The Feasibility of Ultra-Hardness in Nanocomposite Coatings

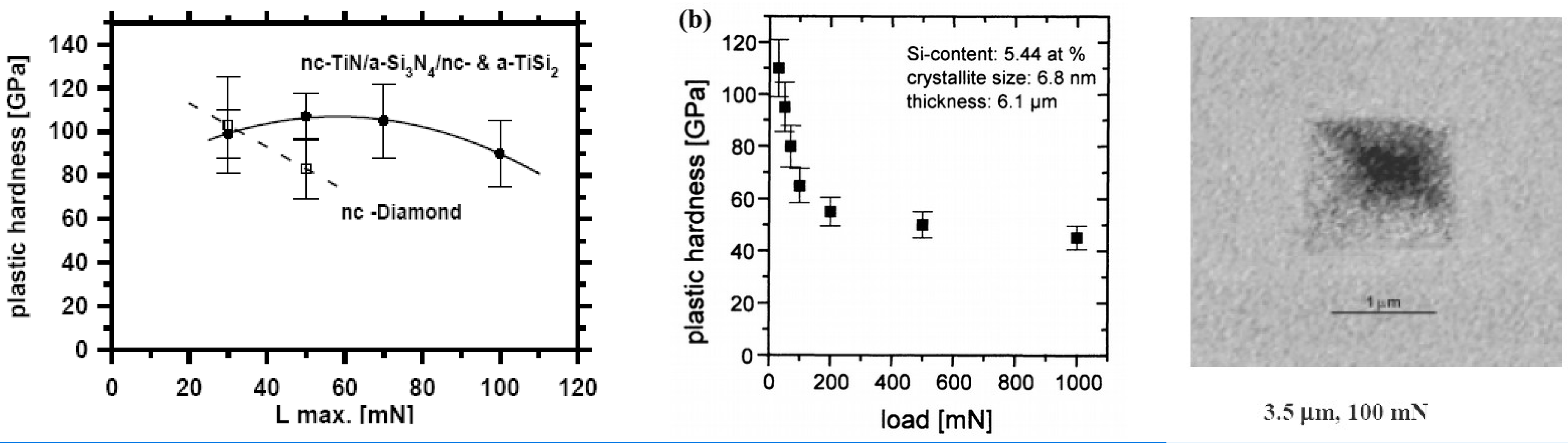
Marcus Fuchs

Saxonian Institute of Surface Mechanics

Sächsisches Institut für Oberflächenmechanik

Motivation

Since 1999 Mr. Stan Veprek claims to have produced nanocomposite nc-TiN/a-Si3N4/TiSi2 coatings with **hardness exceeding 100 GPa** [1, 2], meaning they are at least as hard as regular diamond.



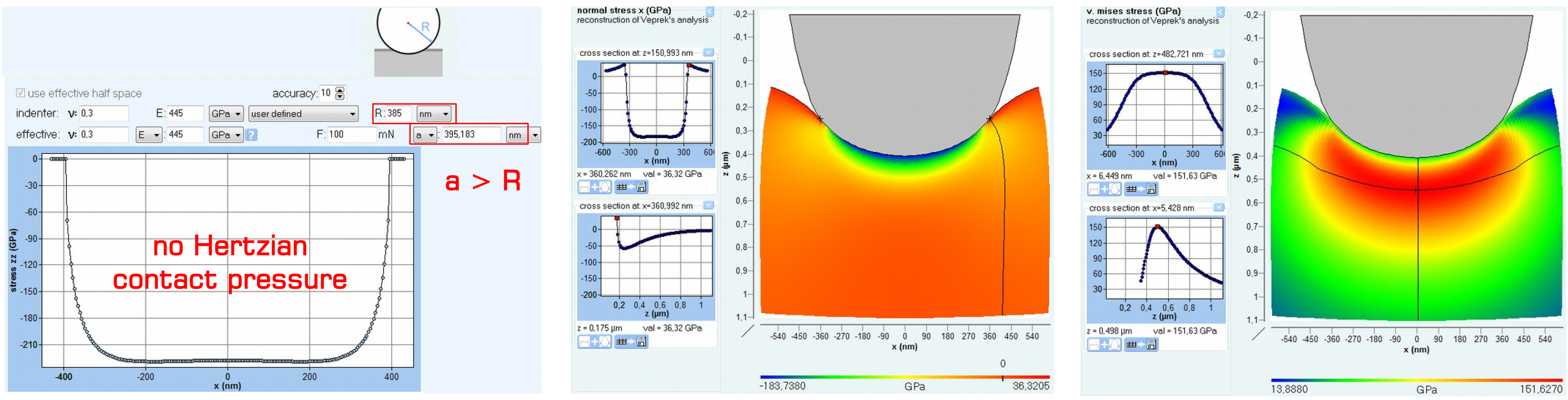
A Few Basic Issues

- **No sample** of ultra-hard nc-TiN/a-Si_3N_4/$TiSi_2$ provided for independent verification.
- **No correct SEM images** provided ever … so far.
- Dozens of publications are all based on only 6 samples (**cross and circular references**).

1st Critical Review revealed sever mistakes in indentation analysis [3, 4]:

- geometry correction factor ε = 1
- linear fit to the unloading curve
- area function calibration based upon H_M
- H_M was assumed to be H_{Knoop}
- fixed power law exponent $F=C(h-h_0)^{1.47}$
- no instrument compliance correction
- no initial penetration correction

Review [6] of Veprek's Theoretical Proof using FilmDoctor [7]



Sticking to his analysis would result … … in a stunning tensile strength of 36 GPa and yield strength of 151 GPa!

Taking Veprek's arbitrarily chosen constraint factor H=2.84 Y, the **lower limit of hardness** would be smashing **430 GPa**!

Theoretical Review Using First Principles [5]

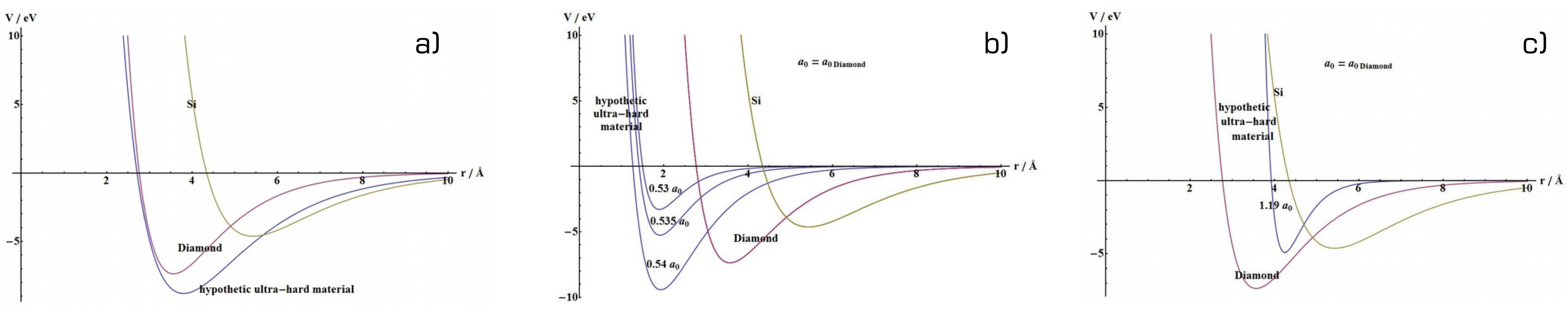
$$V_{Morse} = \varepsilon\left[e^{-2p(r-r_0)} - 2e^{-p(r-r_0)}\right]$$

$$V_{Diamond} = \sqrt{\left[\frac{H_{UH}}{H_{Diamond}}\right]^3 \cdot \left(\frac{r_{0\_UH}}{r_{0\_Diamond}}\right)^3} \cdot V_{UH}$$

$$\Rightarrow r_{0_{UH}} < 0.39\,nm$$

→ more details at booth #43 tomorrow

→ rules out 0.4486 nm found by Veprek [9]!



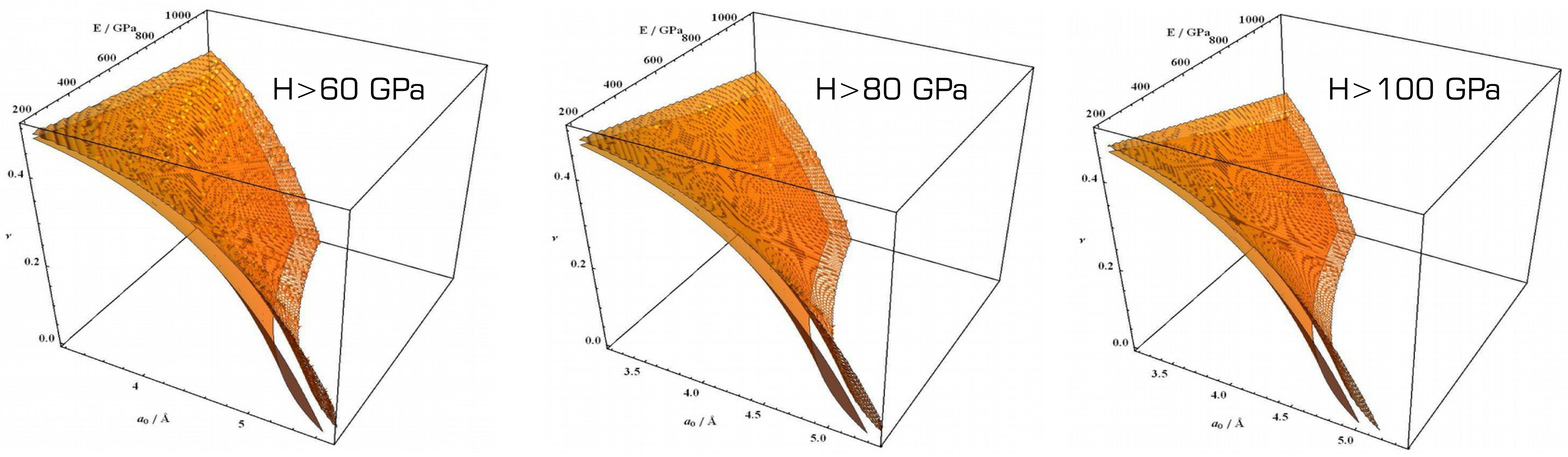
Potentials for Diamond, Silicon, and rather impossible ultra-hard nanocomposite (a), with fcc structure (b), and a **possible fcc-structured nanocomposite with an unimpressive H=40 GPa (c)**.

Possible Solutions for Ultra-Hardness Applying the Energy Approach [8]

Q: Is ultra-hardness ever feasable?

Using the methods introduced here, the „construction parameters" for possible super-hard (H>60 GPa), harder (H>80 GPa), and ultra-hard (H>100 GPa) materials (which are based on diamond structures) will be determined.

A: No, at least not on this planet.



Due to recent events: Is nanotwinned diamond really two times harder than regular diamond?

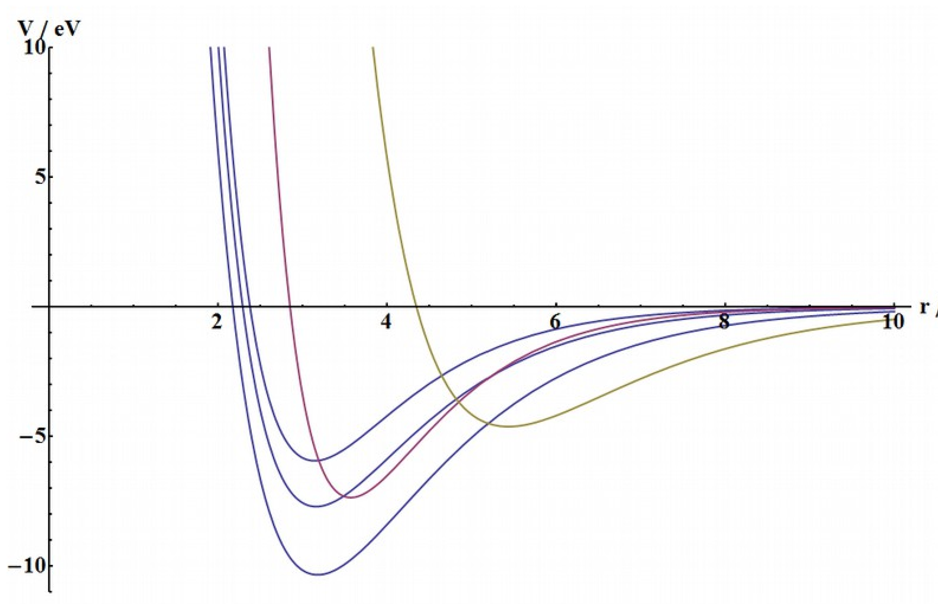
This year, Huang et al. [10] claimed having measured a Vickers hardness of **up to 203 GPa** at a normal load as high as 4.9 N **without any detectable damage of the indenter tip** – which was made of ordinary diamond. It goes without saying that this is **physically impossible!** Thus, nanotwinned diamond can only exist with a lattice constant much smaller than this of ordinary diamond under certain hypothetic conditions [11]:

a) carbon atoms sucking energy from somewhere to be held together strongly (see lowest blue curve in figure)

b) a lattice constant of ≤ 0.885 times the one of diamond (see middle blue curve in figure), **but only if** a diamond crystal bigger than the contact area is *somehow* being compressed by a factor of 1.3

→ **nt-diamond is not harder than ordinary diamond!**

→ **Nature sacrifices quality for impact factor!**



Conclusions

- There is **neither a proof** for the existence of "ultra-hard" coatings
- **nor is there a theory** which could substantiate the existence!
- actually achievable hardness: ca. **40 GPa**
- FilmDoctor allows finding such mistakes
- ultra-hardness is not feasable with earthbound materials (except BF)
- **npn = Nature Publishes Nonsense**

References

[1] Veprek et al., MRS Symposium Proceedings 581 (1999) 321.
[2] Veprek et al., Surface and Coatings Technology 133 (2000).
[3] Fischer-Cripps et al., Surface & Coatings Technology 200 (2006) 18.
[4] Fischer-Cripps et al., Philosophical Magazine 92 (2012) 13.
[5] Schwarzer, Philosophical Magazine 92 (2012) 13.
[6] Fuchs, www.pontifux.de/The-Saga-of-Ultra-Hard-Coatings, 2011.
[7] Software FilmDoctor, www.siomec.de/FilmDoctor
[8] Schwarzer, SIO Online Archive, www.siomec.de/pubs/2013/002, 2013.
[9] Veprek et al., Surface and Coatings Technology 204 (2010).
[10] Huang et al., Nature 510 (2014) 7504.
[11] Schwarzer, www.siomec.de/Nanotwinned-Diamond, 2014.

→ copies of this poster tomorrow at booth #43

www.siomec.de/Ultra-Hardness www.siomec.de/Nanotwinned-Diamond booth #43