

Advanced Materials Research Methods

X Ray Diffraction Part 2

X Ray phase analysis (quantitative)

Structural calculations – Vegard`s Rule

GID configuration for thin films exploration

Atomic Force Microscopy AFM

Principles of operations of microscope

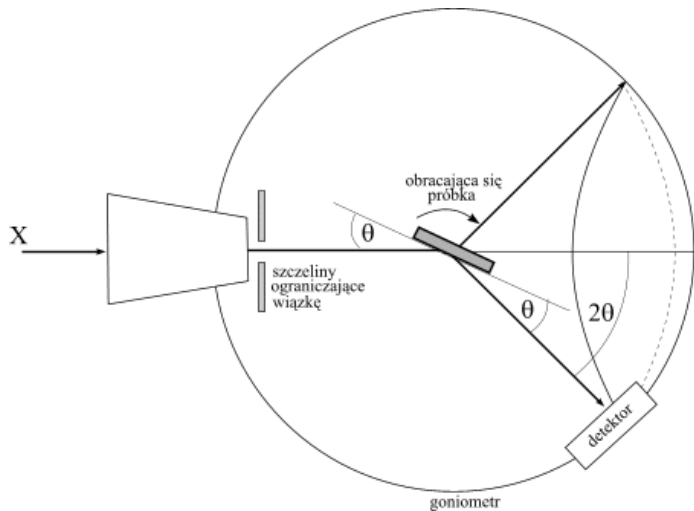
Modes of work of AFM

Application

The powder X Ray diffractometry of polycrystalline samples

sample:

- Polycrystalline powder sample of granulation in the range of $0,1 - 10 \mu\text{m}$ ($0,0001 - 0,001 \text{ mm}$),
- Solid sample (attention on stress and texture)



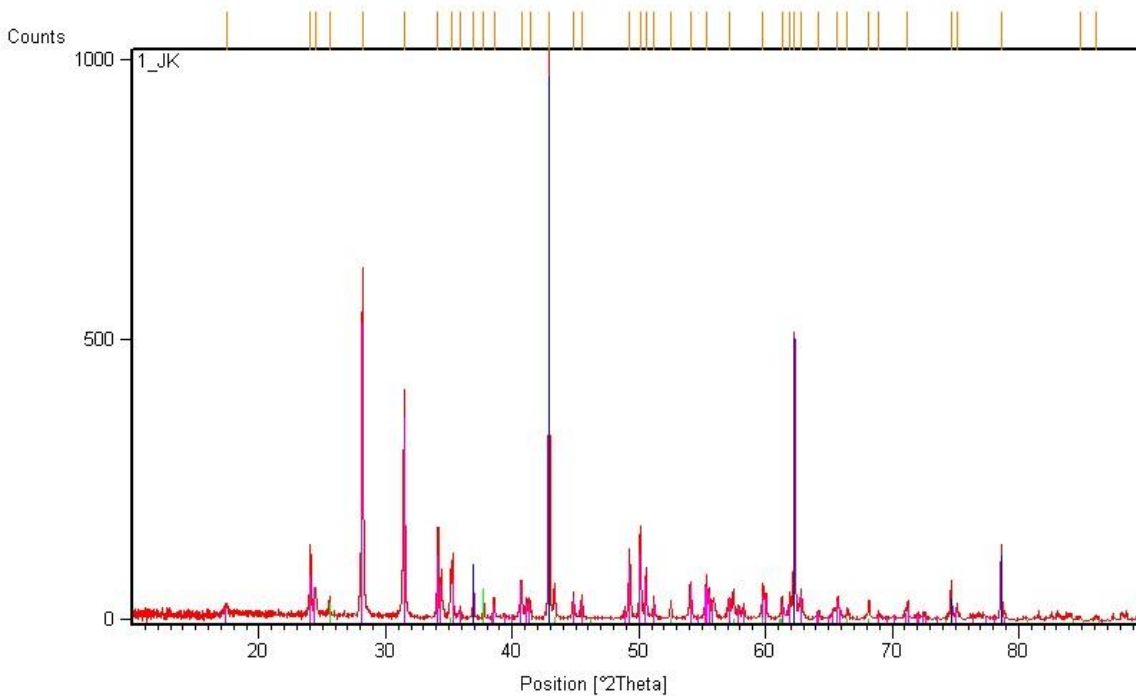
radiation:

- monochromatic $K\alpha$ or $K\alpha^1$,

measure equipment:

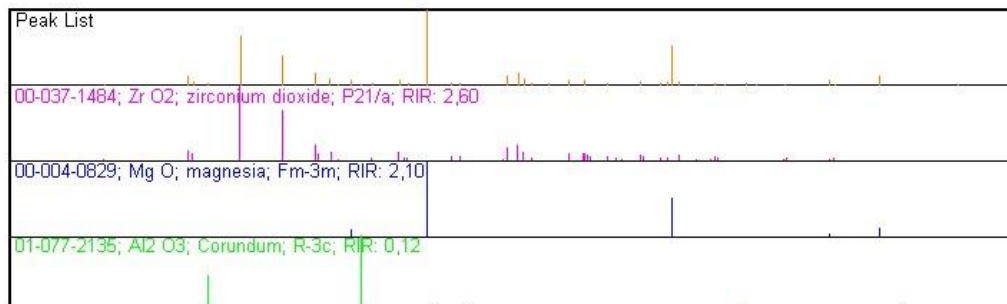
- Two axes goniometer
- Bragg-Brentano geometry (most often)

The powder X Ray diffraction pattern of polycrystalline sample



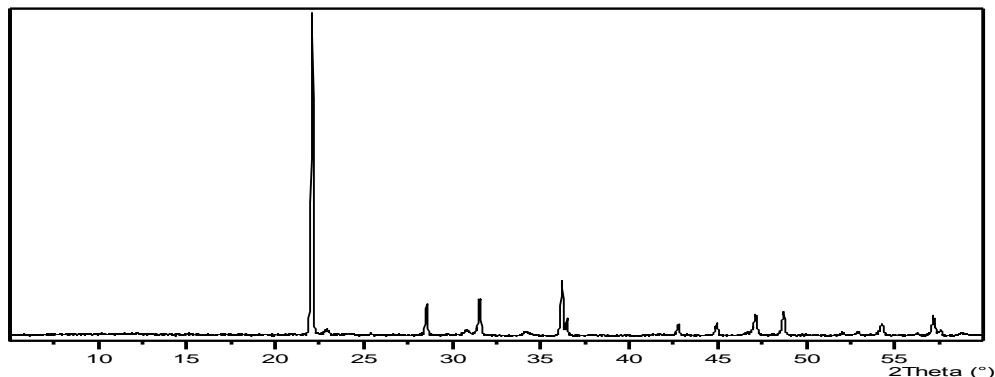
X Ray Phase Analysis

- qualitative
- quantitative



The qualitative phase analysis

Intensity (counts)



$$d_{hkl} = \frac{\lambda}{2\sin\theta}$$

$$I_{rel} = \frac{I_n}{I_{max}} \cdot 100$$

14-0696	Wavelength = 1.5405				
BPO₄ Boron Phosphate	d (Å)	Int	h	k	l
	3.632	100	1	0	1
Rad.: CuKα1 λ: 1.5405 Filter d-sp: Guinier 114.6	3.322	4	0	0	2
Cut off: Int.: Film I/cor.: 3.80	3.067	4	1	1	0
Ref: De Wolff. Technisch Physische Dienst. Delft	2.254	30	1	1	2
The Netherlands. ICDD Grant-In-Aid	1.973	2	1	0	3
Sys.: Tetragonal S.G. I 4̄ (82)	1.862	8	2	1	1
a: 4.338 b: c: 6.645 A: C: 1.5318	1.816	4	2	0	2
α: β: γ Z: 2 mp:	1.661	1	0	0	4
Ref: Ibid	1.534	2	2	2	0
Dx: 2.809 Dm: SS/FOM:F ₁₈ =89(.0102 . 20)	1.460	8	2	1	3
	1.413	1	3	0	1
	1.393	1	2	2	2
	1.372	2	3	1	0
	1.319	4	2	0	4
PSC: tl12. To replace 1-519. Deleted by 34-0132. Mwt: 105.78	1.271	1	1	0	5
Volume [CD]: 125.05	1.268	2	3	1	2
	1.211	2	3	0	3
	1.184	2	3	2	1

The quantitative phase analysis

$$J_{hkl}^n = C \cdot |F_{hkl}|^2 \cdot LP \cdot p \cdot A \cdot V_n \quad \text{in multiphase systems}$$

$|F_{hkl}|^2$ - the structure factor containing temperature factor

LP - Lorentz and polarity factor (angle factor)

p - the plane multiplicity factor

A - the absorption

$$C = J_0 \cdot \lambda^3 N^2 \cdot \left(\frac{\mu_0 e^2}{4\pi m r} \right)^2$$

J_0 - the intensity of primary beam

λ - X Ray radiation length

μ_0 - the magnetic permeability in vacuum

e - the electron charge

m - the mass of electron

r - the distance between an electron and the detection point

N - the number of unit cells in 1 cm^3

V_n - the volume fraction of the n-phase

The absorption coefficient

J_0 - the intensity of X Ray beam passing through the absorbent of dx thickness

dJ - the loss of intensity of X Ray beam passing through the absorbent, proportional to J_0 , dx and μ

μ - the linear absorption coefficient

$$dJ = \mu J_0 dx$$

Beer equation of absorbance

$$J = J_0 e^{-\mu x}$$

$\mu = 1/(2A)$ in a flat samples (in X Ray diffractometers)

μ^* - the mass coefficient of absorption, $\mu^* = \mu/\rho$

X Ray phase analysis - methods

- **the direct comparison of patterns:**

- for two phases of very similar (almost identical) μ^* (a mixture of phases absorbs X Ray in the same way as a single phase);

- **the internal standard method**

- when μ^* of pure, separate phase and of mixture differ from one another

- **the external standard method**

- when μ^* of pure, separate phase and of mixture differ from one another

- **Rietveld refinement method**

- the mathematic profile analysis, independent of the differences in μ^* values of phases in the mixture (sample)

The internal standard method

$$J_{hkl}^a = \underbrace{C \cdot |F_{hkl}|^2 \cdot LP \cdot \rho \cdot A \cdot V_a}_{K_a} \quad \text{standard MgO, Si, } \alpha\text{-Al}_2\text{O}_3 \text{ itp...}$$

K_a, ρ_a - constant values of A phase,

$$A = 1/(2 \mu); \quad \rho_a = m_a/V_a \longrightarrow V_a = m_a/\rho_a$$

K_w, ρ_w - constant values of standard,

$$m_a \longrightarrow X_a \quad X_a - \% \text{ content of A phase}$$

μ^* - mass coefficient of absorption,
 $\mu^* = \mu/\rho$

$$m_w \longrightarrow X_w \quad X_w - \% \text{ content of standard}$$

ρ - the density of a mixture

$$J_{hkl}^a = \frac{K_a \cdot X_a}{\mu^* \cdot \rho_a} \quad \text{for A phase}$$

$$J_{hkl}^w = \frac{K_w \cdot X_w}{\mu^* \cdot \rho_w} \quad \text{for standard}$$

$$J_{hkl}^a = \frac{K_a \cdot X_a}{\mu^*}$$

$$J_{hkl}^w = \frac{K_w \cdot X_w}{\mu^*}$$

The calculation of phase A content - X_A

We choose one analytical reflection for:

$$\frac{J_{hkl}^a}{J_{hkl}^w} = \frac{K_a \cdot X_a}{K_w \cdot X_w}$$

➤ for analyzed phase A J_{hkl}^a
(the strongest one)

➤ for standard J_{hkl}^w
(according to the literature data)

$$\frac{J_{hkl}^a}{J_{hkl}^w} = K \frac{X_a}{X_w}$$

$$X_a = \frac{J_{hkl}^a}{J_{hkl}^w} \frac{X_w}{K}$$

content of phase A

[%] or the mass fraction

The calibration curve (an example for CaCO₃)

Data		Total amount	mass fractions		Intensities			
CaCO ₃	Al ₂ O ₃		CaCO ₃	Al ₂ O ₃	CaCO ₃ int	Al ₂ O ₃ int	x	y
0,095	0,3923	0,4873	0,194952	0,805048	83,04	71,7	0,242162	1,158159
0,1885	0,3009	0,4894	0,385166	0,614834	128,95	44,36	0,626454	2,906898
0,248	0,2447	0,4927	0,503349	0,496651	150,1	32,98	1,013486	4,551243
0,2862	0,2031	0,4893	0,584917	0,415083	163,6	26,76	1,409158	6,113602
0,4002	0,1113	0,5115	0,782405	0,217595	204,38	11,07	3,595687	18,46251

$$J_a/J_w = f(x_a/x_w)$$

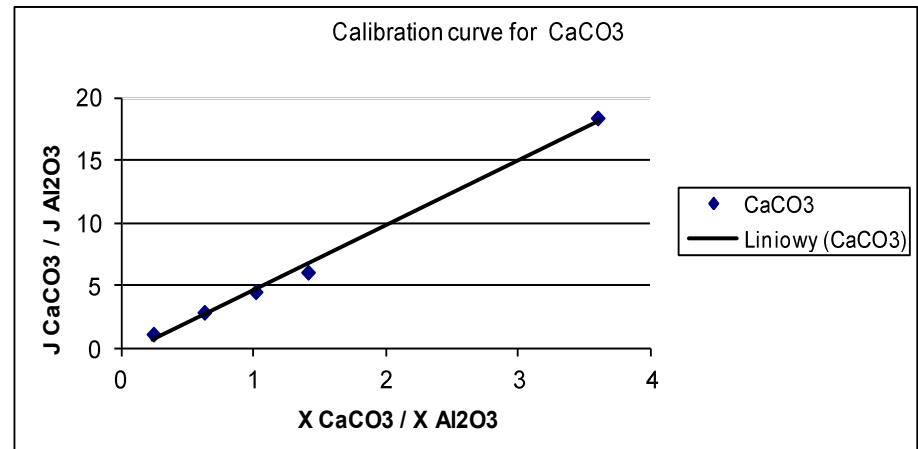
linear function $y = ax + b$

$$a = K \text{ (stała } K) \quad b \cong 0$$

for CaCO₃:

$$y = 5.2115 x - 0.534$$

$$K = 5.2115$$



The integral intensity
– the area under the peak curve

$$J_a/J_w = f(x_a/x_w)$$

The accuracy and errors in the quantitative analysis

Differences between a structure of phases and a standard

- the different $[F_{hkl}]^2$
- the different volume of unit cells
- differences in density
- the possibility of solid solutions presence

Preparation of samples

- the improper homogenization
- the texture of samples
- the improper granulation

Measurement parameters

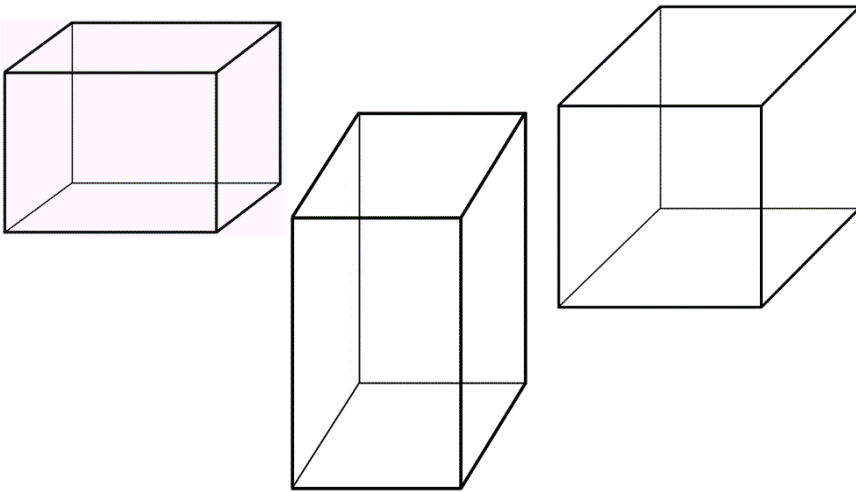
- the unstable X Ray source
- the unstable detector
- errors in a monochromator operating
- errors in a goniometer operating

Structural calculations – unit cell parameters

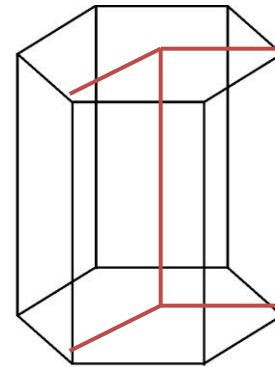
Squared equations:

$$1/d_{hkl}^2 = h^2/a^2 + k^2/b^2 + l^2/c^2 \quad \text{in orthogonal systems}$$

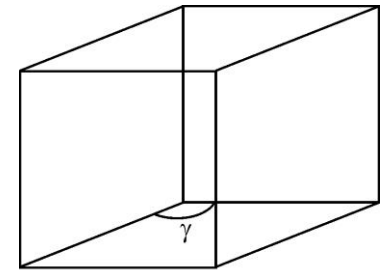
$$1/d_{hkl}^2 = 4/3 [(h^2 + k^2 + hk)/a^2 + l^2/c^2] \quad \text{in the hexagonal system}$$



An orthogonal unit cell



graniastosłup o podstawie sześciokąta foremnego



równoległoscian o kącie $\gamma = 120^\circ$

Unit cells in the hexagonal system

$$n\lambda = 2 d_{hkl} \sin\theta$$

Vegard's Law

Lattice parameters of solid solutions of ionic crystals vary linearly in relation to the increasing content of the component substituted according to the equation:

$$a_r = a_1 + (a_2 - a_1) \cdot C_2 / 100$$

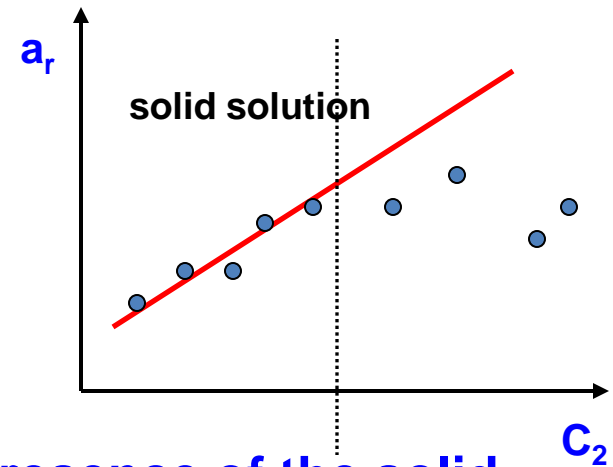
a_r – lattice parameter of solid solution

a_1 - lattice parameter of a solvent

a_2 - lattice parameter of a solute

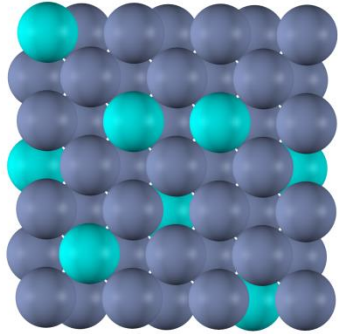
C_2 – content of solute [% mol.]

Diagram: $a_r = f(C_2 / 100)$



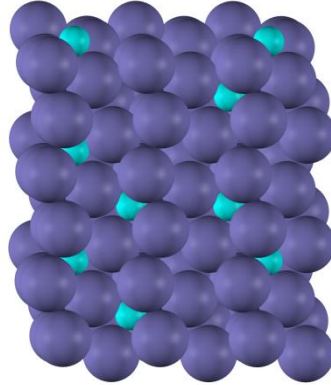
Linear nature of diagram confirms the presence of the solid solution and shows its range.

Solid State Solutions



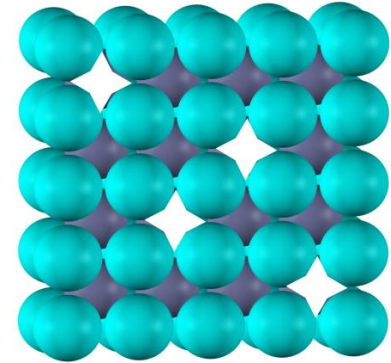
Substitution solid solution

- The similar ion radius (less than 15%)
- The same type of chemical formula
- The same charge
- The same type of lattice
- The similar electronegativity



Interstitial solid solution

- Movable ions in interstitial positions
- The electroneutrality of crystal



Subtraction solid solution

Solid State Solutions

ρ_r – X Ray density (theoretical)

$$\rho_r = \frac{A \cdot Z}{V_k} \cdot 1.6602 \cdot 10^{-24}$$

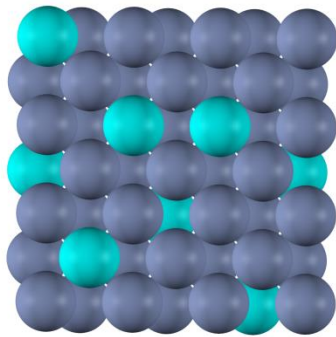
A – the molecular weight

Z – the number of molecules in the unit cell

V_k – the unit cell volume

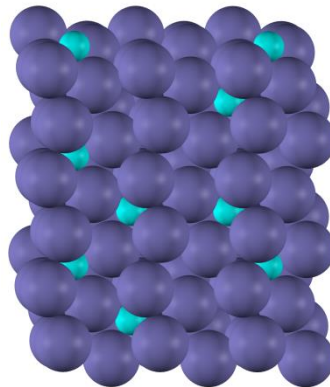
Calculations for the solvent structure

ρ_p – the pycnometer density (real)



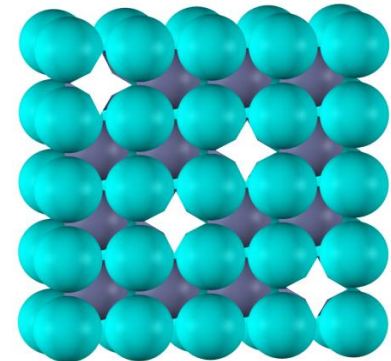
Substitution solid solution

$$\rho_r = \rho_p$$



Interstitial solid solution

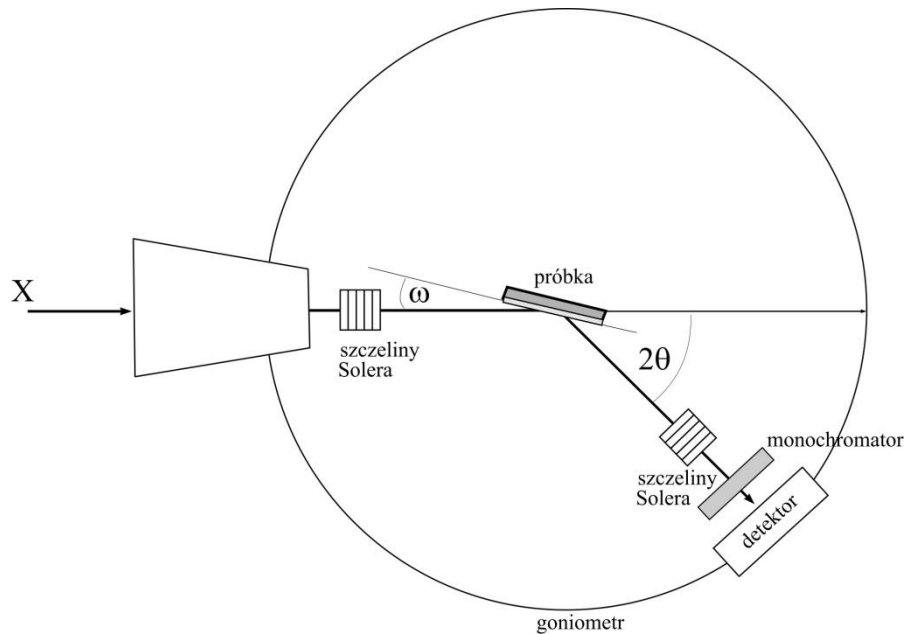
$$\rho_r < \rho_p$$



Substraction solid solution

$$\rho_r > \rho_p$$

Thin films measurements – GID configuration



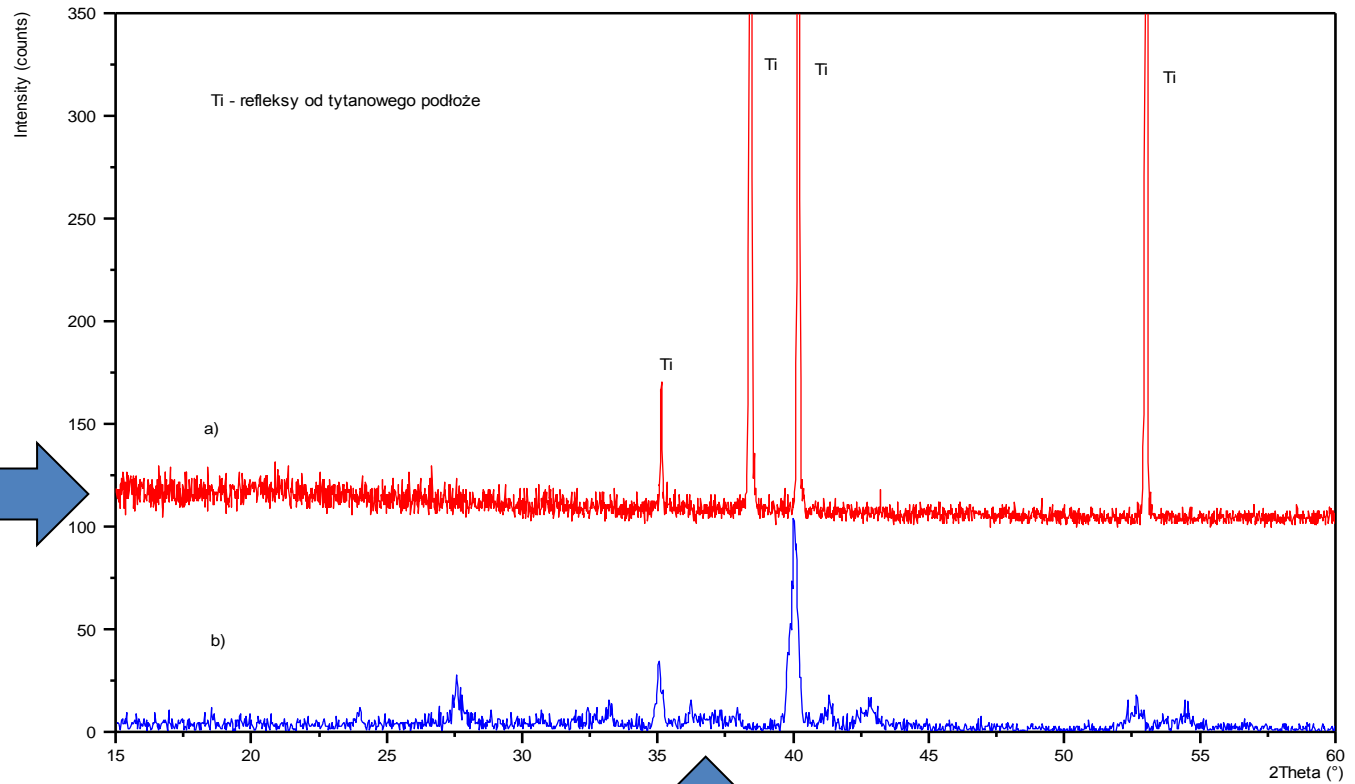
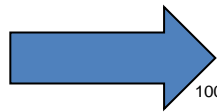
ω – constant, small angle of incidence of values between 1 and 3 °.

Thin films deposited on different substrates (steel, titanium alloys, glass etc.) need special measurement parameters in order to reduce the effect from the substrate and strengthen the reflections originating from coating. Then the measurement configuration with the stable incidence angle (ω) is applied.

GID
Grazing Incidence
Diffraction

Measurements in GID configuration

The diffraction pattern obtained in the standard configuration



The diffraction pattern of the same sample obtained in GID configuration

Crystallites dimensions- Scherrer's equation

$$D_{hkl} = \frac{k \lambda}{\beta \cos \theta}$$

where:

β - the full width at half maximum $\beta = \beta_{\text{obs}} - \beta_{\text{stand}}$, [rad]

λ the length of radiation applied, $\lambda = 1.5406$ [Å]

k - Scherrer constant, in the range of 0.9 - 1.0, $k = 0.9$

D_{hkl} - the average crystallite size (the dimension perpendicular to the plane which gave the reflection)

Where to apply different peak parameters ?

PEAK POSITION

Space symmetry group

Lattice cell parameters

Uniform internal stresses

INTENSITY

Atoms positions in the unit cell

Texture

Quantitative Analysis

FULL WIDTH AT HALF MAXIMUM

Non-uniform internal stresses

Average crystallites size

Scanning Probe Microscopy SPM

Scanning Tunneling Microscopy STM

Atomoc Force Microscopy AFM

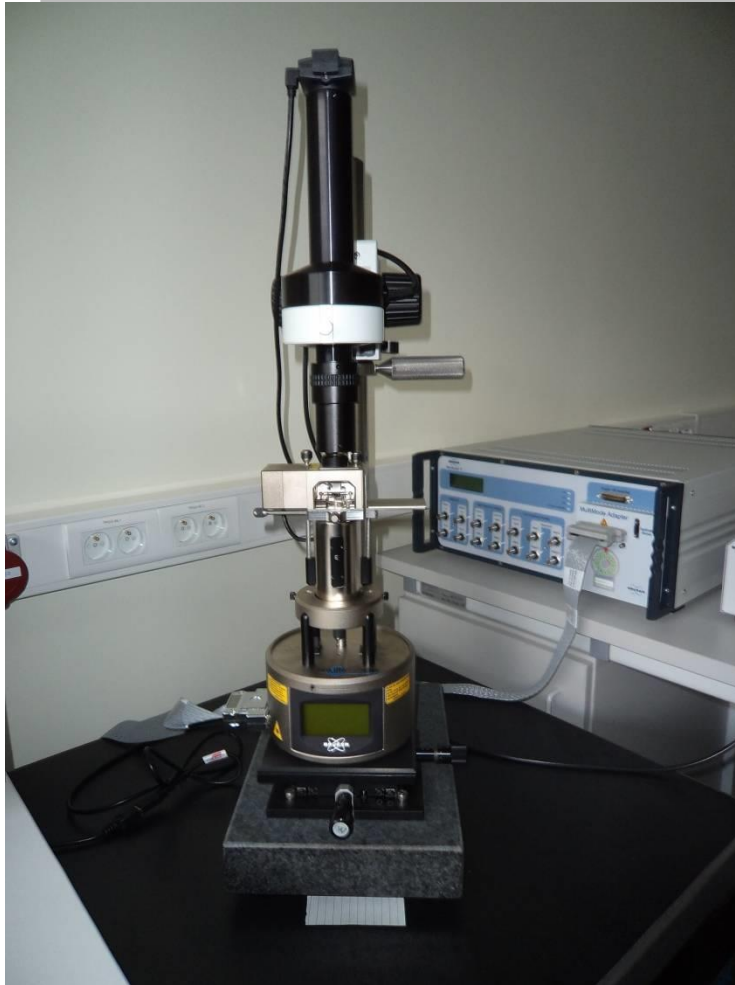
Application of STM

- 1. Imaging of the sample surface is based on the applying of the tunneling current between the tip (the probe is a metal needle) and the sample. So the sample has to be conductive or covered by the conductive coating.**
- 2. The highest resolution mode of SPM (atomic resolution level)**

Applications of AFM

1. Imaging of surface of the sample – the only limit is very !!! clean surface
2. Exploration of some properties distribution:
 - frictional forces
 - an adhesion
 - the spatial distribution of magnetization
 - the spatial distribution of electric charge (the surface potential)
3. The modification of local properties of sample
 - nanolithography

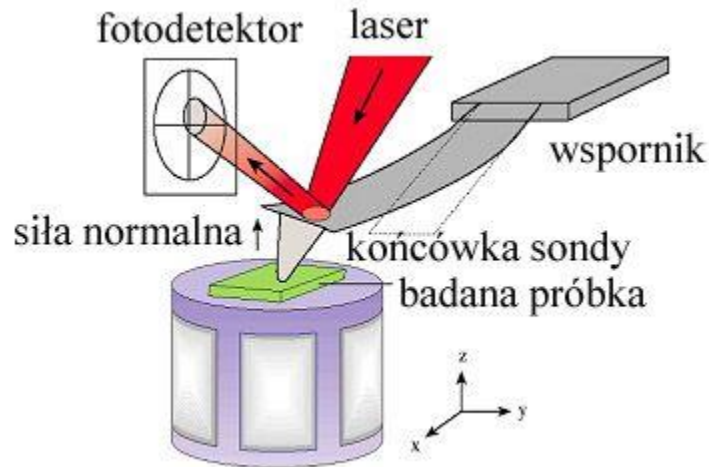
Scheme of AFM Microscope type: Multimode 8.0 by Bruker



AFM operation is based on the interactions between the probe and the surface of sample which cause the deformation of probe, detected by the optical systems.

Exploration of surface in tAFM - how it works?

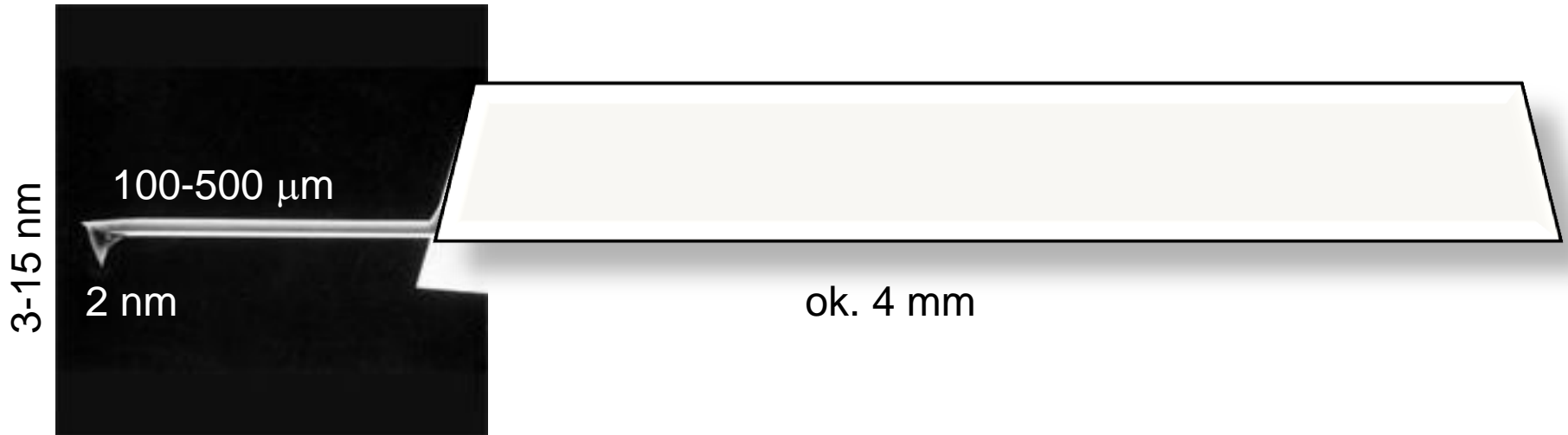
Image is obtained by the detection of forces interacting on the probe



Forces causing the deformation of the probe are detected by the optical laser system (photodetector)

Scanner - piezoelectric tube with six electrodes which enable the tube to move in three directions XYZ. The scanner allows to move the sample under the tip (usually) in XY directions, in proper distance correlating with the strenght of impact and at the same time, with the deformation of the probe. The motion of the scanner in Z direction, closely connected with the probe deformation, reflects the changes in the profile of the surphace.

Sondy



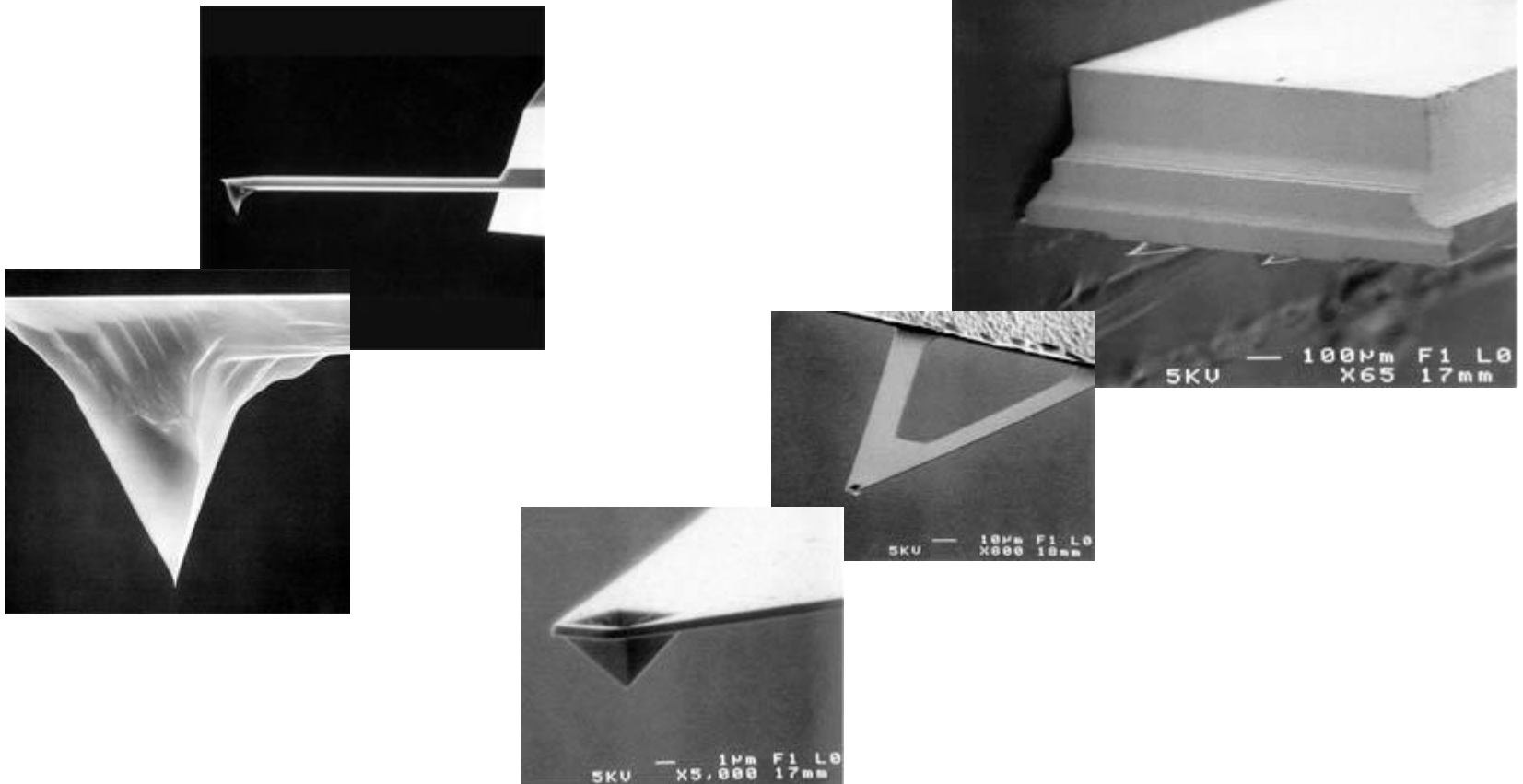
Probe - tip, cantilever, needle, etc.

Parameters:

- length from 100 to 500 μm,
- curve radius about 2 nm
(also 1 nm in high resolution measurements or even 20 nm in case of measurements in liquid cells)
- Force constants 0.01 - 1 N/m
- Resonant frequencies in the range of 2 - 120 kHz



Different types of probes



Source: Bruker 2013

AFM Microscopy

The type of interactions between the tip and the surface atoms influences on the surface topography and the surface properties research:

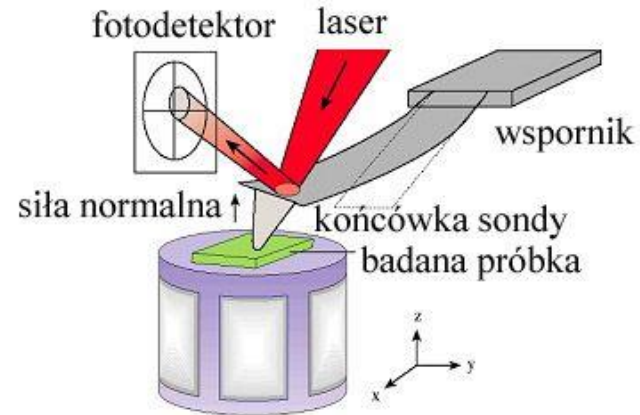
- the local potential distribution research
- the local magnetic field distribution research
- Young Modulus distribution research
- **the topography research:**
 - Van der Waals forces
 - The deformation of the probe according to Hook law
 - Interactions with the water layer on the sample surface

Modes of AFM operations

Modes of operation:

- ✓ **Contact;**
- ✓ **LiftMode (no contact)**
- ✓ **Semi-contact:**
 - Tapping**
 - Peak Force Tapping (Scan Assist)**

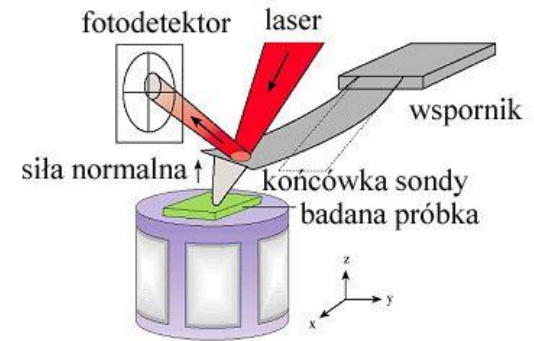
Contact mode



- ✓ First mode applied in AFM
- ✓ Through all measurement, the strength of impact is constant
- ✓ Every change of this force causes the scanner to move up or down in Z direction to come back to primary value of strength.
- ✓ Mode applied to hard and very hard materials

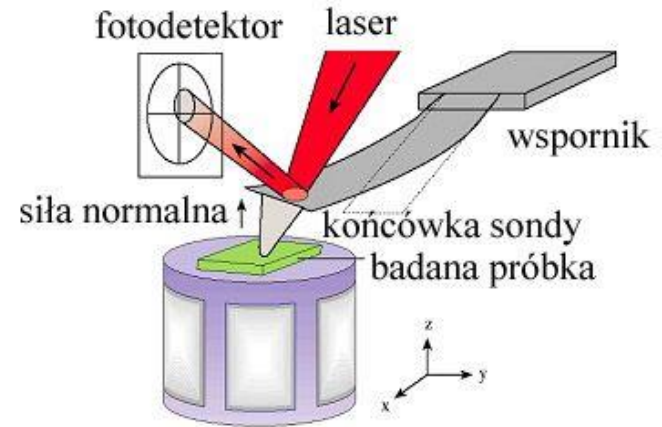
Semi-contact modes:

- Tapping
- Peak Force Tapping



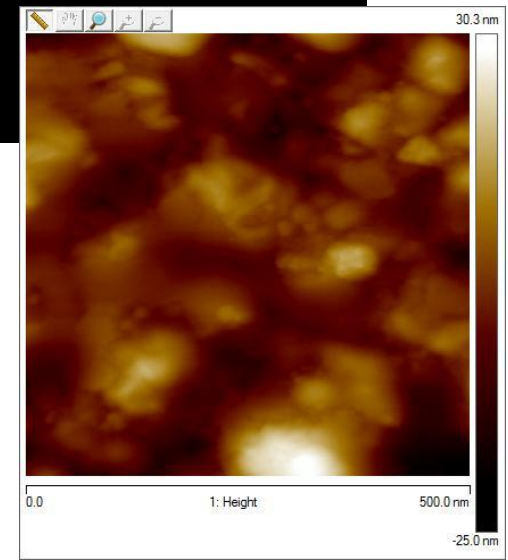
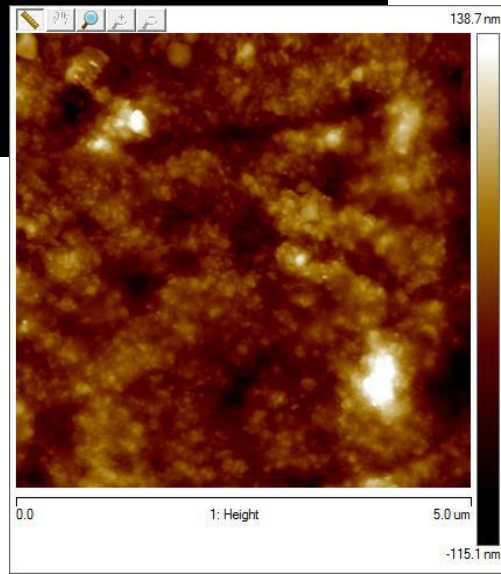
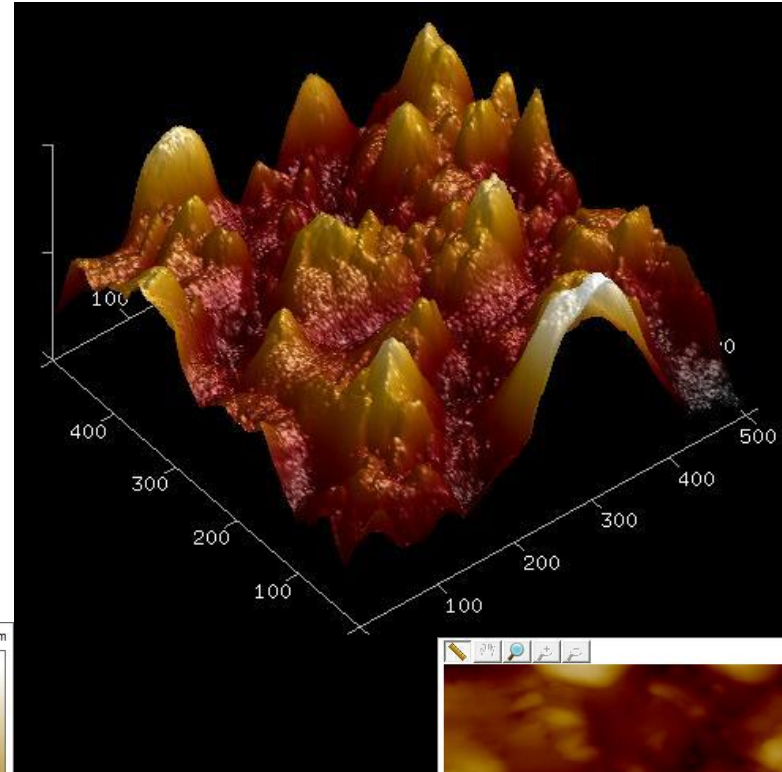
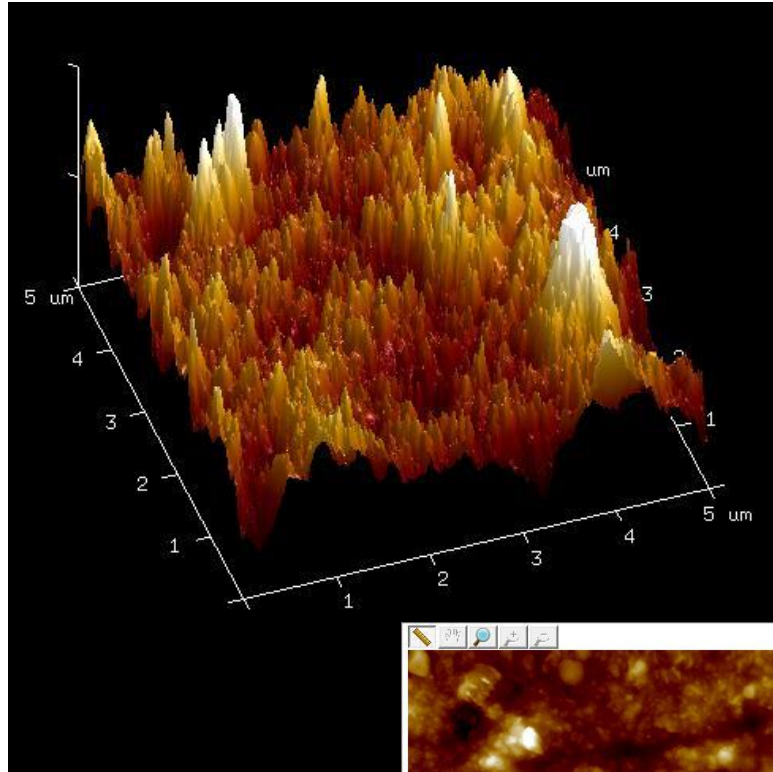
- ✓ The probe vibrates with the constant frequency and amplitude
- ✓ When any change on the surface appears, the amplitude of probe vibrations also changes.
- ✓ Then the system send a signal to the scanner to move itself in Z direction (up or dawn) until the probe will vibrate with the promary amlitude and frequency.
- ✓ The recorded motion of scanner in Z directions reflects changes in surface profile.

LiftMode (no contact)

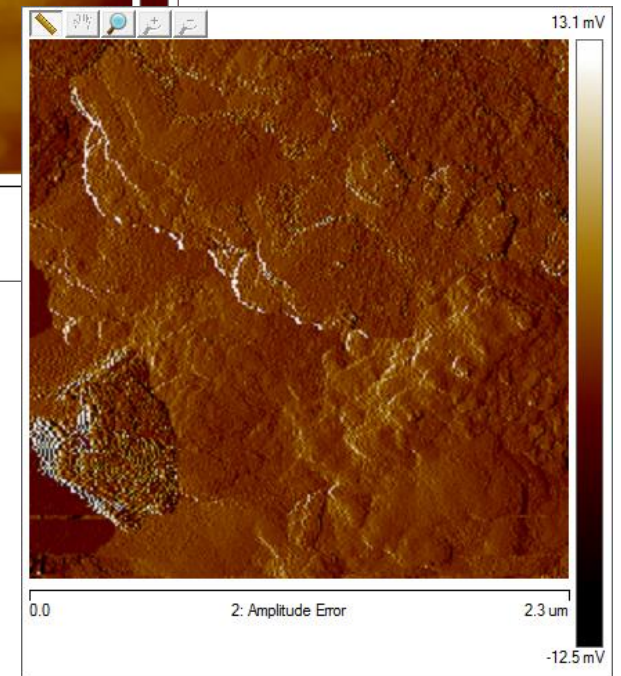
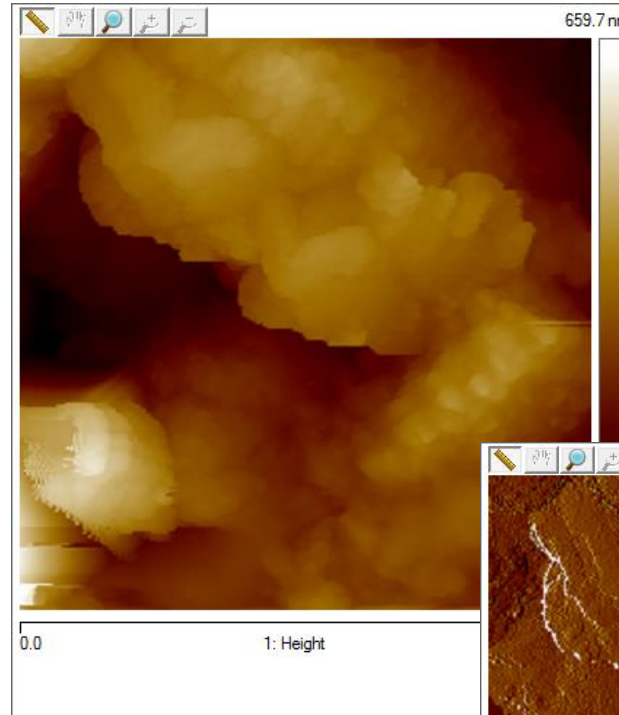
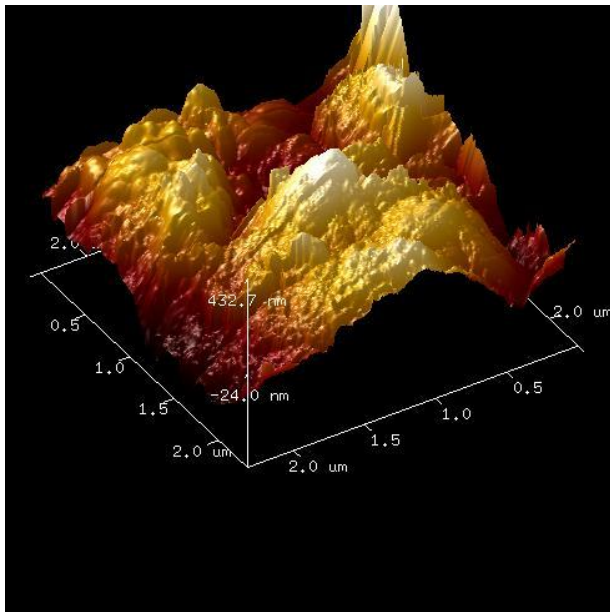


- ✓ Constant distance between the tip and surface what can be treated as the „zero” strength of impact
- ✓ Z direction motion of scanner correlates the changes in the shape of surface
- ✓ Van der Waals forces are main to influence on the probe deformation.

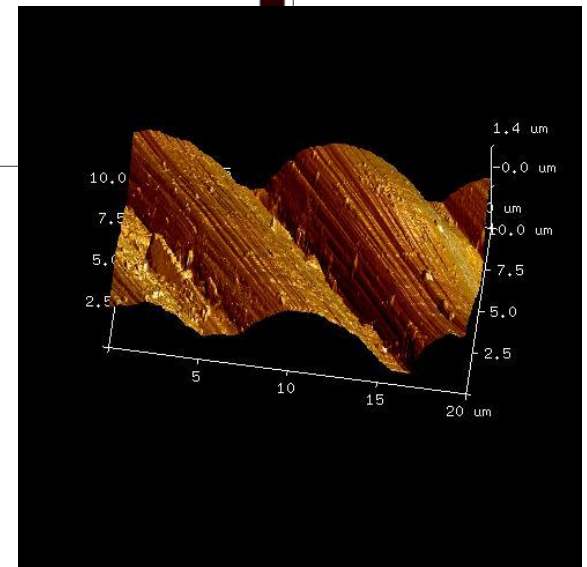
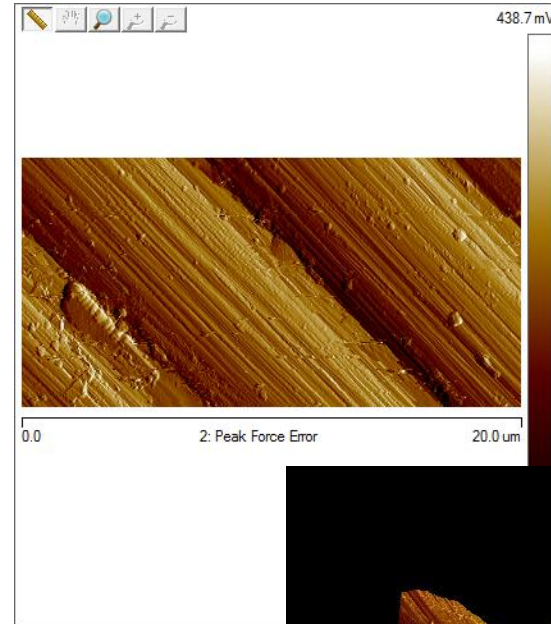
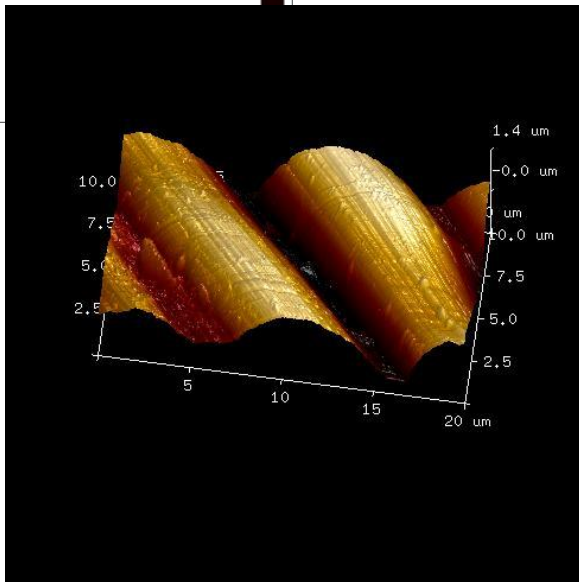
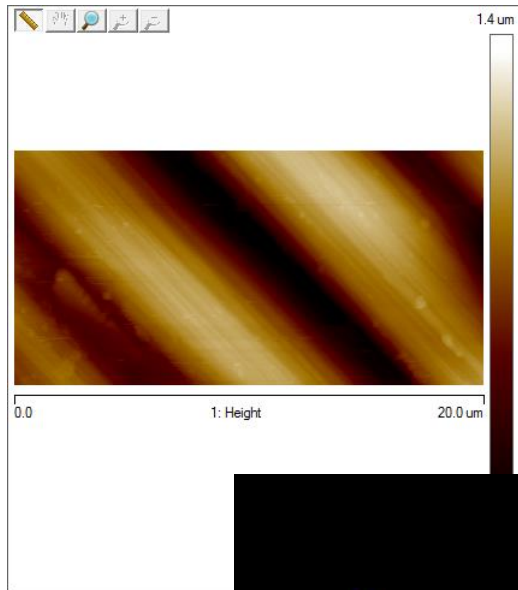
TiO₂ -Al₂O₃ thin film synthesized by sol-gel method and deposited on steel by dip coating technique.



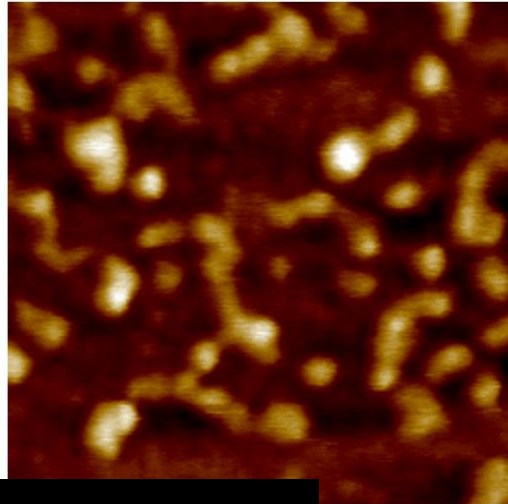
TiO₂ -Al₂O₃ thin film deposited on steel and incubated in SBF for 30 days



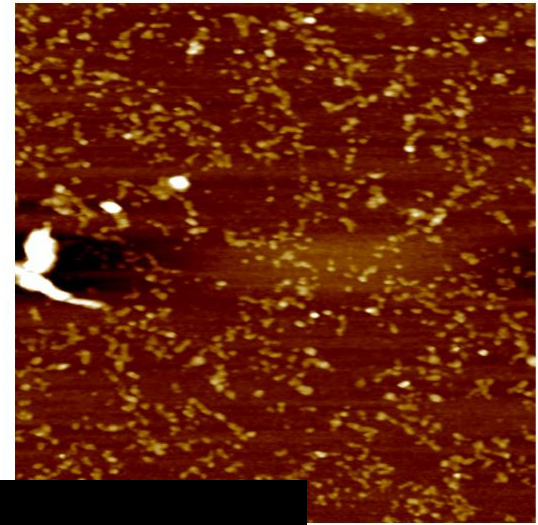
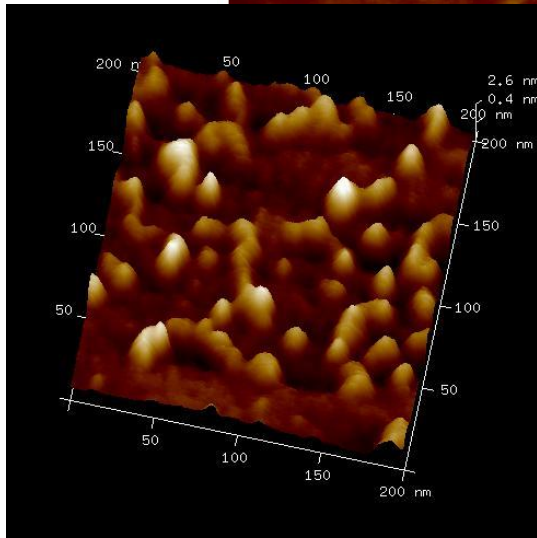
Carbon tubes



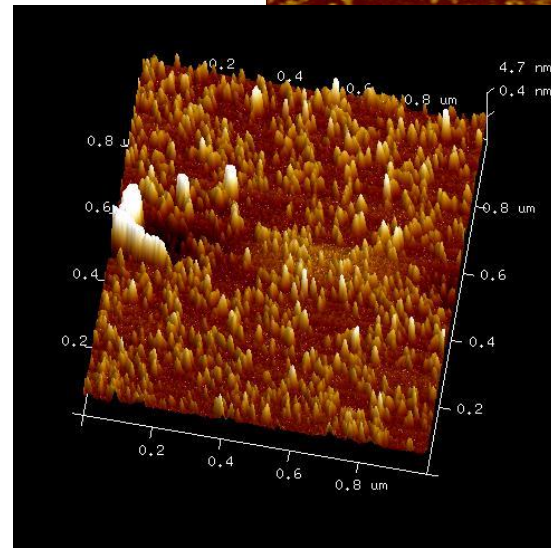
Coatings containing SiO_2 (silsesquioxates) deposited in epitaxial beam



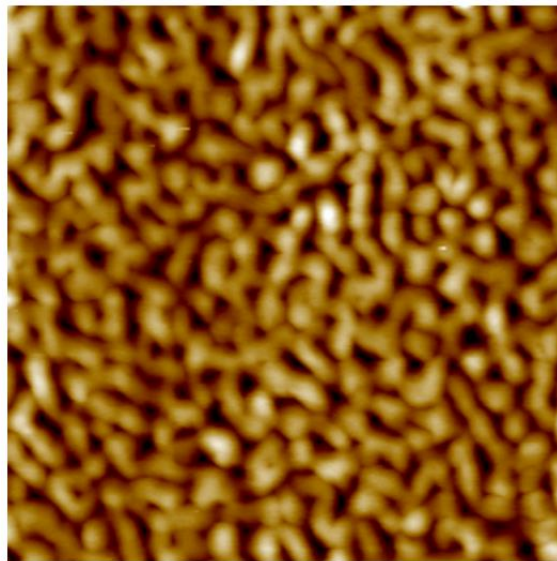
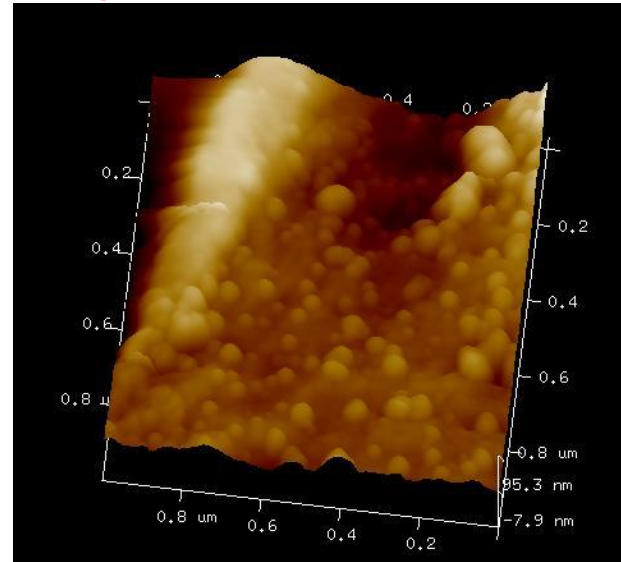
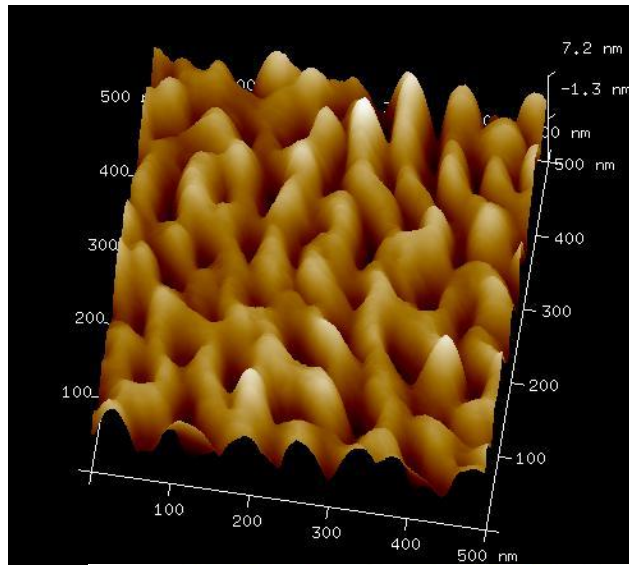
200.0 nm



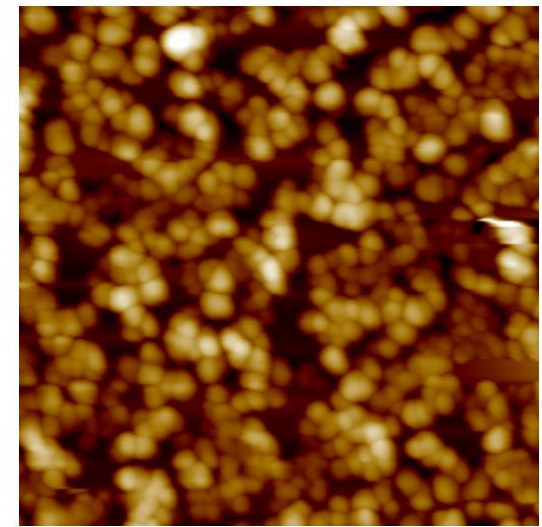
1.0 μm



TiO₂ -Al₂O₃ /Ag thin film synthesized by sol-gel method and deposited on steel by dip coating technique.

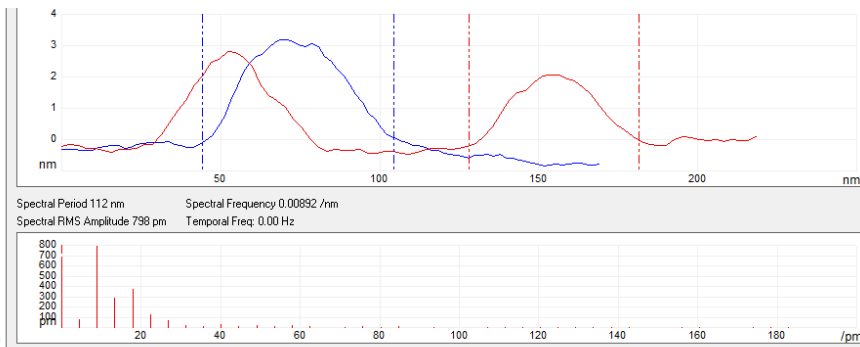
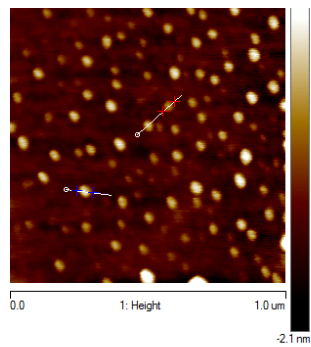
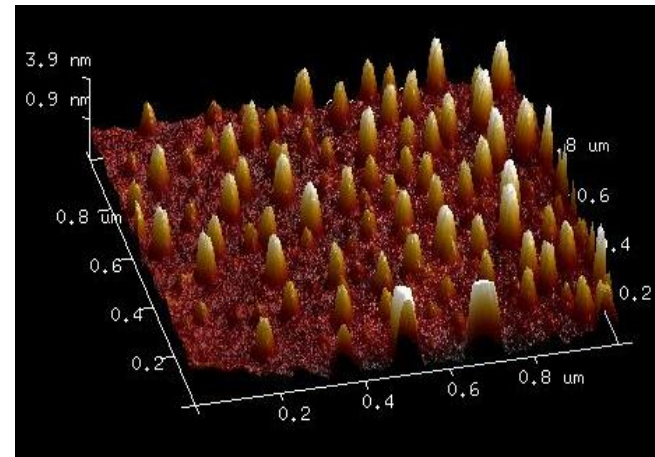
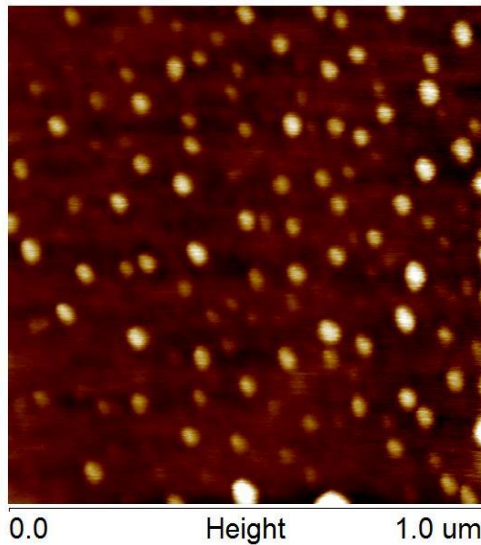


0.0 Height 1.0 μm



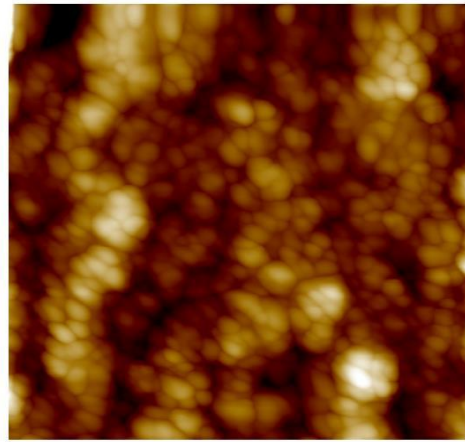
0.0 Height 1.0 μm

SiO₂ (14 % weight) thin film synthesized by sol-gel method and deposited on steel by dip coating technique -section

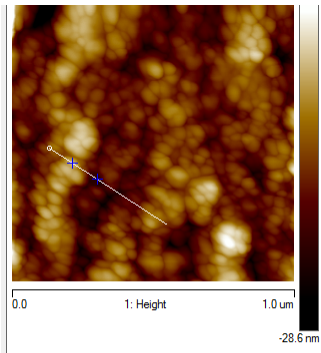
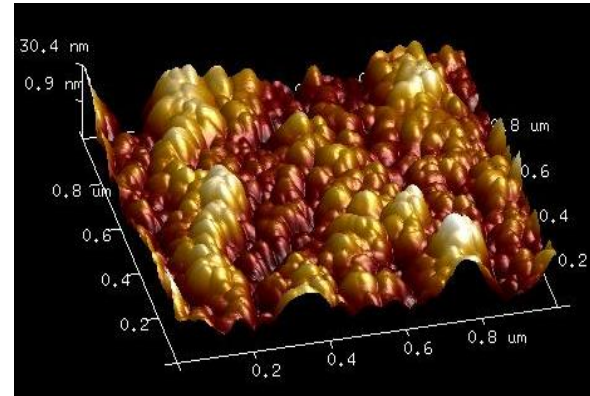


Pair	Horizontal Distance	Vertical Distance	Surface Distance	Angle	Rmax	Rz	Rz Count	Rms	Ra (Frequency Cutoff)	Frequency Cutoff	Radius	Radius Sigma
1	61.160 (nm)	235.535 (pm)	61.641 (nm)	0.221 (g)	3526.156 (...)	3526.156 (...)	2.000	860.538 (pm)	1491.271 (pm)	0.006 (nm)	128.859 (nm)	0.218 (nm)
2	54.768 (nm)	162.750 (pm)	54.998 (nm)	0.170 (g)	2291.599 (...)	2291.599 (...)	2.000	1191.014 (...)	822.406 (pm)	0.009 (nm)	153.109 (nm)	0.179 (nm)

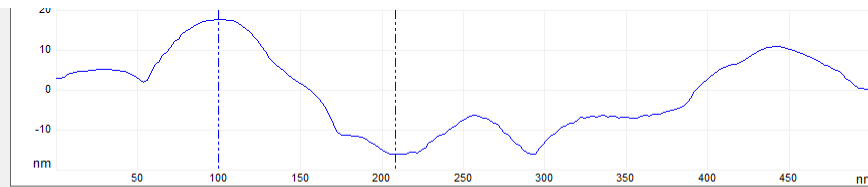
SiO₂ (10 % weight) thin film synthesized by sol-gel method and deposited on steel by dip coating technique -section



0.0 Height 1.0 um



Pair	Horizontal Distance	Vertical Distance	Surface Distance	Angle	Rmax	Rz	Rz Count	Rms	Ra (Frequency Cutoff)	Frequency Cutoff	Radius	Radius Sigma
1	107.572 (nm)	-33.843 (nm)	114.952 (nm)	-17.464 (g)	32.778 (nm)	0.000 (nm)	0.000	5.730 (nm)	9.829 (nm)	0.002 (nm)	158.429 (nm)	2.813 (nm)
0	0.000 (nm)	0.000 (nm)	0.000 (nm)	0.000 (g)	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (nm)	0.000 (nm)	0.000 (nm)
0	0.000 (nm)	0.000 (nm)	0.000 (nm)	0.000 (g)	0.000 (nm)	0.000 (nm)	0.000	0.000 (nm)	0.000 (nm)	0.000 (nm)	0.000 (nm)	0.000 (nm)



Spectral Period 505 nm Spectral Frequency 0.00198 /nm
Spectral RMS Amplitude 7.93 nm Temporal Freq. 0.00 Hz

