SIZE-DEPENDENT DENSITY OF GOLD NANO-CLUSTERS AND NANO-LAYERS DEPOSITED ON SOLID SURFACE

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Firstly, I would like to say, this contribution is written only for this Dedicated Issue of CCCC, only for my sweet boss, dear friend and my heavy critic Zrzek. Time to time I attended some conferences focused on modeling, simulations and I understood this point badly. Many renowned professors spoke about some playing with balls and only gradually I have found out that "playing with small balls" could be useful, important and had many applications. To delight my dear Zrzek, I started to look intensively for some suitable "ball problem" for me. Thanks to my dear colleagues, co-authors of this paper, I got a chance for "balling". I have chosen the special problem of gold nano-clusters and nano-layers sputtered on solid surfaces.

The gold density enters some indirect determination of gold properties as an input parameter. Reported gold density of 19 320 kg m^{-3} at standard conditions is correct for gold bulk or macro-sized specimens. For nano-sized specimens (nano-clusters, nano-layers), however, this standard density value need not be applicable. This work deals with gold density as a function of the nano-structure size. The calculated density was compared with experimental one performed for gold sputtered onto glass or poly(ethylene terephthalate) substrates. Calculated gold density was found to increase from 11 249 to 19 304 kg m^{-3} when the characteristic dimension of gold nano-structures increases from 0.7 to 82 nm. At the same time the free volume fraction in nano-structures decreases from 57 to 26%.

Keywords: Au sputtering; AFM, AAS and FIB-SEM methods; Au density calculation and measurement; Free volume ratio; Lattice parameter; Nanoparticles; Nanotechnology.

Vacuum-deposited metal clusters and thin films play an important role in various fields of technology[1]. Gold in the form of thin films is nowadays used in a vast range of applications such as micro- and nano-electromechanical systems (MEMS and NEMS)[2], sensors[3], electronic textiles[4], bioengineering[5], generators of non-linear optical properties[6] or devices for surface-enhanced Raman scattering[7].

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Bulk gold is a shiny, yellow noble metal that does not tarnish, is non-magnetic, melts at the temperature $T = 1336$ K and has got a density value of $\rho = 19\,320$ kg m^{-3}. However, it is well known that the properties of gold vary depending on their size in the range of nano-dimension rapidly due to the so called surface size and quantum size effects[8,9]. Also different arrangement of Au crystal lattice, lattice parameter values and a certain volume disorder play an important role in property changes of nano-sized materials[9–15]. Both the size effects and the different arrangement of crystal lattice result in that gold nanoparticles exhibit different values of many physico-chemical properties in contrast to the bulk.

For a long time we have studied many physical and physico-chemical properties of thin gold nano-layers and nano-clusters sputtered or evaporated on different substrates, e.g. glass, silicon and some polymers[9,13,16–21]. We have confirmed that the gold properties vary significantly depending on sample dimension, size of clusters or thickness of layers, especially in nano-sized region. For these investigations the precise knowledge of layer thickness is of crucial importance.

There are several methods for determination or measurement of apparent layer thickness, e.g. atomic force microscopy (AFM), focused ion beam with scanning electron microscopy (FIB-SEM) or atomic absorption spectroscopy (AAS)[17,19,22]. All of them have their limitations. AFM and SEM are direct measurement techniques but they belong to less spread technique. Due to this, AAS is applied more often in comparison with others even this is indirect determination method.

For the last one, the density of gold is necessary. As was discussed above, many basic physical properties, between them density, is not constant and they depend on cluster size in nano-region[10–13]. Due to this, we calculated density of gold depending on size of nano-structures and we compared it with experimental data. The experiments were performed on gold layers sputtered onto glass and poly(ethylene terephthalate) (PET) substrates.

EXPERIMENTAL

Substrate and Au Deposition

The gold layers were sputtered on 2 × 2 cm microscopic glass substrate, 1 mm thick, supplied by Glassbel Ltd., Czech Republic. Glass surface roughness of $R_a = 0.34$ nm was determined by AFM method on the square 1.5 × 1.5 μm. Gold layers were also deposited onto 50 μm thick PET film supplied by Goodfelow, UK.

The sputtering was accomplished on Balzers SCD 050 device from gold target (purity 99.99%, supplied by Goodfelow Ltd.). The deposition conditions were following: DC Ar plasma, gas purity 99.995%, discharge power of 7.5 W, Ar flow approximately 0.3 l s^{-1}, pressure of 5 Pa, electrode distance of 50 mm, electrode area of 48 cm^2 and reaction chamber volume ca. 1000 cm^3. The sputtering times vary from 4 to 500 s.

Diagnostic Techniques for Determination of the Apparent Layer Thickness

Apparent layer thickness was determined using 3 independent techniques: (i) AAS, which is indirect method described below, (ii) FIB-SEM image of a cross-section perpendicular to the sample surface, and (iii) AFM with scratch method[23].

The first technique comprises complete removal of the gold layer from a well-defined part of the sample surface, and the determination of gold content using AAS on a Varian AA 880 device using a flame-atomization technique at a wavelength of 242.8 nm, the accuracy of this determination is presented as 10% (see ref.[22]). The procedure consist of dissolution of deposited gold layer in well defined volume of a solvent, determination of concentration of gold in the solution, calculation of gold amount in solution and its conversion into apparent layer thickness. For this calculation we always used the tabulated bulk value[24] of gold density (ρ = 19 320 kg m^{-3}).

One of the direct measurements of the apparent layer thickness was accomplished by SEM (SEM, JSM-7500F). The specimen for SEM examination was prepared by cross-sectioning of the metal–polymer sample on a standard cross-section polisher (CP), with a focused ion beam (FIB, 6 kV acceleration voltage, 2 h operation). Both of these methods (AAS and SEM) are suitable for glass and PET substrates.

Apparent layer thickness for chosen sputtering times was examined using AFM, too. The AFM images were taken under ambient conditions on a Digital Instruments CP II set-up. The samples of 1 cm^2 in area were mounted on stubs using double-sided adhesive. A large area scanner was used, allowing area up to 100 μm^2 to be imaged. A Veeco phosphorus doped silicon probe CONT20A-CP with spring constant 0.9 N m^{-1} was chosen. The scratches were done at ten different specimen positions (for each examined layer thickness) by nanointendation tip. The apparent layer thickness was determined from AFM scan done in contact mode. AFM is not acceptable for polymers because of their low hardness.

RESULTS AND DISCUSSION

The dependence of the gold apparent layer thickness, determined by all mentioned methods (AAS, FIB-SEM and AFM) on sputtering time is shown in Fig. 1. For large thicknesses the values obtained by three different techniques are the same (see Fig. 1, at higher sputtering time). For low thicknesses the values obtained by AAS method are significantly lower than those obtained by two other methods (see Fig. 1, the detail). Also generally it is known the metal layers grow linearly with deposition time for evaporated and sputtered metal structures. This dependence is clear for AAS values of thicker layers and for other methods, but AAS results for thinner structures show non-linearity (see Fig. 1, under 50 s). The reason may be an imperfect dissolution of gold removed from the sample surface. But it was disproved by experiment – we have measured the weight of glass substrate before and after deposition and dissolution of Au structures, and the substrate weights were the same (in terms of experimental error). Another reason may be bulk gold density used for thickness calculation. Obviously a density dependence on the layer thickness should be taken into account. As it was presented previously for evaporated Au structures[10–12], lattice parameter and density depend on the thicknesses.

The changes of the gold density can be related to a free volume fraction within gold clusters which is a decreasing function of increasing cluster size. In Fig. 2 the concept of the free volume fraction is illustrated by 2D images of two clusters of different sizes and lattice parameters. Smaller gold cluster embodies higher lattice parameter[13] that results in larger distance between atoms and higher fraction of the free volume.

Detailed description of gold deposition onto solid surfaces can be found in ref.[1]. It was shown that the layer growth proceeds in four stages (nucleation, lateral growth, coarsening and vertical growth) and it results in creation of metal nano-block[1]. The knowledge of the nano-clusters shape is important information for calculation of nano-clusters volume. In Fig. 3, the layer growth is illustrated by two SEM scans of gold layer sputtered on PET for 30 and 500 s. Thinner layer is not continuous and it consists of separated gold clusters, the shape of which is close to cuboids.

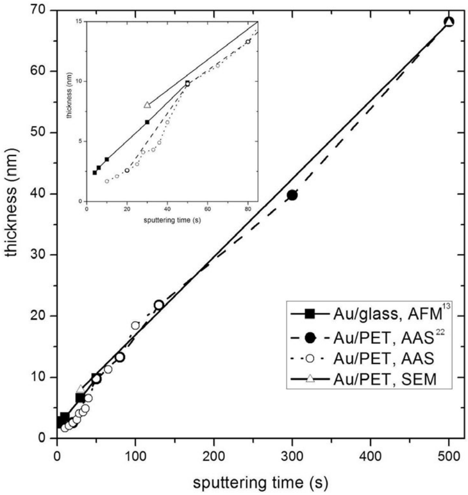

Fig. 1

Thickness of Au layer (or clusters) sputtered on glass and PET obtained by AAS (circles; full circles[22]), AFM [13] (squares) and FIB-SEM (triangles) for different sputtering time

Present density calculation is based on the following basic equation

$$\rho = \frac{m}{V} = \frac{m_{\mathrm{Au}}}{V} = \frac{N_{\mathrm{Au}} M_{\mathrm{Au}}}{(V_{\mathrm{Au}} + V_{\mathrm{free}})} = \frac{N_{\mathrm{Au}} M_{\mathrm{Au}}}{L_i L_j L_k} \qquad (1)$$

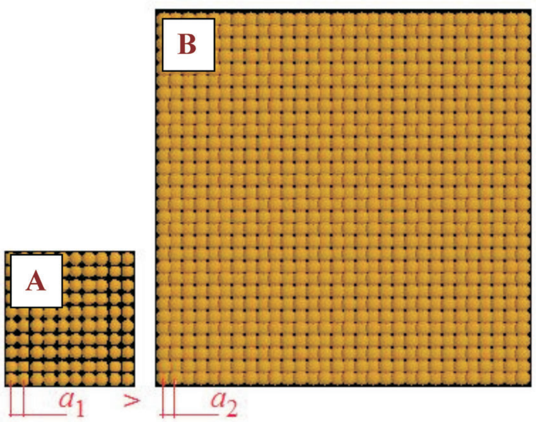

FIG. 2
2D model of gold clusters of different lattice parameters: a_1 (A) and a_2 (B) ($a_1 > a_2$). The smaller cluster means the higher value of lattice parameter and the higher free volume fraction

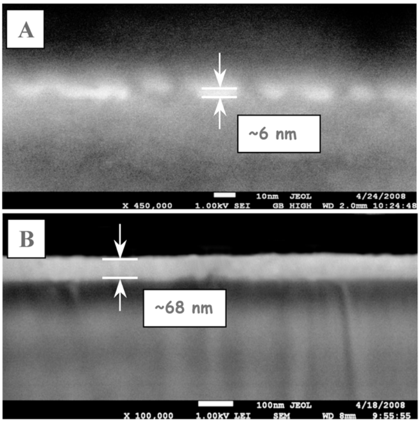

FIG. 3
SEM scan of Au layer sputtered on PET for deposition times 30 s (A) and 500 s (B). The cut was done by the FIB (focused ion beam) method

where m_{Au} is a weight of all Au atoms presented in nano-cluster, V is volume of nano-cluster including the Au atoms volume V_{Au} and free volume V_{free} (the volume between individual atoms in nano-cluster), N_{Au} is a number of all Au atoms in nano-cluster, M_{Au} is a mass of one Au atom, L_i, L_j, L_k are edge lengths of nano-cluster. V and L_i, L_j, L_k are obtained from a lattice parameter a, which presents the distance between individual atoms. Length L (L_i, L_j and L_k, respectively) of nano-cluster is given by the relation

$$L = (N-1)a + 2r_{Au} \tag{2}$$

where N is a number of atoms in the relevant edge of the nano-cluster and $r_{Au} = 0.144$ nm is a radius of Au atom[24]. Lattice parameter a was determined by X-ray diffraction method for layers with apparent thicknesses ranging from 10 to 75 nm (see ref.[13]). We used two extreme lattice parameter values[13] $a_1 = 0.40839 \pm 0.00022$ nm and $a_2 = 0.40731 \pm 0.00011$ nm obtained for the thinnest and the thickest cluster and layer thicknesses, respectively, and it was demonstrated the density determined using Eq. (*1*) depends on the nano-cluster size. We were able to satisfactorily determine the lattice parameter only for apparent layer thicknesses exceeding 10 nm. For thinner layers the lattice parameter must be extrapolated. Here we present new relation for the description of the dependence of lattice parameter a on the layer thickness d, which is similar to one recommended[14]

$$a = A_0 + A_1 \exp(-d/b_1) + A_2 \exp(-d/b_2) + A_3 \exp(-d/b_3) \tag{3}$$

where d is the cluster or layer thickness (in nm), and A_0–A_3 and b_1–b_3 are parameters with the following values $A_0 = 0.40724$, $A_1 = 0.02664$, $b_1 = 3.22086$, $A_2 = 6.52396 \times 10^{-4}$, $b_2 = 30.92880$, $A_3 = 0.03030$, $b_3 = 3.22083$. Parameters of Eq. (*3*) were calculated from values of lattice parameters presented earlier[13]. Equation (*3*) was used instead of the fixed value of the lattice parameter into equations for nano-cluster edge, volume and Au density by Eqs (*1*) and (2).

In Fig. 4 the density as a function of the structure edge (for individual clusters) or of the layer thickness (for homogenous layers) calculated from Eq. (*1*) under different lattice parameters is shown. Curves 1 to 3 present calculated density for two extremes fixed lattice parameters a_1, a_2, (curves 1 and 2) and for lattice parameter calculated from Eq. (*3*) (curve 3). Calculated density is compared with experimental data[13] (curve 4). It is seen that the experimental values roughly follow expected dependence but they lie well below calculated ones. For thinner layers the observed discrepancy may be due to the fact that the layers are discontinuous[13] and the discontinuity was not reflected in the density determination. Regarding that experimental determination of lattice parameter is known only for apparent thicknesses above 10 nm, density values for thinner layers can be affected by surface of substrates and their chemistry[13] and it is only "extrapolated" density unconfirmed by experiments.

We compared our results with once published previously for evaporated Au structures[10–12]. Values of lattice parameters and density are presented for the thicker layer thicknesses[10–12] in comparison with our ones unfortunately. But the trend of dependences of lattice parameters and density versus layer thicknesses are the same.

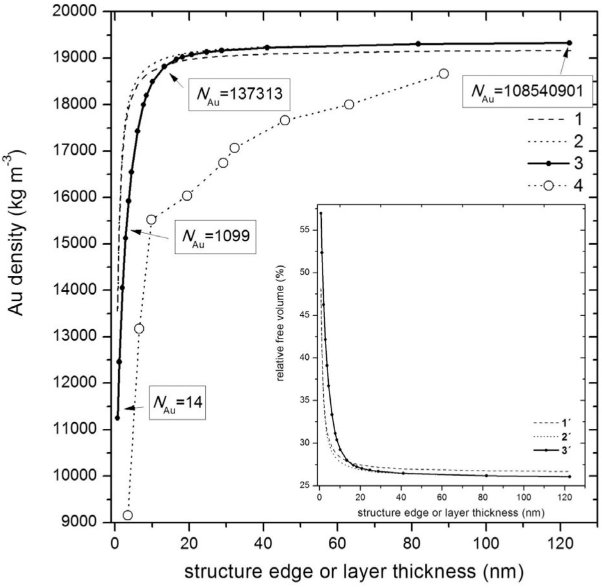

FIG. 4
Density versus layer thickness calculated by Eq. (*1*) under different assumptions: 1, for constant lattice parameter a_1 = 0.40839 nm; 2, for constant lattice parameter a_2 = 0.40731 nm; 3, for lattice parameter determined from Eq. (*3*); 4, for experimental data[13]. N_{Au} is total number of Au atoms in nano-cluster of presented structure edge or layer thickness. In the inset the dependence of the free volume fraction, calculated from Eq. (*4*), on the structure edge or layer thickness is shown under the same assumption: 1′, for constant lattice parameter a_1 = 0.40839 nm; 2′, for constant lattice parameter a_2 = 0.40731 nm; 3′, for lattice parameter determined from Eq. (*3*)

We have also calculated the free volume fraction $(V_{\mathrm{free}})_{\mathrm{rel}}$ from the following equation

$$(V_{\mathrm{free}})_{\mathrm{rel}} = \frac{(V - V_{\mathrm{Au}})}{V} 100 \,. \qquad (4)$$

The calculated values as a function of the layer thickness are shown in the inset of Fig. 4. As could be expected, the free volume fraction is a decreasing function of the structure edge (for individual clusters) or of the layer thickness (for homogenous layers). It varies from 56% for thinner layer to 26% for layer 80 nm thick. That means the saturation of clusters or layers by gold atoms as 74%. The value of 74.05% is tabulated for bulk gold[24].

SYMBOLS

a, a_1, a_2	lattice parameters, nm
A_0–A_3,	parameters of Eq. (*3*)
b_1–b_3	parameters of Eq. (*3*)
d	layer thickness, nm
L_i, L_j, L_k	edge lengths of nano-cluster, nm
m_{Au}	weight of all Au atoms, kg
M_{Au}	mass of one Au atom, $3.2707135763762 \times 10^{-25}$ kg
N	number of atoms in the relevant edge of nano-cluster
N_{Au},	number of all Au atoms in nano-cluster
r_{Au}	radius of Au atom, 0.144 nm
R_a	surface roughness, nm
V	volume of nano-cluster, nm^3
V_{Au}	volume of Au atoms in nano-cluster, nm^3
V_{free}	free volume between individual atoms in nano-cluster, nm^3
$(V_{\mathrm{free}})_{\mathrm{rel}}$	free volume fraction, %
ρ	density, kg m^{-3}

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