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IsGISAXS simulations of the gold clusters growing on PS thin film

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Contents

1 Introduction

The adjustment of size-dependent catalytic, electrical and optical properties of gold cluster assemblies is a very significant issue in modern applied nanotechnology. In this report some simulations for gold growing on the polysterine layer is presented. These simulations enable the extraction of morphological real space parameters, such as cluster size and shape, correlation distance, layer porosity and surface coverage, directly from reciprocal space scattering data. This approach enables a large variety of future investigations of the influence of different process parameters on the thin metal film morphology. Furthermore, this study allows for deducing the wetting behavior of gold cluster films on solid substrates and provides a better understanding of the growth kinetics in general, which is essential for optimization of manufacturing parameters, saving energy and resources.

2 GISAXS (Grazing incedence small angle x-ray scattering)

A sketch of the GISAXS geometry and the general sputter deposition process is depicted in Fig. 1. For direct current (DC) sputter deposition, a voltage is applied to two parallel electrodes at low argon (Ar) pressure resulting in a plasma discharge. Gold atoms are emitted from the target due to impacts of accelerated argon ions onto the target leading to deposition and cluster growth on the substrate. In the present investigation, a micro- focused X-ray beam at a grazing incidence angle ai enables the detection of diffuse scattering $I(2\theta_f, \alpha_f)$ as a function of the exit angle α_f and the out-of-plane angle $2\theta_f$ by any type of roughness or electron density variation in the near surface regime. The components of the scattering vector perpendicular and parallel to the sample surface are

$$q_x = \frac{2\pi}{\lambda}(\cos(2\theta_f)\cos(\alpha_f) - \cos(\alpha_i)) \quad (1)$$

$$q_y = \frac{2\pi}{\lambda}(\sin(2\theta_f)\cos(\alpha_i)) \quad (2)$$

$$q_z = \frac{2\pi}{\lambda}(\sin(\alpha_f) + \sin(\alpha_i)) \quad (3)$$

The scattered intensity $I(q_y, q_z)$ corresponds to a collective momentum transfer of an assembly of particles. It is proportional to the total interference function $S(q_y, q_z)$ and the square of the particle form factor $F(q_y, q_z)$. $S(q_y, q_z)$ is the Fourier transform of the particle autocorrelation function describing the spatial arrangement of particles on the surface and $F(q_y, q_z)$ is the Fourier transform of the electron density correlation function. Consequently, correlations perpendicular to the surface appear in the q_z direction, e.g. height of nanoparticles, roughness and layer thickness (Fig. 1).

In figure . 1. a schematic image of scattering geometry is shown. An X-ray beam arrives at the sample with an incident wave vector k_i and at grazing incidence angle α_{in} and it is scattered under the polar angle α_{out} and the azimuthal angle $2\theta_f$.

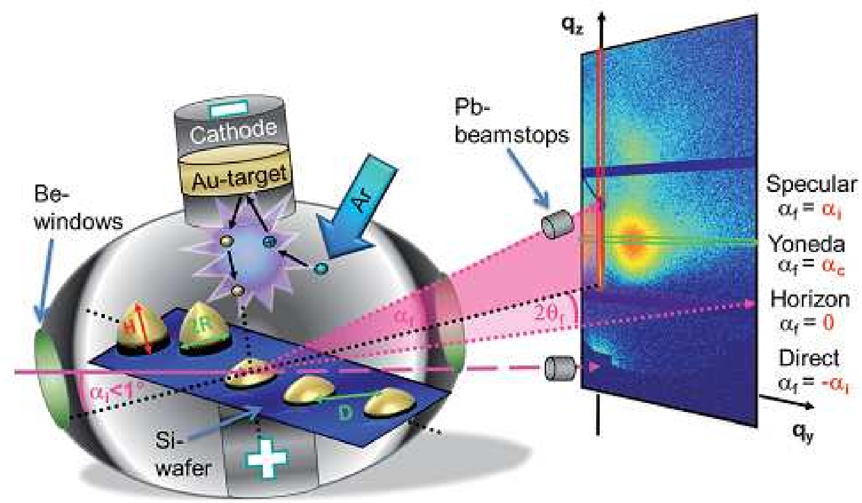


Figure 1: Scheme of the transportable ultra-high vacuum (UHV) sputter chamber in a microbeam grazing incidence small-angle X-ray scattering

3 Model

The model of growth of the gold clusters on the polysterine thin film was made by Matthias Schwartzkopf. This model has experimental confirmation.

The gold clusters are assumed to be hemi-spherical shaped when they are comparatively small ($R < D$) and worm-like shaped when they are comparatively big ($R > D$) .R is a radius of each gold cluster and D is a distance between 2 cluster centers. The influence of different parameters (PS film thickness, roughness of the PS film, size of the clusters, contact angle, incident angle and depth of the clusters) on the GISAXS pattern was studied.

4 Simulations

During the Summerschool several simulations of GISAXS patterns of the gold clusters on PS film with silicon substrate were done using IsGISAXS programm. IsGISAXS is a software dedicated to the simulation and analysis of Grazing Incidence Small Angle X-Ray Scattering (GISAXS) from nanostructures. For the all simulations $\lambda = 0.96$ nm, pixel size 172 nm, distance to detector 2750 nm.

4.1 Growth of the hemispherical gold clusters

The simulation of growth of the hemispherical gold clusters in the first 8nm thickness was done with the step 0.1 nm. The PS film thickness was 100 nm $\alpha_{inc} = 0.5$ deg. As can be seen from the pictures 2, 3, 4 and 5 the shape of the specular rod changes completely due to the size of the hemi-spherical gold clusters.

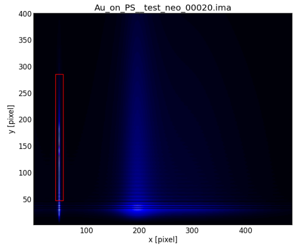


Figure 2: R=2 nm

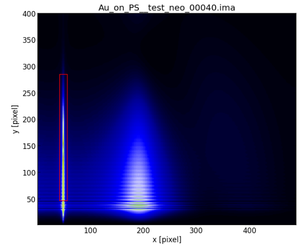


Figure 3: R=4 nm

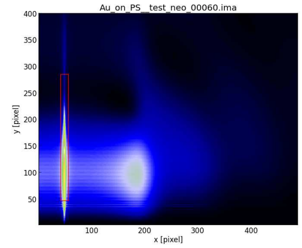


Figure 4: R=6 nm

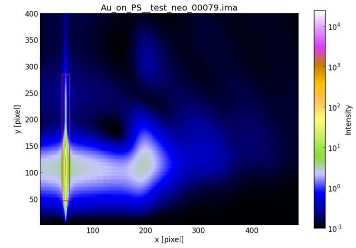


Figure 5: R=8 nm

4.2 Additional box-like clusters

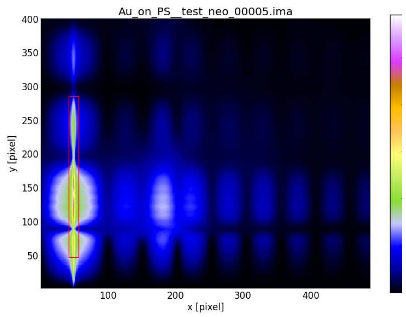


Figure 6:

5% Box-like clusters

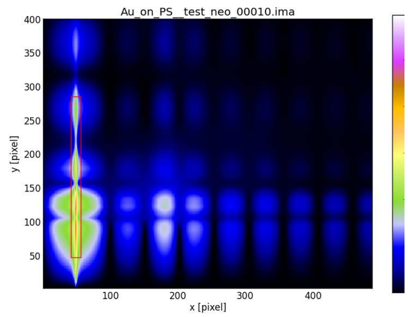


Figure 7:

10% Box-like clusters

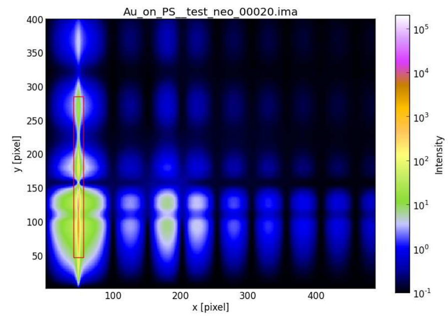


Figure 8:

20% Box-like clusters

When the clusters grow, the distance between them becomes smaller, and if $D < 2R$ the clusters touch each other and form a worm-like clusters. These worm-like clusters were simulated as a box-like clusters and hemi-ellipsoid clusters.

Two sets of simulations ware done. One with the combination of hemi-spherical clusters and additional box-like clusters and another one with combination of hemi-spherical and hemi-ellipsoid clusters.

The first simulation with the box-like clusters shows that these additional clusters change the GISAXS pattern completely even if there is a small amount of them. This GISAXS pattern does not look similar to the experimental one, which means that box-like clusters are not suitable to simulate worm-like clusters.

4.3 Variation of the film thickness

The simulation of GISAXS patterns with different PS film thickness were done. Other parameters were: $R = 5nm$, $H = 5nm$, $\alpha_{inc} = 0.5deg$. Some of the patterns are shown at the figure 9, 10 and 24. From these patterns can be seen that the frequency of the oscillations is changing due to the change of PS film thickness.

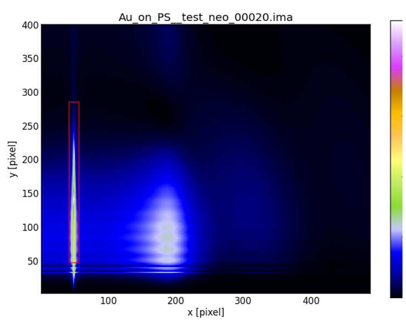


Figure 9: D=36 nm

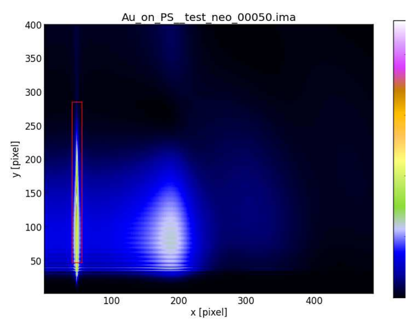


Figure 10: D=98 nm

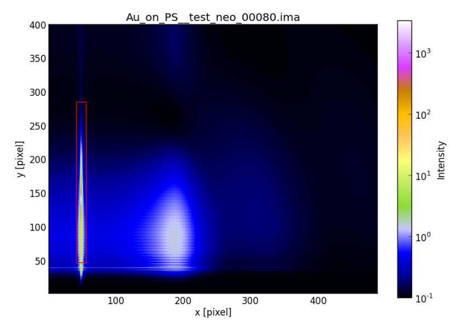


Figure 11: D=158 nm

To calculate the dependance of the oscillations from the film thickness some cuts were dome, and every cut was fit with the $F = H\sin(w(x-c))$ function. For the good statistics the intensity has been integrated over 8 pixels in the q_y direction. The dependence of the frequency of oscillations (w) from the film thickness is shown on figure 12. This was fitted with the linear function

$$F(l) = al + b, \tag{4}$$

where F is a frequency, l - layer thickness. From the fit $a = 0.35 \pm 0.005$ $b = 3.5 \pm 0.6$.

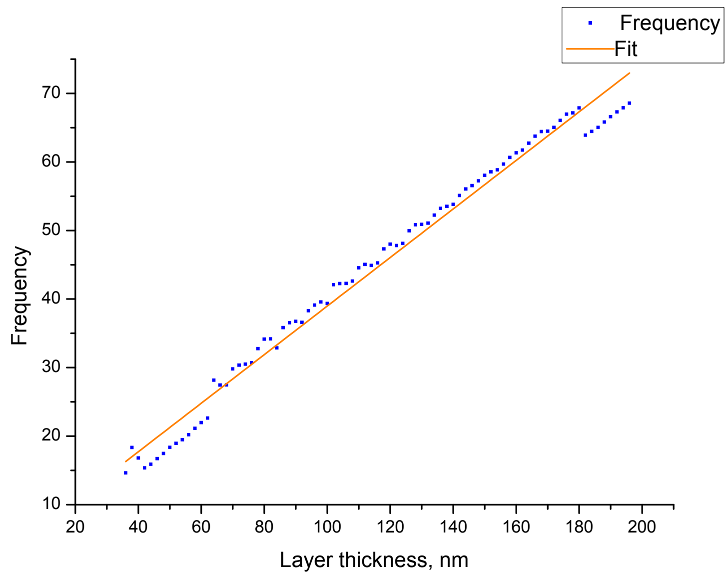


Figure 12: Frequency of oscillations

4.4 Variation of roughness

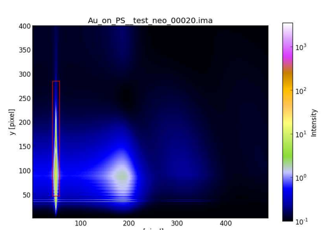


Figure 13: σ=2

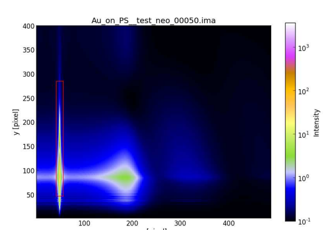


Figure 14: σ=5.5

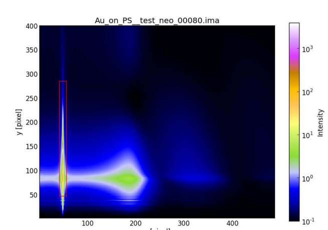


Figure 15: σ=8

The simulation of GISAXS patterns with different roughness (σ) of the PS film were done. The PS film thickness was 100 nm, R = 5 nm, H = 5 nm, $\alpha_{inc} = 0.5$ deg. The roughness was changed from 0.1 to 30 nm with 0.1 nm step. Some of these simulations are shown here. As can be seen from the pictures 13, 14 and 15 in the beginning with the increasing of roughness blur is also increasing, and then Yoneda wing is appearing, and becoming larger.

Also the intensity of the Yoneda wing is changing with the roughness. The dependence is shown on the following graph.

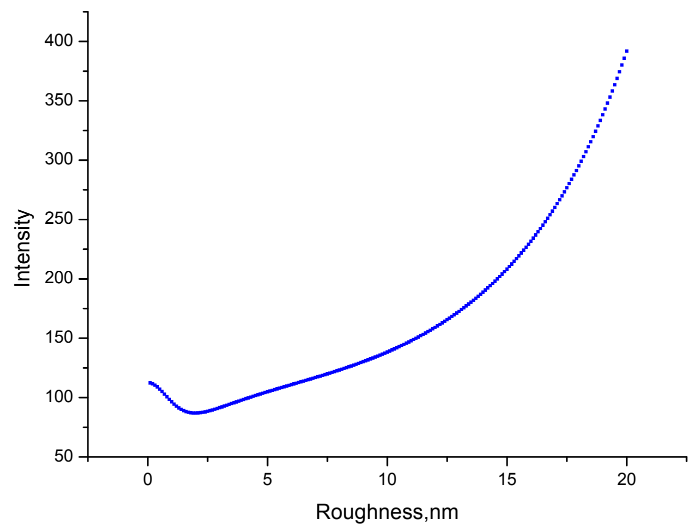
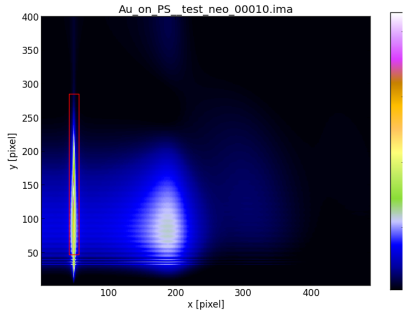
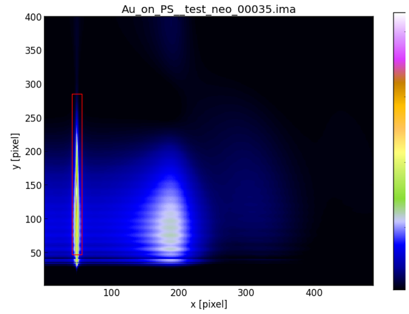


Figure 16: Dependance of the maximum intensity of the Yoneda wing from the PS film roughness

4.5 Variation of depth of clusters

The simulation of GISAXS patterns with different depth clusters were made. The PS film thickness was 100 nm, $R = 5$ nm, $H = 5$ nm, $\alpha_{inc} = 0.5$ deg. The depth of clusters was varied from 1 to 80 nm. As can be seen from the figure 17, 18 and 19 the blur of the oscillations becomes bigger with the increasing of the depth of clusters.





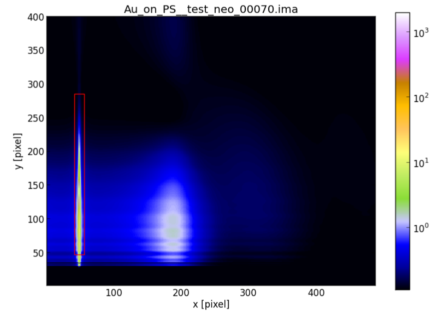


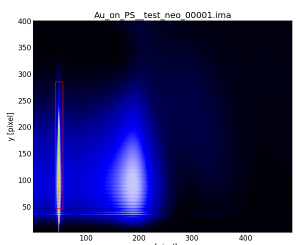
Figure 17: Depth=10 nm

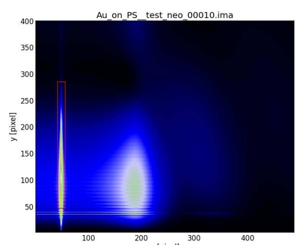
Figure 18: Depth=35 nm

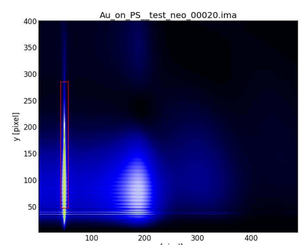
Figure 19: Depth=70

4.6 Variation of the incident angle

The simulation of GISAXS patterns with different depth clusters were made. The PS film thickness was 100 nm, $R = 5$ nm, $H = 5$ nm. The incident angle was changed from $\alpha_{inc} = 0.145$ to $\alpha_{inc} = 0.845$ deg in 0.025 nm step. Some GISAXS patterns are shown at figures 20, 21, 22, 23.







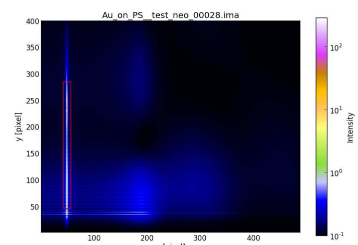


Figure 20: $\alpha = 0.145$ deg

Figure 21: $\alpha = 0.370$ deg

Figure 22: $\alpha = 0.620$ deg

Figure 23: $\alpha = 0.820$ deg

As can be seen from the pictures, the specular rod vanishes when the incident angle increases. Also the shape of the specular rod changes from more elliptical to more round-shaped. These simulations show that the incident angle around 0.5 deg provides best GISAXS patterns.

4.7 Variation of the contact angle

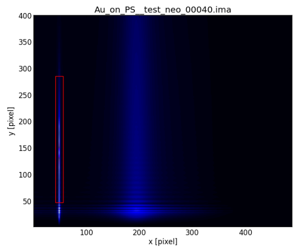


Figure 24:
$\psi = 40$ deg

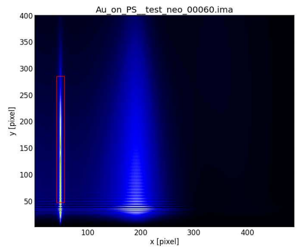


Figure 25:
$\psi = 60$ deg

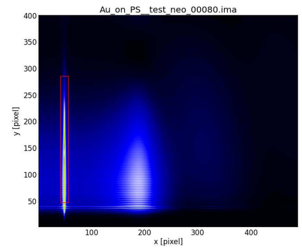


Figure 26:
$\psi = 80$ deg

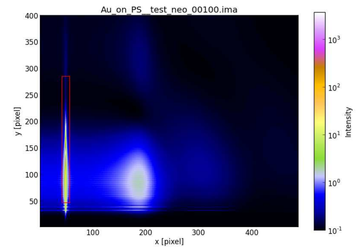


Figure 27:
$\psi = 100$ deg

The simulation of GISAXS patterns with different depth clusters were made. The PS film thickness was 100 nm, $\alpha_{inc} = 0.5$ deg. Simulations were done for $R = 5$ nm and $D = 10$ nm, $R = 4$ nm and $D = 8$ nm, $R = 3$ nm and $D = 6$ nm, $R = 2$ nm and $D = 4$ nm. The contact angle (ψ) was changed from 0 to 100 degrees. For the small R ($R = 2$ and $R = 3$) the GISAXS patterns are not so interesting, because they do not change much due to the change of the contact angle.

GISAXS patterns for the $R = 5$ nm and $D = 10$ nm with different contact angles are shown at the picture. As can be seen from the picture the shape of the rods changes significantly due to the change of the contact angle. For the smaller contact angle ($\psi = 40$ deg) there is no particular shape of the rod, and for the larger contact angle the specular rod is more round-shaped.

The same simulations were done for the $R = 4$ nm and $D = 8$ nm.

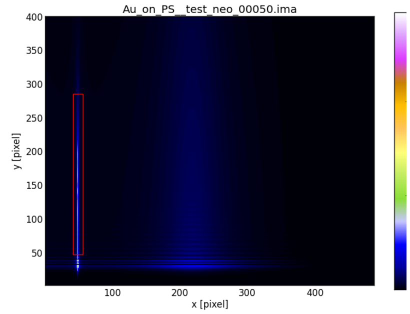


Figure 28: $\psi = 50$ deg

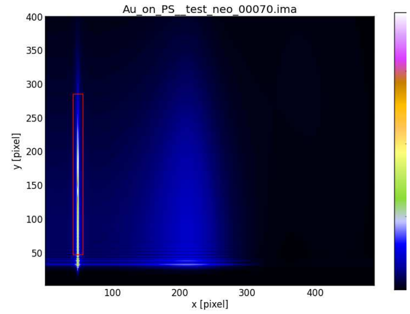


Figure 29: $\psi = 70$ deg

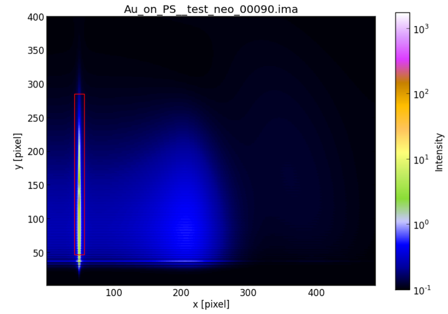


Figure 30: $\psi = 90$ deg

5 Conclusion

Several simulations of GISAXS patterns for the gold clusters on PS film were done, and the influence of several parameters on the GISAXS pattern was measured.

As can be seen from these simulations the oscillations of the rods change due to the PS film thickness and roughness, and depth of the gold clusters inside the PS layer. And the shape of this rod changes due to the shape and the size of the gold clusters. So these parametres can be studied from the GISAXS pattern. However, since both film thickness and roughness influence on the frequency of oscillations it is not so easy to measure these parameters. Also, the simulation of the worm-like clusters shows, that they can not be fitted with box-shapes.

6 Aknowledgements

I'd like to thank my supervisor Matthias Schwartzkopf for guidance throughout the project. He has never been reluctant to answer any questions and his expertise in this field has been crucial in the interpretation of the results. Also I would like to thank Carsten Richter for help with software.

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Nanoscale, 2013, 5, 5053

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