can be high within the boundaries of the structural defects or Si cracks.

Let us estimate the temperature of the CoSi layer during the exothermic reaction $\text{Co} + \text{Si} = \text{CoSi}$ at the CoSi/Si interface. Consider the case when this interface has the width δ and is placed between the boundaries of the defect. Assuming a low thickness of Co layer above the defect ($\sim 1 \text{ nm}$) and supposing that $t \leq 10^{-7} \text{ s}$ (the distance of temperature diffusion $x'' = 2\sqrt{at}$ is lesser than the thickness of the Si sample (a is the temperature conductivity coefficient, $a \approx 10^{-5} \text{ m}^2/\text{s}$) and we can consider the quasi-one-dimensional case of heating the edge of the Si half-infinite rod. The functional solution of the thermal conductivity equation in this case gives the temperature on distance r from the CoSi/Si interface at chosen moment τ [16]:

$$T(r, \tau) = T_0 + \frac{2}{K_\varepsilon} \int_0^\tau \frac{q[T(0, z)] e^{-\frac{r^2}{4a(\tau-z)}}}{\sqrt{\pi(\tau-z)}} dz, \quad (5)$$

where $K_\varepsilon = \sqrt{\lambda_2 c_2 \rho_2}$, with the thermal conductivity λ_2 , the heat capacity c_2 and density ρ_2 of Si; $q[T(0, z)]$ is the heat flux in J/m^2 on the CoSi/Si interface due to the exothermic reaction:

$$q[T(0, \tau)] = \tilde{Q} \rho_1 V(T, \tau), \quad (6)$$

ρ_1 is the concentration of Co at the interface, \tilde{Q} is the heat effect of the reaction. The temperature at the interface can be obtained from this relation:

$$T(0, \tau) = T_0 + \frac{2}{K_\varepsilon} \int_0^\tau \frac{q[T(0, z)]}{\sqrt{\pi(\tau-z)}} dz. \quad (7)$$

The change of the factor $\frac{r^2}{4a\tau}$ is small, and further we

will suppose that the interface does not move in the process of the reaction. Then, we can solve the system (3), (4), (6), (7) using the numerical method proposed in [17, 18] for $\tau_{m-1} < z < \tau_m$:

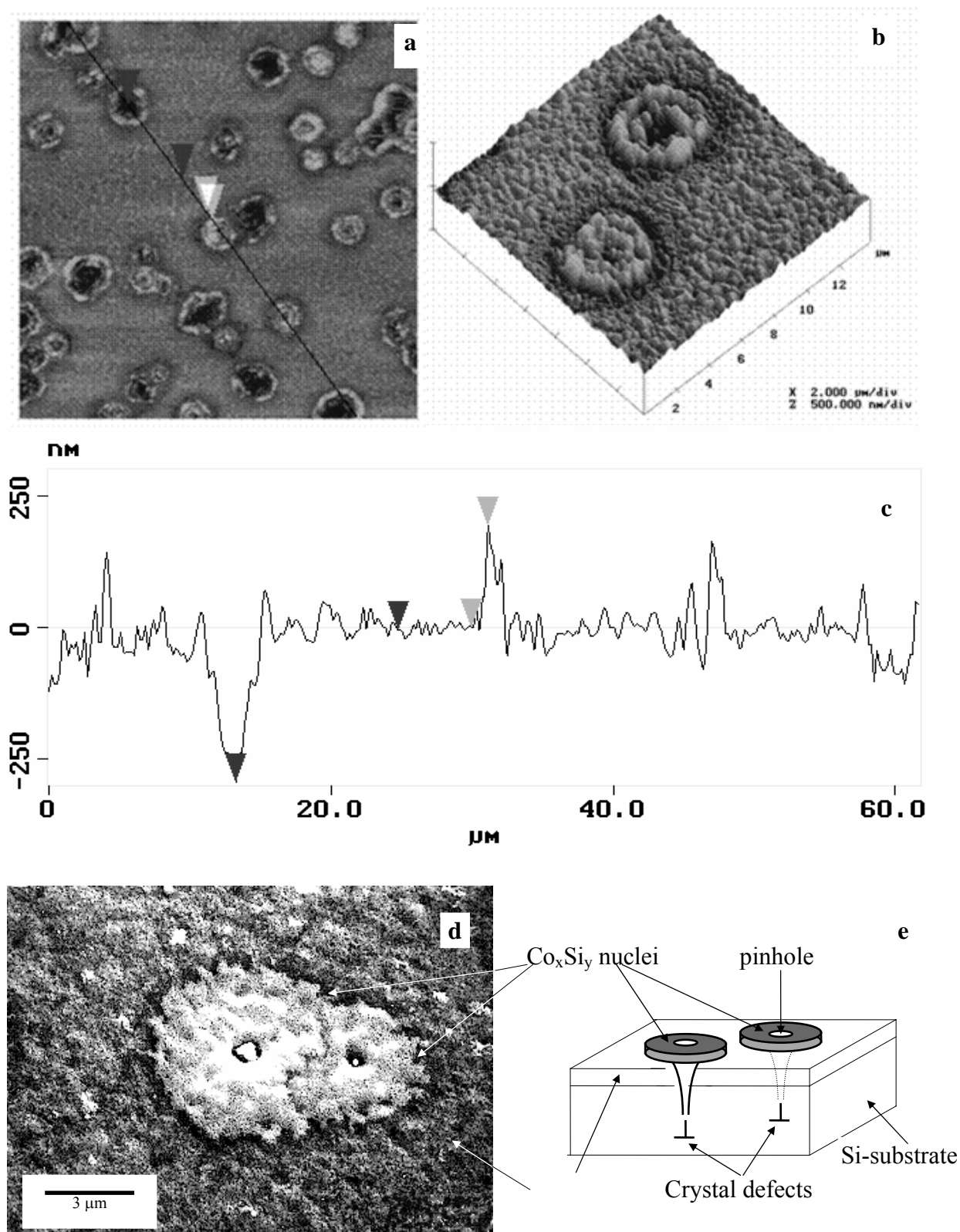


Fig. 1. AFM images (a, b), surface profile (c) and SEM image (d) for the Co/Si structure after vacuum annealing at 873 K. The scheme of the lateral silicide crystallites and pinholes formation (e).

$$T(0, \tau_m) = T_0 + \frac{2}{K_\varepsilon} \int_0^{\tau_{m-1}} \frac{q [T(0, z)]}{\sqrt{\pi(\tau-z)}} dz + \frac{2q [T(0, \tau_{m-1})]}{K_\varepsilon} \int_{\tau_{m-1}}^{\tau_m} \frac{1}{\sqrt{\pi(\tau-z)}} dz. \quad (8)$$

The temperature dependence of the velocity of layer growth is determined by the temperature dependences of the velocity constants

$$v = v_0 e^{-\frac{U_r}{kT}}, \quad v' = v'_0 e^{-g \frac{U_r}{kT}} \quad (9)$$

and coefficients of diffusion:

$$D = D_0 e^{-\frac{U_d}{kT}}, \quad D' = D'_0 e^{-\frac{U_{def}}{kT}}, \quad (10)$$

where v_0 , v'_0 , D_0 , D'_0 are pre-exponential factors, U_r is the activation energy of the reaction, U_d is the diffusion energy barrier, U_{def} is the energy barrier on the diffusion inside the defect, g is a factor $0 < g < 1$.

3. Results and discussion

The dependences $D(T)$ and $D'(T)$ were chosen as follows: $D = 10^{-5} e^{-\frac{1.9\text{eV}}{kT}}$, $D' = 10^{-5} e^{-\frac{3 \cdot 1.9\text{eV}}{5 \cdot kT}}$. The value $U_d = 1.9$ eV was experimentally found in [4] for the CoSi layer growth. Because there are no experimental data on the linear growth of layer in Co-Si

system, we used the expression $v' = 10^3 e^{-g \frac{1.9\text{eV}}{kT}}$, which at 1000 K and $g = 1$ gives the same velocity 10^{-7} m/s as was found experimentally for the system Ni-Si [19]. Using the factor g in this expression, we can model the change of the reaction activation energy due to the surface charge inside the defect. The initial temperature $T_0 = 1000$ K was chosen. The energy effect of the

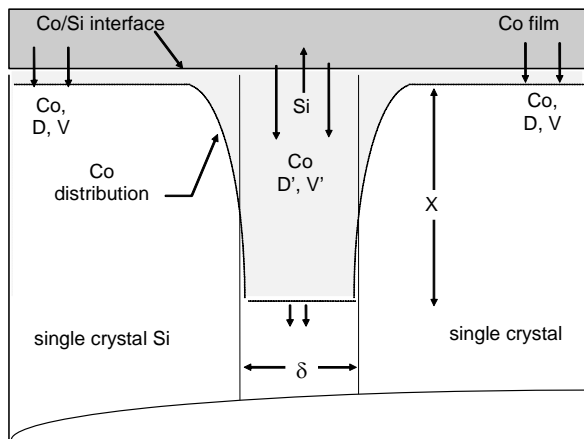


Fig. 2. Fisher's model for the diffusion of Co atoms into the dislocation and Co atom displacement x .

reaction \tilde{Q} is equal to $1.15 \cdot 10^6$ J/kg [5]. Dependences $T(0, t)$ are shown in Fig. 3 for various values of g and δ parameters. At small δ , the sufficient exponential growth of the interface temperature is reached only at great velocities (or small values of g , Fig. 3a, curves 1, 2). Then the temperature decreases due to the transfer to the diffusion growth of the layer. The decrease of the temperature obeys the $t^{-1/4}$ law accordingly to the chosen model. At larger values of g , the growth of the layer is slow (Fig. 3a, curves 3, 4), and the temperature decreases after peaking which does not reach the melting point of Si (~ 1696 K).

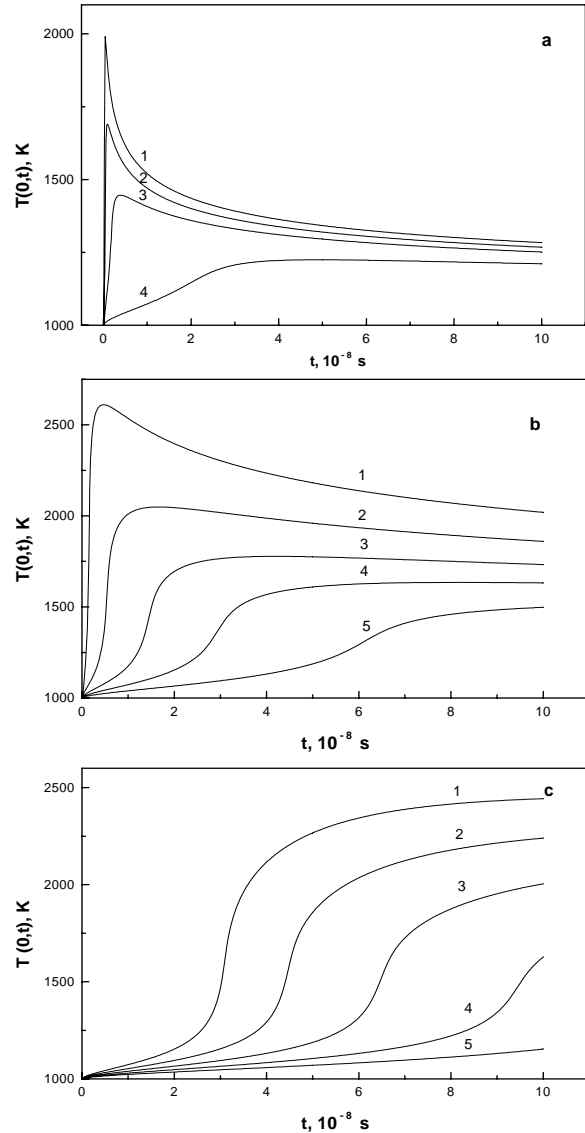


Fig. 3. Dependences of the CoSi/Si interface temperature $T(0, t)$ on time at various values of the parameters δ and g : a) $\delta = 10^{-8}$ m, $g = 0.18$ (1), 0.25 (2), 0.32 (3), 0.40 (4); b) $\delta = 10^{-7}$ m, $g = 0.30$ (1), 0.35 (2), 0.38 (3), 0.40 (4), 0.42 (5); c) $\delta = 5 \cdot 10^{-7}$ m, $g = 0.40$ (1), 0.41 (2), 0.42 (3), 0.43 (4), 0.44 (5). Lines denote the CoSi melting temperature $T_{\text{melt}} = 1737$ K.

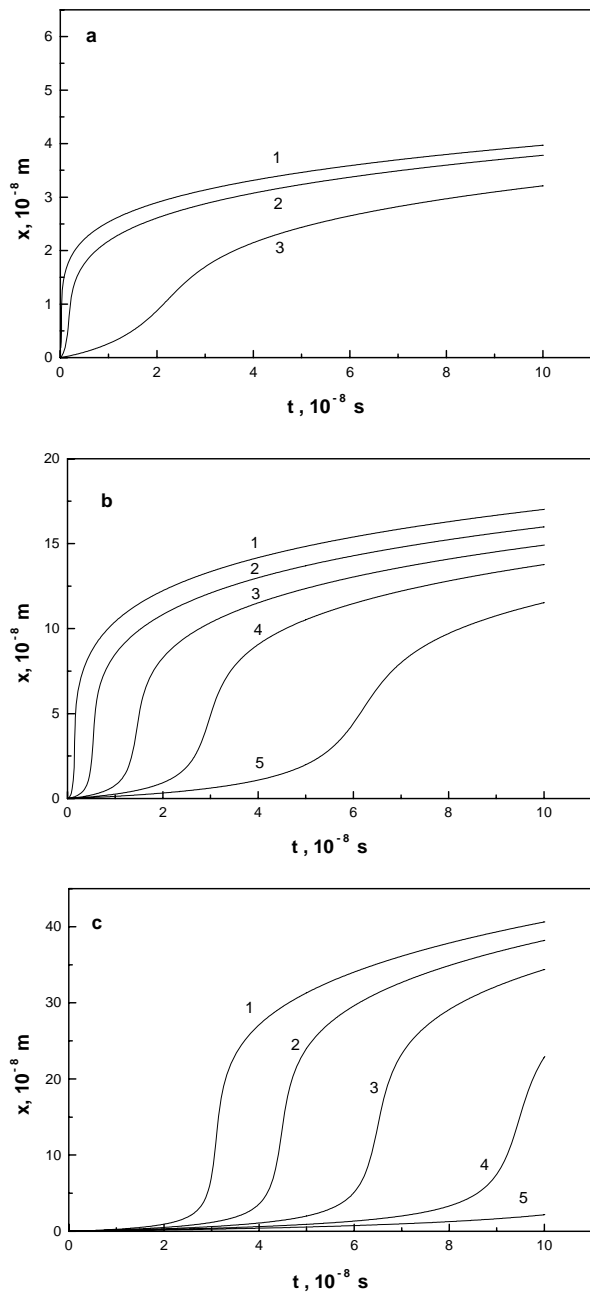


Fig. 4. Dependences of the CoSi layer thickness x on time at various values of the parameters δ and g : a) $\delta = 10^{-8}$ m, $g = 0.18$ (1), 0.32 (2), 0.40 (3); b) $\delta = 10^{-7}$ m, $g = 0.30$ (1), 0.35 (2), 0.38 (3), 0.40 (4), 0.42 (5); c) $\delta = 5 \cdot 10^{-7}$ m, $g = 0.40$ (1), 0.41 (2), 0.42 (3), 0.43 (4), 0.44 (5).

Increasing the parameter δ leads to increase of g at which the transition to high temperatures occurs (Figs 3b, c). The peak in the $T(t)$ dependences is shifted to large times and decrease of the temperature is moderate. The range of the parameters g in which the change of temperature regimes appears is reduced ($\Delta g \approx 0.2$ at $\delta = 10^{-8}$, $\Delta g \approx 0.12$ at $\delta = 10^{-7}$ and $\Delta g \approx 0.04$ at $\delta = 5 \cdot 10^{-7}$). The dependence of the thickness of the

CoSi layer x on time is shown in Fig. 4. At $\delta = 10^{-8}$ and small g , the thickness obeys the $t^{1/4}$ law, as it follows from Eq. (3) (Fig. 4a, curve 1). While the parameter g increases, the dependence $x(t)$ turns to the exponential growth at small t and $t^{1/4}$ growth at large t (Fig. 4a, curves 2, 3). The increase of the parameter δ leads to significant enhancement of the layer thickness (Fig. 4b, c).

The temperature of the interface can reach the melting temperatures of CoSi, Si and Co especially at larger values of $\delta = (1 \dots 5) \cdot 10^{-7}$ m (Fig. 3b, c). If the activation energy of the reaction is small, the temperature in the reaction area at the interface increases to very high values (Fig. 3b, curves 1-3) and decays with small decrement, which leads to melting of the CoSi layer during this time. Moreover, the Co layer with the thickness ~ 10 nm will be melted too, accordingly to the chosen model of heating of the half-infinite rod. At larger thickness of the Co layer, the exponent in the equation (5) has to be taken into account, and the temperature of the Co layer will be lower than that inside the defect. Note that, when the temperature of the reaction area will reach the melting points of Co, Si and CoSi phases, the chosen model will not describe heating the interface because the specific heats of melting do not take into consideration. It means that the temperature in the reaction area will not increase higher then in melting points or will decrease when the reaction will be finished. Calculations show that the melted CoSi is extracted by capillary forces on the Co surface for $\sim 10^{-7}$ s and after the process of crystallization CoSi_2 is formed on the top Co film. Thus, the melting of the CoSi layer arises during the exothermic reaction because of the small activation energy of the reaction in the structural defect and as a result of this local melting process the pinhole channel is formed.

4. Conclusions

We considered the growth of the cobalt silicide layer in the frames of the model of grain boundary diffusion. The diffusion front of Co in this model shifts obeying the $t^{1/4}$ law. Because of this law, the layer thickness can grow up to $0.1 \mu\text{m}$ at large velocities of the chemical reaction. This growth rate leads to a great extraction of heat due to the exothermic reaction at the CoSi/Si interface. We calculated the time dependence of the temperature of the reaction area at the interface CoSi/Si and found that for $t \sim (10^{-8} \dots 10^{-7})$ s the temperature can increase to the melting points of Co, Si and CoSi. The liquid alloy spills out on the top of the Co film and pinholes are formed into silicide film as well as lateral silicide crystallites.

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