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ADVANCED SURFACE MECHANICS

# Mechanical characterization of ultra-thin coatings

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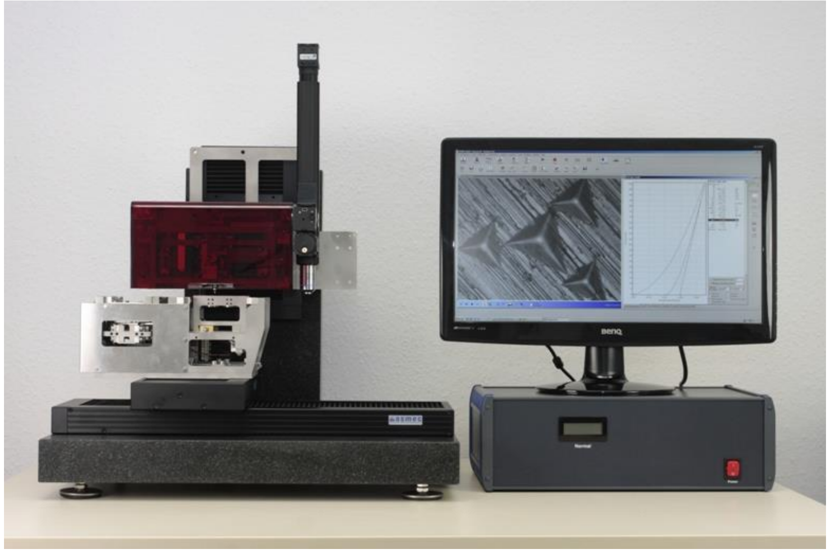
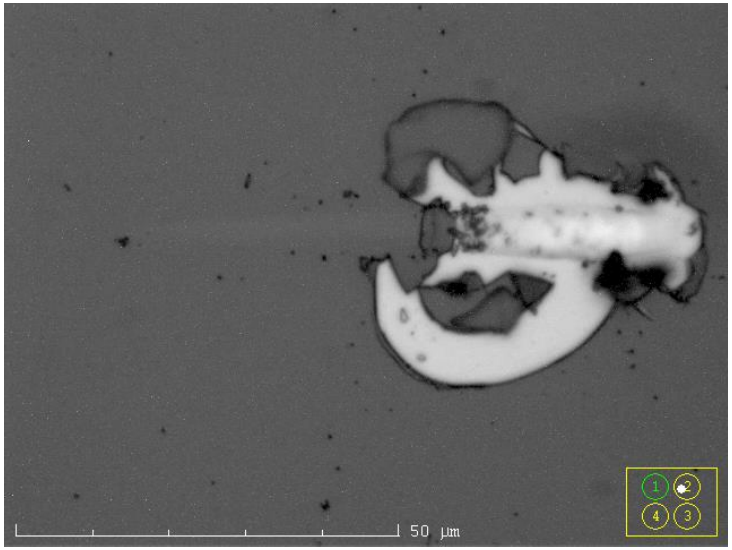
ASMEC Advanced Surface Mechanics GmbH





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## 1) Limits for hardness and modulus measurements

## 2) Accurate determination of tip rounding and area function

## 3) Solutions for ultra thin coatings

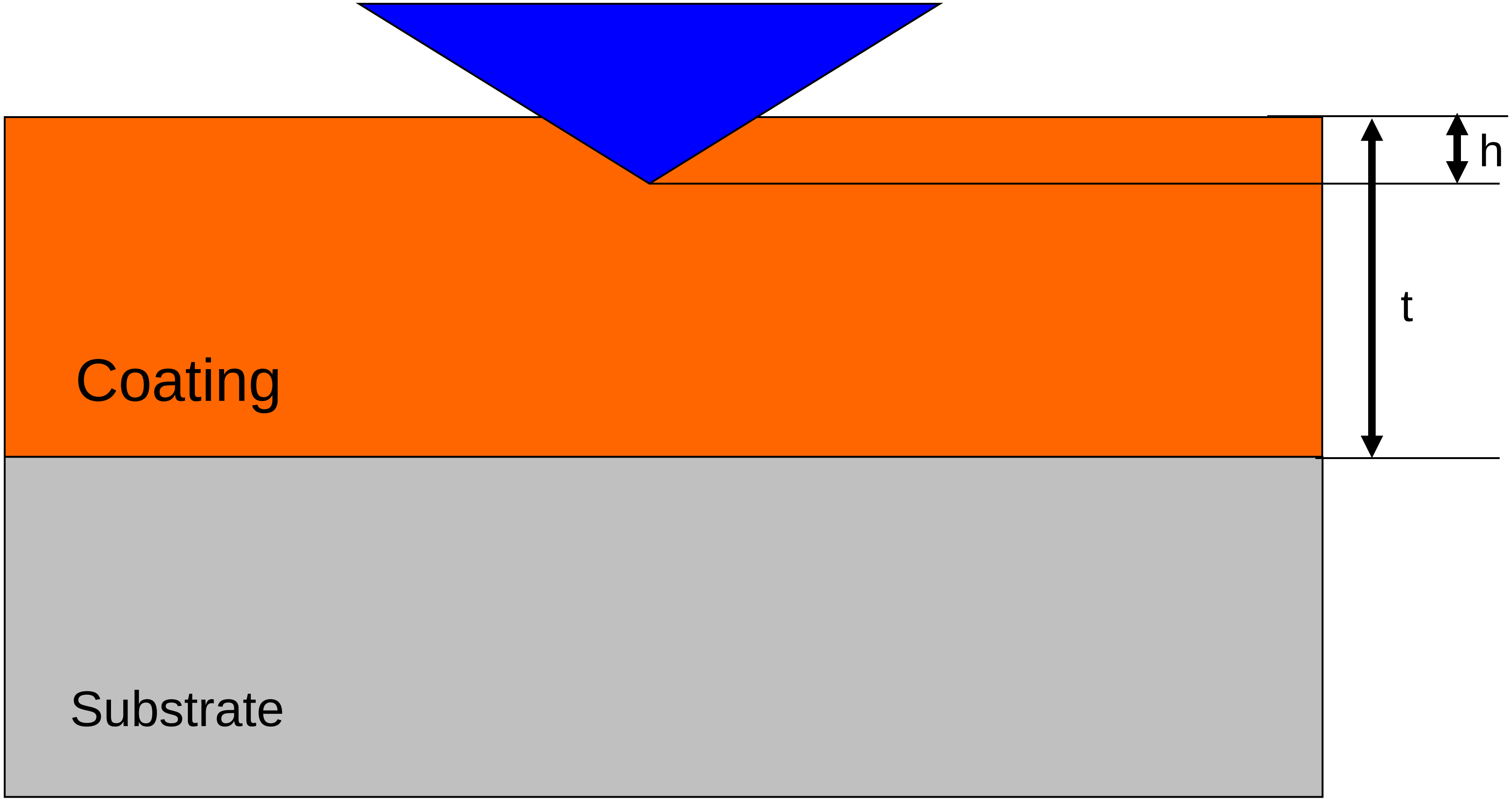
- Ultra sharp tips, ultra low forces
- Extrapolation to zero depth
- Eliminating the substrate influence for fully elastic measurements with spheres
- Eliminating the substrate influence for elastoplastic measurements with sharp tips
- Determining yield strength instead of hardness using micro scratch tests

# Measurement limits for ultrathin coatings

## Limit 1: Substrate influence

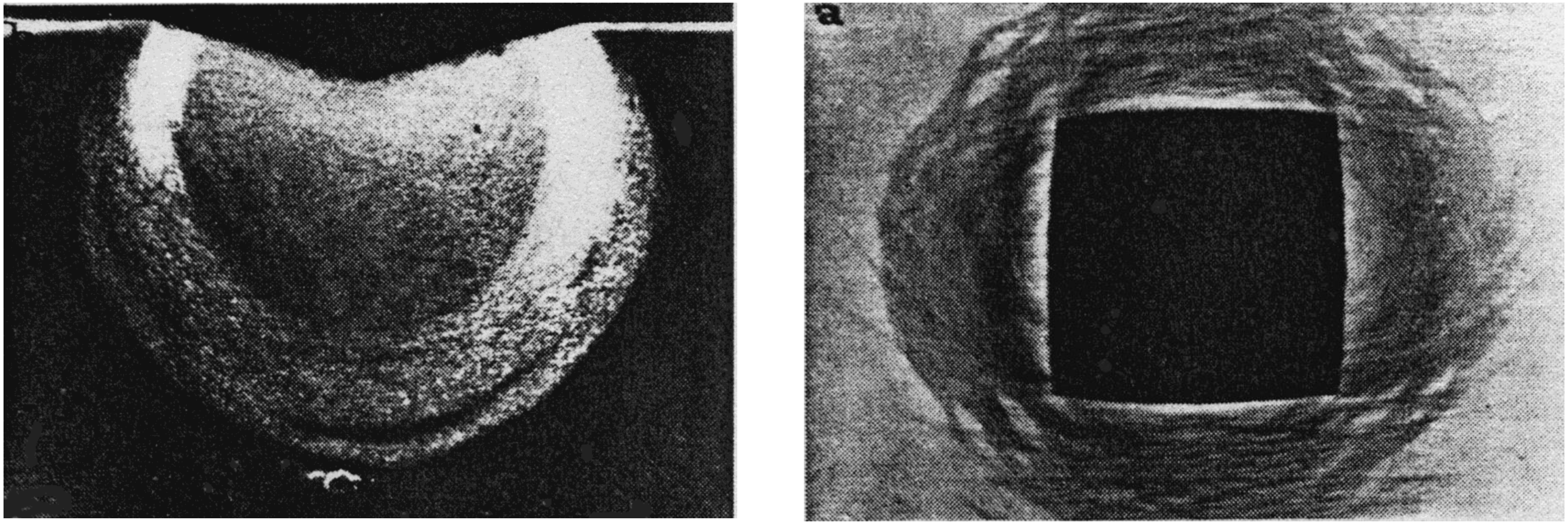
# Depth limit for coatings hardness

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 to10 times the indentation depth.



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

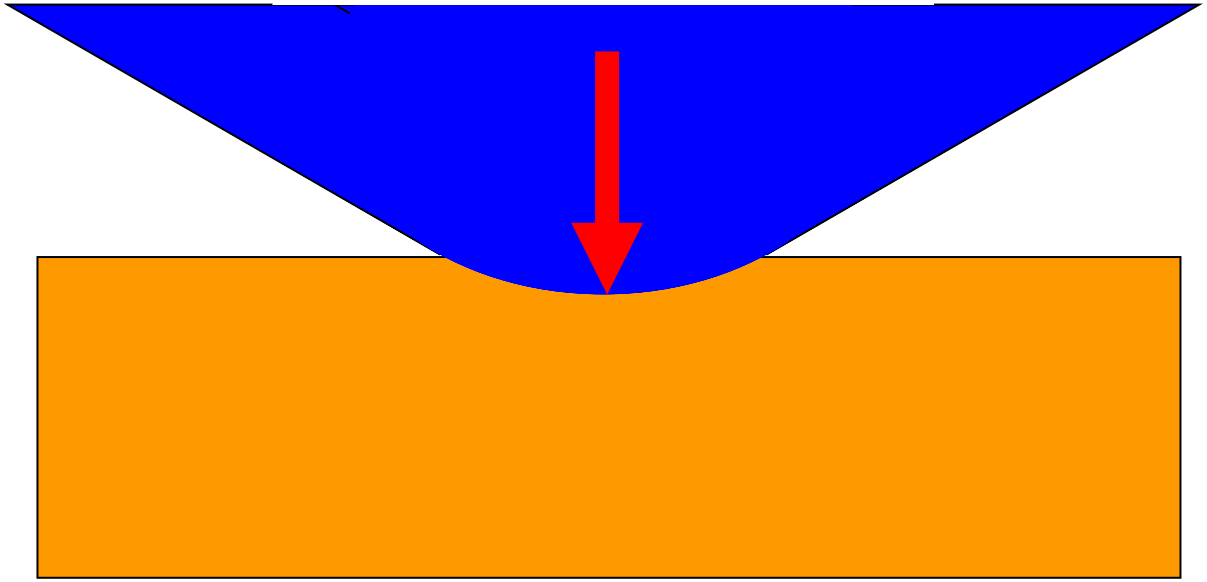
# Limit 2:  Tip rounding

# 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



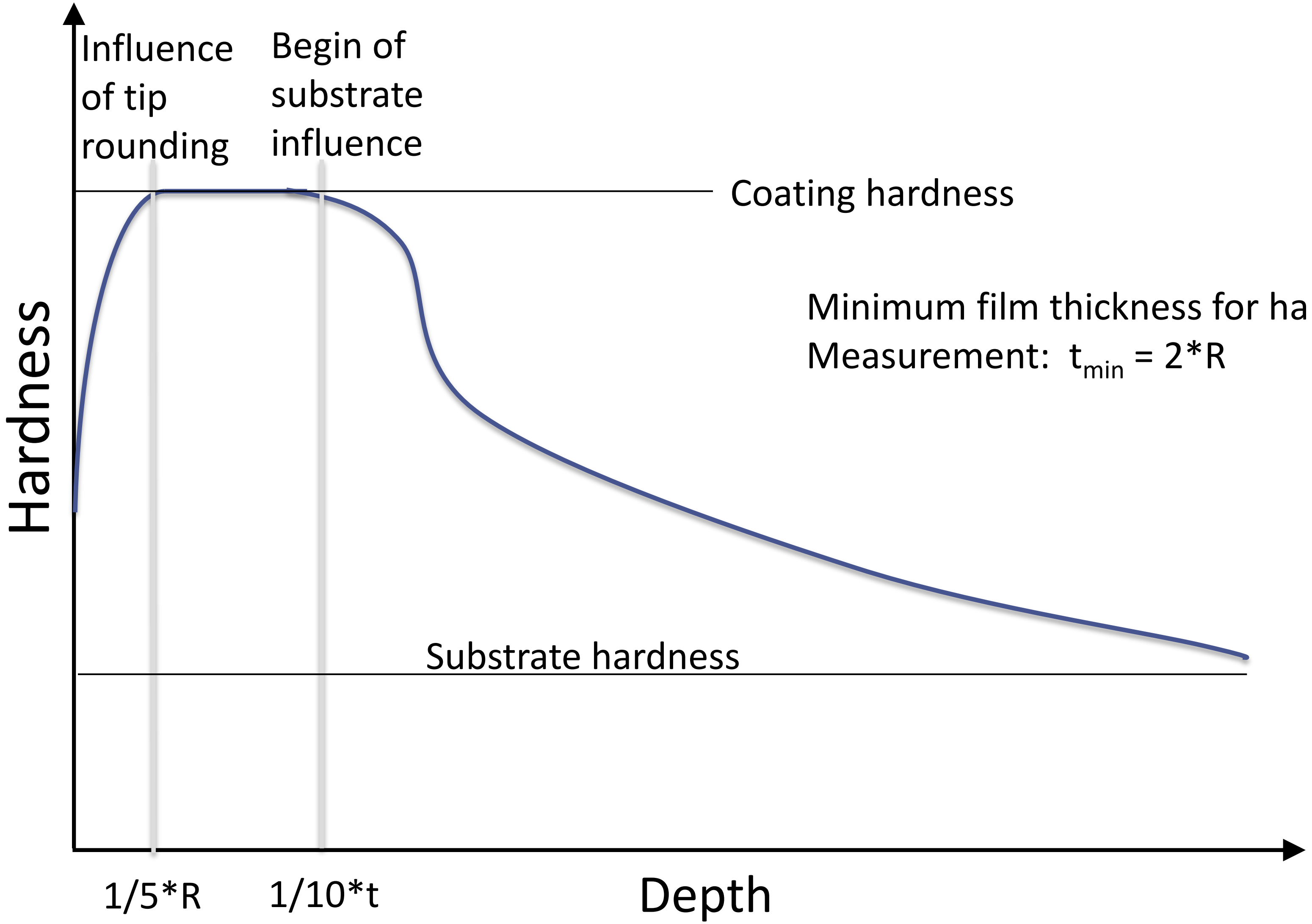
Minimum depth for hardness tests:

$h_{min} = 0.2 \cdot R$

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

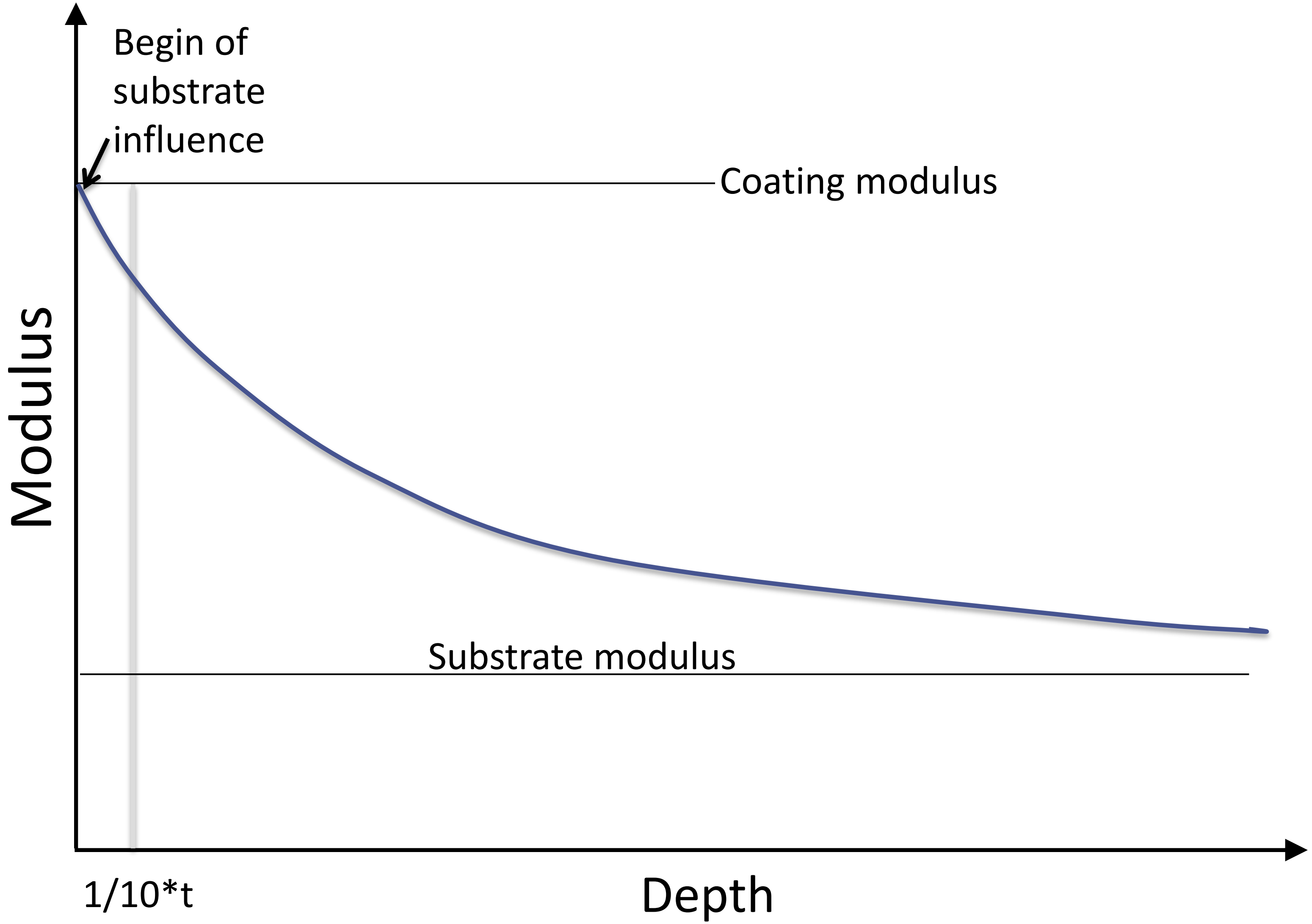
| Tip radius (nm) | Minimum film thickness (nm) |
|---|---|
| 50 | 100 |
| 75 | 150 |
| 100 | 200 |
| 150 | 300 |
| 200 | 400 |
| 250 | 500 |
| 300 | 600 |

# Substrate influence on hardness



Minimum film thickness for hardness Measurement: $t_{min} = 2*R$

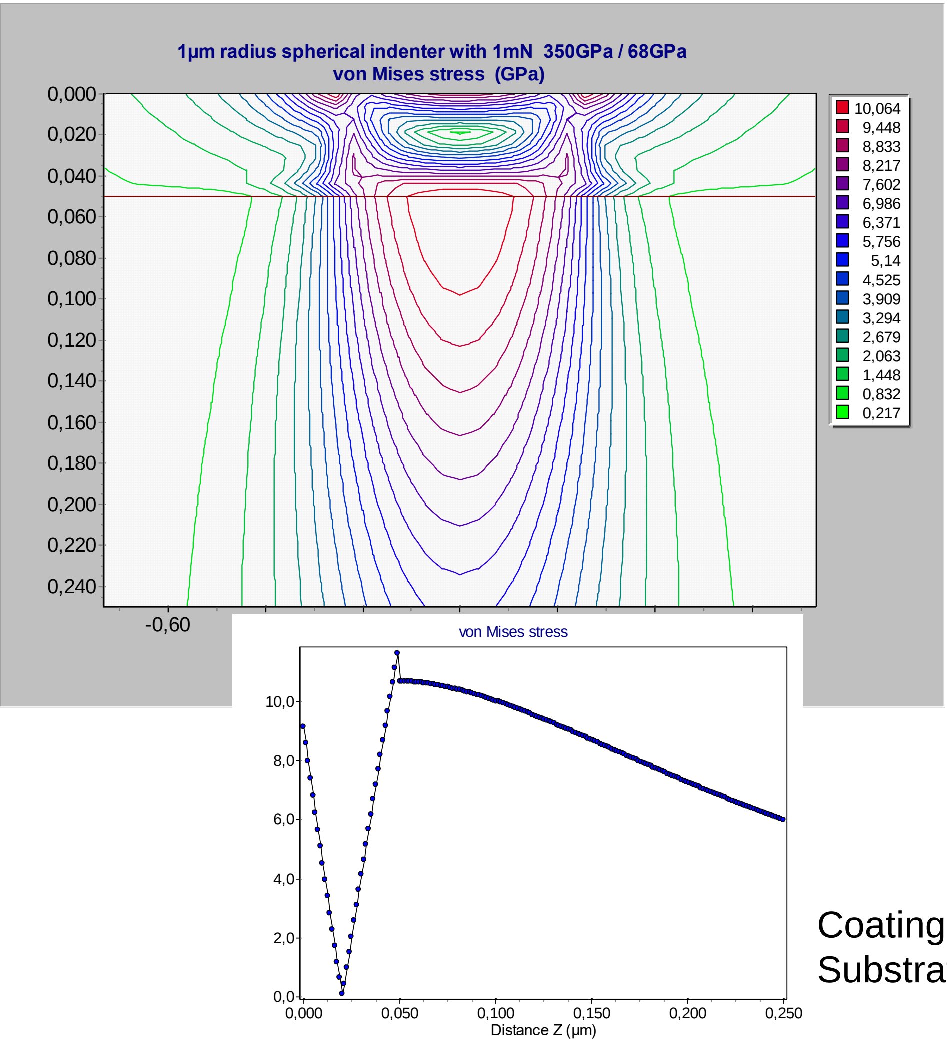
# Substrate influence on modulus



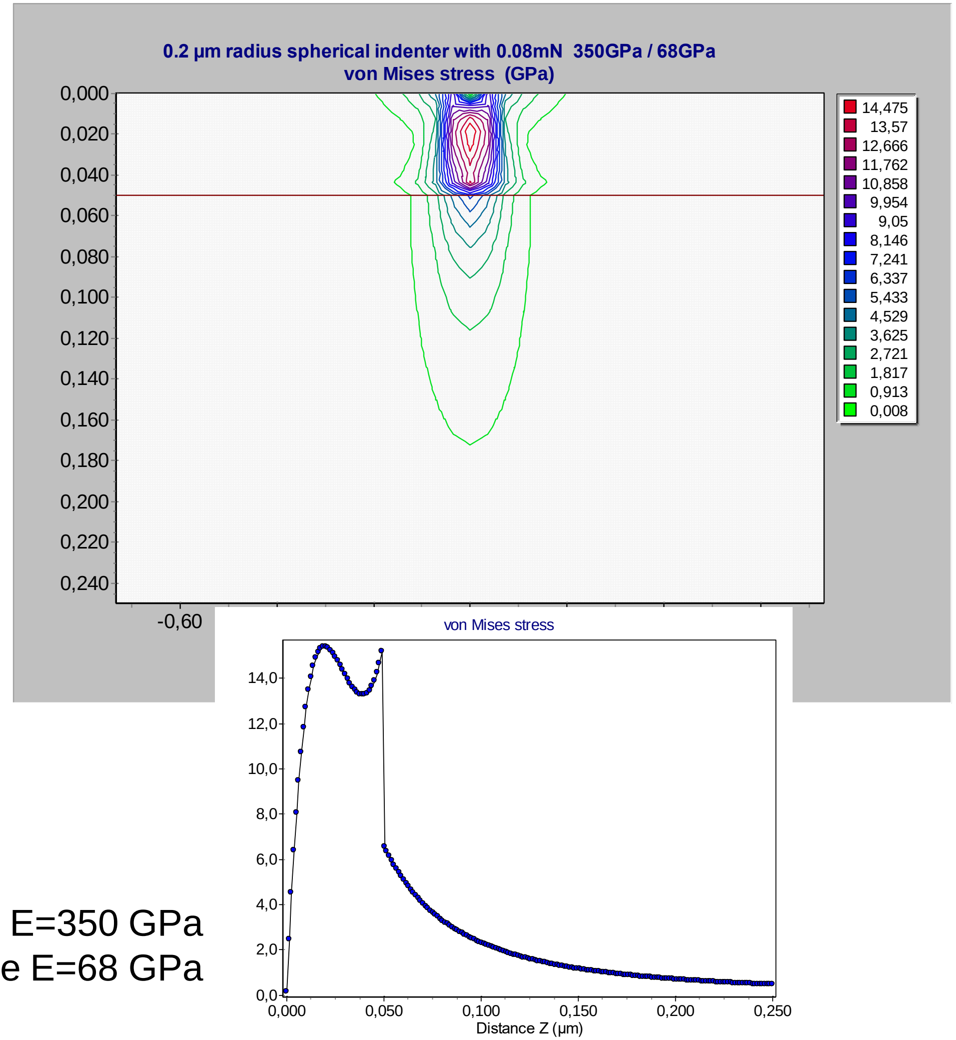
# Limit 3:  Position of first plastic yielding

# Von Mises stress field for a 50nm thin hard coating on glass in dependence on indenter radius

## 1 µm tip radius



## 0.2 µm tip radius

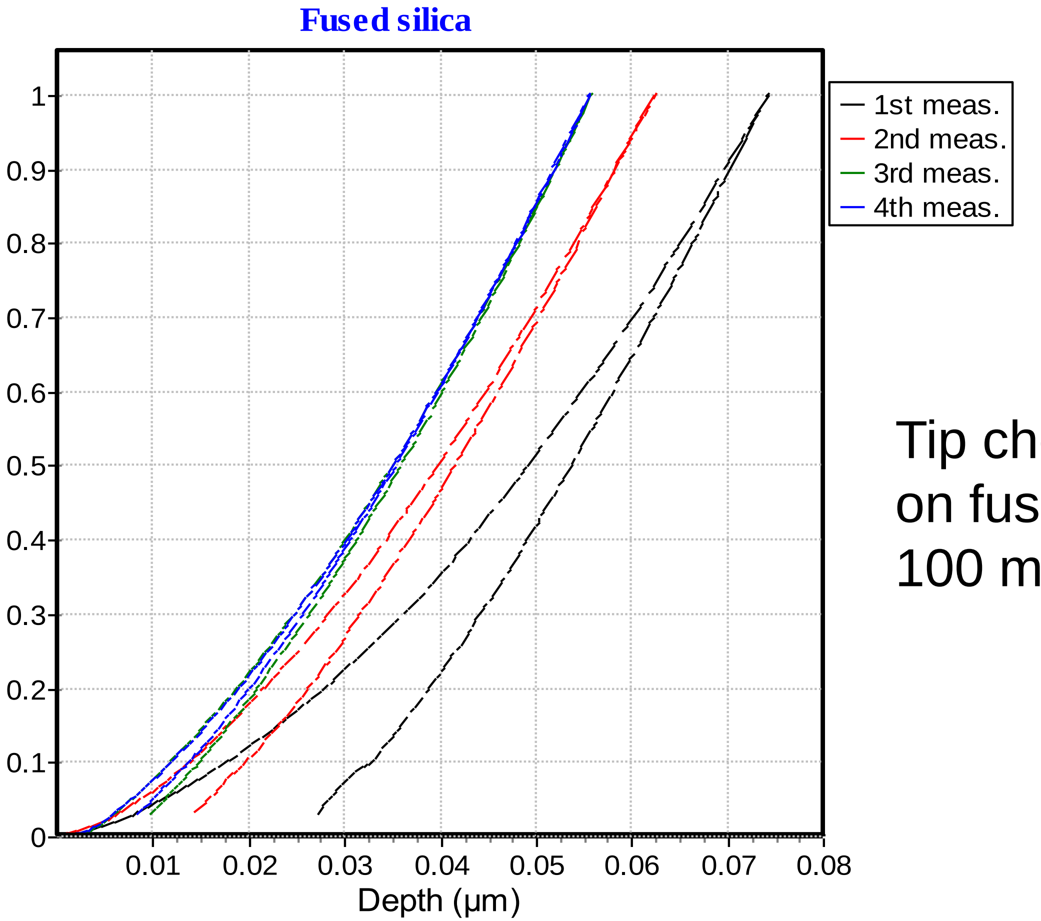


Coating: E=350 GPa
Substrate E=68 GPa

## Low depth measurements require an accurate

## Determination of tip rounding and area function

There is a permanent wear of the diamond tip.
The tip status has to be checked regularly.

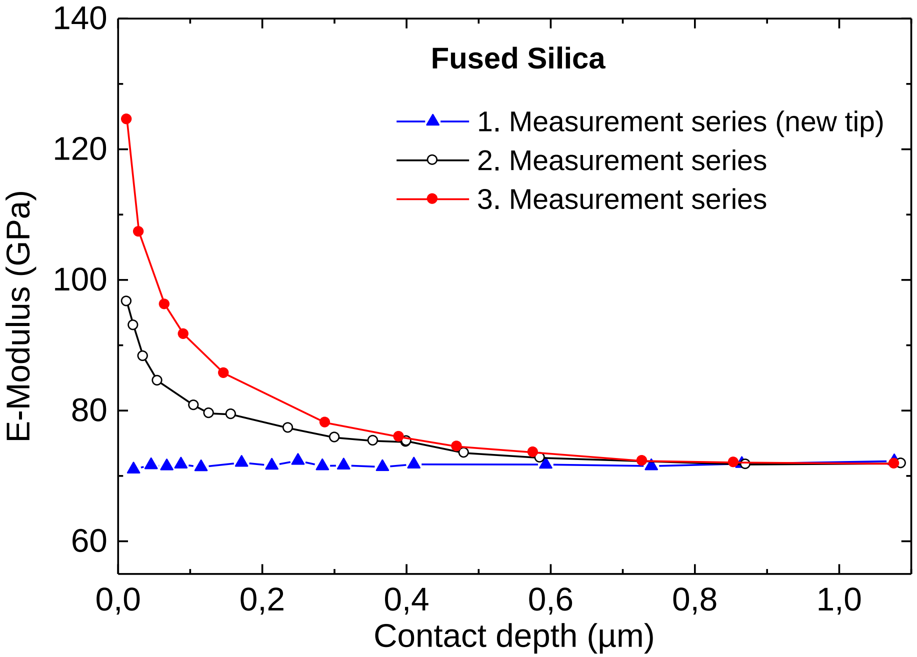


Tip check measurements
on fused silica with several
100 measurements in between.

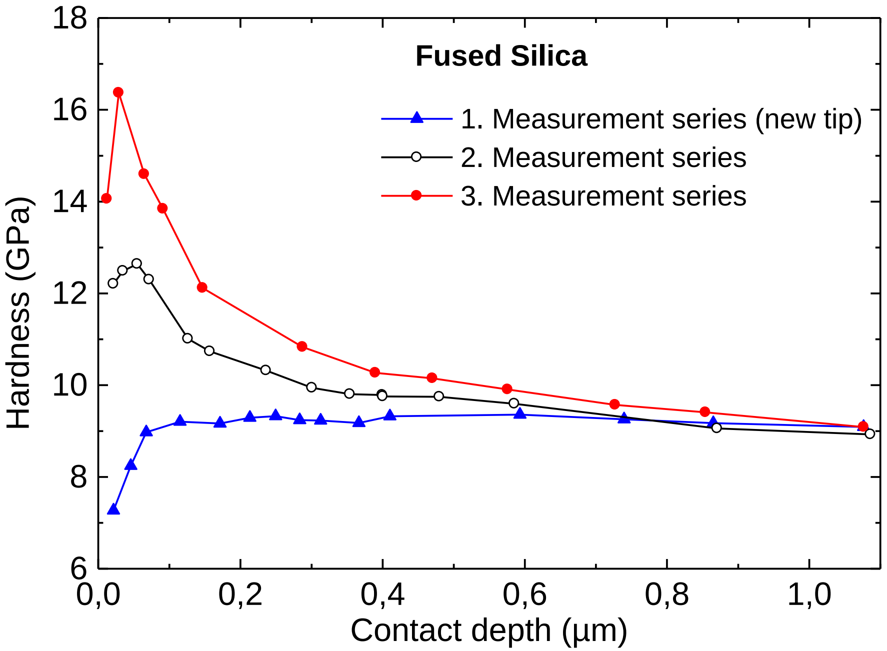
# Error due to incorrect tip area function in dependence on depth

## Example: fused silica

### Modulus



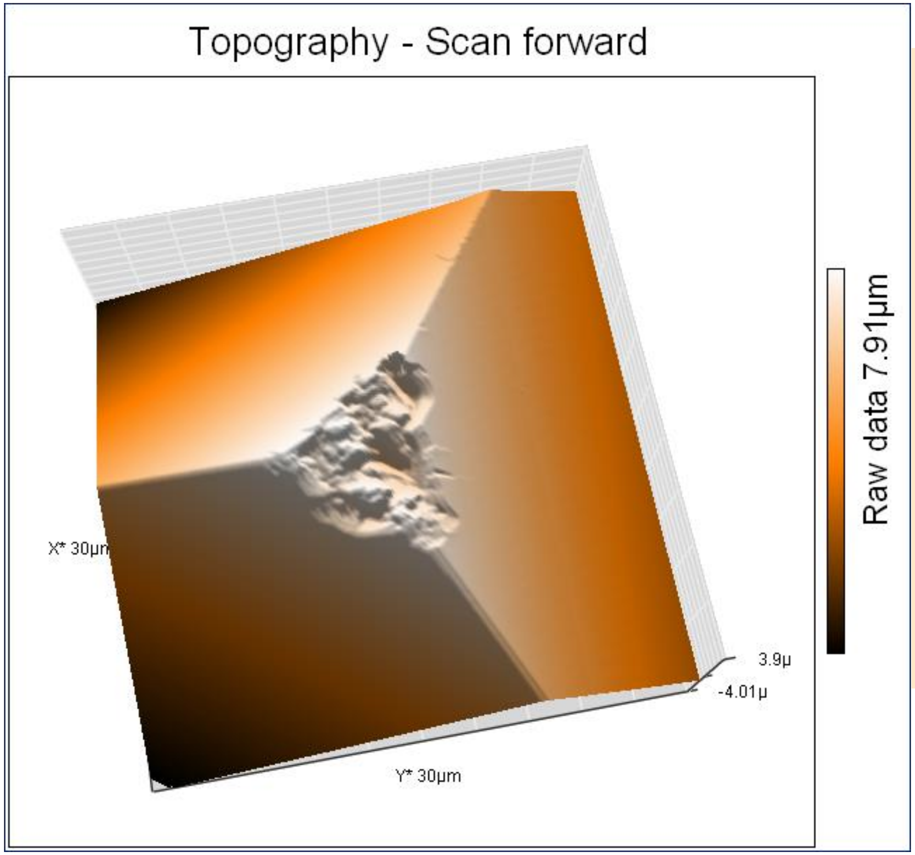
### Hardness

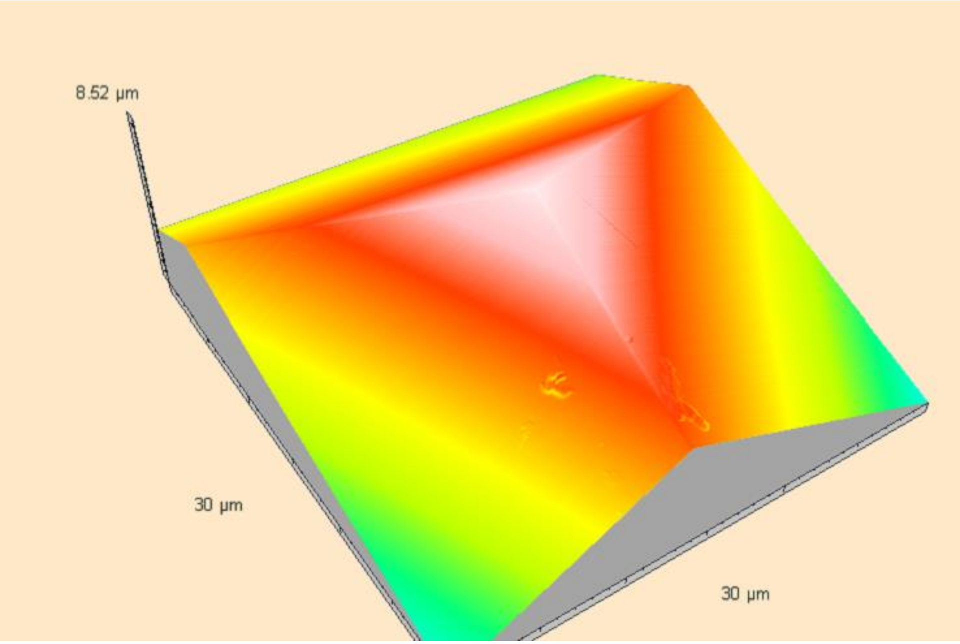


Tip radius: 1. ≈ 150 nm (fresh tip)
2. ≈ 350nm
3. ≈ 700 nm

# Determination of area function

## Direct method: AFM scan of the tips





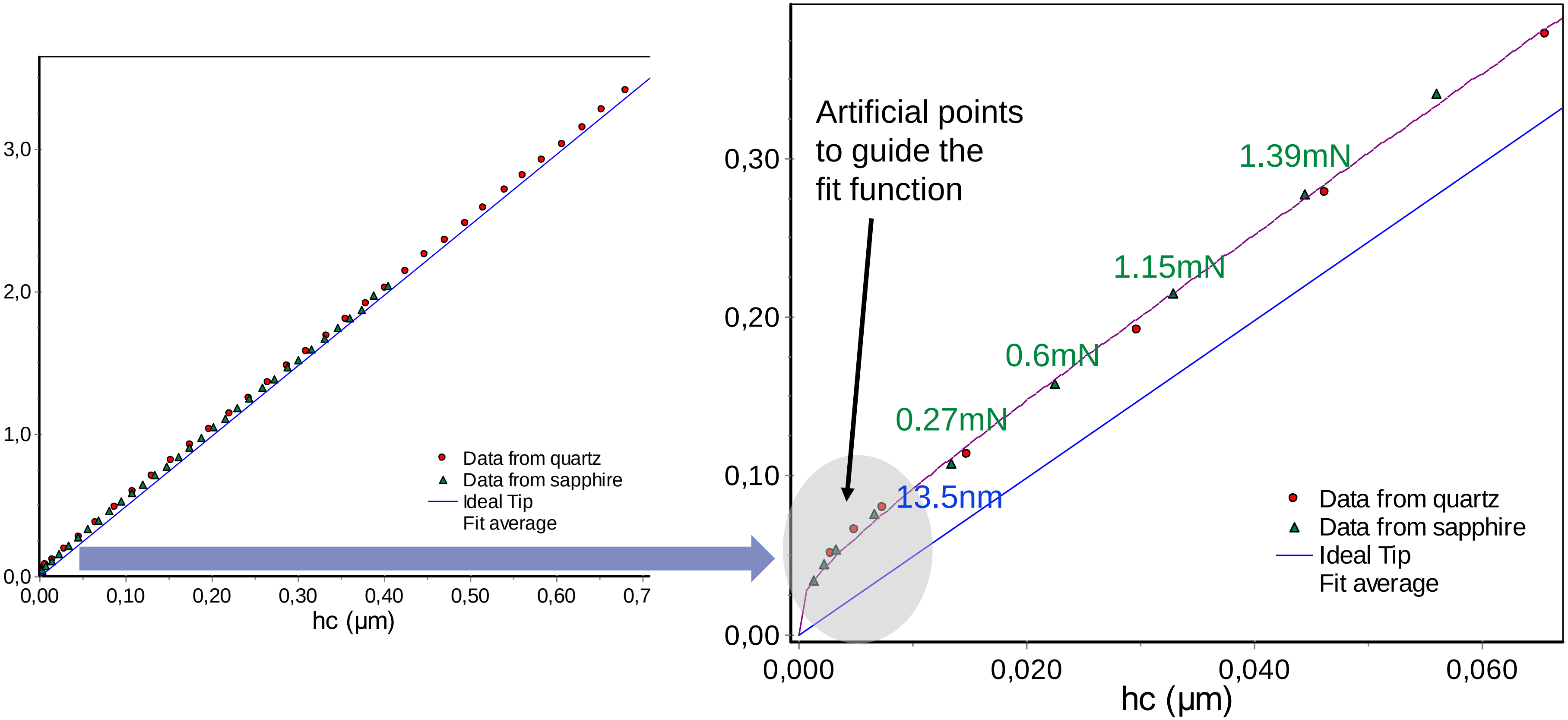
Left: broken diamond tip

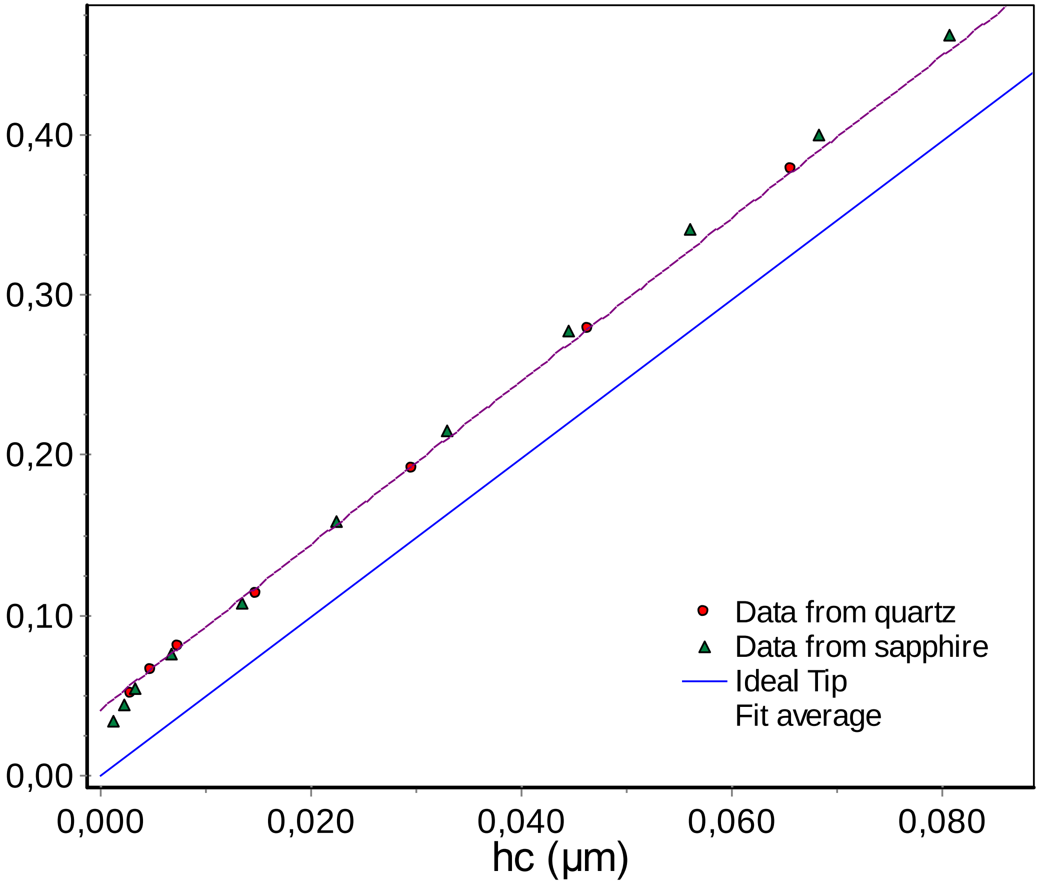
Right: new tip without defects

# Determination of area function

**Direct method:** Measurement with metrological AFM

**Indirect method:** Indentation measurements on homogeneous reference materials

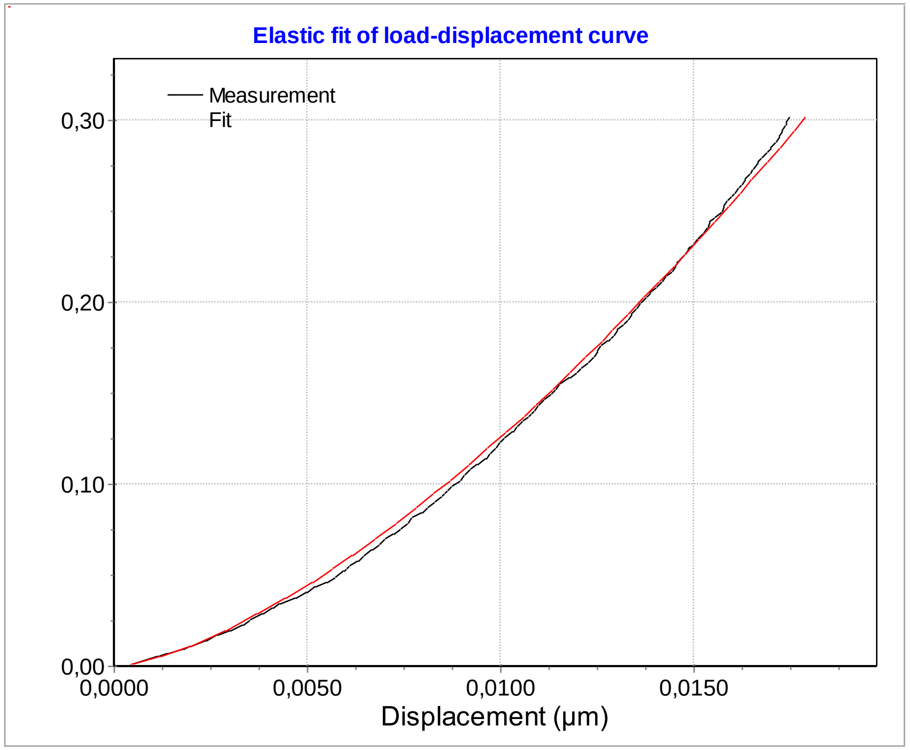




Inadequate fit function with insufficient term number

# How to determine the real tip radius?

→ Elastic measurements on a hard reference material
→ Hertzian contact calculation

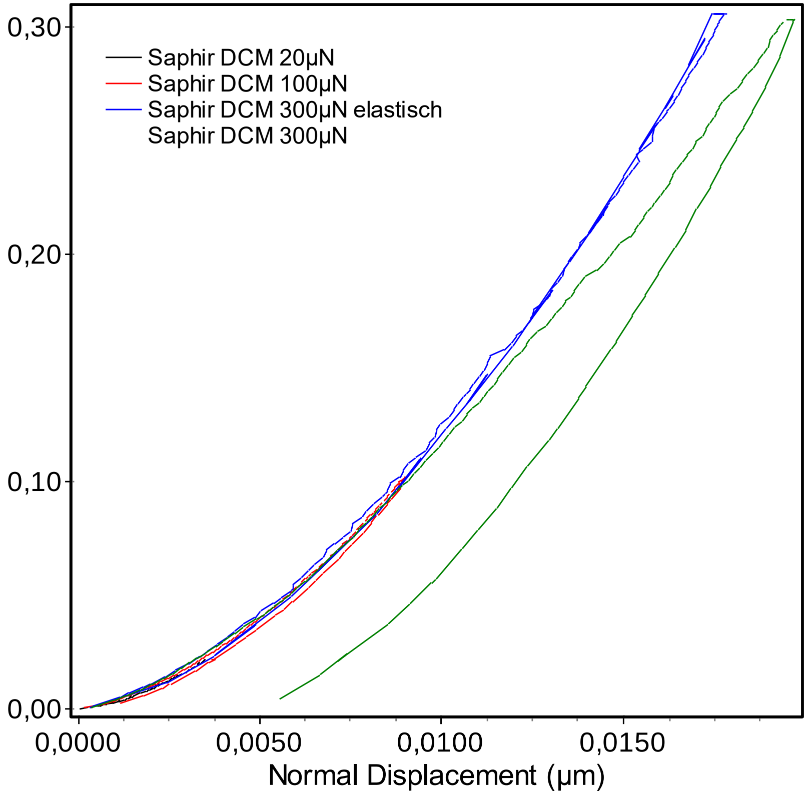


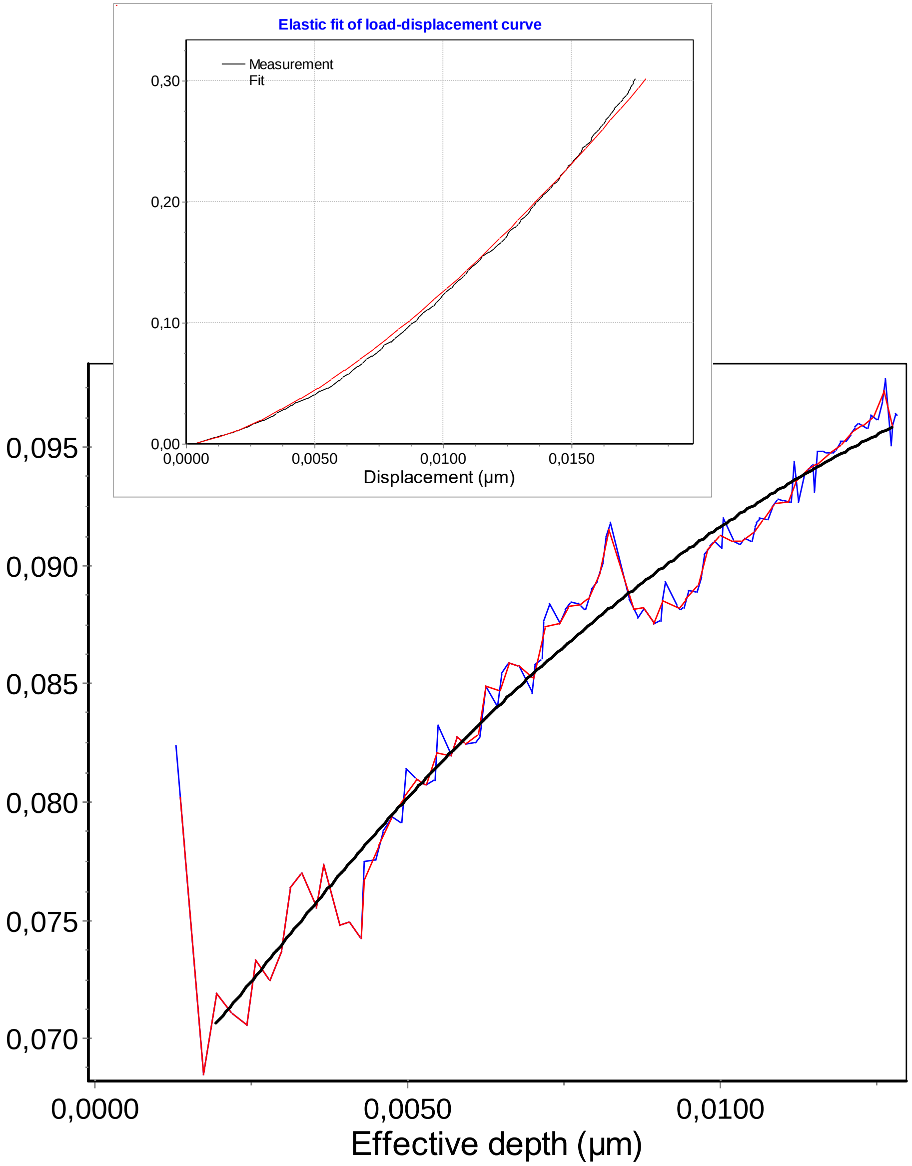
Measurement and fit curve of sapphire

Elastic – plastic transition force for a defect free Sapphire single crystal with strength of 40 GPa (maximum)

| Tip radius (nm) | Transition force (µN) |
|---|---|
| 50 | 31 |
| 75 | 68 |
| 100 | 120 |
| 150 | 280 |
| 200 | 490 |
| 250 | 760 |
| 300 | 1100 |

# Measurements at BAM with Agilent DCM head



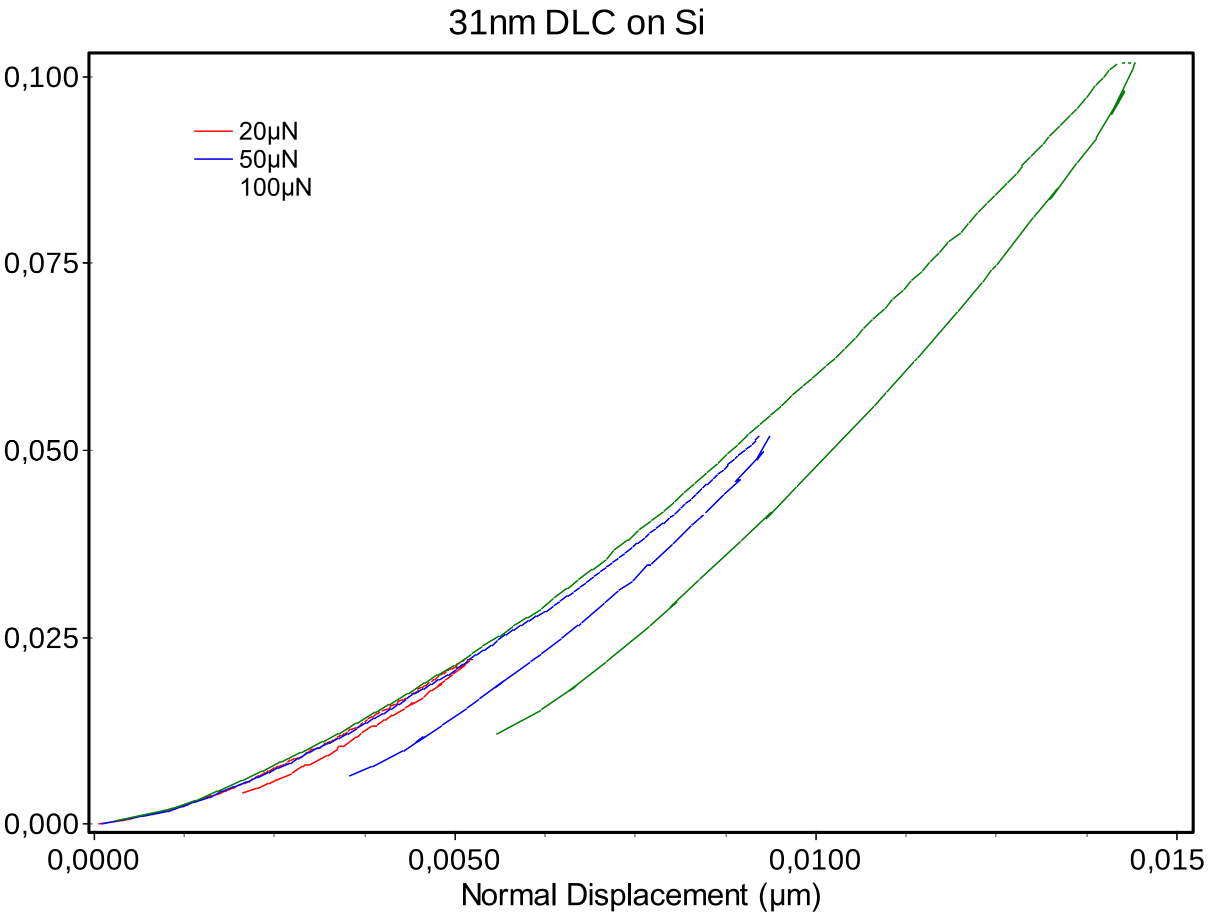


Sapphire measurements and fit curves (0001) Single crystal

# Solutions for ultra thin coatings

1) Modulus measurement
2) Hardness (yield strength) measurement

# Solution 1: Ultra sharp tips, ultra low forces



Example:

Tests with Agilent DCM head

Averaged curves from 10 single measurements

Tip radius 70nm

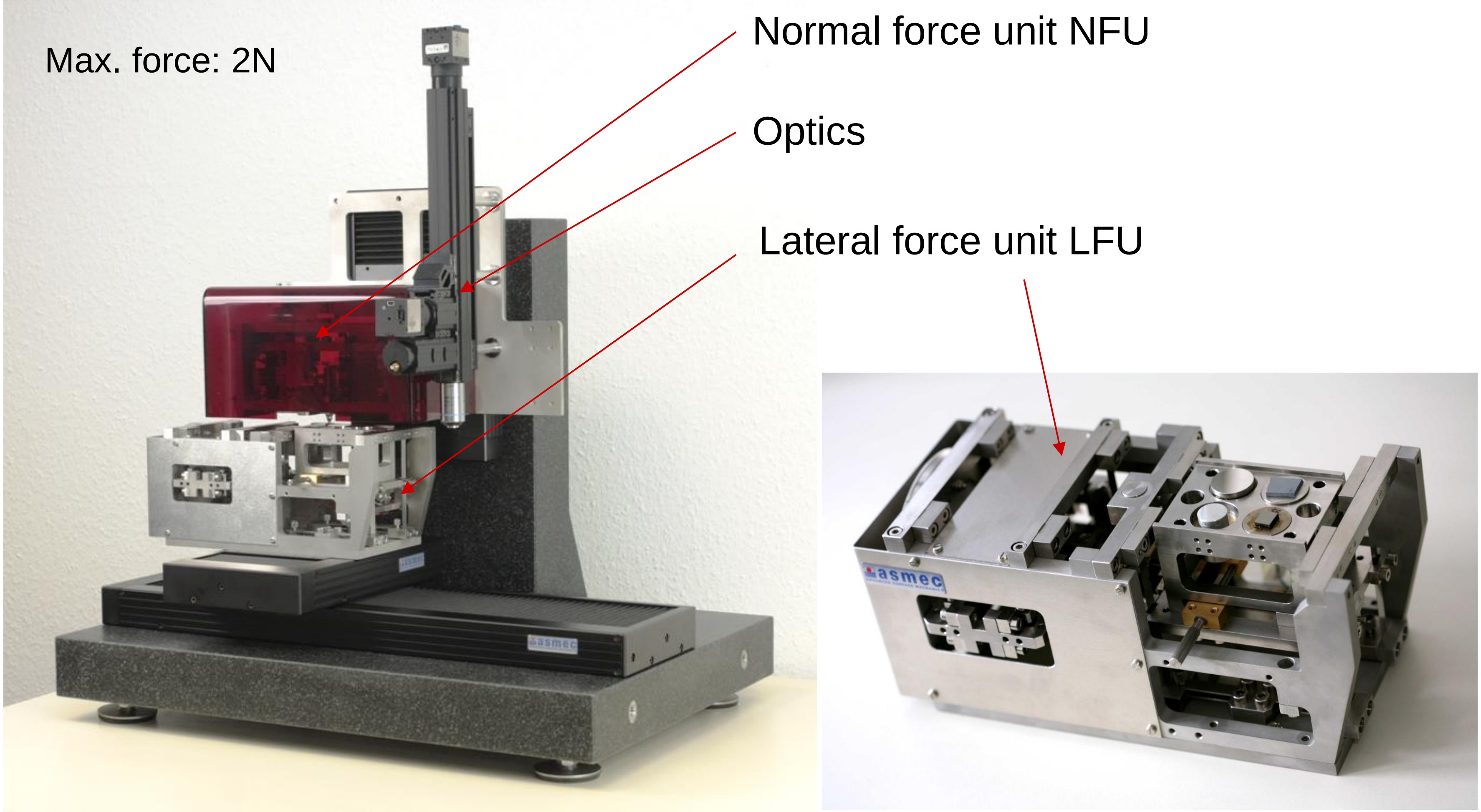
20µN is already to much for a 31nm coating

50µN allow measuring 100nm DLC coatings

For 100nm coatings tip radius should be 50nm and not 70nm

The following tests were done with a

## UNAT – Universal Nanomechanical Tester



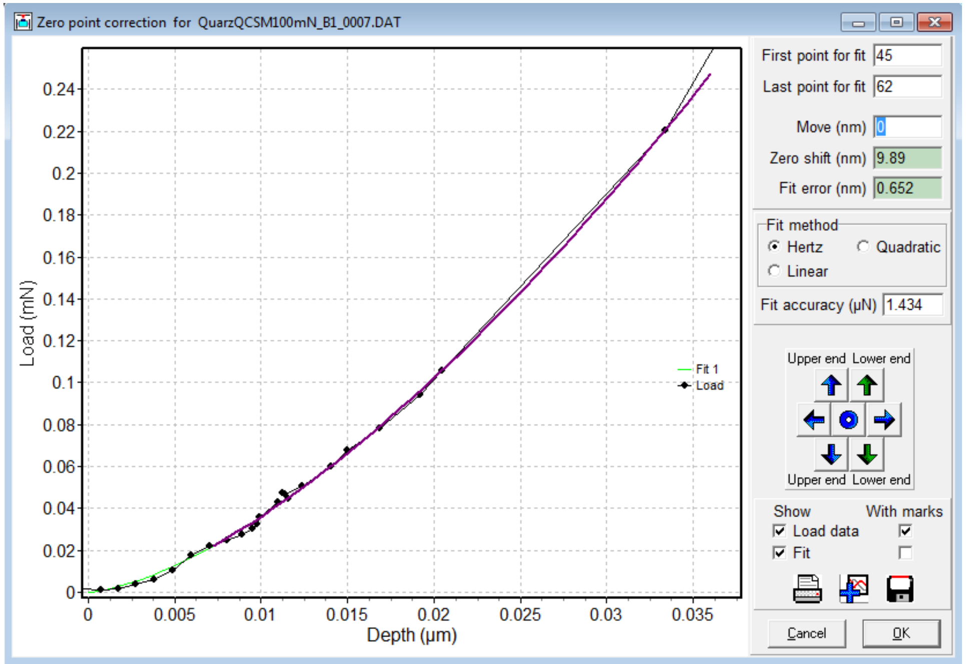
Max. force: 2N

Normal force unit NFU

Optics

Lateral force unit LFU

# For highly accurate results two corrections are necessary



Zero point correction for QuarzQCSM100mN_B1_0007.DAT

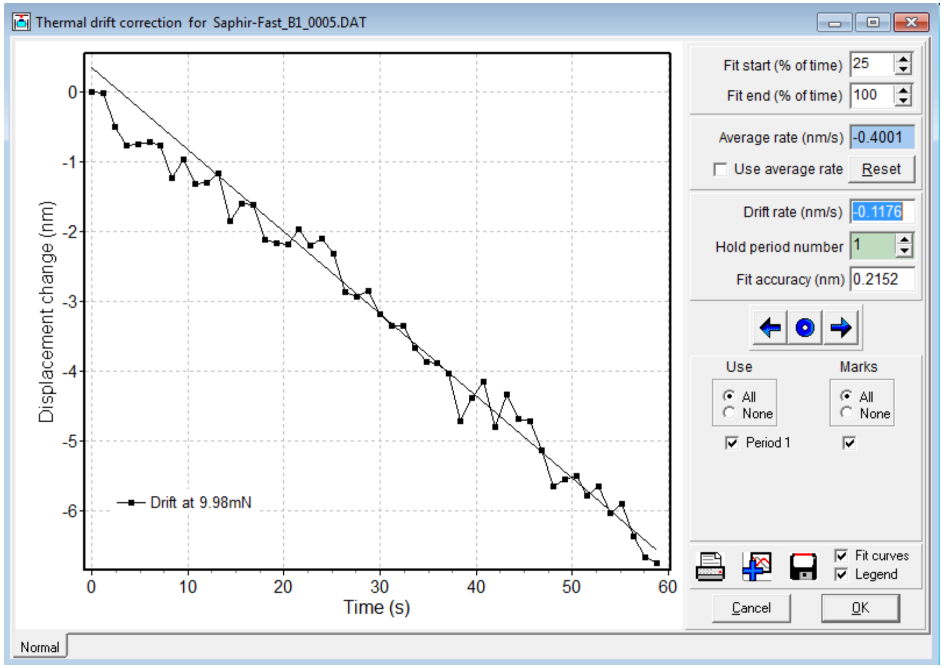
First point for fit: 45
Last point for fit: 62
Move (nm): 0
Zero shift (nm): 9.89
Fit error (nm): 0.652

Fit method
● Hertz
○ Quadratic
○ Linear

Fit accuracy (µN): 1.434

Show / With marks
☑ Load data ☑
☑ Fit ☐

Zero point correction



Thermal drift correction for Saphir-Fast_B1_0005.DAT

Fit start (% of time): 25
Fit end (% of time): 100
Average rate (nm/s): -0.4001
☐ Use average rate
Drift rate (nm/s): -0.1176
Hold period number: 1
Fit accuracy (nm): 0.2152

Use: ● All ○ None
Marks: ● All ○ None
☑ Period 1 ☑

☑ Fit curves
☑ Legend

Thermal drift correction

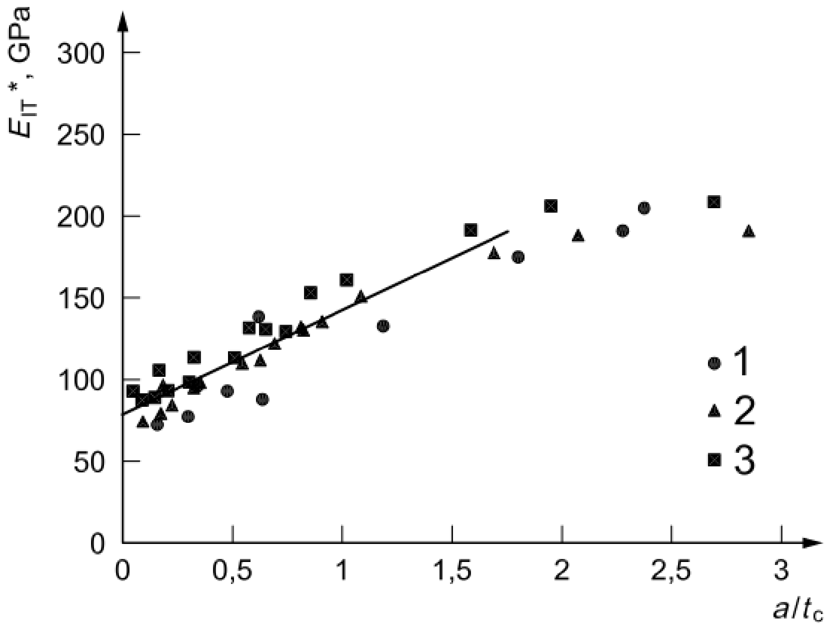
# Solution 2 for modulus measurements:

## Extrapolation to zero depth

The quasi continuous stiffness measurement (QCSM) method is used to generate enough data over depth

# ISO 14577 Part 4

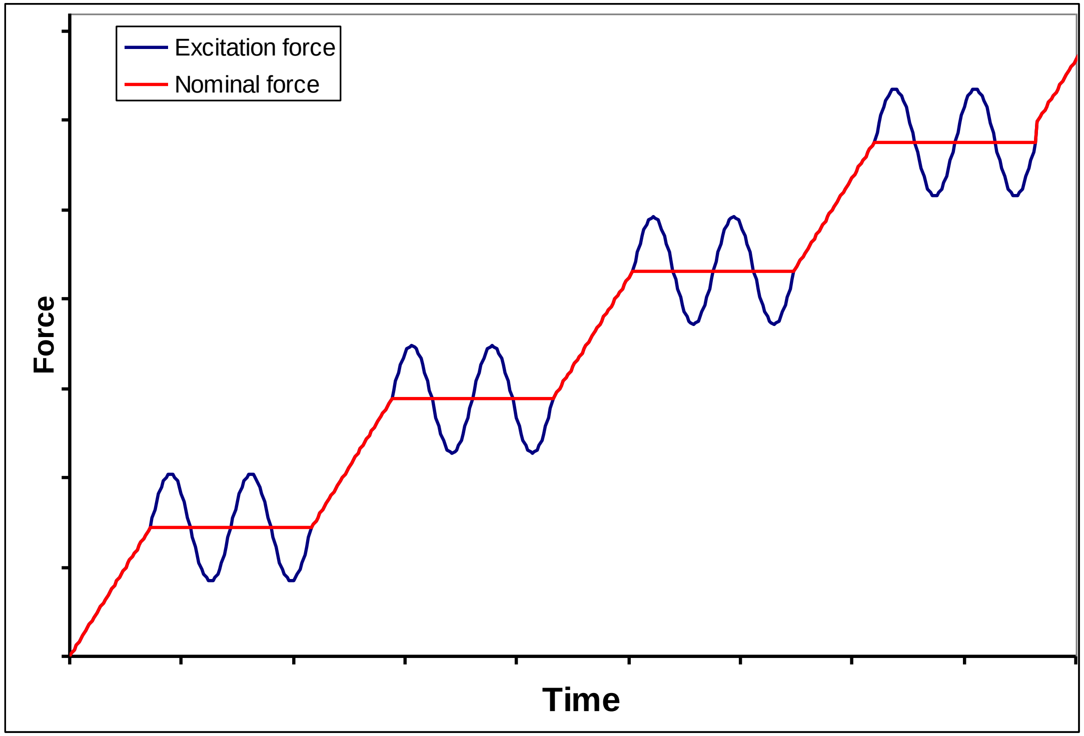
In the case of soft/ductile coatings, indentation force or displacement and indenter geometry shall be chosen such that data shall be obtained in the region where $a/t_c < 1{,}5$. The plane strain indentation modulus of the coating $E_c{}^*$ is obtained by taking a series of measurements at different 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

# QCSM method of ASMEC
# Quasi continuous stiffness measurement

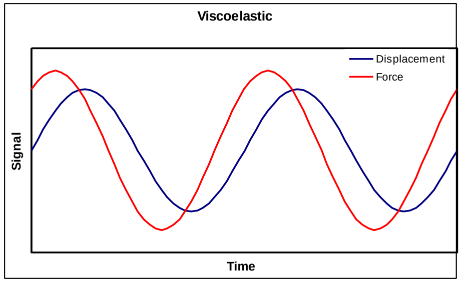


A sinusoidal oscillation is used in superposition to the force signal.

A sinusoidal oscillation is switched on during short dwell times of 2-4 s

Average normal force is kept constant at every point.

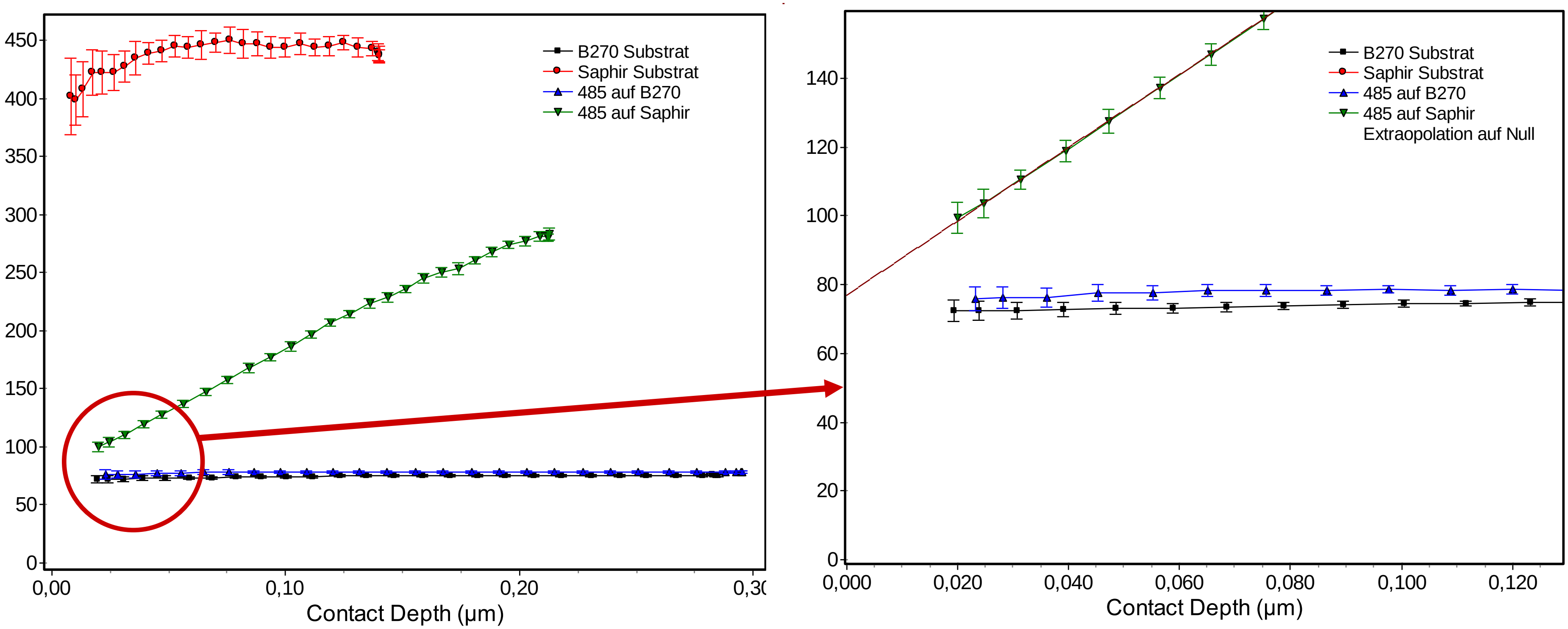
First 20% of the dwell time not used to reduce creep influence.



Amplitude ratio Force/Displacement = contact stiffness

Viscoelastic components result in a Phase shift

# Example: equal $SiO_2$ coatings on glass and sapphire

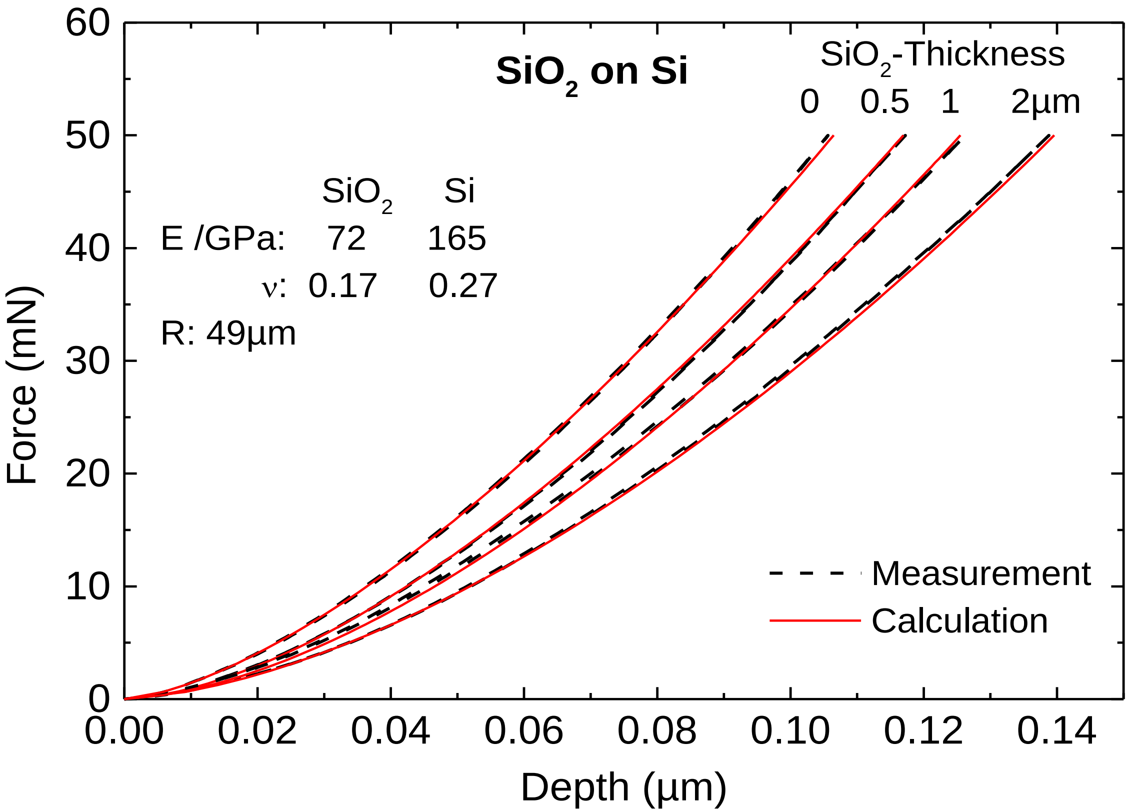


**260nm** oxide coatings on sapphire and glass substrates, maximum force 18mN

First point at (20 nm; 0,24 mN).

# Solution 3 for modulus measurements:

**Eliminating the substrate influence**
**for fully elastic measurements with spheres**
by application of the
**Hertzian contact model for coatings**



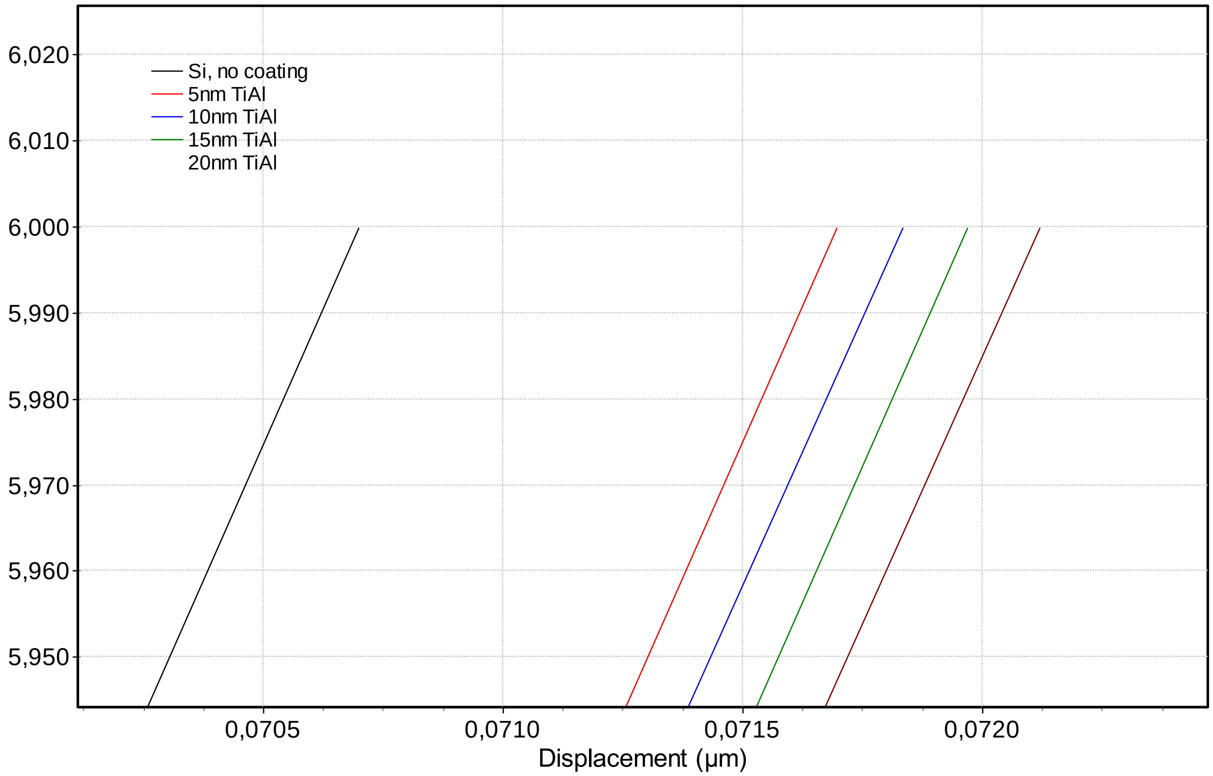
T. Chudoba, N. Schwarzer, F. Richter
Surf. Coat. Tech. 127 (2002) 9-17

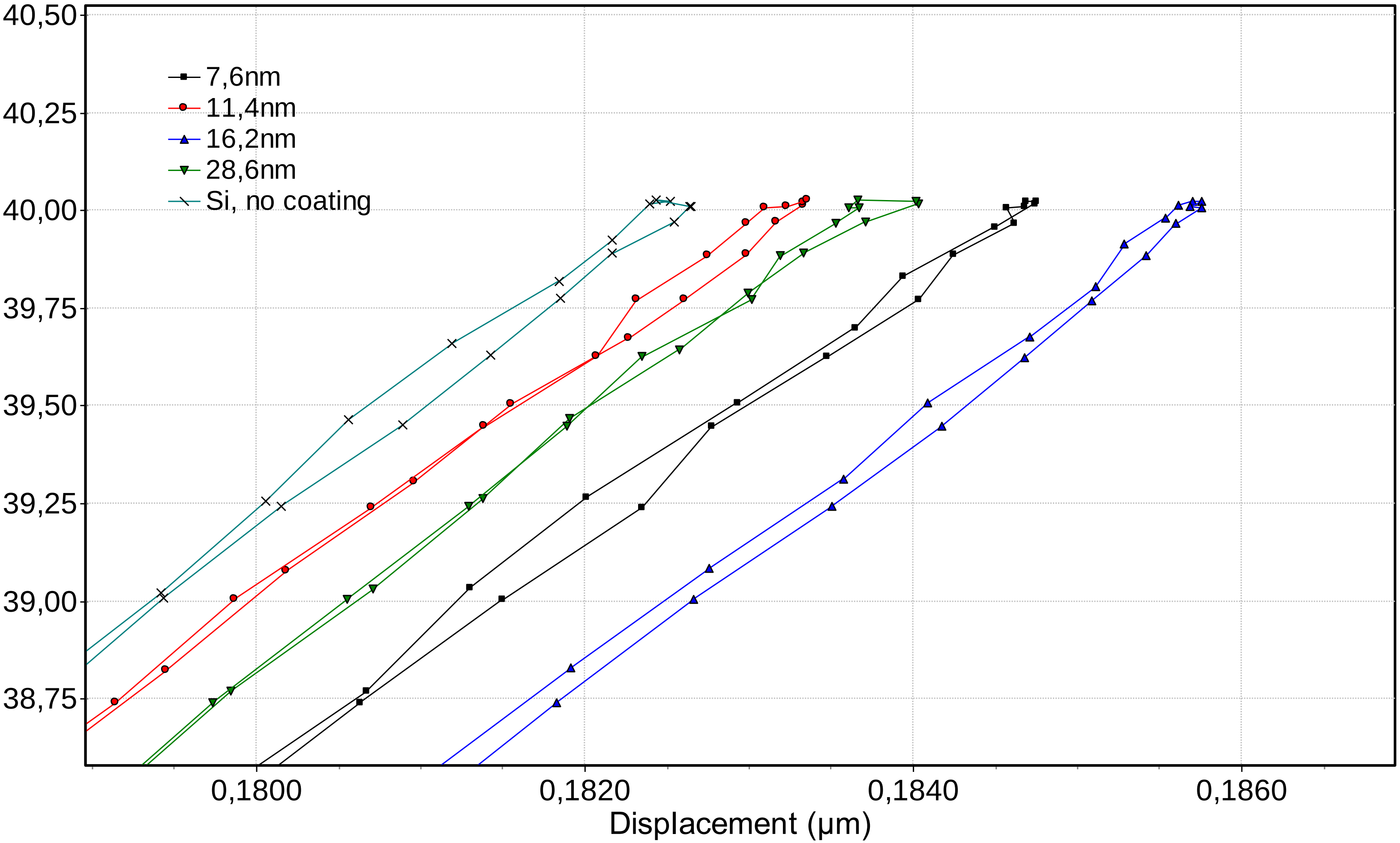
Fit of the measurement data with a theoretical load-displacement curve.

Known substrate properties; fit parameter: film modulus

Useable software ELASTICA, FilmDoctor

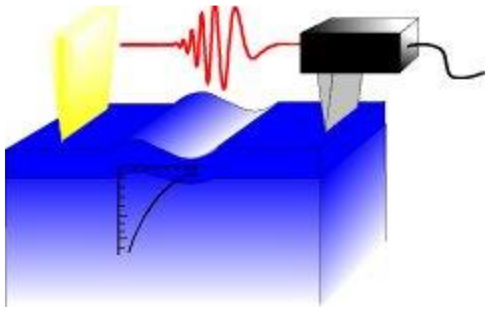
## Thin coatings with 80 GPa on substrate with 165 GPa
## Theoretical force-displacement curve





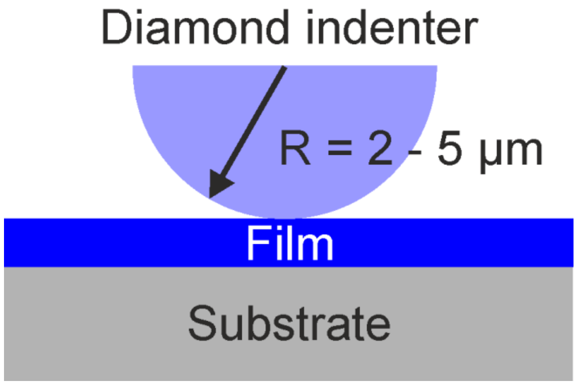
Measured curves for SiO2 films on Si using a 6.5 µm radius indenter at 40mN
Maximum depth difference < 3.5 nm

## SAW (“LAwave”)

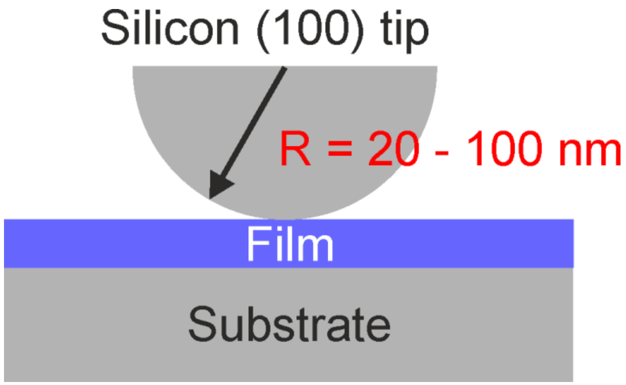


*Source: IWS, Dresden*

## Nanoindentation



## Atomic force acoustic microscopy



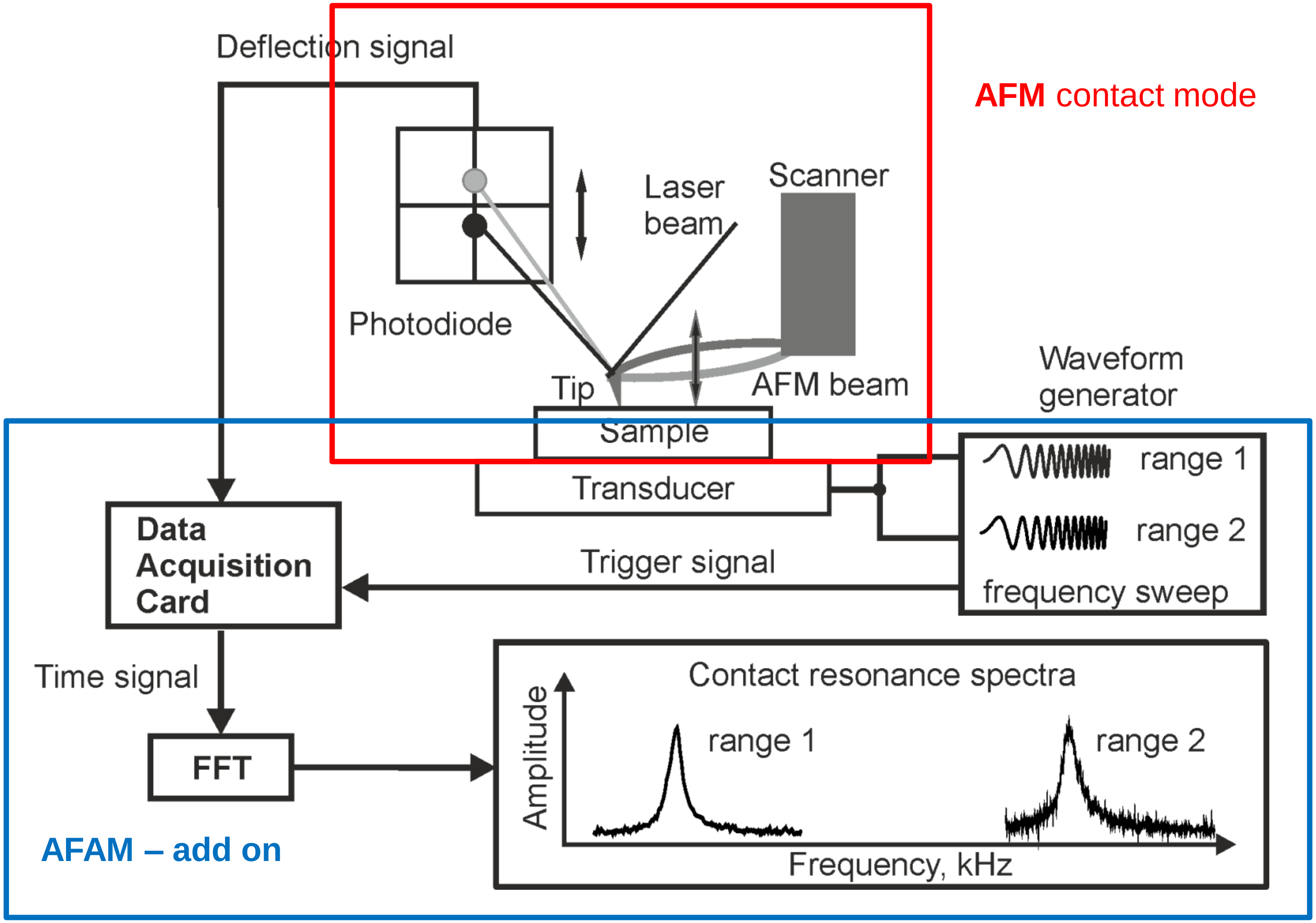
**Acoustic method**

Measures: **Young’s modulus**
Needs: film density and thickness

**Contact methods**

Measures: **Indentation modulus**
Needs: film thickness and substrate properties

AFAM measurements done at Fraunhofer Institute, IzfP, Dresden

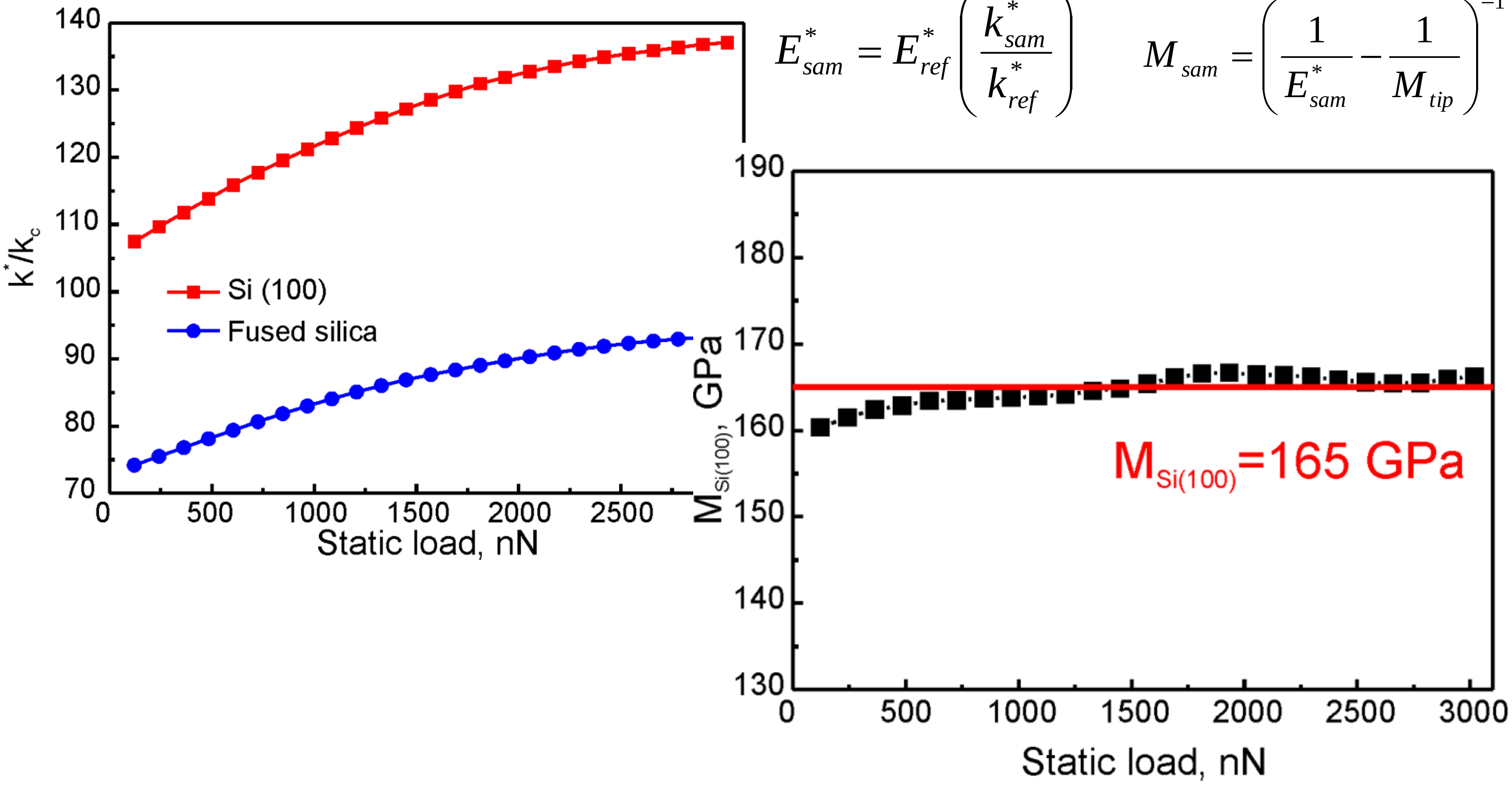


**AFM contact mode**

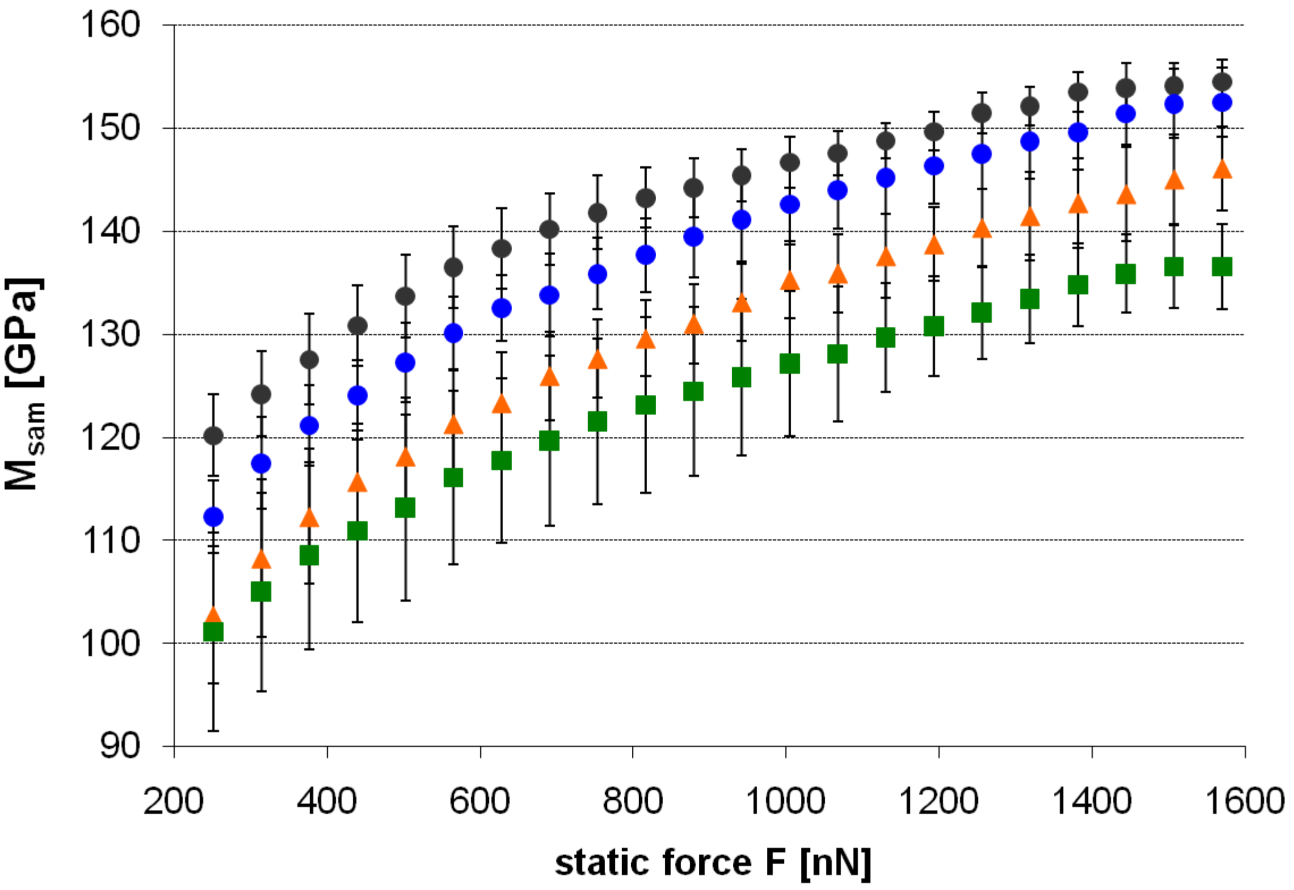
**AFAM – add on**

# Example: Indentation modulus M for Si(100)

$$E^*_{sam} = E^*_{ref}\left(\frac{k^*_{sam}}{k^*_{ref}}\right)^{1.27} \qquad M_{sam} = \left(\frac{1}{E^*_{sam}} - \frac{1}{M_{tip}}\right)^{-1}$$



# Example: nano-thin films of TiAl



Substrate: Si(100)

Samples prepared at Fraunhofer Institute, IPMS, Dresden

# AFAM vs. Nanoindentation

| **Sample** | **Film thickness t, nm** | **AFAM $M_f$, GPa** | **Nanoindentation $M_f$, GPa** |
|---|---|---|---|
| **Titanium aluminide** | 5 | **92** | 90 |
| | 10 | **84** | 88 |
| | 15 | **79** | 79 |
| | 20 | **82** | 82 |

**The values of the indentation modulus obtained by use of the AFAM method agree very well with those obtained by nanoindentation!**

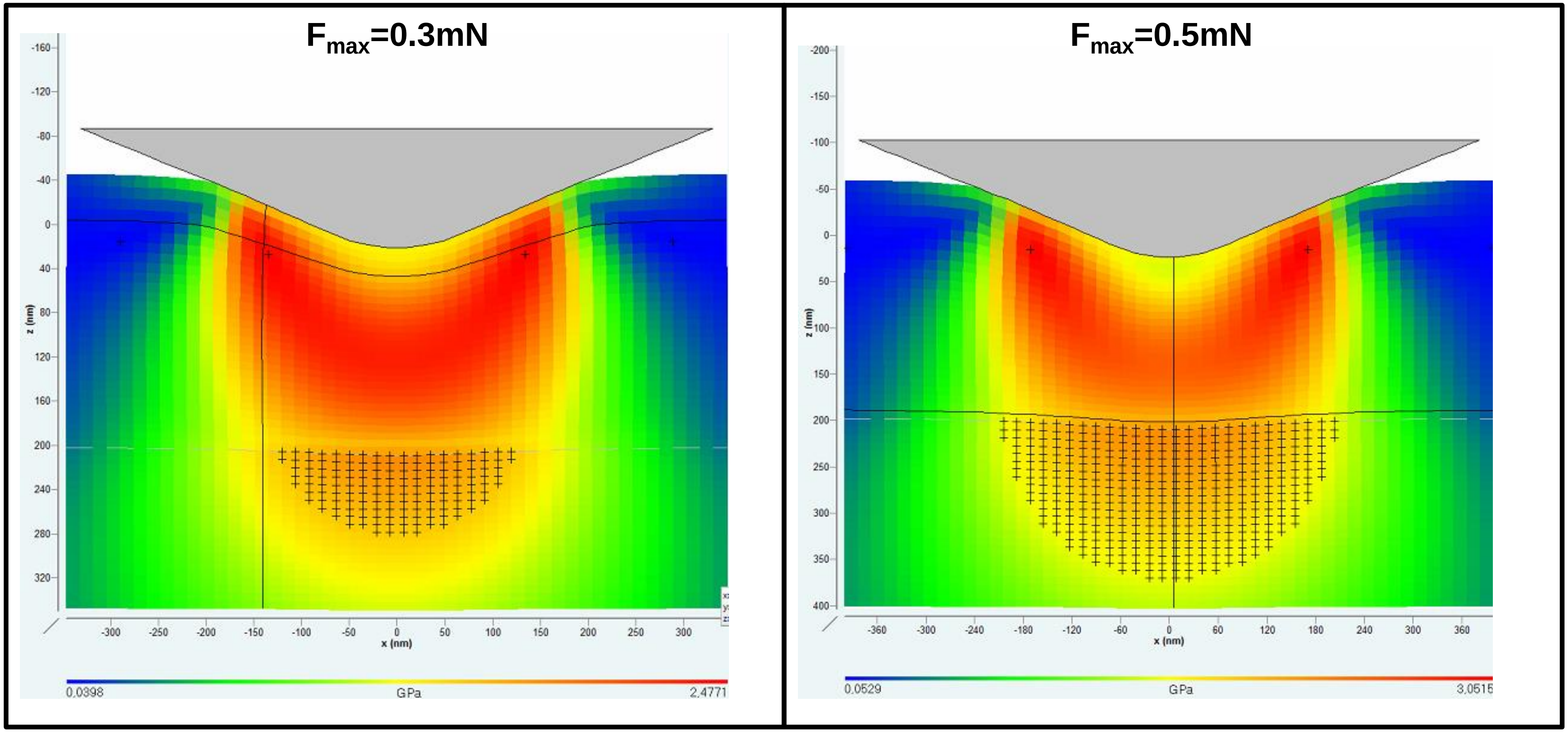
Nanoindentation measurements performed and analyzed by Dr. T. Chudoba, Asmec, GmbH

# Solution 4 for modulus and hardness measurements:

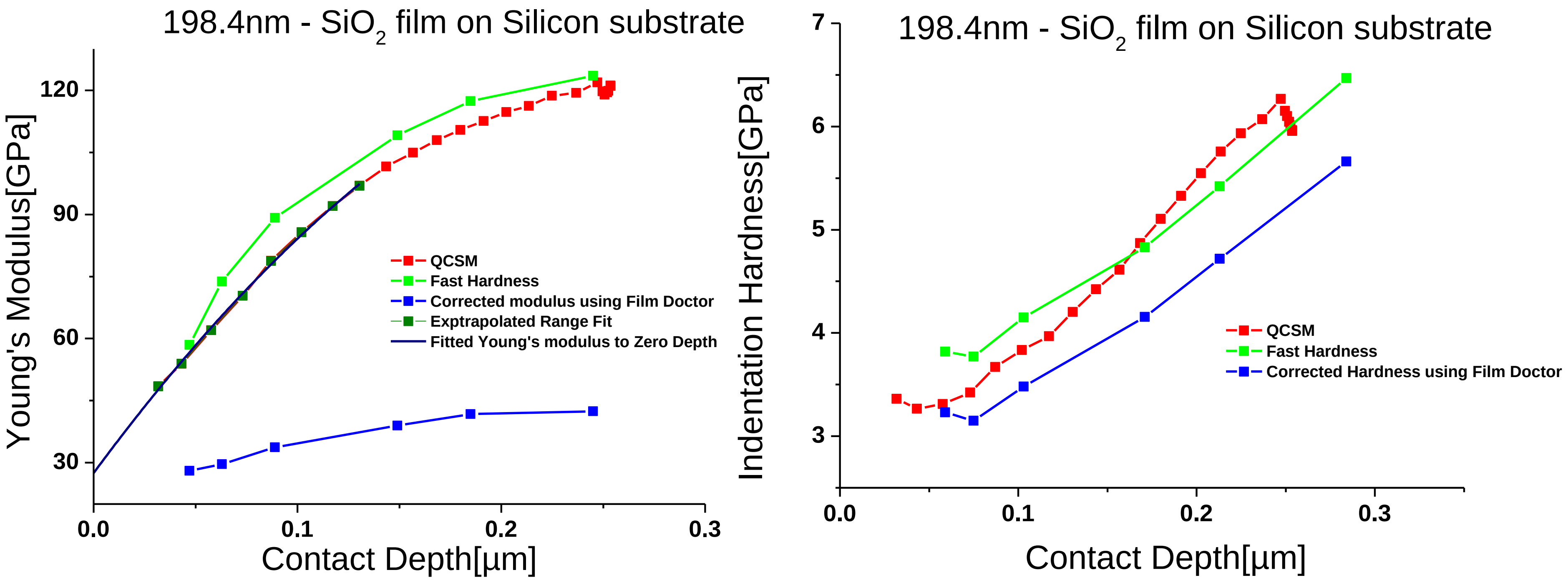
**Eliminating the substrate influence**
**for elastoplastic measurements with sharp tips**
by application of a
**sophisticated contact mechanical model**

# 198.4nm - SiO2 film on Silicon substrate

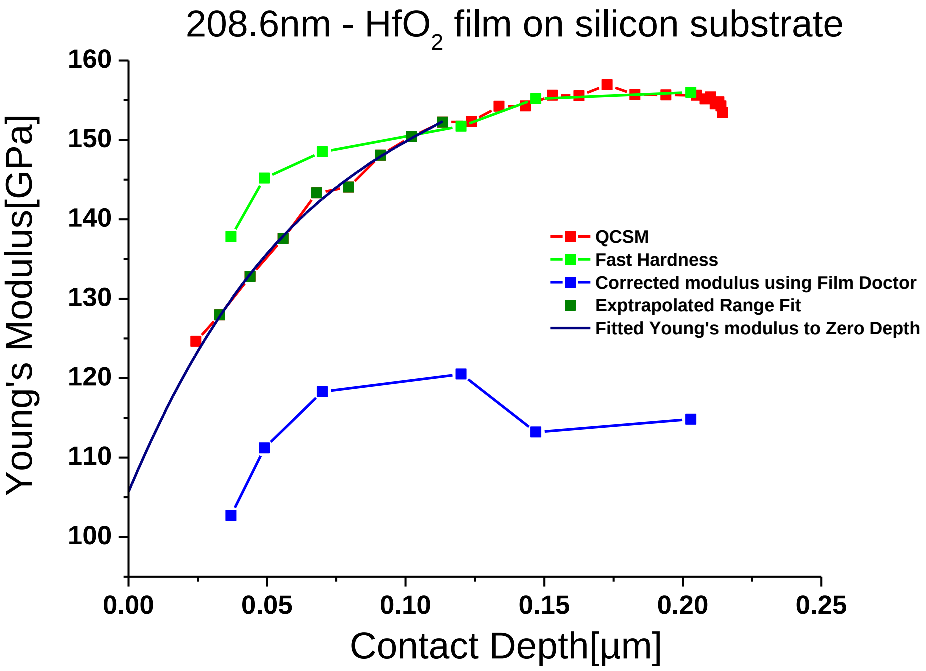
## von Mises Stress (GPa)

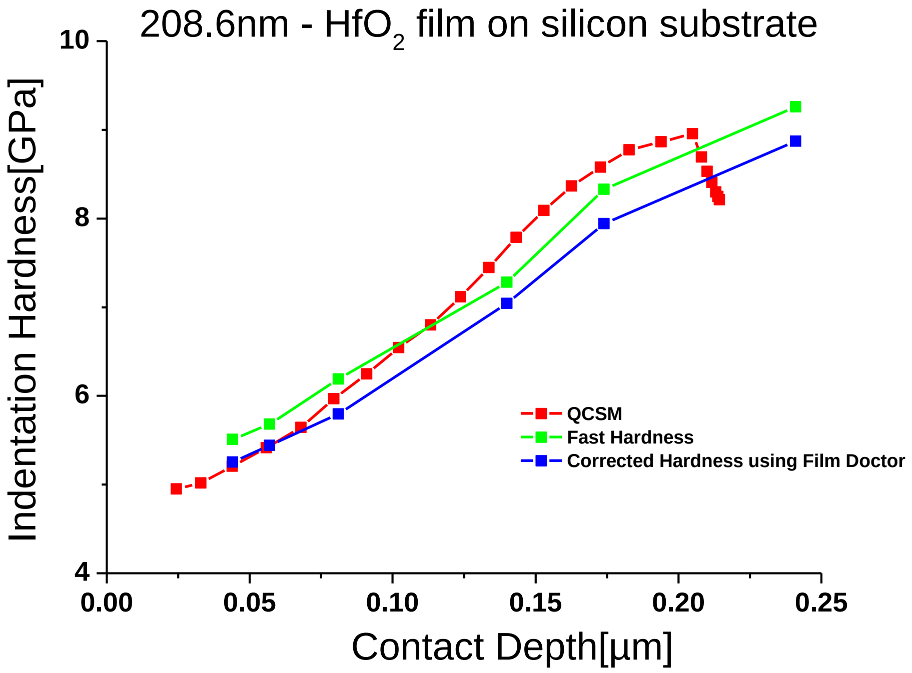

$F_{max}$=0.3mN

$F_{max}$=0.5mN



Comparison between measurements and calculations for force range 0.3mN -10mN





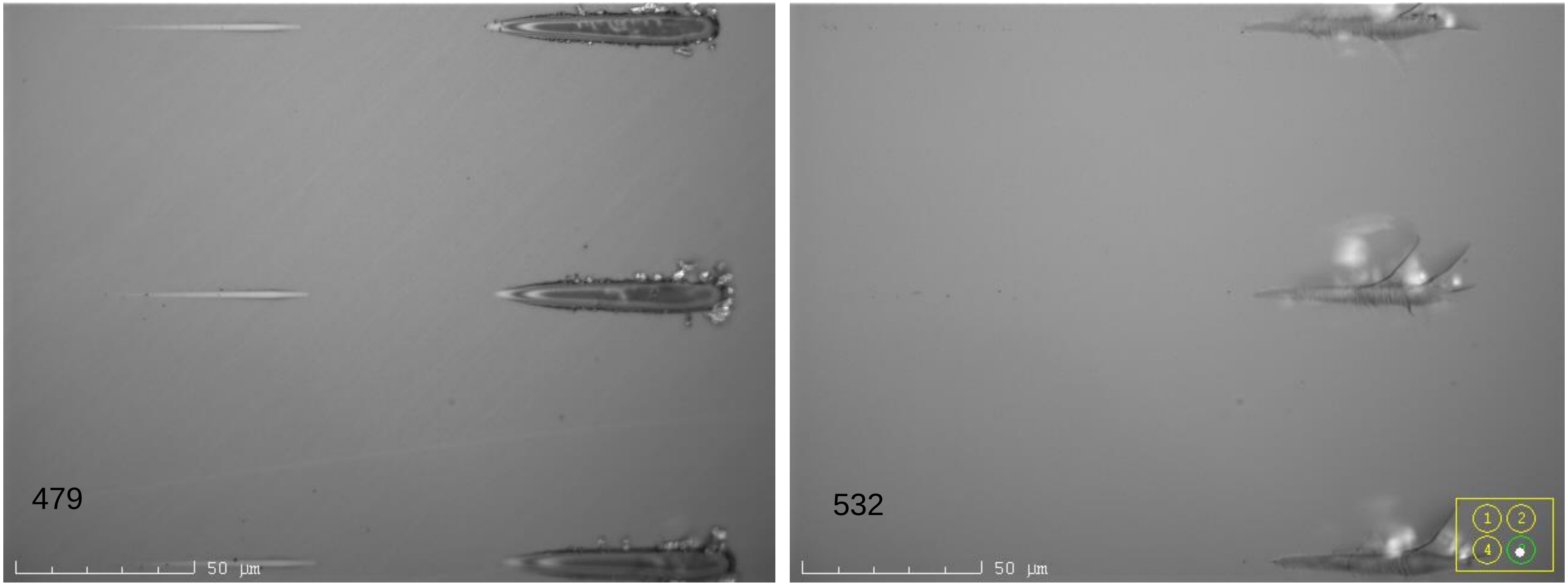
Comparison between measurements and calculations for force range 0.3mN -10mN

# Solution 5 for hardness (yield strength) measurements:

Determining yield strength instead of hardness using micro scratch tests and stress calculations

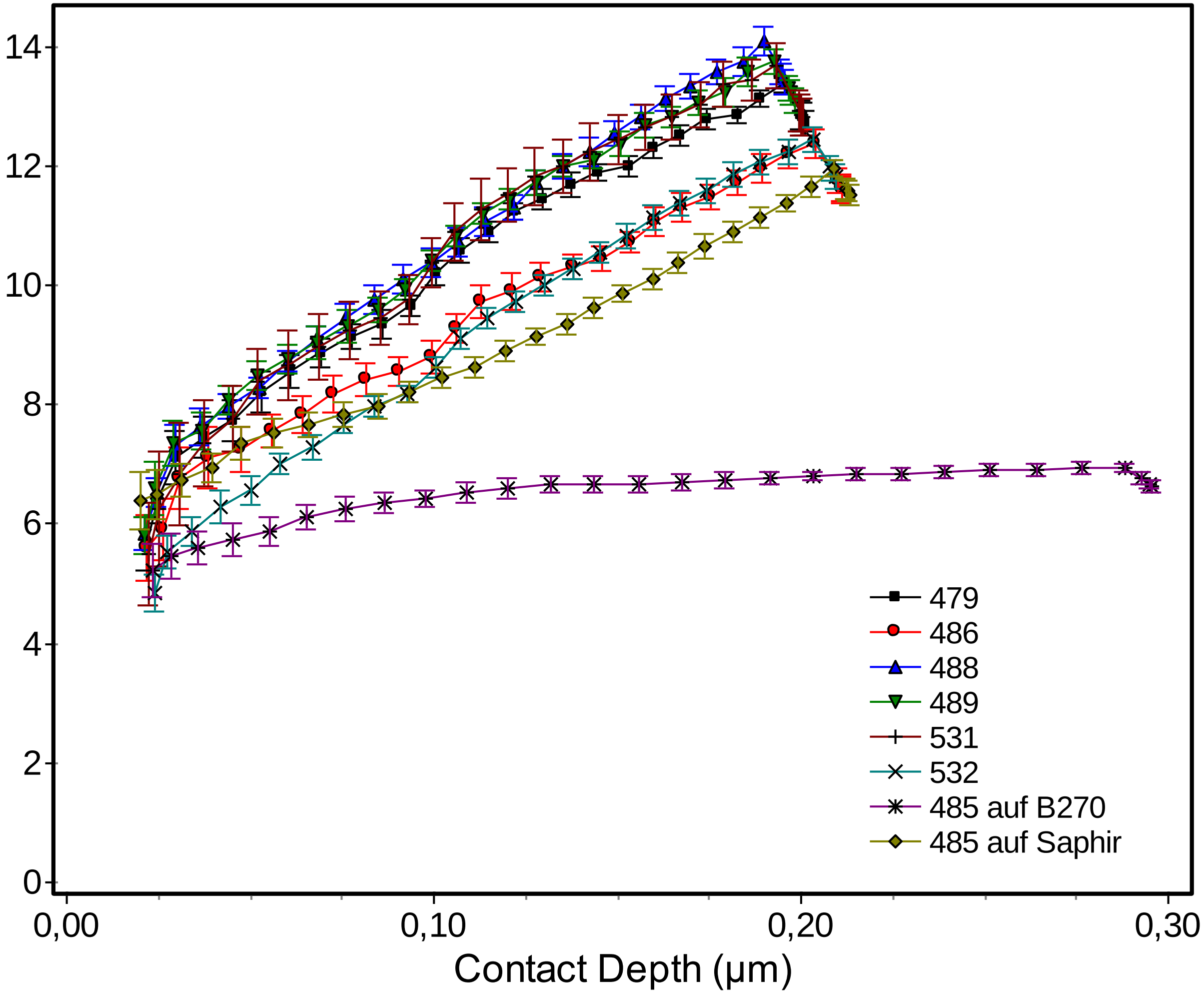
# 240 nm thick optical coatings on sapphire

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

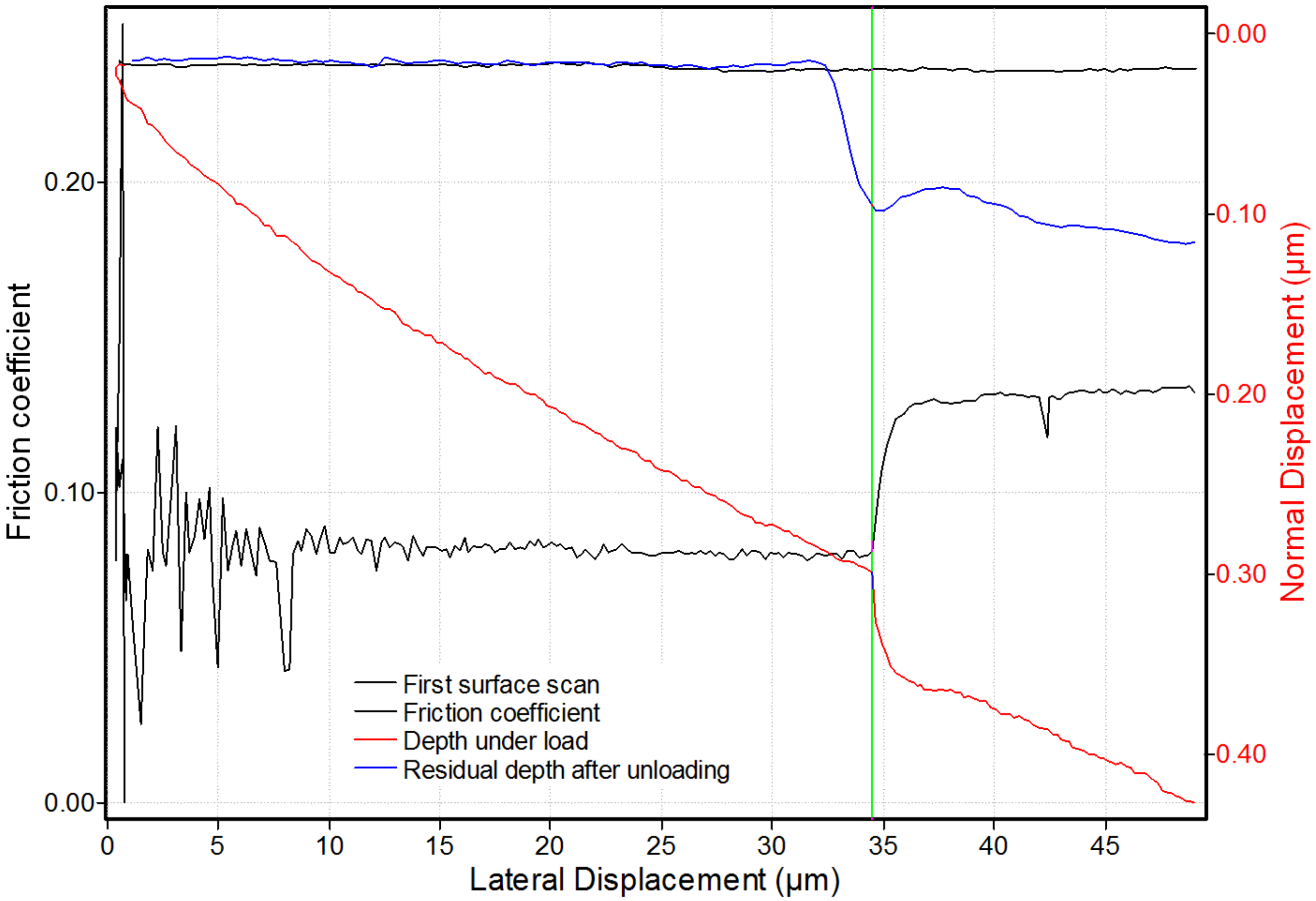


The two coatings show different failure modes

It was not possible to resolve hardness differences with a conventional tip (radius abut 200nmm)



The difference between pre-scan and post-scan of the surface allows detection the elastic-plastic transition

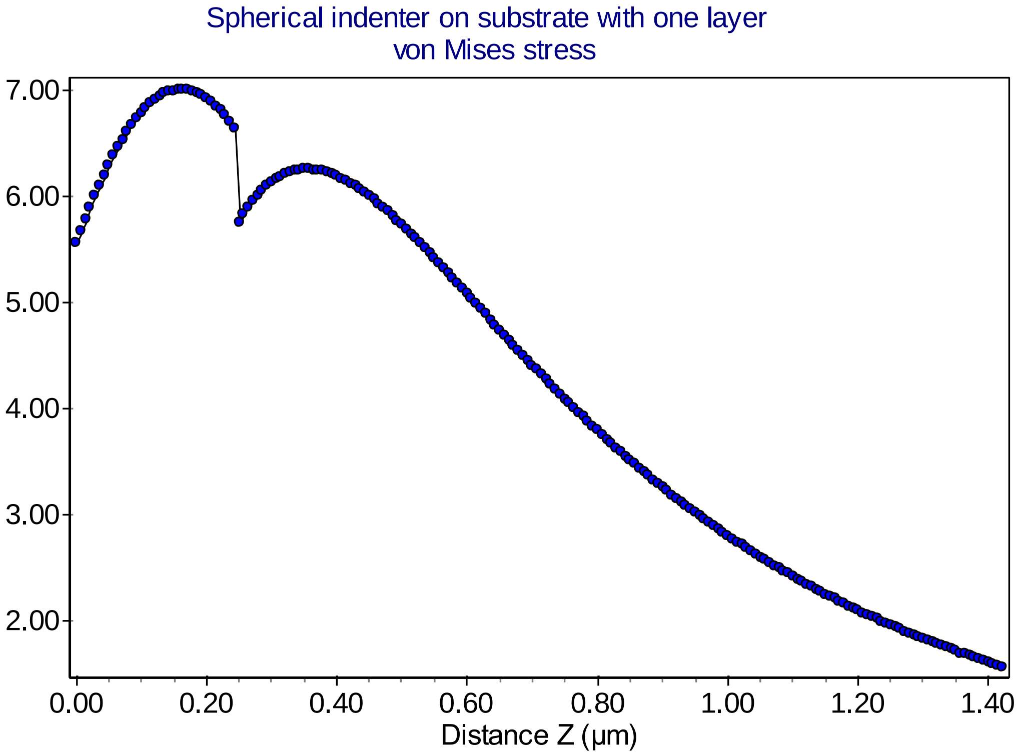


Failure of the coating at: X: 34.48 µm Fn: 174.94 mN µ: 0.081

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

# Thank you for your attention !

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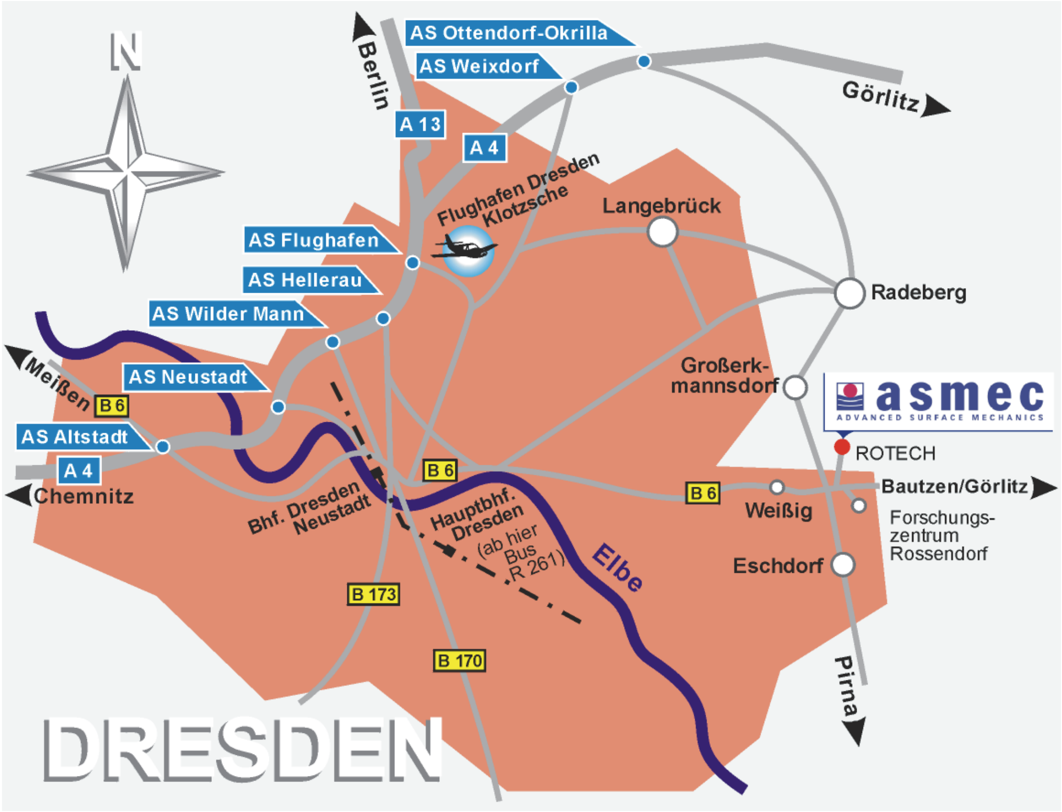
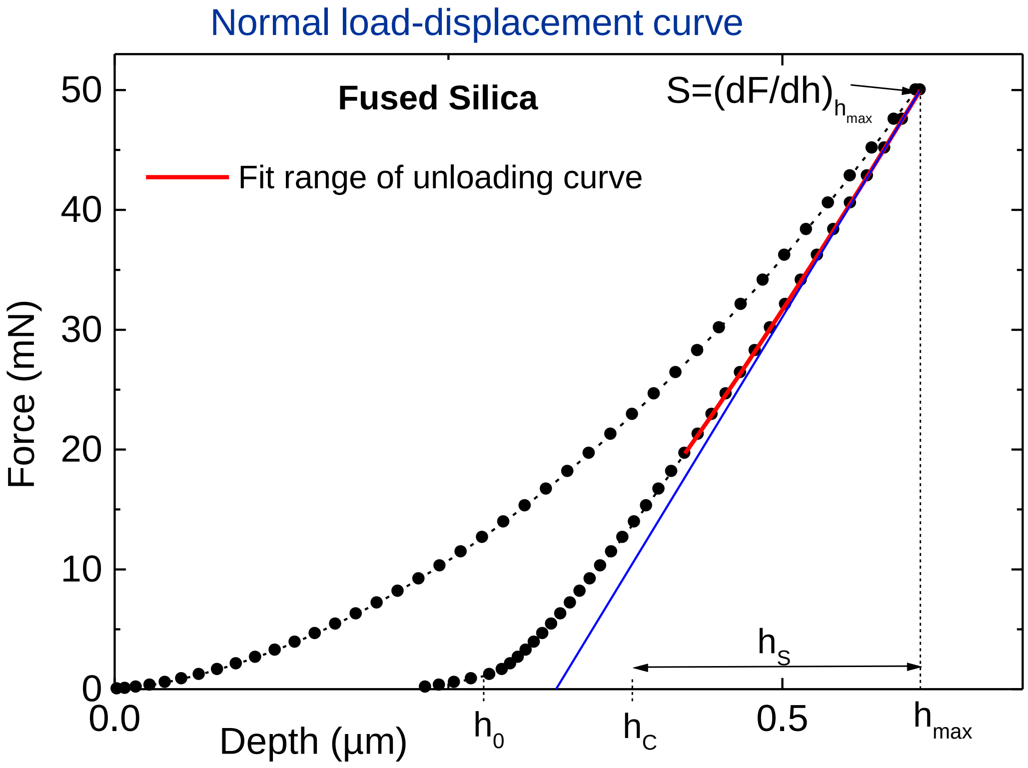


# Nanoindentation: state of the art


Normal load-displacement curve

Measured depth

Contact depth

$$h_C = h_{max} - \varepsilon \cdot \frac{F}{S}$$

Contact area

$$A_C = f(h_C) \propto 24.5 \cdot h_C^2$$

Hardness

$$H = \frac{F}{A_C}$$

Reduced E-Modulus

$$E_r = \frac{\sqrt{\pi}}{2} \cdot \frac{S}{\sqrt{A_C}}$$

Sum of Indenter (i) and sample (s) contribution

$$\frac{1}{E_r} = \frac{1-\nu_i^2}{E_i} + \frac{1-\nu_S^2}{E_S}$$

Maximum force F, displacement h and the unloading stiffness S are used for the calculation of hardness H and modulus E.

The contact area $A_c$ has to be calculated from the indentation depth. This requires a model.