Introductory Guide on the determination of geometrical properties of nano-objects under different adhesion levels

EMRP Project NEW05 **MechProNO** Traceable measurement of mechanical properties of nano-objects

Key criteria for the determination of geometrical properties of nano-objects under different adhesion levels

We discuss criteria that have been identified as key elements for determining the geometrical properties of nano-objects that exhibit different levels of adhesion. We divide the report in sections relative to different aspects to be considered:

- Substrate material
- Tip material
- Tip shape

Measurements are reported in order to provide evidence to support the conclusions presented. Unless stated otherwise, atomic force microscope (AFM) measurements were taken in a semi-clean, temperature controlled room (20 ± 0.1 °C) using an AFM working in closed-loop tapping mode. We used a fibre interferometer with light at 785 nm to detect the cantilever deflection and an NPL Plane Mirror Differential optical interferometer, fibre-fed with a frequency stabilized laser (632.8 nm), was employed to traceably measure the height of the features on the surface.

Substrate material

Starting our discussion from the material of the substrate, we report the results of AFM measurements of nanoparticles on silicon or silicon dioxide substrates. The measurements were taken using a silicon AFM tip with nominal tip radius < 10 nm and the nanoparticles were made of different materials and of different sizes. Given that they are round or cylindrical laying on the substrate, we can extract the diameter using the traceable vertical component of the AFM measurements.

	Nominal value (nm)	Average µ (nm)	Standard deviation σ (nm)	Number of particles measured
TiO_2 on Si <100>	< 150 nm	27.6	10.8	114
TiO_2 on SiO_2	< 150 nm	27.3	11.2	527
(25x77 nm) Au nanorods on Si <100>	25	20.0	1.9	44
(25x77 nm) Au nanorods on SiO_2	25	21.3	2.2	56
60 nm Au on Si <100>	60	57.1	6.8	10
60 nm Au on SiO_2	60	48.3	7.9	10
Ag on Si <100>	50	46.1	6.2	20
Ag on SiO_2	50	50.4	8.7	33

For the particles measured, we did not observe any trend associated with the substrate in the measurement of the NP's height. As an example the average diameter of Au nanorods on Si <100> (20.0 nm) is smaller than the ones on SiO_2 (21.3 nm), whereas spherical Au NP on Si <100> have a larger diameter (57.1 nm) than on SiO_2 (48.3 nm). This highlights that for the NPs considered the two substrates used do not appear to affect the measurement of their diameter.

If we consider a single NP type, we can observe that the difference between the diameter measured on Si and the one measured on SiO_2 is within the size distribution (σ) of the nanoparticles. In the case of Au nanorods σ is as low as 1.9 nm, and we can conclude that in this case the effect of adhesion on the measurements is smaller than this value.

As a conclusion, no clear indication of the effect due to different adhesion/interaction of the NPs with the different substrates can be inferred if the variation in height caused is lower than the distribution of sizes of the nano-objects.

Tip material

We also checked if the change of tip material could result in variation of the diameter measurements due to a change in the interaction/adhesion between the tip and sample/NPs. The following table shows the measurements of the diameter of Au NPs on Si <100> or SiO_2 substrates, taken with either Si tips or diamond coated tips.

	Nominal value (nm)	Average diameter (nm)	Standard deviation (nm)	Number of particles measured
Ag on Si <100> w/ Si tip	50	46.1	6.2	20
Ag on SiO_2 w/ Si tip	50	50.4	8.7	33
Ag on Si <100> w/ diamond tip	50	47.0	8.1	47
Ag on SiO_2 w/ diamond tip	50	51.8	7.7	122

The results show that there is a difference of 4.3 nm in the average height of the NPs when measured on a Si substrate (46.1 nm) and when measured on a SiO_2 one (50.4 nm). A similar difference (4.8 nm) was measured in the case the measurements where performed with a diamond tips (47.0 nm on Si vs. 51.8 nm on SiO_2). Interestingly when using a diamond tip, the average diameter of NPs on either Si or SiO_2 increases by 0.9 nm and 1.4 nm, respectively. Also in this case, however, the standard deviation of the nanoparticles is larger than the difference observed and therefore it not possible to uniquely relate the different results to the effect of adhesion between tip and sample/substrate as a result of the tip material.

Tip shape

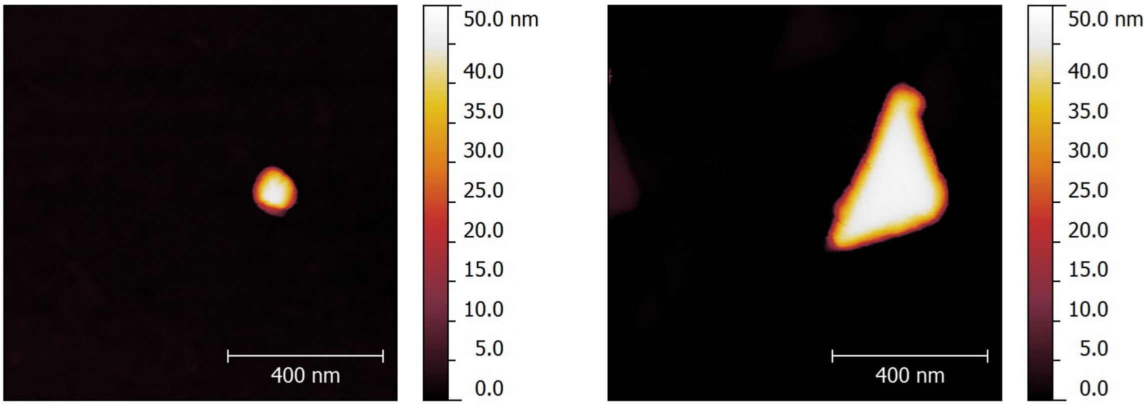
We also checked the effect of tip diameter in the extraction of the diameter of the nanoparticles. In this case we compared the results obtained with a sharp tip (tip radius < 10 nm) with the ones obtained with a blunter tip (tip radius ~ 150 nm).

Also in this case we observed that the distribution of particle size is larger than the difference in average diameter.

		< 10 nm tip radius			150 nm tip radius		
	Nominal value (nm)	Average (nm)	Standard deviation (nm)	# of particles measured	Average (nm)	Standard deviation (nm)	# of particles measured
TiO_2 on Si <100>	< 150 nm	27.6	10.8	114	25.8	9.1	137
TiO_2 on SiO_2	< 150 nm	27.3	11.2	527	25.1	8.3	138
Au nanorods on Si <100>	25	20.0	1.9	44	21.1	2.7	46
Au nanorods on SiO_2	25	21.3	2.2	56	20.7	4.7	63
60 nm Au on Si <100>	60	57.1	6.8	10	57.8	9.0	48
60 nm Au on SiO_2	60	48.3	7.9	10	57.0	9.2	39
Ag on Si <100>	50	46.1	6.2	20	48.7	8.7	37
Ag on SiO_2	50	50.4	8.7	33	55.0	5.9	41

Within the scope of understanding the effect of tip shape we tested how tip wear affects the measurement of the nanoparticle diameter. We used the AFM in contact mode (CM) and non-contact mode (NCM) with silicon tips with diameter of <10 nm. For both cases we first measured a group of Ag nanoparticles dispersed on a SiO_2 substrate, we then eroded the tip by pressing it against an area free of NPs while scanning, and finally we took AFM measurements of the same nanoparticles. We show here the direct comparison between the NP's height measured before and after eroding the tip.

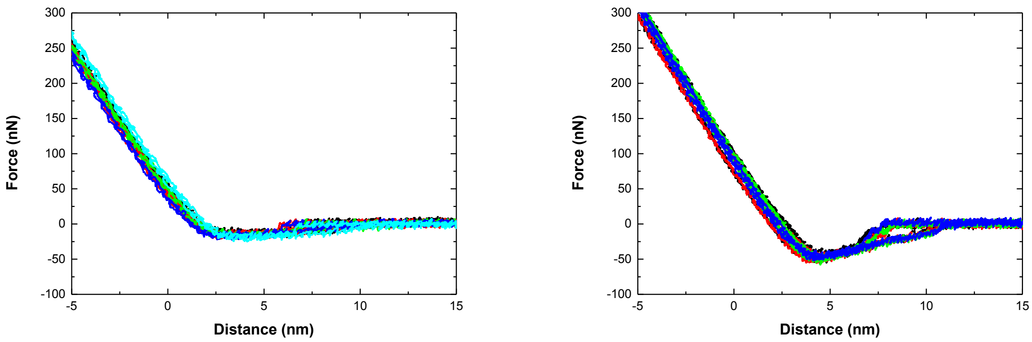
As an example Figure 1 reports the image of a nanoparticle before and after eroding the tip. Although the NP is expected to be round with a radius of about 45 nm, the AFM image results dilated on the XY plane, due to the finite size of the tip (tip radius of ~ 10 nm). The AFM image is in fact given by the "dilation" of the NP and the tip, thus resulting in a larger diameter in the XY plane, compared to the height along Z. This effect is even more evident after eroding the tip (Fig. 1 (b)), as in this case the tip is worn and the size of its apex becomes bigger than the size of the NP. As a result the AFM image is mainly of the tip rather than the nanoparticle. It is, however, to be noted that despite the dilation in XY, the height of the imaged NP should remain the same in both cases (~45 nm).



(a) (b)

Figure 1. AFM scan in non-contact-mode of a nanoparticle before and after eroding the tip

The change in adhesion between the tip and the substrate can be observed through force distance curves as in Figure 2. They show an increase of the adhesion force from -20 nN before the erosion to -58 nN after the erosion, due to the increase of the contact area between the tip and the substrate.



(a) (b)

Figure 2. Multiple force distance curves taken in the same sample point (a) before and (b) after eroding the tip

The results obtained from the AFM measurements, showed that when working in NCM the diameter of the nanoparticles reduces by an average of 1 nm, whereas in CM it increases by an average of

4 nm. We associated the increase of the NP diameter in CM mainly with an increase of the adhesion between the tip and the substrate (not to the NP) and the reduction of the indentation of the NP when the tip wears out. On the other hand, in NCM the tips have a much softer interaction with substrate and NPs, and are not expected to induce any indentation. The reduction of diameter was instead attributed to the increase of repulsive force due to an increase of the tip/substrate contact area when the tip is eroded. It is to be noted that the contact area between the tip and the NPs do not increase as much as the tip/substrate contact area because it is limited by the dimension of the NPs and their spherical shape.

Conclusion

The information gathered with these experiments allowed us identifying few key criteria to be considered for the measurement of nano-objects.

Firstly we suggest that NCM is used instead of CM for measuring NP and nano-objects in general. CM could apply an excessive force to the nano-objects and cause their deformation, or ever move them if not properly anchored to the substrate.

Secondly we suggest checking the level of adhesion using force distance (FD) curves. Given that FD curves can contribute to tip erosion, it is important to leave the FD curve as last test, so as to prevent altering the shape of the tip during series of measurements.

Thirdly we did notice a change in the measurement associated to tip wear. Further investigation of this effect is recommended, in particular relative to the effect of the scan parameters such as oscillation amplitude or amplitude damping for NCM AFM scans. We suggested that the variation in diameter is due to the change in contact area for both CM and NCM. For the aim of measuring the dimensions of nano-objects, we recommend that the measurements are taken with the sharpest possible tip available. This is because adhesion effects have a larger influence with blunter tips, and, therefore, minimizing the contact area between tip and substrate or sample contributes to minimize these effects.

Finally, in this case the diameter was extracted by using the height measurement from AFM images and the effect of adhesion could be measured directly. In the case of extraction of the diameter from the lateral dimensions of the nano-objects, further sources of uncertainty need to be considered (e.g. uncertainty on the stage position, size of the scan step, etc.). Among these is the shape of the tip. It is known that the AFM image is the dilation of the sample by the tip and therefore, whereas the height of the features mainly remains unaffected by the shape of the tip, their lateral dimensions are highly influenced. Also in this case, using a sharp tip helps reducing the uncertainty, however, for better results, “eroding” the AFM image by the shape of the tip is a further improvement. For this purpose, knowing the shape of the tip is a requirement and can be achieved by different methods such as using ad-hoc samples (e.g. “tip characterizers” or “tip check”), using SEM images of the tip or using software techniques, e.g. the “blind tip reconstruction” routine.