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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: GISAXS study of self-organized multilayers of carbon encapsulated transition metal nanoparticles**	**Experiment number**: 20-02-685
Beamline:	**Date of experiment**: from: 28/08/2009 to: 01/09/2009	**Date of report**: 18/05/2010
Shifts:	Local contact(s)**:** Nicole Jeutter	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Self-organized nanostructures in C:Ni nanocomposite thin films have been investigated *ex-situ* by means of grazing-incidence small-angle x-ray scattering (GISAXS). Films were grown by ionized physical vapour deposition (iPVD) in the form of pulsed filtered cathodic vacuum arc. This approach provides a flux of depositing species in the form of hyperthermal (~10-100 eV) ions whose energy and direction can be easily controlled by an electromagnetic field. During thin film growth, atomic displacements are caused by impacting energetic ions, resulting in phase separation in an advancing surface layer. No additional thermal sample heating has been applied thus suppressing any considerable surface diffusion of ad-atoms.

The transmission electron microscopy (TEM) and GISAXS results of C:Ni films grown at various conditions are summarized in Figure 1. Deposition normal to the substrate surface results in an alternating carbon-rich and nickel-rich layered structure. The undulations of Ni concentrations within each layer are correlated to the metal distribution in adjacent layers which indicates that the nanoparticle nucleation is dependent on the morphology of the underlying layer. This demonstrates that after an initial growth period, the ‘active’ layer switches to an oscillatory mode which results in the emergence of a periodic precipitation pattern. It must be noted that any considerable surface diffusivity destroys the periodic pattern formation and results in the growth of columnar Ni rich nanoparticles.

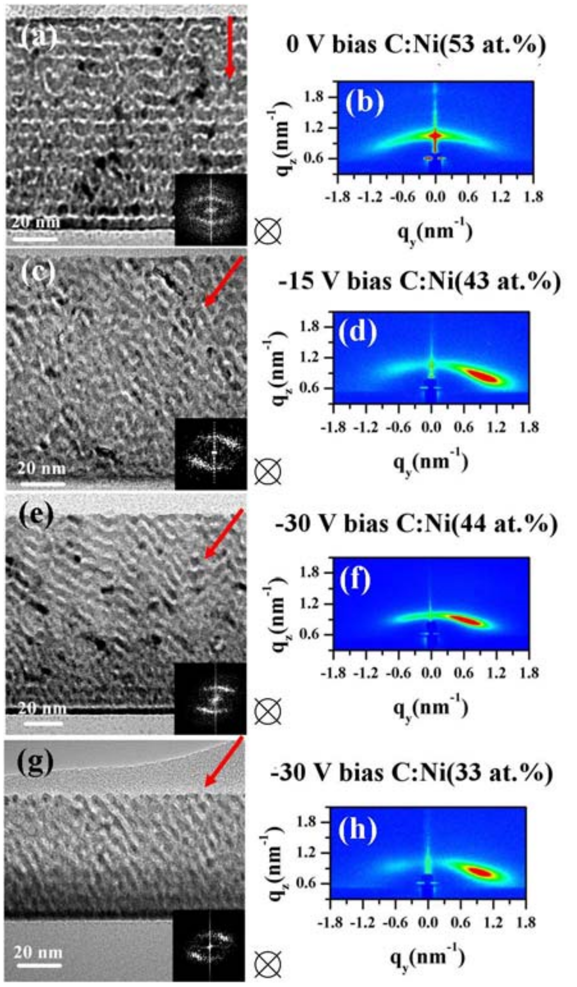

Figure 1. C:Ni film morphologies by TEM (left column) and GISAXS (right column) Growth parameters are indicated on the corresponding panels. The red arrows on the TEM images schematically indicate the incoming ion direction. The insets are FFTs of the corresponding X-TEM images. The crossed circles indicate the direction of the x-ray beam for the corresponding GISAXS measurements (extracted from Ref. [1]).

Ion impacts off-normal to the surface tilt the alternating carbon rich and nickel layers (Figure 1 (c)-(h)). *The metal nanopatterns no longer align with the advancing surface, but with the incoming ions.* At the very beginning of the deposition process a few precipitate layers form parallel to the substrate surface before the layers tilt. An increase of Ni content and ion energy results in a decrease of the tilt angle and an increase of the pattern period. After tilting the sample, the fast Fourier transform (FFT) of the TEM images exhibit rotational rather than mirror symmetry. GISAXS images from a macroscopic sample region (~5mm^2) closely resemble the upper part of the FFT patterns of the local area probed by TEM, confirming that the observed asymmetries are a global property of the material. A comparison of the fast fourrier filtered TEM images and GISAXS one can conclude that the structure consists of two composition modulation waves represented by two spots in GISAXS patterns – one ‘moves’ during the film growht roughly towards the ions and the other one with a significanlty lower amplitude in the direction perpendicular to the incident ions. In addition, GISAXS at different in-plane angles (now shown here) shows that the density correlations become symmetric and significantly weaker when approaching the plane which is perpendicular to the plane of incoming ions and sample surface normal.

GISAXS in combinations with TEM has allowed us to establish a dependence of the nanopattern morphology on the film composition, ion energy and incidence angle, and demonstrate a method for controlling the nanopatterning. From the fundamental point of view this study shows that phase separation processes at the nanoscale may be externally controlled by controlling the velocity and proportion of the depositing species. The approach is generally applicable to all ionized physical vapour deposition techniques and a large range of nanocomposite systems. This opens new prospects in controlled bottom-up synthesis of nanostructured composite materials or even of sculpted complex encapsulated 3D nanostructures such as chevrons or helices if the ion incidence angle is changed during the growth. A publication has been prepared and is under consideration in the Journal of Applied Physics.

In-situ heating experiments could not be carried out due to technical problems related with the sample alignement. The optimized procedure was established to carry out ex-situ measurements. However, the remaining time was sufficient for ex-situ GISAXS experiments only.

[1] G. Abrasonis, T. W. H. Oates, Gy. J. Kovács, J. Grenzer, P. O. Å. Persson, K. H. H. Heinig, A. Martinavičius, N. Jeutter, C. Baehtz, M. Tucker, M. M. M. Bilek, W. Möller, “Nanoscale precipitation patterns in carbon-nickel nanocomposite thin films: period and tilt control via ion energy and deposition angle”, J. Appl. Phys. *submitted* .