Thermal-activated granulation of ultrathin Au films. Structural and phase transformations

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Abstract. This paper represents the results of time, temperature, and dimension factors influence on the formation dynamics and structural-phase transformations in ultrathin and islands metallic films during their synthesis by methods of thermal-activated granulation and gradient coatings deposition. It's shown that the efficiency of metallic coatings granulation depends on the temperature and time of the TAG and determined by the effective thickness of the granulated coating. At a certain effective thickness, the second-order phase transition occurs in the film during the granulation process (percolation transition).

1. Introduction
Ultrathin and nanoislands metallic films are often used in planar microelectronic technologies, in plasmon and magnetoplasmon sensing systems, to create the control elements of fiber-optic communication lines, in optical systems, and nanocatalysis [1–7]. It's known that a structural-phase transition of the second type (percolation transition) is observed at thermal-activated granulation of ultrathin films. This phase transition leads to the formation of ensembles of self-assembled nanoparticles (nanoisland structures).

Many factors influence on formation dynamics and parameters of self-assembled nanoparticles: such as method of islands formation, the materials of film and substrate, surface type and structure, system temperature, coating thickness, time of the process, etc. [8,9]. So, an actual problem is to study the dynamics of self-assembled nanoparticles formation and also structural and phase transformations in thin films during the percolation transition from continuous coating structure to nanoisland structure.

2. Experimental technique
The samples of Au ultrathin and nanoisland films were synthesized by thermal vacuum deposition on a GGG (gallium-gadolinium garnet) substrates. Before deposition of coatings, the substrates were cleaned with ethanol and treated with vacuum annealing (the pressure is not more than 6·10^{-4} Pa, $T = 400 ^\circ C$, $\tau = 30$ min) and with ion-beam cleaning in glow HF-discharge.

In this work two methods for the synthesis of self-assembled nanoparticles were used. There are vacuum annealing method and thin-screen method (Figure 1). The first method was based on coatings thermal-activated granulation (TAG) caused by surface self-diffusion. The second method was based on the formation of coatings with gradient of effective thickness [10]. In this case in the ultrathin area of the gradient the coating has a nanoisland structure, i.e. composed of self-assembled nanoparticles.

The using of both these methods together is the most interesting in practice. It makes possible to synthesize a gradient coating on one sample in a single technological process and this coating is
granulated by annealing then. This technique is very effective to make investigations of the dimensional factors influence on the physical properties of nanoisland coatings.

Figure 1. Thin-screen method: (a) Scheme of thin-screen method for Au films formation with gradient of effective thickness: 1 – evaporator with molten material, 2 – GGG substrate, 3 – thin-screen, 4 – “half-shadow” zone (film’s area with gradient of effective thickness), 5 – film’s area with constant thickness, 6 – “free” zone (area of substrate without coating); (b) The approximate distribution of the film’s effective thickness along the gradient in the "half-shadow" zone for the case of a circular evaporator.

3. Results and discussion
At the firstly let's consider the temporal dynamic of film’s thermal-activated granulation (TAG). In this experiment the Au film on GGG substrate has continuous thickness about 10 nm. We synthesized 6 identical samples in single deposition process and annealed them on air at $T_{\text{TAG}} = 680^\circ C$ during different time $\tau_{\text{TAG}}$, such as: 1, 2, 5, 10, 30 and 60 min.

The results of surface morphology investigation by scanning electronic microscopy (SEM) are shown on figure 2. It’s shown SEM-images of coating’s nanoisland structure (self-assembled gold nanoparticles) and diagrams of nanoparticles size distribution. As can see, at low annealing time (1 and 2 min.) the complex chain-clusters consisting of three or more islands are presented in granulated coating. In this case the real nanoparticles size distribution (dotted line) is different from the symmetric Gaussian (solid line) and has asymmetric in the bigger clusters side. So, as nanoparticles size, we mean the parameter $d$ associated with the planar projection area of a complex chain-cluster $S$ through the equation:

$$d = \frac{2\sqrt{S}}{\pi} \quad (1)$$

At annealing time increasing (5 and 10 min.) as complex only binary clusters are observed and the nanoparticles size distribution became symmetric (better approximated with Gaussian). At high $\tau_{\text{TAG}}$ (30 and 60 min.) only single nanoparticles are observed and as longer the annealing time, as smaller the average particles size.
Figure 2. Temporal dynamics of TAG. Film Au_{NP}/GGG (h_{eff} = 10 nm, T_{TAG} = 680°C). SEM-images of the granular coatings surface and size distribution of self-assembled nanoparticles are presented. Insets shown the granulation time.

At figure 3 the dependences of distribution asymmetry index Δ and most probability particles size d_0 from annealing time τ_{TAG} are shown. The distribution asymmetry index Δ can be determined as:

\[ \Delta = \frac{d_{\text{max}} - d_0}{d_0 - d_{\text{min}}} \]  

where \( d_{\text{max}} \) – the maximum size of observed nanoparticles, \( d_{\text{min}} \) – the minimum size, respectively.

 Dependencies on figure 3 are demonstrated the classical percolation transition (a second-order phase transition) [11], during which became the destruction of complex chain clusters into individual nanoparticles.
At the secondly let's consider the temperature dynamics of film’s thermal-activated granulation (TAG). In this experiment the Au film on GGG substrate has continuous thickness near 10 nm. We synthesized 4 identical samples in the single deposition process and annealed them on air during 10 min at different temperatures $T_{TAG}$ such as 680°C, 750°C, 850°C and 950°C. The results of surface morphology investigation shown on figure 4.

As can see at low annealing temperature binary clusters are observed. At $T_{TAG}$ increasing only single nanoparticles are presents. Symmetrical size distribution of nanoparticles (well approximation with Gaussian) is observed in all cases. At figure 5 the dependences of standard deviation $\sigma$ and most probability particles size $d_0$ from $T_{TAG}$ are shown.
Figure 5. Temperature dynamics of TAG (Figure 4 analyses). The dependence of standard deviation $\sigma$ and most probability particles size $d_0$ from annealing temperature $T_{TAG}$.

As can see the standard deviation and most probability particles size are decreases when the annealing temperature is increased. It’s obvious that when approaching the melting point ($T_{TAG} / T_{TAG} = 1$), the parameters $d_0$ and $\sigma$ will tend to some constant values which characteristic for gold in the liquid state (a first-order phase transition).

At the thirdly let's consider the dimensional percolation transition in film with gradient of effective thickness $h_{eff}$ at TAG. In this experiment the effective thickness of Au coating on GGG-substrate was variable along the gradient from 5 nm (in the “thick” area) to zero thickness (clean substrate). After deposition the film was treated by vacuum annealing at 450°C during 120 min. The film was annealed immediately after deposition without removing the samples from the vacuum. This technique avoids additional contamination of the coating. It should be emphasized that the granulation temperature in this experiment was significantly lower than the melting point of gold.

As can see on presented SEM-images (Figure 6), at the “thickest” area of the film ($h_{eff} \approx 5$ nm) after the TAG some separated defects began to forming in the coating continuity. These defects have type as “cracks” with wide up to 20 nm and long up to 150 nm (Figure 6a). But in this area the coating retains its integral continuity.

On figure 6b shows film area with a smaller effective thickness ($h_{eff} \approx 4$ nm) than in the previous area. As can see the film in this area has many extended defects with type as “crack” which made a chaotic grid on the surface. In this area defects have a greater length up to 200–250 nm and a complex branched structure, with a crack width smaller than in the previous area (2–10 nm). It should focus that the metal coating areas still form continuous percolation channels.

On figure 6c showed the film surface morphology at area with $h_{eff} \approx 3$ nm. As can see in this area defects with the “crack” type form a continuous connected grid. In this case the percolation channels are destroyed and discrete flat islands with irregular shape are formed. Images on figures 6b and 6c visually demonstrate the phenomenon of percolation transition in the coating structure (a second-order phase transition).

Figures 6d, 6e, and 6f demonstrate the successive stages of coating island structures evolution when its effective thickness decreases. On figure 6d ($h_{eff} \approx 2$ nm) are shown isolated discrete islands with irregular form which separated by “wide” intervals up to 20 nm. On figure 6e ($h_{eff} \approx 1$ nm) individual discrete islands are also visible, but these islands have smaller sizes (about 5 – 50 nm) and more regular form (it's nearly rounds or may be approximated as a system of two or more rounded elements). In the end of gradient ($h_{eff}$ tends to 0 nm) we can observe on figure 6f separate islands with form become to round and with size 20 – 50 nm, which located from each other on considerable distance 0.3 – 1 μm.
Figure 6. Surface morphology of the Au/GGG film with a thickness gradient $h_{\text{eff}}$ after annealing at 450°C during 120 min. (a–f) – different areas of the film along the gradient (insets – area 200 × 200 nm).

4. Conclusions
In the presented work it has been experimentally shown that the efficiency of metallic coatings granulation depends to the temperature and time of the TAG and determined by the effective thickness of the granulated coating.

When the TAG time changes, a second-order phase transition (percolation transition) is observed in the structure of a thin-film coating. At "low-temperature" granulation (the annealing temperature is significantly lower than the melting temperature), complex clusters of two or more islands are present in the structure of Au/GGG granulated coating ($h_{\text{eff}} = 10$ nm). It's leads to a significant dispersion and asymmetry of the nanoparticles size distribution.

It has been also experimentally established that the effective thickness parameter $h_{\text{eff}}$ significantly affects to the processes of “low-temperature” granulation in ultrathin films. In experiment clearly demonstrated the processes of percolation transition in a granular film. It is shown that effective “low-temperature” granulation with formation of a discrete island structure occurs in films with $h_{\text{eff}} \leq 3$ nm. For such thicknesses at diffusion motion the kinetic energy of Au atoms in the TAG process becomes higher than sum of interatomic bonds energy and adhesion energy at the GGG/Au interface.

Acknowledgments
This work was supported by the RF Ministry of Science and Highest Education in the framework of the base part of the state task (Project No. 3.7126.2017/8.9) and partially supported by the V.I. Vernadsky Crimean Federal University Development Program (Projects No. ВГ22/2018).
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