Nanostructured and Nanocluster Thin Films

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Abstract. Metal and metal oxide nanoclusters were prepared by means of the cluster source of a Haberland type. Two types of nanocluster sources assembled in our laboratory and implementing 2" and 3" magnetrons were operated in a DC mode in order to prepare silver and aluminium clusters. Large fraction of clusters was electrically charged both negatively and positively. Formation of nanoclusters and their charging was studied in dependence on experimental conditions using SEM, TEM, QCM and XPS.

Introduction
Preparation of structures with characteristic sizes about 100 nm and smaller has been in the focus of interest in the past years due to tremendous difference the nanoscale surfaces provide with respect to the bulk matter. New or different attributes of the nanoparticles arise from the fact that they have greater ratio of surface to volume than the bulk matter. Atoms on the surface have different electronic structure because they miss neighbours to fit in all of their valence electrons. This fact is valid for all materials but only sufficiently small particles have the ratio of surface atoms high enough to have any measurable influence.

There are many ways to prepare nanoparticles but this paper is devoted to their preparation by a vacuum method implementing the Haberland type cluster source. The original Haberland source, with a schematic view shown on fig. 1, utilized magnetron sputtering. It was also equipped with differential pumping of the aggregation chamber, time-of-flight mass separation and the walls of the aggregation chamber were cooled by liquid nitrogen. Such configuration allows effective production and analysis of mass-separated clusters, yet at expense of high capital cost. Our goal was to utilize the basic Haberland’s concept of magnetron sputtering but with significant simplification of the experimental arrangement. Our main research concern was to master the deposition process of metal and metal oxide clusters and to make basic characterisations with respect to deposition conditions.

Formation of clusters
As described in the literature [3-5], most cluster sources including ours proceed with formation of clusters through condensation of supersaturated vapour on an inert gas. Most generally, the source material for cluster formation is somehow (usually by evaporation or sputtering) converted into vapour. The vapour is consequently mixed with cool inert gas, which results in supersaturation of the

Figure 1. The schematic view of the original Haberland source [1, 2]
vapour and condensation into clusters. Clusters along with the gas are then usually ejected through an orifice into vacuum and allowed to land on a substrate.

Process of vapour condensation and cluster formation was described theoretically in the literature [3, 4]. It is dependent on several parameters including material of vapour, type of buffer gas and its temperature, impurities (especially reactive gases) and so on. There are two main ways in which cluster formation may go: homogeneous nucleation and coagulation. Which way is preferred is determined by a parameter called critical radius [5] which may be defined as

$$r^* = \frac{2\sigma m}{kT\rho \ln(\phi_k)}$$

where \(\sigma\) is the surface tension of a forming cluster, \(\rho\) is is density, \(m\) is molecular or atomic mass, and \(\phi_k = p_k/p_s\) where \(p_k\) and \(p_s\) are vapour pressure and saturation vapour pressure, respectively. The value of critical radius determines the stability of a forming cluster. The cluster will be stable if its size is larger than the critical radius. If it is smaller, the cluster will eventually evaporate unless it grows fast beyond the critical radius. Magnitude of the critical radius (determined mainly by the deposited material) determines if the cluster growth will follow the homogeneous nucleation or coagulation. If the critical radius is much smaller than the product molecule, then the clusters will be formed by coagulation, otherwise their formation will proceed through the homogeneous nucleation.

In either way (homogeneous nucleation or coagulation), a first dimer is formed by a three body process

$$M+M+A \rightarrow M_2+A$$

where \(M\) is a molecule of the cluster precursor and \(A\) is a molecule of the buffer gas [4]. As soon as the first dimer is created, more atoms or molecules can attach to the growing nucleus by only two body process, thus forming the cluster.

**Experimental**

As mentioned above, the Haberland type cluster source was specially designed and assembled in our laboratory. Two types of the source using either 2” or 3” planar magnetrons were studied. Schematic picture of the source is shown on figure 2.

Both 2” and 3” magnetrons were operated in a DC mode and were equipped with silver or aluminium targets. The walls of the cluster source were cooled by water to enhance cluster formation process. The length of the chamber could be enlarged by a set of spacers which were mounted between the water cooled body of the cluster source and the exit cone. The cone itself was replaceable and this allowed mounting the orifices with different diameters.

![Diagram](image-url)

**Figure 2.** The scheme of the cluster source used in our experiments.
The entire assembly of the cluster source was mounted on a vacuum chamber pumped by diffusion and rotary pumps. Argon was used as a buffer gas. Typical pressure inside the cluster source was in the range from several tens to several hundreds of pascals.

The cluster deposition was monitored by 5MHz quartz crystal microbalance. Clusters were deposited on glass and silicon substrates as well as on TEM grids for further SEM, TEM and XPS analyses.

Results and discussion

Silver was chosen as a starting material because of its high sputtering yield and low reactivity. This allows studying the processes of cluster formation and deposition unperturbed by chemical reactions. Furthermore, availability of the literature dealing with silver nanoclusters allows deeper understanding of the processes involved. It was experimentally found that the deposition parameters should be optimized for both 2” and 3” cluster sources to obtain stable fluxes of nanoclusters. For example, the pressure in the 2” cluster source without spacer below 150 Pa and higher than 450 Pa was not efficient for the cluster formation and no deposition of the silver clusters was observed. Magnetron current of 200 mA was used for most experiments as it gave high deposition rate without excessive thermal stress to the target. Nevertheless, other values of current were tried without significant influence on cluster formation. Fig. 3 shows the typical SEM images of the silver clusters prepared using the 2” cluster source. The images were taken on the samples prepared at ultimate limits of the working pressure window, i.e. at 150 and 400 Pa. Apparently, the clusters tend to get larger with increasing pressure.

It is generally known that nanoclusters exiting the orifice may be and often are electrically charged, however a thorough experimental data are lacking in the literature. Knowledge of charge distribution allows mass filtration and cluster energy manipulation. After the window of the deposition parameters had been established, charging of the silver clusters was studied. Two electrostatic systems for cluster deflection were tested. The first utilized two stainless steel grids where the frontal grid was grounded while the rear grid could be biased positively, negatively or also grounded, see fig. 4. A QCM was placed behind the grids to measure the deposition rate. This experiment allowed determining mass percentage of the charged clusters with respect to their polarities and percentage of the neutral clusters. The experiment was carried on the 3” cluster source with pressure of 75 Pa inside the source and DC current of 200 mA.

The experiments were conducted with the second grid biased to either +900 V or -900 V. Such values were sufficient to reject all the charged clusters of the same polarity as the grid and to allow through only the clusters of the opposite polarity and neutral clusters. With both grids grounded, the entire flux of the charged and neutral clusters is deposited on the QCM. Thus, three experiments

Figure 3. Silver nanoclusters prepared using the 2” cluster source. Both samples were prepared with magnetron current of 0.2 A and orifice diameter of 1.5 mm but at different pressures a) 150 Pa, b) 400 Pa.
Figure 4. The experimental scheme for determination of cluster charging

Table 1. Mass amount of charged and neutral clusters

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<tr>
<th>Clusters</th>
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<tr>
<td>negative</td>
<td>24</td>
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<td>32</td>
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<tr>
<td>positive</td>
<td>39</td>
<td>positive</td>
<td>37</td>
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<tr>
<td>neutral</td>
<td>37</td>
<td>neutral</td>
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allowed determining the mass ratio between the positively charged, negatively charged and neutral clusters. The amount of the clusters passing through the grids and depositing on the QCM was measured both in the centre of the beam and on its edge. The results summarized in Table 1 shows the difference in amount of negative clusters between both positions: the negative clusters tend to concentrate on the edge of the beam. Similar experiment can be done by applying high potential directly on the substrate, which is not possible in case of QCM but works well in case of usual conducting substrates.

Another experiment was done with two deflection plates positioned as shown on fig. 5. The QCM was placed at the fixed position outside the spot of the undeflected beam and the voltage between the plates was changed from 0 to 700 V for both polarities. Electrostatic field deflected the trajectories of the positively and the negatively charged clusters to the opposite directions whereas the flux of the neutral clusters remained uninfluenced. The angle of deflection of the charged clusters depended on their mass-to-charge ratio. If one elemental charge per one cluster is assumed as is commonly done in the literature for metal clusters [4, 6], it is possible to determine the mass distribution of the charged particles. For this purpose, the QCM was complemented with a narrow slit with 1 mm width in order to separate only a narrow fraction of the deflected beam and thus only particular cluster size. The conditions of cluster deposition were the same as for the previous experiment with the deflection grids: 75 Pa pressure in aggregation chamber and 0.2 A discharge current. The results of the measurement are given on fig. 6 along with TEM images on fig. 7 obtained when the QCM was replaced by TEM grid.

Fig. 7 shows that under the low deflection voltage of 30 V only the small clusters with sizes about 10 nm were sufficiently susceptible to electric field to reach the out-of-axis substrate. The bigger particles were not sufficiently deflected from the beam axis and passed by the substrate. At the 100 V voltage the smallest particles were strongly affected by the field, their trajectories further shifted and missed the substrate. Instead, the particles with the size about 20 nm were detected. Finally, at the voltage of 400 V only the heavier particles with the size of about 30 nm reached the substrate.

Figure 5. Experiment for determination of the cluster charge
Figure 6. Cluster charge distribution for deposition conditions of magnetron current 200 mA and pressure 75 Pa; a) absolute deposition rate of charged clusters; b) mass distribution of charged clusters described by deflection voltage

Figure 7. TEM micrographs of clusters deflected by various voltages; a) 30 V; b) 100 V; c) 400 V

The next step of the research was focused on deposition of aluminium clusters. These were fabricated by using the 3" cluster source. The working window of operation conditions was significantly narrower this time than in the case of silver. The pressure window was shifted to lower values of 15 Pa while the upper threshold of 30 Pa was dependent within the error of 5 Pa on power of the magnetron. At lower power the upper border shifted to higher pressure which seems to be due to temperature changes inside the aggregation chamber. The best results with the highest deposition rate were achieved in the range from 20 to 25 Pa. Fig. 8 shows a TEM image of aluminium clusters prepared at pressure 25 Pa and magnetron current 0.2 A. Unlike silver, the aluminium clusters show very narrow size distribution with diameter between 20 and 25 nm. Cubic, triangle and hexagonal shapes can be observed whereas spherical particles are in minority if not present at all. The aluminium clusters also tend to get smaller with increasing power which might be due to change of temperature regime. However, the size reduction is more probably related with creation of higher concentration of nucleation centres as the amount of sputtered material increases.

The deposition of the aluminium clusters was found to be extremely sensitive to presence of oxygen. The amount of oxygen needed to dramatically change the operation conditions is extremely low but it causes widening of pressure window by 50 Pa by shifting the upper border to 80 Pa. In order to prevent oxygen contamination, surface oxide layers of the target must be sputtered off prior to each deposition.

Due to chemical reactivity, aluminium clusters are also strongly susceptible to reaction with oxygen after removal from the deposition chamber into air. Unlike silver, where the silver/oxygen ratio measured by XPS was about 10, the aluminium/oxygen ratio was only about 1. High resolution XP spectra of the silver peak revealed almost only metallic bonds, while the aluminium peak measured immediately after air exposure showed 57% of aluminium oxides and after 1 month of aging it showed as much as 79% of aluminium oxides.
Figure 8. The TEM images of the aluminium clusters: a) 5 cm from the orifice, 10 s deposition; b) 25 cm from the orifice, 3 minute deposition.

Conclusions

Silver clusters were successfully prepared using both 3" and 2" cluster sources. Cluster size was characterised by SEM and TEM with respect to deposition conditions. Cluster charging was studied by electrostatic deflection using QCM with result that 60 to 70% of the clusters are charged. Aluminium clusters were prepared on 3" cluster source. The window of operation was significantly narrower than in case of silver, but clusters seemed to be of almost uniform size.

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References