Bruker AXS

Application Note # AFM-01

AFM and GISAXS Study of Self-assembled FeO Nanoparticles

Self-assembled iron oxide nanoparticles were investigated using atomic force microscopy (AFM) and grazing-incidence small-angle X-ray scattering (GISAXS).
The atomic force microscopy was carried out using a Bruker N8 TITANOS system and showed a dense particle distribution across the sample surface. Its depth and lateral profiling provides an estimate of the particle size and shape and preliminary information on the ordering of the objects. The X-ray measurements were performed with a D8 DISCOVER diffractometer with VÅNTEC-2000 2-D area detector. This permits a long-range, statistically-averaged analysis over the whole surface of the investigated FeO nanoparticle sample. The shape and size of the particles as well as the inter-particle distance were evaluated using distorted-wave Born approximation (DWBA) implemented in the LEPTOS software. Several models were verified to analyze the correlation characteristics of the nanoparticles position.

The results obtained demonstrate a consistency of the nanoparticle dimensions as measured with AFM and X-ray methods. The conventional non-synchrotron X-ray diffraction setup provides sufficient data quality for comprehensive evaluation of the investigated samples.

Sample Preparation

The iron oxide nanoparticles were synthesized through a high-temperature solution phase reaction of metal acetylacetonates ($Fe(acac)_3$) with 1,2-hexadecanediol, oleic acid and oleylamine in phenylether. Toluene was used as a solvent. The FeO nanoparticles are super-paramagnetic at room temperature (the blocking temperature T is 22 K). For self-assembling studies, 5 µL drops of a colloid solution were deposited manually onto Si substrates with a native SiO_2 layer over an area of 1 cm^2. The drops were dried in air at room temperature.

Experimental Setup for AFM (N8 TITANOS)

Atomic force microscopy (AFM) is a surface inspection technique. A very sharp tip (radius < 10 nm) which is attached to a cantilever is scanned along the sample surface and detects the topography.

Scanning can be done either in contact or dynamic mode. In dynamic mode the cantilever oscillates near its resonant frequency. The oscillation amplitude and the damping determine whether the measurement is done in intermittent contact or non-contact mode. With the Bruker Nano AFM these values can be adjusted very accurately as the oscillation amplitude is automatically calibrated in nm.

The N8 TITANOS is a large sample AFM for analyzing samples up to 300 mm x 300 mm with a very low noise level in Z below 0.05 nm.

AFM measurement results

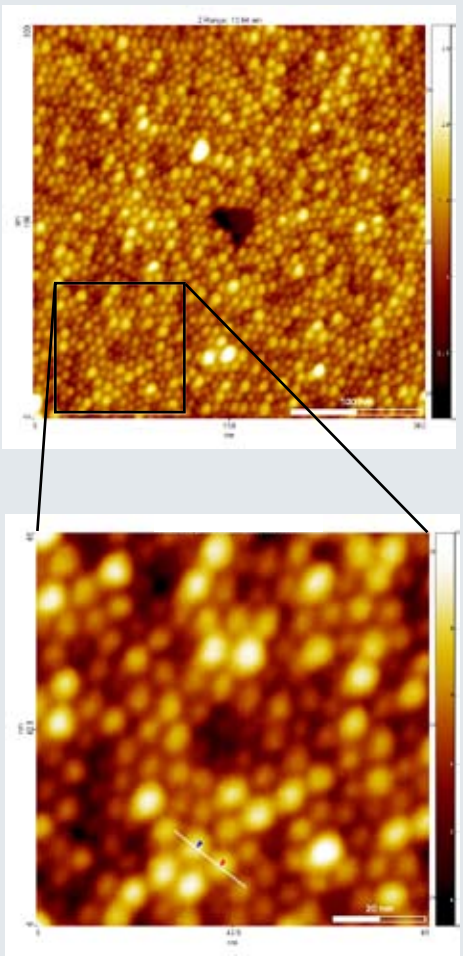


Fig. 1 a – b Top: a) 300 nm x 300 nm topography scan of FeO particle sample. Bottom: b) Zoom into a), scan size 85 nm x 85 nm. The white line with arrows indicates position of a line profile.

AFM results

The results shown in figures 1 to 3 were achieved using regular cantilevers measuring in intermittent contact mode (8 nm free amplitude, 39% damping).

The appearance of the particles in fig. 1 leads to the assumption that they are of spherical shape and closely packed. To determine the size of these particles a cross section was drawn across the center of a number of adjacent particles as indicated in fig. 1b. The profile shown in fig. 2 was extracted from this cross section. The blue and red arrows (figs. 1b and 2) indicate the position of height maxima of two representative neighboring particles. The distance of 6.44 nm between maxima leads to the conclusion that particles have a diameter of ca. 6.4 nm. Fig. 3 shows a 3D representation of the scan. It confirms both the assumptions that the particles are spherical and closely packed.

Line profile evaluation

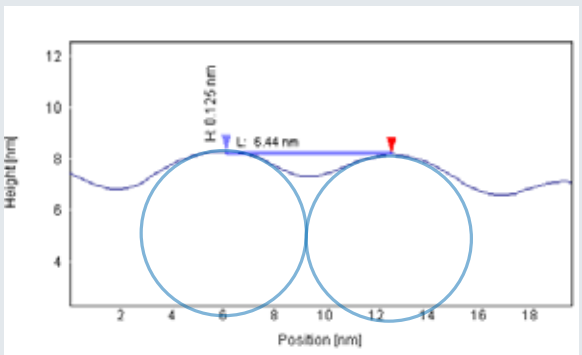


Fig. 2 Line profile from fig. 1 b). The blue circles indicate the spherical particles, the arrows the positions of maximum height (particle tops) used for size determination.

3D image of AFM scan

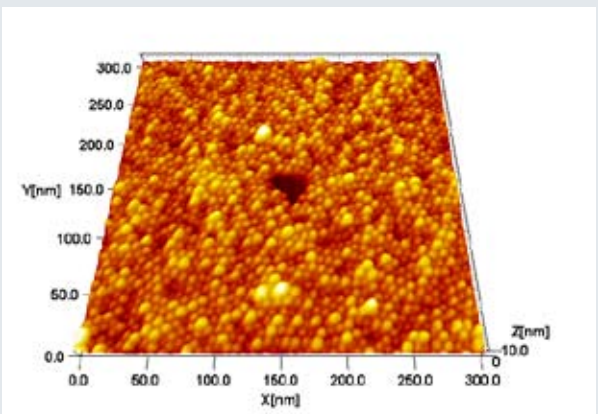


Fig. 3 3D representation of the 300 nm x 300 nm AFM scan. The spherical shape and close packing of particles is clearly visible.

Experimental Setup for GISAXS (D8 DISCOVER)

Grazing-Incidence Small Angle X-Ray Scattering (GISAXS) was first introduced in 1989 [2] as a novel technique for investigating structures on or close to the surface. At grazing incidence, the incident beam undergoes total external reflection if the angle is below the critical angle. Scanning the angle of incidence from below to above the critical angle is therefore a kind of non-destructive depth profiling. This is used for conventional X-ray reflectivity (XRR) measurements, which are sensitive to electron density differences along the surface normal. GISAXS on the other hand is sensitive to in-plane correlations in the surface and interfaces. Therefore periodically distributed electron density variations (height-height correlations e.g.) on or slightly below the surface can be investigated. Additionally the GISAXS signal is very sensitive to surface roughness.

Today, GISAXS is a commonly used technique for investigations of quantum dots, thin organic films, or nanomaterials arranged on surfaces. Grazing incidence SAXS experiments require both a high primary beam intensity and a low beam divergence so until now most GISAXS experiments have been performed at synchrotrons. Now the D8 DISCOVER using the Micro Focus X-ray Source (IμS) and the VÅNTEC-2000 2-D detector opens up this exciting field to laboratory instruments.

GISAXS Theory

Scattered X-ray Intensity within the DWBA includes both coherent and incoherent (diffuse) components:

$$I(\alpha_i,\alpha_f,2\theta_i,2\theta_f)=|\chi_0|^2|T_i|^2|T_f|^2\,[I_d + I_c],$$

$$T_i = \frac{2k^i_z}{k^i_{z+} k^i_{zs}} \quad , \quad T_f = \frac{2k^f_z}{k^f_{z+} k^f_{zs}}$$

$$k^i_{zs} = k_0\sqrt{1 + \chi_s - \cos^2\alpha_i} \quad , \quad k^f_{zs} = k_0\sqrt{1 + \chi_s - \cos^2\alpha_f}$$

I_d is diffuse scattering, caused by the fluctuations of geometrical sizes of nanoparticles, it depends on the one-particle distribution functions near the average values:

$$I_d = [<|F_l(\vec{q})|^2> - |<F_l(\vec{q})>|^2],$$

The coherent component I_c depends on the pair correlation function $g_l(r)$ for distribution of nanoparticles within the plane, which is parallel to the surface:

$$I_c = \sum_{l=1}^{l_0} |<F_l(\vec{q})>|^2\, S_l(\vec{q}_\perp)$$

$$S_l(\vec{q}_\perp) = \rho_s^{(l)}\delta(\vec{q}_\perp) + 1 + \rho_s^{(l)} \int dr_\perp [g_l(\vec{r}_\perp) - 1]\exp[-i\vec{q}_\perp\vec{r}_\perp]$$

$$F_{sph}(q) = \exp[iq_z(H - R)] \int_0^H 2\pi R_z^2 \frac{J_l(q_l R_z)}{q_l R_z} \exp(iq_z z)dz$$

D8 DISCOVER

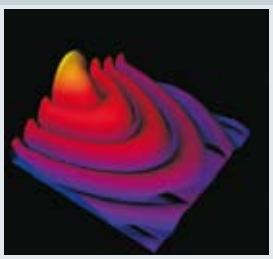
Fig. 4 D8 DISCOVER with enclosure

Measurement Parameters

Source	Micro Focus X-ray Source (IμS)
	Cu Kα radiation, 45 kV / 650 mA
Sample holder	Eulerian cradle
Laser video microscope	Sample alignment & imaging
Detector – sample dist.	210 mm
Detector	VÅNTEC-2000 (2-D Detector)
Angular Range	35° coverage in 2Θ and γ
	at 200 mm detector distance
Detector Resolution	2048 x 2048 pixels
Beam Size	covers the whole sample area
Data collection time	10 min/frame

Calculated scattering intensities

Spherical particles
FeO on Si substrate
R = 3 nm, ΔR = 0.3 nm,
Correlation model:
Hard sphere, L = 9 nm



Cylindrical particles
FeO on Si substrate
R = 3 nm, ΔR = 0.3 nm,
H = 6 nm, ΔH = 0.6 nm,
Correlation model:
Hard sphere, L = 9 nm

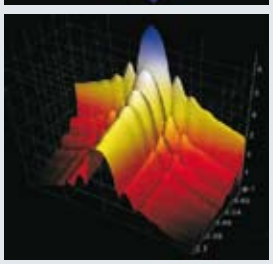


Fig. 5 Scattering intensities for spherical and cylindrical particles, calculated with LEPTOS G.

GISAXS Results

The software package LEPTOS G was used for the evaluation of the GISAXS maps.
Several GISAXS 2D maps have been recorded at different incidence angles. For each angle, several map sections have been fitted simultaneously with fixed sample models (Hard-Sphere correlations, Gaussian parameter distribution, Full sphere particle shape), variable particle size values (diameter D) and interparticle distances (lateral correlation length L). The particular result obtained for a spherical particle shape is:

D = 6.4 ± 0.5 nm; L = 6.2 nm

Screenshots of the LEPTOS program

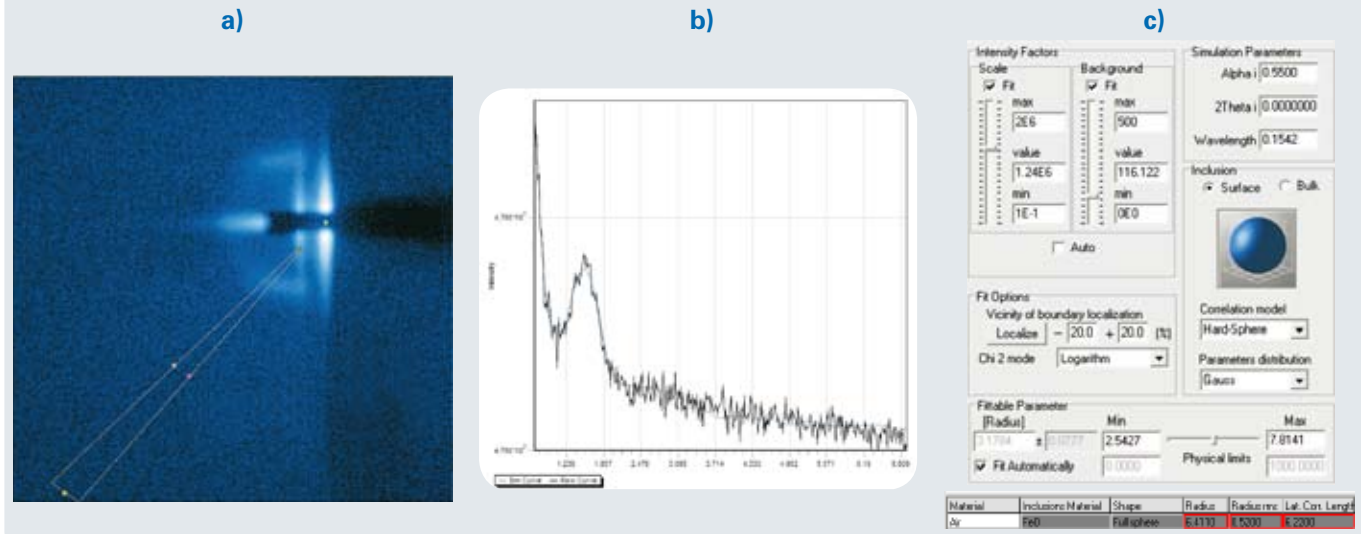


Fig. 6 a – c Left: a) 2D GISAXS map. b) Radial section from the map in a). c) Sample model used for the measurements

Conclusion

The present work proves the GISAXS technique as a reliable method for comprehensive evaluation of nanoscale objects. The wavelength of X-rays allows the characterization of nanoparticles with dimensions down to the nanometer-scale. The X-ray beam size makes it possible to evaluate the statistically-averaged parameters over a large illuminated area. Precise data analysis, accounting for both coherent and diffuse scattering, delivers a wide set of the nanoparticles' parameters (shape, size, correlations, distributions).

Modern X-ray sources and detectors permit in-house evaluation without recourse to external laboratories. AFM results confirm the GISAXS data, and supply short-range structural information to complement the long-range GISAXS results.

References

[1] A. Ulyanenkov. 2004 Proc. of SPIE Vol. 5536 1 (SPIE, Bellingham, WA, 2004).
[2] J.R. Levine, J.B. Cohen, Y.W. Chung, P. Georgopoulos, 1989 J. Appl. Cryst. 22, 528-532

Sample courtesy of

L. Chitu[1], G. Maier [2], E. Majkova[1], P. Siffalovic[1],
[1] Instute of Physics, Slovak Academy of Science, Slovakia
[2] Department Materialphysik - Montanuniversität Leoben (DMP), Austria

Authors

A. Thöne[1], A.Ulyanenkov[2]
[1] Bruker Nano, Herzogenrath, Germany
[2] Bruker AXS GmbH, Karlsruhe, Germany

Contact us for more details:

Bruker Nano
www.bruker-nano.com

Bruker AXS GmbH
www.bruker-axs.com