

Guideline for the preparation of fixed nano-objects on hard substrates, like nanoparticles and nanowires

The following nano-objects were selected to be produced for MechProNO partners:

- Gold nanoparticles (60 nm, spherical)
- Gold nanorods 650 and 700 (25 nm x 66 nm and 25 nm x 77 nm respectively)
- Silica nanoparticles (100 nm, respectively 304 nm, spherical)
- Silver nanoparticles (50 nm, spherical)
- Silver nanowires (60 nm x 10 µm)
- Titanium dioxide (<150 nm)

The fabrication of these nano-objects consists of the following steps:

- substrate cleaning
- calculation of the desired particle surface concentration
- application of a small preparation volume of nano-object solution onto the substrate
- drying

Substrate cleaning

A small silicon wafer piece <100> or <100> with 1-2 µm SiO₂ is cleaned by wet chemical **SC-1** procedure (NH₄OH (29%), H₂O₂ (30%) and DI water in a volume ratio of 1:1:5; 10 min., 80°C) respectively by **piranha etch** (H₂SO₄ (40%) +H₂O₂ (30%) in a volume ratio of 4:1; 15 -20 min., 90°C). Other approved methods are dry cleaning procedures in a **plasma** apparatus or using **DUST- AID Cleaning Strips**.

Particle surface concentration

To deposit nano-objects in a defined distance to each other it is necessary to calculate well-directed an appropriate particle surface concentration c_A [1/mm²], the particle number per substrate area. The equation shows the relation between surface concentration c_A , number concentration c_N , volume concentration c_V , mass concentration c_m , depending on particle size x , preparation area A_{PR} and preparation volume V_{PR} (for spherical particles):

$$c_A = \frac{N_P}{A_{PR}} = c_N \cdot \frac{V_{PR}}{A_{PR}} = c_V \cdot \frac{6}{\pi x^3} \cdot \frac{V_{PR}}{A_{PR}} = c_m \cdot \frac{1}{\rho_s} \cdot \frac{6}{\pi x^3} \cdot \frac{V_{PR}}{A_{PR}}$$

Conventional drop drying

In case of drying the nano-objects were deposited by liquid droplet application with following fluid evaporation if the gaseous phase still isn't saturated with vapour. In MechProNO the drying method was applied to all of selected materials: silica and titanium dioxide particles, gold particles, gold rods and silver particles.

1. The cleaned wafer piece is stored in a laminar flow box.

2. The wafer piece is applied to a drop of diluted homogenized dispersed suspension (5-10 μl , droplet size 3.5-5.5 mm) with a micro pipette or a very thin cannula. The supplied nano-object concentration depends on the particle size and on their density as well as on the surface properties of substrate. By total drop drying (all particles remain on the substrate) is it possible to estimate an expedient degree of dilution in case of separated particle deposition per known area. It makes sense to calculate the particle surface concentration c_A [$1/\text{mm}^2$] before.
3. The suspension remains on the substrate for a defined time. Normally a droplet volume of 10 μl needs about 30 minutes for total drying in a laminar flow box. Another possibility is to remove the excess solvent with an optic tissue after 5 minutes; the realization depends on the compound and adsorption behaviour of material.

Drop-Drying by Marangoni Effect

To overcome the drying rings as well as better nano-object separation and uniform deposition over the silicon surface can be attained by Marangoni-Flow-Assisted Drop-Drying.

In this connection the aqueous nano-object suspension with high surface tension pulls more strongly on the surrounding liquid with low surface tension (ethanol vapour atmosphere), the presence of a gradient in surface tension will naturally cause the liquid to flow away from regions of low surface tension. Such flow induces a strong recirculation in the droplet, which removes particles from the contact line and moves them along the free surface toward the droplet centre and leads to uniform deposition (Majumder et al, 2012).

1. The cleaned wafer piece is placed on a small plastic holder into a Petri dish highly filled with ethanol.
2. The wafer piece is applied to a drop of homogenized dispersed and diluted suspension ($< 5 \mu\text{l}$) with a micro pipette or a very thin cannula and the Petri dish is closed.
3. The drop of suspension spreads over the surface; the contact angle decreases and the drop volume grows with time. Then it is allowed to dry (this may take several hours).

Rinsing

In Rinsing the nano-object deposition is realized by diffusion (based on Brownian motion) during the particle contact on substrate. Particularly in case of titanium dioxide the rinsing method is suitable and well-reproducible.

1. The cleaned wafer piece is stored in a laminar flow box.
2. The wafer piece is applied to a drop of diluted homogenized dispersed suspension (approximately 10-20 μl) with a pipette or a very thin cannula. The adequate nano-object concentration depends on the particle size and on their density as well as on the surface properties of substrate again. By rinsing the deposited particle concentration is not to quantify previously, therefore an appropriate particle concentration supplied must be estimated empirically.
3. For nano-objects 10-15 minutes adsorption time is sufficiently for safe particle sticking. Then the remaining liquid was sucked off with an optics cloth and the substrate is rinsing with deionised

water, afterwards the silicon wafer is dried with N₂. The particles remain on the substrate based on van der Waals forces.

4. A more homogeneous deposition rate can be achieved when at first the suspension is dispersed by bath sonication and heated to about 40°C, thus on the one hand is prevented the agglomeration of the nano-objects and on the other hand the viscosity of fluid is decreased.

Dip-coating

In the so-called Dip-coating method the particle deposition is effected also by diffusion (based on Brownian motion) during the immersion of substrate in a nanoparticle suspension. This preparation method was applied for all of selected materials with the aim of no-clustered particle deposition.

1. The cleaned wafer piece is held with clean tweezers or fixed to a device and immersed in the diluted suspension for defined time.
2. After usually 10 minutes the substrate is pulled out jitter free with a constant speed. Whereas pulling out a thin film remains on the substrate and the solvent evaporated. Afterwards the silicon wafer is dried with N₂ carefully.
3. The deposit rate depends on the particle concentration in the diluted suspension, the time of immersion, the pull out speed and the surface properties of particles and substrates. When the particle concentration of the suspension is chosen suitably, the particles can be deposited well reproducible, well separated and homogeneous on the substrate surface. Then the dip-coating method could be interesting especially for AFM measurements.

Restrictive to remark, in case of polydisperse suspensions the particle deposition can be size-selective, because the particle mobility in the suspension depends on their diameter.

Electrostatic precipitation

Previous studies have shown that the electrostatic deposition of aerosols within Electrostatic Precipitators (ESP), in which the particles are deposited by electrostatic field forces, can provide substrates with separated particles depending on the quality of the generated aerosols.

To avoid re-agglomeration or sedimentation, particulate suspensions are provided in combination with stabilizers. The stabilizers are the source for residual particles during typical aerosolization processes with atomizers. Thus, it is difficult to distinguish between target particles and residuals.

To advance this problems and to obtain very fine raw aerosols (in size range below 100 nm), to aerosolize the colloidal suspension we've also operated an Electrospray Aerosol Generator (ESG Model 3480, TSI Inc., Shoreview, USA) in combination with an ESP (Prototype of NAS Model 3089, TSI Inc., Shoreview, USA). The employed ESP (Fissan et al, 1999) consists of a corona needle as ion-source for unipolar, negative particle charging. Afterwards, the charged particles are passed through an electrical field where they are moved on the lines of electric flux to the substrate. The specific surface particle deposition rate depends on the material characteristics and the presence of stabilizers.