EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

http://193.49.43.2:8080/smis/servlet/UserUtils?start

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Self Assembly of Nanoscale Crystallites	**Experiment number**: 28-01-68
Beamline: BM 28	**Date of experiment**: from: 19th – 26th July 2000	**Date of report**: 28th February 2000
Shifts: 18	**Local contact(s)**: Simon Brown	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

* Dr. Chris Nicklin (University of Leicester)

* Prof. Colin Norris (University of Leicester)

* Mr. Simon G. Alcock (University of Leicester)

* Dr. Mathias Brust (University of Liverpool)

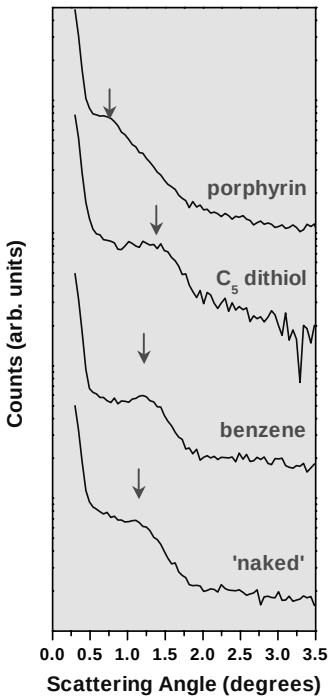
* Dr. Simon Brown (XMaS)

Prof. R.E. Palmer (University of Birmingham)

Report:

A grazing incidence small angle X-ray scattering (GISAXS) study was carried out at the XMaS beamline in July 2000 by the University of Leicester in collaboration with Birmingham and Liverpool Universities. The samples consisted of gold nanoparticles (~4.5nm in diameter) surrounded by organic thiol terminated molecules that self-assemble on the gold surface. As a solution containing the clusters evaporates, the organic cage mediates a self-organising process whereby the clusters form close packed, ordered arrangements. The aim of this beamtime was to study the effect of external parameters, such as the sample temperature during evaporation, on the quality of the ordering. All results were obtained by solvent evaporation on an oxidised silicon (111) sample.

Figure 1



Initial measurements focused on the small angle scattering from the particles in solution, subjected to different chemical treatment. A variety of 'linker' molecules were added to the solution in order to study their effect on the average particle separation. Figure 1 shows the small angle scattering features for the uncoated gold particles and with three different linker molecules (based on the names in the figure) added. The peak shifts indicate that the molecules are attaching to the surface of the gold clusters causing them to interact with each other. Specifically, the C5 dithiol is a short chain molecule that has a thiol group at both ends and therefore forms a strong short link between neighbouring clusters. This leads to the increase in peak position indicated. The benzene based thiol leaves the peak at approximately the same position,

although the shape is more pronounced. This indicates that the average separation remains the same, but more of the clusters sit at this distance, through mediation by the molecule. Porphyrin is a large molecule and it's thiol based derivative shifts the SAXS peak to a lower value. This is due to the constraint of having to fit the large molecule between neighbouring clusters.

Figures 2 and 3 show GISAXS scans of the resulting films after solvent evaporation at the temperatures indicated, for a layer of gold particles equivalent to 10 close packed cluster layers. All measurements were made with a constant X-ray angle of incidence and the detector scanning in the out-of-plane direction for the vertical scattering and in-plane for the horizontal scattering. In figure 2, at room temperature and just below (16.7°C) there is a single peak corresponding to a separation of the nanoscale crystallites of 5.7±1.0nm. In this case they are separated by dodecanethiol (C_{12} based chain) which has a chain length of ~1.5nm. This result, therefore, indicates that the average separation is caused by interdigitation of the C_{12} molecules from neighbouring clusters. At lower temperatures, there is a significant transition which results in the narrowing of the first peak and the appearance of additional peaks at higher scattering angles. The first peak in the 10.1°C plot corresponds to a separation of the scattering centres of 5.9±0.3nm. Further reduction in the temperature causes a splitting of the narrow features, indicating the presence of two length scales in the direction of the sample normal.

Comparison of the out-of-plane and in-plane scattering (Figure 3) shows that the layers have good polar alignment (I.e. they are aligned almost parallel to the surface) but poor azimuthal alignment. These results may be caused by diffusion limited aggregation or the presence of small domains which are disordered in the plane but well ordered in the direction of the layering. Further investigations (including AFM measurements) and additional GISAXS studies are planned to understand this transition and the effects of other external parameters (e.g. gas pressure). Similar results are obtained for 2.5nm particles.

This work has been presented at the CMMP-2000 conference held at Bristol in the U.K.

Figure 2

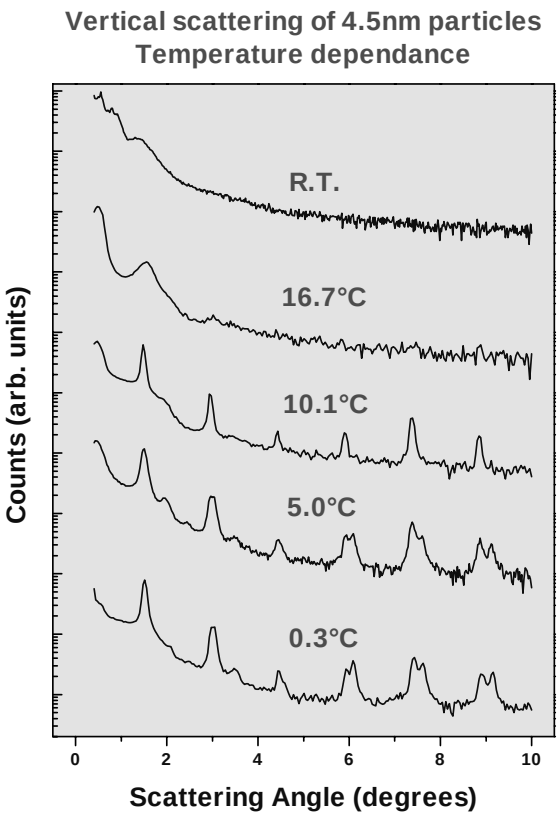


Figure 3