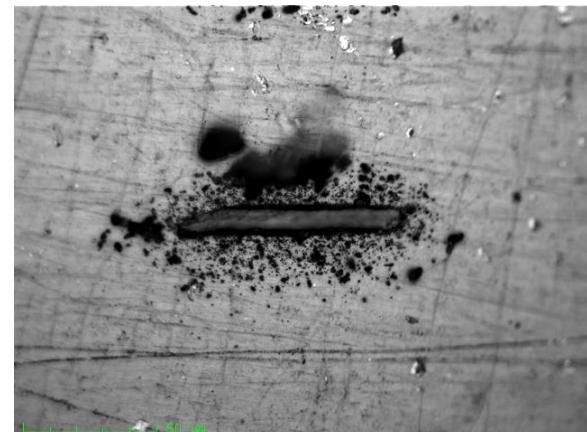
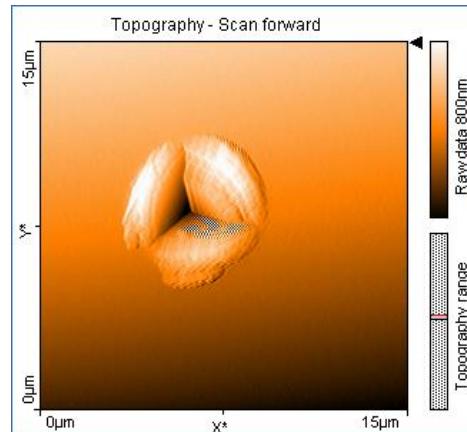
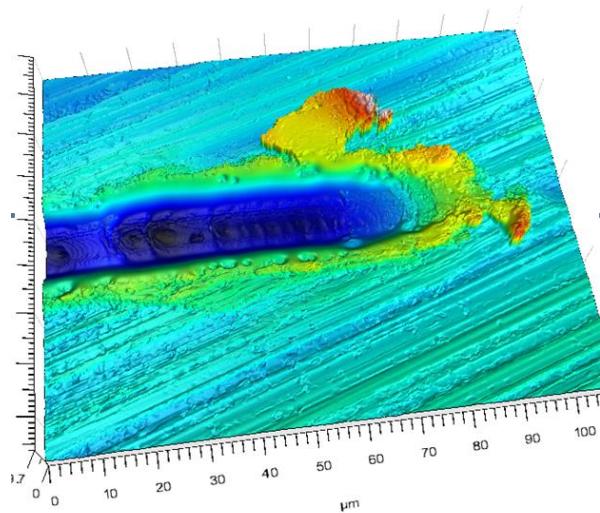


Mechanical Property Characterization of Coatings and Surfaces within the Nano- and Micro-Scale

Thomas Chudoba

ASMEC Advanced Surface Mechanics GmbH



This talk contains contributions from

M. Griepentrog, U. Beck – BAM, Berlin, Germany

A. Clausner, F. Richer – TU Chemnitz, Germany

N. Schwarzer, N. Bierwisch – SIO, Tankow, Germany

A. Gies – Oerlikon, Lichtenstein

D. Schneider – Fraunhofer IWS, Dresden, Germany

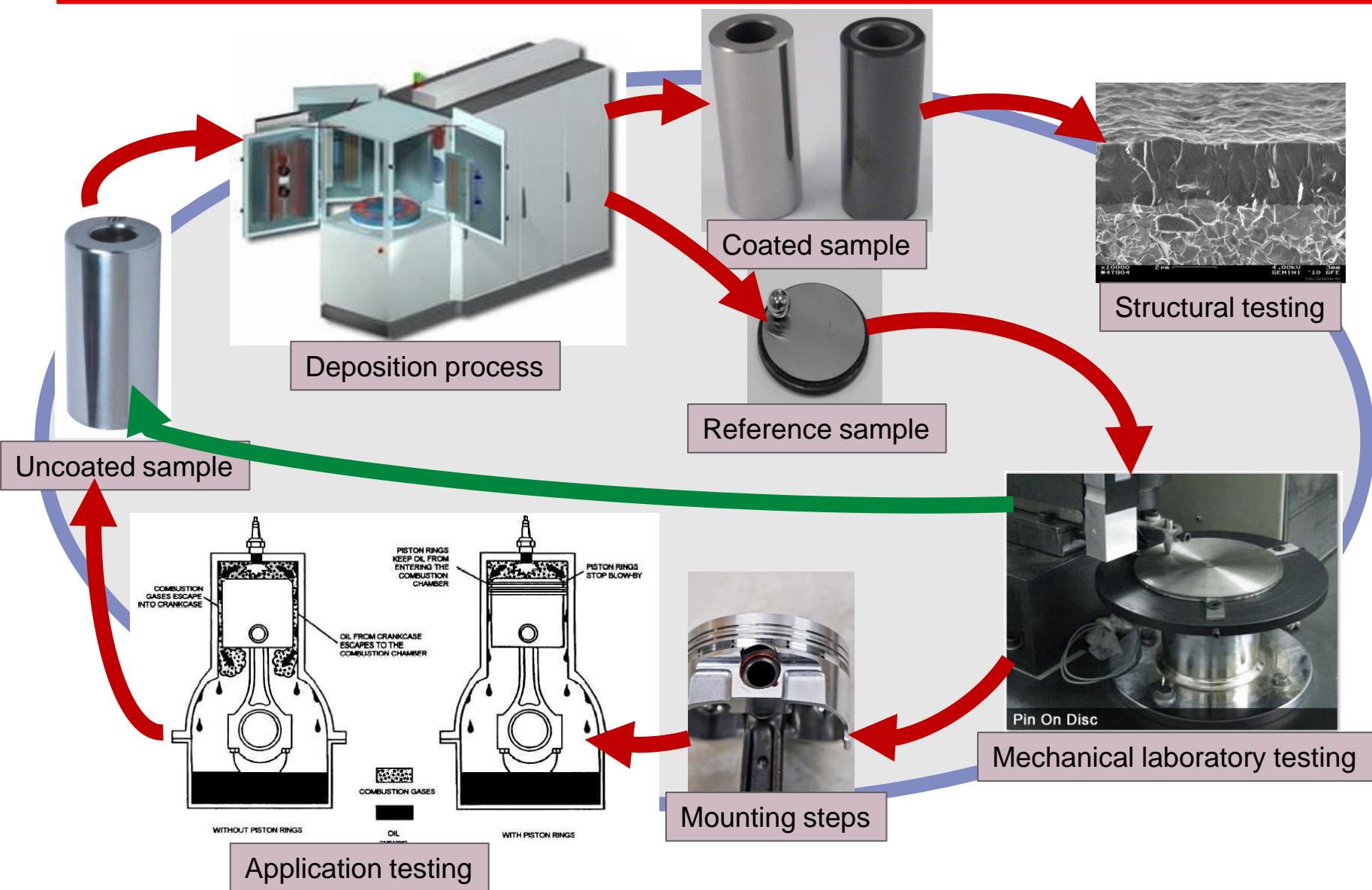
M. Kopycinska-Müller – Fraunhofer IzfP, Dresden, Germany

Content

- 1) Motivation for mechanical testing**
- 2) Mechanical material parameters**
- 3) Comparison of test methods – the difficulty of quantification**
- 4) Conclusions**

Mechanical surface tests are used for:

- 1) Development** → Finding an optimum surface/coating for a certain application
- 2) Failure analysis** → Finding out why certain surfaces/coatings fail
- 3) Quality control** → Guarantee stable surface/coating properties over time



Trial and error development process in a multi parameter space

Example: Double layer coating

Testing of:

- 10 materials for each single layer (10×10)
- 10 process parameters per material
- 10 film thickness combinations

= $10 \times 10 \times 10 \times 10$ combinations

= **10000** samples

Problems of surface mechanics for coated systems

The search for the optimum coating material is
time consuming and expensive.

Mechanical parameters of thin coatings and small structures are
difficult to measure.

Laboratory measurements and simulations often
differ from the conditions in a real application.

Core messages at the beginning:

It is hard to get accurate data!

You need a higher level of modelling and calculations!

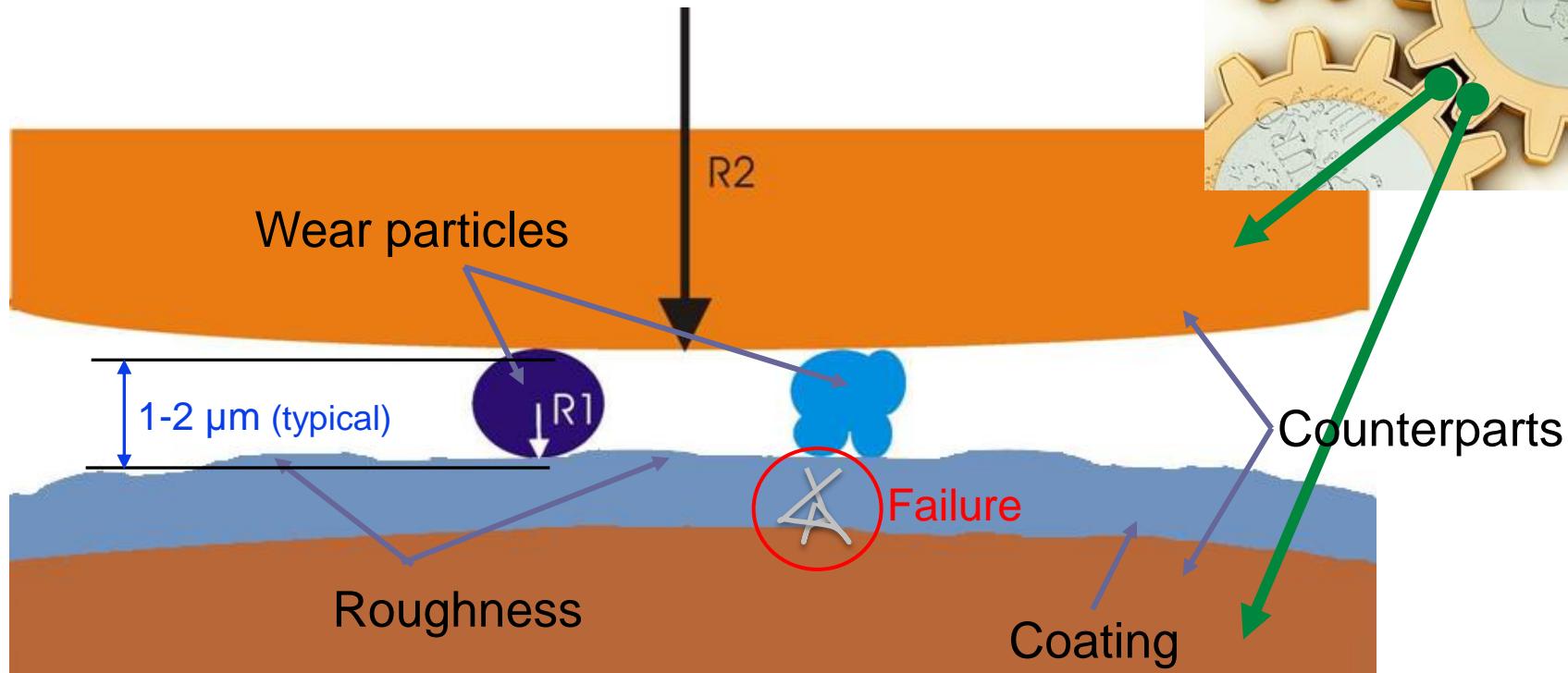
Steps for a reduction of the development effort

Identify the most critical conditions in the application, which cause failures

Identify the most critical mechanical (physical) material parameters

Combine tests with a higher level of modelling and calculations

Analysis of characteristic loading conditions

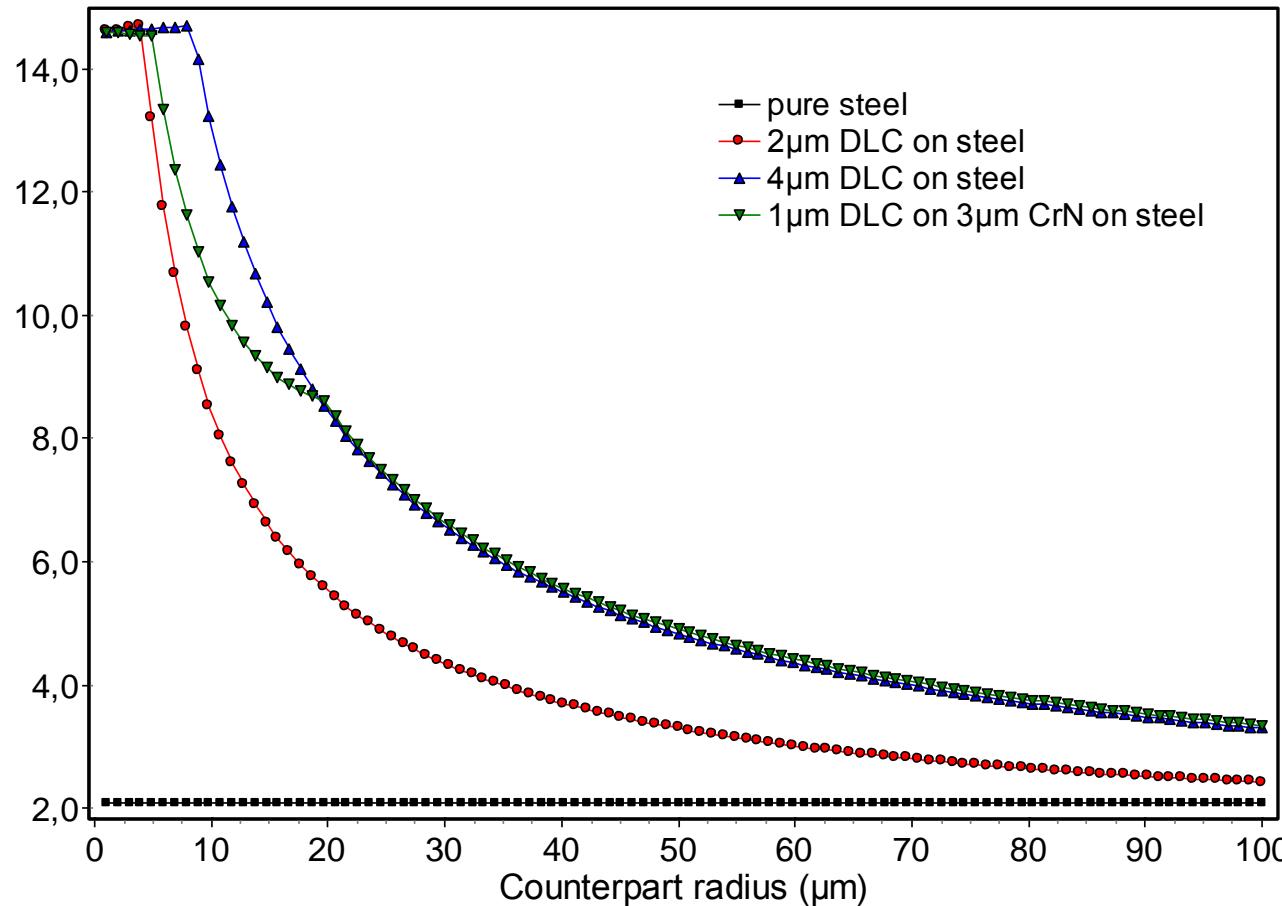


To understand the failure reasons one has to go down to the dimension of roughness and wear particles → This requires high resolution.

Example for modelling

Load carrying capacity of different coating systems on steel

Load carrying capacity



Input parameter required:
E – Young's modulus
v – Poisson's ratio
Y – Yield strength
(T – Tensile strength)

Steel	DLC	CrN	
E	200	270	300 GPa
v	0.3	0.2	0.25
Y	2	15	8 GPa

2) Mechanical material parameters

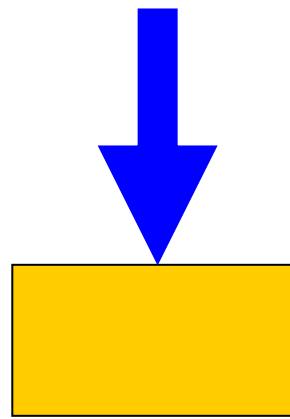
Mechanical behavior	Parameter	Test methods for coatings
Elastic behavior	Young's modulus, Poisson's ratio	Nanoindentation+LFU, ultrasonic surface waves, AFAM, impulse excitation technique
Plastic behavior	Hardness, Yield strength, Stress-strain-curve, hardening exponent	Nanoindentation+LFU
Brittle behavior	Fracture toughness, tensile strength	Nanoindentation+LFU, 4-point bending
Time dependent behavior	Creep, fatigue resistance, strain rate dependence	creep test, impact test, cavitation test, fatigue test (cyclic contact loading)
Frictional and wear behavior	Friction coefficient (not intrinsic) Wear coefficient (not intrinsic) Stribeck curve (not intrinsic)	Friction test, wear test, nanoindentation+LFU
Adhesion	Adhesive strength Scratch resistance (not intrinsic)	Scratch test (LFU), peel test, centrifuge test, cavitation test, Rockwell test

For all parameter it also has to be considered:

LFU = Lateral Force Unit

- Internal stress
- Dependency on temperature
- Dependency on sample homogeneity: failure density, gradients, thickness constancy, roughness

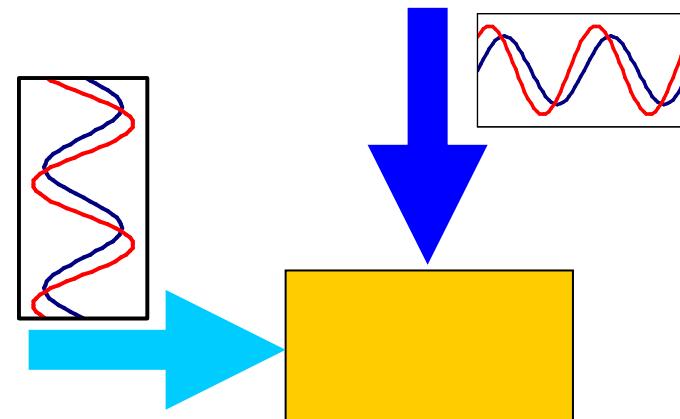
Default Nanoindenter



1 degree of freedom:

- Normal load-displacement-curve

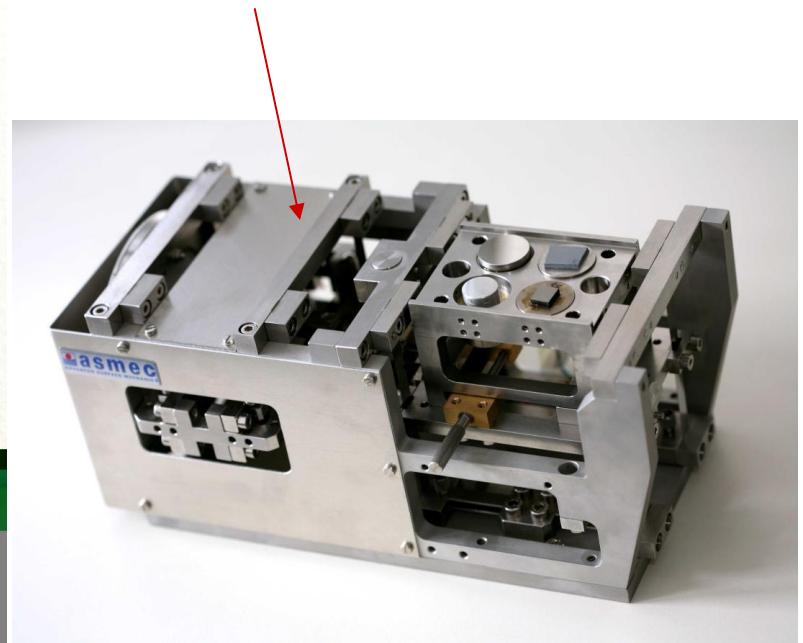
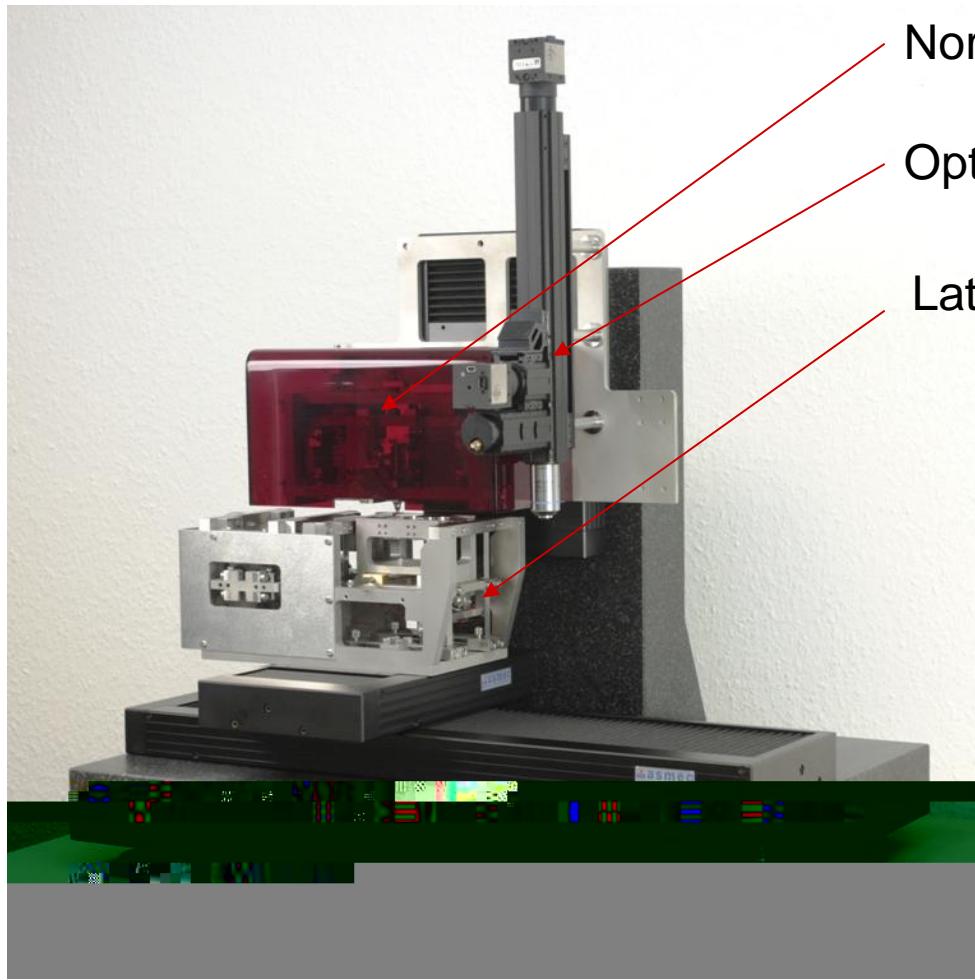
Universal nanomechanical tester



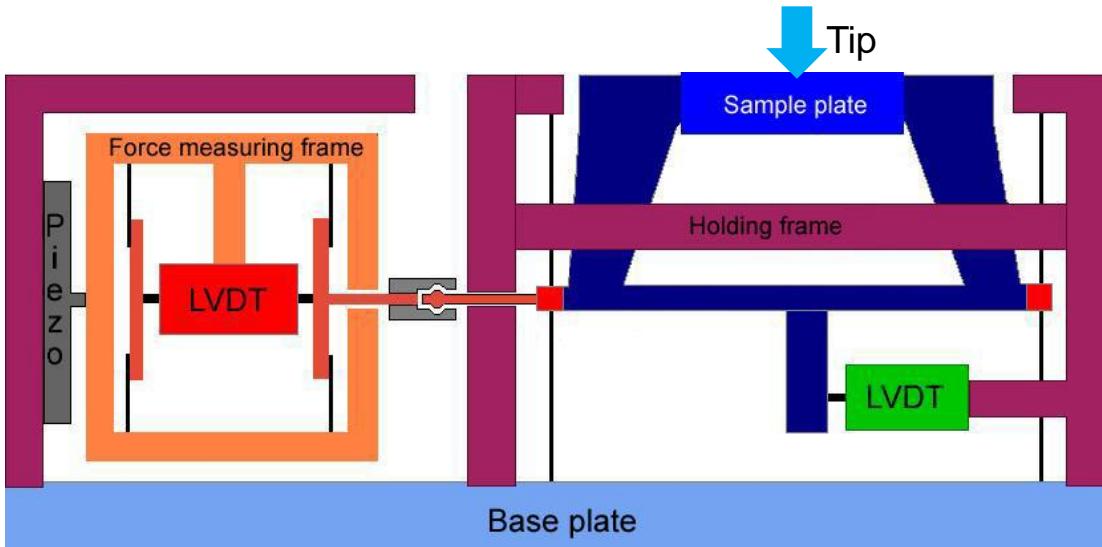
4 degrees of freedom:

- Normal load-displacement-curve
- Lateral load-displacement-curve
- Oscillation normal (dynamic mode)
- Oscillation lateral (dynamic mode)

UNAT – Universal Nanomechanical Tester



Lateral force head – the new component



- Nanometer resolution like in normal direction
- The sample is moved laterally (not the tip)
- High stiffness in normal direction
- No height change during lateral movement
- Force generation independent on movement

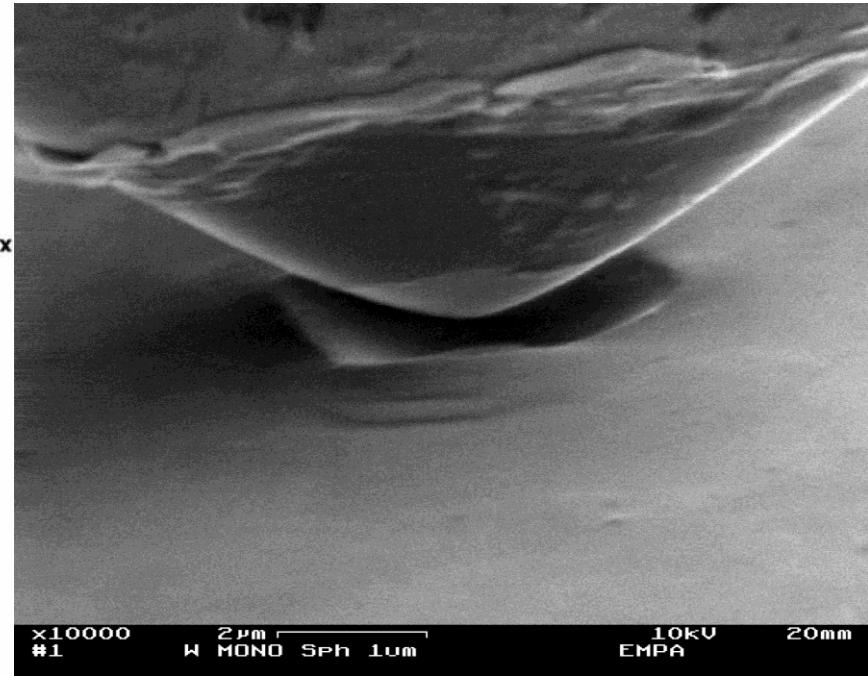
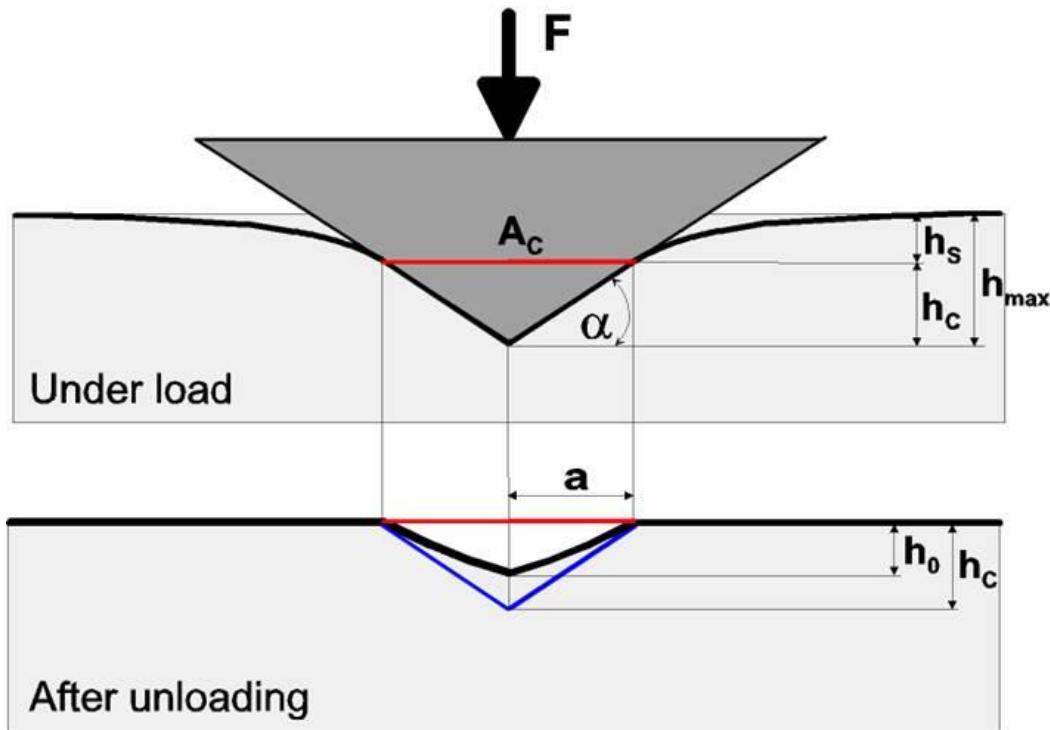
- A force can be applied and measured without any movement of tip or sample
- No rolling motion of the tip due to bending of the indenter shaft
- Transition sticking- sliding friction highly resolved

Elastic behavior

Young's modulus
Poisson's ratio

Nanoindentation ISO 14577

Quantitative: Yes
Local



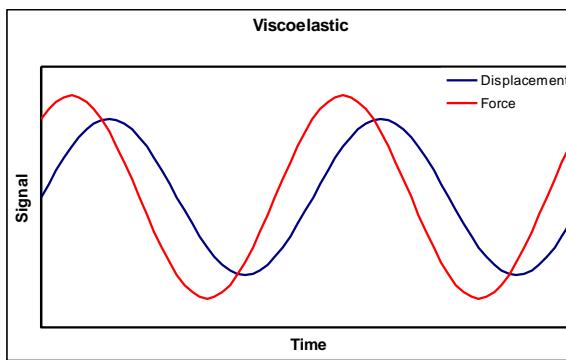
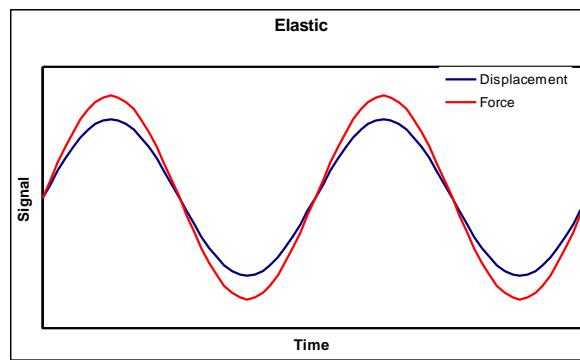
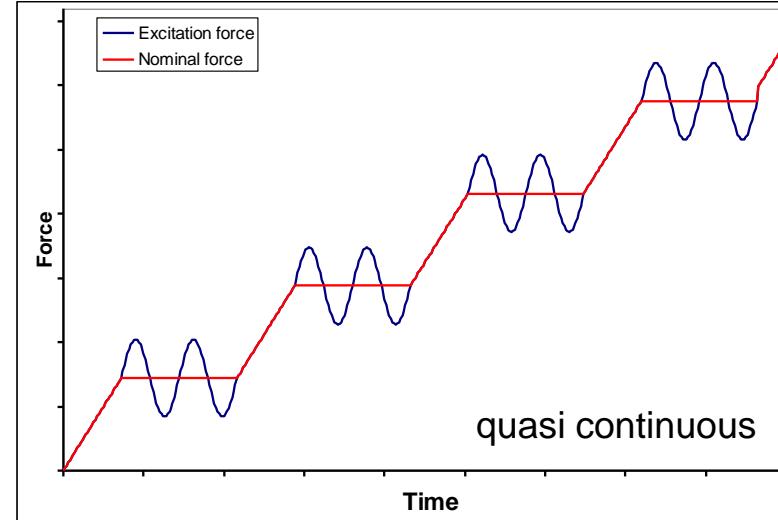
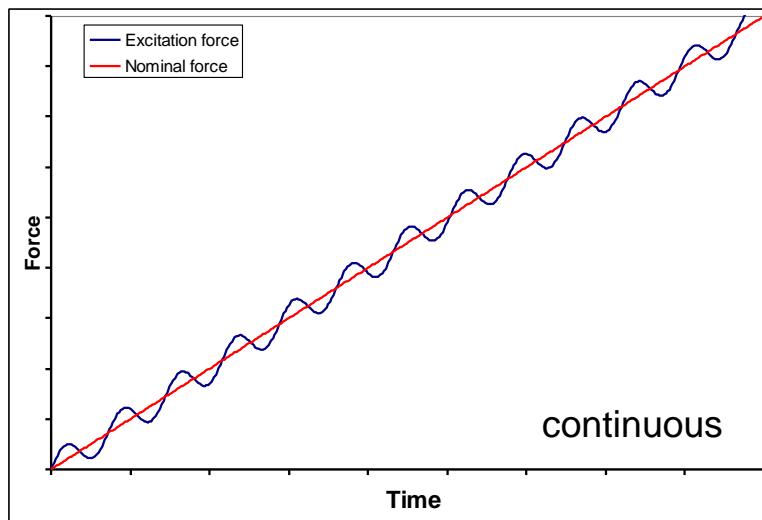
Determination of Hardness and Modulus

Only normal forces

Counterpart always diamond

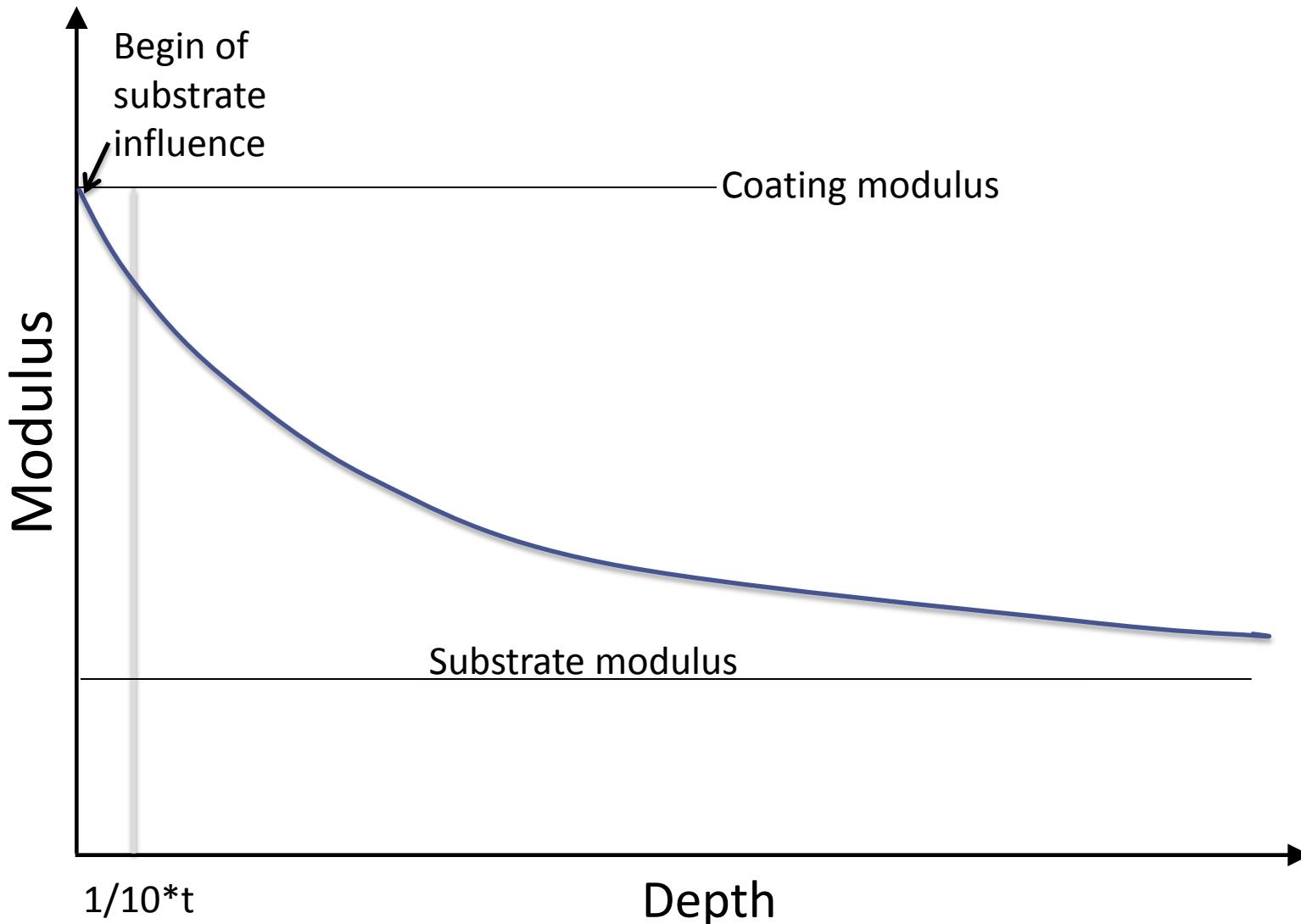
QCSM – Quasi Continuous Stiffness Measurement

A sinusoidal oscillation is superposed to the force signal.
Force/Displacement amplitude ratio ~ contact stiffness S



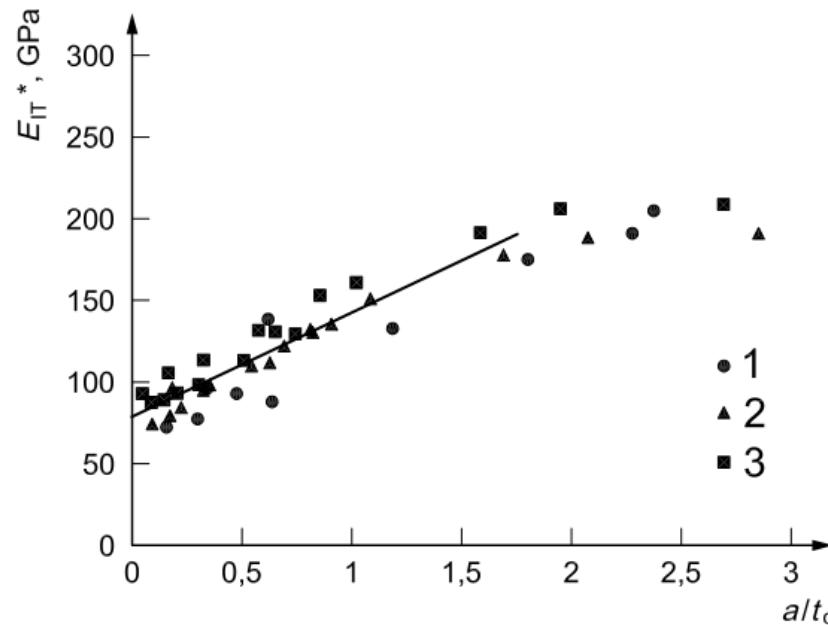
Viscoelastic behavior results in a phase shift between force and displacement.

Substrate influence on modulus



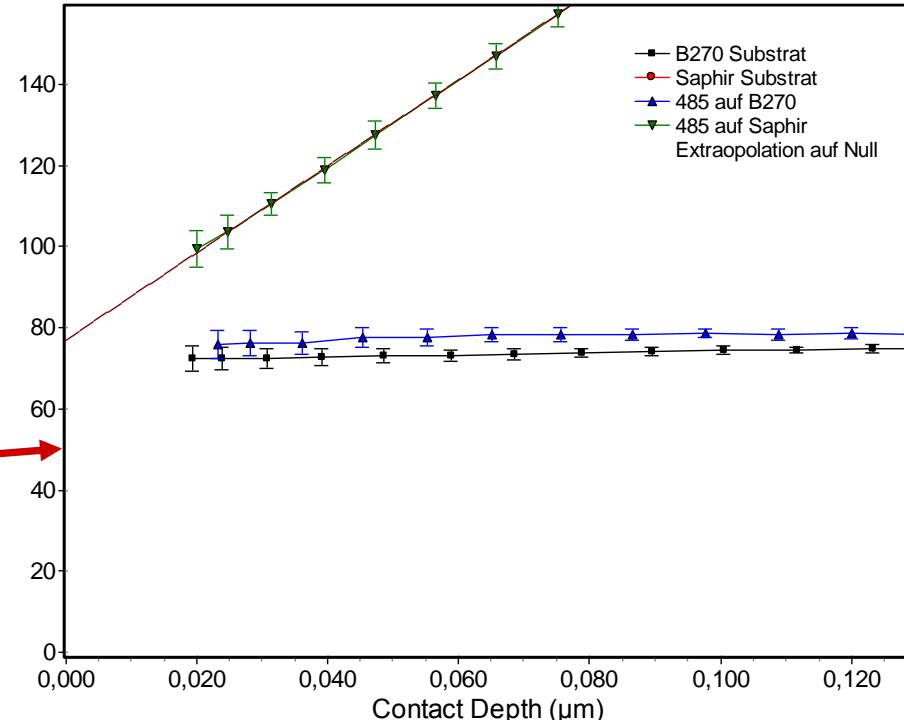
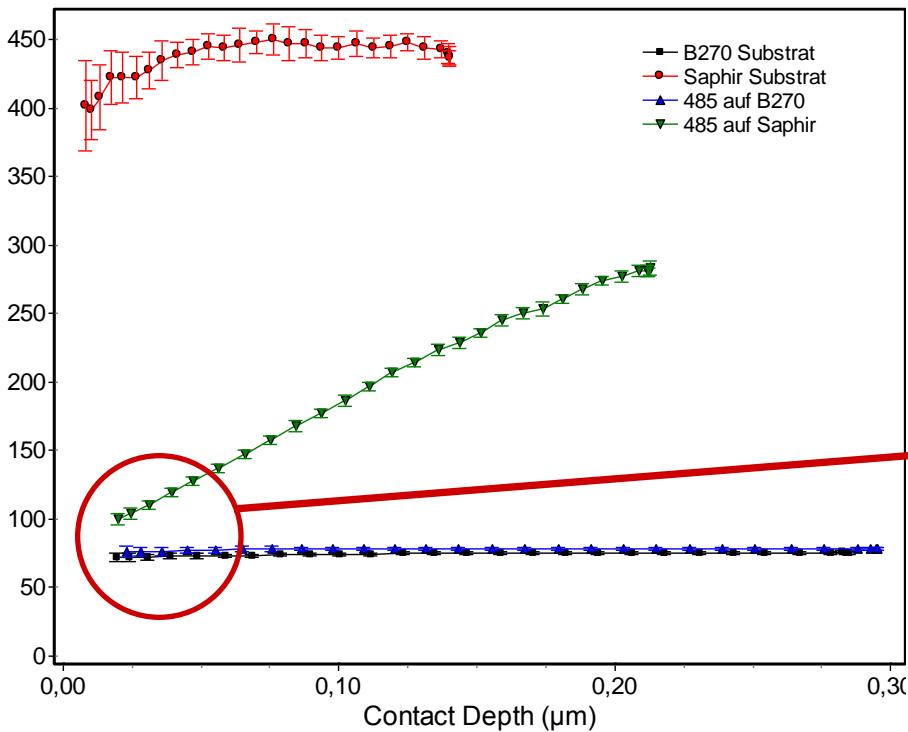
ISO 14577 Part 4

In the case of soft/ductile coatings, indentation force or displacement and indenter geometry shall be chosen such that data shall be obtained in the region where $a/t_c < 1.5$. The plane strain indentation modulus of the coating E_{IP}^* is obtained by taking a series of measurements at different indentation depths and extrapolating a linear fit to plane strain indentation modulus vs. a/t_c to zero, see Figure 4.



Key

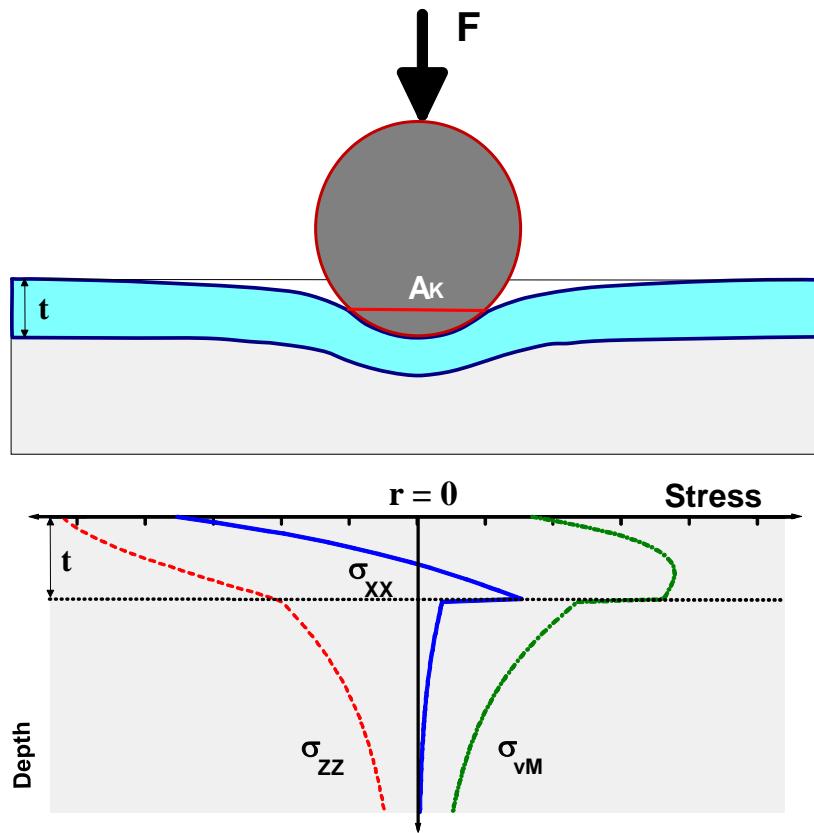
- 1 spherical indenter
- 2 Berkovich indenter
- 3 Vickers indenter

Example: 260nm SiO₂ coatings on glass and sapphire

Maximum tip radius for hardness measurements: 120nm

Maximum force for all measurements: 18mN, first point at (20 nm; 0,24 mN).

Elastic indentation with spherical indenter



Requirements

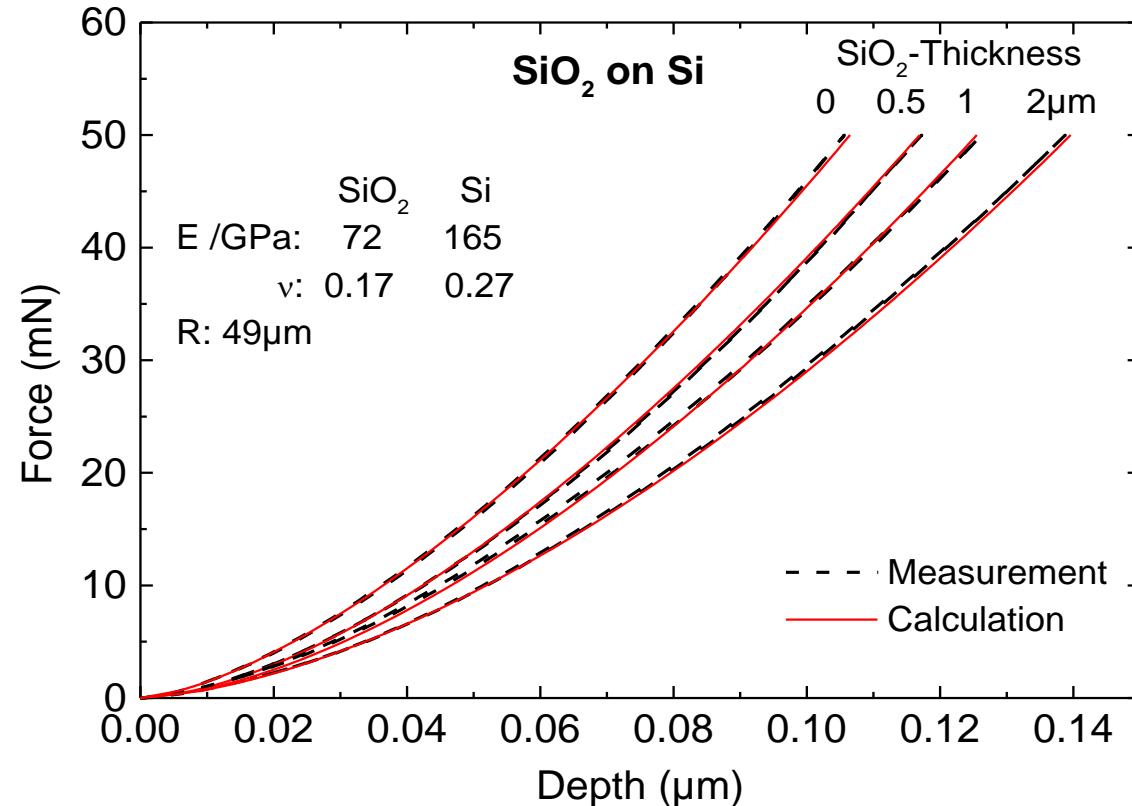
Wholly elastic indents

High accurate measurements with resolution < 1 nm

Accurate knowledge of tip radius and frame compliance

Combination with elastic modelling

Elastic calculation of Hertzian pressure profile for coated systems



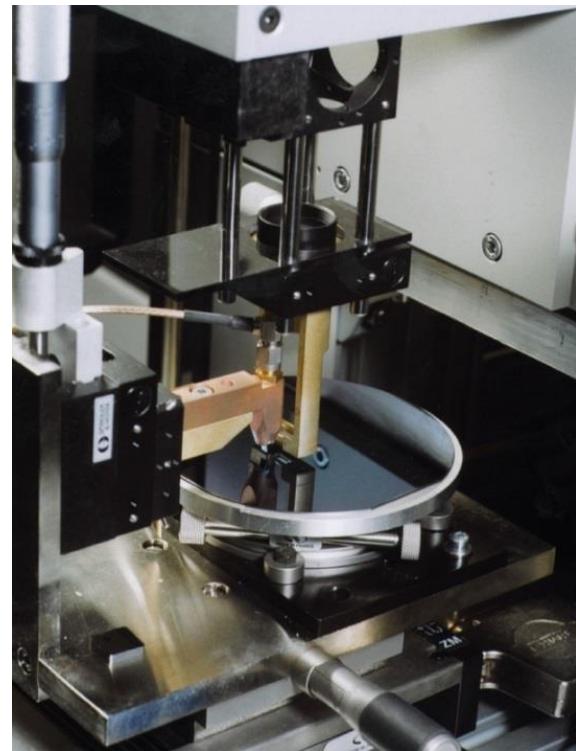
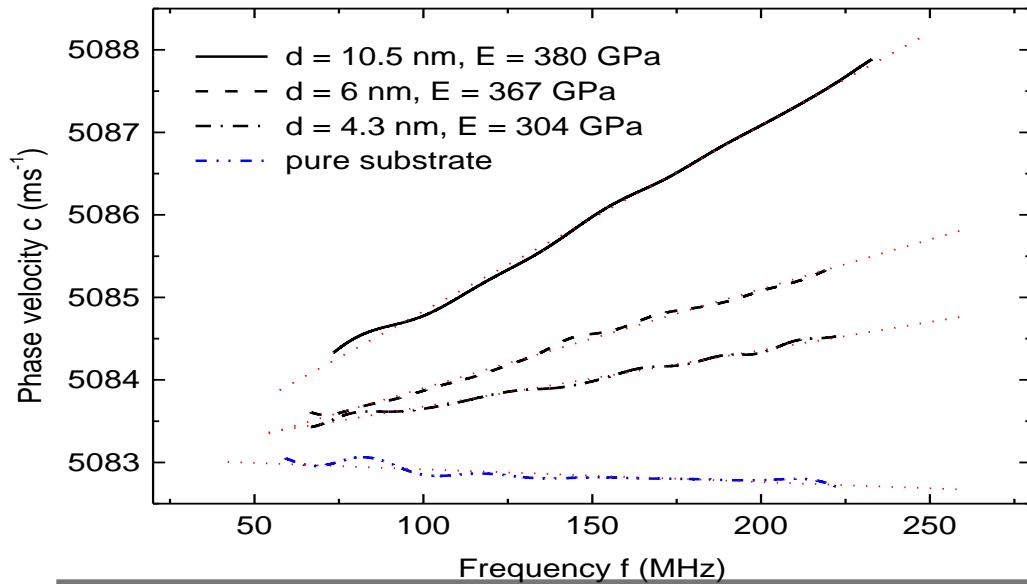
T. Chudoba, N. Schwarzer, F. Richter
Surf. Coat. Tech. 127 (2002) 9-17

Fit of the measurement data with a theoretical load-displacement curve.
Known substrate properties; **fit parameter:** film modulus

Useable software **ELASTICA**, **FilmDoctor**

Acoustic surface waves
DIN 50992-1

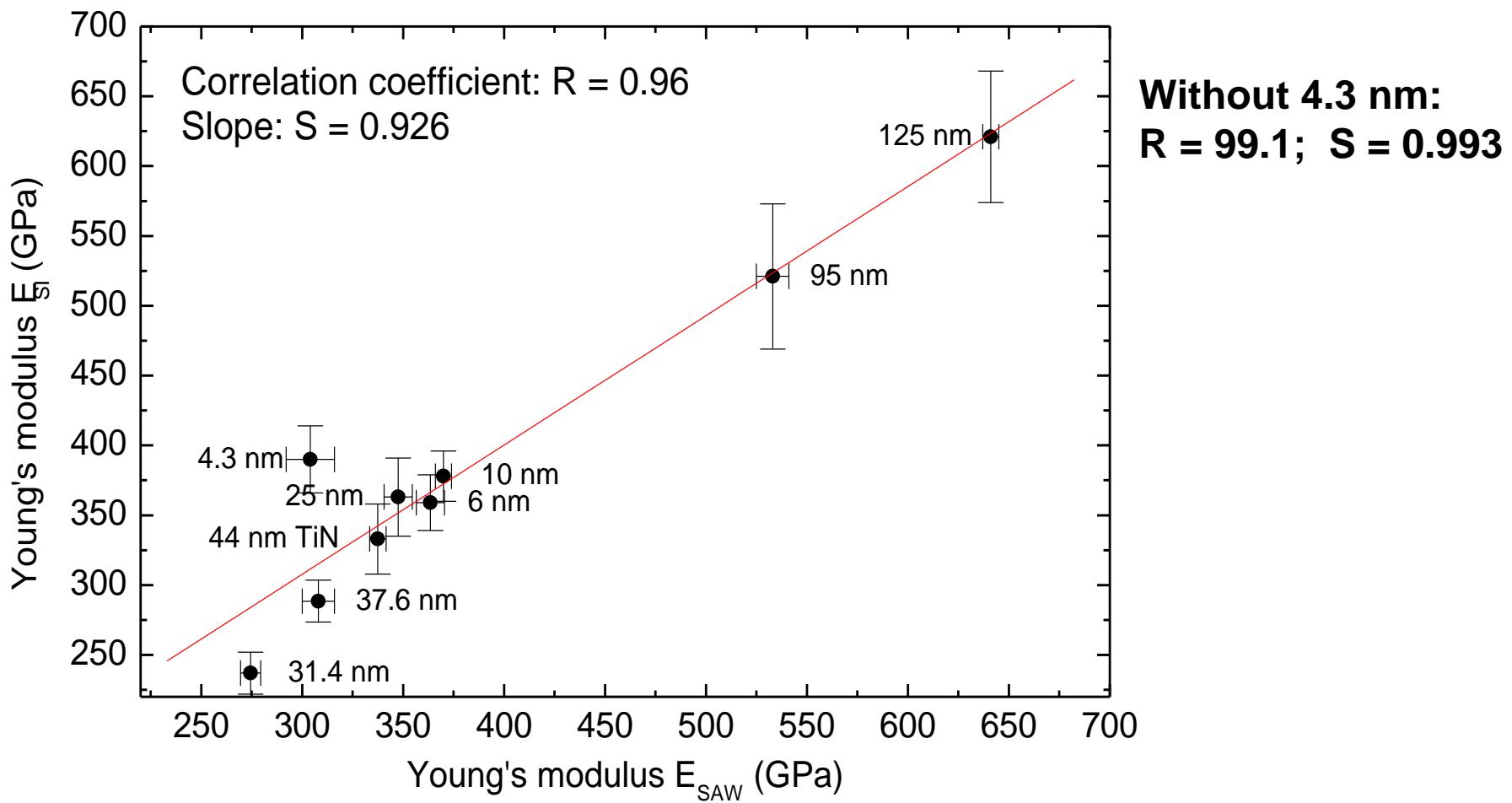
Quantitative: Yes
Integral



Comparison SAW - Nanoindentation

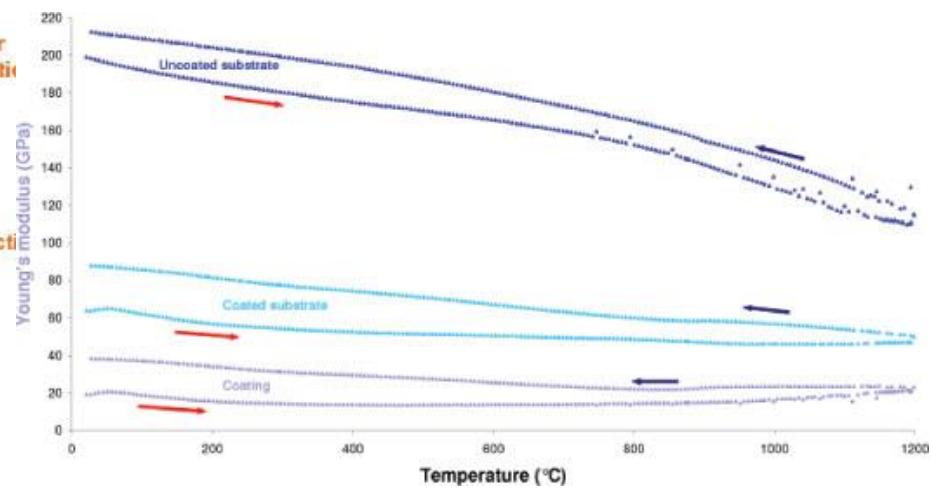
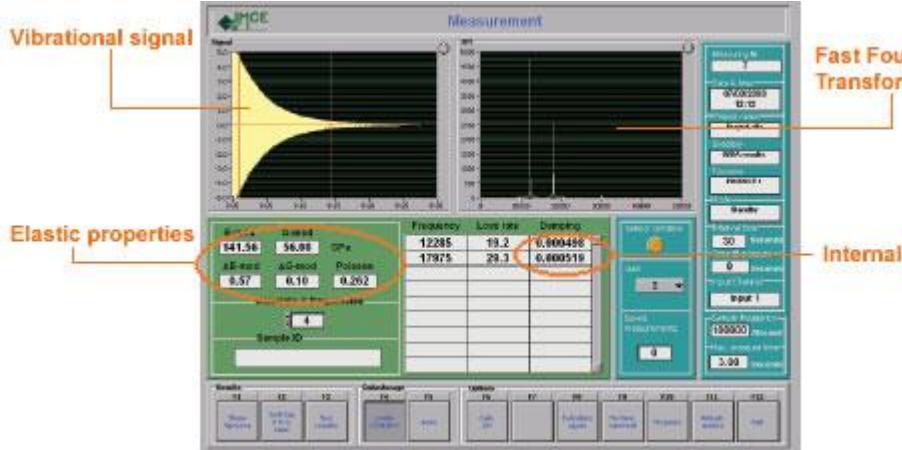
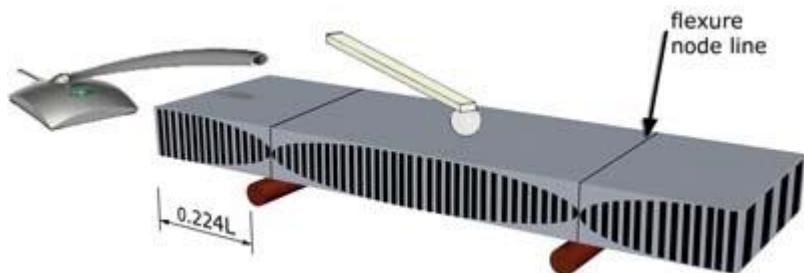
	SAW (IWS)	SAW (BAM)	Sphere (75 nm)	Sphere (3 μm)
Thickness	E (GPa)	E (GPa)	E (GPa)	E (GPa)
4.3 nm	304	246 ± 6	Not elastic	390 ± 24
6 nm	367	360 ± 5	Not elastic	359 ± 20
10 nm	380	360 ± 4	Not elastic	378 ± 18
25 nm	370	325 ± 6	367 ± 81	359 ± 28
31.4 nm	272	277 ± 2	236 ± 42	238 ± 15
37.6 nm	315	301 ± 5	291 ± 37	286 ± 15
44 nm TiN	339	336 ± 1	Not elastic	333 ± 25
95 nm	533	530 ± 12	521 ± 52	Not measured
125 nm	641	638 ± 6	621 ± 47	Not measured

Comparison SAW - Nanoindentation



Impulse excitation technique ASTM E1876

Quantitative: Yes
Integral

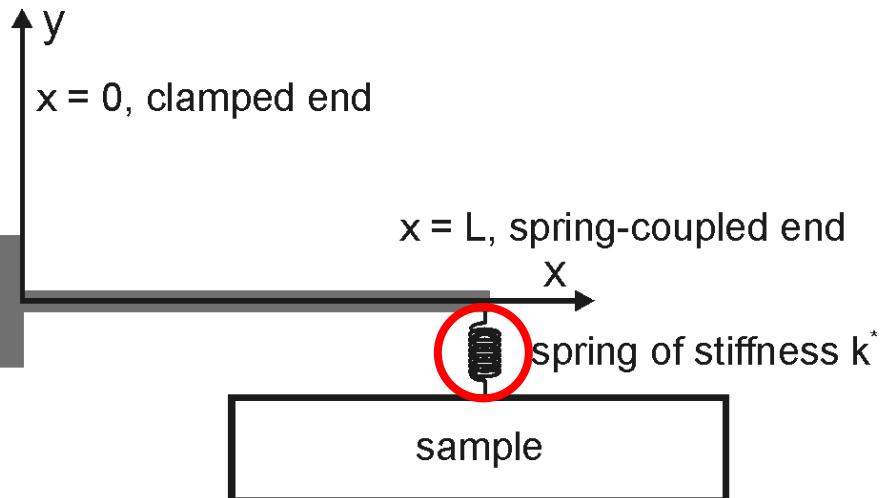


from IMCE, Belgium

Atomic force acoustic microscopy AFAM

Quantitative: partially
Local

Contact resonance frequencies of an AFM cantilever



Contact resonance

Frequency

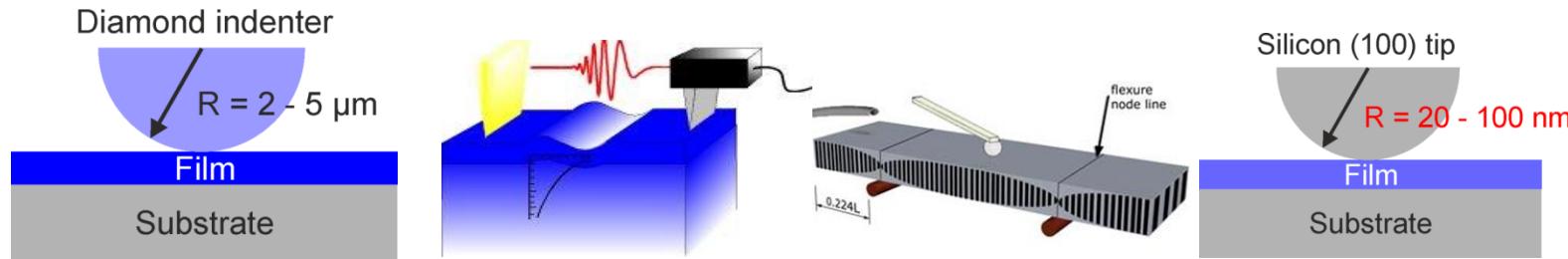
contact mechanics

$$f_n = F_i(k^*, k_c, L_1, L)$$

$$k^*$$

$$\frac{1}{E^*} = \frac{1}{M_{tip}} + \frac{1}{M_{sam}}$$

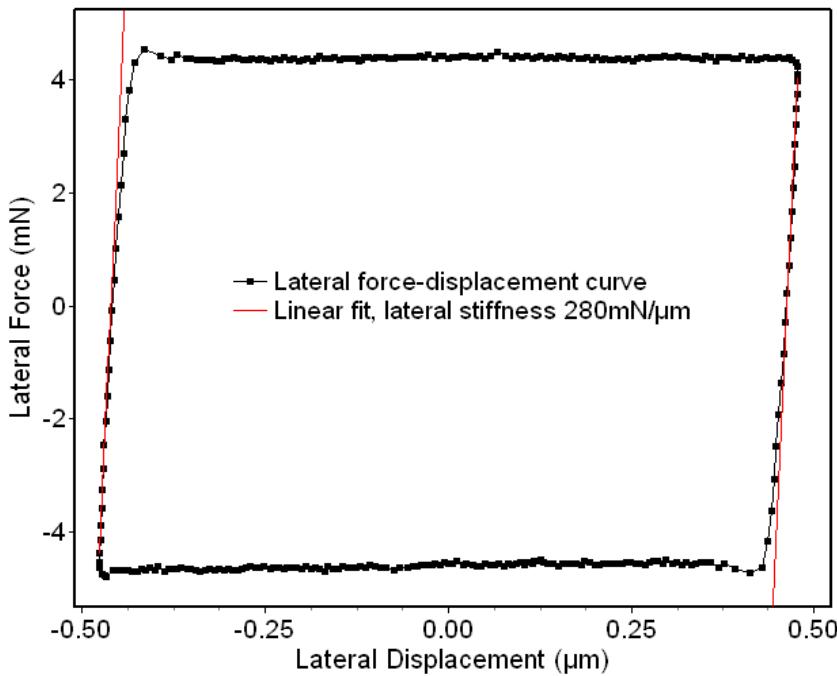
Source: Kopycinska-Müller, Fraunhofer IZFP, Dresden



Method	Nanoindentation	Surface acoustic waves	Impulse excitation technique	Atomic force acoustic microscopy
Locality type	Local	Integral	integral	Local (high)
Knowledge required	Tip and substrate properties, Poisson's ratio	Substrate properties, density , (Poisson's ratio)	Substrate properties	Tip properties
Surface requirements	Very smooth, Hard (elastic indents)	Light absorbing, low damping	No special	smooth
Deviating conditions	High pressure	none	none	High pressure
High temperature testing	Up to 700°C (1000°C)	no	Up to 1600°C	no

Poisson's ratio measurement by nanomechanical testing

Measurement of **lateral** contact stiffness
(lateral instrument stiffness corrected)



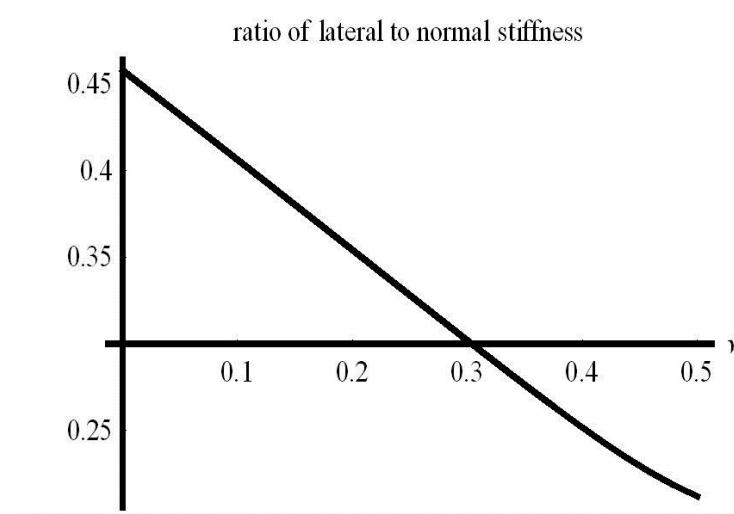
Poisson's ratio can be determined → Contact model required

Two unknown Parameters:

- Young's modulus **E**
- Poisson's ratio **V**

Two measured parameters (same position)

- Normal stiffness **S_N**
- Lateral stiffness **S_L**

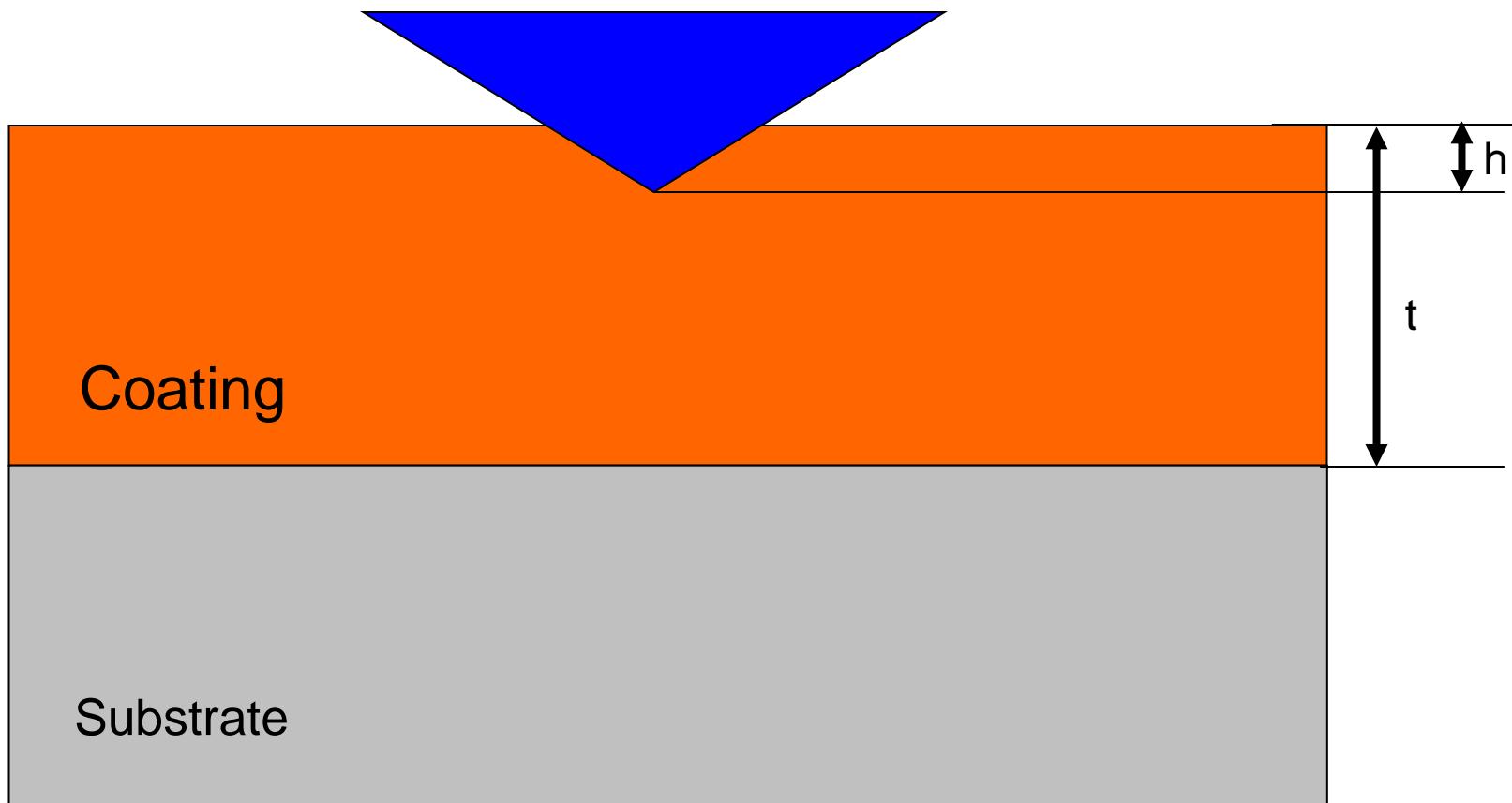


Plastic behavior

Hardness
Yield strength
Stress-strain curve
Hardening exponent

Depth limit for coating hardness tests

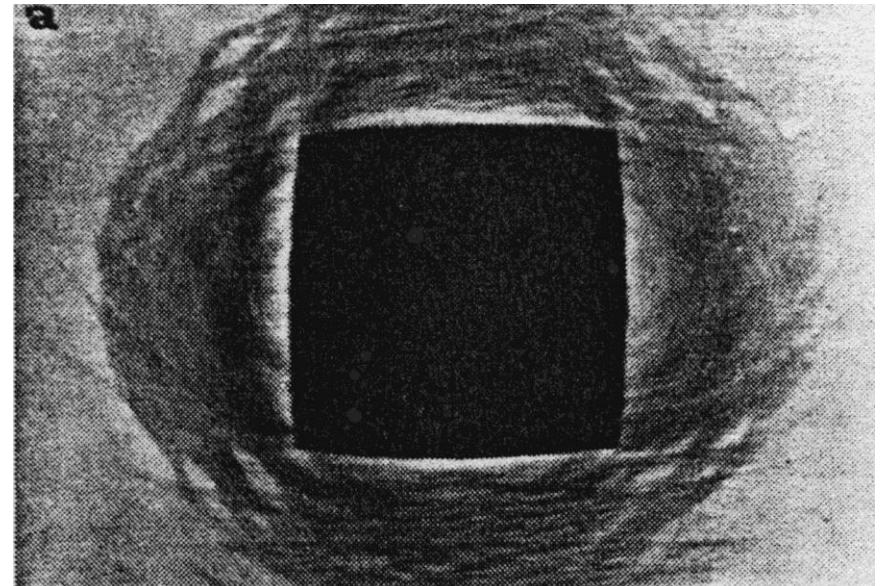
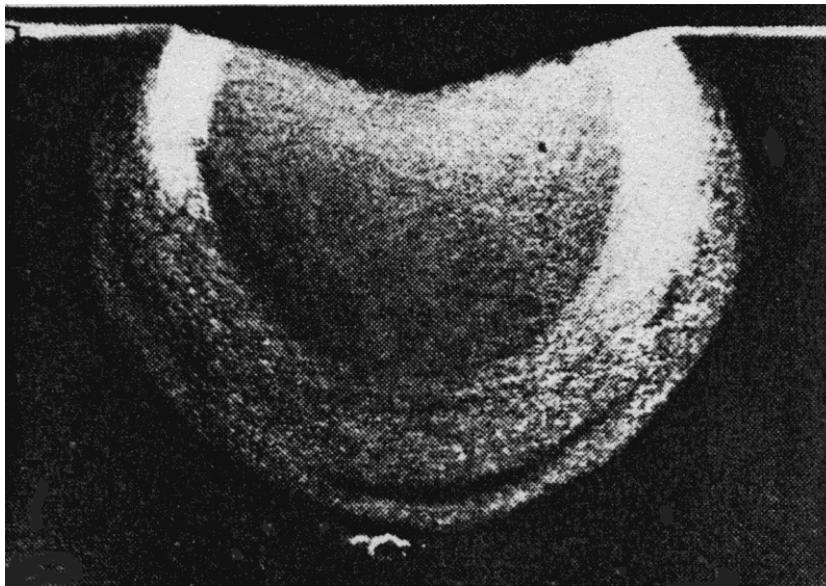
One tenth rule $h < \frac{t}{10}$



Reason for depth limit

The plastic zone is much larger and deeper than the indent.

Therefore the information in the load-displacement curve comes from a depth of up to 10 times the indentation depth.



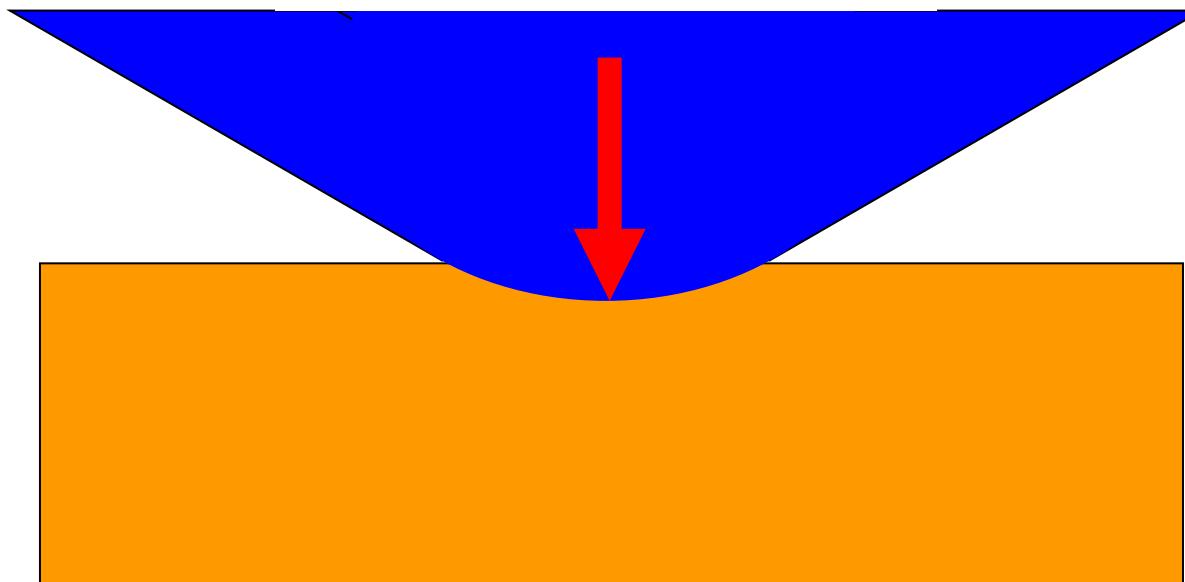
Presentation of the plastic zone in steel using a special etching technique

Limited resolution due to tip rounding

Area function with high accuracy needed

Minimum indentation depth for comparable hardness results:
20% of tip radius

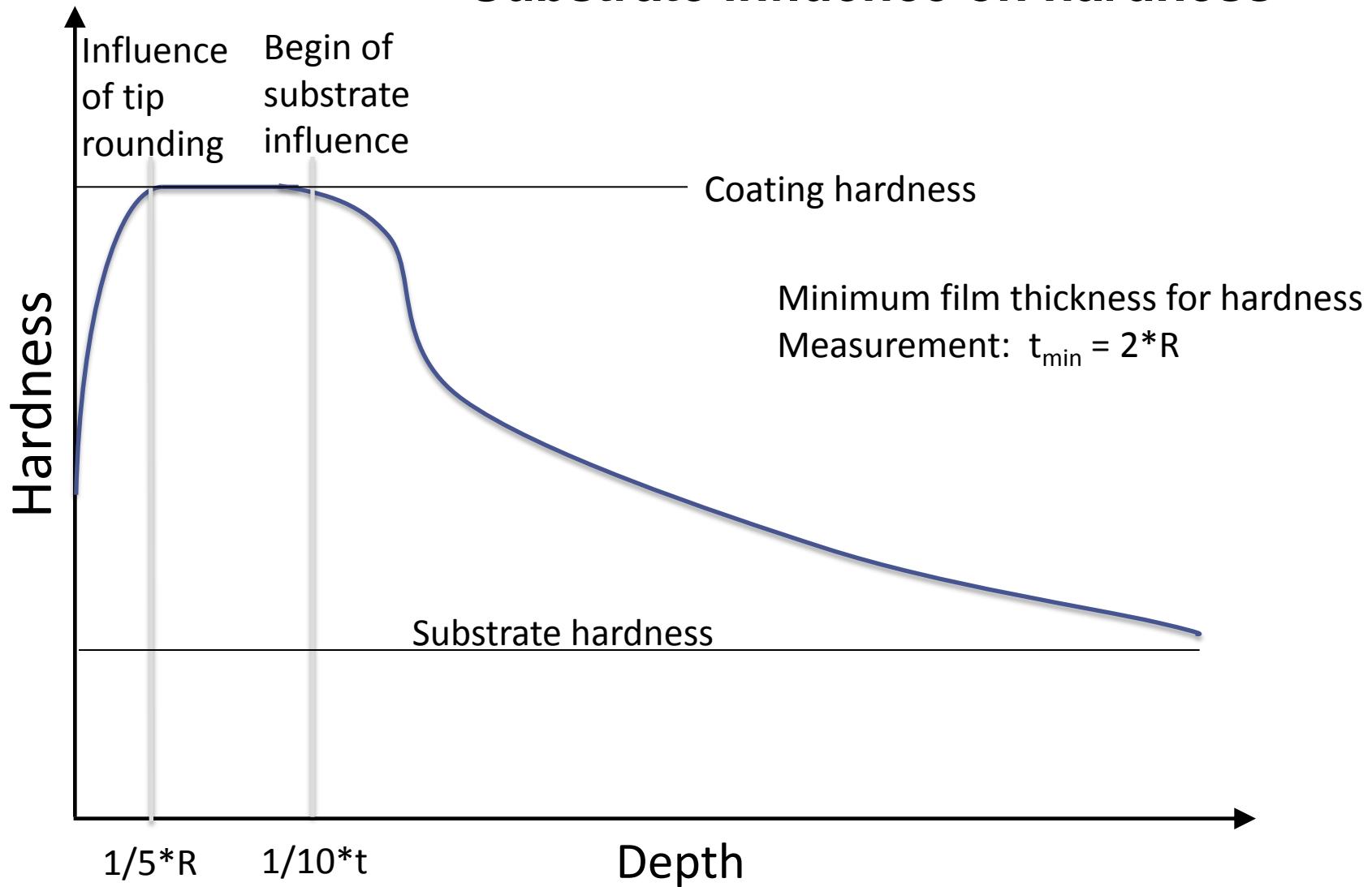
A Berkovich tip has a typical tip radius between 100 – 300 nm



Minimum depth for
hardness tests:

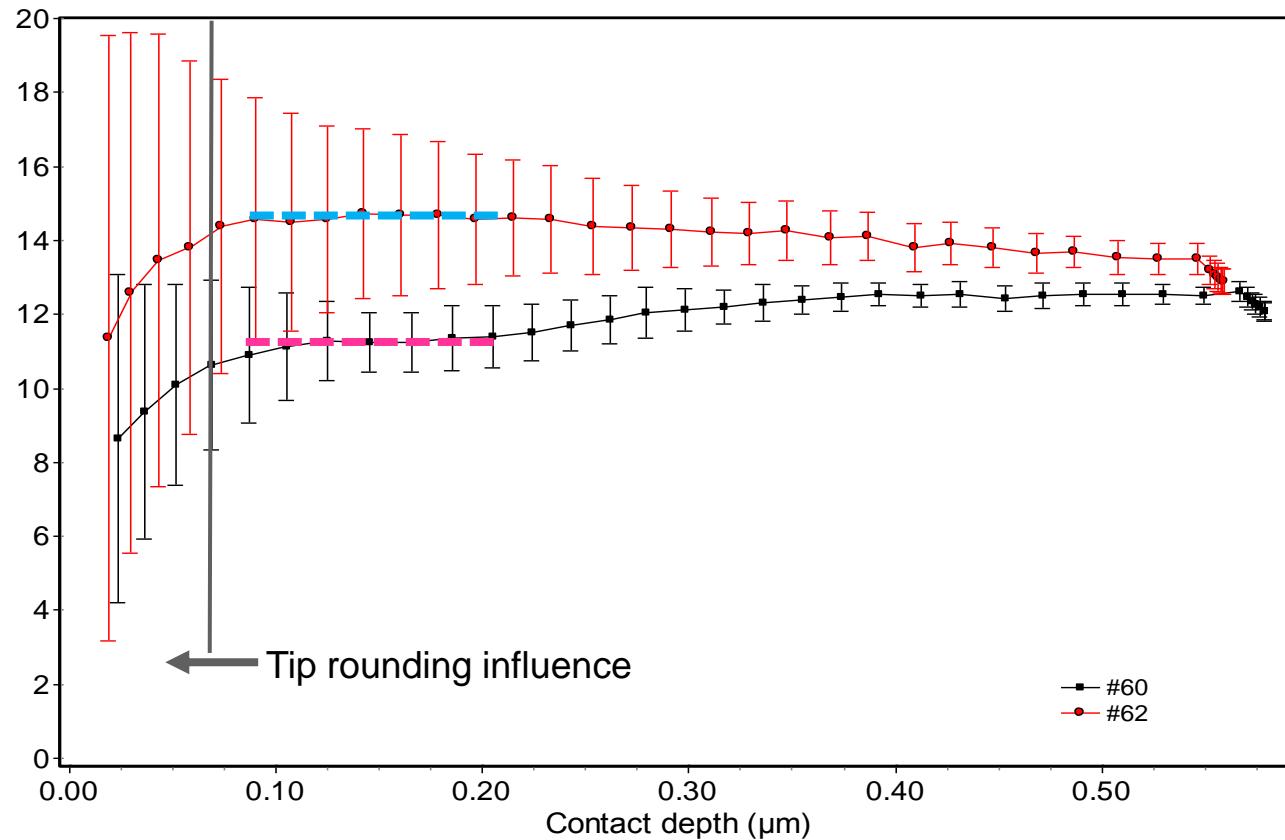
$$h_{\min} = 0.2 * R$$

Substrate influence on hardness



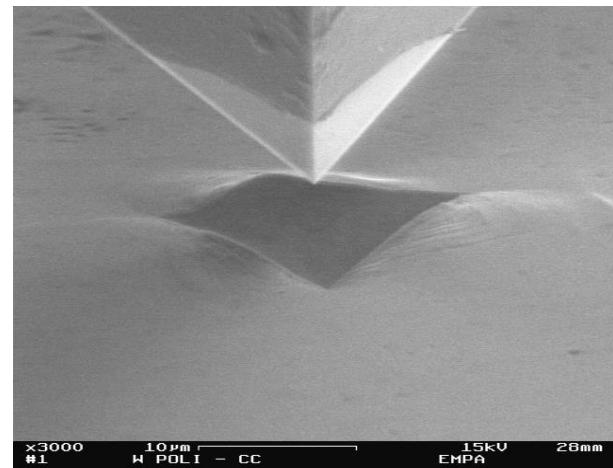
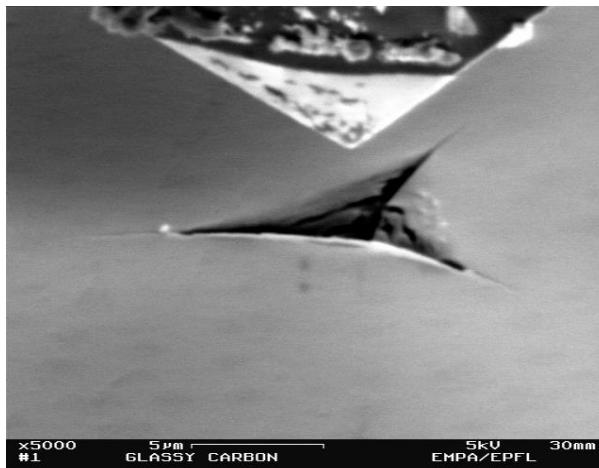
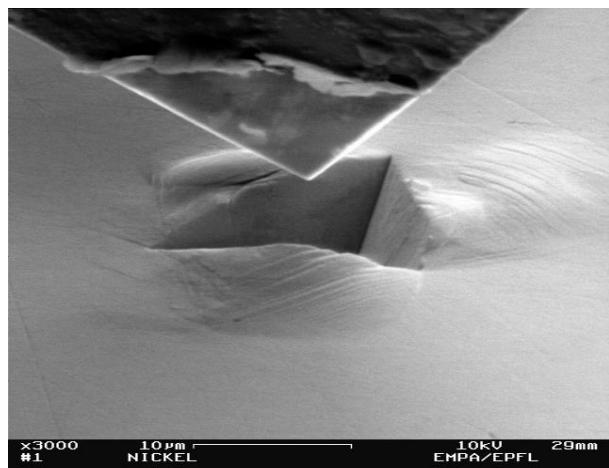
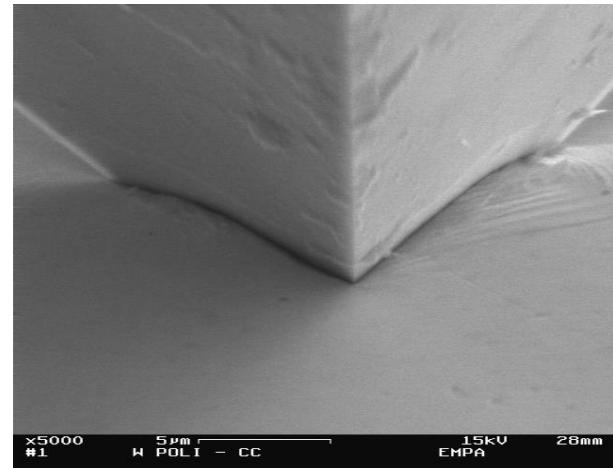
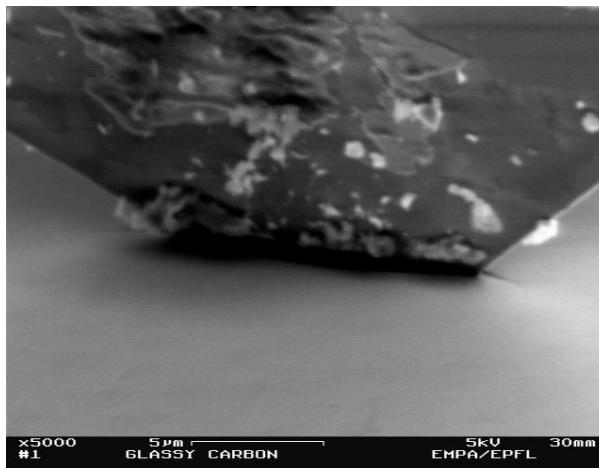
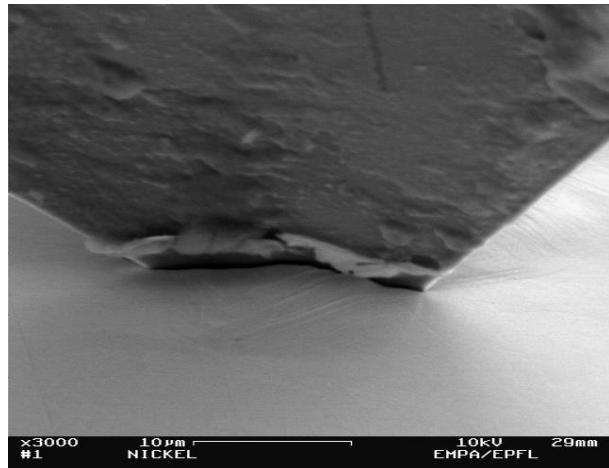
Minimum film thickness for **hardness** measurements
in dependence on tip radius (not for modulus)

Tip radius (nm)	Minimum film thickness (nm)
50	100
75	150
100	200
150	300
200	400
250	500
300	600



H (#60) < H (#62)
11.3 GPa 14.8 GPa

SEM images from indents with Cube Corner indenter

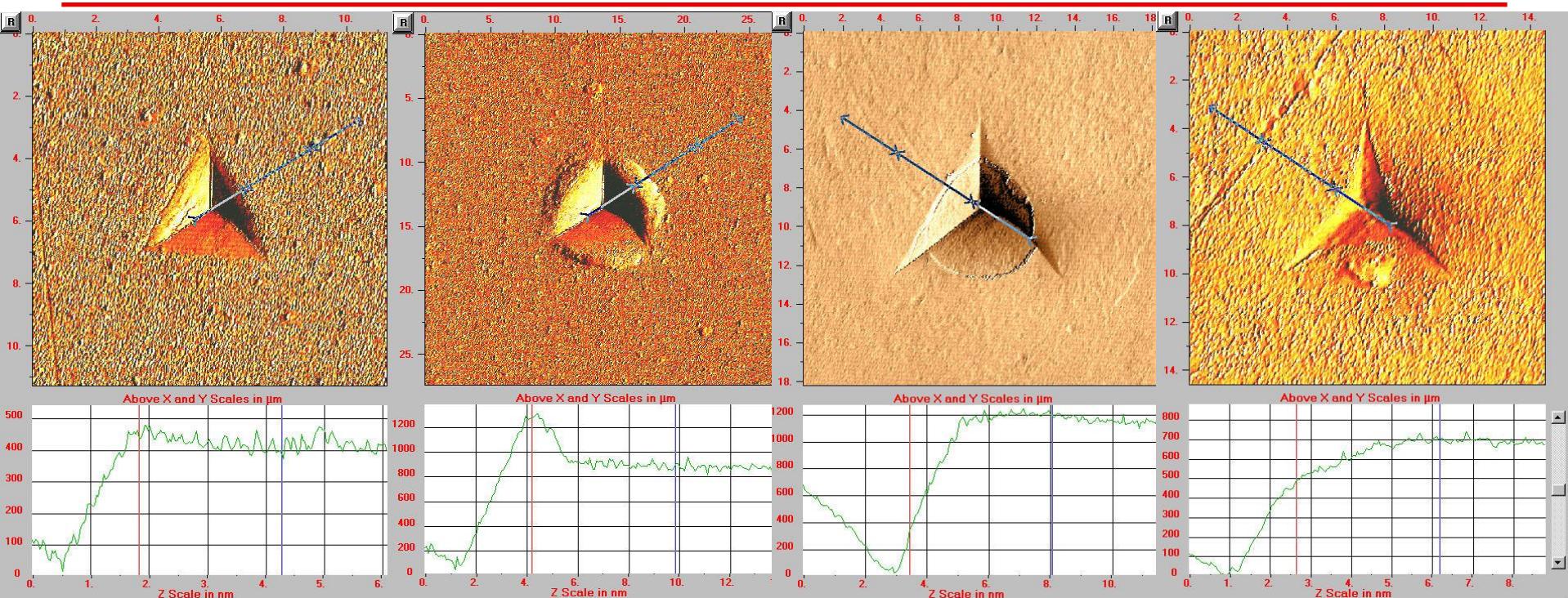


Nickel

Glassy carbon

Tungsten

Source: EMPA, Switzerland



normal

Al on BK7 glass

0,4 μm / 1,1 μm

Load: 10 mN

pile-up

Al on BK7 glass

0,9 μm / 1,1 μm

50 mN

cracks

Al₂O₃ on Nickel

1,2 μm / 0,9 μm

100 mN

sink-in

Al₂O₃ on Nickel

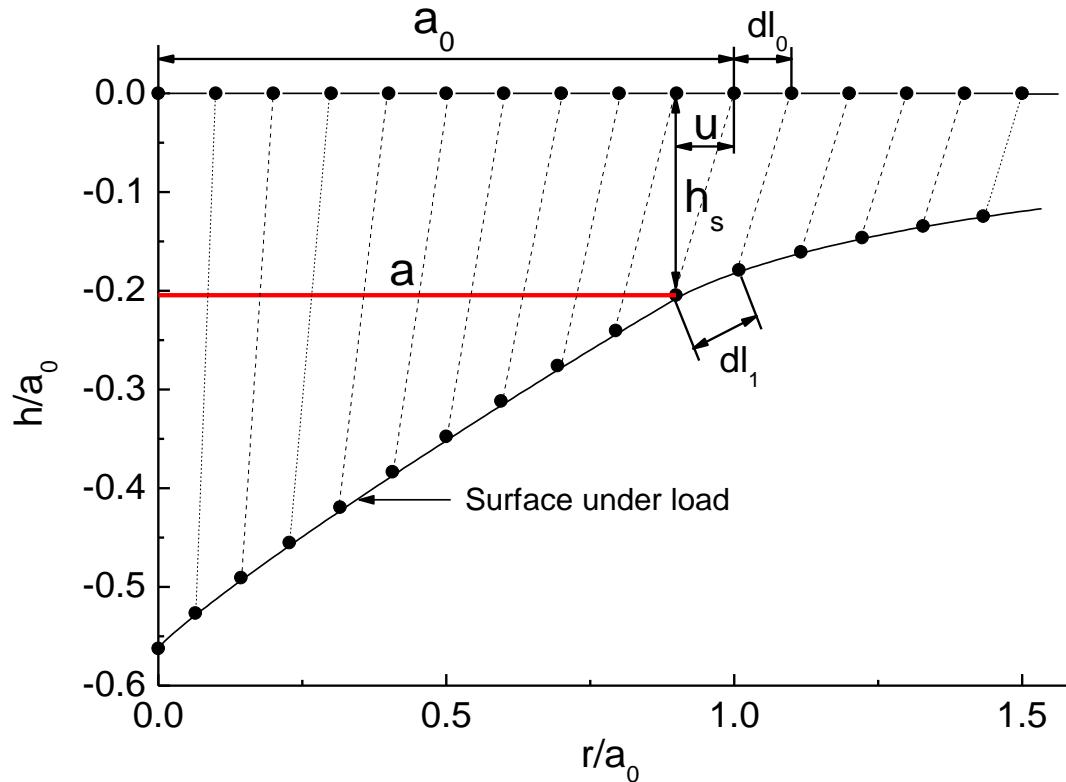
0,7 μm / 2 μm

100 mN

green = depth / film thickness

Additional correction: radial displacement correction

Included in the new revision of the standard ISO 14577



Example for influence:

	with	without	correction
H:	30 GPa	→ 31,5 GPa	
E:	400 GPa	→ 413 GPa	

$$u_r = \frac{(1-2\nu)(1+\nu)}{2} \frac{F}{E \cdot a^2} \cos\left(\arctan\left(\frac{h_0}{a}\right)\right)$$

T. Chudoba, N. M. Jennett, Higher accuracy analysis of instrumented indentation data obtained with pointed indenters, J. Phys. D: Appl. Phys. 41 (2008)

Theoretical limit for plastic deformation with pyramidal/conical indenter:

$$\frac{H}{E_r} = \frac{\tan \alpha}{2}$$

With $\alpha = 19.7^\circ$ follows

$$\frac{H}{E_r} \leq 0.179$$

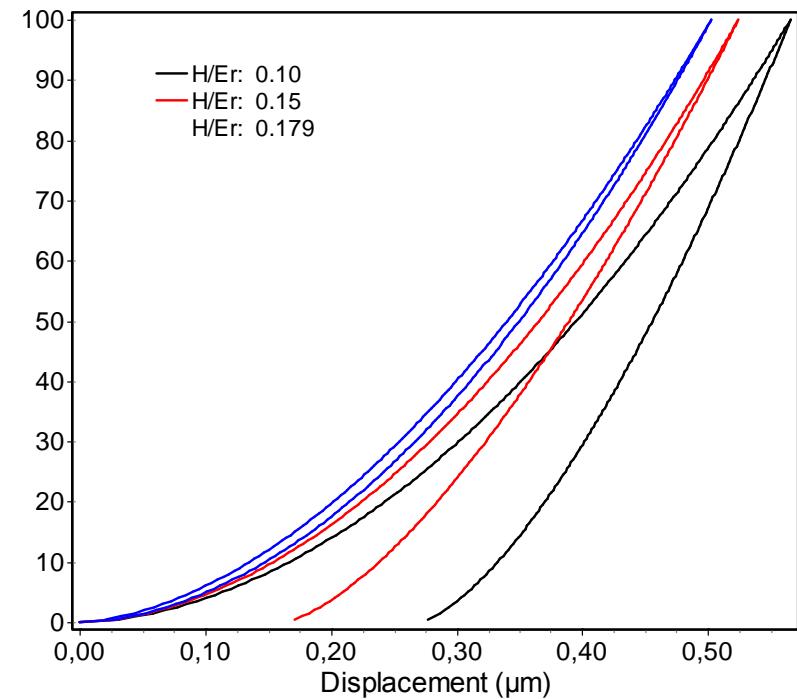
for Berkovitch and Vickers

Examples: Fused silica: $H/E_r = 0.14$

DLC $H/E_r = 0.10$

CrN $H/E_r = 0.07$

Steel $H/E_r = 0.01 \dots 0.05$

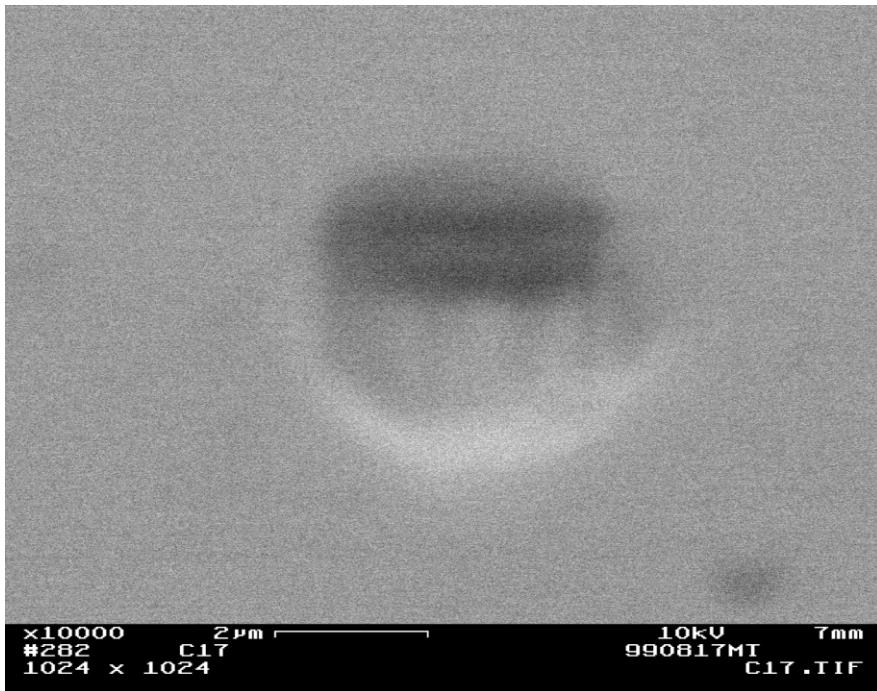


Seen in this conference: $H = 50 \text{ GPa} / E = 300 \text{ GPa} \rightarrow H/E_r = 0.197 \quad (E_r = 254 \text{ GPa})$
 \rightarrow Not possible

Yield strength

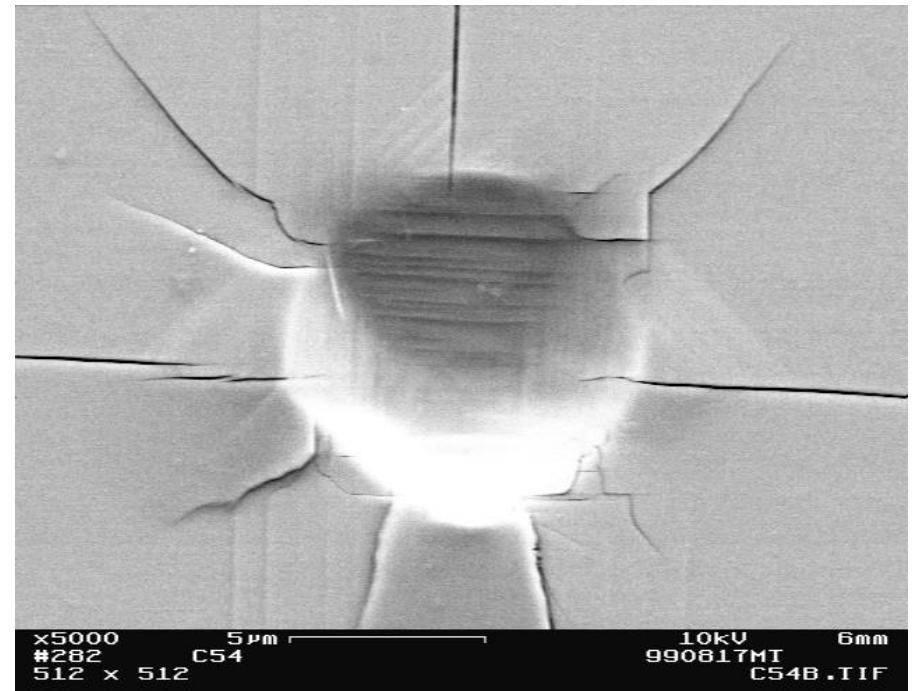
Can we measure the yield strength of hard and brittle materials?

Yes, it is a question of dimension!



small load

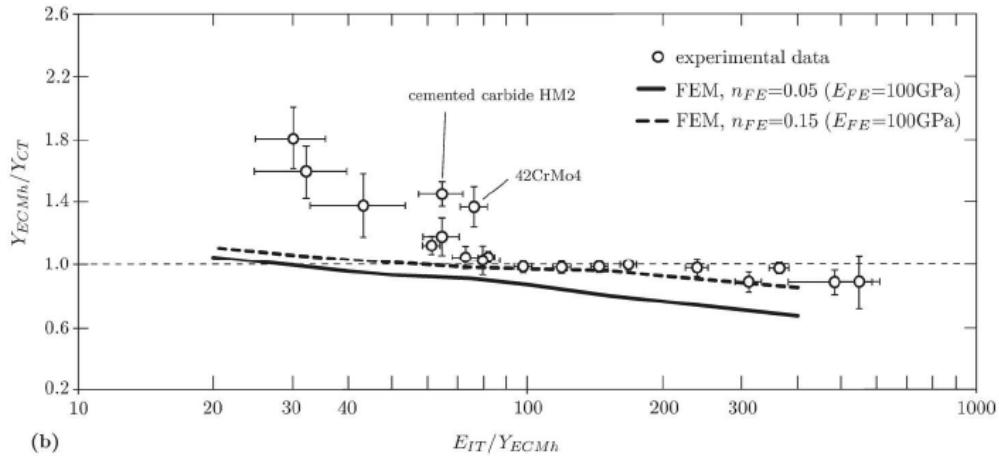
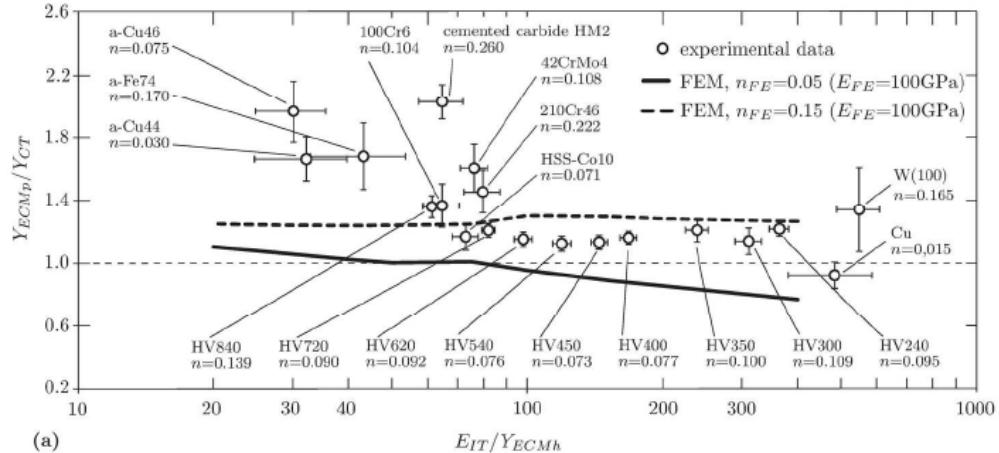
$4\mu m$ radius indenter in GaAs



higher load

Yield strength determination

Quantitative: Yes
local



Clausner, Richter, JMR 2014, accepted for publication

Tabor relation for metals

[D. Tabor, The hardness of metals, Oxford University Press (1951)]

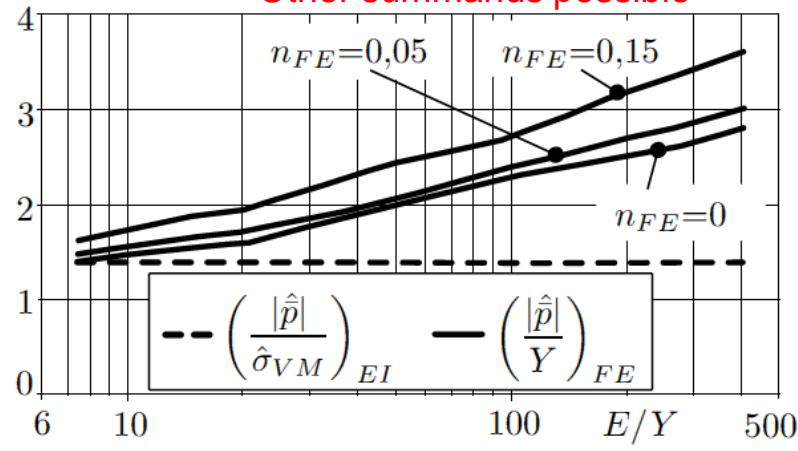
$$H = 3Y$$

Expanding cavity model of Marsh

[D. M. Marsh, Proc. Roy. Soc. A279 (1964) 420]

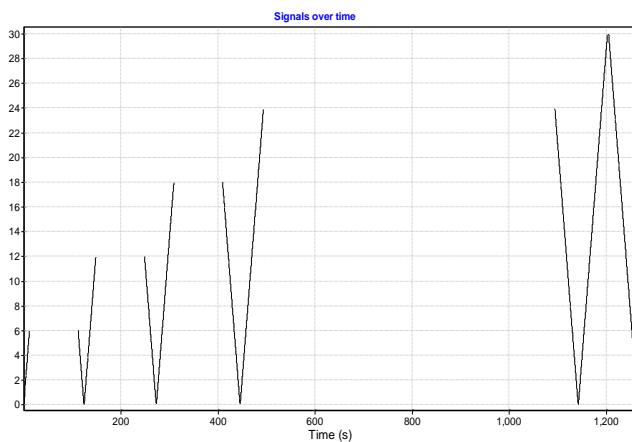
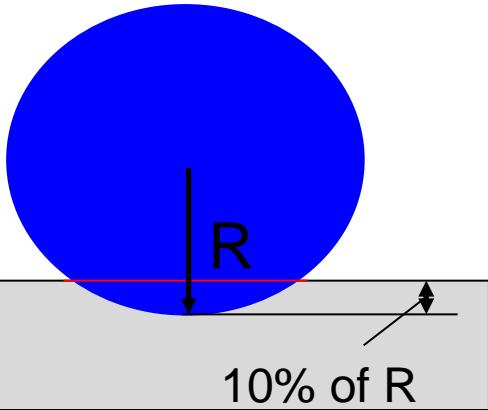
$$\frac{H}{Y} = 1.25 + \frac{2}{3} \ln \left(\frac{1}{3} \frac{E}{Y} \tan \beta \right)$$

Other summands possible

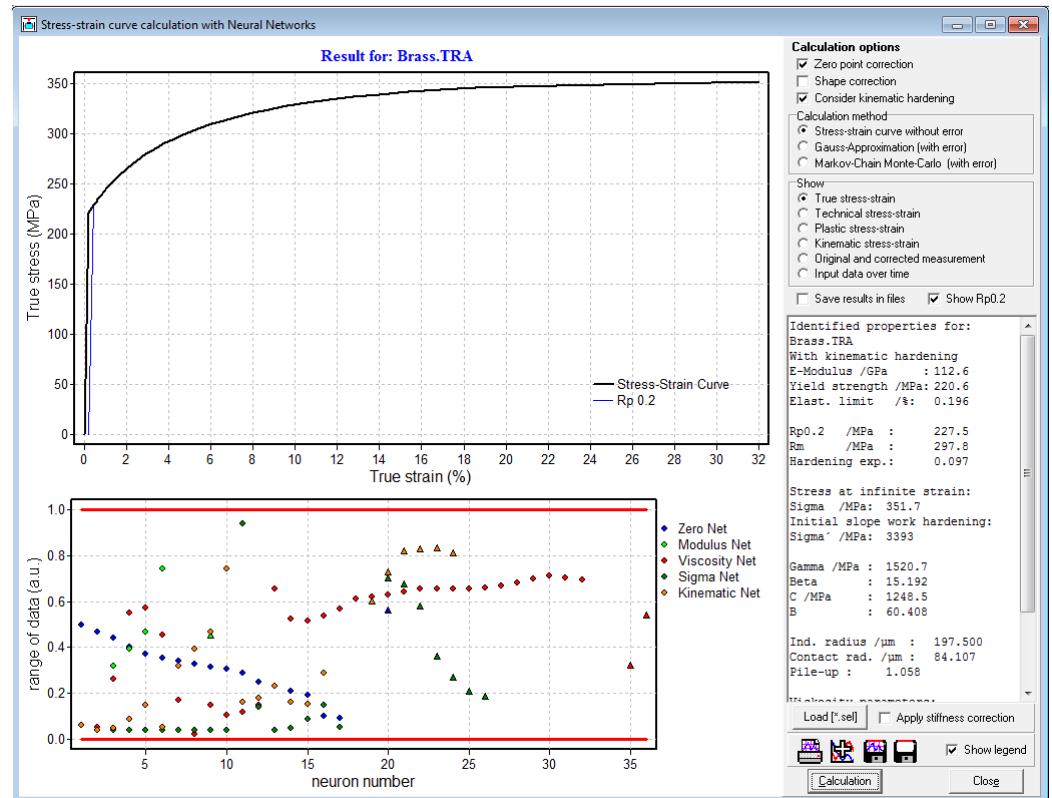


Stress strain curve determination with spherical indenter and neural network

Quantitative: Yes
local



$$\sigma(\varepsilon_p) = k_0 + \frac{\gamma}{\beta} \left(1 - e^{-\beta\varepsilon_p}\right) + \frac{3c}{2b} \left(1 - e^{-b\varepsilon_p}\right)$$



In the model the stress consists of 3 terms.
first term k_0 is the yield stress
second term the isotropic hardening
third term the kinematic hardening

Brittle behavior

Fracture toughness
Tensile strength

Fracture toughness estimation from indentation tests

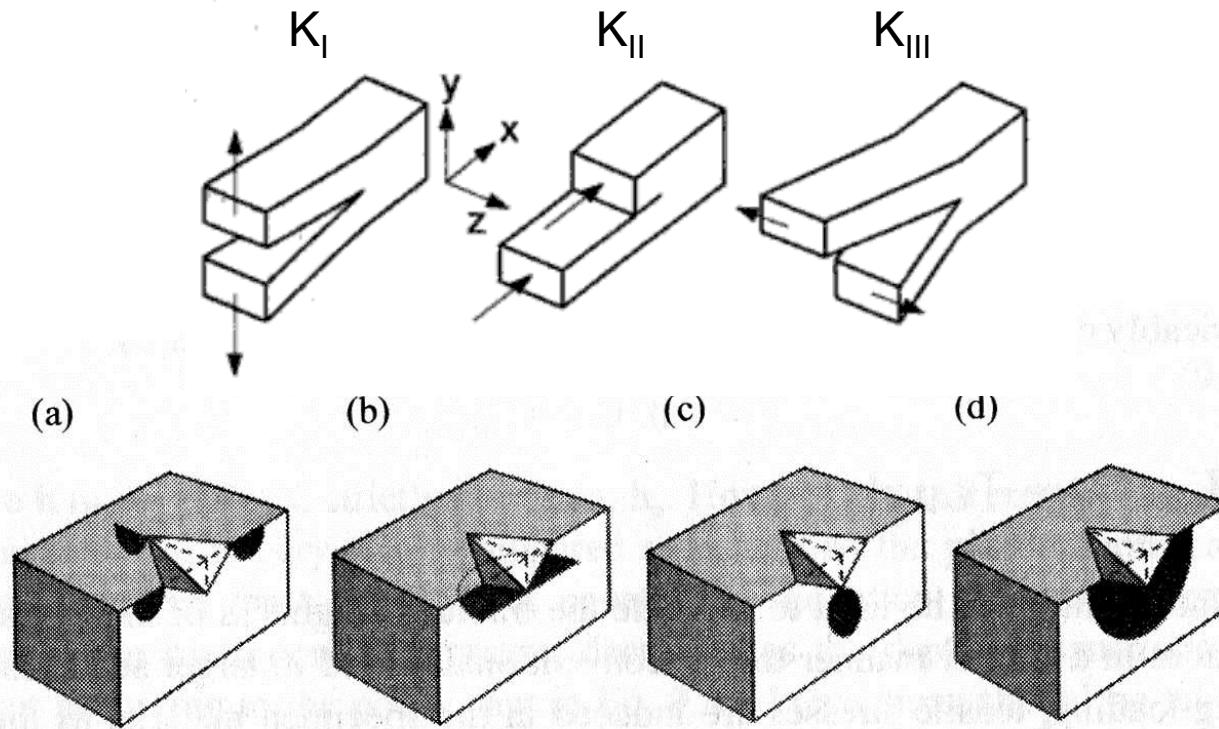


Fig. 9.2 Crack systems for Vickers indenter: (a) radial cracks, (b) lateral cracks, (c) median cracks, (d) half-penny cracks (after reference 13).

(a) Also known as Palmquist cracks

Image from: A.C. Fischer-Cripps, Nanoindentation, Springer

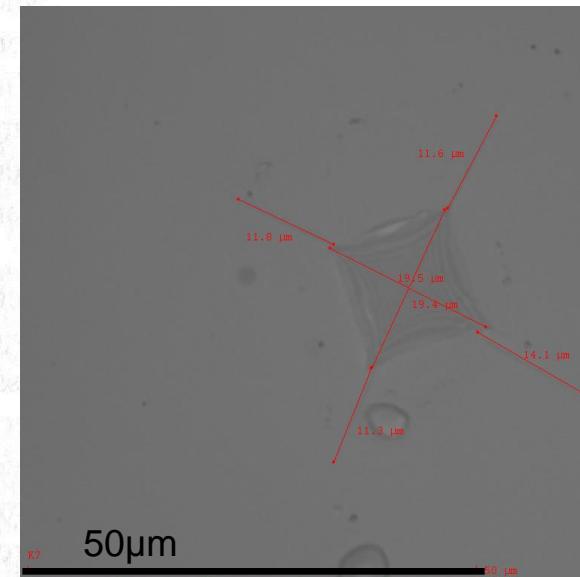
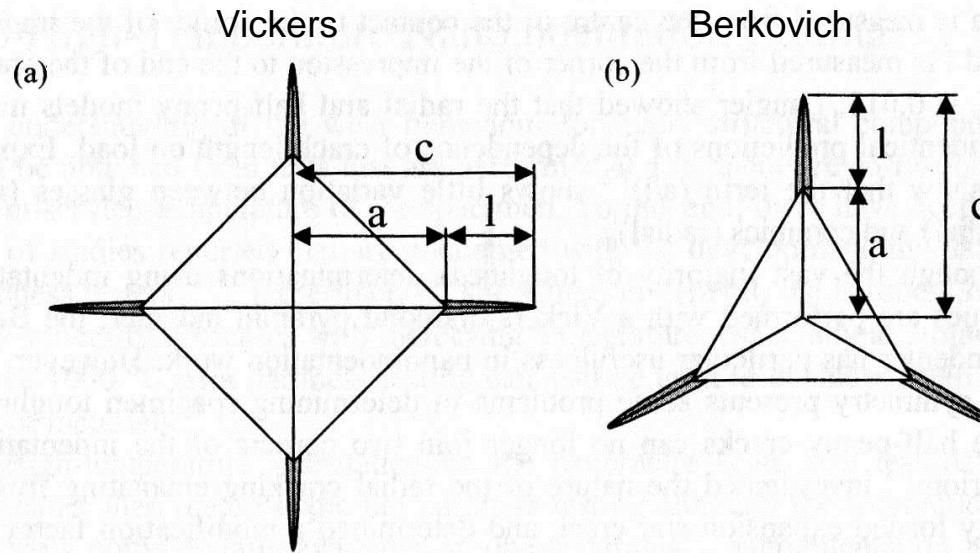


Fig. 9.3 Crack parameters for Vickers and Berkovich indenters. Crack length c is measured from the center of contact to end of crack at the specimen surface (After reference 13).

Image from: A.C. Fischer-Cripps, Nanoindentation, Springer

For $c/a > 2.5$ Median crack shall form

$$\text{Median } K_C = 0.016 \cdot \left(\frac{E}{H} \right)^{0.5} \cdot \frac{F}{c^{1.5}} \quad c = a + l$$

$$\text{Median } K_C = 0.015 \cdot \left(\frac{a}{l} \right)^{0.5} \cdot \left(\frac{E}{H} \right)^{2/3} \cdot \frac{F}{c^{1.5}}$$

F - Force Factor	Vickers	Cube corner
0.016		0.032
0.015		0.016

Palmquist crack: $I \propto F$
Median crack: $c \propto F^{2/3}$

Fracture toughness from indentation using sharp tips

$$K_c = 0.087 \cdot \left(\frac{E}{H} \right)^{2/3} \cdot (\cot \phi)^{2/3} \cdot \frac{F}{c^{2/3}}$$

Half opening angle Vickers: 68° Cube Coner: 35°

Quantitative: partially
Local

1.5 N indents with Vickers indenter into:

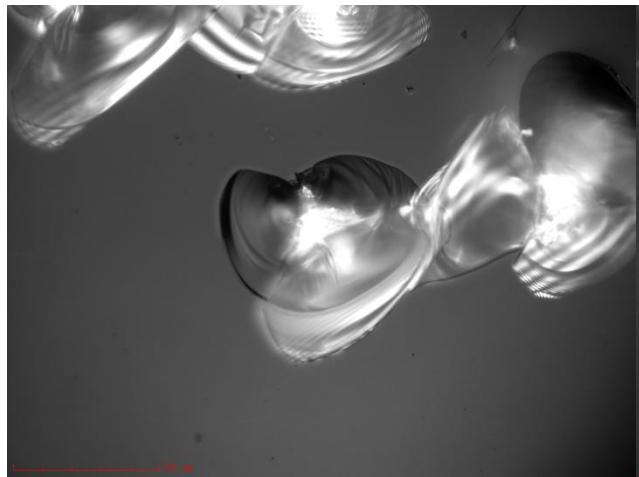
Fused silica

K7 glass

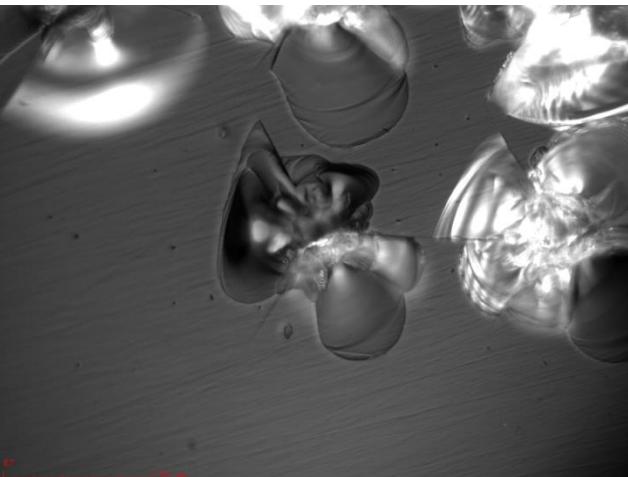
BK7 glass

10µm

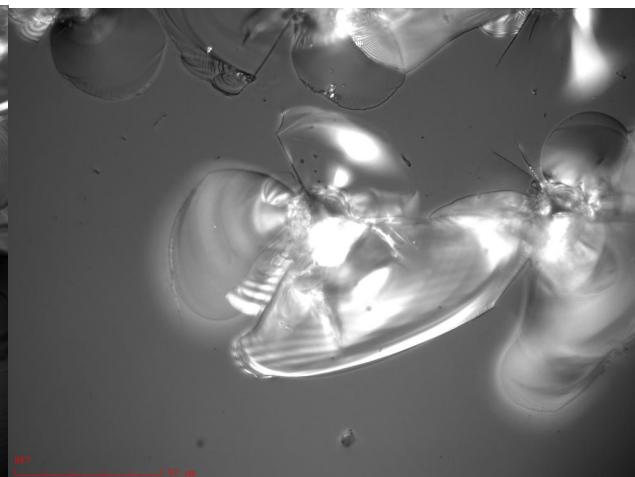
Cube corner 1.5N: Silica



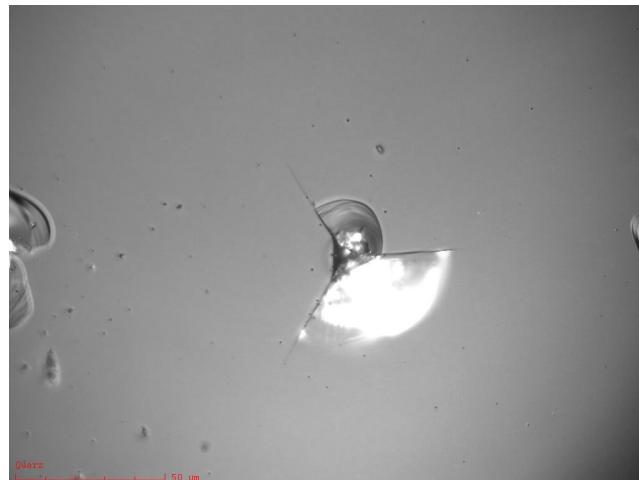
K7



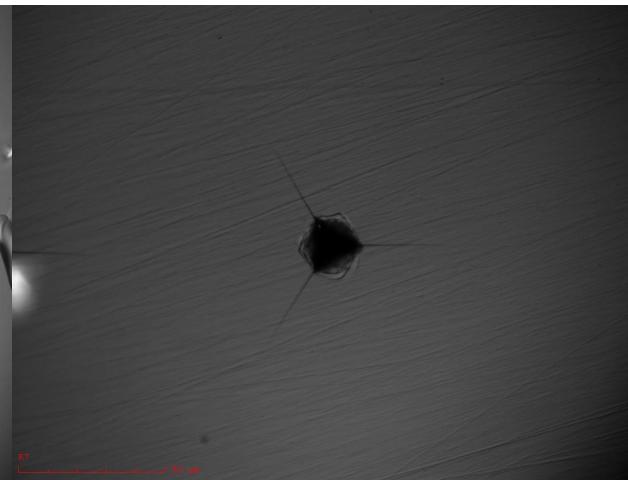
BK7



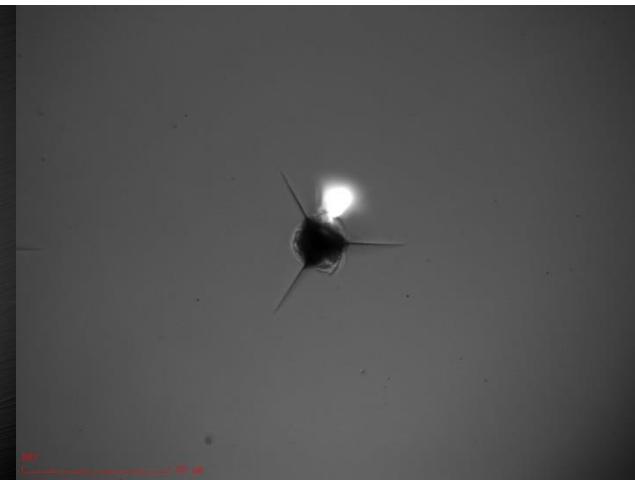
Cube corner 1.0N: Silica



K7



BK7



Parameter	FS	K7	BK7
H / GPa	9.3	5.7	7.4
E / GPa	72	69	82
Poisson's ratio	0.17	0.214	0.206
Klc Literature	0.75	0.95	0.82
Fracture toughness MPa*m ^{1/2}			
Kc (Eq. 1) Vickers	1.4	0.60	0.84
Kc (Eq. 1) Berkovich	0.71	0.56	0.95
Kc (Eq. 2) Vickers	2.0	0.6	0.8
Kc (Eq. 2) Berkovich	0.4	0.4	0.9
Kc (Eq. 3) Vickers	4.6	0.8	1.1
Kc (Eq. 3) Berkovich	0.4	0.4	0.9
Kc (Eq. 4) Vickers	0.6	0.4	0.5
Kc (Eq. 4) Berkovich	0.4	0.5	0.7
Mean	0.50	0.56	0.84

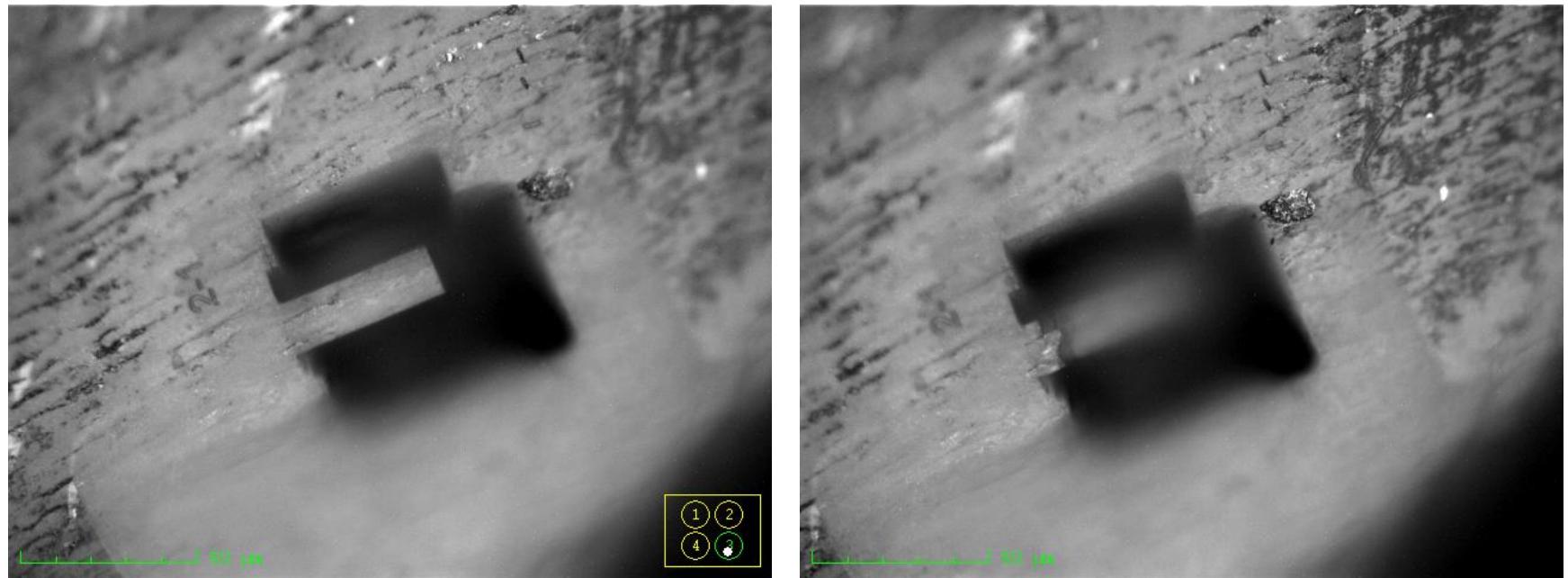
Mean without blue numbers

- It is possible to determine fracture toughness data from Vickers or cube corner indentations in the micro range
- Results depend on indenter type
- Accuracy decreases with decreasing indent size
- High load indents with cube corner indenter result in severe crack formation.
- For thin coatings the substrate influence has to be considered → quantitative results only in combination with FE modelling

Tensile strength from beam bending experiments in combination with FE calculations

Quantitative: partially
Integral

Quantitative results for coatings only possible in combination with FE modelling

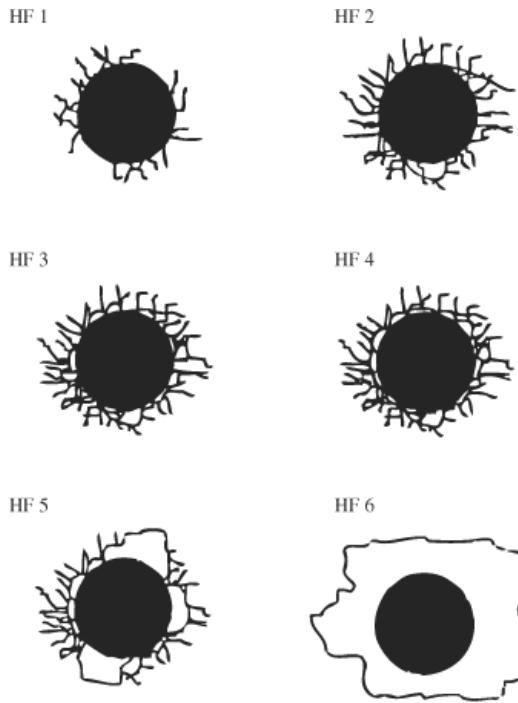
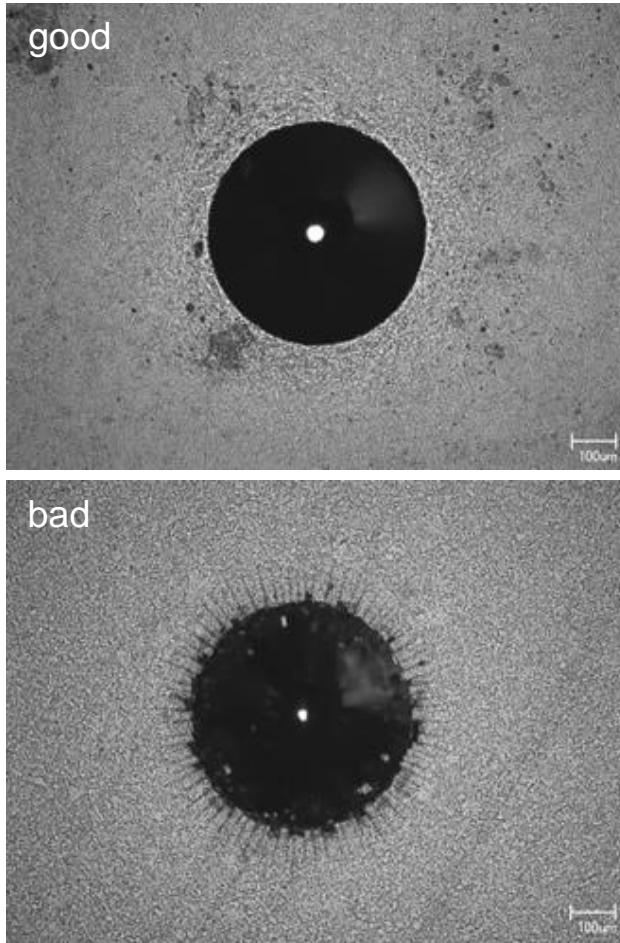


Example: micro beam bending experiment on tooth material

Adhesion

Rockwell adhesion test VDI guideline 3198

Quantitative: No
Local



VDI guideline 3198

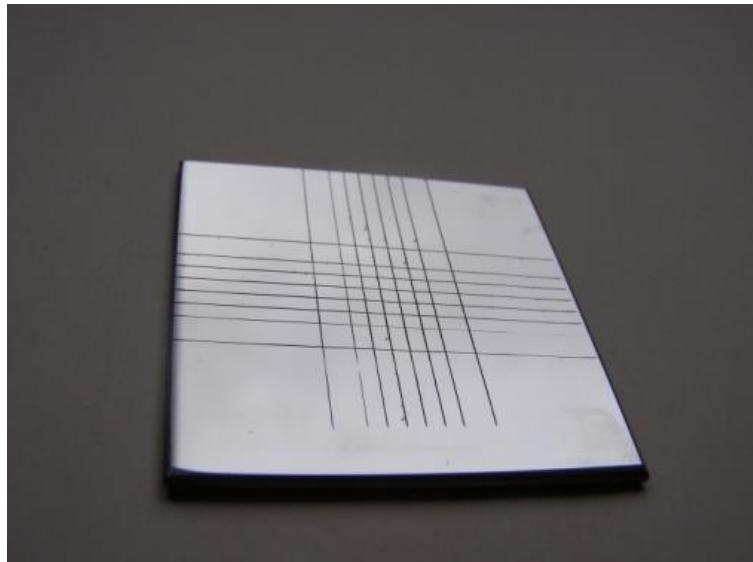
Figure 5. Adhesion strength quality HF 1 to HF 6⁶.

Mat. Res. vol.10 no.3 São Carlos July/Sept. 2007

JAPAN PROXIMO INC.

Cross-cut test
 ISO 2409 (paints and varnishes)
 ISO 9211-4 (optical coatings)

Quantitative: No
Integral



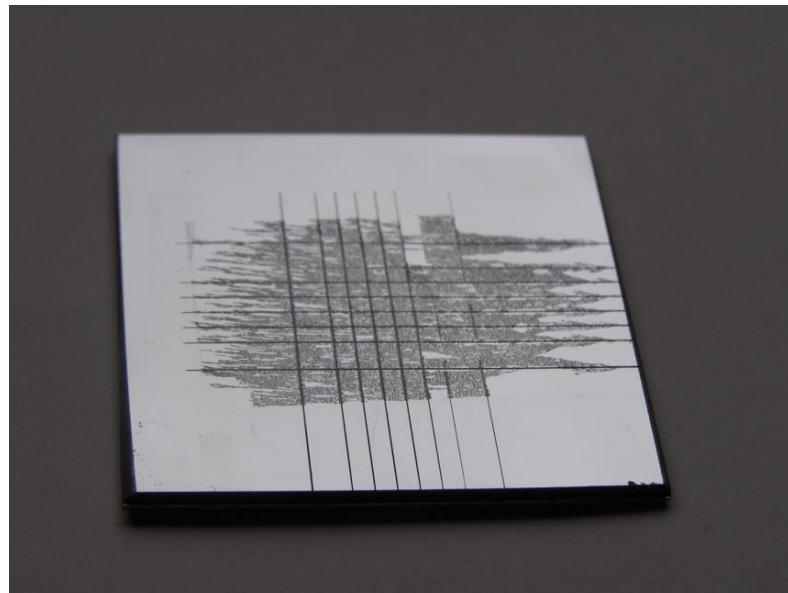
100 nm Cr on PC – passed (class 0)

class	description	pattern
0	no delaminated square, no visible defects	-
1	no delaminated square, small defects at cut- crossings, delaminated area less than 5%	
2	defects at cut-crossings and -lines, delaminated area between 5% and 15%	
3	additional areal defects and/or delaminated squares, delaminated area in between 15 % and 35 %	
4	additional areal defects and/or delaminated squares, delaminated area in between 35 % and 65 %	
5	beyond class 4	-

Courtesy Beck, BAM

Peel test
EN 28510

Quantitative: No
Integral



100 nm Cr on PC

Cross-cut: passed
Peel test: failed

Courtesy Beck, BAM

Peel test for flex-rigid bonded composites
(according to ISO 8510-1)

Peel width: (25 ± 0.5) mm

Testing length: 150 mm

T-sized substrate, 5 samples

90° pull direction for peel vs. 60° pull
direction for cross-cut tests

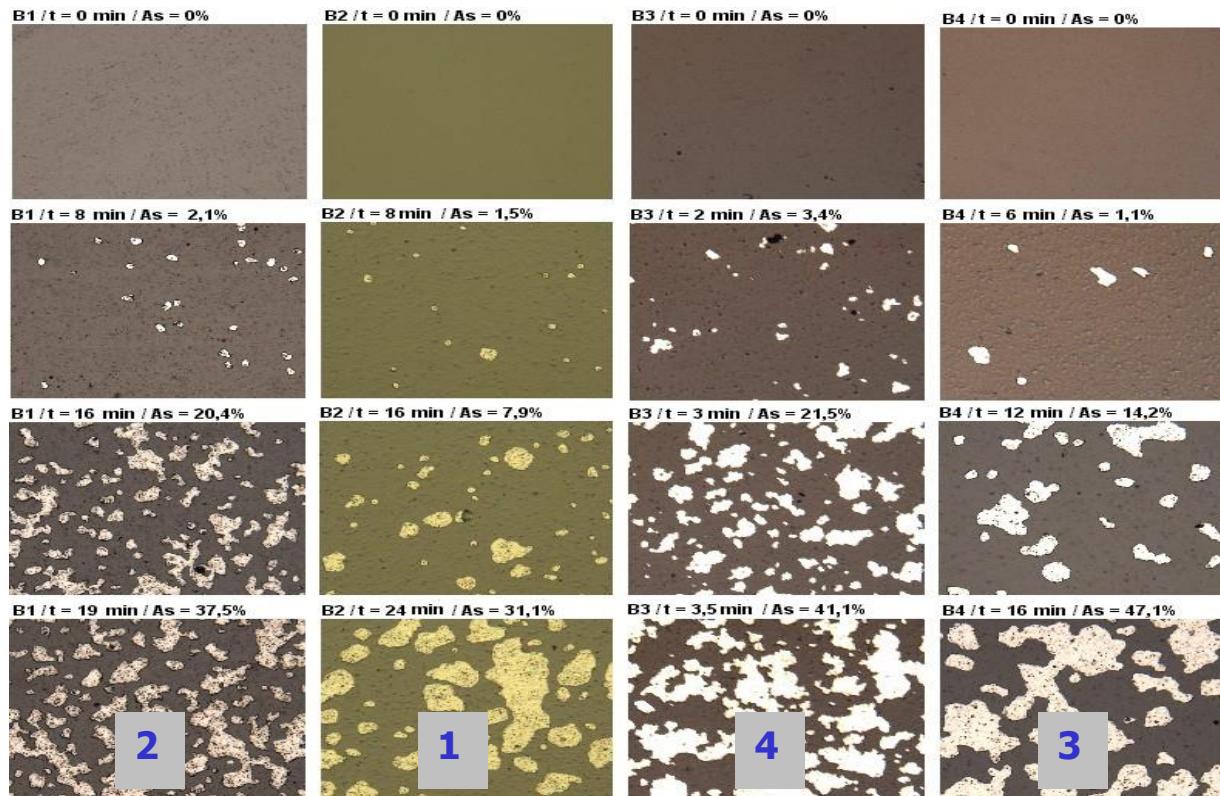
Testing velocity: (50 ± 5) mm/min

Peel force: N/m

Cavitation test ASTM G32

Quantitative: No
Integral

DLC – coatings, different pre-deposition treatment

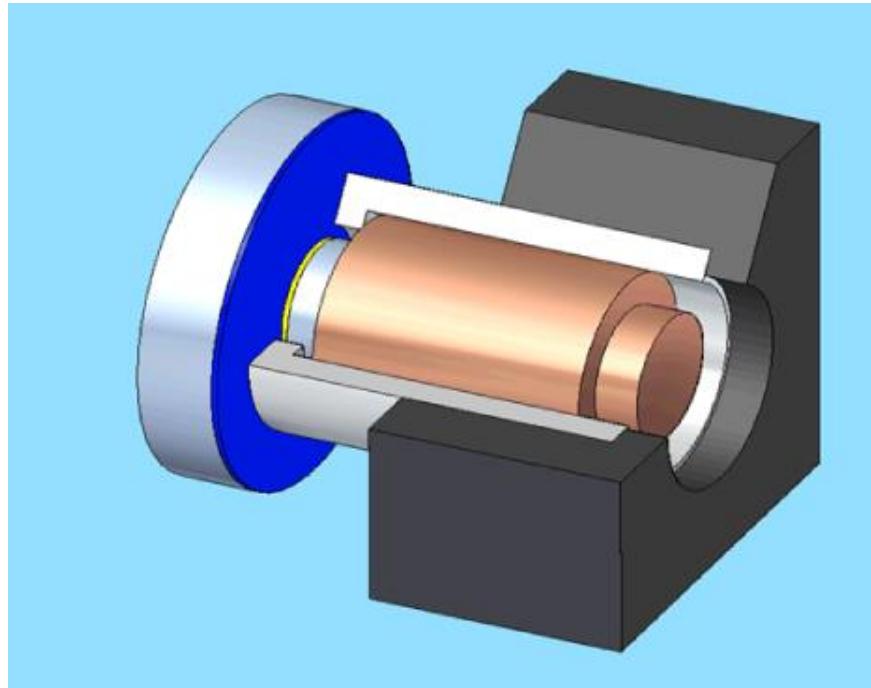


$s = 1 \text{ cm}$, $f = 20 \text{ kHz}$

The cavitation resistance is measured in **s** to reach a distinct degree of coverage (DoC).

Courtesy Beck, BAM

Centrifuge test

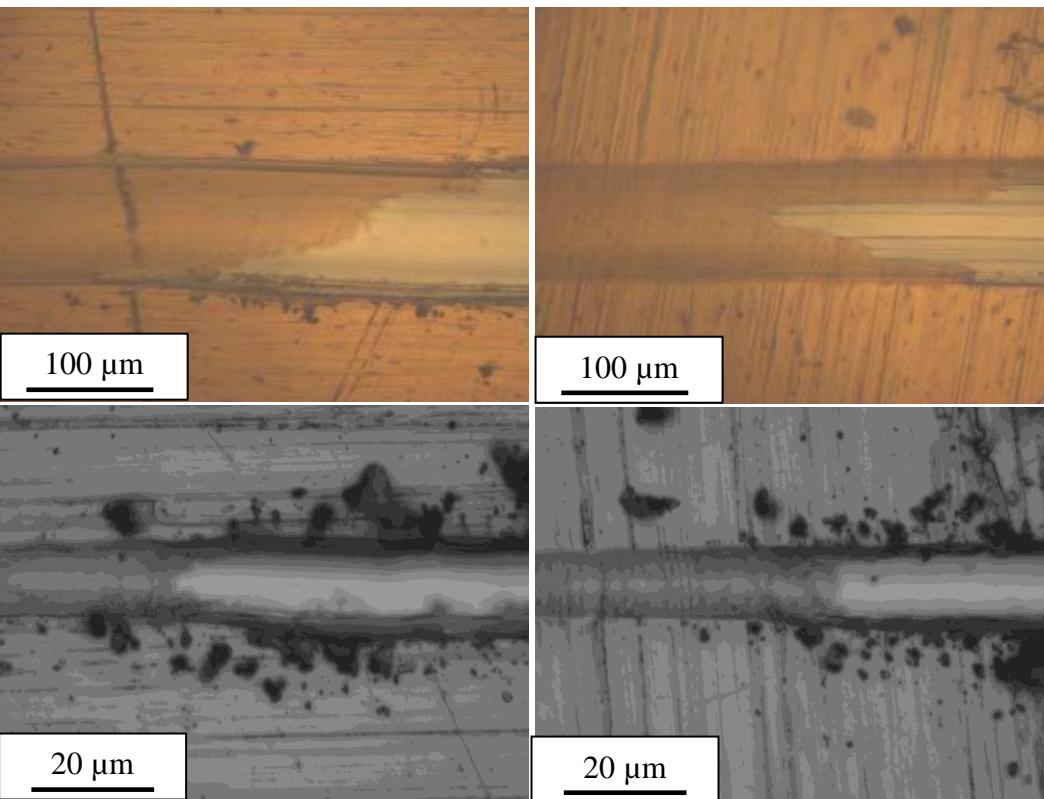


Courtesy Beck, BAM

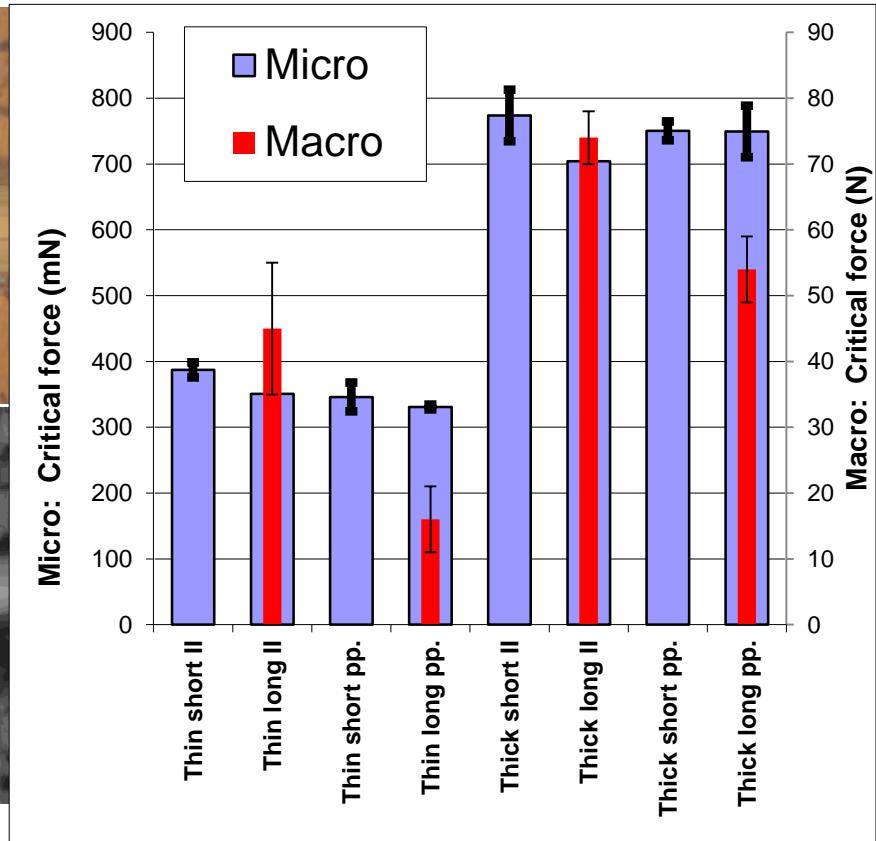
substrate/coating – adhesive – adherend – test stamp – guiding sleeve – testing unit

**Scratch test --- Micro scratch test
EN 1071 none**

**Quantitative: partially
Integral**

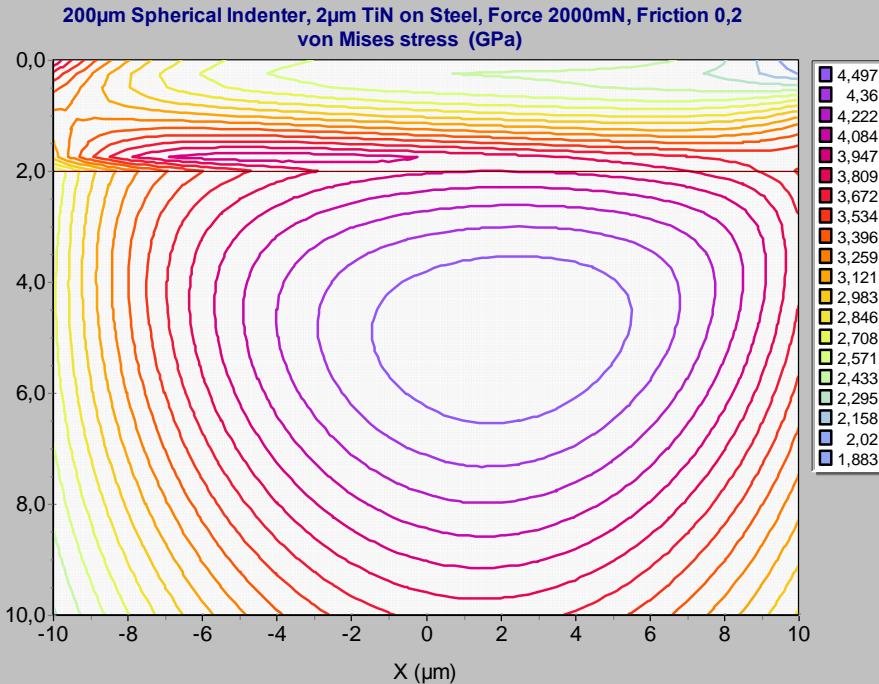


550 nm TiN on steel

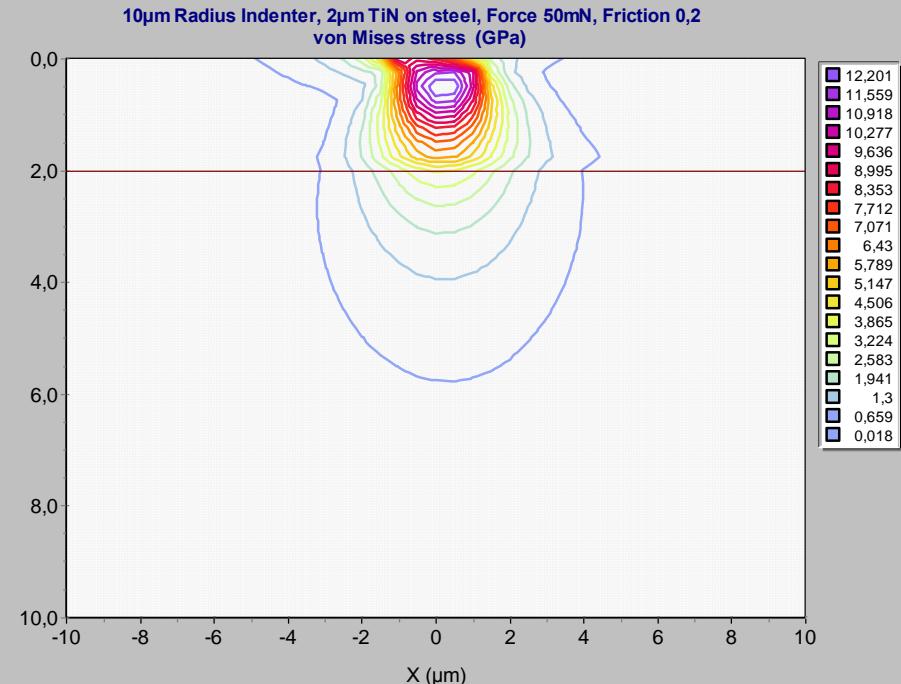


Thin = 550 nm TiN
Thick = 1500 nm TiN

Von Mises stress field in the surface of a $2\mu\text{m}$ thick hard coating on steel for a scratch test with tips of different radius.



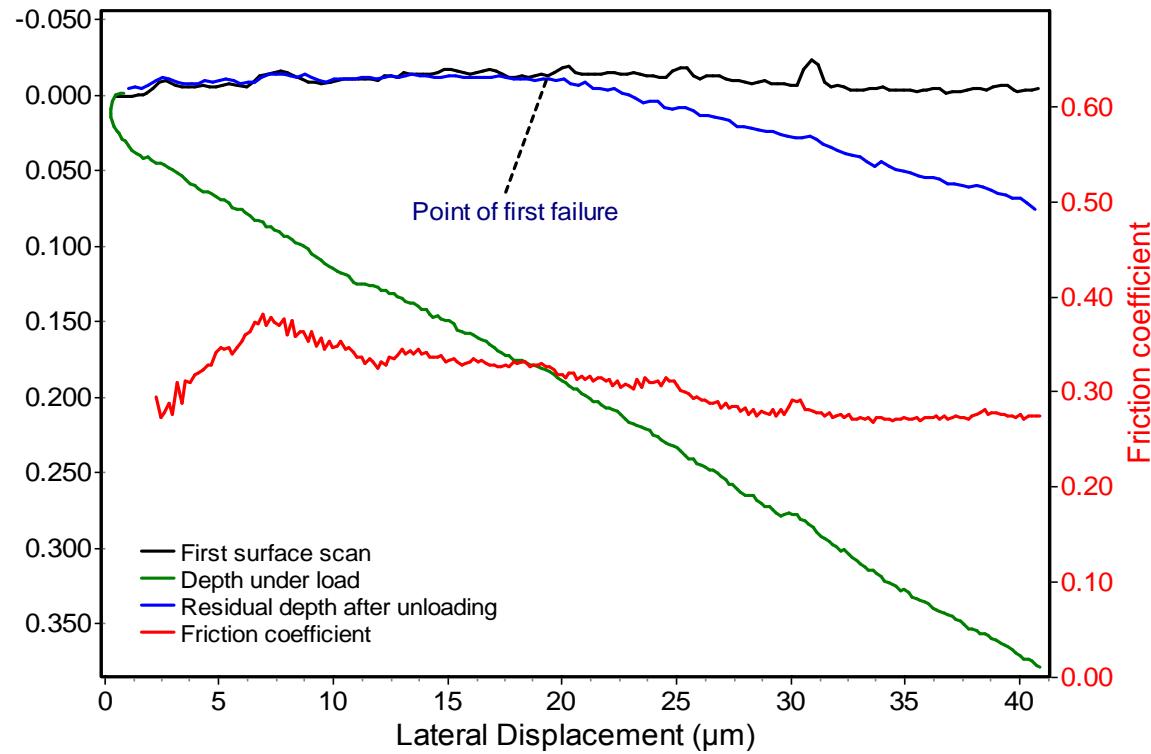
200 μm radius



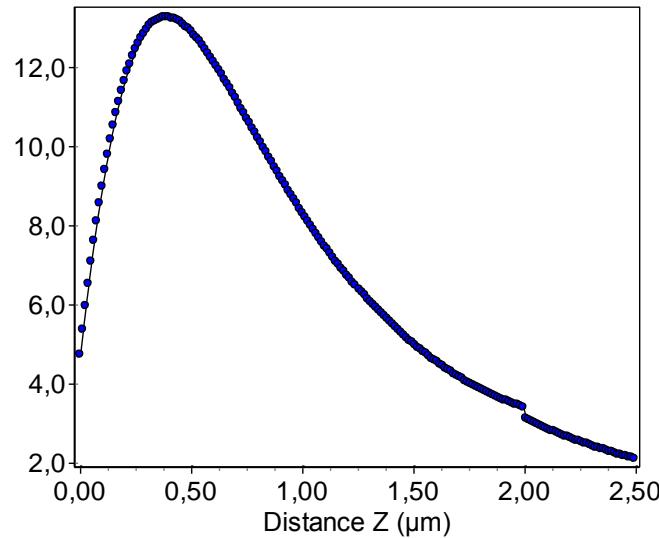
10 μm radius

The first failure of a conventional scratch test occurs normally in the substrate.

Elastic-plastic transition gives yield strength

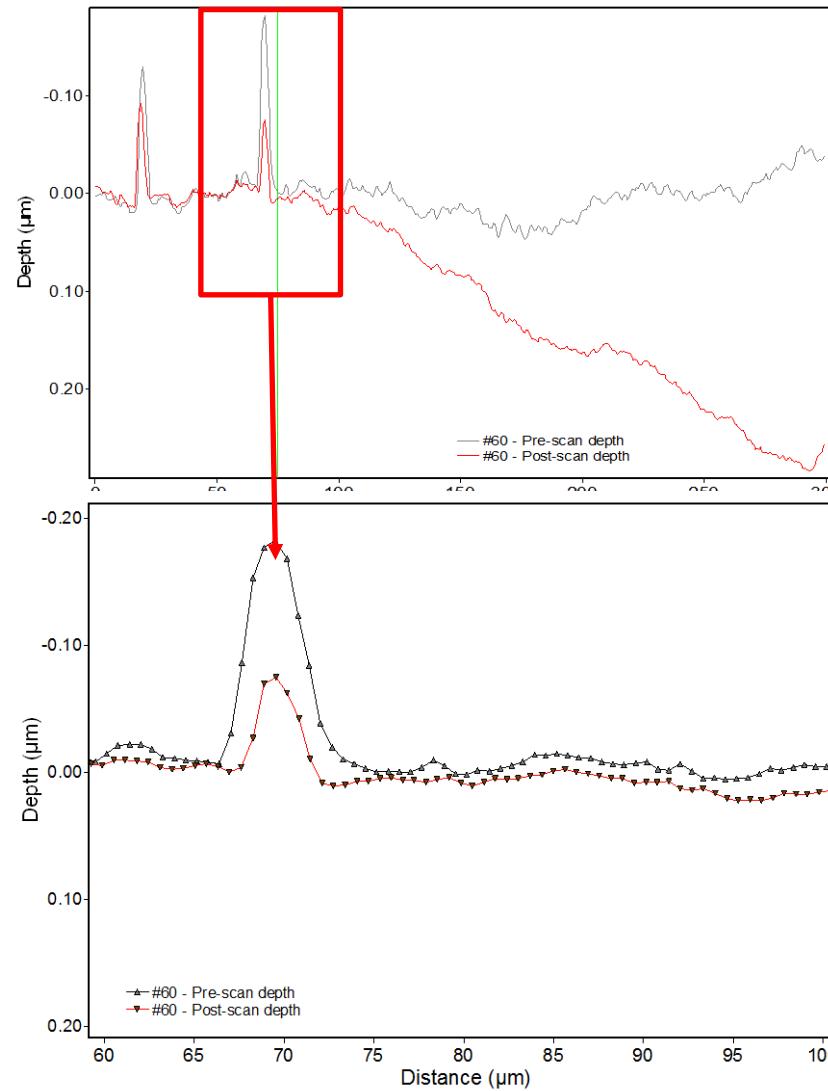
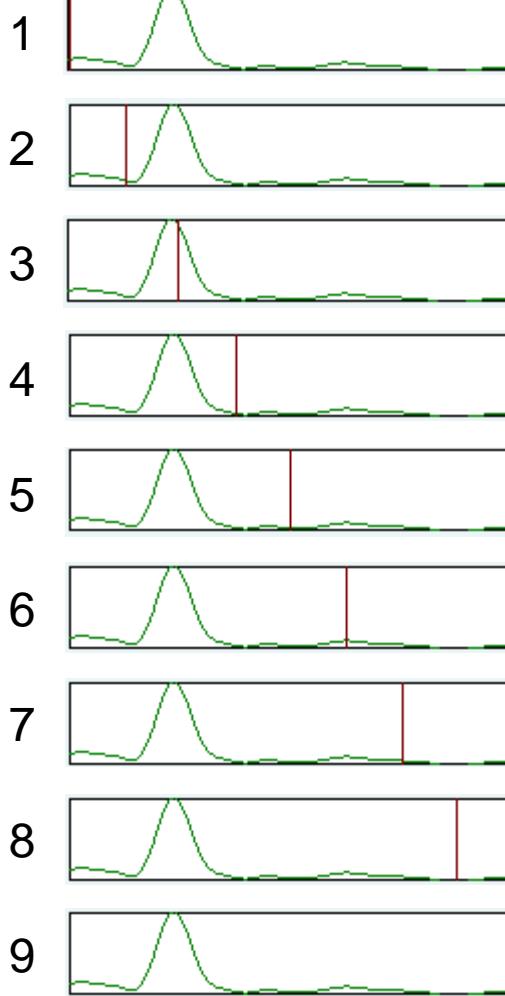


Spherical indenter on substrate with one layer
von Mises stress

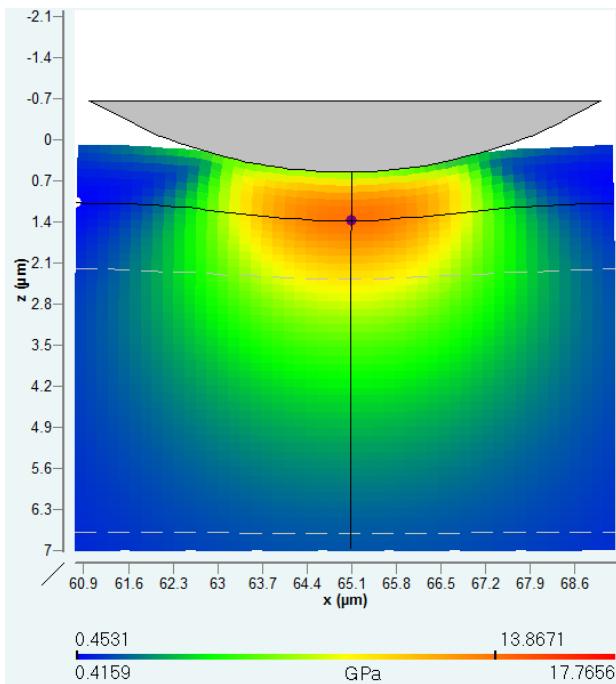


Scratch test with load ramp from 0 mN (left) to 35 mN (right).
The high displacement resolution in both directions allows to detect the point of first failure.

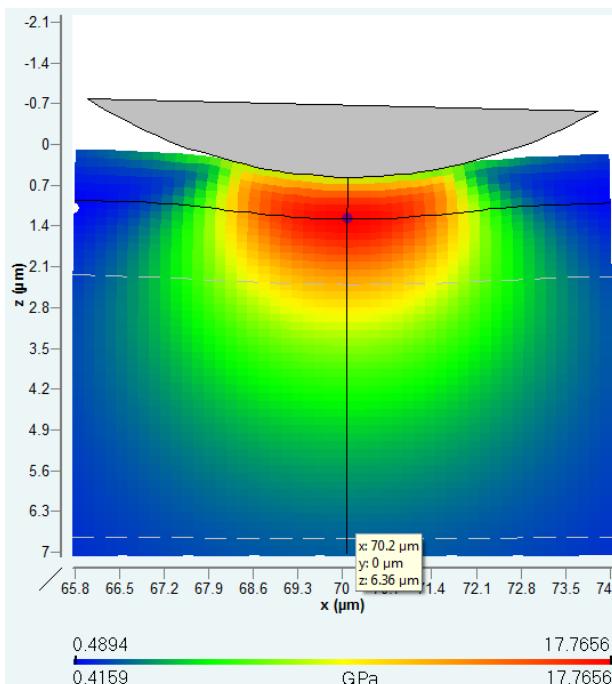
Scratch tests on **a:C:H:W** coatings (DLC) #60 and #62



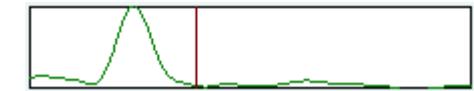
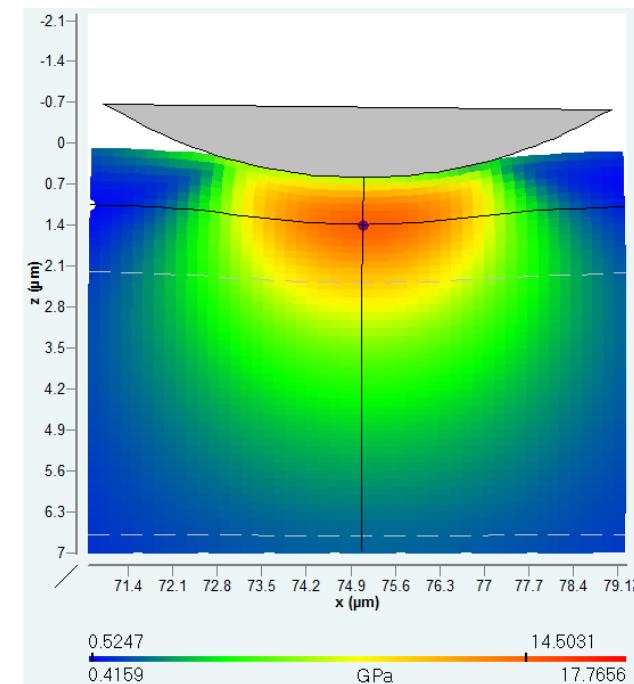
Von Mises stress profile, *FilmDoctor* calculation



180.8mN

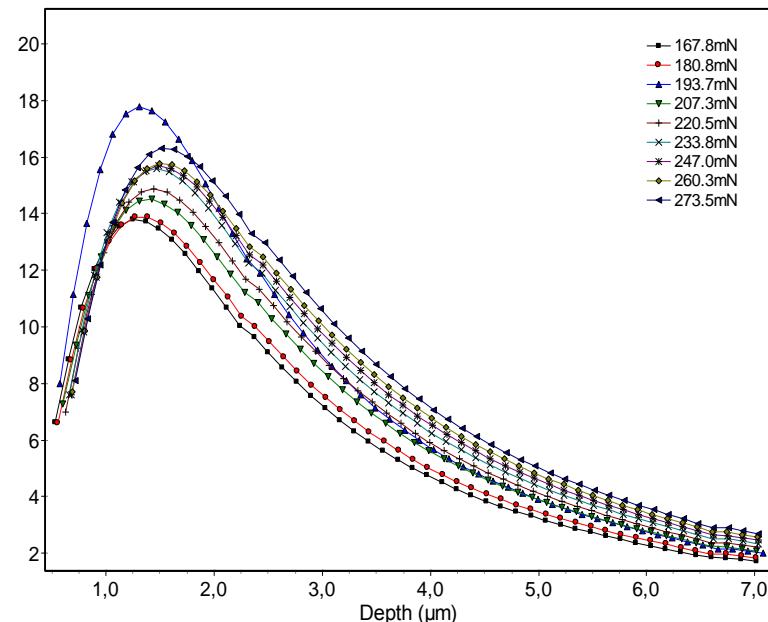
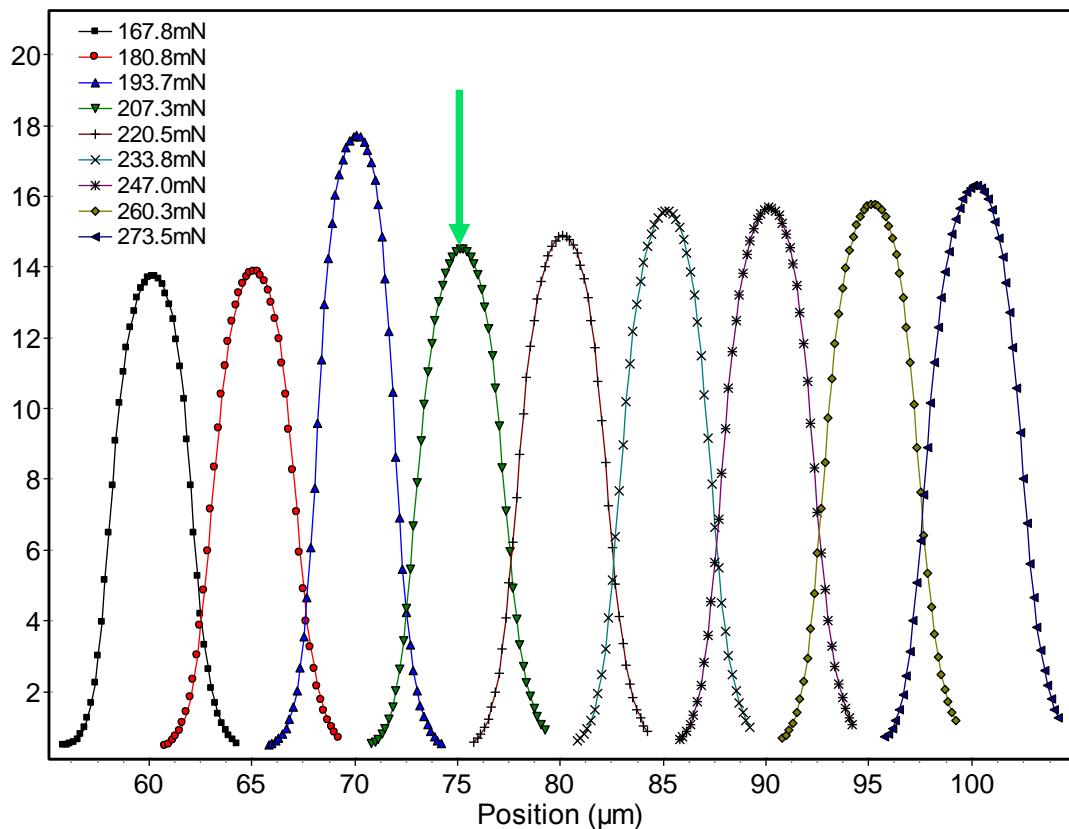


193.7mN

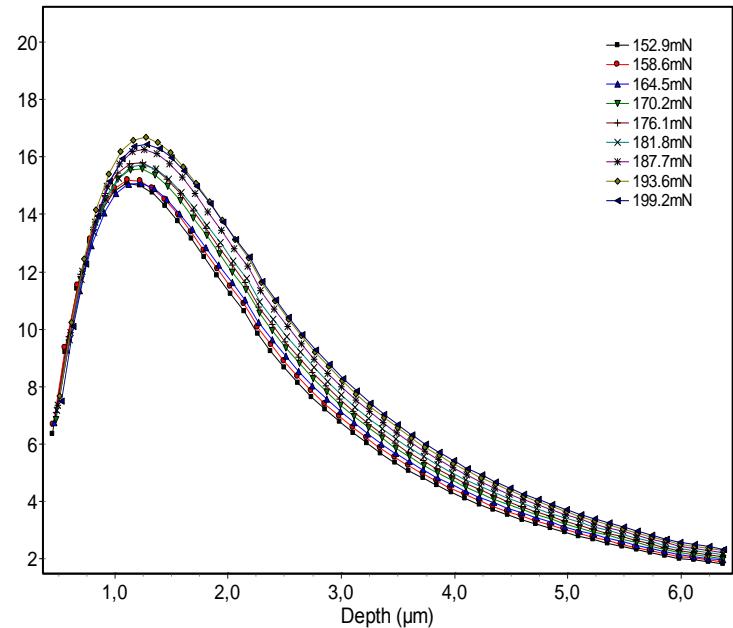
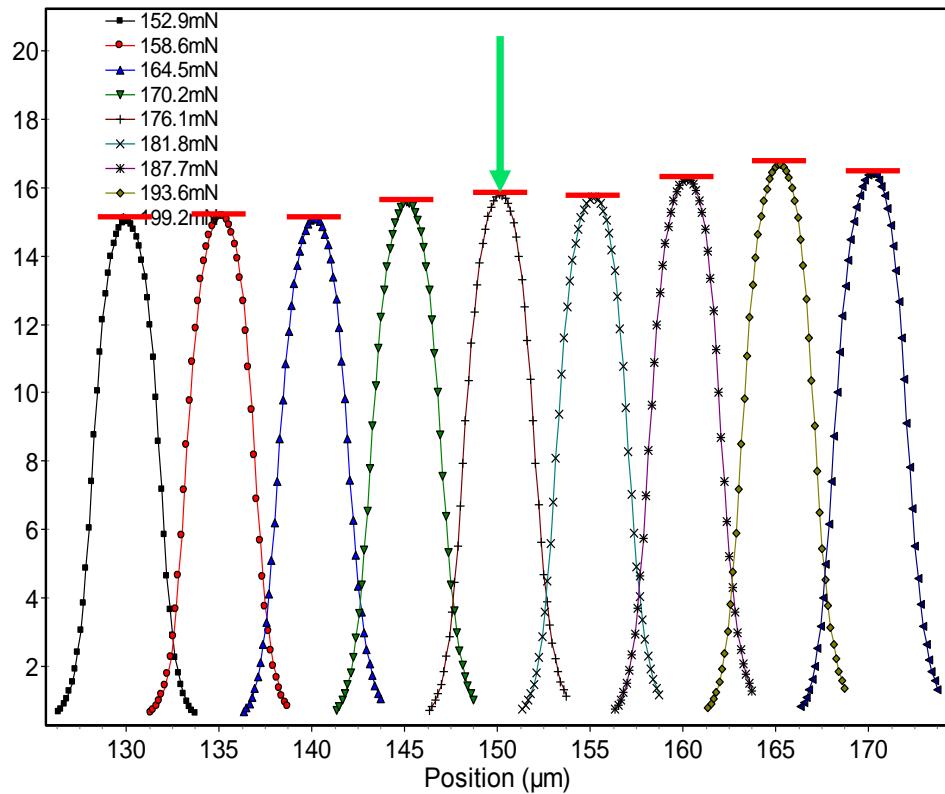


207.3mN

The von Mises stress is considerably higher on top of the peak



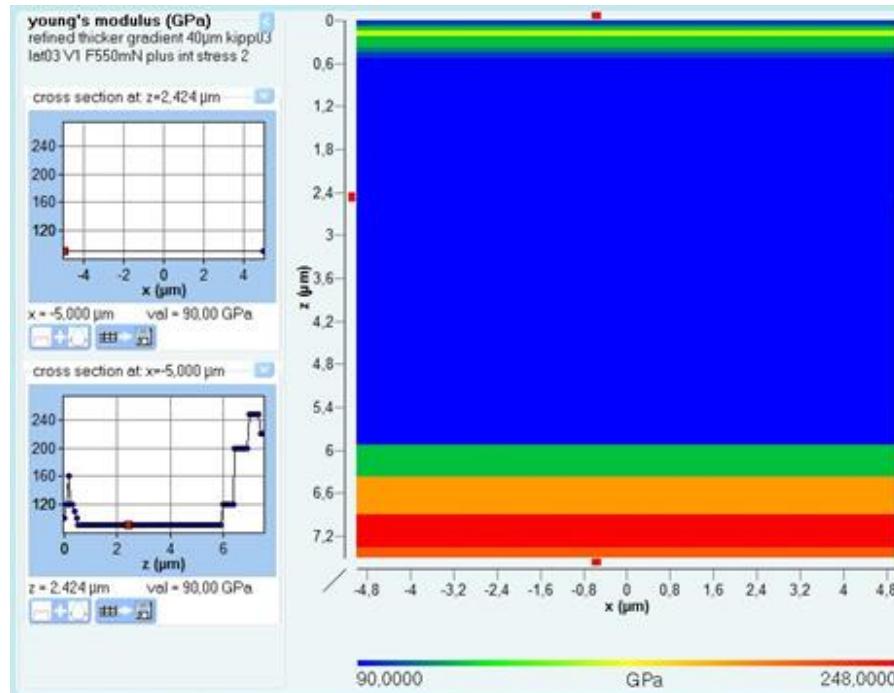
Comparison of stress profiles from different positions



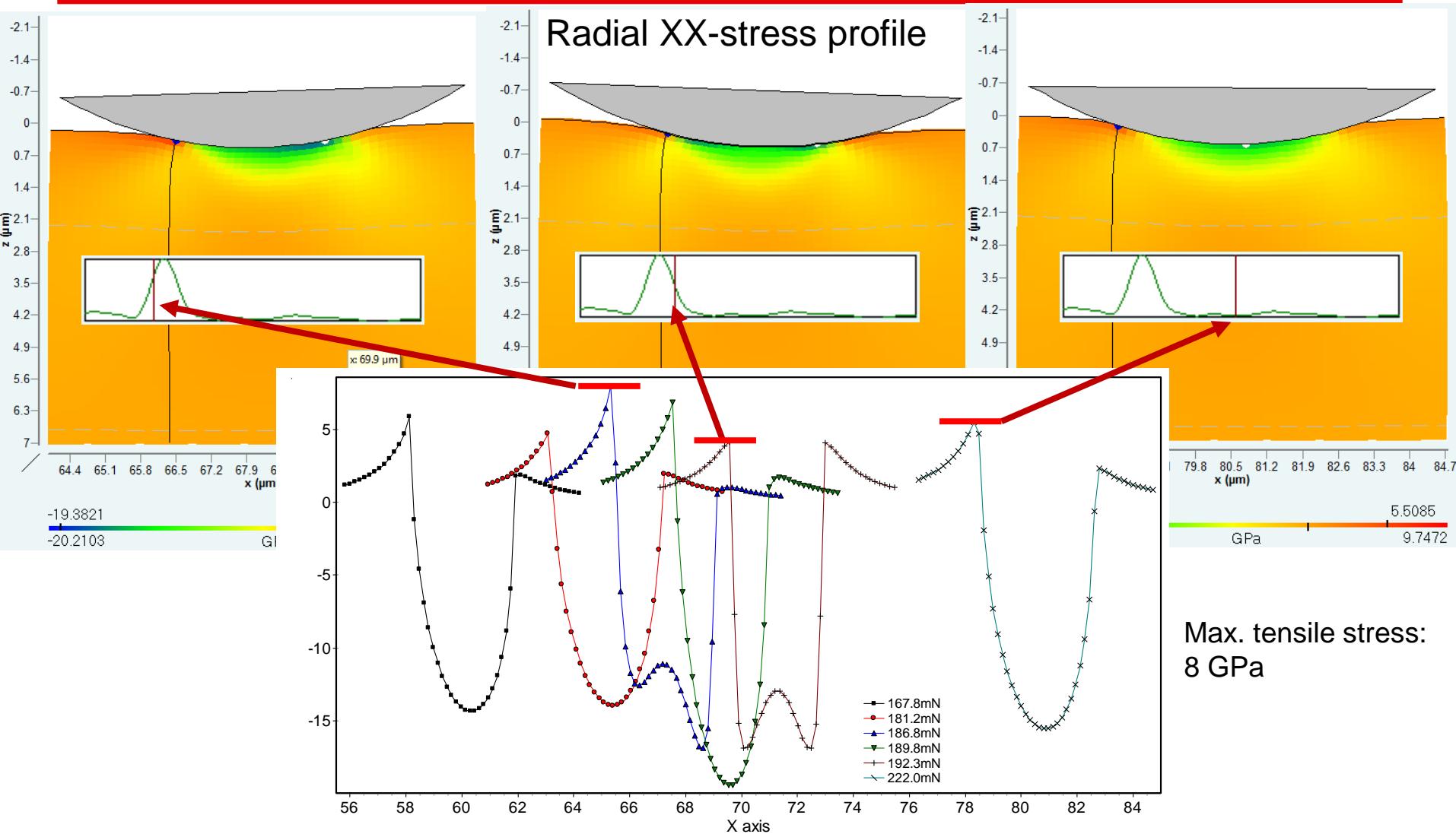
Comparison of stress profiles from different positions
The stress is not steadily increasing with force

Sample	#60	#62
Hardness H	11.3 GPa	14.8 GPa
Critical force	207 mN	176 mN
Yield strength Y	14.5 GPa	15.8 GPa

Sample #60 = gradient coating thickness 6.5µm
 Sample #62 = homogeneous coating thickness 7.8µm



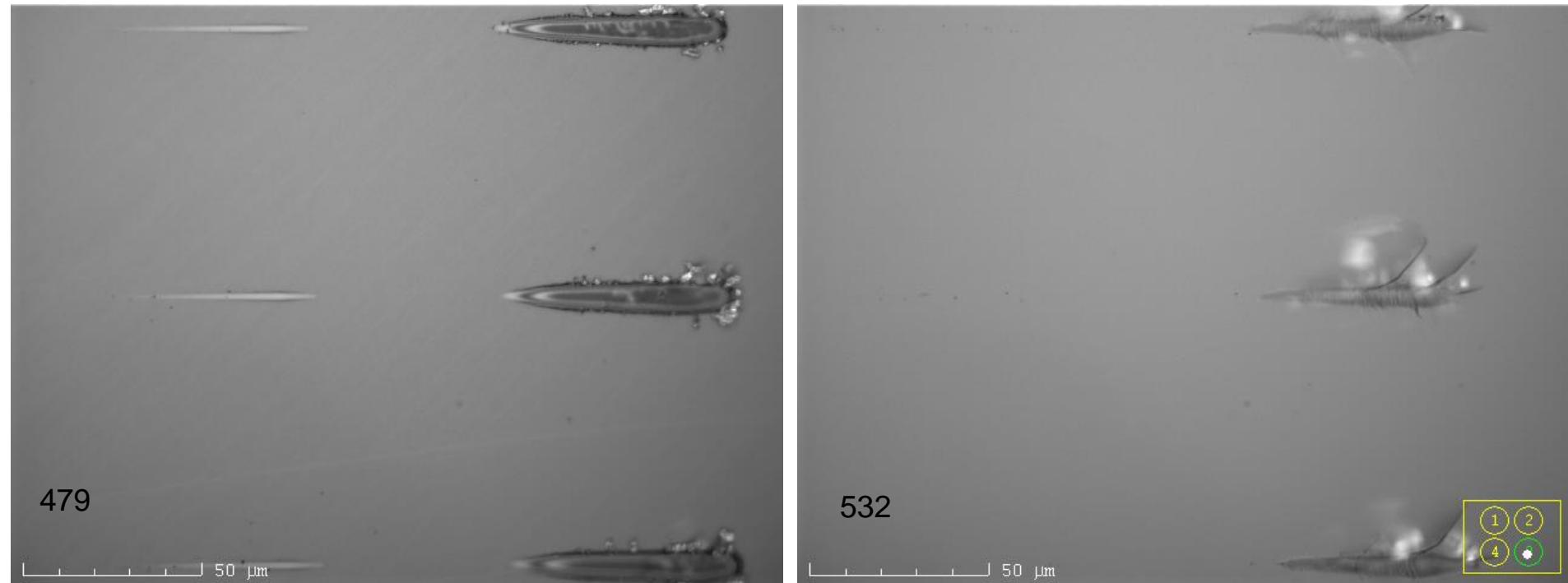
Example for a gradient coating



The tensile stress is considerably higher in regions with increasing surface profile

240 nm thick optical coatings on sapphire

Three 50mN und 700mN micro scratch tests over each other

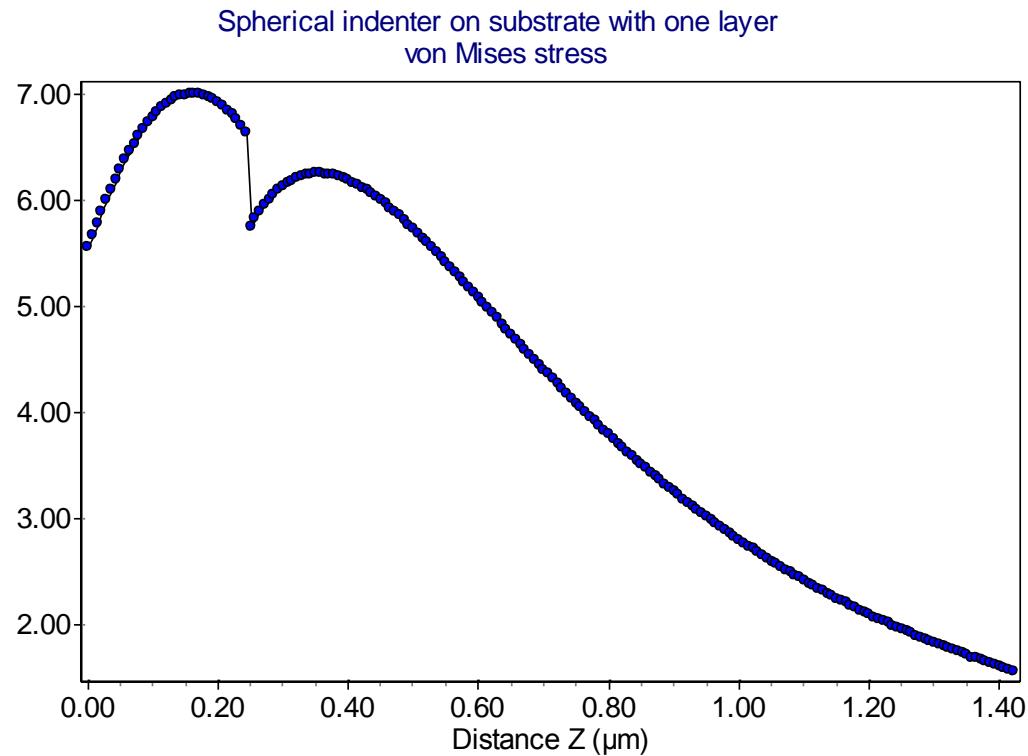


The two coatings show different failure modes

Yielding starts in the coating since the substrate was hard enough for these samples

Yield strength results

Sample number	Fcrit mN	μ	Yield strength GPa
479	6.89	0.061	6.97
486	6.60	0.067	6.5
488	8.30	0.078	7.4
489	8.49	0.088	7.64
531	12.75	0.110	8.79
532	131.79	0.069	20.8
485/sapphire	8.93	0.065	6.31
485 /glass	31.92	0.057	6.25
Sapphire	171.500	0.084	27.7



Von Mises stress profile for sample 479

Frictional and wear behavior

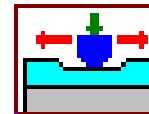
No sample but combinatorial properties

Friction coefficient

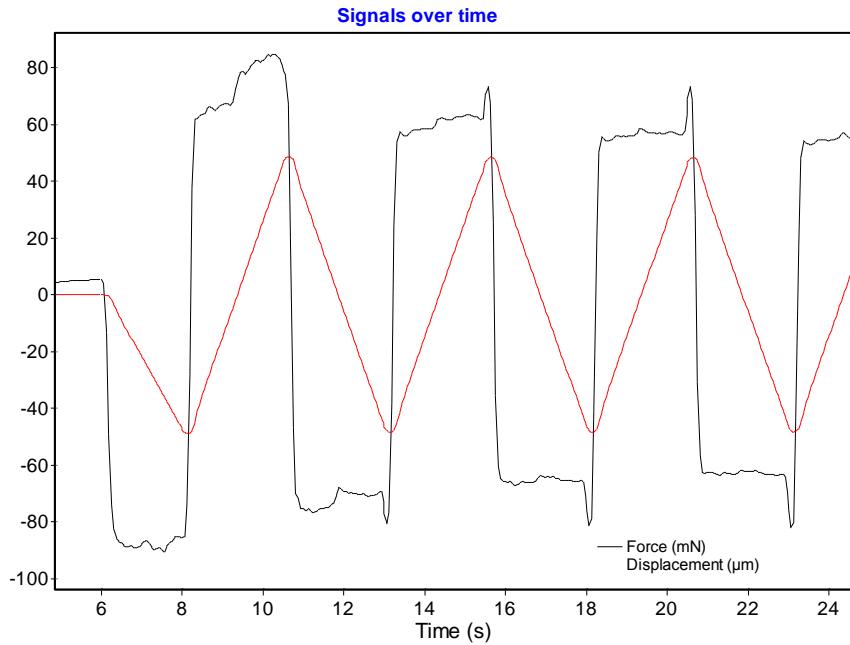
Wear coefficient

Stribeck curve

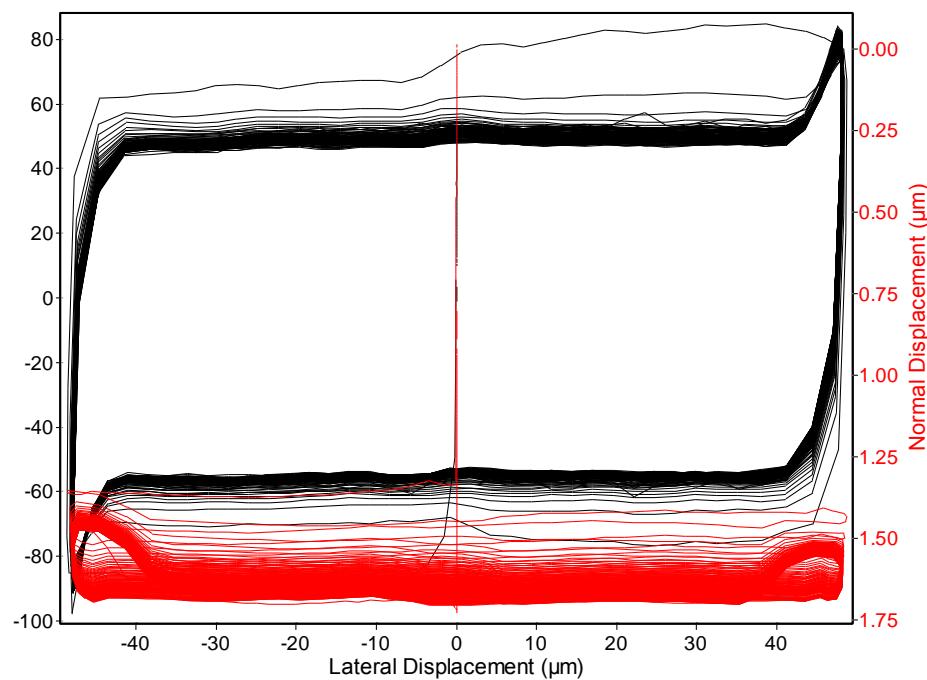
Micro wear test with LFU



Example for DLC on steel, normal force 500mN
Diamond tip with 10 μ m radius



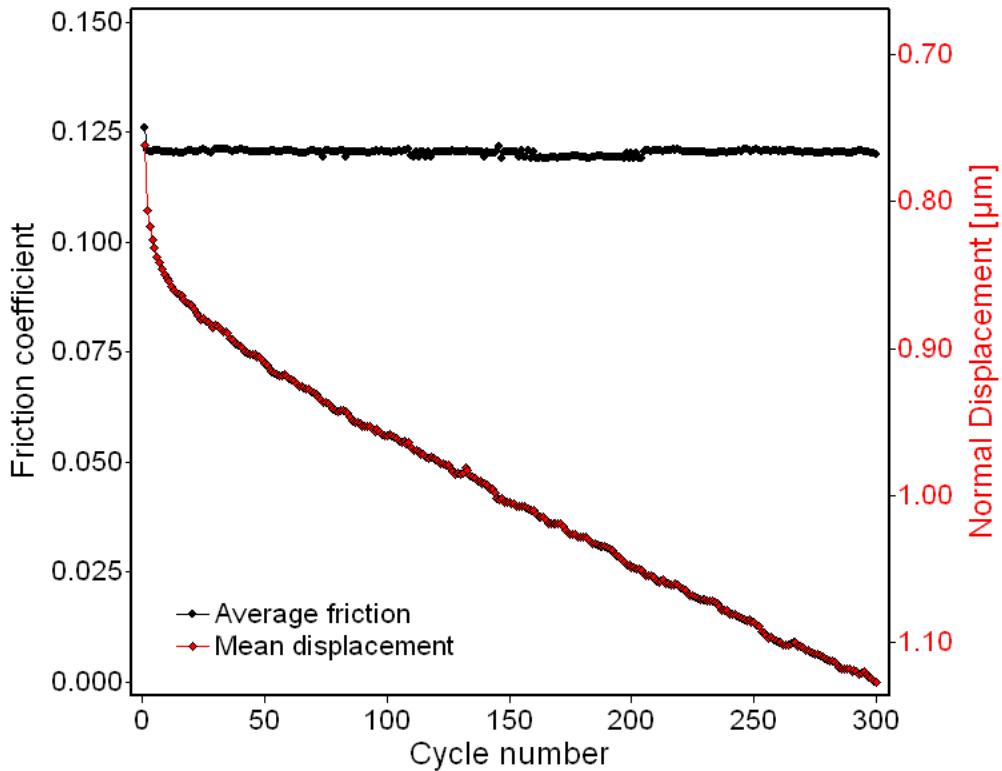
Force and displacement signal of first 3 cycles over time



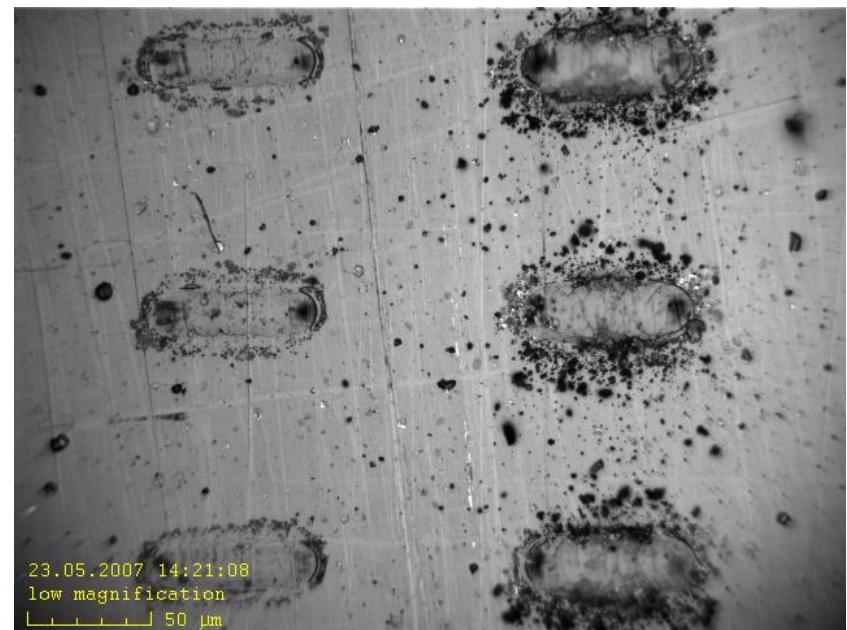
Data from 100cycles in one graph

Micro wear test
No intrinsic property test

Quantitative: No
Local



Wear rate: 1 nm / cycle



Force	1000mN	1500mN
Contact pressure	7.2 GPa	8.4 GPa

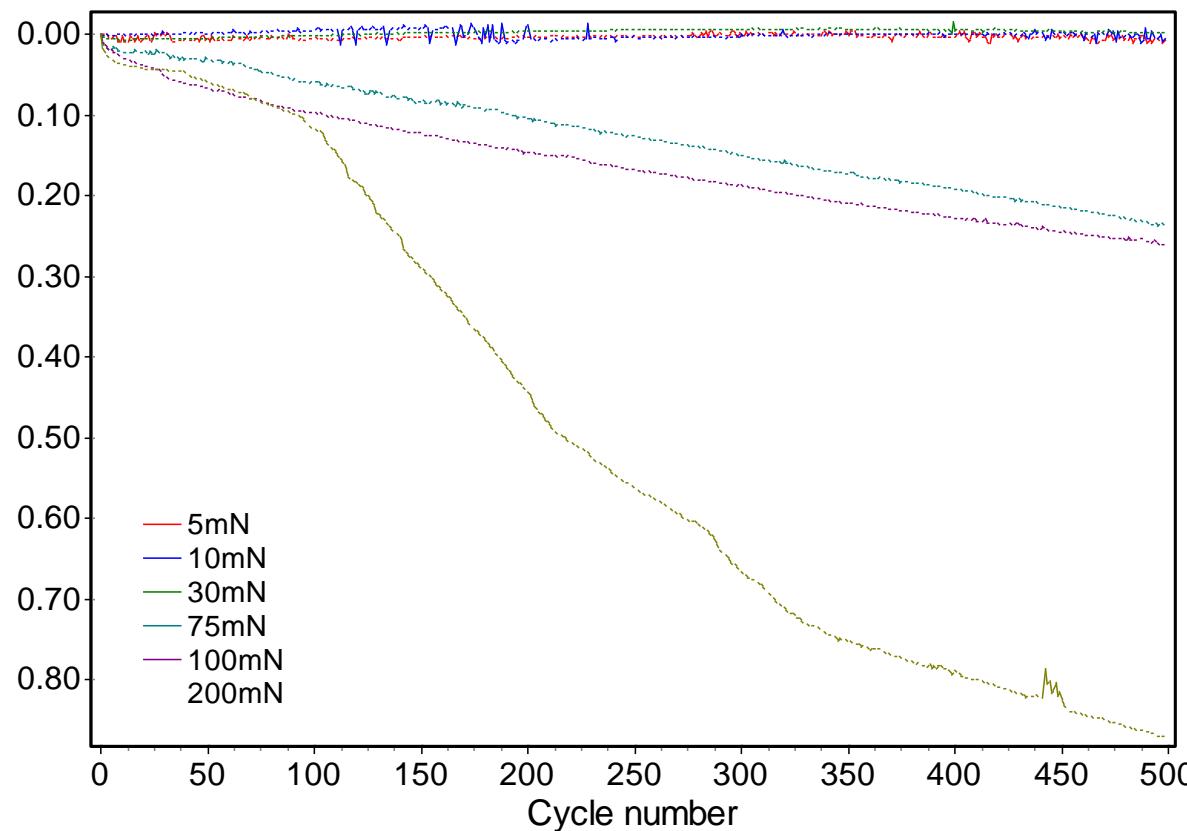
2.5μm DLC on steel, 55μm tip radius
Amplitude 50 μm, Measuring time 1800 s

CVD DLC on steel

5,7 μ m film thickness, Film modulus: 100 GPa, Hardness: 12 GPa

Indenter: diamond sphere, 6 μ m radius

Displacement amplitude 80 μ m measurement time 3144s

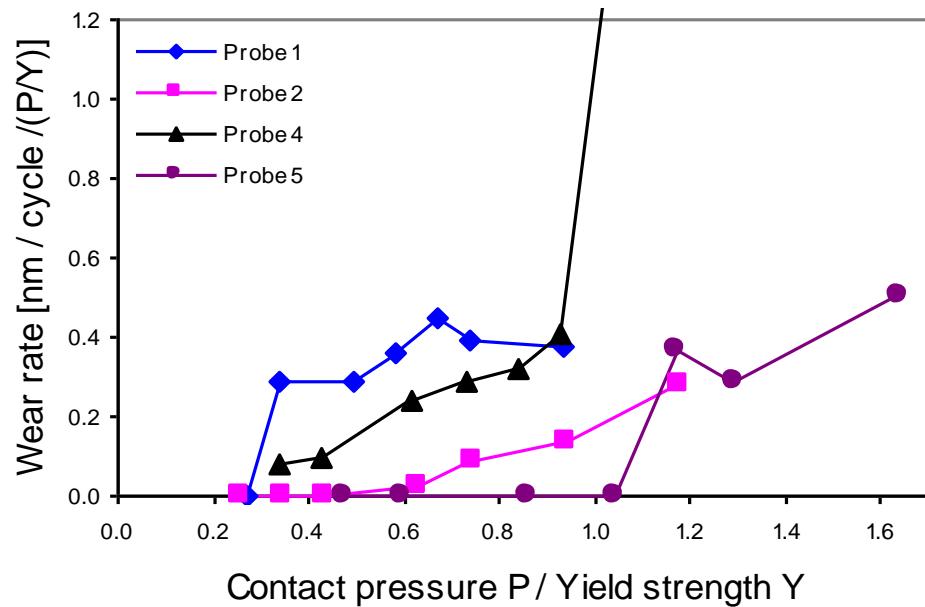


No wear until 50mN normal force

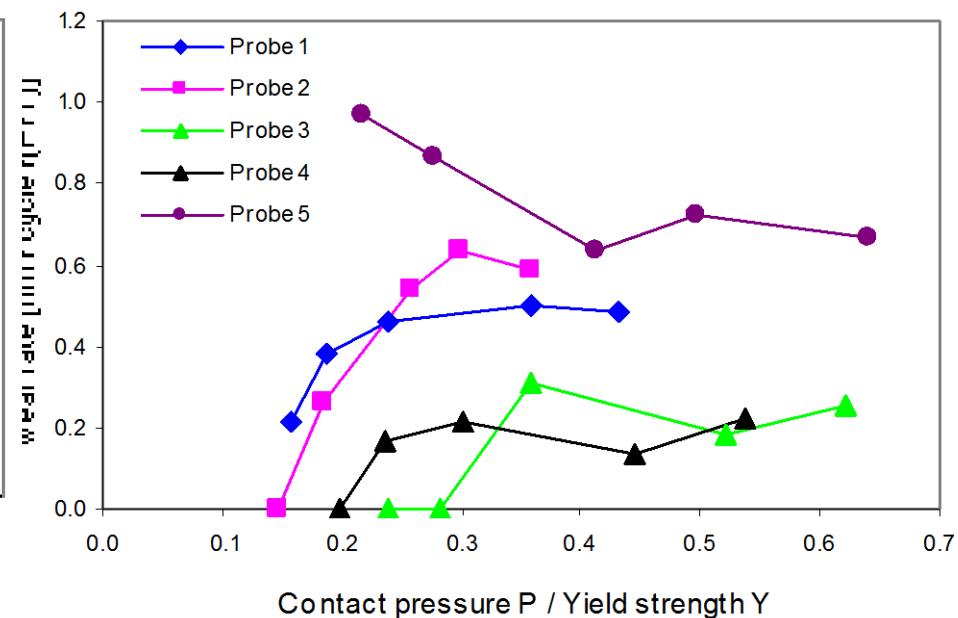
Wear rate at 75mN and 100mN: 0,4nm/cycle

Wear tests on different DLC coatings (a-C:H and t-aC)

Tests with diamond indenter of 6 μm radius

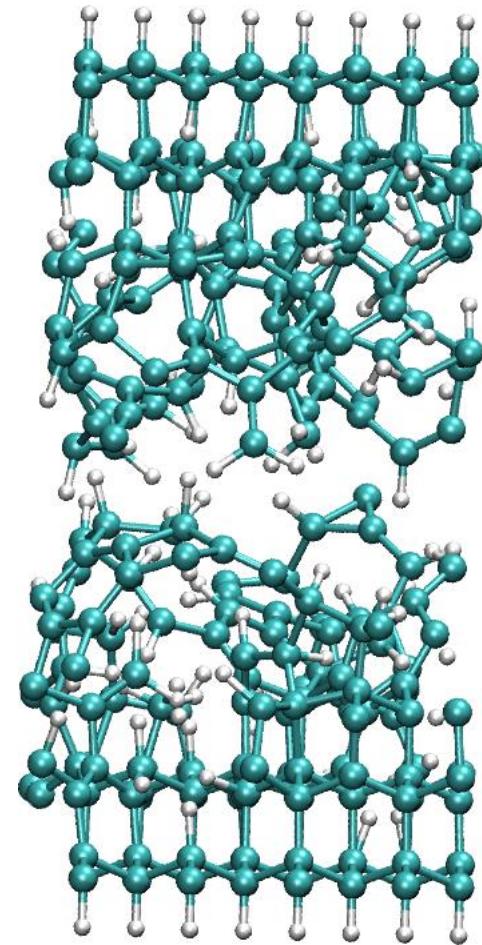
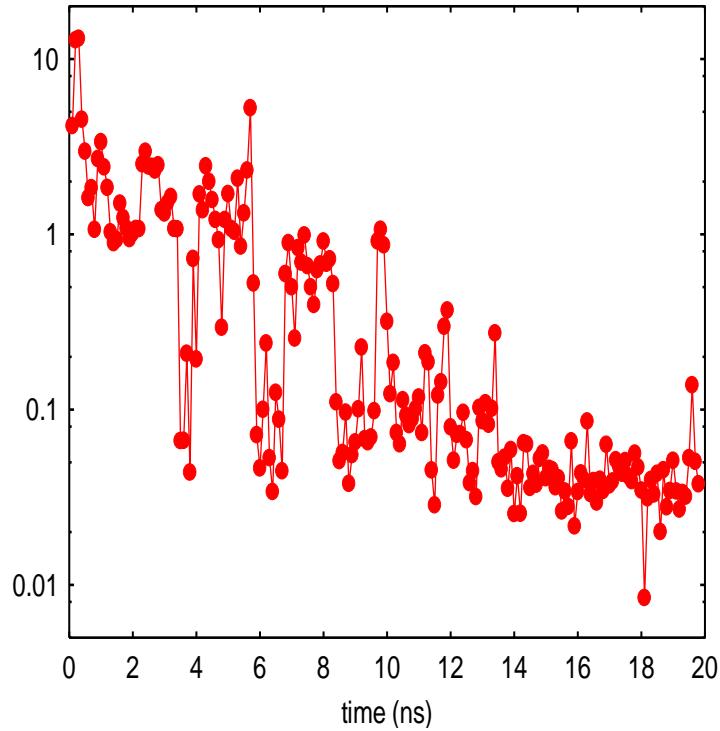
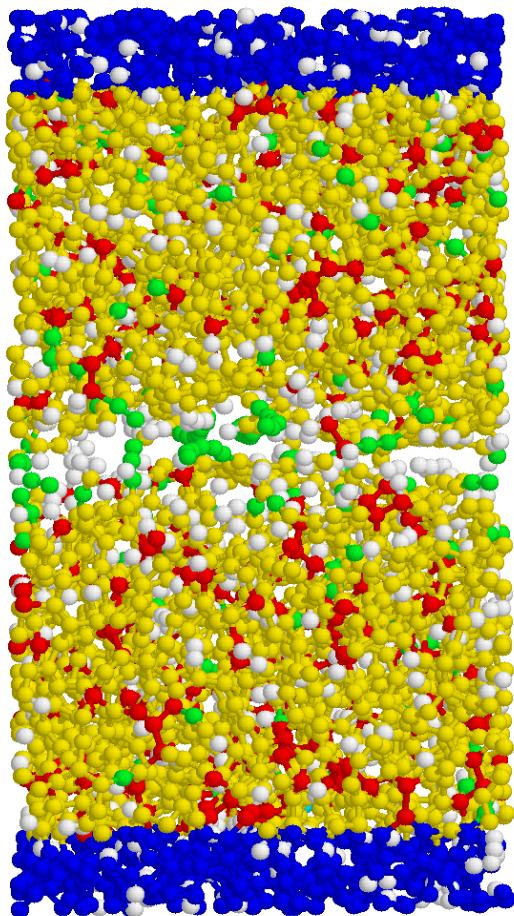


67 μm radius



Normalization with yield strength Y (X-axis)
and P/Y -ratio (Y-axis)

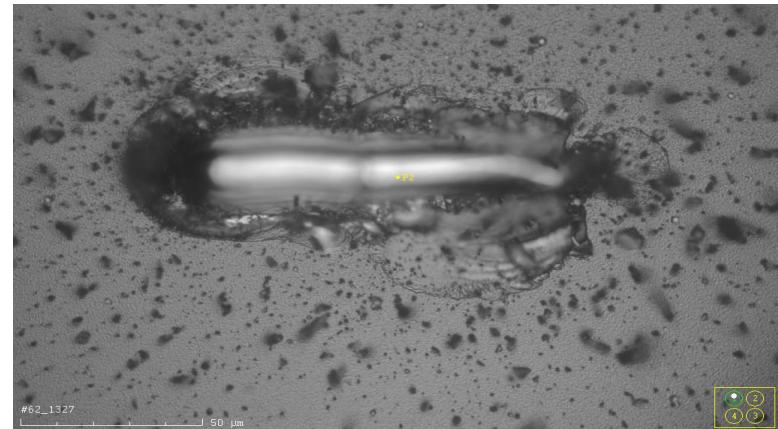
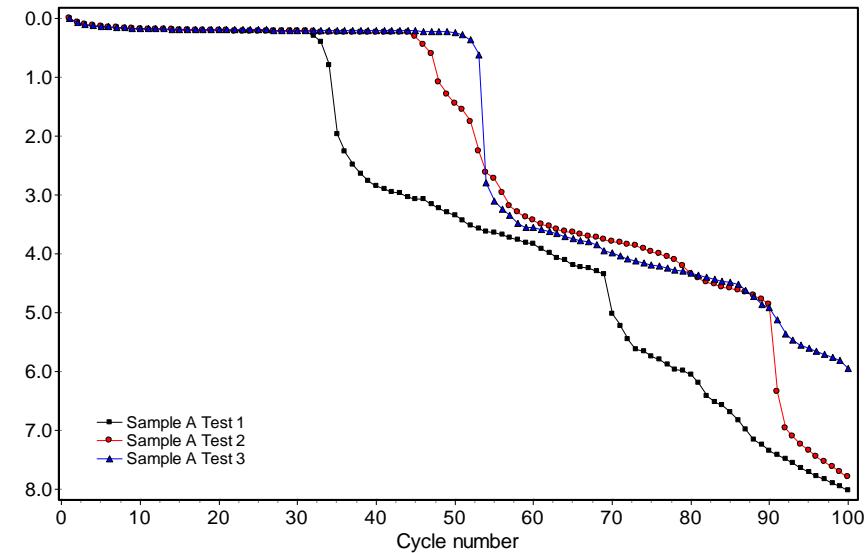
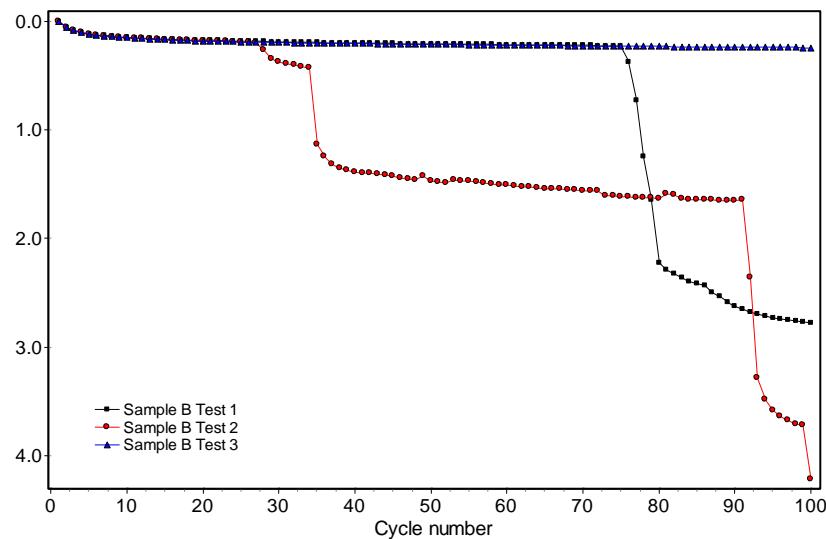
Moleculardynamic simulation of running in behavior of DLC → graphitization observed



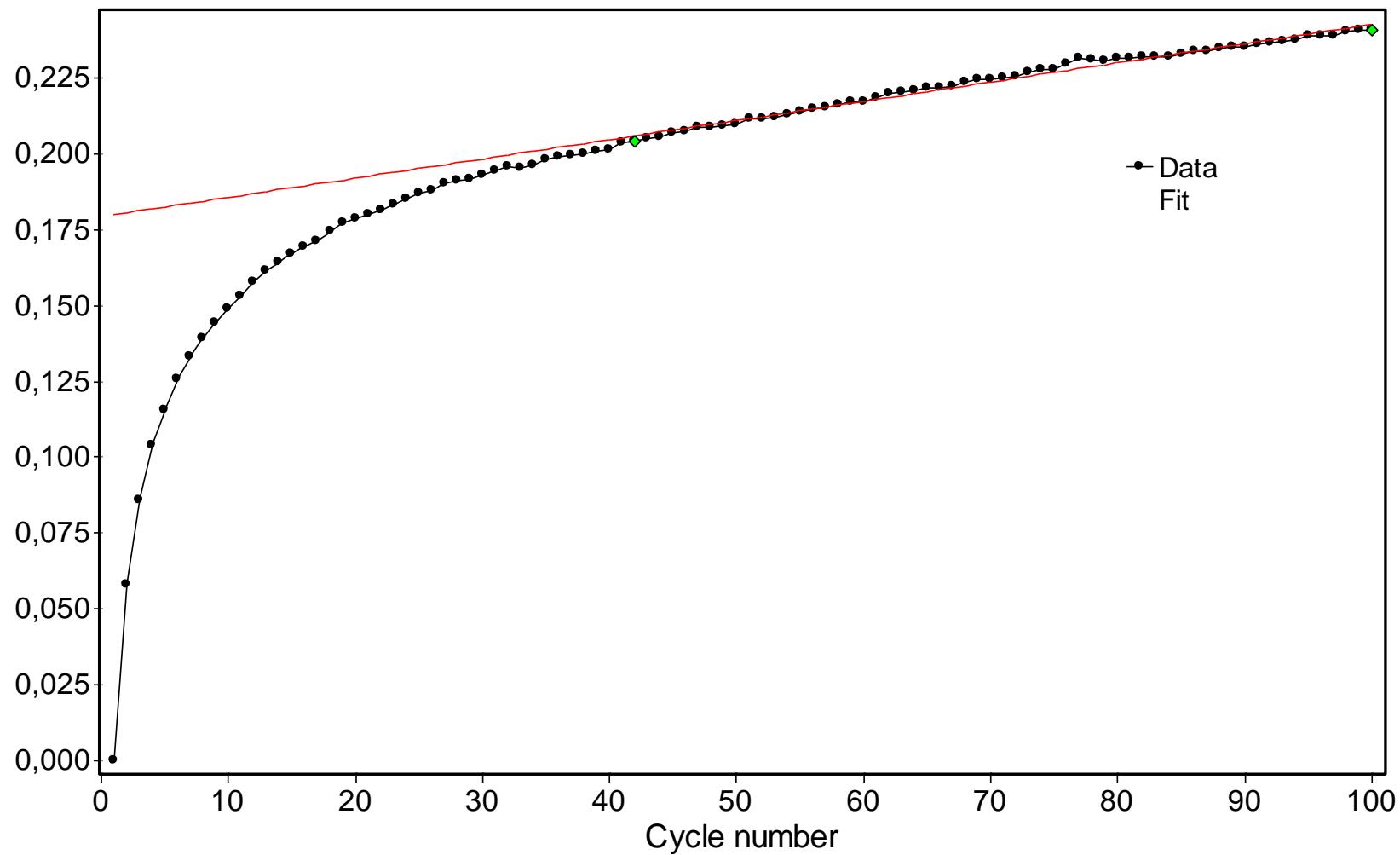
Source: Moseler, Fh IWM, Freiburg, Germany

Wear behavior of sample #60 is better than for sample #62
although the hardness is lower

Test conditions: 500mN, 9.3 μ m radius indenter



#60: wear rate = 0.63 nm/cycle



Conclusions

- Finding the mechanically best behaving coating-substrate combination for a certain application is time consuming and expensive.
- The quantification of the mechanical behavior is still a challenge. Not all necessary mechanical parameters of coatings can be measured with standard test methods up to now.
- For the understanding of failure mechanisms it is necessary to measure with nanometer resolution.
- A larger inclusion of modelling tools (FE, analytical) can considerably shorten the development process. For the calculations accurate and relevant mechanical parameters are necessary.
- A better reproduction of the conditions in an application is necessary in laboratory tests.
- This requires the inclusion of lateral force-displacement measurements with high precision
- In the future the significance of multi-axial testing in combination with stress calculation will increase.