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# *About the characterisation of ultra thin coatings via nanoindenter*

## *Analysing system for the investigation of ultra-thin coatings [1, 2] – determination of their Young's modulus, hardness and yields strength using the method of the „Effective Indenter" [3-5]*

This study should be considered as a documentation for two important tools (modules) of the software FilmDoctor [5]. These modules are:

1. the fit-curve-module and
2. the „tool" „calculate Young's modulus" (in the menu „tools").

## Motivation: Why a special procedure or rather analysing system for ultra-thin coatings? → Why must classical analysing procedures like Oliver and Pharr or tools like ELASTICA and IndentAnalyser fail here?

For very thin coatings, let us say well below 500nm there are two important points which have to be taken into account and which have almost no effect in the case of thicker coatings:

1. In the case of elastic measurement with spherical or parabolic indenterns it usually is impossible to produce contact radii, which are small in comparison with the coating thickness. In dependence on the difference between the Young's moduli of coating and substrate this can result in dramatic deviations from the Hertzian pressure distribution (Fig. 1). Analysing of such indentation data using the method of Field and Swain or with the help of ELASTICA, using the Hertzian theory, is not possible then.
2. In the case of "sharp indenters", very low loads and inelastic measurements, we have the following problems
    a. indenter tip rounding and
    b. an often dramatic violation of the 1/10-Rule (penetration depth / coating thickness) for the determination of coating hardness.

## Solution of the problem

To 1. In this case we simply find the solution by applying the extended Hertzian theory [3] to the measured load-depth-curve. As we see in fig. 1, this theory allows the evaluation of a great variety of different surface stress distributions. This gives us the means for the modelling of contact problems for coating-substrate systems.
In the software FilmDoctor we have installed a module for the fit of the coatings Youngs' modulus for an arbitrary parabolic indenter of the form

$$Z(r)=\frac{r^2}{d_0}+\frac{r^4}{d_2}+\frac{r^6}{d_4}+\frac{r^8}{d_6}. \tag{0.1}$$

The use of this module is elaborated in the next section (to 2). The only difference to this section is the fact that we here consider an elastic indent while in the next section an elastic-inelastic indentation will be considered.

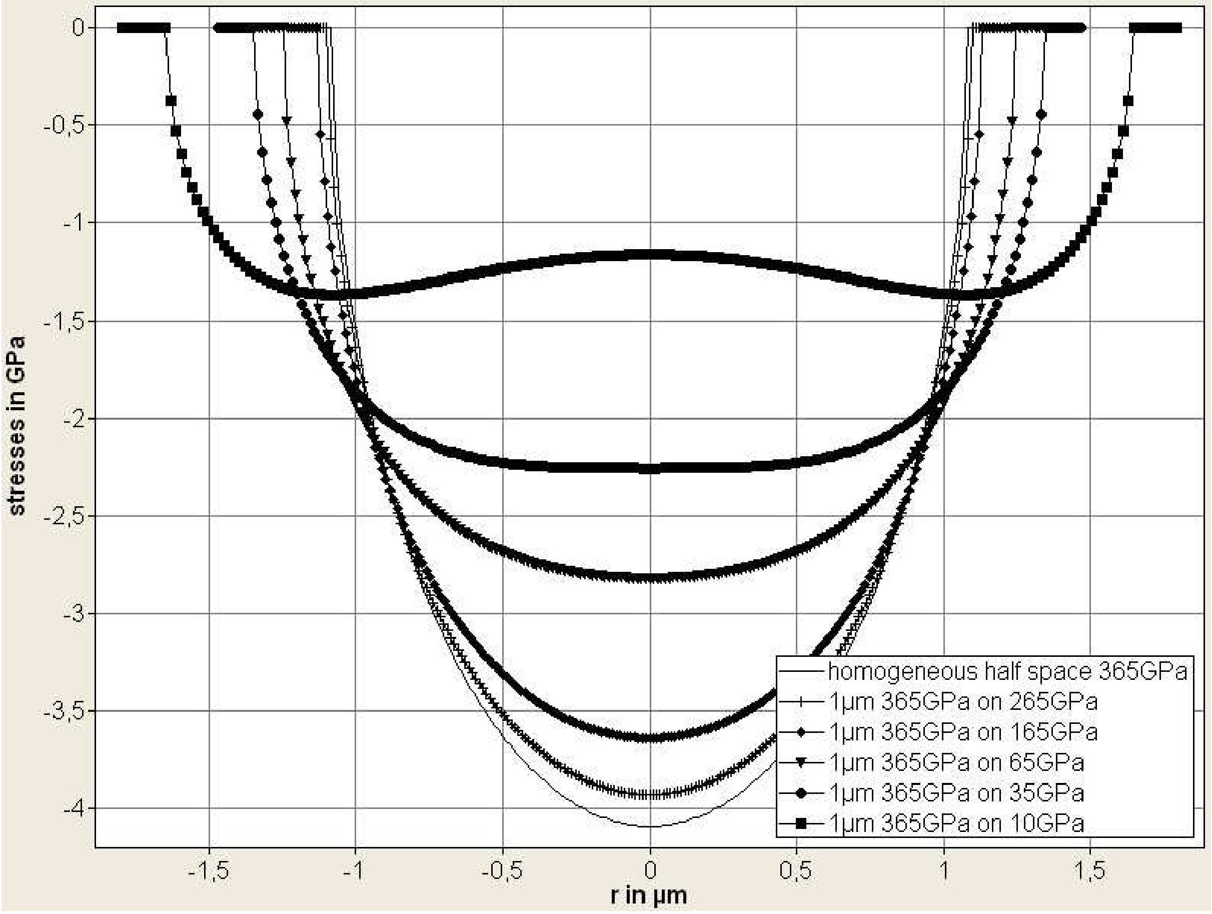
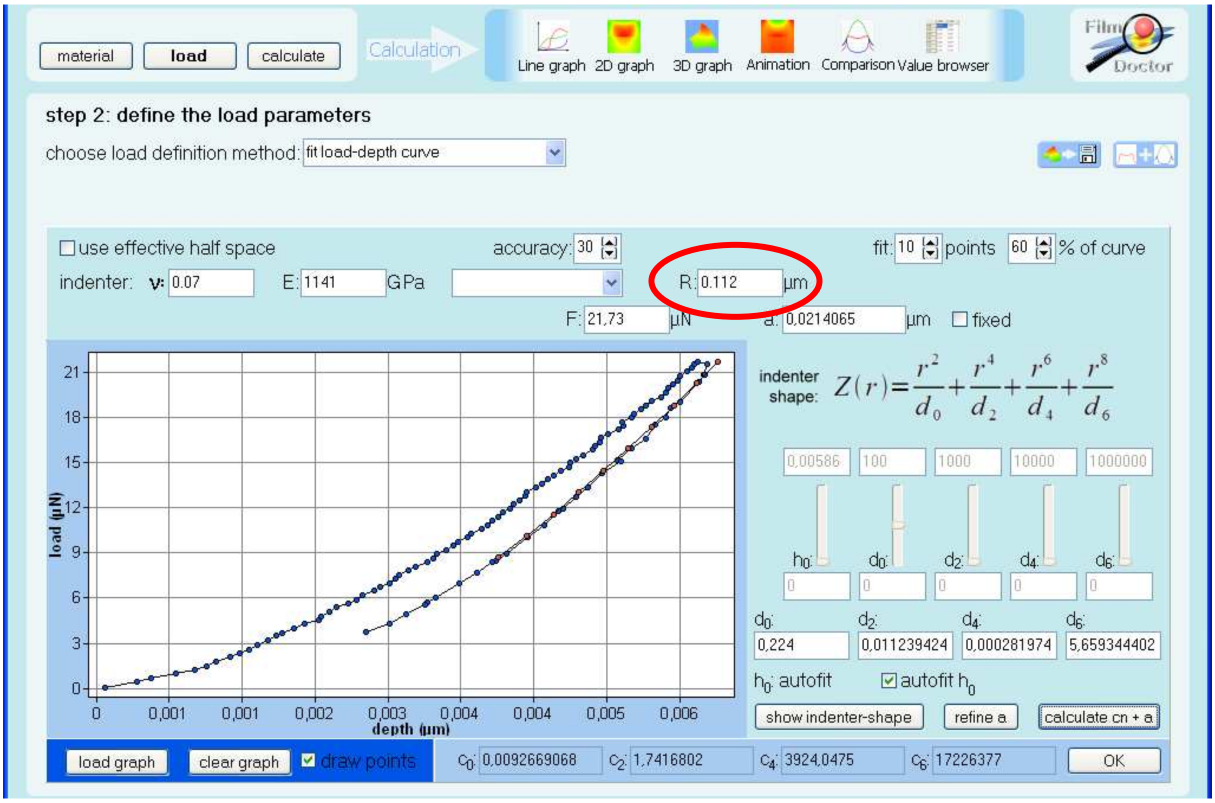


**Fig. 1:** **Resulting normal surface stress distribution for a variety of coating-substrate systems under contact pressure produced by a 50µm-diamond sphere.**

To 2. In the case of an inelastic measurement with sharp indenters (Vickers-, Berkowich- or others) of a thin coating, one first need to determine the „effective half space Young's modulus“ as determined with the Oliver and Pharr (e.g. [4]) method (e.g. with the software IndentAnalyser from the company ASMEC GmbH → www.asmec.de). As an example we consider here a 4.3nm-DLC-coating on silicon. The „effective half space Young's modulus“ was 171GPa. As effective indenter we obtain almost a sphere with the radius of R=0.112µm (Fig. 2a). In fig. 2b a more general indenter shape is fitted to the unloading curve



step 2: define the load parameters

choose load definition method: fit load-depth curve

☐ use effective half space accuracy: 30 fit: 10 points 60 % of curve

indenter: ν: 0.07 E: 1141 GPa R: 0.112 µm

F: 21,73 µN a: 0,0214065 µm ☐ fixed

indenter shape: $Z(r)=\frac{r^2}{d_0}+\frac{r^4}{d_2}+\frac{r^6}{d_4}+\frac{r^8}{d_6}$

0,00586 100 1000 10000 1000000

$h_0$: 0 $d_0$: 0 $d_2$: 0 $d_4$: 0 $d_6$: 0

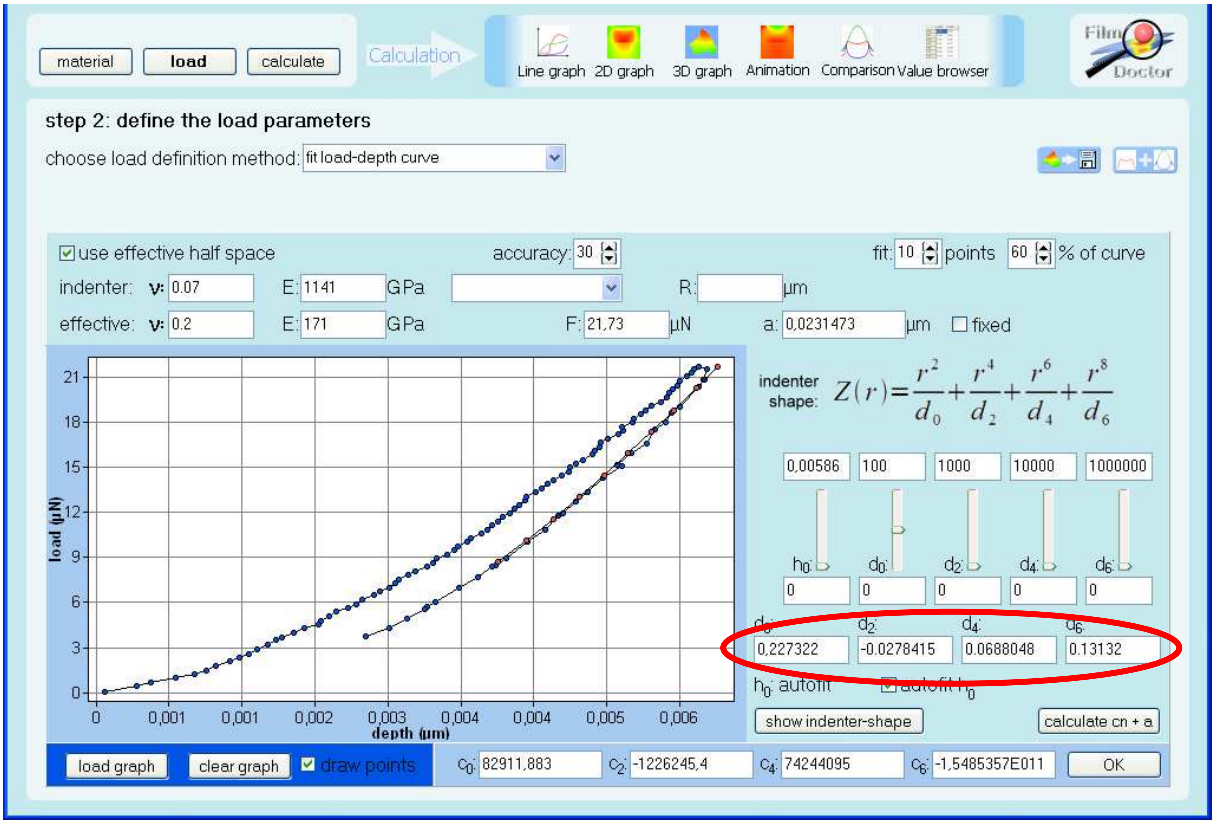
$d_0$: 0,224 $d_2$: 0,011239424 $d_4$: 0,000281974 $d_6$: 5,659344402

$h_0$: autofit ☑ autofit $h_0$

☑ draw points

$c_0$: 0,0092669068 $c_2$: 1,7416802 $c_4$: 3924,0475 $c_6$: 17226377

**Fig. 2a:** **Example for a Berkowich measurement with a so called AKKU-Tip into a 4.3nm-DLC-coating on silicon (maximum load: 21µN). The software IndentAnalyser evluated an „effective half space Young's modulus" of 171GPa for the coating-substrate system. The red dots show the effective indenter (a sphere with radius R, see red ellipse) fit to the unloading curve.**



step 2: define the load parameters

choose load definition method: fit load-depth curve

☑ use effective half space accuracy: 30 fit: 10 points 60 % of curve

indenter: ν: 0.07 E: 1141 GPa R: µm

effective: ν: 0.2 E: 171 GPa F: 21,73 µN a: 0,0231473 µm ☐ fixed

indenter shape: $Z(r)=\frac{r^2}{d_0}+\frac{r^4}{d_2}+\frac{r^6}{d_4}+\frac{r^8}{d_6}$

0,00586 100 1000 10000 1000000

$h_0$: 0 $d_0$: 0 $d_2$: 0 $d_4$: 0 $d_6$: 0

$d_0$: 0,227322 $d_2$: -0.0278415 $d_4$: 0.0688048 $d_6$: 0.13132

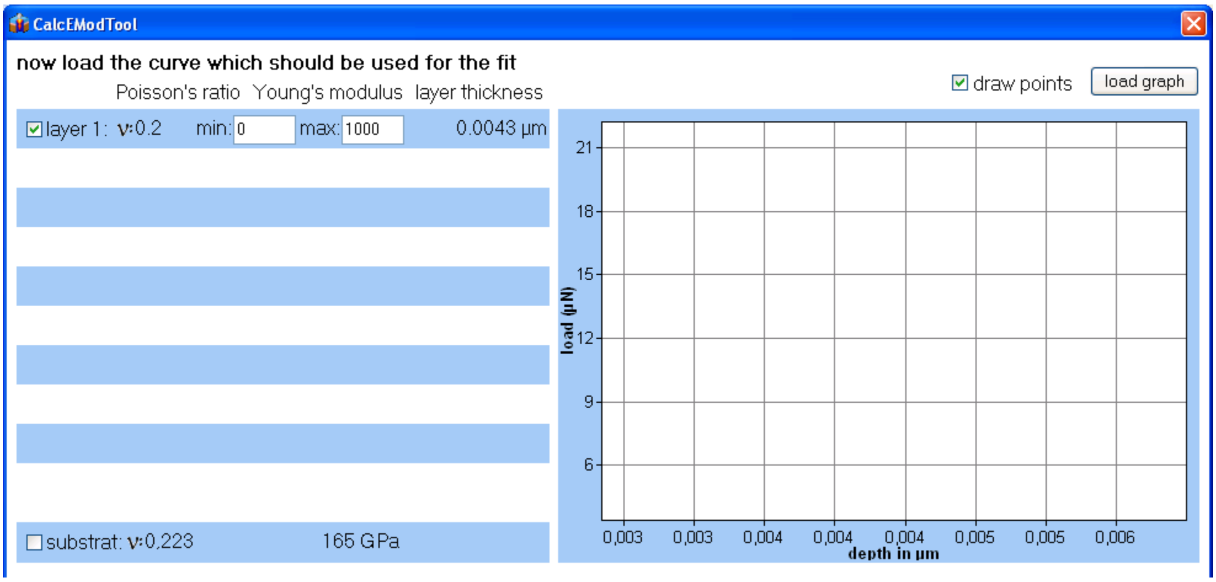
$h_0$: autofit ☑ autofit $h_0$

☑ draw points

$c_0$: 82911,883 $c_2$: -1226245,4 $c_4$: 74244095 $c_6$: -1,5485357E011

**Fig. 2b:** **Berkowich indentation of Fig. 2a. The red dots show the effective indenter fit to the unloading curve. In contrast to fig. 2a this time a more general indenter shape (parabolic) was fitted to the unloading curve (see red ellipse).**

Next step is to open the „tool“ „Calculate Young’s modulus“ in the menu line. There we chose the coating where we intent to fit the Young’s modulus for and load the load-depth-curve (Fig. 3 and Fig. 4).



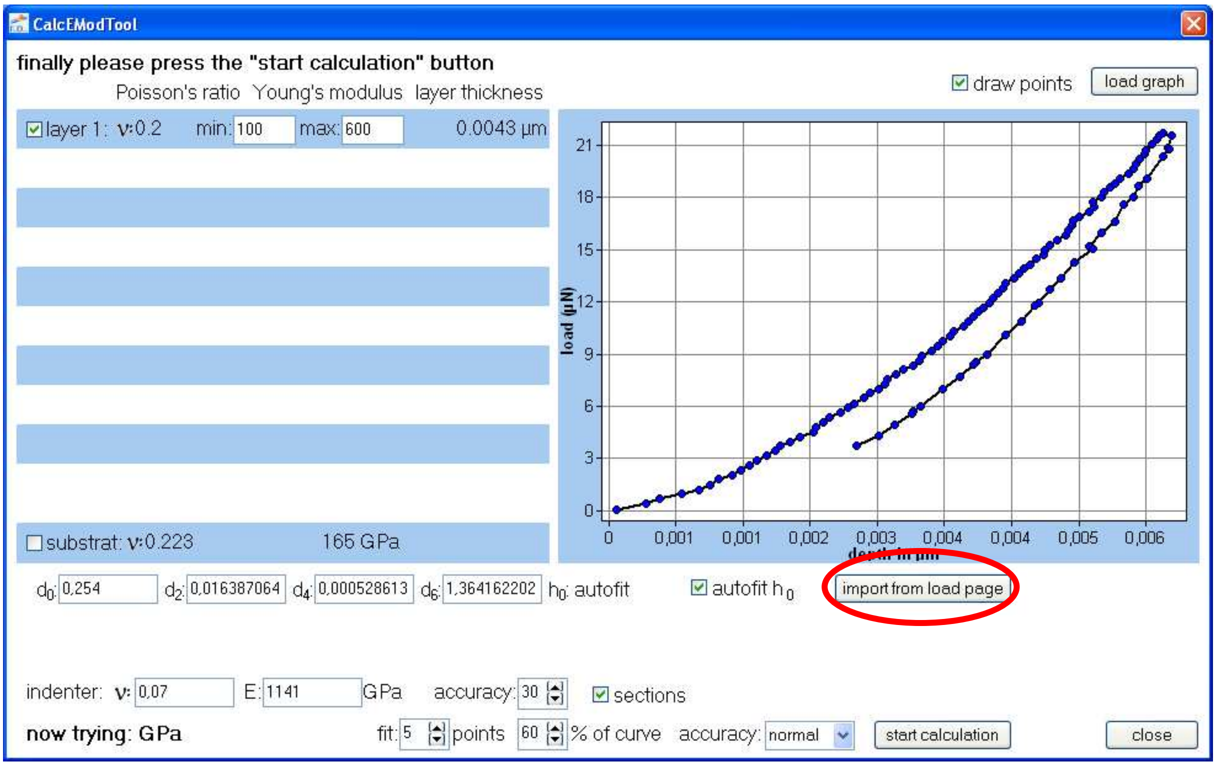
now load the curve which should be used for the fit

☑ layer 1: ν:0.2 min: 0 max: 1000 0.0043 µm

☐ substrat: ν:0.223 165 GPa

**Fig. 3:** „Tool“ „Calculate Young’s modulus“ with the coating selected for the fit (tick).

After loading the curve into the program we chose the effective indenter found with the „fit load-depth curve” module previously (see Fig. 2a), which was a sphere of radius R=112nm (Fig. 4).



finally please press the "start calculation" button

☑ layer 1: ν:0.2 min: 100 max: 600 0.0043 µm

☐ substrat: ν:0.223 165 GPa

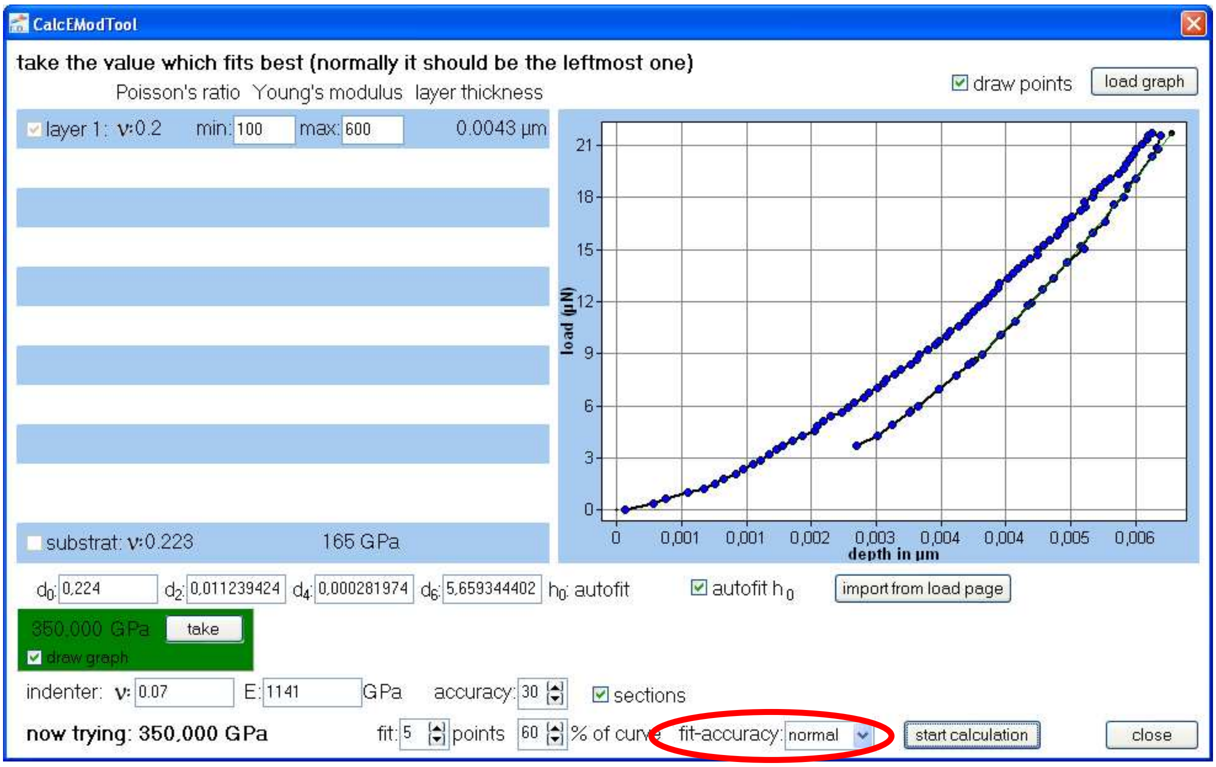
$d_0$: 0,254 $d_2$: 0,016387064 $d_4$: 0,000528613 $d_6$: 1,364162202 $h_0$: autofit ☑ autofit $h_0$

indenter: ν: 0,07 E: 1141 GPa accuracy: 30 ☑ sections

now trying: GPa fit: 5 points 60 % of curve accuracy: normal

**Fig. 4:** Choosing the right (effective) indenter (here „import from load page“ – red ellipse) and setting of the limits for the fit (here min=100 und max=600).

With the button „start calculation“ the fit starts and provides us a coating Young’s modulus of 400GPa (Fig. 5).


CalcEModTool

take the value which fits best (normally it should be the leftmost one)

Poisson's ratio Young's modulus layer thickness

☑ layer 1: ν:0.2 min: 100 max: 600 0.0043 µm

☐ substrat: ν:0.223 165 GPa

$d_0$: 0,224 $d_2$: 0,011239424 $d_4$: 0,000281974 $d_6$: 5,659344402 $h_0$: autofit ☑ autofit $h_0$

350,000 GPa ☑ draw graph

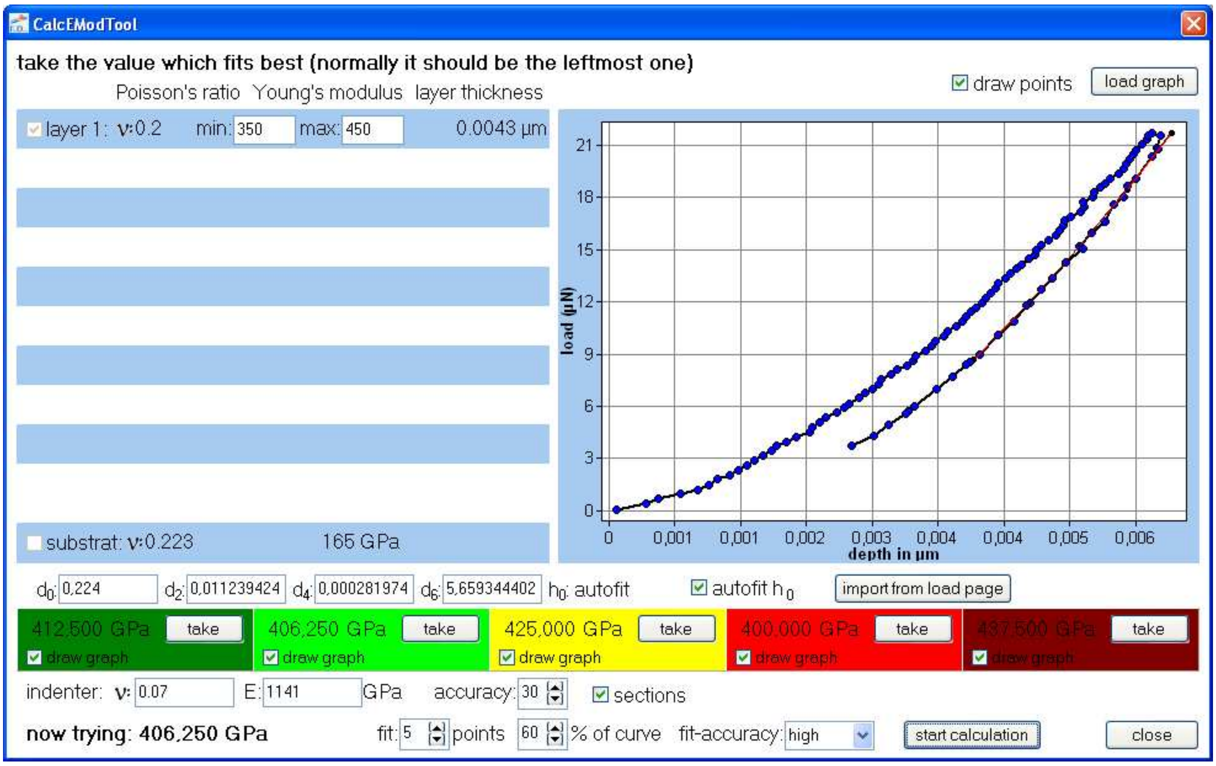
indenter: ν: 0.07 E: 1141 GPa accuracy: 30 ☑ sections

now trying: 350,000 GPa fit: 5 points 60 % of curve fit-accuracy: normal

☑ draw points

**Fig. 5:** **Result of a first rough fit (The limits where chosen in wide range of min=100 und max=600). Now the fit will be repeated with new boundaries 350GPa and 450GPa and an increased fit-accuracy set to high (red circle) → see next figure.**

Now we refine the limit min and max and start the fit again (Fig. 6a and 6b). For the spherical effective indenter (Fig. 6a) we found a result which is in very good agreement with the known 390GPa ± 24GPa of this ultra-thin coating [2] measured with a 3µm spherical diamond indenter and analysed using a pure Hertzian approximation. However, we obtain a significantly different value for the more accurate parabolic effective indenter (Fig. 6b). Here the results of about 306GPa is in almost perfect agreement with the SAW measurement performed at the IWS which provided 304GPa ± 12GPa [2].



CalcEModTool

take the value which fits best (normally it should be the leftmost one)

Poisson's ratio Young's modulus layer thickness

☑ draw points

☑ layer 1: ν:0.2 min: 350 max: 450 0.0043 µm

☐ substrat: ν:0.223 165 GPa

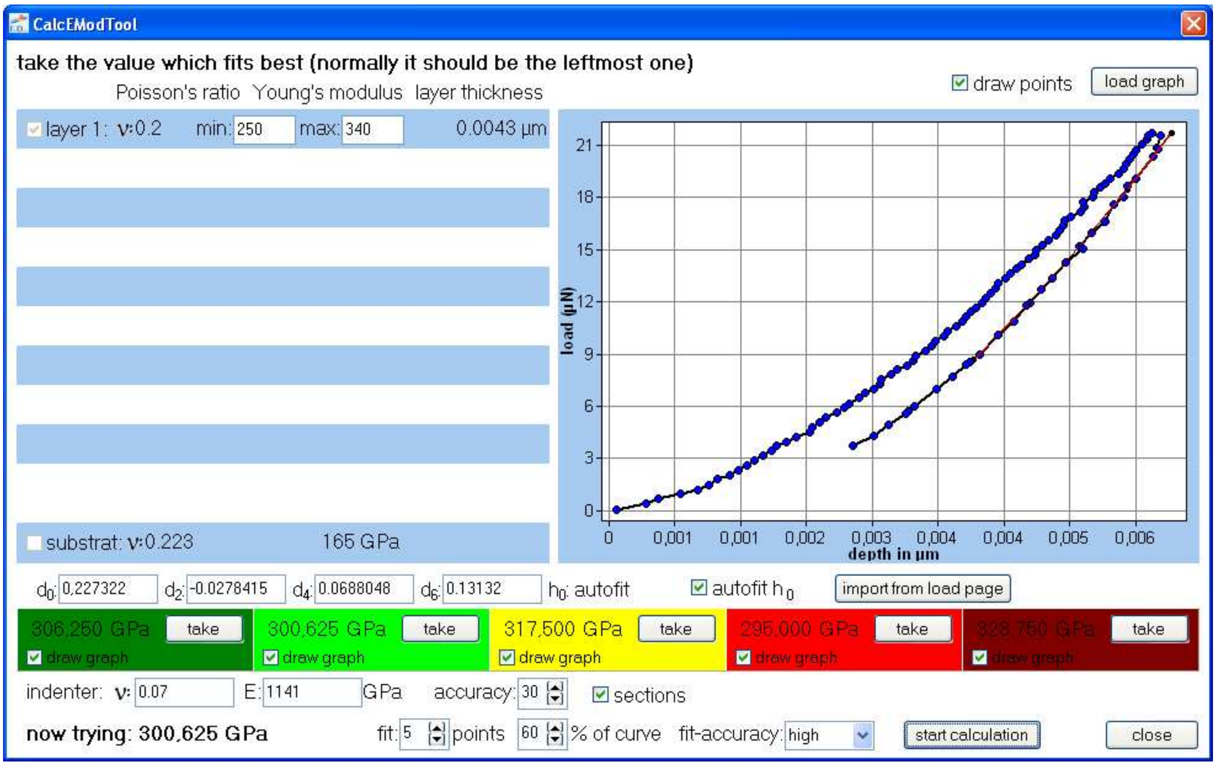
$d_0$: 0,224 $d_2$: 0,011239424 $d_4$: 0,000281974 $d_6$: 5,659344402 $h_0$: autofit ☑ autofit $h_0$

412,500 GPa ☑ draw graph | 406,250 GPa ☑ draw graph | 425,000 GPa ☑ draw graph | 400,000 GPa ☑ draw graph | 437,500 GPa ☑ draw graph

indenter: ν: 0.07 E: 1141 GPa accuracy: 30 ☑ sections

now trying: 406,250 GPa fit: 5 points 60 % of curve fit-accuracy: high

**Fig. 6a:** **Results of the second Fit after refining the limits for the coating Young's modulus (here min=350 und max=450) for the spherical effective indenter.**



CalcEModTool

take the value which fits best (normally it should be the leftmost one)

Poisson's ratio Young's modulus layer thickness

☑ draw points

☑ layer 1: ν:0.2 min: 250 max: 340 0.0043 µm

☐ substrat: ν:0.223 165 GPa

$d_0$: 0.227322 $d_2$: -0.0278415 $d_4$: 0.0688048 $d_6$: 0.13132 $h_0$: autofit ☑ autofit $h_0$

306,250 GPa ☑ draw graph | 300,625 GPa ☑ draw graph | 317,500 GPa ☑ draw graph | 295,000 GPa ☑ draw graph | 328,750 GPa ☑ draw graph

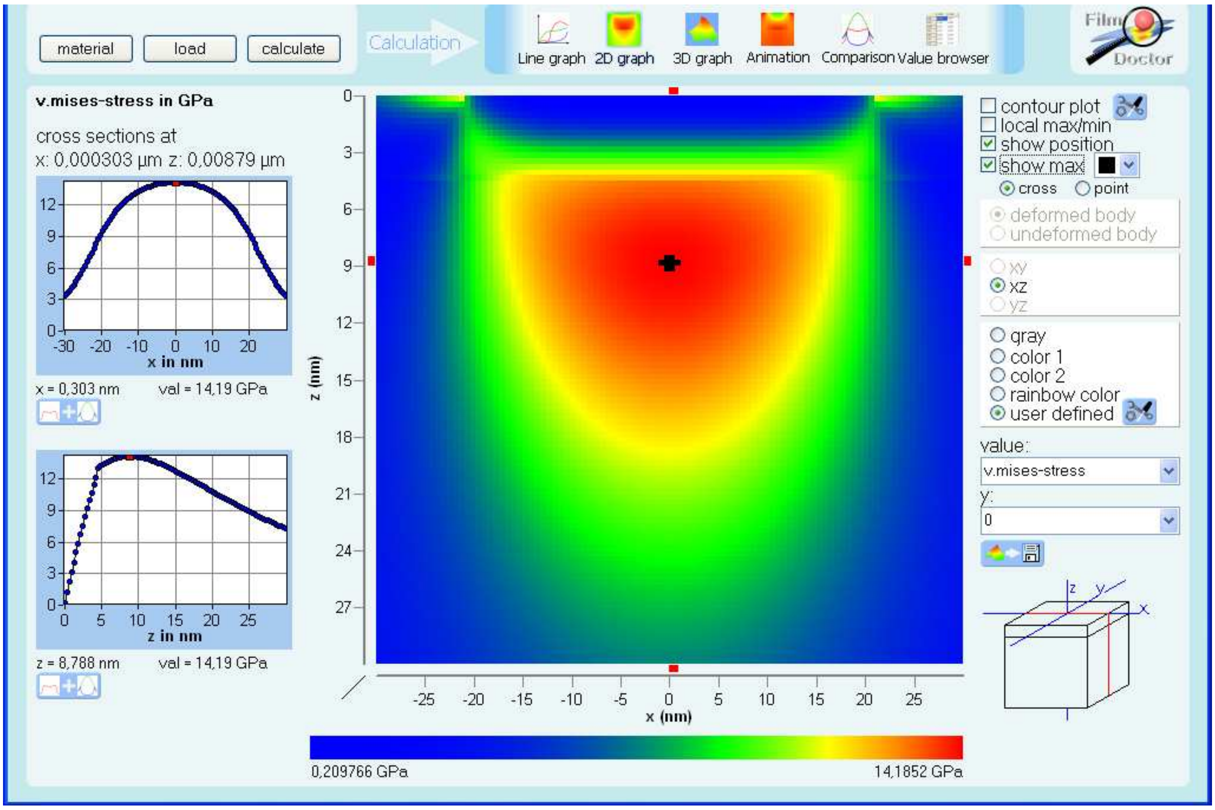
indenter: ν: 0.07 E: 1141 GPa accuracy: 30 ☑ sections

now trying: 300,625 GPa fit: 5 points 60 % of curve fit-accuracy: high

**Fig. 6b:** **Results of the Fit after refining the limits for the coating Young's modulus (here min=250 und max=340) for the parabolic effective indenter.**

Now the found coating Young's modulus is being used as material parameter for the material input page. We evaluate the stress field in the moment of maximum depth (load approx. 21µN). We find a maximum for the von Mises stress of 14.2GPa in the substrate and 11.5GPa

in the coating (Fig. 7a) in the case of the spherical effective indenter. The parabolic indenter result is 13.7GPa in substrate and 11.6GPa in the coating.
If we could be sure, that the substrate would have been completely elastic during the penetration process, we could use the maximum coating stress as yield strength measure for the coating. However, in this case we know from other investigation, that the substrate is responsible for the inelastic behaviour of the coating-substrate system [1].



v.mises-stress in GPa

cross sections at
x: 0,000303 µm z: 0,00879 µm

x = 0,303 nm val = 14,19 GPa

z = 8,788 nm val = 14,19 GPa

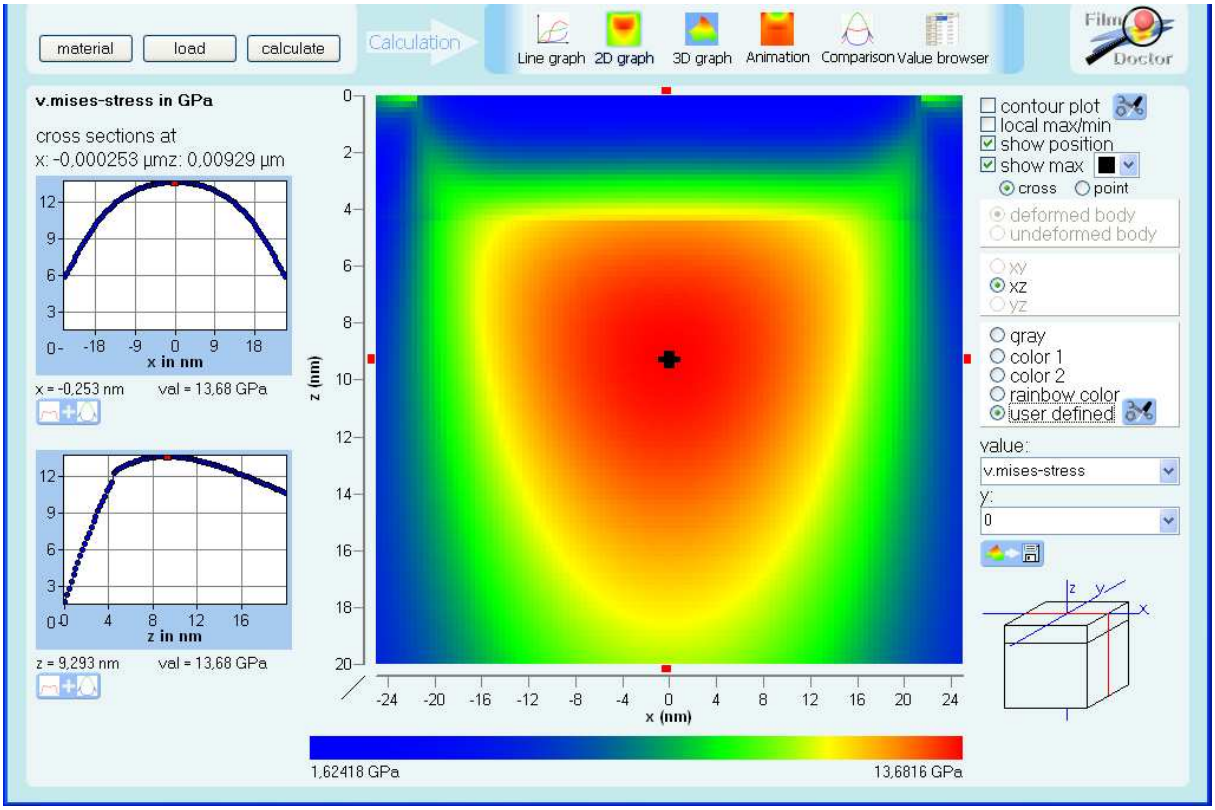
☐ contour plot
☐ local max/min
☑ show position
☑ show max
● cross ○ point
● deformed body
○ undeformed body
○ xy
● xz
○ yz
○ gray
○ color 1
○ color 2
○ rainbow color
● user defined

value: v.mises-stress

y: 0

0,209766 GPa 14,1852 GPa

**Fig. 7a: von Mises stress in the moment of beginning unloading for the spherical effective indenter.**



**v.mises-stress in GPa**

cross sections at
x: -0,000253 µmz: 0,00929 µm

x = -0,253 nm val = 13,68 GPa

z = 9,293 nm val = 13,68 GPa

☐ contour plot
☐ local max/min
☑ show position
☑ show max
● cross ○ point
● deformed body
○ undeformed body
○ xy
● xz
○ yz
○ gray
○ color 1
○ color 2
○ rainbow color
● user defined

value: v.mises-stress

y: 0

1,62418 GPa 13,6816 GPa

**Fig. 7b:** **von Mises stress in the moment of beginning unloading for the effective indenter of parabolic shape.**

## References

[1] N. Schwarzer, T. Chudoba, F. Richter: „Investigation of ultra thin coatings using Nanoindentation”, Surface and Coatings Technology, Vol 200/18-19 pp 5566-5580, online at doi: `http://dx.doi.org/10.1016/j.surfcoat.2005.07.075`

[2] T. Chudoba, M. Griepentrog, A. Dück, D. Schneider, F. Richter, Young’s modulus measurements on ultra-thin coatings, J. Mater. Res., 19 (2004) 301

[3] N. Schwarzer, "Elastic Surface Deformation due to Indenters with Arbitrary symmetry of revolution", J. Phys. D: Appl. Phys., 37 (2004) 2761-2772

[4] G. M. Pharr, B. Bolshakov, "Understanding nanoindentation unloading curves", J. Mater. Res., Vol. 17, No. 10, Oct 2002.

[5] FilmDoctor: software package for the evaluation of the elastic field of arbitrary combinations of normal, rotating and lateral loads of the type $\sim r^n\sqrt{a^2-r^2}$ (with n=0,2,4,6), available from the internet at: http://www.siomec.de/downloads (contact: service@siomec.de).