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Study of silver cluster formation from thin films on inert surface

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ABSTRACT

We investigated the evolution of 6–130 nm silver thin films during vacuum annealing. The bimodal character of cluster size distribution was observed for 12–130 nm films. One average cluster size is 40–80 nm, other average size is 380–420 nm. At the same time it is shown that two simultaneous processes occur: coalescence and evaporation. The bimodality distribution character is associated with these two simultaneous processes. The initial 6 nm Ag film is found to be not continuous and to consist of aggregates of stuck clusters. The heating of this film up to 230 °C leads to the separation of clusters and unimodal character of cluster size distribution (average cluster size is up to 10 nm). The differences in behavior of 6–130 nm Ag thin films are discussed in terms of classical nucleation theory.

1. Introduction

Recently special attention has been paid to metal nanoclusters (or nanoparticles) due to their original properties and technological applications. For example, nanoclusters are used as effective catalysts for carbon nanotubes [1–3], silicon [4,5] and other semiconductor nanowires [6]; as chemical catalyst [7,8]; for creation of memory cells [9–11], lasers [12] and photonics [13,14]. The size of clusters and the distance between them are the main factor determining functional characteristics for applications.

One of nanocluster formation method is disintegration of thin film [15–20], that is caused by low-temperature melting effect [21]. For these technological applications it is important to control geometrical parameters and stability of the cluster array system. For this reason we investigated silver thin film evolution depending on heating conditions in vacuum and film thickness in the range from 6 to 130 nm.

2. Materials and methods

625 μm-Thick and 100 mm-diameter Si (100) wafers were used as substrates for the deposition of silver films. Si wafers were cleaned by a sulfuric acid–hydrogen peroxide mixture (97% H_2SO_4–30% H_2O_2, 1:1 v/v) during 10 min. Then they were rinsed in deionized water and dried by jet of isopropyl alcohol vapor.

The silver film was deposited on silicon wafers by resistive vacuum-thermal evaporation method at the residual gas pressure 1×10^{-5} Torr. Silver film thickness varied in the range from 6 to 130 nm and was controlled by atomic force microscopy (AFM).

The samples with various silver film thicknesses were annealed in vacuum at different temperatures during different periods of time in accordance to the data obtained in [15]. The sample surface was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The number of clusters per the unit of area and their size were calculated and measured by Axio Vision software.

3. Results

We can divide our experimental results into two groups in accordance with the behavior of clusters. The first group includes cluster arrays obtained from 12 to 130 nm silver thin films. The second group includes cluster arrays obtained from 6 nm silver thin films.

The common characteristic of all histograms for the first group is bimodal distribution of the clusters in size. Fig. 1 shows the cluster size distribution histogram for 65 nm film. The first average diameter was estimated to be 40–80 nm, while the second one corresponds to 380–420 nm. It should be noted that the first average diameter was the same for all first group samples, while in the second one changed for various film thicknesses. The similar bimodal characteristic of cluster size distribution was observed by Ruffino et al. for gold [22], Bandarenka et al. for copper [23] and Arslan et al. for aluminum [24].

The annealing time was found to influence cluster array evolution. Fig. 2 shows that cluster size increases up to several micrometers after annealing for 40 min. But cluster sizes and their number decrease, and distance between clusters increases after annealing for 80 and 120 min. Cluster size distribution bimodality remains independent on the duration of annealing, although the cluster number decreases. Thus, for this group there take place two simultaneous processes:

- coalescence (increase of clusters sizes up to several microns and of distances between clusters for different annealing duration);
- evaporation (120 min annealing leads to almost full evaporation).

The second group includes samples with 6-nm-thick silver thin films. Interestingly, as-deposited 6-nm-thick Ag film is non-continuous and consists of cluster

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agglomerates (Fig. 3a). But these agglomerates break up into separate clusters when heated up to 230 °C (Fig. 3b).

Fig. 4 demonstrates the cluster size distribution histogram for 6 nm film. Only one range of size i.e. 5–10 nm dominates. In the inset of Fig. 3b we can see that clusters of this size are monoclusters. It should be noted that there are other reports in the references on the distribution of clusters with one dominant size. In particular, this kind of sizes distribution of Ag clusters was observed by Xu et al. on the amorphous carbon, S_3N_4 and SBS-copolymer [25].

SEM studies of samples with different annealing time show that cluster array remains unchanged. Geometrical parameters of silver cluster array do not change even after 2 h of annealing at 230 °C.

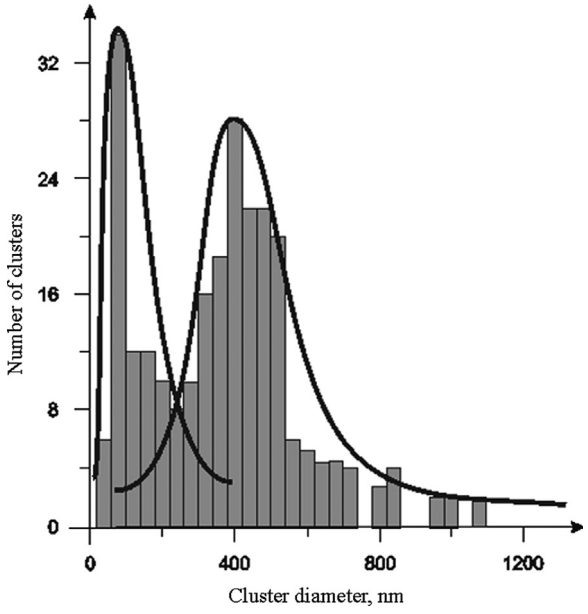

Fig. 1. The cluster size distribution histogram of a $30 \times 20\ \mu m^2$ surface for 65 nm-thick silver film annealed at 750 °C during 5 min.

4. Discussion

In our opinion the behavior of the samples from the first group is obvious. The surface melting has the significant influence on cluster formation from thin film. This phenomenon was discussed in detail in [15,21,26]. Any real system is semi-infinite, since it is limited by surface. For this reason, melting of such a system is heterogeneous and starts from the surface.

Therefore, there are several thermodynamic features for the heterogeneous melting process:

- A liquid layer of certain thickness exists on a solid state material surface at temperatures lower than the reference melting temperature. The liquid layer is in equilibrium with the solid state phase. The lower the temperature, the thinner the liquid layer on the solid surface is.
- The equilibrium between the liquid and solid state is noticeably displaced in the area of the lower temperature for low-dimension systems such as thin films, nanoclusters, nanowires.

Disintegration of silver thin films from the first group of 20 nm happens at temperature 660 °C, which rises up to 800 °C with the increase of film thickness up to 130 nm. According to the heterogeneous melting concept, all clusters are surrounded by a certain thickness liquid shell at a certain heating temperature. At the starting moment of film disintegration process only monoclusters appear. The existing liquid shell and surface tension provides a slip of clusters on the surface. Thus, due to surface tension force clusters can move to distances several times exceeding the diffusion migration distance. This causes a coalescence process; when clusters migrate, merging into each other and becoming globular. The free surface area of the cluster array and the surface energy reduces which leads to the decrease of the whole system's energy. Thus, some monoclusters of 40–80 nm coalesce into globular clusters of 380–420 nm. Some globular clusters can grow up to several micrometers during the annealing process, as it can be seen in Fig. 2. Coalescence is supposed to lead to a fadeaway of monoclusters. However, the evaporation process takes place simultaneously with coalescence, therefore some

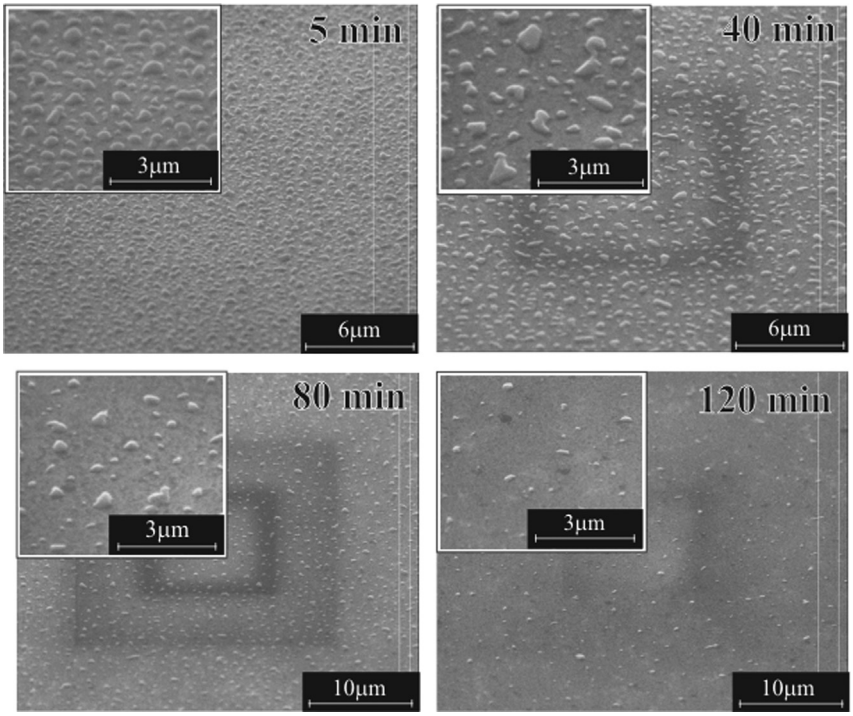

Fig. 2. SEM images of 20 nm-thick silver thin film after annealing at 660 °C for 5, 40, 80 and 120 min.

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