DELIVERABLE REPORT

WP10 JRA5 – Nano-Object Transfer and Positioning

D10.4

Methods for deposition of hierarchical markers

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Contents

Executive Summary

This deliverable report D10.4 of the Joint Research Action JRA5 "Advanced Nano-Object Transfer and Positioning" describes how hierarchical markers can be created on sample surfaces in a controlled way and optimized for several applications based on different processing and deposition methods. As selected examples, we are dealing here with the following approaches: i) E-beam lithography, ii) electron- (EBID) and ion- (IBID) beam induced deposition of a precursor material, and iii) parallel markers using the direct laser writing via multiphoton polymerization.

For a given application, the appropriate method should be carefully chosen depending on the process steps involved in the sample preparation, the sample size, and the spatial resolution and scanning range of the nano-science and focused X-ray beam instruments planned to be used, and finally, the precision, size and total amount of the markers required.

An optimal marker system to ensure an easy and quick nano-transfer comprises hierarchically arranged markers at dedicated marker positions with a designed lateral size and thickness. From the methods listed above, e-beam lithography and direct laser writing can be employed in case many markers at given positions on larger areas are needed. On the other hand, the strategy followed exploiting the EBID/ IBID process permits a pre-selection of regions of interest that contain the nano-objects, and a subsequent placement of the highest level hierarchical markers in their close vicinity.

Here, we are describing all three techniques with experimental details on the methods, discuss advantages and limitations for each of the technique, and give examples on how and where these methods are ideally used for, and how they have been tested within the framework of NFFA - JRA5. Moreover, this report contains guidelines and suggestions that may be considered to optimize the hierarchical arrangement and shape of the markers in order to further simplify the search algorithm for the nano-objects of interest.

1. Concept

This deliverable report D10.4 is part of a set of deliverable reports and milestones dealing with the creation and utilization of a (hierarchical) marker system on a sample surface to re-locate nano-objects. In order to compile this deliverable report in full detail, topics have been partially selected from the following deliverable and milestone reports:

- JRA5 - D10.1: "SOFTWARE ROUTINE FOR COORDINATE DEFINITION AND RELOCATION OF SINGLE NANO-OBJECTS"
- JRA5 - D10.2: "IMPLEMENTATION OF TRANSFER AND POSITIONING SYSTEM AT NANOLABS AND ALSFS"
- JRA5 - MS8 "VALIDATION OF FLUORESCENCE MARKERS WITH A LATERAL LINE RESOLUTION OF ~ 50 NM"
- JRA5 - D10.5 "DEMONSTRATION OF RELOCATING NANOOBJECTS BASED ON IN-SITU DEPOSITED FLUORESCENCE"
- JRA5 - MS13 "DESIGN AND PROTOCOLS ACCEPTED AT NANOCENTERS AND ALSF", AND THE CROSS-JRA DELIVERABLE REPORT JRA2

- D7.14 "TEST OF RE-ALIGNMENT OF NANOSTRUCTURES IN SYNCHROTRON EXPERIMENT BY IN-SITU MARKER DEPOSITION" BETWEEN JRA2 – RESEARCH ON HIGH PRECISION MANUFACTURING AND JRA5.

The proposed "marker design on demand" developed within JRA5 relies on all the JRA2 and JRA5 achievements described in these reports. It integrates the marker hierarchy in the phase of sample preparation and processing according to the working flow sketched in Figure 1:

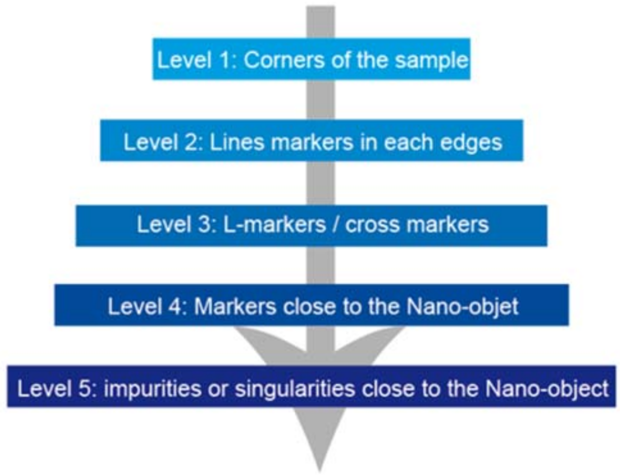


Figure 1: Hierarchical marker strategies. (M. Abuin, T.F. Keller, A. Stierle, DESY)

1.1 Electron-beam lithography

E-beam lithography can be used to create nanoscale nano-structures and marker patterns, with lateral sizes down to ~ 10 nm. The involved processes can be quite diverse depending on the structure that is aimed for, and the used materials (substrates, photo-resist, etc.). Its strength lies in writing repeated, equidistant structures, but can also introduce variations and gradients in the nano-structure sizes and in particular the lateral nano-structure distance, etc. It usually requires several processing steps like, e.g., spin-coating of a photo-resist, development, and a lift-off process that for some work flows is combined with an etching process, and a final post-annealing step.

1.2 Ion- (IBID) and Electron- (EBID) beam induced deposition

Ion- (IBID) and electron- (EBID) -beam induced deposition are based on a gas injection system (GIS) inside an SEM or dual beam focused ion beam (FIB) instrument. At DESY NanoLab [2], a commercial Pt containing precursor gas is inserted into the chamber system at around 40 °C through a GIS injection nozzle positioned in close proximity to the sample surface, and as such ensures optimal deposition conditions. This permits to create markers on specific positions onto a sample surface, and manually arrange their location in order to create an optimal hierarchy for guidance to the nano-regions of interest that are pre-selectable by this technique.

1.3 Parallel markers using the direct laser writing via multiphoton polymerization

The multiphoton polymerization process can be used to create marker arrays. It utilizes an organic–inorganic hybrid composite [3]. As described in milestone MS8 of this JRA5, line patterns down to 50 nm can be reached providing a tool to localize nano-objects by an array- and line- counting based navigation. This is in particular useful as template onto which the nano-objects are deposited by wet chemistry, like, e.g., from a liquid solution in an evaporating solvent. Then, using nanoscience-center instrumentation, specific nano-objects can be considered and pre-selected for the nano-transfer to a focused X-ray experiment at an analytical large scale facility (ALSF).

2. Design specifications

Within the JRA5 "Advanced Nano-Object Transfer and Positioning", it has been realized that combined nano-science and synchrotron-based focused X-ray beam experiments exhibit a significant heterogeneity with respect to the substrates, the arrangement of nano-objects, and the instrumental settings. This fact led us to propose and develop a "marker design on demand" that is specific and optimized for a given experiment and application for the nano-transfer.

Among other specifications, this "marker design on demand" includes several hierarchy levels. It furthermore takes into account the lateral instrumental resolution of all instruments within the experiment, at which the nano-objects need to be re-localized, all travel ranges of the sample stages or microscopes, as well as all spatial resolutions during sample scans for searching the markers.

In addition to the sketch in Figure 1 the marker selection, marker positioning and marker writing need to consider the following aspects:

- 0th order hierarchy: Sample corners serving as 0th order hierarchical markers are usually damaged. The markers should therefore be located not right but in close vicinity to a corner. Thick markers with a large lateral extension should be used, simplifying the first search and alignment step. 0th order hierarchy serve to bridge distances on the order of several mm, with a precision of 10-100 µm.

- 1st order hierarchy: Intermediate guiding markers are useful, which are located in well-defined distances to the region of interests (ROIs), but still sufficient far to serve as central navigation points to reach several nano-objects of interest. 1st order hierarchy could be used as a divider of the sample area into several regions with different process conditions for each nano-object, or serve as fillers to bridge large distances between markers on the order of several 100 µm, with a precision of 10-50 µm. Furthermore, with the intermediate 1st order hierarchy markers the "Advanced Nano-Object Transfer and Positioning" nano-navigation can be fine-tuned.

- 2nd order hierarchy: Fine markers should be placed in close vicinity to the pre-selected nano-object. An optimized marker thickness is required for different applications depending on the detection schemes and in turn different sensitivities at the ALSFs operating the focused X-ray beams to ensure i) an easy (re-) localization and ii) avoid any contamination from the EBID / IBID processes.

- Moreover, the marker design itself can simplify the search process by an appropriate shape: Asymmetric markers are useful, as they exclude an accidentally wrong mounted sample, and guide into the right direction by the shape itself, knowing the map of the sample from the pre-analysis at the nanoscience-centre.

- A detailed review of the area of interest in the nanoscience centres (like by AFM, SEM, etc.) is mandatory. A limited amount of high resolution images can be taken at the focused X-ray beamline, with, optimally, a continuous scanning mode to save X-ray beamtime.

- An optical light microscope and/or X-ray fluorescence detector can significantly reduce the time for re-localizing the markers.

- Markers on the sample holder can help (to be developed and implemented in subtask 10.3.2 of JRA5, where an industry-friendly platform of interoperability between nano-instruments and nanofocused beamlines based on the Advanced Nano-object Transfer and Positioning is developed by the JRA5 partners (ESRF, CEA, DESY).

"Anti-markers" can be employed, like a milled region created by focussed ion beam (FIB), or any pre-existing defects that could create a contrast in the X-ray beam (like absorption in the Bragg peak of the substrate), is an alternative approach to consider.

Further detailed descriptions of the proposed "Tailored Design for an Advanced Nano-Object Transfer & Positioning" can be found within the deliverable report D10.2 "Implementation of transfer and positioning system at nanolabs and ALSFs".

3. Results

3.1 Electron-beam lithography

Figure 2a shows an SEM overview image of a hierarchical marker arrangement with guiding marks as created by an e-beam lithography process. The guiding letters and descriptions can be seen, directing to specific regions of interests, as originally written by the e-beam into the photoresist.

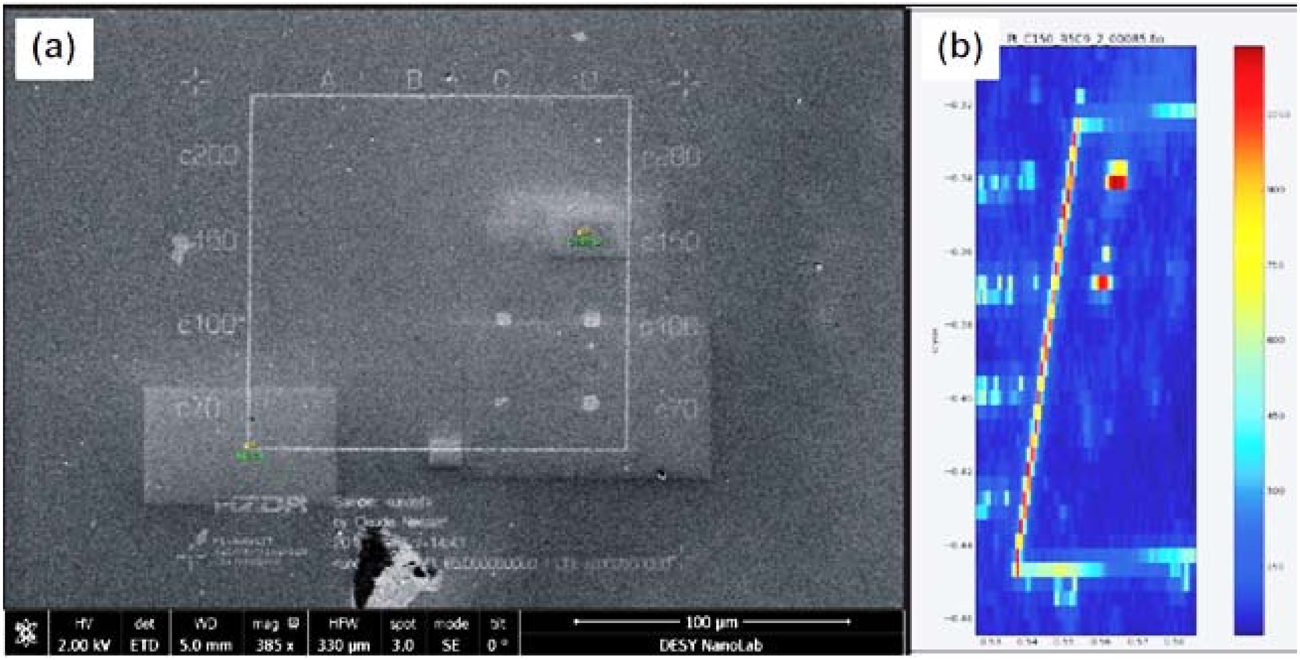


Figure 2: SEM image (left) and Pt X-ray fluorescence image (right) of electron-beam lithography prepared Pt nano-arrays with surrounding localization frames and marker numbers (S. Kulkarni, T. F. Keller, R. Shayduk, A. Stierle et. al, DESY)

Figure 2b shows an X-ray scanning image obtained at beamline P10 at PETRA III, DESY using the Pt L_3 X-ray fluorescence at an X-ray energy of around 12 keV. Inside the surrounding square, nano-objects are located on a regular array. In this case, the nano-objects itself consist of arrays of single Pt nanoparicles ordered equidistantly with a varying lateral distance / pitch from field to field.

3.2 Ion (IBID) and Electron (EBID) beam induced deposition

The images in Figure 3 result from a post-analysis after an X-ray beamtime at ID01, ESRF. Using Bragg coherent diffraction imaging (B-CDI), a single Pt nano-particle was analysed in a reducing gas atmosphere at elevated temperature. Back at the nano-science centre (DESY NanoLab), auxiliary IBID/ EBID markers where designed to guide the search inside a UHV-AFM/STM to the nano-region containing the nanoparticle analysed in the X-ray beam at ID01.

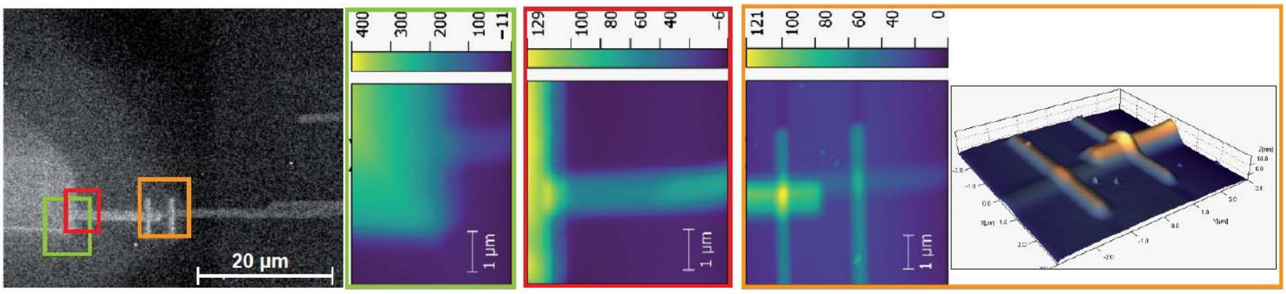


Figure 3: SEM, 2D- and 3D-AFM images of the EBID/IBID written Pt based markers during the navigation to the pre-selected nano-object (E. Graanaes, .S Kulkarni, M. Abuin, T. F. Keller, A. Stierle, DESY).

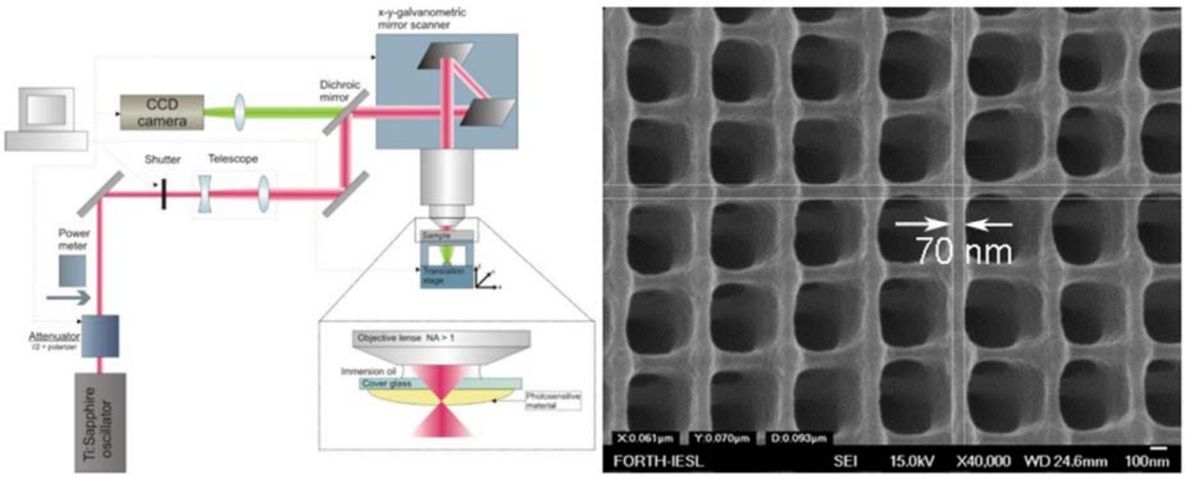
The image on the left of Figure 3 is an SEM image of the auxiliary markers that have been added to the existing markers created before the ID01 beamtime. These markers were specifically designed to guide the search towards the nanoparticle inside a UHV AFM-STM. The AFM scanning images are shown in 2D in the centre and in 3D view on the right.

Most importantly, detailed lateral information like, in particular, calibration markers with well-defined lateral distances was incorporated into the marker structures to ensure a simply re-location.

3.4 Parallel markers using the direct laser writing via multiphoton polymerization

Figure 4 shows a sketch of the experimental setup and a resulting array pattern consisting of a cross-arrangement of two perpendicular line patterns. In this experiment, a line width of 70 nm was achieved, and the square inside the lines is of the order of 100 nm, showing the high resolution benefical for a precise re-location of nano-objects located inside the squares.

Within the JRA5 milestone report MS8, the capability of creating and validating fluorescence markers by EDX with a lateral line resolution of ~ 50 nm is described in more detail. Currently, an X-ray beamtime at SOLEIL is currently prepared and will be scheduled end of 2018 in the framework of a research project to scientifically exploit this technical development within JRA5.



Direct laser writing via multiphoton polymerization workstation at **FORTH**

Marker arrays via laser-based direct-write non-linear lithography, exhibiting a lateral line resolution of ~ 70 nm (**FORTH**)

Figure 4: Marker preparation for position re-location by direct-write lithography / multiphoton polymerization (fluorescence, absorption, etc.). The feasibility of writing patterns with a 50 nm pitch size was reported in milestone 8 (JRA5-MS8). (E. Stratakis, FORTH)

3.4 Hierarchical marker design on demand

Figure 5 sketches and summaries the main hierarchical concepts developed within the JRA5 – Advanced Nano-Object Transfer and Positioning in a logo. Markers at different, known positions with different lateral sizes and thicknesses are the framework for the hierarchical approach for re-localization. At the same time, the logo shows two different detection schemes used to image a navigation marker, i) SEM on the top left at the nano-science centre, and ii) an X-ray fluorescence scanning image of the very same marker at a focused X-ray beamline.

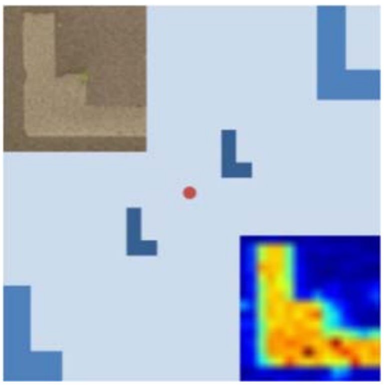


Figure 5: Logo of the JRA5 offer “Nano-Object Transfer & Positioning” of the transnational NFFA user program, indicating several hierarchical levels and the SEM and X-ray florescence images taken from the same marker at DESY NanoLab in Hamburg and at the X-ray beamline ID01 at ESRF in Grenoble (T F. Keller, M. Abuin, A Stierle, DESY).

This logo is used since beginning of 2018 to advertise the outcome of JRA5 to potential NFFA users to attract them to pre-select their nano-objects with our newly developed design, software protocol and hardware implementation at selected X-ray beamlines, see, e.g., https://www.nffa.eu/offer/lithography-patterning/installation-1/nano-object-transfer-positioning/

4. Conclusions and Perspectives

Within this deliverable report JRA5 D10.4 we describe the methodologies to employ a hierarchical system to facilitate a nano-navigation based on a designed array or marker arrangement that have been developed or used by the partners within the JRA5.

Since beginning of 2018, the outcome of the JRA5 development has become a new offer of the transnational access. This offer provides i) hierarchical markers with electron- or ion beam induced deposition (EBID/IBID) at DESY NanoLab, ii) the software scripts, and iii) a tailored design of the marker size like thickness, lateral arrangement, etc. in order to optimize the search for the nano-ROI. With new NFFA user proposals the Advanced Nano-Object Transfer and Positioning tool will we refined, expand and adopted. Furthermore, the developments within the JRA5 “Advanced Nano-Object Transfer and Positioning” on the hierarchical nano-navigation schemes are offered to all users with accepted regular PETRA III proposals.

The number of X-ray beamlines with focusing options will significantly grow in the next few years, not only at PETRA III but at all 3rd generation synchrotron sources in Europe and worldwide. This stresses the need for a well-defined nano-transfer protocol. Hierarchical concepts like being implemented in JRA5 and described in this report will play a prominent role.

In perspective, for the emerging 4th generation diffraction limited storage rings a systematic nano-navigation system will be ultimately required. The outcome of the JRA5 “Advanced Nano-Object Transfer and Positioning” is one first step and possible way to continue, as it already has been spread to the participant institutions, several European synchrotrons and focused X-ray beamlines. Even more, is has raised interest at the Advanced Photon Source in Chicago, USA for their upgrade program APS-U.

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