GISAXS *insitu* Sputter Deposition of different metals and alloys on PMMA films

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Abstract

Dealing with the polymer-metal interfaces is a good challenge for the today's advanced materials science field. Grazing Incidence Small-Angle X-Ray Scattering (GISAXS) is a versatile technique to determine sample surface structures as well as inner electron density variations of the deposited material. An investigation of *insitu* GISAXS Sputter Deposition of metals (Au, Ag and Cu) and alloys (AuAg and AgCu) on Polymethyl methacrylate (PMMA) has been done using advanced synchrotron radiation facilities at P03 / MiNaXS beamline, PETRA III, DESY (Hamburg, Germany). GISAXS data has been processed using the software DPDAK. The simplified geometrical (hemispherical) model of clusters' growth has been used to determine the different average real parameters like correlation distance, cluster radius, average particle density, Surface coverage, layer porosity, clusters' height, percolation threshold, etc. This investigation gives understanding towards the growth kinetics of nano clusters during deposition and their organization mechanism .

Contents

I INTRODUCTION

In the advanced synchrotron radiation experiments, Grazing Incidence Small-Angle X-Ray Scattering (GISAXS) is a good technique for the characterisation of discontinuous thin films. In this technique, the incident x-ray beam gets totally reflected externally from the surface of the substrate, then the scattering of the refracted beam takes place at smaller angles by the surface of thin film.. The advanced technique of GISAXS has many advantages over the other techniques such as Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM). Both of these techniques are performed in the real space while GISAXS takes place in the reciprocal space (momentum space). AFM has the access only to topographies over the surfaces but GISAXS is accessible to the buried structures also. The metals and the alloys are deposited on the polymer thin films (prepared by spin coating) by the Sputter Deposition technique and the *insitu* GISAXS experiment on these metal-polymer interfaces yield the complete information about the size distribution, structural arrangement and some internal morphologies of the films.

II GISAXS

GISAXS is a surface-sensitive technique which is frequently used in the field of nano-science. It is a powerful technique which enables us to study the nano-scale objects objects deposited on surfaces, thin and ultra-thin layers of nano-materials and nano-structured surfaces.

History and Background of GISAXS

The first experiment based on GISAXS was performed in 1989 by Levine and his co-workers when they were experimenting on the structure of gold nano-particles on silicon. Several years later, in 1997, Peter Müller-Buschbaum introduced the technique of GISAXS in the field of polymers and soft matter.

Geometry of GISAXS

The GISAXS geometry is represented in fig.1

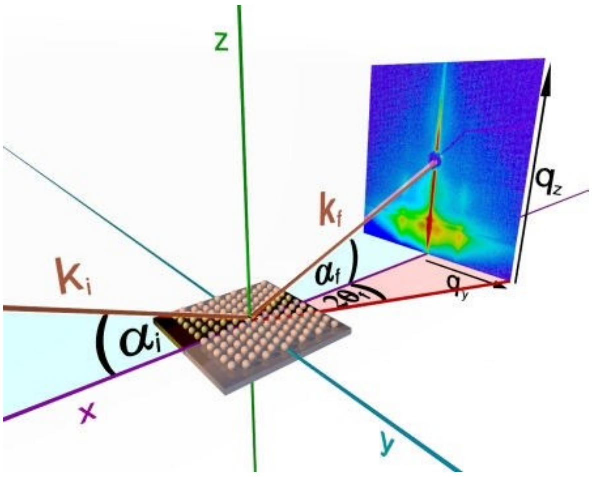


Fig. 1 : Geometry of GISAXS

A monochromatized x-ray beam with wave vector $\mathbf{k_i}$ is made to get incident on the surface at very low angle of incidence α_i with respect to the surface. The x-direction is along the plane of the surface of the beam

III DPDAK

Working of DPDAK :

At the time of experiment at the synchrotron beamline,the user controls the beamline by the use of present infrastructure and the the raw data gets created and stored in the form of scanned scattering images. The user can read the raw data from the file system directly through the DPDAK installation running in parallel. DPDAK stores the results in different forms such as plots, images, etc.

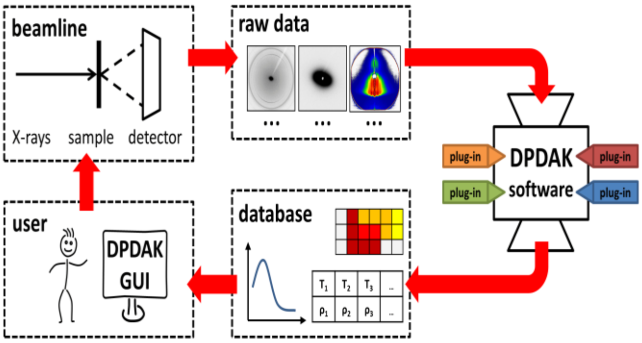
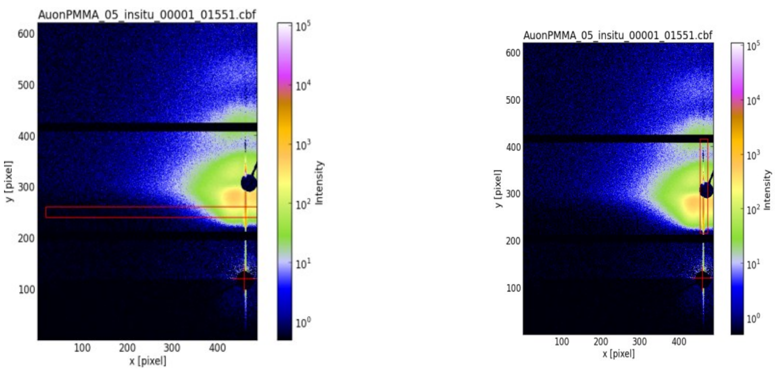


FiGURE 2 : Working of DPDAK during synchrotron experiment

Features of DPDAK

The software, DPDAK(directly programmable data analysis kit) is an open-source software which was developed to process the data and information obtained from synchrotron radiation experiment. This software works on the basis of plug-in structure model. DPDAK is a flexible tool kit for processing large amount of offline and online analysis of SAXS and GISAXS data. This software is written in Python. The various kinds of file formats supported by DPDAK are edf, tif, cbf and mar. SciPy and NumPy are the packages of Python which are used for fitting and numerical operations in DPDAK. The python package Matplotlib enables the user to display graphs from 1-D to 2-D. DPDAK can correct the scattering images for intensity and background and bin them for integration.

Cuts : In GISAXS experiment, DPDAK enables the user to make horizontal line cuts (also known as out-of-plane cuts) along $q_y = (2\pi/\lambda)(\cos\alpha_f \sin 2\theta_f)$ and the vertical line cuts (known as detector cuts) along $q_z = (2\pi/\lambda)(\sin\alpha_f + \sin\alpha_i)$. By the horizontal line-cuts, one can get the information regarding particle size, interparticle distance and correlation assembling and by the vertical cut, the information about clusters' helight can be extracted. So as a whole, one can obtain information about particle size, shape, density variation, assembling, etc. in lateral and vertical directions. So, DPDAK is designed to extract dta from the region of interest (ROI).



(a) (b)

FIGURE 3 : (a) Horizontal cut and (b) Vertical cut made in DPDAK

Peak Fitting in DPDAK : DPDAK has a tool for peak fitting which can be used for fitting one-dimensional data with arbitrary combination of Lorentzian, Gaussian and background functions.

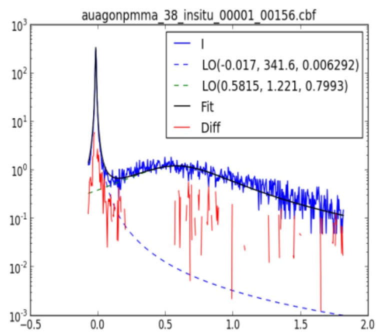


FIGURE 4: Fitting done in DPDAK by peak fitting tool for the sample AuAgonPMMA_38_insitu_00001

DPDAK Plug-ins : There are three different plug-ins in DPDAK : Base, Display and Export plug-ins.

1) The base plug-in enables the user to read and process data(text files, detector images, etc.). The data processing includes arithmetic operations and fitting.

2) The display plug-in displays the data, e.g., a plot

3) The export plug-in enables one to export the data from database to any type of format.

II Experimental Section

The GISAXS experimental measurements were performed at MiNaXS / P03 beamline of PETRA III storage ring at DESY, Hamburg (Germany).

1) Cleaning of Silicon Substrate

Due to atmospheric exposure of silicon, oxidation occurs which creates a thin oxide layer on the surface of the silicon wafer. In order to remove these organic residuals, cleaning of silicon surface is required to have deposition of good quality of films. In the process of cleaning of substrate, all the bonds between the

contaminants and substrate are broken up without harming the surface of the substrate. Substrate cleaning is important for the reproducibility of the films as it affects the smoothness, uniformity, adherence and porosity of the films and also, it has influence on layer growth characteristics. The silicon pieces (each of dimensions 12 x 15 mm^2) were cleaned in acetone using ultrasonic bath for 15 minutes and then they were rinsed with acetone, isopropanol and ultra clean water. The silicon substrates were further cleaned using piranha etching in an acid bath (200mL 0f 96% H_2SO_4 , 88mL of 35% H_2O_2 and 37.5mL of deionised water) for 15 minutes at 80˚C. Then, the treated substrates were rinsed with ultra clean water 4-5 times and then they were dried in nitrogen flow.

2) Preparation of PMMA thin film (Spin Coating)

Spin-coating is the best coating method for getting uniform and smooth thin films over a large range of thickness (30nm to 2000nm). It is based on the action of centrifugal force which enables the solution to spread on the substrate surface.

After cleaning of the substrate, the substrate was spin coated with of a solution of PMMA using the spin coater (6-RC, SÜSS Micro Tec Lithography, Germany). The deposition parameters were optimised before to get desired thickness of the film (80-85nm). As this was the comparative study to understand the growth behaviour of metal and metal alloy nanostructure, the polymer thickness of all the samples were kept constant. By the action of centrifugal force, the solution was uniformly distributed on the silicon wafer surface in the end of cycle. In this technique, the solvent got evaporated and a thin uniform film of PMMA was obtained on the silicon wafer. The various parameters involved in the spin-coating process are listed in table 1 as follows :

TABLE 1 : DFG Samples : optimized deposition parameters

Concentration : 12mg / 1000mL in toluene

Material	rpm	ramp	Time (s)	Approx. Thickness (nm)	Substrate Si(100)
PMMA	850	9	30	80 ± 5	12 x 15 mm^2

3) Preparation of Samples (Sputter Deposition)

Five set of samples using different metal and alloy targets have been deposited on prepared PMMA thin films. The rate of deposition in sputtering have also been optimized initially to get same thickness in all the samples. In order to make a comparative analysis, the combination of sputtering parameters have been chosen to get the desired constant thickness of each metal and metal alloy over polymer. The different sputtering parameters for all these samples are listed in the following table 2 :

TABLE 2 : Sputter Deposition Parameters

S.No.	Sample Name	Target	Power (W)	Voltage (V)	Argon flow rate (sccm)	Deposition Time (s)	Desired Thickness (nm)
1	Au on PMMA	Au	10	311	10	77	10
2	Ag on PMMA	Ag	9	308	10	77	10
3	AgAu on PMMA	AgAu	10	319	10	77	10
4	Cu on PMMA	Cu	23	313	10	77	10
5	AgCu on PMMA	AgCu	17	331	10	77	10

4) Grazing Incidence Small-angle X-ray Scattering (GISAXS)

(i) Layout of P03 / MiNaXS beamline, PETRA III,DESY

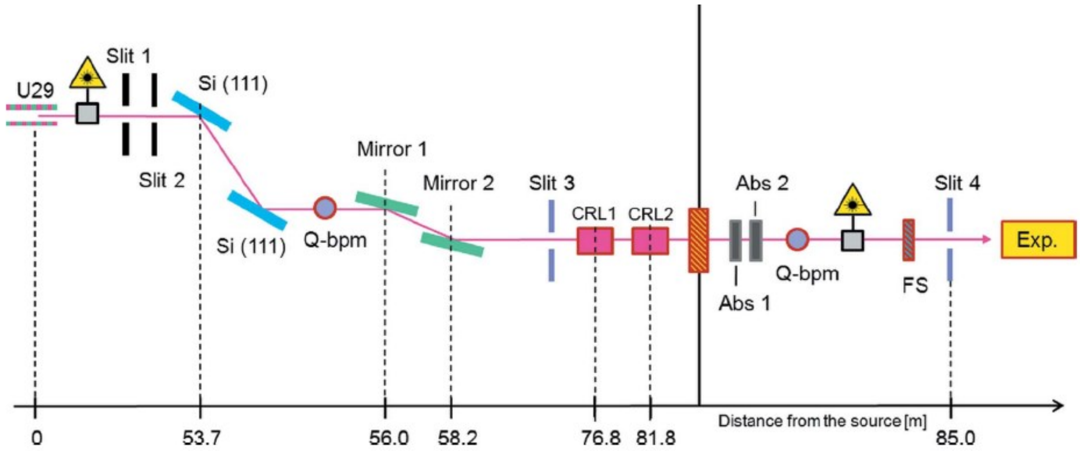


FIGURE 5 : Layout of P03 Beamline

(ii) GISAXS Experiment

A monochromatized x-ray beam of photon energy 13KeV (wavelength λ 0.953nm) was incident on the samplesurface at 0.4268˚ with respect to the sample surface. The scattered intensity was observed by a two-dimensional detector PILATUS 1M having a pixel size of (0.172 x 0.172)mm^2. The experimental value of sample to detector distance (SDD) taken was 2320mm. The specularly reflected beam and the direct beam were covered by individual beamstops so as to prevent the saturation condition or damage of the detector.

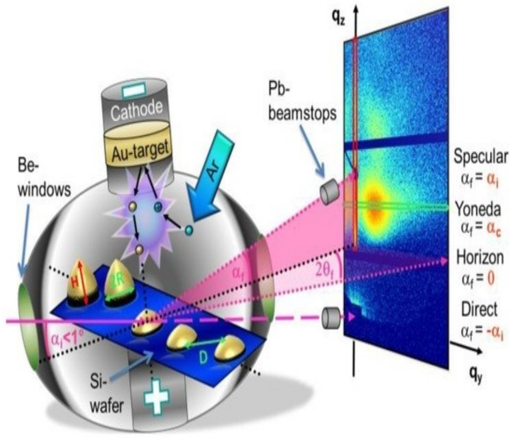


FIGURE : Scheme of an insitu sputter deposition experimentcombined with GISAXS. The angle between the incident monochromatic X-ray beam and the surface is denoted by α_i, the corresponding exit angle by α_f, the out-of-plane angle by $2\theta_f$. A reciprocal space (q_y , q_z) coordinate system is indicated. The origin of coordinates of q_y and q_z is indicated by the direct beam positions. The red and green rectangles in the 2D GISAXS pattern mark the region of the detector cut and out-of-plane cut, respectively. [*Matthias Schwartzkopf and Stephan V. Roth , J.Nanomaterials 2016, 6,239*]

5) Data Analysis

The *insitu* GISAXS experimental data was analysed using DPDAK software. Horizontal and vertical line cuts were made on the two-dimensional detected data so as to extract information regarding the morphological parameters and the clusters' growth kinetics. Then, the horizontal cuts were fitted using appropriate Lorentzian parameters, hence the Correlation Distance(D) of the clusters can be extracted as

$$D = 2\pi/q_0$$

where, q_0 is the fitted correlation peak position maxima.

Then, other morphological parameters such as Cluster Radius(R), Percolation threshold($\delta(2R/D = 1)$), Surface Coverage (θ), Layer Porosity (Φ), Average Particle Density(ρ), Average Cluster Height(H), etc.

Results and Discussion

1. Geometrical Model of Cluster Growth

In the hemispherical geometrical model [*Matthias Schwartzkopf*], the uniform hemispherical clusters have been considered to be arranged in 2-D hexagonal lattice plane. For the calculation of Cluster Radius(R), effective deposition thickness(δ) is required.

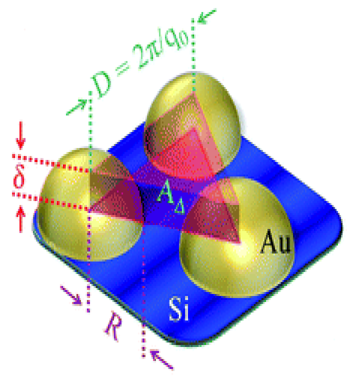


FIGURE : 3-D scheme of the geometrical model

An equilateral triangle of side length D is assumed which connects the centres of the three hemispherical gold clusters. This gives the equation

$$R = [3^{3/2} D^2 \delta / 4\pi]^{1/3} = [3^{3/2} \pi\delta / q_0^2]^{1/3}$$

The surface coverage (θ) can be determined as the ratio of the area covered by the clusters in the triangular region (A_c) to its total area (A_T) i.e.,

$$\theta = A_c / A_T$$

$$= (\pi R^2 / 2) / \{(\sqrt{3}) D^2 / 4\}$$

$$\theta = 2\pi R^2 / (\sqrt{3}) D^2$$

$$\theta = R^2 q_0^2 / 2\pi (\sqrt{3})$$

The layer porosity (Φ) can be calculated as the ratio of the volume of the void (V_v) to the total volume of the unit cell (V_T) i.e.,

$$\Phi = V_v / V_T$$

$$= \{(\tfrac{\sqrt{3}}{4}) D^2 (R-\delta)\} / \{(\tfrac{\sqrt{3}}{4}) D^2 R\}$$

$$\Phi = 1 - (\delta / R)$$

The average particle density (ρ) within the triangular unit cell can be calculated as

$$\rho = 2 / (\sqrt{3}) D^2$$

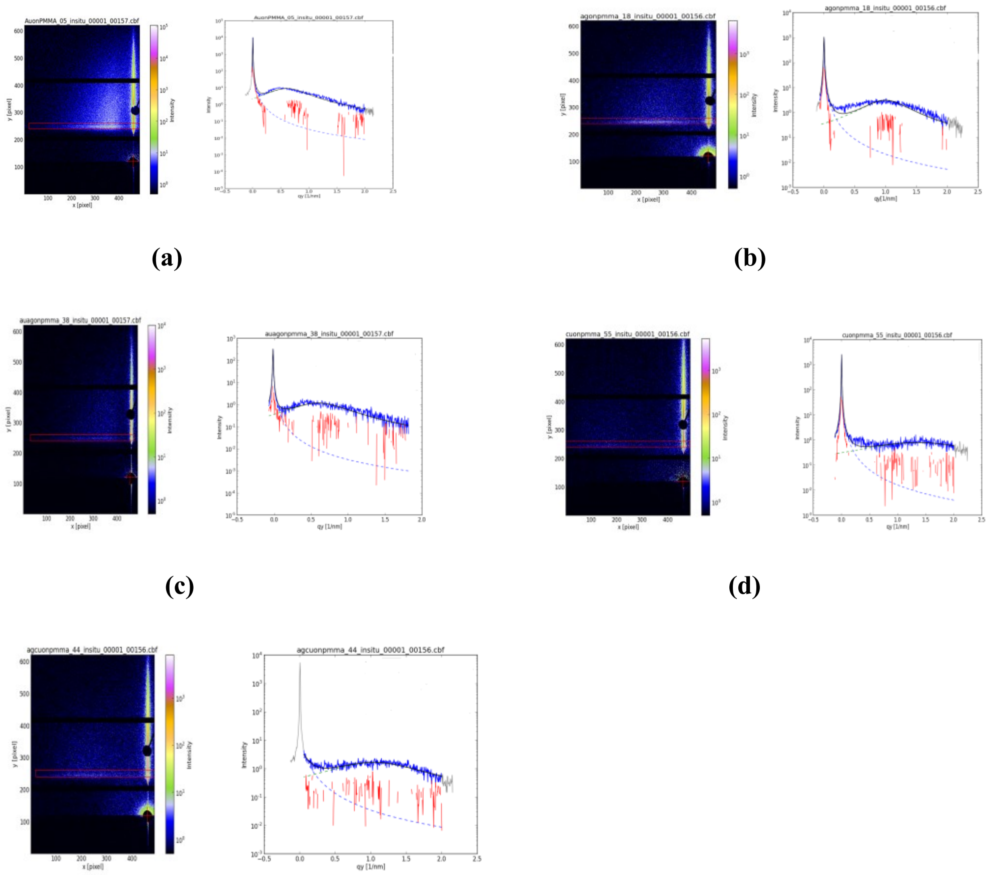
The average particle height is given as

$$H = 2\pi / \Delta q_{z(max.)}$$

where, $\Delta q_{z(max.)}$ is the difference in the maxima or minima of the peak fit obtained by vertical cuts.

2) Results of different samples

To give a glance over the growth execution of metal and alloy on polymer following Figure 8 represents selected 2-D GISAXS pattern of the samples studied in the present study. After starting the sputter deposition, a broad side peak occurs at large q_y position that represents short range order in successive clusters.



(a) (b)

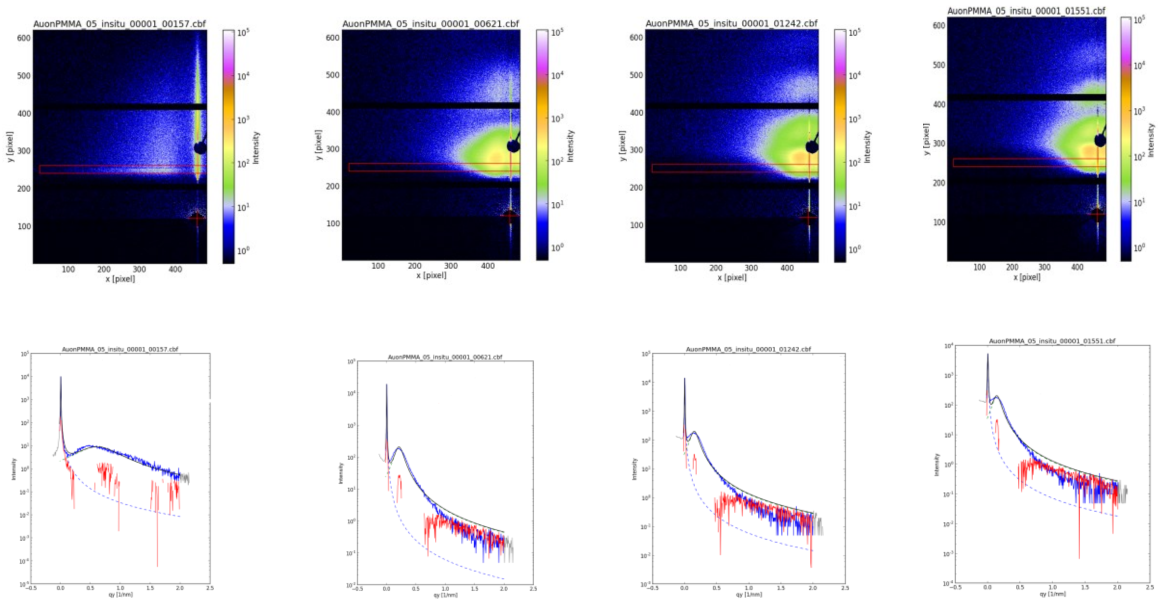
(c) (d)

(e)

FIGURE 8 : GISAXS pattern of the samples at first stage of deposition and their extracted profile :

(a) Au_PMMA, (b) Ag_PMMA, (c) AuAg_PMMA, (d) Cu_PMMA and (e) AgCu_PMMA

As the deposition proceeds, the correlation peak gets shifted towards the origin which shows the growth of nanoparticle in lateral direction. Figure 9 shows the GISAXS images of Au_on_PMMA sample after acquiring 1nm, 4nm, 8nm and 10nm thickness (the images of other samples are not shown in this report).



(a) (b) (c) (d)

FIGURE 9 : GISAXS pattern of the sample Au_on_PMMA after (a) 1nm, (b) 4nm,

(b) 8nm and (d) 10nm thick deposition

In q_z direction, the height modulation represents the total thicknessof the film deposited. The result shows rather good correlation in both horizontal and vertical direction. For some samples (Cu_PMMA and AgCu_PMMA), the percolation threshold occurs below 10nm, i.e., the clusters are touching each other indicating nanocluster growth limit in lateral direction. Over this thickness, it will acquire layered structure. Our analysis shows good agreement with the hemispherical model. From this, we have calculated, correlation distance, cluster radius, average particle density, Surface coverage, layer porosity, percolation threshold, etc. All the calculated parameters after 10nm thick deposition are listed in TABLE 3.

TABLE 3 : Calculated Parameters ater 10nm deposition

Sample	Au_PMMA	Ag_PMMA	Cu_PMMA	AuAg_PMMA	AgCu_PMMA
Correlation Distance (D) [nm]	46.0 ± 0.7	32.6 ± 0.2	15.4 ± 0.5	49.8 ± 2.1	20.5 ± 0.14
Cluster Radius (R) [nm]	20.6 ± 0.2	16.4 ± 0.05	9.9 ± 0.2	21.7 ± 0.6	12 ± 0.05
Lateral Aspect Ratio (2R/D)	0.9 ± 0.02	1.0 ± 0.008	1.3 ± 0.08	0.87 ± 0.06	1.2 ± 0.012
Surface Coverage (θ)	0.73 ± 0.04	0.92 ± 0.03	1.5 ± 0.05	0.69 ± 0.09	1.22 ± 0.002
Layer Porosity (Φ)	0.51 ± 0.005	0.39 ± 0.002	0.02± 0.0008	0.54 ± 0.01	0.17 ± 0.003

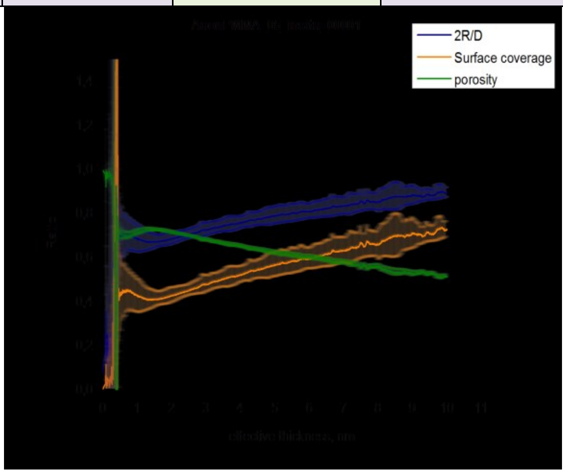


FIGURE : Au deposition on PMMA : Evolution of Aspect Ratio (2R/D) , Surface Coverage (θ) and Layer Porosity(Φ) as a function of effective thickness

This result indicates that percolation has not been approached till 10nm in this sample. Only 72.8% of surface coverage and 51.4% of layer porosity in the film of 10nm has been found.

Conclusion

Owing to the combinational *insitu* sputter deposition during GISAXS measurement, it is possible to study the kinetic growth of nanoparticles at diffferent stages of deposition. As the effective thickness increases, interparticle distance decreases due to higher particle density and so does the surface coverage increases. The percolation threshold of metal in metal-polymer nanocomposite is important, as near the percolation threshold value, electrical and optical properties change very significantly.From the processed calculation of Au, Ag and Cu on PMMA, it is clear that Au clusters are bigger in size than Ag and then Cu and thus the inter-particle distance and porosity are in the same ordering sequence in the three samples. While the surface coverage and percolation threshold are in the opposite manner i.e., Au< Ag<Cu, this result is as per the expctation. In comparison of alloys AuAg and AgCu, the cluster size and interparticle distance is higher in AuAg while the percolation is faster in case of AgCu. It seems that the growth kinetics in AuAg is more dominated by Au and in AgCu, the kinetic growth is more overshadowed by Cu. This is kind of first time resolved study on *insitu* growth of metal and metal alloy on polymer. The results are in close proximity with the hemispherical model by *Matthias Schwartzkopf.*

Outlook

The results presented here have provided the good understanding about the deposition stages of metal sputter deposition technique on the polymer PMMA. In future experiments, I will try to make an experiment in which the desired deposition thickness will be greater than 10nm so that the percolation threshold value for Au on PMMA and AuAg on PMMA can be determined. In the next step, the metal deposition on PS thin films and on the diblock of PS and PMMA (PS_b_PMMA) and the comparison of the results with the results obtained in the present case of PMMA films will provide a good understanding. The experiments based on Wide-Angle X-Ray Scattering (WAXS) and X-Ray Reflectivity (XRR) will be a good opportunity. The future investigations may be based on biopolymers, that will provide a good approach for nano-composite and nano-structured thin films.

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