Structure of the metallic films deposited on small spheres trapped in the rf magnetron plasma

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Abstract. Metallic coatings were deposited onto glass spheres having diameters from several to one hundred micrometers by the magnetron sputtering. Two different experimental schemes were exploited. One of them had the traditional configuration where a magnetron sputter was placed at one hundred millimeters from particles. In this scheme, continuous mechanical agitation in a fluidized bed was used to achieve uniformity of coatings. In the second scheme the treated particles (substrates) levitated in a magnetron rf plasma over a sputtered rf electrode (target) at the distance \(d\) of few mm from it and at gas pressure \(p\) values of 30–100 mTorr. These parameters are essentially different from those in the traditional sputtering. Agitation due to the features of a particle confinement in dusty plasma was used here to obtain uniform coatings. Thickness and morphology of the obtained coatings were studied. As it is known, film growth rate and structure are determined by the substrate temperature, the densities of ion and neutral atom fluxes to the substrate surface, the radiation flux density, and the heat energy produced due to the surface condensation of atoms and recombination of electrons and ions. These parameters particularly depend on the product of \(pd\). In the case of magnetron rf dusty plasma, it is possible to achieve the \(pd\) value several times lower than the lowest value proper to the first traditional case. Completely different dependencies of the film growth rate and structure on the \(pd\) value in these sputtering processes were observed and qualitatively explained.

1. Introduction
Deposition of a uniform metallic coating on small particles is required in producing metal-ceramics composites, hydrogen storage micro containers, laser fusion targets, electromagnetic radiation screens etc. To deposit coatings on microspheres it is necessary to retain the particles at the fixed distance from the source forming the coating atoms—magnetron sputtered target, to sustain their constant separation from each other during the whole process, which provides the safety of the coating. In [1], Lowe and Hosford studied the rf magnetron sputter deposition of a coating on single particles (size of 500 \(\mu m\)) and found that, if the particle to be coated was levitated in the gas and did not contact with solid surfaces, the resulting surfaces were the most uniform and smooth. Such a process design should just be envisioned. The magnetron sputter deposition relates to line-of-site technologies, i.e. it does not suggest any shielding objects between the treated surface and the sputtered material. Mechanical separation of particles from each other with the use of vibrations of different frequencies was applied in [2, 3]. Magnetron
sputtering allowed uniform coatings to be deposited on 10–100 \( \mu \)m particles, but the results with particles smaller than 10 \( \mu \)m were poor, because the problem of dispersing small particles had not been solved completely. The widely used fluidized bed technology is efficient with particles not smaller than 50 \( \mu \)m and having the low mass density [4,5]. A classical fluidized bed technology is unsuitable at low gas pressures [4]. One of the ways to enhance the efficiency of this technology is the introduction of gas discharge plasmas to the process. Thus, Snyder et al. [6] complemented the process of dispersion of 50 \( \mu \)m particles by the fluidized bed technology by the initiation of an inductive rf discharge in the chamber filled with particles. It was experimentally established that in the presence of plasma the concentration of particles in the bed increased several times.

There are a few techniques based on magnetron sputtering to coat spherical particles whose sizes are greater than 5 \( \mu \)m [7,8], and one was introduced by Kersten et al. [9] for smaller particles. The main feature of the latter technique is confining the treated microparticles in a dusty plasma trap. It is possible to trap the particles in plasma due to their charging. The like negative charges suppress agglomeration of particles [10]. In [9], the trap is formed using the proper electric field distribution over a special relief electrode or over a segmented one. In [11], another kind of the method was realized. The microparticles are confined in a trap formed in the rf magnetron discharge plasma. Planar magnetron discharge is characterized by non-uniform plasma density along the negatively biased electrode. The potential distribution in the magnetron discharge plasma [12,13] and the corresponding electric field lines ensure formation of an electrostatic trap for negatively charged particles in such plasma near to the electrode, even if the electrode does not have macroscopic deviations from a plane shape. Just below this trap the ions bombard the electrode closely to the particles at a distance which is of the order of the rf sheath thickness. The electrode surface is sputtered here and an atomic beam arises to form the coating on the particles in the trap.

The aims of the work were to obtain the particles coated with metal films both by means of confining them in the plasma of a magnetron rf discharge and by means of traditional sputtering method, particularly in the condition of similar product \( pd \) value, to find and describe the structure features typical for the coating in the plasma trap.

2. Experiment
In the first part of the experiment on coating small particles they were confined in magnetron rf plasma using the setup which is described in [11]. The scheme of the process is given in figure 1.

The capacitive rf discharge of 6 MHz in argon gas at pressure in the range of 30–100 mTorr and flow rate up to 2 sccm was used. The discharge plasma looks from the top like a circular glowing ring. It was separated from the sputtered electrode by the dark space of less than
1.5 mm thick in the experiments. The discharge peak-to-peak voltage was up to 400 V (the rf discharge power was up to 30 W). The negative self-bias of the sputtered electrode was up to 100 V. We use copper or silver sputtered grounded targets. After the discharge was turned on the sputtered area appeared below the plasma glow as a closed circular contour of 45 mm in diameter (see figure 1).

Glassy spheres with diameters in the range of 30–100 µm and monodisperse silica balls of 5.35 µm mean diameter (microParticles GmbH) were injected into the discharge plasma using the method described in [11]. The levitating cloud was visualized by the laser-light scattering technique. The deposition time was varied from 5 up to 40 minutes. The coated microspheres were collected on the special substrate placed near the sputtered area at the side opposite to the injecting electrode. By shifting the magnetic system and inclining the chamber one can locate the trap with microspheres above the substrate (the dashed line in figure 1). The substrate was covered by the movable screen that shielded it from the undesired untimely collection of microspheres and from the sputtered atom deposition. At the end of each treatment the screen was removed, the trap was shifted to the drain region, the rf voltage was turned off and the coated microspheres were collected on the substrate. To get the reference samples of the coating two flat polished oxidized silicon substrates were located closely to the discharge in a separate run. One of them was put horizontally with the flat surface faced upward on the target near the sputtered track. The other was hung vertically with the flat surface faced to the discharge glowing ring and was at floating potential.

In the second part of the experiment the already noted big glassy spheres as well as the cenospheres (from conventional power station waste) with diameters in the range of 30–250 µm were coated with copper and aluminum by DC magnetron sputtering. The cenospheres have the larger wall thickness of several microns and a lot of defects on the outer surface. The fluidized bed technique was used to agitate the particles. The particles were placed in a metal container open from above. The magnetron sputter with a copper or aluminum target was placed above the container at the distance of 100 mm from the bottom. The sputter was run at DC discharge power of 1 kW, at the argon gas pressure of 2 mTorr and flow rate of a few sccm. To get a uniform coating over the whole surface of microspheres they were used to form a cloud inside the container. On this purpose the inertial dispenser created container vibrations with the frequency of 50 Hz. The maximal amplitude of vibrations was 1.5 mm and the optimum one was selected in the experiments. For that the cloud was illuminated by a laser beam. The amplitudes were considered optimal when, firstly, a dense cloud of microspheres was created inside the container of 1–3 cm in height (it was established at the atmospheric pressure) and, secondly, the microspheres did not leave the container, i.e. above the container only individual particles were registered in the laser beam (it was established in the evacuated chamber). The temperature of the container was measured in the process with the thermocouple. The structure of the particles was studied using scanning electron microscope (SEM) images and their elemental composition was investigated by the energy dispersive X-ray (EDX) method. To determine the average film growth rate on the particles we broke them in some parts and estimated the film thickness using the SEM images of the disruptions in the film.

3. Results

The initial surfaces of the silica balls and glassy spheres were quite smooth, at least according to the SEM images. The coatings obtained in both schemes demonstrated the island mode of the growth. First we describe the structure of the coatings obtained in the traditional sputtering scheme on conditions of a high DC magnetron discharge power, a large distance between the microsubstrates and the target, and a low sputtering gas pressure.

A part of high DC discharge power is consumed to heating the container with the spheres inside it. The value of temperature close to the stationary one was 520 K. The image of the
Figure 2. Cu island coating on the surface of the fractured glass sphere obtained in the fluidized bed is seen to the right. The cleavage of the glass wall is seen in the middle.

Figure 3. Fractures of the copper coating on the glass sphere. The films were obtained in the fluidized bed.

copper film typical for the beginning of the growth is given in figure 2. There are crystallites of substantially different sizes in the film. The observed structure can be described taking the measured temperature value as the temperature of microsubstrates. The wide island size distribution is typical for the incomplete regime of condensation at low supersaturation value. A considerable decrease in the condensation coefficient takes place at increasing the substrate temperature $T_s$ in the range of $(0.3–0.4)T_m$ [14], where $T_m$ is the melting point temperature. According to the temperature measured results the bottom value is reached in the first stage of the copper sputtering process. This resulted in a high desorption rate and led to the observed development of incomplete condensation regime.

After sputtering for 30–60 minutes a continuous metal layers of submicron thickness were obtained at the particles in the sample of 10 cm$^3$ volume. The fracture of the copper coating on the glass sphere is given in figure 3. In the given stage of the growth the film is coarse-grained keeping the high roughness typical for the film at the earlier stage. One may suggest from the image analysis that the crystallites of submicron size which are the main structure element of the film are bounded firmly. The structure of the film and the sputtering conditions ($T \sim 0.4T_m$, $p = 2$ mTorr) correspond to zone 2 of the Movchan–Demchishin–Thornton model of a thick film growth [15].

The optical images of the cenospheres before and after coating with aluminum are given in figure 4.
Figure 4. Cenospheres with diameters in the range of 30–250 µm (a) before and (b) after coating with aluminum.

Figure 5. Image of the radial crosssection (left part) of the particle cloud consisted of small silica balls and glassy spheres in rf magnetron plasma (millimeter scale is given).

Figure 6. Mean value of the distance between the target and the region of confinement for particles of different masses and diameters compared to the discharge dark space width.

Microspheres levitated above the sputtered track at the height of 1.5–2.2 mm. Small silica balls were confined at the height of 2.5–4 mm, see figures 5 and 6. The particles were illuminated by the green laser beam expanded in the vertical direction. In figure 5, the horizontal green line is due to the intersection of the beam with the target surface under the cloud. The top view of the cloud in our experiment was geometrically similar to the form of the sputtered track.

The temperature of the particles levitating in the discharge was estimated by the method of [16], based on the energy flow balance at the particle surface. The particles are supposed to be heated by recombination of ions and electrons at its surface, by transfer of kinetic energy of electrons, ions, fast gas atoms and sputtered atoms, by condensation of the latter and by heat radiation towards the particle. Cooling of the particles was due to heat radiation and thermal conduction of the gas.

The particle temperatures obtained for various plasma parameters are given in table 1. The main differences of our study from the results of [16] are the more considerable contribution of the sputtered atoms to heating and the lower contribution of the radiation to the heat losses because of the smaller values of the metal film emissivity in our case. The temperature of
the particles is less than 450 K, so the coating deposition occurs without re-evaporation. The incoming flow of sputtered atoms is absorbed completely (condensation coefficients are close to unity [14]). The sputtered metal atom flow to particle surface $R$, estimated using an average coating growth rate, was in the range of $4 \times 10^{14} - 1.8 \times 10^{15}$ cm$^{-2}$s$^{-1}$.

We can determine surface island density not earlier than at the final stage of their growth, just before the initial stage of their coalescence, using SEM image similar to the one given in figure 7. The surface island density $n_x$ in this stage is in the range of $(1 - 6) \times 10^{10}$ cm$^{-2}$. These values are somewhat lower than the ones typical for the growth of silver coatings on flat surfaces of oxidized amorphous silicon at the room temperature and some lower value of $R$ [16]. This does not contradict the conclusions of the classical theory of island growth of the film, according to which the dependence of $n_x$ on the surface temperature is stronger than on the atomic flux density [14].

All the particles had uniform coatings after the treatment. The coating morphology was special for each type of particles (figures 8–10) and depended essentially on the region of particle levitation relative to the target location and on the target material. During the growth of a silver coating and in most cases of a copper coating the enlargement of lateral dimensions of all the crystallites was observed (at different levitation conditions on $p$ and $d$). In some cases it corresponded to the geometric crystal selection rule. On the contrary, in silver coatings on small particles the relatively large, 300–400 nm in size, well-faceted separate Ag crystals were formed, figure 8. That does not directly correspond to the classic zonal Movchan-Demchishin-Thornton film growth model [15]. According to it the temperature of not less than $0.4T_m$ is necessary for the formation of faceted crystallites in a thick film. The estimations gave approximately the same values of the order of $10^{15}$ cm$^{-2}$s$^{-1}$ for the densities of the metal atom flux from the target and for the ionic one from the bulk plasma to the particle. Therefore, the observed growth of large faceted grains on the prominent parts of the coating seems to be promoted by the relatively low density of a sputtered atom flux and by presence of flux of ions, having energy of a few tens of electron-volts, to these parts of the floating particles. The intergrowth of the crystallites is hampered because the metal adatom diffusion on the developed surface relief between the crystallites is suppressed due to the high surface density of argon adatoms under the high argon pressure in the process.

Both the copper coatings and the silver ones on small silica balls demonstrate the attributes of the spherulitic growth. The copper coated silica particles have the appearance of the closed spherulites and the silver ones have the appearance of the open spherulites, compare figures 8
Figure 8. The silver coating on the silica ball.

Figure 9. The copper coating on the silica ball.

Figure 10. The copper coating on the glass sphere with diameter of 57 µm. The film was obtained in the dusty trap.

Figure 11. The silver coating on the flat substrate located on the sputtered electrode on one side of the discharge ring.

and 9. Essential distinctions of silver and copper films morphologies may be explained by the greater defect quantity on the copper surface. The occurrence of the defects is connected with the incorporation of impurity atoms, for example, oxygen into a Cu lattice. It has been known that even 2 ppm admixture (Cd in Au) [14] enhances the density of islands. In our case the inclusion is a copper oxide.

Nodular growth [18] within a coating is observed in some cases. A lot of nodules grow on the surfaces of cenospheres that are rich of relief defects. In the case of using a copper target the nodules grow on smoother surfaces too, e.g. on the surfaces of small silica balls. Both the nodules and the rest part of the film consist of smaller crystallites. It means that the continuous splitting of the growing crystals took place all over the film surface in the case. Due to this fact the nodules have plane or broken induction border surfaces, that is distinct from results of [18], where the border surfaces were hyperboloid-like. On reaching the film thickness of several hundreds of nanometers the branch cracks may appear in the film (figure 9). They rounded the nodules or other micron-sized film surface regions. The weak bonding between crystallites is typical for the film growth on condition of low temperatures and high pressures.
of tens of millitorrs. The cause is the high rate of the argon atom adsorption on the condition, which induces the decrease in the metal atom diffusion rate on the surface. It is known that high intrinsic tensile stress is observed in metal films that are obtained in the deposition process where the oblique component of sputtered atom flux to the substrate surface is substantial [19]. It is this off-normal incidence that is proper to our deposition process due to the 3D form of the substrates used.

Thus in both cases the temperature of small particles was insufficient to provide the strong crystallite coalescence at this stage of the growth.

On the contrary the film obtained on glass spheres with the diameter of 30–70 µm demonstrated coalescence of crystallites (see figure 10). The fact may be described by the enhanced ion bombardment of the heavier particles that were confined in the region of the large electric field strength. The similar structure was observed in the coating obtained on the flat ion-bombarded native oxidized silicon substrate that was located on the target near the discharge ring, given in figure 11. And in the coating on the floated flat substrate the crystallites had more pronounced faces. The influence of ion bombardment on the film growth characteristics requires the development of the modified zone model, for instance as in [20].

The mean growth rates $G$ of the films on the glass spheres with diameters 30–60 µm and on the small silica balls were: about 0.15 nm/s for the copper and 0.3 nm/s for the silver. On the contrary, no films were obtained on the big glass spheres with diameters of 80–100 µm levitated close to the copper target, at the distance $d$ that was less or equal to the dark space width. After the deposition process their surfaces saved high initial smoothness that is proper to glass. The growth rates of the silver films obtained on such particles levitating close to the silver target at the same distance were equal to approximately one quarter of the growth rate on the silica balls. In many deposition processes the dependence of the growth rate on the distance between the target and the substrate, $d$, is well described by the Keller-Simmons formula [21] that predicts the monotonic decrease in $G$ with increasing $d$ and $p$. The formula was obtained from analysis of the sputtered atoms transport in the gap between the target and the substrate which did not take into account the resputtering of the coating by the high-energetic species and the reflection of sputtered atoms from the coating. Deviations from the formula predictions may be connected with these processes. In [21], 5–10% decrease in the growth rate of a copper film with the decrease in gas pressure $p$ in the low gas pressure range was observed. The observation was interpreted as the result of the decrease of sticking probability for elements of low surface binding energy caused by the bombardment of the film by the fast argon atoms reflected from the target.

The decrease in the metal atom sticking coefficient with the decrease in $d$ was observed in [22]. The effect was described by the raised heating of the substrate with the decrease in $d$ on the conditions of the experiment. Growth of the surface temperature may cause a higher desorption rate. In our case the distance between the target and substrate particles is smaller by 1–2 orders of the magnitude, and, therefore, their heat exchange will define the heat balance. The significant difference of our scheme is the proximity of the microsubstrates to the cold target, so the conditions to obtain the supersaturation, both of material income sufficiency and quite low substrate temperature of $T_s = (0.2 – 0.3) T_m$, would be fulfilled. Therefore the suppression of the film growth on the heaviest spheres levitated near the sheath edge may be interpreted as the result of the adatom desorption caused by the direct ion bombardment.

4. Conclusions
Metallic coatings were deposited onto glass spheres levitating in the plasma of a magnetron rf discharge at a distance of less than 3 mm from the sputtered target. To confine the larger dust particles in plasma a higher electric field is required, so the distance between the levitation region and the target decreases with increasing the dust particle mass. Both the growth rate and the
structure of the coatings strongly depend on the particle size. The growth of metal films on the surface of the dust particles levitating in the upper part of the trap in these conditions obeys the following laws: the growth mode is an island one at moderate fluxes of metal atoms and low temperatures of the substrate; increasing the flux of metal atoms and increasing the number of defects result in reducing the size and in increasing the surface density of the crystallites; the crystallites are loose-bonded at high pressure of the gas in the sputtering process.

The growth of metal films on the surface of the dust particles levitating in the middle region of the trap is characterized by a solid intergrowth of crystallites and the relatively small roughness of the coating. This is due to the increased ion bombardment of the film with the approach of dust particles to the electrode sheath edge.

To obtain the coatings with the required properties in this experimental scheme it is necessary to study the levitation region in the near-electrode sheath of the discharge and select the discharge parameters: the gas pressure, the rf power and the electrode-target temperature.

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References
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