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MISCELLANEOUS

MODELING OF DIFFUSION SYNTHESIS OF TITANIUM DISILICIDE

V. A. Pilipenko,[a] V. V. Molofeev,[b] V. N. Ponomar',[a] A. N. Mikhnyuk,[b] and V. A. Gorushko[a]

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An analytical model of diffusion synthesis of titanium disilicide, which describes the regularities of phase transitions in the titanium–silicon system depending on the temperature and the heat-treatment time, has been proposed.

The reproducibility and stability of silicide-formation processes ensuring required contacts with shallow *p–n* junctions and low resistances of interconnections of polysilicon gates play a large role in creation of high-quality, fast semiconductor devices of integrated circuits (ICs). The use of silicides on polycrystalline silicon in formation of gates and interconnections enables one to improve the quick operation, reproducibility, and reliability of circuits and decrease the delay time of the signal due to the lower resistance of current-conducting elements. A current-conducting system from titanium silicide on polysilicon ensures an improvement of about an order of magnitude in the properties as compared to polysilicon. An increased spread in electrophysical parameters and microstructural instability are observed at the present time because of the low controllability of the processes of silicide formation, which is caused by the inertia of long-duration heat treatments; this makes it difficult to use the data of the processes in the technology of submicron ICs.

Modeling of diffusion synthesis of titanium disilicide enables one to develop the process of its formation; this process ensures the stability and reproducibility of the parameters of the film, which is the necessary condition for bringing the submicron technology to a new level in microelectronics.

Since the process of diffusion synthesis of titanium disilicide of films is probabilistic in character, to model it we use the Monte Carlo method, namely, the single-particle method of modeling of transition of particles from one state to another. The essence of this method is that one considers the random movement of a single particle and then the averaging of movements of particles over the ensemble and time.

The process of modeling can be subdivided into three main steps: formation of a stochastic structure, modeling of the process of diffusion mixing, and statistical processing of the results.

The first step is preparatory; a structure of the film–substrate system on which we will carry out modeling is formed at this step. In our case this system is represented as follows. Since the titanium film is polycrystalline, it is subdivided into grains, whereas the substrate representing monocrystalline silicon is subdivided into cells, i.e., arbitrary regions which are subsequently the centers of formation of grains. The grains and cells in the initial structure have a rectangular shape of different size. Thus, the initial structure of the titanium–silicon system in section represents the form of a "brickwork."

In the second step of modeling, zones having different diffusion coefficients for Ti and Si were separated. These are the boundaries of the grains, their internal volume, and intergranular regions (Fig. 1). For the substrate it was assumed that the diffusion of silicon between the cells occurs without allowance for the boundaries and the mechanism of self-diffusion, and only the concentration of the diffusant in uniformly distributed silicon cells was taken into account.

[a]"Belmikrosistemy" Unitary Enterprise, "Integral" Scientific-Production Association, 12 Korzhenevskii Str., Minsk, 220064, Belarus; [b]Belarusian State University, Minsk, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 78, No. 3, pp. 185–189, May–June, 2005. Original article submitted February 12, 2004.

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The diffusion synthesis of the silicide phases of titanium in the silicon cells was assumed to be completed if the heating temperature of the sample ensured the heat of formation required for it and the concentration of titanium in silicon attained the corresponding value. An islet of the silicide phase was formed in this case in place of the cell.

In the process of modeling, for the titanium film we took into account that diffusion processes at the grain boundaries and in the intergranular regions are more intense than those in the volume. It is only titanium that diffuses from titanium grains, whereas the diffusion of titanium and silicon from the grains of different phases of silicides is absent; they are only accumulated. When the concentration of silicon in a titanium grain attains the required value, the corresponding phase of titanium disilicide is formed under certain temperature conditions.

Since current equipment makes it impossible to model the behavior of each atom, we made a number of assumptions in the model:

(a) the titanium film and the silicon substrate consist of individual atoms;

(b) each element represents an atomic group called a cluster, which participates in diffusion processes;

(c) clusters can be of two forms — those of silicon and titanium with different size.

Thus, a thin-film titanium–silicon system may be characterized by the following parameters: phase type (Si, Ti, Ti_5Si_3, TiSi, and $TiSi_2$), element composition (Si and Ti), coordinate, position of the cluster in the film (grain, volume, grain boundary, and intergranular boundary), and whether a given coordinate is occupied. Each active cluster participating in diffusion is described by the lifetime and the coordinate.

In the process of diffusion, clusters may move along the grain boundaries, in intergranular regions, and inside the grain volume (only for the clusters of titanium in a silicon single crystal). At the initial instant of time, we assume that there are no active atoms and they leave the corresponding volumes to reach the boundaries of the grains (titanium clusters) and cells (silicon clusters). The time of reaching the boundary is the lifetime in the volume. Each cluster may change to one vacant state according to the scheme shown in Fig. 2. The probabilities of these events are equal to

$$P_1 = \frac{1}{t_1 P_t}, \tag{1}$$

$$P_2 = \frac{1}{t_1 P_t} + \frac{1}{t_2 P_t}, \tag{2}$$

$$P_3 = \frac{1}{t_1 P_t} + \frac{1}{t_2 P_t} + \frac{1}{t_3 P_t}, \tag{3}$$

$$P_4 = \frac{1}{t_1 P_t} + \frac{1}{t_2 P_t} + \frac{1}{t_3 P_t} + \frac{1}{t_4 P_t}, \tag{4}$$

$$P_5 = \frac{1}{t_1 P_t} + \frac{1}{t_2 P_t} + \frac{1}{t_3 P_t} + \frac{1}{t_4 P_t} + \frac{1}{t_5 P_t}, \tag{5}$$

$$P_6 = \frac{1}{t_1 P_t} + \frac{1}{t_2 P_t} + \frac{1}{t_3 P_t} + \frac{1}{t_4 P_t} + \frac{1}{t_5 P_t} + \frac{1}{t_6 P_t}, \tag{6}$$

$$P_7 = \frac{1}{t_1 P_t} + \frac{1}{t_2 P_t} + \frac{1}{t_3 P_t} + \frac{1}{t_4 P_t} + \frac{1}{t_5 P_t} + \frac{1}{t_6 P_t} + \frac{1}{t_7 P_t}, \tag{7}$$

$$P_8 = \frac{1}{t_1 P_t} + \frac{1}{t_2 P_t} + \frac{1}{t_3 P_t} + \frac{1}{t_4 P_t} + \frac{1}{t_5 P_t} + \frac{1}{t_6 P_t} + \frac{1}{t_7 P_t} + \frac{1}{t_8 P_t}, \tag{8}$$

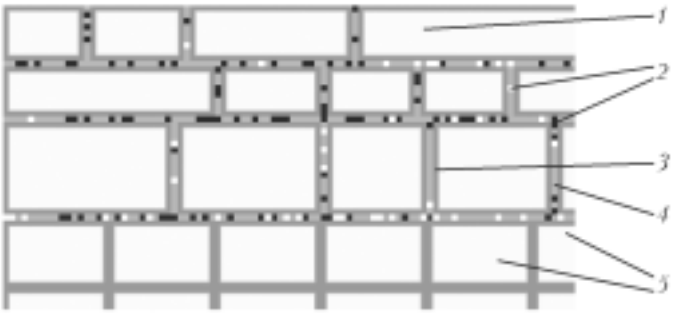

Fig. 1. Model representation of the vertical section of the film of titanium and silicon in diffusion synthesis of titanium disilicide: 1) grains of the Ti film; 2) clusters of Si and Ti; 3) grain boundary; 4) intergranular boundary; 5) silicon cells.

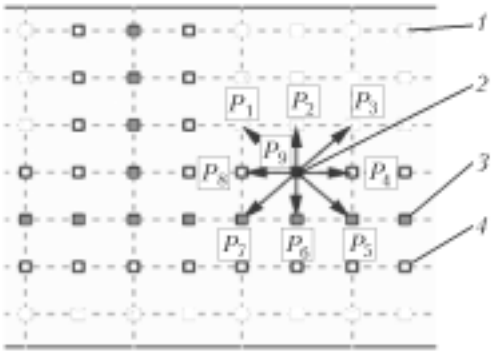

Fig. 2. Diagram of possible motions of the cluster: 1) grain volume; 2) titanium cluster; 3) intergranular space; 4) grain boundary.

$$P_9 = 1\,, \tag{9}$$

$$P_t = \frac{1}{t_1} + \frac{1}{t_2} + \frac{1}{t_3} + \frac{1}{t_4} + \frac{1}{t_5} + \frac{1}{t_6} + \frac{1}{t_7} + \frac{1}{t_8} + \frac{1}{t_9}\,. \tag{10}$$

In each direction, we calculate the transition time t as a function of the diffusion coefficient D from the expression

$$t = \frac{a^2}{4D}\,. \tag{11}$$

The direction of motion of a particle is determined by comparison of the randomly generated number q uniformly distributed on the interval [0, 1] to the probabilities P_1, P_2, P_3, P_4, P_5, P_6, P_7, P_8, and P_9 calculated above.

We assume that, in heating, the temperature in the film changes abruptly, at a prescribed interval within which it is constant. Within the interval of thermostability, we have the following processes: the emergence of clusters at the corresponding boundary with a time shorter than the running time from the volume, the jump of a cluster with a minimum lifetime, and the modification of the film structure. Changes in the film depend on the present and future positions of the cluster executing a jump. If the cluster after the jump is at the grain boundary or in the intergranular region, the parameters (occupied/vacant) of the position of the cluster are simply renewed (restored). In the case where the new position of the cluster is in the grain (silicon cluster) or in the cell of monocrystalline silicon (titanium clusters), the conditions of formation of the new phase are checked and, when the result is positive, the grain in the film or the cell in monocrystalline silicon is transformed to the corresponding phase of titanium disilicide.

TABLE 1. Constants of Diffusion for Titanium and Silicon in Silicon and Titanium and in Different Phases of Titanium Silicide for Volume and Intergranular Diffusion

Material in which diffusion proceeds	Type of diffusing element	Constants of diffusion D_0	
		intergranular, $E_a = 0.8$	volume, $E_a = 0.9$
Silicon	Si	$2 \cdot 10^{-7}$	$2 \cdot 10^{-9}$
	Ti	$2 \cdot 10^{-7}$	$2 \cdot 10^{-9}$
Titanium	Si	10^{-7}	$5 \cdot 10^{-10}$
	Ti	$2 \cdot 10^{-8}$	$5 \cdot 10^{-10}$
Ti_5Si_3	Si	10^{-7}	10^{-11}
	Ti	10^{-7}	$5 \cdot 10^{-10}$
TiSi	Si	10^{-7}	$2 \cdot 10^{-11}$
	Ti	$2 \cdot 10^{-8}$	$2 \cdot 10^{-10}$
$TiSi_2$	Si	10^{-8}	10^{-13}
	Ti	$2 \cdot 10^{-8}$	$2 \cdot 10^{-10}$

To model the process of diffusion synthesis of titanium disilicide with different character of temperature action in the model, we allowed for the time variation of the temperature with the corresponding correction of the lifetime and the diffusion coefficient of clusters in the model. Furthermore, we prescribed the parameters of the regime of treatment: the modeling time, the phase of conversion of the lifetime, the initial and final temperatures of the sample, the heating time, the conditions (temperature and concentration relation Si/Ti) of formation of Ti_5Si_3, TiSi, and $TiSi_2$, the number of layers in the "brickwork" for the titanium film and the silicon substrate adjacent to it, and the size of a titanium grain and a silicon cell. Depending on the diffusion mechanism dominant in synthesis and on the type of material (Si or Ti) and the phase of titanium silicide (Ti_5Si_3, TiSi, or $TiSi_2$), we prescribed the values of the diffusion constants E_a and D_0 given in Table 1. Modeling is performed as long as $t_{runn} < t_{mod}$. Upon its completion, the information obtained on the process of silicide formation is statistically processed, namely, diagrams of change in the phase composition of the titanium–silicon system with treatment temperature are constructed and the table of the percentage of silicon and titanium in each layer for the grain volume and boundaries and the intergranular space is given.

The results of modeling of the process of diffusion synthesis of titanium disilicide depending on the temperature of fast heat treatment that have been obtained based on the model proposed are presented in Fig. 3. Their analysis shows that the diffusion mixing of silicon and titanium (Fig. 3a) begins at a temperature of 510°C. Upon the attainment of 610°C, we have the formation of titanium silicide enriched with the metal of Ti_5Si_3 (Fig. 3b). In the first step, the main diffusing material in this case is titanium.

Noteworthy is one feature of the course of the mutual diffusion of titanium and silicon. The predominance of the diffusion of titanium into silicon over the diffusion of silicon into titanium occurs until metal-enriched titanium silicide is formed at the titanium–silicon boundary, after which silicon becomes the main diffusing element. At the same time, in the second layer of the film of titanium where its silicide phases have not been formed yet, the main diffusing element into silicide is titanium, whereas at the silicide–silicon boundary, it is silicon. On the whole, the main diffusing element into the layer of the titanium silicide boundary with silicon is titanium. Thus, in this layer, the concentration of titanium amounts to 63% and that of silicon amounts to 37%.

An increase in the temperature to 620°C produces an increase in the silicide-layer thickness to form Ti_5Si_3 over the entire thickness of the titanium film (Fig. 3c). What this means is that, at this temperature, titanium is totally transformed to metal-enriched titanium silicide.

Further increase in the temperature to 640° causes the formation of titanium silicide containing all three phases of it: Ti_5Si_3, TiSi, and $TiSi_2$ (Fig. 3d). A feature of this process is that these phases are now formed due to the diffusion of silicon into the silicide film formed. In heating of the sample to 660°C, the titanium-silicide phase $TiSi_2$ is intensely formed and the content of the phase TiSi decreases (Fig. 3e). An increase in the treatment temperature to 720°C leads to the disappearance of the TiSi phase and the predominance of the $TiSi_2$ phase (Fig. 3f).

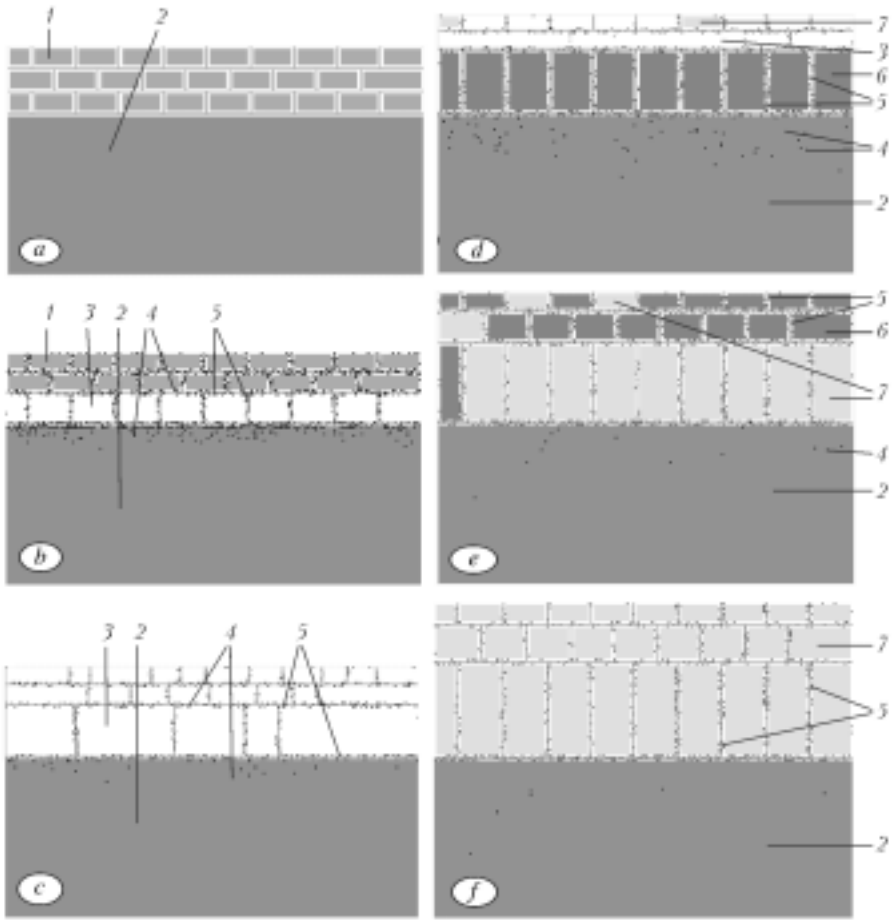

Fig. 3. Results of modeling of a change in the phase composition in the thin-film Ti–Si system (a) in fast heat treatment with a temperature of 610°C (b), 620°C (c), 640°C (d), 660°C (e), and 720°C (f): 1) Ti grains; 2) monocrystalline silicon; 3) Ti_5Si_3 grains; 4) Ti cluster; 5) Si cluster; 6) TiSi grain; 7) $TiSi_2$ grain.

Statistical processing of the results of modeling of the diffusion synthesis of titanium disilicide of ten processes enables us to state the following. In the temperature range 515–545°C, we have mutual diffusion of silicon into titanium and titanium into silicon with the predominance of the latter without formation of silicide titanium phases. In this case, silicon is accumulated in titanium grains and titanium is accumulated in silicon cells. At a temperature of 600–630°C, three titanium-silicide phases are formed and silicon becomes the main diffusing element. In the range 650–680°C, we observe a decrease in the content of the Ti_5Si_3 phase and an increase in the TiSi and $TiSi_2$ phases, with the predominance of $TiSi_2$. An increase in the temperature to 700–715°C ensures an increase in the content of the $TiSi_2$ phase, a decrease in the percentage of TiSi, and virtually a total disappearance of Ti_5Si_3. A total transition to the $TiSi_2$ phase is carried out at 720°C. Further increase in the temperature produces no changes in the phase composition of the titanium disilicide formed. In all these transitions, silicon is the main diffusing element.

A comparison of the results obtained by modeling to experimental data [1–3] has shown their complete identity, which demonstrates the reliability of the proposed model of diffusion synthesis of titanium disilicide in different types of heat treatment.

NOTATION

a, distance between lattice sites, or intercluster distance, cm; $D = D_0 \exp(E_a/kT)$, diffusion coefficient, $cm^2 \cdot sec^{-1}$; D_0, constant of the diffusion coefficient, $cm^2 \cdot sec^{-1}$; E_a, activation energy, eV; k, Boltzmann constant,

eV/^{o}C; q, randomly generated number uniformly distributed in the interval [0, 1]; P_1, P_2, P_3, P_4, P_5, P_6, P_7, and P_8, probabilities of transitions in the directions indicated in Fig. 2; P_9, probability of constancy of the position of a cluster; T, temperature, ^{o}C; t_1, t_2, t_3, t_4, t_5, t_6, t_7, and t_8, time of possible transitions in the directions indicated in Fig. 2, sec; t_9, time of rest, sec; t_{runn}, running time of modeling, sec; t_{mod}, time during which the process of modeling is carried out, sec. Subscripts: a, activation; 0, value of the quantity at $T \to \infty$; runn, running; mod; modeling.

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