Certifications

Pontificia Universidad Católica de Chile

Characterization results for the copper nanoparticle sample using AFM

Analysis: 28 june 2016

Analysis time: 1 hour

Number of samples: 3

Equipment specifications:

Location: Surfaces Laboratory, Physics Institute, PUC

AFM: JPK Instruments, NanoWizard 3 model

Tip type: Pyramidal shape with curvature radius ~10 nm

Gold-coated cantilever dimensions: height 10-15 µm, length 125 µm, width 30 µm. Resonance frequency 45-115 kHz, force constant 0.5-9.5 N/m, obtained from NanoAndMore, Watsonville, CA, USA. Equipment calibration is sporadically verified with calibration samples, e.g., "HS-20MG Height Calibration Standard, 20 nm" from NanoAndMore, Watsonville, CA, USA.

Sample preparation: 5 µl of the provided sample dissolved in 1.5 ml ultrapure water. 10 µL of this solution deposited on a crystalline and ultra-flat silicon substrate, previously cleaned using the Tidswell method and dried with ultrapure nitrogen gas. Spin coating performed at 2 speeds: 3 seconds at 200 RPM, then 10 seconds at 8,000 RPM.

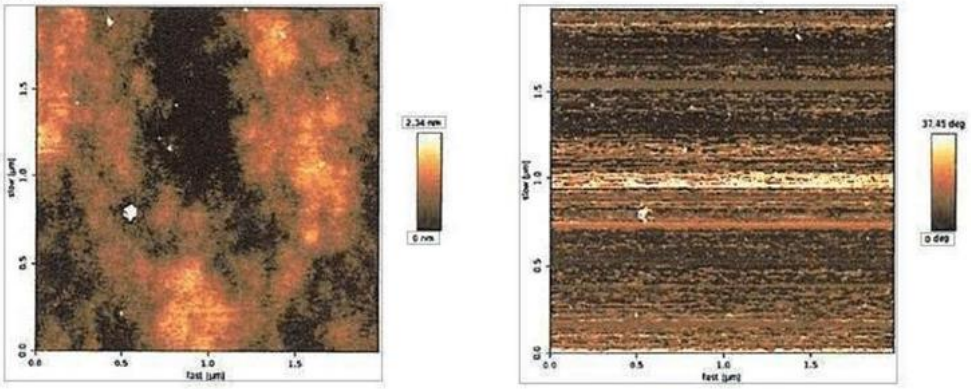
AFM analysis performed immediately after sample preparation

Results:

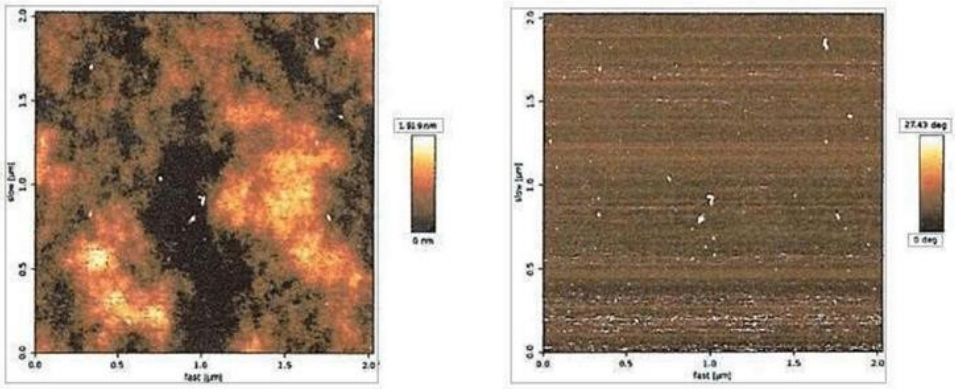
Background roughness (silicon (100) crystal substrate) is 408,52 pm, with a standard deviation of 29,95 pm.

Topographies (left) along with their phase image (right) obtained were:

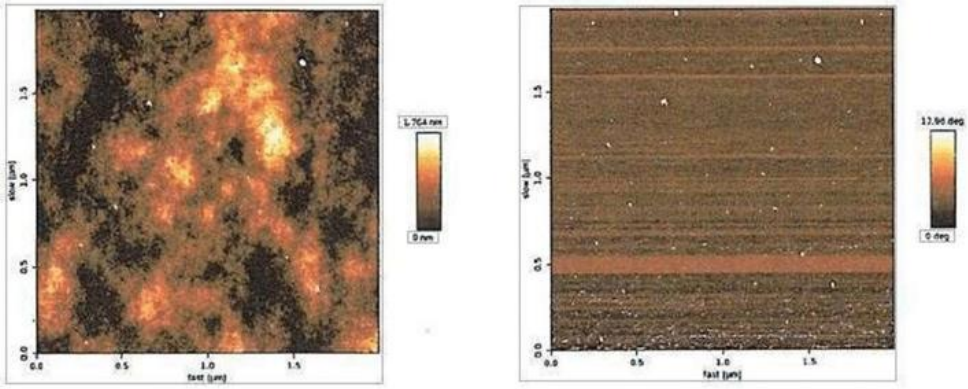
Zona 1:



Zona 2:



Zona 3:



La topography describes the height variations present on the sample. The phase image shows the differences in the type of material on the sample; in other words, the phase signal indicates whether the tip encounters softer or harder materials, which results in a change in the phase.

In this case, the phase changes match perfectly with the changes observed in the topography. Therefore, it can be inferred that there are particles that differ from the silicon substrate. These particles correspond to the nanoparticles provided by the client, which, according to the information supplied, are copper nanoparticles.

The particle size was determined by measuring the recorded height and the recorded width of the nanoparticles. From the recorded width, the actual width ΔW can be obtained by calculating the ideal width that the AFM should register. The particle height d and the tip radius R of the cantilever are related to the ideal width by the expression $d = w_{ideal}^2 / 8R$. The cantilevers used (Pointprobe® model) guarantee a tip radius smaller than 12 nm, typically R ranges from 8 to 12 nm. The actual width is then given by the difference ΔW between the measured width and the ideal width, i.e. $\Delta W = w_{recorded} - w_{ideal}$.

Results for a total of 34 particles analyzed:

The average particle height was 4.25 nm, with a standard deviation of 2.902 nm. The average particle width was 18.308 nm, with a standard deviation of 11.228 nm.

Observations

The measured width is determined by the cantilever tip and may also be affected by potential cantilever torsion; therefore, the width data obtained for the particles are less reliable than the corresponding height measurements.

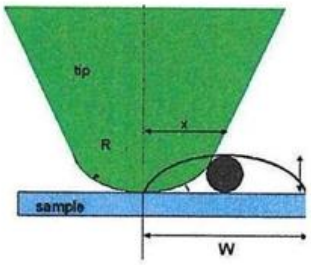
These measurements are valid for the nanoparticles extracted from the sample provided by the client, at the date and time when the measurement was performed, and may depend on the sample preparation.

Atomic Force Microscopy (AFM) is a more direct method than other techniques operating at the nanometer scale and enables the measurement of individual nanoparticles. Scanning Electron Microscopy (SEM) methods do not provide the nanometer-scale resolution of AFM; the minimum resolution of a conventional SEM is typically limited to particles larger than approximately 60 to 80 nm. With AFM, it is possible to detect nanoparticles on the order of 1 nm in size, considering the particle height.

AFM scans smaller areas than SEM; therefore, AFM cannot provide information regarding the chemical composition of the particles. SEM, however, when combined with an EDX or EDS detector, can provide information on the surface composition of the nanoparticles. X-ray measurements can provide information on the chemical composition and crystalline structure of a nanoparticle agglomerate.

Height(nm)	Recorded width(nm)	Ideal width(nm)	Actual width(nm)	
1	2,836	42,29	15,063	27,227
2	4,603	26,98	19,190	7,790
3	5,34	46,97	20,669	26,301
4	2,905	23,17	15,245	7,925
5	3,723	24,61	17,258	7,352
6	2,636	22,26	14,522	7,738
7	3,777	21,13	17,383	3,747
8	1,548	18,86	11,128	7,732
9	5,175	37,36	20,347	17,013
10	3,387	22,77	16,461	6,309
11	15,22	53,86	34,894	18,966
12	3,398	30,09	16,488	13,602
13	3,49	30,57	16,709	13,861
14	6,458	73,95	22,730	51,220
15	3,583	33,63	16,930	16,700
16	3,212	28,96	16,030	12,930
17	1,774	23,42	11,913	11,507
18	5,271	33,05	20,535	12,515
19	3,575	35,05	16,912	18,138
20	6,208	65,75	22,285	43,465
21	6,256	46,34	22,371	23,969
22	3,457	64,77	16,630	48,140
23	3,636	30,47	17,055	13,415
24	1,65	22,72	11,489	11,231
25	3,935	40,09	17,743	22,347
26	2,138	40,54	13,078	27,462
27	13,82	49,63	33,251	16,379
28	3,221	43,01	16,052	26,958
29	2,869	31,26	15,150	16,110
30	3,211	32,84	16,027	16,813
31	1,985	29,47	12,602	16,868
32	2,831	31,89	15,049	16,841
33	4,574	40,32	19,129	21,191
34	2,786	27,46	14,929	12,531
Promedio	4,250	36,045	17,743	18,303
Desviación	2,902	13,422	5,093	11,228

Calculation of nanoparticle diameter from the recorded width



$$x^2 = R^2 - (R-d)^2$$

Para $R \gg d$

$$W = \sqrt{8dR}$$

Important note: Nanoparticles of various metals, including copper nanoparticles, tend to form oxides from the moment they are manufactured. The degree of oxidation increases over time. Depending on storage conditions, nanoparticles may change their structure and initiate sintering, agglomeration, dendrite formation, and crystallization processes, which may be accelerated by changes in temperature, pressure, and exposure to radiation (for example, cosmic radiation during air transport).

These measurements are valid for the nanoparticles extracted from the sample provided by the client, at the date and time the measurement was performed, and may depend on the sample preparation.

These results cannot be extrapolated to the full manufacturing batch or to other nanoparticle products from this or other companies.

Dr. rer. nat. Ulrich Volkmann
Profesor Titular Facultad de Física UC
SurfLab, Instituto de Física UC

Nicolás Moraga
Licenciado en Física UC
Cand. Master en Física UC