Quantitative Characterisation of Surface Nanostructures by Dual Polarisation Interferometry

Introduction

Dual Polarisation Interferometry (DPI) provides an important quantitative tool for the nanotechnologist[1]. This application note describes the use of DPI for the real time measurement and analysis of the construction of a layer consisting of nanoparticle components.

The aim of these experiments was to measure the physisorption of polyethyleneimine (PEI) polymer onto a silicon oxynitride surface and the subsequent physisorption of 80nm silica spheres to the surface. The characteristics of the layer as it formed were determined from the adsorption profiles. We were interested in the mechanism and behaviour of the 80nm spheres under the experimental regime deployed.

Experimental

The experiments were performed on a Farfield ***Ana*****Light**® dual polarisation interferometer. The surface used in all studies was a silicon oxynitride ***Ana*****Chip**™ with no further pre-treatment. The temperature of the samples was controlled throughout to 20°C. Water used in buffer preparation was deionised and free of organic impurities. All buffers and reagents were analytical grade or higher, and solutions were degassed prior to use.

Polyethyleneimine (PEI) polymer deposition: HEPES running buffer (aqueous 10mM, pH7.4) was flowed over the ***Ana*****Chip**™ surface at 50µl/min. PEI polymer (mol. wt. 25,000) solution (0.1mg/ml in running buffer) was added to the flow for 15 mins, followed by a rinse with running buffer.

Silica sphere physisorption: Once the deposited PEI polymer layer was stable in the running buffer, 0.1% w/w 80nm silica spheres in running buffer (HEPES) was added to the buffer flow for 13 minutes at a slower flow rate of 20µl/min. Following a buffer rinse, a second addition of Silica spheres (1% w/w) was injected for 3.8 minutes.

Subsequent structured layer formation: The surface generated by addition of silica spheres was then treated with a second injection of PEI solution (0.1mg/mil in RB) and this layer was once again subjected to an injection of 1% w/w silica spheres in running buffer.

The layer thickness and density were measured in real time throughout the entire experimental procedure described above.

Results and Discussion

Figure 1 shows the “layer” data acquired at key points during the time course of the experiment.

Layer	Event	RI Density	Thickness (nm)	Mass Change ($ngmm^{-2}$)
3	**PEI deposition**	**1.47994**	**0.737**	**0.619**
4	**0.1% silica sphere physisorption**	**1.36457**	**78.192**	**41.532**
5	**1% silica sphere physisorption**	**1.36578**	**76.114**	**0.480**
6	**Second PEI additions**	**1.36772**	**76.920**	**1.005**
7	**1% silica sphere addition**	See **Note (a)**	See **Note (a)**	

Figure 1: Quantitative layer values at key points throughout the experiment

PEI Polymer deposition: PEI adsorbed very rapidly on the silicon oxynitride surface to form a layer 0.74nm thick with a refractive index of 1.4799. From the known physical characteristics of PEI, it is possible to calculate the surface

[1] GH Cross, A Reeves, S Brand, MJ Swann, LL Peel, NJ Freeman, JR Lu – **The Metrics of Surface Adsorbed Small Molecules on the Young’s Fringe Dual-Slab Waveguide Interferometer**. *J. Phys. D: Appl. Phys.*, 2004, 37, 74-80.

coverage as approximately 79%, and we were able to extend this to calculate the mass coverage of PEI as $0.619 ngmm^{-2}$. **Figure 2** shows the thickness, mass and density profiles for the PEI physisorption process. The process can be seen to be very rapid, illustrating the advantage of DPI as a real time technique.

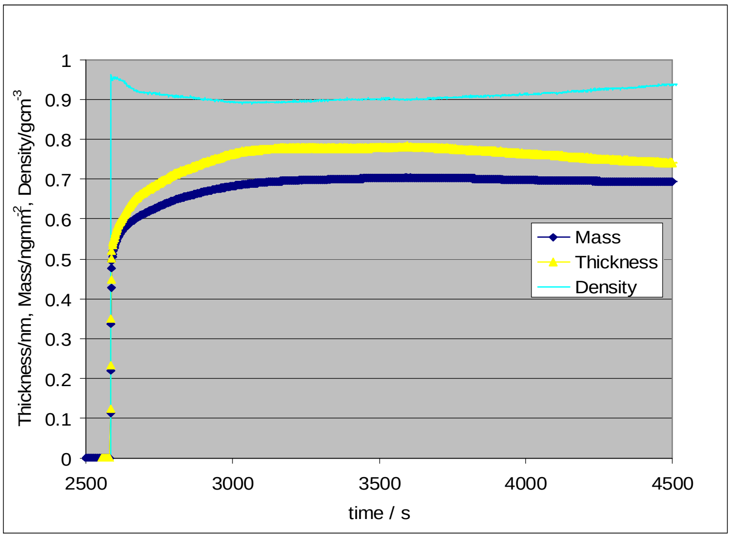

Figure 2: Real time thickness, density and mass responses on PEI physisorption

Silica sphere physisorption: Figure 3 shows the adsorption of the 0.1% solution of 80nm silica spheres produces a diffuse, thick layer on the silicon oxynitride surface. Within three minutes, a layer of spheres forms on the PEI surface, giving thickness measurement of 78.19nm, refractive index of 1.3646 and mass coverage of 41.532 $ngmm^{-2}$. This is consistent with a surface coverage of 25.2% for the silica spheres.

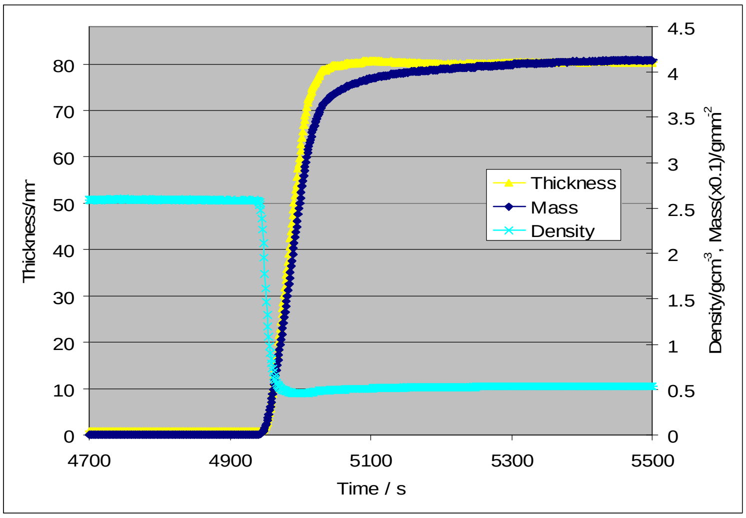

Figure 3: Real time thickness, density and mass profiles for physisorption of 0.1% 80nm silica spheres to PEI surface

Introduction of the 0.1% silica spheres caused an increase in mass and thickness and a drop in density of the surface layer (which includes the polymer layer). The almost linear increase in the mass implies mass transport limitation, as would be expected from particles as large as 80nm. Initially the mass and thickness correlate, indicating a progressive deposition of spheres on the ***Ana*****Chip**™ surface. However, the thickness reaches its final value before the mass, implying that infilling is the predominant mechanism during the latter stages of the process. **Figure 4** shows a visual schematic of the PEI polymer deposition and the subsequent silica sphere physisorption.

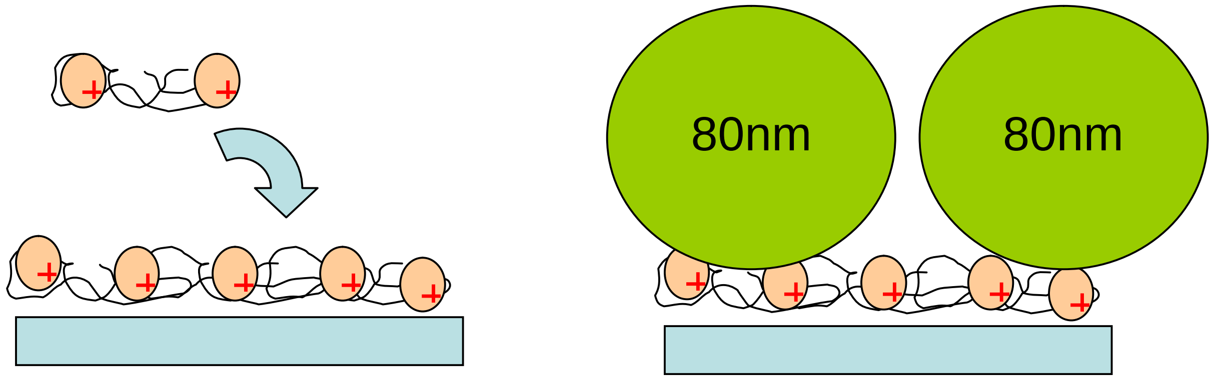

Figure 4: Visual schematic of PEI polymer deposition (left) and 80nm silica sphere physisorption (right). Not to scale

Subsequent addition of 1% silica spheres to the surface caused a small amount of additional mass to be deposited (0.480ngmm^{-2}) and a modest thickness decrease (2.08nm) as shown in **Figure 1**. These observations are consistent with driving the surface loading of silica spheres to saturation. These measured values are in good agreement with values obtained using other methods[2].

Subsequent structured layer formation: Treatment of the silica sphere surface from above with a second injection of PEI causes an additional layer to adsorb to the spheres. **Figure 1** shows a small increase in the thickness (0.81nm), mass (1.005 ng/mm^2) and RI (0.0019) upon addition of the polymer, as would be expected.

Note (a): *Addition of further silica spheres (1% w/w) onto this layer causes responses which are consistent with further increases in thickness and physisorbed mass. However, the thickness range of the* ***Ana*****Light®** *instruments is arbitrarily limited to 100nm, and therefore the values obtained were outside the current measurement range, as the layer would be expected to be in the region of 160nm thick. This data does suggest that there may be some rearrangement of the surface structure upon the second addition of 1% silica spheres, leading to a slow bedding down and increasing their interaction with the PEI polymer more closely attached to the surface of the chip.*

Conclusions and Benefits

These experiments confirm that DPI is capable of accurately measuring and characterizing the formation of complex layer structures incorporating 80nm silica spheres. Typical layer structures determined fall within expected ranges, for example 78nm increase being measured by DPI on addition of 80nm spheres.

Farfield's ***Ana*****Light®** instruments enable the study of the behaviour and quantitative determination of the structures of a diverse range of molecular systems. ***Ana*****Light®** gives the researcher a unique combination of high-resolution data in real time on thickness, refractive index (density) and surface coverage in a benchtop format. DPI is an important surface characterization tool for the nanotechnologist and surface scientist, giving access to:

- Clear understanding of surface processes in real time
- Data on surface structure dimensions at sub-Ångstrom resolution
- Quantitative data for comparison with other analytical techniques (such as neutron reflectivity and ellipsometry)
- Access to absolute, and therefore less ambiguous, results – no complex model fitting is required with DPI

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[2] Unpublished data from Dr Marcus Textor, Biointerface Group at ETH Zurich, Switzerland.