Mechanism and Conditions of Nanoisland Structures Formation by Vacuum Annealing of Ultrathin Metal Films

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The paper presents theoretical and experimental results of studies of nanoisland metallic coatings on semiconductor substrates obtained by vacuum annealing of ultrathin solid films. It is shown experimentally that the formation of islet structure is possible only for films with thickness above a certain value. The study of surface morphology of the films was carried out using SEM.

Keywords: Thin film, Vacuum annealing, Diffusion, Nanoisland, SEM.

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1. INTRODUCTION

One of the promising areas of nanophysics is production and characterization of heterogeneous nanocatalysts. Such catalysts usually are ordered systems of nanoislands of metals or their compounds on substrates of various types [1].

Formation of such ordered systems (in particular palladium (Pd) nano-islands on silicon (Si) substrates) is a complex engineering problem. One of the possible and the cheapest method is vacuum annealing of ultrathin continuous metallic films deposited on a substrate [2-4].

This method is realized in two stages. First stage is a vacuum deposition of ultrathin continuous metal coating on a substrate; the second stage is a vacuum annealing of obtained samples. For this reason, this method has some drawbacks.

Firstly, the presence of two process steps reduces the reproducibility of results. Secondly, due to statistical straggling of islands size and location it is impossible the formation of ordered system of nanocatalysts in principle. Thirdly, interdiffusion of the film and the substrate materials lead to the formation of the transition diffusion layer which is a negative factor.

2. THEORETICAL SPECULATIONS

2.1 Processes in the Film-Substrate Interface

A Consider in details processes in the film-substrate interface during vacuum annealing.

Due to the diffusion at the interface between the film and the substrate there will be the intermixing (interdiffusion) of two materials. This process can be described by Fick's first law:

$$\phi = -D_x \frac{\partial C}{\partial x}, \qquad (2.1)$$

where ϕ is the diffusive flux of atoms, D_x is the diffusion coefficient (diffusion constant), $\partial C / \partial x$ is concentration gradient in the x direction.

The diffusion coefficient D_x is defined by the Arrhenius equation [5]:

$$D_x = D_{0x} \exp\left(-\frac{E_a}{k_B T}\right), \qquad (2.2)$$

where E_a is the diffusion activation energy.

Pre-exponential factor D_{0x} is the diffusion coefficient at $E_a = 0$ and can be expressed as:

$$D_{0x} = \nu a^2, \qquad (2.3)$$

where ν is an average frequency of thermal vibrations (the number of collisions with the potential barrier E_a), a – interatomic distance.

Consider a simplified model for which the diffusion coefficient D_x is a constant and lattice parameters of the diffusing materials are equal, i.e. flux is proportional to the concentration gradient. Let's carry out a step by step analysis of the mass transfer during the formation of a diffusion layer on the film-substrate interface (Fig. 1).
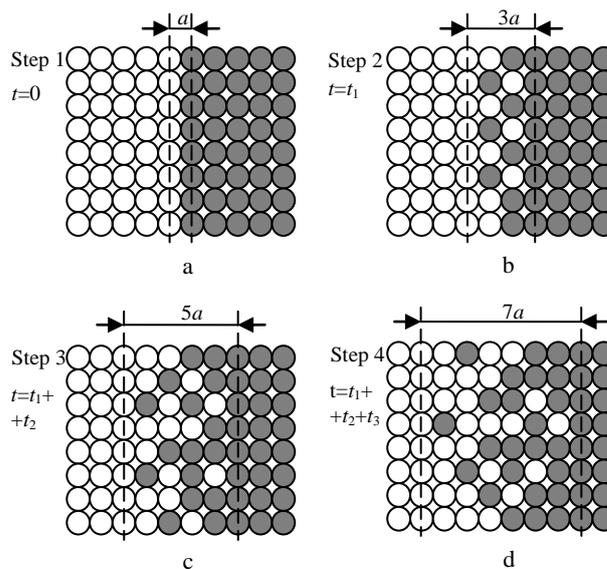
Fig. 1 – Step by step model of the mass transfer during the formation of a diffusion layer on the film-substrate interface

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At the initial time $t_0 = 0$, gradient $\partial C / \partial x = C / a$ (Fig. 1a). Then equation (2.1) takes the form $\phi_0 = -D_x (C / a)$.

During time t_1 one atomic layer of the film material will be "mixed up" with a one atomic layer of the substrate material forming diatomic diffusion layer (Fig. 1b). The distance from the pure film material to pure substrate material becomes $3a$, gradient $\partial C / \partial x = C / 3a$. The diffusive flux $\phi_1 = -D_x (C / 3a) = \phi_0 / 3$.

Accordingly time of interdiffusion of two next atomic layers of the film and the substrate $t_2 = (\phi_0 / \phi_1) t_1 = 3t_1$. Now the distance from the pure film material to pure substrate material is $5a$ (diffusion layer – four atomic layers, see Fig. 1c), the gradient $\partial C / \partial x = C / 5a$ and the diffusive flux $\phi_2 = -D_x (C / 5a) = \phi_0 / 5$.

Similarly for the mixing of the third layer (Fig. 1d) we have: $t_2 = (\phi_0 / \phi_2) t_1 = 5t_1$, $\partial C / \partial x = C / 7a$, $\phi_3 = -D_x (C / 7a) = \phi_0 / 7$.

Summarizing we receive:

– as a result of interdiffusion of n layers of the film and the substrate, the diffusive flux:

$$\phi_n = -D_x \frac{C}{(2n+1)a} = \frac{\phi_0}{(2n+1)} ; \qquad (2.4)$$

– time of n layers diffusion:

$$t = \sum_n t_n = \sum_n (2n-1) t_1 = n^2 t_1 . \qquad (2.5)$$

Fig. 2 graphically illustrates formulas (2.4) and (2.5).

As one can see, the diffusive flux after "mixing" of n atomic layers of the film with the substrate material decreases by a hyperbolic law. A total diffusion time $t(n)$ increases by a quadratic dependence.

2.2 Mechanism of Formation of Island Structures

Now consider the mechanism of formation of island structures on the surface of the metal film during its annealing. We assume that the annealing temperature is less than the melting point of the film. In this case the only mechanism of the formation of atomic clusters (islands) on the continuous film surface is the mechanism of surface self-diffusion. In this process an atom diffusing on the surface jumps from "occupied" lattice site into the "free" lattice site. That is, in the case of surface self-diffusion the concentration gradient is always constant $\partial C / \partial x = C / a$. The flux in this case will be determined by a change of the diffusion coefficient. That is, at steady-state thermal conditions, according to (2.2) and (2.3), the rate of mass transfer will depend only on the value of activation energy and interatomic distance.

Consider as an example the surface of fcc structure which is typical for many metals (Fig. 3).

Fig. 3a illustrates structure of the fcc (100) surface. The black color highlights an arbitrary surface atom, for which bonds with the nearest neighbors (bold black) and bonds with the length equal to the lattice parameter (bold grey) are defined. The coordination number of surface atom is $z = 8$, the number of bonds with the length equal to the lattice parameter is $x = 5$. Fig. 3b shows that the location of the atom above the plane of the fcc (100) surface leads to the formation of four bonds with its nearest neighbors and one bond equal to the lattice parameter. Analyzing the possible directions of diffusion one can conclude that the elementary displacement of the diffusing atom (from one lattice site to the neighbor) occur along the $\{1\bar{1}0\}$ and $\{110\}$ directions.

The structure of the fcc (110) surface is presented on Fig. 3c. The coordination number of surface atom in this case is $z = 7$, the number of bonds with the length equal to the lattice parameter is $x = 4$. Location of the diffusing atom above the fcc (110) surface (Fig. 3d) suggests the presence of 5 bonds with its nearest neighbors and 2 bonds with the length equal to the lattice parameter. As can be seen from the figure, the diffusion of the atom on the fcc (110) surface is possible in two directions with a different probability of diffusion jumps. The first direction (less likely) coincides with $\{001\}$ crystallographic direction, the second (more likely) – with $\{1\bar{1}0\}$ direction. The difference in transition
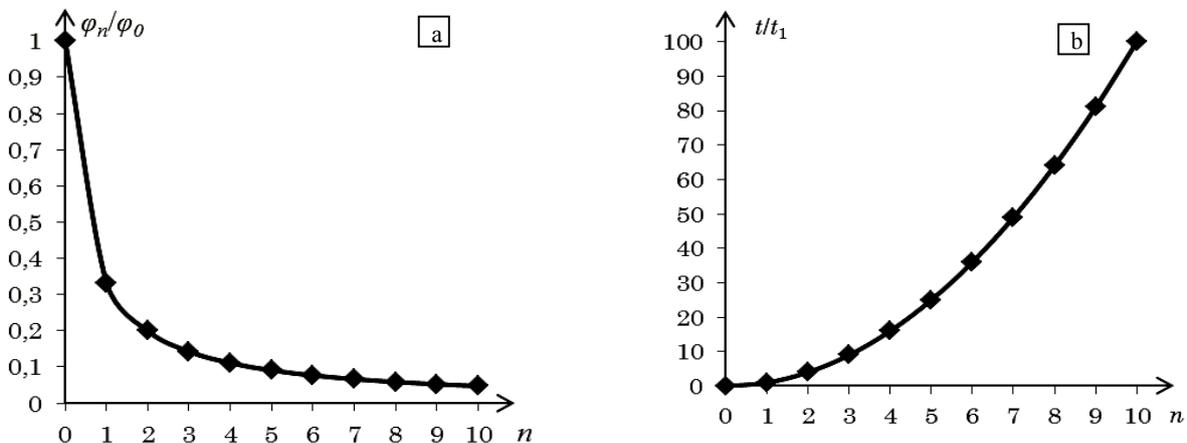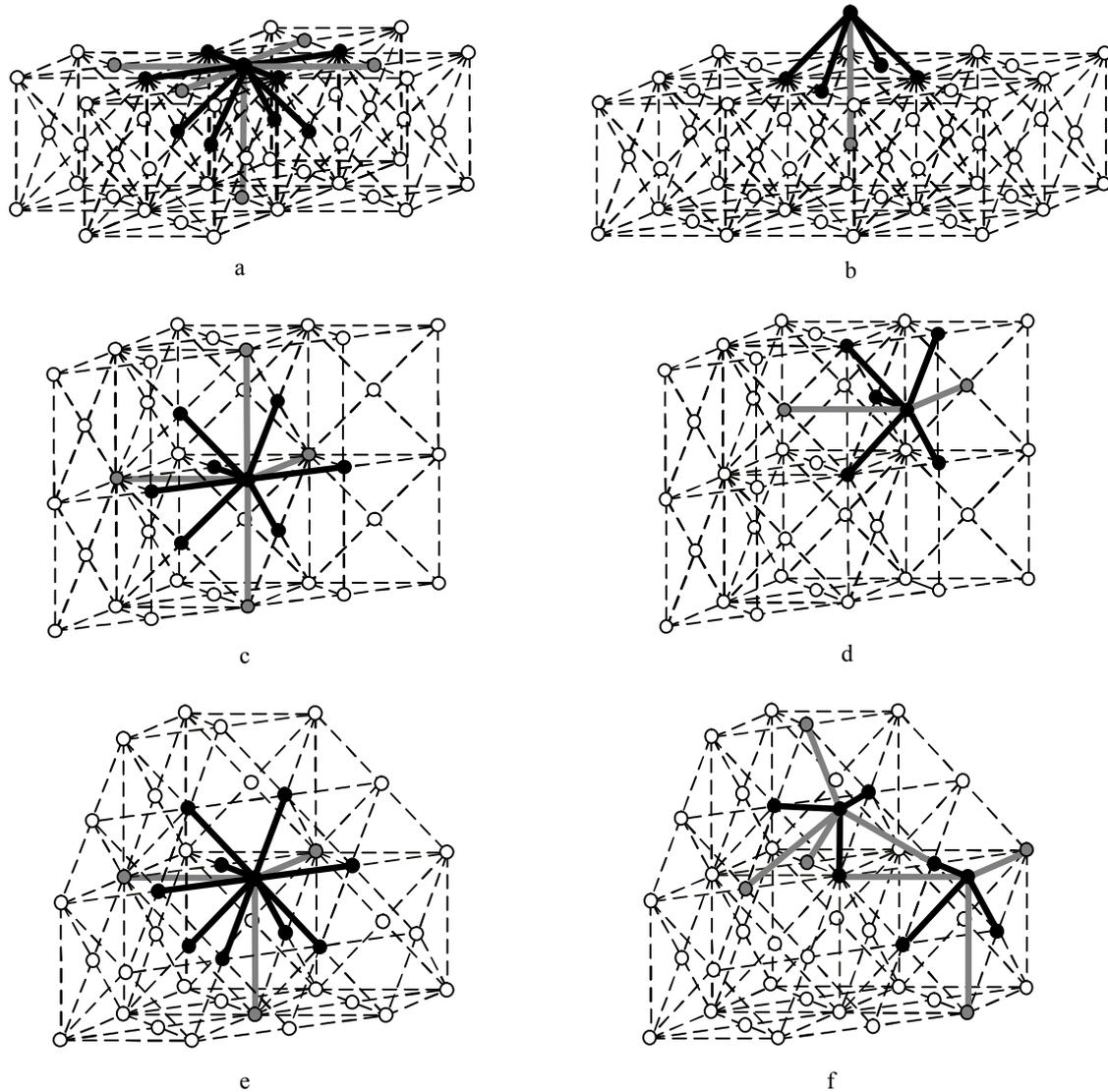

Fig. 2 – The relative change of the diffusive flux during interdiffusion of n atomic layers of the film and substrate materials (a) and relative total time of diffusion (b)

Fig. 3 – Surface structure: (a), (b) – fcc (100); (c), (d) – fcc (110); (e), (f) – fcc (111). Bonds of the atoms located "in" and "above" the surface are denoted (bold black – bonds with nearest neighbors, bold grey – bonds with the length equal to the lattice parameter)

probabilities is due to the difference in the distance between the surface atoms and the number of broken bonds. Thus, in the atomic rows perpendicular to the {001} direction, the distance between atoms is the distance between nearest neighbors a as well as in rows perpendicular to the {1$\bar{1}$0} direction it is a parameter of cubic lattice $a\sqrt{2}$. Then, according to (3), the pre-exponential factor which determines the diffusion coefficient will be: for the {001} direction $D_{0\{001\}} = \nu a^2$, and for {1$\bar{1}$0} direction $D_{0\{1\bar{1}0\}} = 2\nu a^2 = 2D_{0\{001\}}$.

The structure of the fcc (111) surface is presented in Fig. 3e. The (111) plane of fcc structure is the most close-packed, and the coordination number of surface atom is $z = 9$. Besides this atom forms three bonds with the length equal to the lattice parameter. Fig. 3f presents the possible location of the atom above the fcc (111) surface. Two possible examples, corresponding to the fcc and hcp structure are presented. In both cases the coordination numbers are the same ($z = 3$). The

difference is only in a number of bonds with the length equal to the lattice parameter (for fcc packing $x = 3$, for hcp packing $x = 4$). Possible directions of atom diffusion above fcc (111) surface coincide with the directions {11$\bar{1}$}, {1$\bar{2}$1} and. The transition of the diffusing atom to a neighboring site will be accompanied always by a change in the type of packing.

Let's estimate the values of the binding energy of a surface atom and the surface self-diffusion activation energy for different surfaces of the fcc structure.

The binding energy of the atom with the crystal is proportional to the number of bonds with neighboring atoms. Herewith bonds with nearest neighbors and bonds with the length equal to the lattice parameter should be considered. If the coordination number of the atom in the crystal is z_0, the number of bonds with the length equal to the lattice parameter is x_0 and the binding energy per atom is E_0, we can write:

$$E_0 = z_0 \cdot E_z + x_0 \cdot E_x = E_z\left(z_0 + kx_0\right), \qquad (2.6)$$

where E_z is the binding energy with nearest neighbor; E_x – binding energy of bond with the length equal to the lattice parameter; $k = E_x/E_z$.

As was shown above, for the fcc packing the lattice parameter is $\sqrt{2}$ times larger than the interatomic distance. If we present the interatomic interaction energy in the form of Lennard-Jones potential, then $k \approx 0.23$. For surface atom with coordination number z and the number of bonds with the length equal to the lattice parameter x, the binding energy is

$$E_s = E_z \left(z + 0.23x \right). \qquad (2.7)$$

In the case of palladium (Pd) (the binding energy of atom in a crystal is 3,936 eV [5], $z_0 = 12$, $x_0 = 6$) we have $E_z = 0,294$ eV. The results of calculations of E_s are presented in Table 1.

Thus, for realization of surface self-diffusion the atom located "in" the surface must jump into position "above" the surface (Schottky mechanism) As was shown (Fig. 3) during the surface self-diffusion atomic transitions from one site to another are not accompanied by energy consumption (z and x are constant). Restriction in movement creates only the presence of a periodic potential barrier (diffusion activation energy E_a), whose value is determined by the number of broken bonds with its nearest neighbors z_{bb} and bonds with the length equal to the lattice parameter x_{bb} (Table 2).

On the basis the foregoing discussion it is clear that diffusing atom has relatively weak binding energy with the surface and can move overcoming the potential barrier E_a by its thermal energy. Taking into account the described properties, the state of the diffusing atoms can be considered as "quasi-liquid". Herewith stresses, arising due to decreasing of the coordination number of atoms in the surface "quasi-liquid" layer, leads to the formation of forces similar to the surface tension forces in liquids. Thus, the system will spontaneously relax with a decrease of surface energy i.e. freely diffusing atoms will form clusters (islands). A similar mechanism of formation of island structures during solid thin films growth is called "Stranski-Krastanov" mechanism [7].

Consider the kinetics of island structures formation [8]. The primary stage of an island growth is the formation of a stable nucleus of supercritical size. As a

result of the island growth a so-called capture zone of diffusing atoms around the island is formed. The radius of such a zone is:

$$r \approx \sqrt{D \cdot \tau}, \qquad (2.8)$$

where D is surface self-diffusion constant, τ is mean stay time of the diffusing atom on the surface.

Then the surface coverage (by islands and capture zones) can be described by an expression:

$$F(t) = N(t)D\tau, \qquad (2.9)$$

where $N(t)$ is the average number of supercritical nuclei per square unit, t is annealing time.

Further formation of new nuclei is possible only on the surface which does not belong to the capture zones. Rate of change of the nuclei number on the surface square unit can be described by the expression:

$$\frac{d}{dt}N(t) = I \cdot [1 - F(t)], \qquad (2.10)$$

where I – rate of formation of supercritical nuclei. From (2.9) and (2.10) the surface coverage

$$F(t) = 1 - \exp(-ID\tau \cdot t). \qquad (2.11)$$

Accordingly, the number of nuclei per square unit is:

$$N(t) = \frac{F(t)}{D\tau} = \frac{1}{D\tau}[1 - \exp(-ID\tau \cdot t)]. \qquad (2.12)$$

3. EXPERIMENTAL RESULTS

Consider the results of experimental studies of ultrathin palladium films morphology on Si(111) substrate after vacuum annealing.

The metal film of 1 and 2 nm thickness were deposited on the semiconductor surface by thermal evaporation from a tungsten crucible in a vacuum (the basic pressure $(8 \pm 0,5) \cdot 10^{-5}$ Torr). As the substrates semiconductor-grade silicon wafers were used (surface orientation (111), both sides polished (surface roughness < 10 nm), thickness 400 ± 20 μm). Deposition was carried out simultaneously on 4 samples in order to create an identical coverage. One sample was not annealed,

Table 1 – The binding energy E_s of surface atom for the various surfaces of the fcc lattice of palladium (Pd)

Surface	Atom «in» surface			Atom «above» surface		
	z	x	E_s, eV	z	x	E_s, eV
fcc (100)	8	5	2.690	4	1	1.244
fcc (110)	7	4	2.328	5	2	1.605
fcc (111)	9	3	2.849	3	3(4)[a]	1.085(1.152)*

* In brackets the value for hcp packing is indicated

Table 2 – Surface self-diffusion activation energy for the various surfaces of the fcc lattice of palladium (Pd)

Surface		z_{bb}	x_{bb}	E_a, eV	Data from [6] E_a, eV
fcc (100)		2	1	0.656	0.15, 0.71, 0.74
fcc (110)	Direction {001}	3	2	1.017	–
	Direction {1$\bar{1}$0}	3	1	0.95	–
fcc (111)	fcc packing	1	2	0.429	0.1, 0.031, 0.059
	hcp packing	1	3	0.497	–

and the other three were annealed in vacuum at a temperature of 450 ºC during 1, 2 and 3 hours, respectively. The study of surface morphology was carried out by scanning electron microscopy (SEM) (Carl Zeiss Inc.).

Fig. 4 illustrates the results of SEM study of palladium film samples (2 nm thickness) on Si substrate after vacuum annealing.
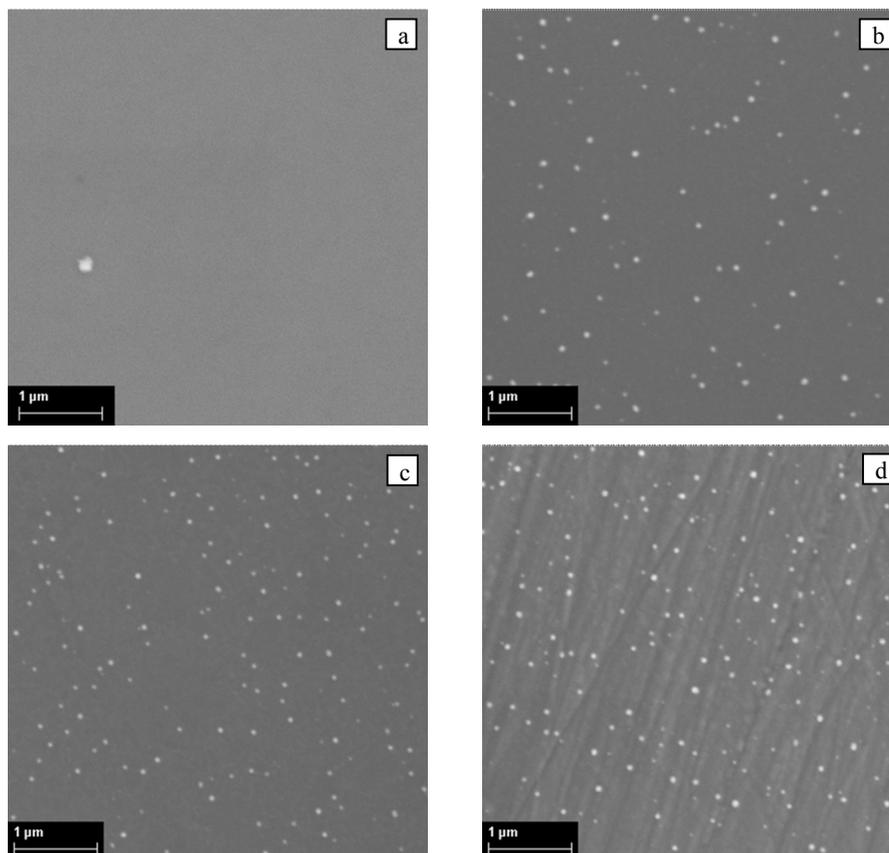
Fig. 4a illustrates a pattern of the continuous Pd film surface on Si substrate which has not been annealed. It is evident that the film has a high degree of homogeneity (for clarity a contrast defect is shown). For the sample annealed during one hour (Fig. 4b) the formation of separated islands on the surface of a continuous film is observed that is consistent with the mechanism described above in the theory. In the case of a two-hour annealing (Fig. 4c) we have the same continuous film with islands on the surface, but the number of islets per square unit has increased, despite the fact that their sizes have not changed. In the case of the "three-hour" sample (Fig. 4d), we have a completely nanostructured film (the relief of silicon polishing is observed).

In table 3 the results of the analysis of the structural characteristics of island formations are presented. In

calculations hemispherical approximation for island shape was used.

Fig. 5 graphically illustrates the results of analysis of the SEM patterns. The points on the graph correspond to the experimental data, solid line – theoretical calculation based on (2.10) and (2.12). As can be seen, the experimental results are in a good agreement with theory.

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Fig. 4 – SEM study of Pd film samples (2 nm thickness) on Si substrate: (a) – 0 hours annealing, (b) – 1 hour annealing, (c) – 2 hours annealing, (d) – 3 hours annealing.

Table 3 – Nanoislands parameters

Annealing time, hour	Island diameter, nm	Prevalent island diameter, nm	Island number per µm²	The equivalent of film thickness, nm
1	30-85	70	4.5	0.283
2	30-85	70	6.85	0.474
3	30-85 (some 100)	70	8.15	0.556

In calculations hemispherical approximation for island shape was used.

Fig. 5 graphically illustrates the results of analysis of the SEM patterns. The points on the graph correspond to the experimental data, solid line – theoretical calculation based on (2.10) and (2.12). As can be seen, the experimental results are in a good agreement with theory.

On the basis of these data we can calculate the following parameters: the rate of supercritical nuclei formation $I = 5.97 \, \mu m^{-2} \, hour^{-1}$, the radius of the atom capture by the island $r = 0.32 \, \mu m$, the maximum number of islands on the surface $N_{max} = 10 \, \mu m^{-2}$.

It should also be noted that the recalculation of the material volume in the island structures per total square of the sample gives an equivalent coating thickness much lower than the initial thickness of the metal film before annealing (see Table. 3). So, in the case of the "three hours" sample only about 25 % of the film material is in the island formations, despite the fact that the coating was completely nanostructured. The rest of the film material preferably has diffused into the substrate to form silicide diffusion layer, which is also consistent with the described theory and is observed in [9, 10].

Fig. 6 illustrates the results of SEM study of annealed palladium film samples (1 nm thickness) on Si substrate. The annealing parameters are the same.

As one can see from these figures already for a "one-hour" sample (Fig. 6b), there is complete absence of metallic coating, including the island structures. The same surface morphology have samples which were annealed during two (Fig. 6c) and three (Fig. 6d) hours, although the initial film surface morphology has the form shown in Fig. 6a. Thus it is possible to make the assumption that all the metal film have diffused into the substrate.

Such a result has quite reasonable explanation. Considering that the film with thickness of about 2 nm have diffused completely into the substrate during less than 3 hours (see Fig. 4), then according to (5) film with 1 nm thickness should be fully diffused during less than 45 minutes and this is observed in experiment. The formation of islands is not observed because of the ultra-low thickness of the initial film and its good adhesion, which makes it impossible realization of the Stranski-Krastanov mechanism.

4. CONCLUSIONS

Thus, it has been shown both theoretically and experimentally that during annealing of continuous ultrathin metal films on semiconductor substrates it's possible the formation of nanoisland structures at temperatures much lower than the melting point of the film material.

The formation of nanoisland structures is realized by Stranski-Krastanov mechanism. Islands growth take place on a continuous film surface from "quasi-liquid" layer (the surface self-diffusing atoms).

It is shown experimentally that during annealing of ultrathin Pd films of 1 nm (or less) thickness deposited on the Si (111) surface the nanoisland structures don't form experiments confirm the formation of transition silicide layers at the interface between the Pd film and Si substrate during annealing. The rate of this process is significantly lower than was claimed in some works [9, 10] and in general depends on the annealing time.
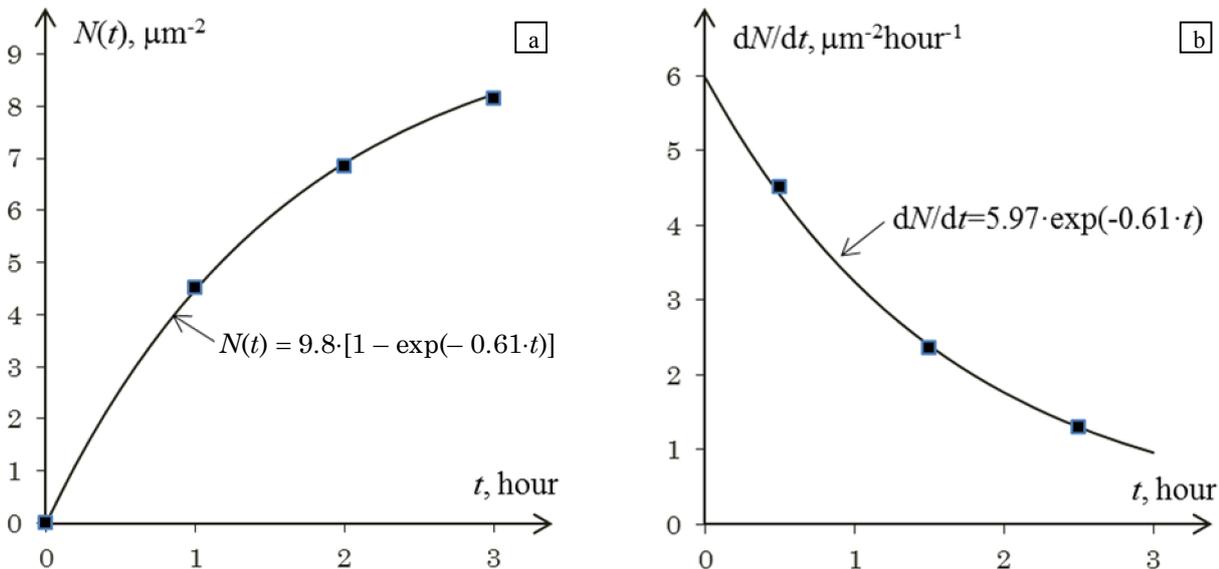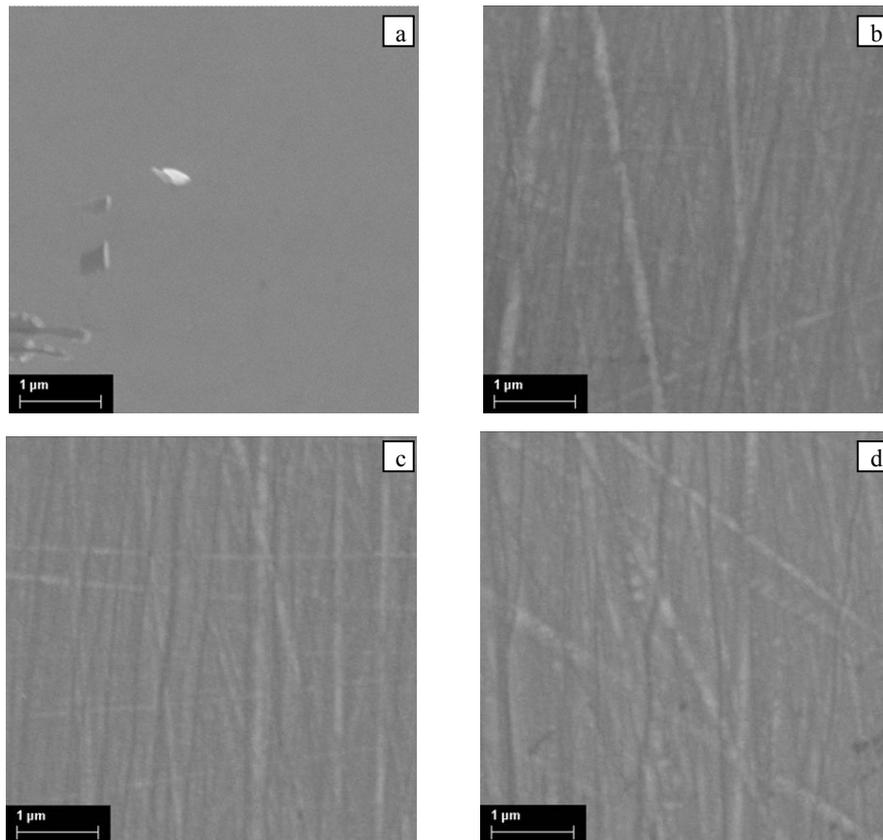

Fig. 5 – The average number of islands per surface square unit vs the annealing time (a), the rate of change of islets number per square unit vs the annealing time (b)

Fig. 6 – SEM study of Pd film samples (1 nm thickness) on Si substrate: (a) – 0 hours annealing, (b) – 1 hour annealing, (c) – 2 hours annealing, (d) – 3 hours annealing

Механизм и условия формирования наноостровковых структур при вакуумном отжиге сверхтонких металлических плёнок

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В работе представлены теоретические и экспериментальные результаты исследований наноостровковых металлических покрытий на полупроводниковых подложках, полученных при вакуумном отжиге сверхтонких сплошных плёнок. Экспериментально показано что формирование островковой структуры возможно только для плёнок с толщиной более некоторого значения. Исследование поверхностной морфологии плёнок производилось с использование РЭМ.

Ключевые слова: Тонкая плёнка, Вакуумный отжиг, Диффузия, Наноостровок, РЭМ.

Механізм та умови формування наноострівцевих структур при вакуумному відпалі надтонких металевих плівок

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В роботі представлені теоретичні та експериментальні результати досліджень наноострівцевих металевих покриттів на напівпровідникових підкладках, отриманих при вакуумному відпалі надтонких суцільних плівок. Експериментально показано, що формування острівцевої структури можливе тільки для плівок з товщиною більшою за деяке значення. Дослідження поверхневої морфології плівок проводилось з використанням РЕМ.

Ключові слова: Тонка плівка, Вакуумний відпал, Дифузія, Наноострівець, РЕМ.

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