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Formation of Nanostructured Thin Film Coatings for Nanocatalysts

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The paper presents the results of theoretical basis of possibility of nanostructured thin-film formation by mechanical stress creation in ultra-thin films deposited on a substrate during their thermal annealing. The experiment results of palladium (Pd) ultra-thin films obtained on silicon (Si) substrates and their vacuum annealing are also presented. The samples were studied by AES and SEM methods.

Keywords: Nanostructuring, Palladium, Vacuum deposition, Thermal annealing, Mechanical stress, Yield stress.

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1. INTRODUCTION

In modern physical chemistry such a concept as nanocatalysts is established. Nanocatalysts are solid nanoscale particles of a substance (usually metal) with high catalytic activity and the possibility of selective heterogeneous catalysis. The nanocatalysts properties are due to two effects: the electronic and geometrical.

Electronic effect is divided conventionally into primary and secondary. The primary electronic effect is associated with increasing of the distance between discrete energy levels in the conduction band (due to the small number of atoms in the nanoparticle). In this case, if the distance between the levels exceeds kT, the particle loses properties of solids in terms of band theory of crystalline structures [1]. Secondary effects associated with changes in distortion of the electron shells of surface atoms (compared with bulk solid), due to the small number of bulk atoms. Thus, we can conclude that the decrease of number of atoms in the nanoparticle below a certain value will lead to the loss of the catalytic properties characteristic of a massive solids.

Geometrical effect is due to high specific catalytically active surface (the ratio of catalyst surface area to volume of spent material). In terms of the geometric effect reducing the size of the nanoparticles will lead to an increase of catalytic activity.

The real dependence of the nanocatalysts catalytic activity on their size is due to the interaction of the electronic and geometric effects and, consequently, has a characteristic maximum.

Thus, for synthesis of efficient nanocatalysts it is necessary to have technology which allows to specify the desired size of the nanoparticles.

One way of creating nanocatalysts satisfying the proposed requirements is the formation of metallic nanostructure (nanoisland) coatings on non-metallic substrates.

2. CALCULATION MODEL OF NANOSTRUCTURED COATINGS FORMATION

For the formation of nanostructured coatings method of annealing of ultrathin films deposited on the substrate is often used. In this process due to the difference between the coefficients of thermal expansion of film and substrate materials mechanical stresses appear in interface layer. If the thickness of the substrate is D and the film thickness is d, for the films of nanometer thickness ($D >> d$) substrate stress can be neglected, i.e. to assume it strainless. Let the film and substrate materials have coefficients of linear expansion α_1 and α_2, respectively. Then, if the sample temperature change is ΔT, corresponding change in the length of the film and substrate is:

$$\Delta l_1 = l_0 \alpha_1 \Delta T \ , \ \Delta l_2 = l_0 \alpha_2 \Delta T \qquad (1)$$

where l_0 – length of the sample before annealing.

Since the substrate is strainless and the sample length for the substrate and for the film is the same, the film will be strained (deformated):

$$\Delta l = l_0 \alpha_1 \Delta T - l_0 \alpha_2 \Delta T = l_0 \Delta T (\alpha_1 - \alpha_2) \qquad (2)$$

According to Hooke's law and subject to (1) and (2) stress arising in the film during elastic deformation can be calculated by the formula:

$$\sigma = -E\varepsilon = -E\frac{\Delta l}{l_0 + \Delta l_1} = -E\frac{l_0 \Delta T(\alpha_1 - \alpha_2)}{l_0 + l_0 \alpha_1 \Delta T} = -E\frac{\alpha_1 \Delta T - \alpha_2 \Delta T}{\alpha_1 \Delta T + 1} \qquad (3)$$

where E – Young's modulus of film material, ε – elongation.

It should be noted that this expression is valid only for elastic deformation of the film, i.e. as long as the stresses in the film do not exceed the proportional limit of material σ_0. Nevertheless, it allows calculating the annealing temperatures at which the film undergoes only elastic deformation (the minimum annealing temperature). Transforming (3) it is easy to show that this temperature is equal to:

$$\Delta T = \frac{\sigma_0}{E\left[\alpha_2 - \alpha_1\left(1 - \frac{\sigma_0}{E}\right)\right]} \qquad (4)$$

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If there is no chemical bond between the substrate and the film, formulas (3) and (4) need to be clarified taking into account the stress σ_s created by surface tension on the film – substrate interface:

$$\Delta T = \frac{\sigma_0 + \sigma_s}{E\left[\alpha_2 - \alpha_1\left(1 - \frac{\sigma_0 + \sigma_s}{E}\right)\right]} \quad (5)$$

In the case of a palladium (Pd) film on the silicon (Si) surface we have the following. The coefficient of linear expansion of silicon $\alpha_к = 2{,}33 \cdot 10^{-6}$ К$^{-1}$, palladium $\alpha_n = 11{,}8 \cdot 10^{-6}$ К$^{-1}$, palladium Young's modulus $E_n = 117 \cdot 10^9$ N/m^2, palladium yield stress $\sigma_{0n} = 5 \cdot 10^7$ N/m^2, the maximum elongation of palladium $\varepsilon_{\max} \approx 0{,}25$. Then, for a minimum annealing temperature $\Delta T_{\min} = 45$ К. Taking into account (3) one can obtain for the elongation:

$$\varepsilon(\Delta T) = \frac{\alpha_1 \Delta T - \alpha_2 \Delta T}{\alpha_1 \Delta T + 1} \quad (6)$$

So when the sample temperature exceeds the room temperature at $\Delta T = 1500$ К (which is close to the melting point of palladium) the relative elongation $\varepsilon = 0{,}014$, i.e. $\varepsilon << \varepsilon_{\max}$.

Thus, one can conclude that in all possible annealing temperature range palladium film is in the yield range of material, which leads to it "structuring".

3. EXPERIMENTAL RESULTS AND DISCUSSIONS

This paper describes a method of formation of nanoisland coatings by vacuum annealing of continuous ultrathin films of palladium (Pd), deposited on silicon (Si) substrate, as well as the results of its study.

The deposition of thin-film metal coatings on silicon surface was carried out by condensation of metal on a prepared substrate from the vapor phase in vacuum (10^{-5} Torr). The flow of metal vapor was created by thermal evaporation of thin filaments of palladium.

Control of the deposited films thickness was carried out by resistive express method. Obtained film thicknesses are between 10-20 nm.

To study the correlation between the annealing parameters of the films and their structural properties samples were produced by series (6 samples) in the similar deposition conditions. As a substrates low-doped polished silicon wafer with surface orientation (111) and a thickness of 400 ± 20 microns were used. The heating of the substrates was carried out up to 150 °C.

After deposition films were cooled to room temperature and then were heat treated in vacuum. As variable parameters of heat treatment were selected maximum heating temperature and heating time at maximum temperature.

Study of films chemical composition was carried out by Auger electron spectroscopy (AES). Results of the analysis after ion bombardment reveal a sharp peak of pure palladium and weak peaks of oxygen, carbon, silicon.

Studies of the surface morphology of the samples were performed using scanning electron microscopy (SEM).

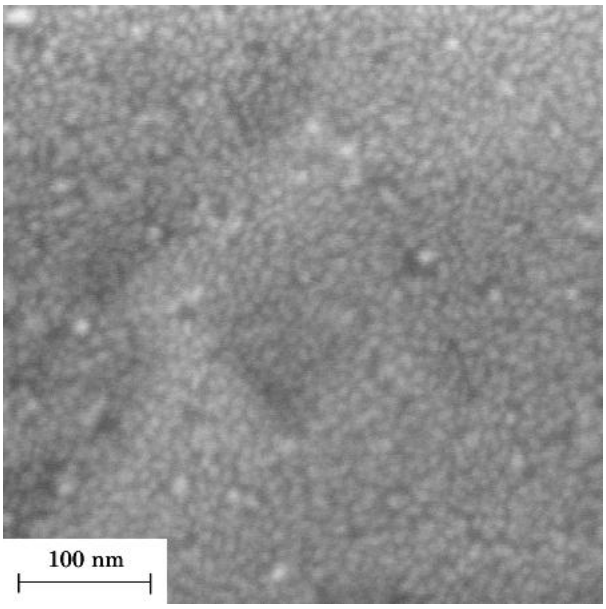

Fig. 1 – Film surface structure after vacuum annealing ($T = 250$ °C, $\tau = 60$ min)

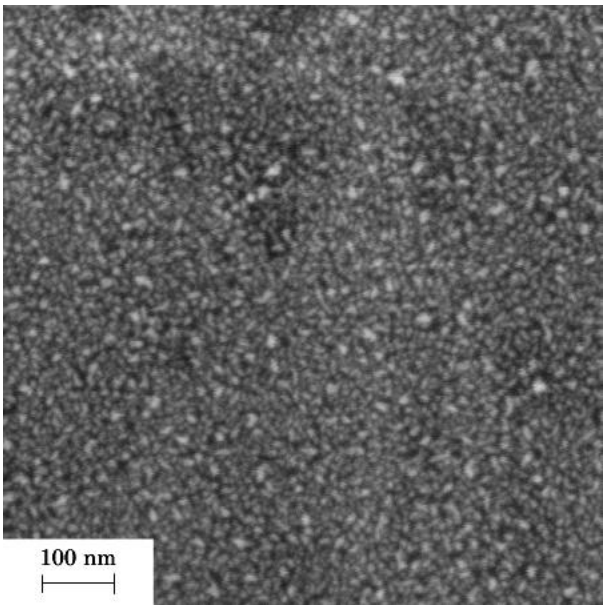

Fig. 2 – Film surface structure after vacuum annealing ($T = 250$ °C, $\tau = 120$ min)

Figures 1 and 2 presents the results of SEM study of samples surface after heat treatment at 250 °C. Figure 1 shows that the film surface slightly structured with separate small nanoobjects. Figure 2 shows pattern of the sample annealed at the same temperature during twice time. It is clearly seen small separate islet formation on the surface of the film on all the area of the figure (although the total structuring not yet been observed), the average size of formation is 10-15 nm.

Figures 3 and 4 presents SEM study of surface morphology of the samples after annealing at 350 °C during 60 and 120 min respectively. In general the character of changes in the structure of the film is similar to the previous couple of samples. The differences

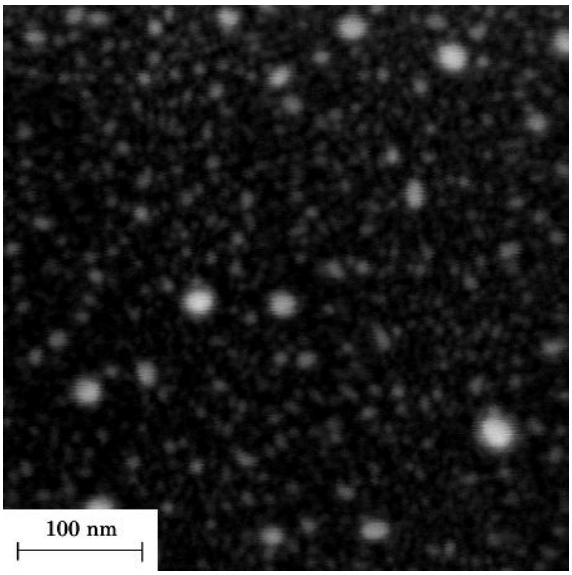

Fig. 3 – Film surface structure after vacuum annealing (T = 350 °C, τ = 60 min)

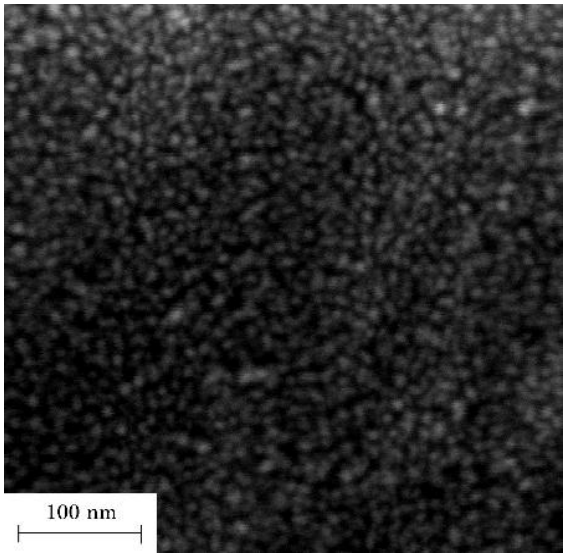

Fig. 4 – Film surface structure after vacuum annealing (T = 350 °C, τ = 120 min)

are in more structuring of the film due to increased mechanical stresses in it. Also size of island nanostructures is slightly different (9-12 nm).

Figures 5, 6, presents patterns of samples annealed at 450 °C during 60 and 120 min respectively. One can see that annealing time also affects the degree of film structuring and the temperature affects the rate of structurization. In this example, for the sample on figure 6, we have almost entirely unstructured film with a distinct island nanostructure. The average size of the structures is 8-11 nm.

Studies have revealed the influence of annealing parameters on the size of the nanostructures (Fig. 7). As can be seen from the graph the average characteristic size of the nanostructures is decreasing with increasing of annealing temperature, and is increasing with increasing of annealing time.

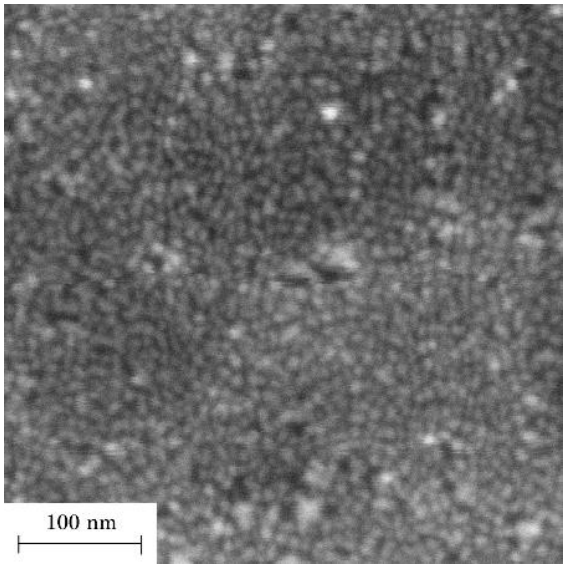

Fig. 5 – Film surface structure after vacuum annealing (T = 450 °C, τ = 60 min)

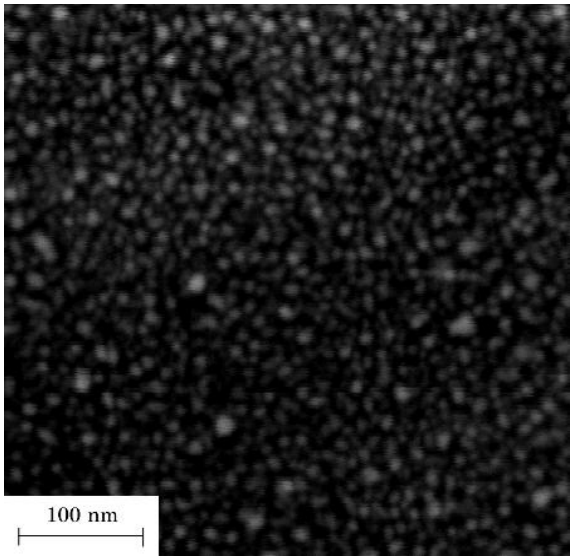

Fig. 6 – Film surface structure after vacuum annealing (T = 450 °C, τ = 120 min)

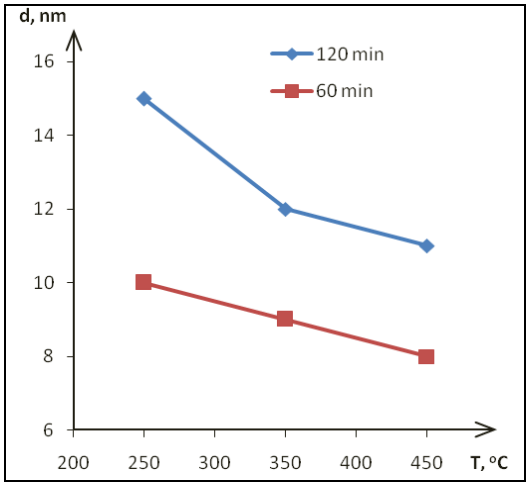

Fig. 7 – Average size of nanostructures as a function of annealing parameters

Such an effect can be explained by the formation of nanocrystalline phases in the bulk of the film [5]. At that temperature increase affects the amount of generated nucleus of a crystals. Accordingly, the increase of annealing time leads to an increase of the size of crystalline nanostructures.

4. CONCLUSIONS

Thus, it is shown that for formation of nanostructured coatings by annealing of films deposited on a substrate it is necessary to create mechanical stresses which exceed the yield strength of the film material. It is possible only when there is a large difference in the coefficients of linear expansion of the film and substrate materials.

It is established that for efficient annealing of the films it is necessary to exceed a certain minimum temperature, whose value depends on the linear expansion coefficients of film and substrate materials, the yield strength of the film material and the stresses in the film – substrate interface.

It was experimentally established that the excess of the estimated minimum annealing temperature leads to an effective structuring of film with the formation of nanoisland surface morphology. The dimensions of the nanostructures are comparable with the thickness of the film. It was found that increasing of annealing temperature increases the rate of structuring, and the annealing time effect on the degree of structuring of the film surface. The influence of annealing parameters on the size of the nanostructures has been revealed.

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