PRELIMINARY VERSION

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0.1 Introduction

This project focuses on the bottom up self assembly of a monolayer consisting of polymer nanospheres

0.2 Radio-Frequency Sputter Deposition

Sputter deposition is an industrial standard technique that has been widely used to fabricate thinlayer coatings since the 1800s. It is physical vapour deposition technique, which deposits the coating material atom-wise onto the substrate. The process uses a plasma to eject sputter atoms from a target material towards a substrate. It can produce uniform, dense, deformity-free coatings with high-throughput and reproducibility, and provides flexibility to specify coating thickness and substrate/target material.

In general, the sputter system is contained within a vacuum chamber at a working pressure of $10^{-6}mbar$. The chamber is filled with argon gas, an inexpensive inert gas that won't react with the target or substrate. The substrate is placed on top of an anode and the target material is placed onto a cathode directly above the substrate (Figure 1).



Figure 1: RF magnetron sputter chamber with the cathode, containing the magnetron and target material, in line-of-sight of the sample stage that is connected to an anode.

With a voltage applied across the anode and cathode, the resulting electric field strength is sufficiently large enough to cause free electrons to collide with high enough energy to ionise argon gas molecules. The further release of electrons referred as a Townsend avalanche is triggered. Positive gas ions travel to the cathode following the external electromagnetic field and stimulating the secondary release of electrons from the cathode. The magnetron localises secondary electrons by the target. The energetic gas ions collide with atoms from the target material. The ion momentum is transferred to the targets surface atoms which gain sufficient energy to overcome the surface binding energy. The released target atoms travel towards the substrate, creating a layer.

Comparing to the other deposition methods (direct current (DC), radio-frequency (RF) magnetron, Pulsed DC and alternating current (AC) sputtering), RF magnetron sputtering has the highest sputter rate and also allows for the use of insulator, semiconductor and polymer targets [1]. The oscillatory motion of the electrons due to the high-frequency alternating voltage increases the number of ionisation's of argon atoms and therefore increases sputter rate. The high-frequency alternating voltage continuously neutralises positive ions on the target to prevent a build-up of positive charge on the target and termination of the process. A magnetron is used to localise the electrons to the target surface, increasing the plasma density and therefore increasing deposition rate.

0.3 Grazing-Incidence Small-Angle X-Ray Scattering



Figure 2: GISAXS scattering set-up [2]. The incoming x-ray beam has a wave vector k_i (lies in x-z plane) and an incident angle to the sample surface α_i . The scattered x-ray beam has a wave vector k_f (lies in x-z plane) and an incident angle to the sample surface α_f . The intensity pattern is in reciprocal space. Beam stoppers are positioned to block the high intensity specular and direct beam from reaching the detector, preventing detector saturation and damage.

GISAXS is a non-invasive, non-destructive technique used to measure nanostructures at surfaces or interfaces, probing information such as structure size, shape and lateral distance between adjacent structures. It relies on the reflection of incident light to produce a 2D intensity pattern (Figure 2). In the case that the sample being measured is homogeneous, all incident light would be scattered by the same angle resulting in a dot on the 2D detector. Dispersity in size, shape and distances between structures will cause the incident light to be scattered by different amounts via different mechanisms [3]. The intensity patterns contain two main features:

- Specular Peak: Produced by light scattered when the incident angle α_i equals angle of reflection α_f .
- Yoneda Region: Yoneda region contains a peak where the incident angle is equal to the critical angle of the material. This region arises from off-specular scattering ($\alpha_i \neq \alpha_f$) and contains information about the morphology of the sample.

Unlike other techniques, GISAXS gives the ability to examine specific depths inside the material by choosing incident angles that fulfill the specular scattering condition. In-plane inter-particle distance and morphological information can be probed by off-specular scattering. The technique can be carried out ex-situ, in-situ and real-time, providing the opportunity to study morphological evolution during processes such as sputter deposition [4].

The intensity depends on the interference function, representing the surface topology, and the form factor which models object shape [1]. A polydispersive (variation in object shape and size) nanostructured surface will cause a smearing of the form factor. Information on object height can be extracted from intensity along the q_z direction.

$$q_y = \frac{2\pi}{d} \tag{1}$$

By taking a vertical cut (detector cut [1]), information such as average nanoparticle height and layer thickness can be calculated. Horizontal (Yoneda) cuts provide insight into average particle size and inter-particle distances. Inter-particle distance, d, can be calculated by finding the q_y value of the Yoneda cut maxima and using eq.1.

0.4 Methods

0.4.1 Sample Preparation

 $11 \times 15mm^2$ boron-doped silicon wafers were cleaned using a Pirahna solution (similar to method in [5]) to remove organic contaminants on the surface and to cause the surface to become more hydrophilic. The wafers were stored for maximum duration of a week in a pure water bath. Before use, substrates were rinsed with de-ionised water and dried with nitrogen.

0.4.2 Monolayer Production

The aim was to fabricate a close-packed, uniform monolayer with high coverage of polystyrene nanospheres (Kisker Biotech GmbH and Co. KG, Germany). The polystyrene solutions (PPs) used contained nanospheres with diameters 4μ m, 3μ m, 2μ m, 1011nm, 381nm, 194nm, 48nm & 25nm. Spin coating, LangmuirBlodgett coating and Drop casting were tested. All resulting samples were imaged with an optical microscope.



Figure 3: Overview of fabrication of silver nanoparticle array. Side view of silicon wafer (top row). Aerial view of silicon wafer (bottom row). (a) & (d) polystyrene nanosphere monolayer. (b) & (c) polystyrene monolayer sputtered with silver. (c) & (e) Silver nanoparticle arrays remaining after polystyrene monolayer removal.

Spin Coating

Spin coating was performed in two steps. The initial spin was performed at low speed with gradual acceleration up to max. speed over a long time. The aim of this was to spread the solution over the substrate. The second spin step was higher speed and acceleration for a short time period. This would in principle cause the clusters to break into a monolayer, roll bi-layer particles into gaps and expel any excess material. $50\mu L$ of $4\mu m$ PPs solution was spun varying individually the speeds (100RPM-250RPM) and time duration (60s-600s) of the first step and the acceleration (1-9). The second step speed was set to 1000RPM, acceleration 9 and a times durations were tested between 10s-60s.

To investigate the effect of a surfactant on spin coating results, methanol and ethanol were separately mixed with the polymer solution in specific ratios (See ??). Solutions were created with 10, 20, 30, 40&50% amounts of surfactant for nanosphere diameters above 1011nm. These samples were all spin coated with step 1: 160RPM, 9 acceleration & 120s and step 2: 1000RPM, 9 acceleration & 10s.

Drop Casting

Methanol-polymer solutions were used for drop casting. The different volumes of solution drop casted included $25, 35, 40, 50 \mu L$. This was performed for $3\&4\mu m$ polystyrene solutions for all the methanol amounts between 10% & 50%.

Langmuir-Blodgett Coating

The Langmuir-Blodgett coating technique uses an air-water interface to form a close-packed colloid monolayer which can be transferred onto a substrate by an angled lifting of the substrate from under the monolayer. Subsequent drying involves positioning the substrate at an angle to encourage optimal evaporation of solvent [6]. Between $100\&300\mu L$ of surfactant-polymer solution (separately using ethanol and methanol) was applied on the surface of de-ionised water in a flask. The substrate was dipped and removed at an angle as to collect the surface layer of polystyrene and was positioned at an angle to dry for 24 hours. This was performed using 10%-50% methanol for $3\&4\mu m$ colloids.

0.4.3 Sputter Deposition

Spin coated samples produced with colloids of 50nm diameter were coated with silver (Ag) in a radio-frequency magnetron sputter chamber for 1000s at a $10^{-6}mbar$ working pressure. A mask was positioned to only sputter half the sample area. Before deposition, the sample was covered with a quartz crystal micro-balance to measure the rate of deposition (0.11A/s).

0.4.4 Sonication

The sputtered sample was placed in a sonication bath for 15 minutes to remove the polystyrene nanospheres leaving a silver nanoparticle array. Once sonicated, samples were dried with nitrogen.

0.4.5 Measurement

The 50nm sample was measured using GISAXS before and after the polystyrene was sonicated off the wafer leaving the silver nanoparticle array. A GISAXS y-direction scan was conducted which scanned across the wafer such to measure the silver sputtered area, the non- silver sputtered area and the interface between them. Scaning electron microscopy was used to image the sample after sonication. GISAXS data was analysed using DPDAK. Detector distance was calculated by calibrating the direct beam images with the calibrant image. The calibrant used was silver behenate. Detector distance for the GISAXS of the 50nm sample was 4050mm.

0.5 Results & Analysis

0.5.1 Polystyrene Monolayer

Overview

Langmuir-Blodgett coating appeared to be limited to working well for colloids above 1011nm diameter. Smaller colloids below 1011nm in the presence of a surfactant were not able to produce monolayers on the water surface. Spin coating was used to create monolayers consisting of the small diameter colloids. The 48nm colloids produced the most homogeneous, close-packed monolayer compared with other small colloids.

Spin Coating

Spin coating performed with $4\mu m$ nanoparticles without the use of a surfactant produced inhomogeneous polystyrene films consisting of sparse clusters in the centre of the film and double layers on the film edge (Figure 4). During the second step of the spin process a double expulsion of the material on the wafer was observed. The time of the first step was decreased to 120s and the second to 10s prevented the double expulsion of material, resulting in a centre more densely populated with polystyrene nanoparticles (Figure ??).





Figure 4: $4\mu m$ Polystyrene nanospheres spun with step 1: 150RPM, ramp 1, duration 600s, step 2: 1000RPM, ramp 9, duration 60s (Left) and spun with step 1: 160RPM, ramp 1, duration 120s, step 2: 1000RPM, ramp 9, duration 10s (Right).

Spinning methanol mixed with $3\mu m$ and $4\mu m$ polystyrene nanoparticles in the ratios 2:8 and 3:7 respectively produced the close packed films that contained bilayers. This bilayer could be further invesigated in the future to create nanoparticle arrays with more complex shapes using the bilayers as a template. The ramp 6 setting used for the $3\mu m$ solution with a methanol-polymer ratio 40:60, produced the best monolayer (Figure 5).





Figure 5: Optical microscope image (a) and SEM image (b) of sample made with $3\mu m$ solution with a methanol-polymer ratio 40:60, spun with settings: Step 1, 160*RPM*, 120*s*, ramp 6; Step 2, 1000*RPM*, 10*s*, ramp 9.



Figure 6: Spin coated sample using ethanol- $(3\mu m)$ polymer solution in the ratio 40:60.

Spin coating ethanol- $(3\mu m)$ polymer solutions using the standard spin setting: step 1, 160RPM, 120s, ramp 6; step 2, 1000RPM, ramp 9, 10s, all ratios resulted in films that contained homogeneous monolayers with some areas containing bi-layers (Figure 6). Ethanol is a less toxic, cheaper surfactant, therefore could replace methanol.

Spin coating was tested on 25nm at standard spin setting caused all the material to expel from the film leaving an inhomogeneous distribution of nanoparticles (Figure ??). Using an optical microscope on this sample revealed that the film was empty except for a few layers of nanoparticles arranged in a ring, showing as a coloured ripple effect (Figure ??). The 48nm colloids were mixed with ethanol, filtered and spun at 2000RPM, ramp 9 for 30s. The samples showed a homogeneous brown coloured layer with a few domains with multilayers and contaminants (Figure 9). The brown colour is due to thin film interference and corresponds to a 100nm monolayer.



Figure 7: Optical microscope image of sample made with 25nm solution with a methanol-polymer ratio 1:1, spun with settings: Step 1, 160RPM, 120s, ramp 6; Step 2, 1000RPM, 10s, ramp 9.



Figure 8: Sample made with 25nm solution with a methanol-polymer ratio 1:1, spun with settings: Step 1, 160RPM, 120s, ramp 6; Step 2, 1000RPM, 10s, ramp 9.

Drop Casting

Drop casting was tested for 3 and 4 micrometers polystyrene methanol solutions of different concentrations. The resulting film consisted of close packed bi-layers with occasional domains of monolayers and no nanoparticles. Some films showed a ripple effect (Figure 10), perhaps being the coffee ring effect. This could be caused by the termination of motion of the edge of the solution droplet due to surface tension. Since the edge of the droplet is exposed to more air than the centre, the methanol at the edge will dry faster and to compensate for this a flow of solution (methanol and polymer) to the edges arises therefore reducing the amount of polymer in the centre. When fully dry, there is a ring concentrated with polymer particles. Since the substrate is hyrophilic (from pirahna cleaning), the static edge of the droplet will be near the center of the droplet creating a stain [7].

The films fabricated using angled Langmuir-Blodgett coating had large areas of uniformly densely packed monolayers. The most successful samples has concentrations 20:80 and 50:50. The use of surfactants has been known to improve the mechanical stability [8]. When a solution of surfactant mixed with polymer is put onto the surface of water, the surfactant will lie on the air-water



Figure 9: Spin coated sample using ethanol-(48nm) polymer solution.

interface and will cause the polymer particles to push together, creating a closepacked monolayer on the water. The surfactant will reduce surface tension which aids the movement of spheres on the surface to configure into a monolayer [6]. An advantage of this method is minimal number of parameters that need to be varied to create a closepacked, homogeneous monolayer.



Figure 10: Photo of sample made with $4\mu m$ solution with a methanol-polymer ratio 10:90





Figure 11: $4\mu m$ Polystyrene nanospheres produced by angled Langmuir-Blodgett coating using a 2:8 ratio of methanol to polystyrene solution. Optical microscope image (left) and photo of sample (right)





Figure 12: SEM images for $4\mu m$ Polystyrene nanospheres produced by angled Langmuir-Blodgett coating using a 2:8 ratio of methanol to polystyrene solution.

0.5.2 GISAXS & SEM

When the silver sputtered on the PPS monolayer is sonicated off, the broad peak decreases to lower q_{y} values (Fig.13d than that of the silver sputtered PPS monolayer (Fig13a). This suggests the distances between object centres is larger for the Ag nanostructures left after sonication compared with the non-sonicated silver sputtered PPS monolayer. There are two possibilities for the distances probed for the non-sonicated silver sputtered PPS monolayer (Figure 14). For small clusters of gold particles present on the polymer nanospheres, the distance probed are that between gold atoms or the gold atoms form large clusters on the nanospheres and the distance probed would be that between nanosphere caps. To investigate this, the log graphs of the Yoneda linecuts for the plain PPS monolayer, the silver sputtered PPS monolayer and the Ag nanoparticle arrays left after sonication of the PPS layer (Figure 19). The average distances probed for a PPS monolayer, Ag sputtered on a PPS monolayer and an Ag nanoparticle array resulting from sonicated sputtered monolayer were $D_{PPS} = 41.0nm, D_{Ag} = 50.3nm\&D_{Ag,nano} = 82.1nm$ (calculated with 1). The value of the distance probed for gold sputtered on a polymer monolayer is approximately equal to the diameter of the colloids which suggests that the distance probed is that between the gold caps present on the nanospheres. The average distance for the Ag on PPS layer is larger than for a pure PPS monolayer, further implying the presence of the gold caps. The distance between the nanoparticle arrays is much larger than that of the polystyrene nanospheres, therefore, it is implied that there is no templating effect [3]. Sonicating off the silver capped nanospheres leaving silver nanoparticles results in an increase of particle distance. This could signify that unlike the nanospheres which have 6 equidistant neighbour particles, the silver nanoparticles 3 short distant neighbours and have 4 long distance neighbours. Therefore, the most prominent in-plane particle distance will be longer for the silver nanoparticles compared with capped polystyrene nanospheres. SEM images of the sonicated sample exhibit areas of silver covered polystyrene nanospheres. Higher resolution SEM images would be required to examine whether silver caps can be observed.



Figure 13: 2-Dimensional GISAXS patterns taken from y-scan raw data. (a), (b), (c) are the scans of the silver sputtered on the polymer monolayer side of the wafer, the monolayer side of the wafer and the interface between the two respectively.(d), (e), (f), are the scans of the silver nanoparticle array side of the wafer, the silicon after the monolayer was sonicated off and the interface between the two sides respectively.

Smearing around the Yoneda region of fig13e could hint at the presence of leftover polystyrene or other contaminants on the silicon surface. This confirms the incomplete sonication of the sputtered monolayer. Traces of leftover polystyrene nanospheres are visible on the SEM images fig16a, d, e, f.

The critical angle of silicon found from the vertical line cut, $\alpha_{c,linecut} = 0.135^{\circ}$, was lower than the reference value for silicon probed at energy 11850eV, $\alpha_{c,ref} = 0.151^{\circ}$ [9]. This difference could originate from the silicon having a different density to the reference density, the existence of organic, PPS, or oxide layers on the silicon, or the detector incident angle being set wrong. The detector distance was thought to be 3.9m but using the calibrant images, it was calculated to be 4.05m. The incident angle that was calculated with the 3.9 metres would be wrong in fact instead of 0.38 deg it should be 0.366 deg. This could have caused a systematic error for the vertical linecuts.

In fig.13b, there are two horizontal peaks, the top is the critical angle for silicon and the bottom is the critical angle for the polymer. The lower horizontal peak is stronger, implying that there is a high coverage of polymer on the silicon. Evanescent waves in the silicon polymer interfere



Figure 14: Illustration for the different distances probed in GISAXS for (1) PPS monolayer on silicon, (2) silver sputtered onto PPS monolayer on silicon and (3) sonicated silver sputtered onto PPS monolayer

and produce a smeared intensity between the Silicon and polymer peaks.Bragg rods are visible suggesting the presence of a monolayer on the silicon.

There is an asymmetry visible in the linecut interface between the plain polystyrene monolayer and the silver sputtered polystyrene monolayer (fig.15c). The symmetry of all other linecuts, implies this feature is unique to only this interface. This result could be pointing to an asymmetry in the sputter coating of the masked atoms at the interface. When a mask is placed over the centre of a wafer, the sputter atoms in the atmosphere of the chamber could in principle sputter the sides of masked atoms exposed to the air. Placing the masks, overhanging the edges of the wafers could reduce probability of sputter atoms reaching the masked atoms. The asymetry of the silver coating on the nanosphere would lead to scattering in different directions therefore creating an asymetry in the scattering intensity.

Examining the beauty shot taken of the Ag nanoparticle array remaining after sonication (fig.18, an angled peak is visible on the left hand-side of the image. Similar angled peaks were observed in [10], that were due to the facets of a 3D pentagonal structure. The cause of the streak in this data could be a result of the facets of the Ag nanoparticles which theorically are tetrahedron shaped. Further investigation into these angles peaks could be done by rotating and measuring the sample. Other facets of the shaped nanoparticles would be expected to have different angles streaks.



Figure 15: Yoneda linecuts taken from y-scan raw data. (a), (b), (c) are the scans of the silver sputtered on the polymer monolayer side of the wafer, the monolayer side of the wafer and the interface between the two respectively. (d), (e), (f), are the scans of the silver nanoparticle array side of the wafer, the silicon after the monolayer was sonicated off and the interface between the two sides respectively.

0.6 Conclusion Further work

Three coating techniques were explored in order to find a method that will produce homogeneous, close-packed, high-coverage monolayers on silicon with high reproducibility. The techniques were tested for different sized particles ranging from $4\mu m$ to 25nm, the 48nm nanoparticles produced better monolayers when spin coated whereas the larger nanoparticles produced very good monolayers when using Langmuir Blodgett coating. More time would be required to explore the spin parameters for other small colloids. A focus was put on the 48nm particles and GISAXS measurements were taken for a 48nm monolayer.

Comparison between the GISAXS measurements for the polystyrene monolayer and the Ag nanoparticle arrays helps rule out templating effects since the distances between polystyrene spheres do not coincide with that of the Ag nanoparticles. The comparison between the GISAXS measurements before and after sonication hint to the prescence of silver caps positioned on the polystyrene nanospheres and reveal that sonicating leads to an increase in particle distance. The possible reason for this is that the Ag nanoparticles will have more distant than close neighbours compared to silver capped nanospheres, which has 6 equidistant neighbours. This would lead to the average particle distance being larger. The prescence of a monolayer is verified by the clear Bragg peaks on the GISAXS taken of the polystyrene monolayer. An asymmetry was observed at the interface between silver covered polystyrene and plain polystyrene. It has been suggested that this is originates from an asymmetry in the silver coverage on the nanospheres. This could be explained by an penumbra effect that occurs when the sputtering particles are able to reach nanospheres under the edge of the



Figure 16: SEM images for sonicated silver sputtered PPs monolayer. (a)View of material not fully sonicated. (b) closer view of unsonicated material. (c) view of interface between spouttered and non sputtered area. (d)-(e) Unsonicated material, (f) remaining polystyrene nanospheres.

mask, therefore coating one side of them. This could be avoided in future work by positioning the masks to hang over the outer edge of the sample substrate. An angled streak that appeared in the long exposure scan of the Ag nanoparticle array, could be evidence for facets of the theoretically tetrahedral shaped silver nanoparticles. For future work, more closely packed homogeneous samples of small colloids should be made and measured in GISAXS. The samples should be rotated so the angled streak can be investigated to see whether it changes position when probing other facets. Work should be done to explore the structure property relationship of the Ag nanoparticle arrays. This could be done by taking UV-Vis spectroscopy and ellipsometry to measure the optical properties and correlate them with the structural findings.



Figure 17: Detector (vertical) linecuts taken from y-scan raw data. (a), (b), (c) are the scans of the silver sputtered on the polymer monolayer side of the wafer, the monolayer side of the wafer and the interface between the two respectively. (d), (e), (f), are the scans of the silver nanoparticle array side of the wafer, the silicon after the monolayer was sonicated off and the interface between the two sides respectively.



Figure 18: Long exposure taken of silver nanoparticle arrays left after monolayer was sonicated off.



Figure 19: Log graph of linecuts taken for the polystyrene monolayer, the silver sputtered on the polystyrene monolayer and the sonicated silver sputtered polystyrene monolayer.

Appendices

Sample	Diameter (µm)	Surfactant type	Surfactant (%)	Polymer Solution (%)	
SE1	4	Methanol	50	50	
SE2	4	Methanol	40	60	
SE3	3	Methanol	30	70	
SE4	3	Methanol	20	80	
SE5	4	Methanol	10	90	
SE6	3	Methanol	50	50	
SE7	3	Methanol	40	60	
SE8	3	Methanol	10	90	
SE9	3	Methanol	50	50	
SE10	3	Methanol	40	60	
SE11	2	Methanol	32	68	
SE12	2	Methanol	35	65	
SE13	2	Methanol	37	63	
SE14	3	Ethanol	50	50	
SE15	3	Ethanol	40	60	
SE16	3	Ethanol	30	70	
SE17	3	Ethanol	20	80	
SE18	3	Ethanol	10	90	
SE19	4	Methanol	99	1	
SE20	3	Methanol	99	1	
SE21	2	Methanol	99	1	
SE22	2	Methanol	35	65	
SE23	3	Methanol	50	70	
SE24	1.011	Methanol	30	70	
SE25	1.011	Methanol	20	80	
SE26	0.8	Methanol	30	70	
SE27	0.8	Methanol	20	80	
SE28	4	Methanol	10	90	
SE29	1.011	Methanol	50	50	
SE30	1.011	Methanol	40	60	
SE31	1.011	Methanol	30	70	
SE32	1.011	Methanol	20	80	
SE33	1.011	Methanol	10	90	
SE34	3	Methanol	40	60	
SE35	0.025	Methanol	50	50	
SE36	0.194	Methanol	50	50	
SE37	0.194	Methanol	40	60	
SE38	0.194	Methanol	30	70	
SE39	0.194	Methanol	20	80	
SE40	0.194	Methanol	10	90	
SE41	1.011	Methanol	20	80	
SE42	1.011	Methanol	50	50	
SE43	1.011	Methanol	10	90	
SE44	0.381	Methanol	10	90	

Figure 20: Table to show surfactant-polymer solutions produced.

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