The influence of deposited surface structures on mechanical properties

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Introduction

processing → structure → properties

Parameters, e.g.:

- temperature
- pressure
- flow/deposition rate
- times/timing
- system geometry
- target/substrate materials and their specifics
- voltage
- current
- and so forth

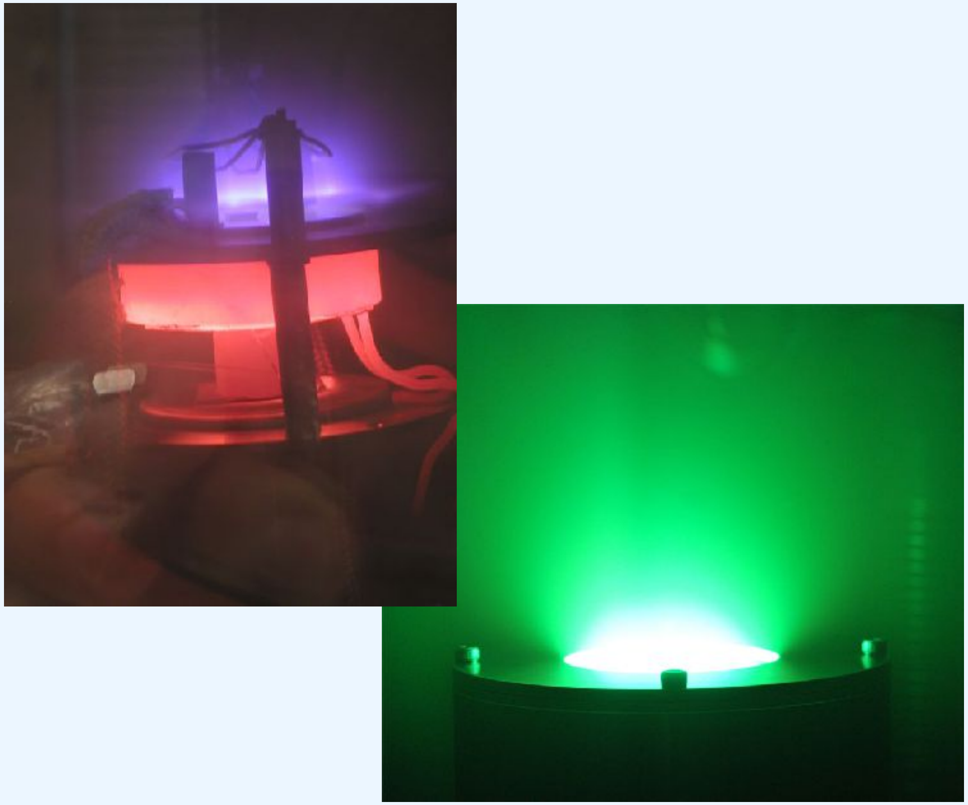
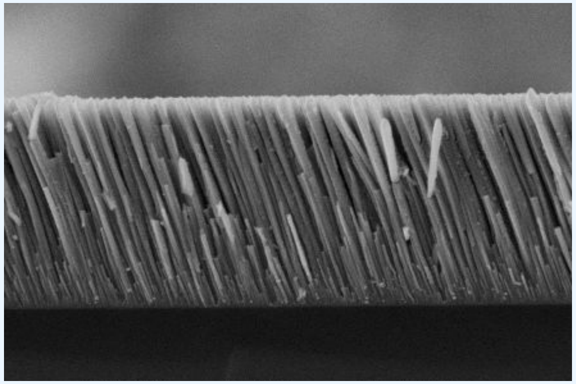
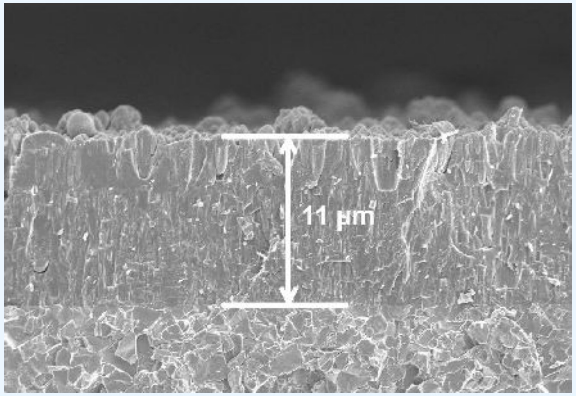


Photo courtesy of A. Anders, LBNL

Introduction

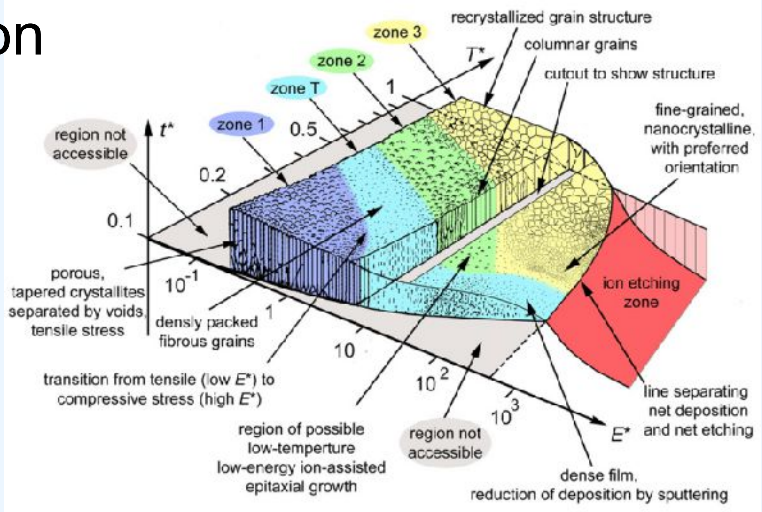
processing → **structure** → properties





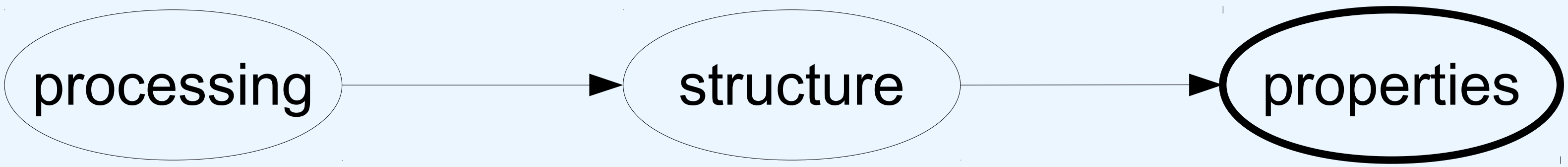
Possibly affected surface structures:

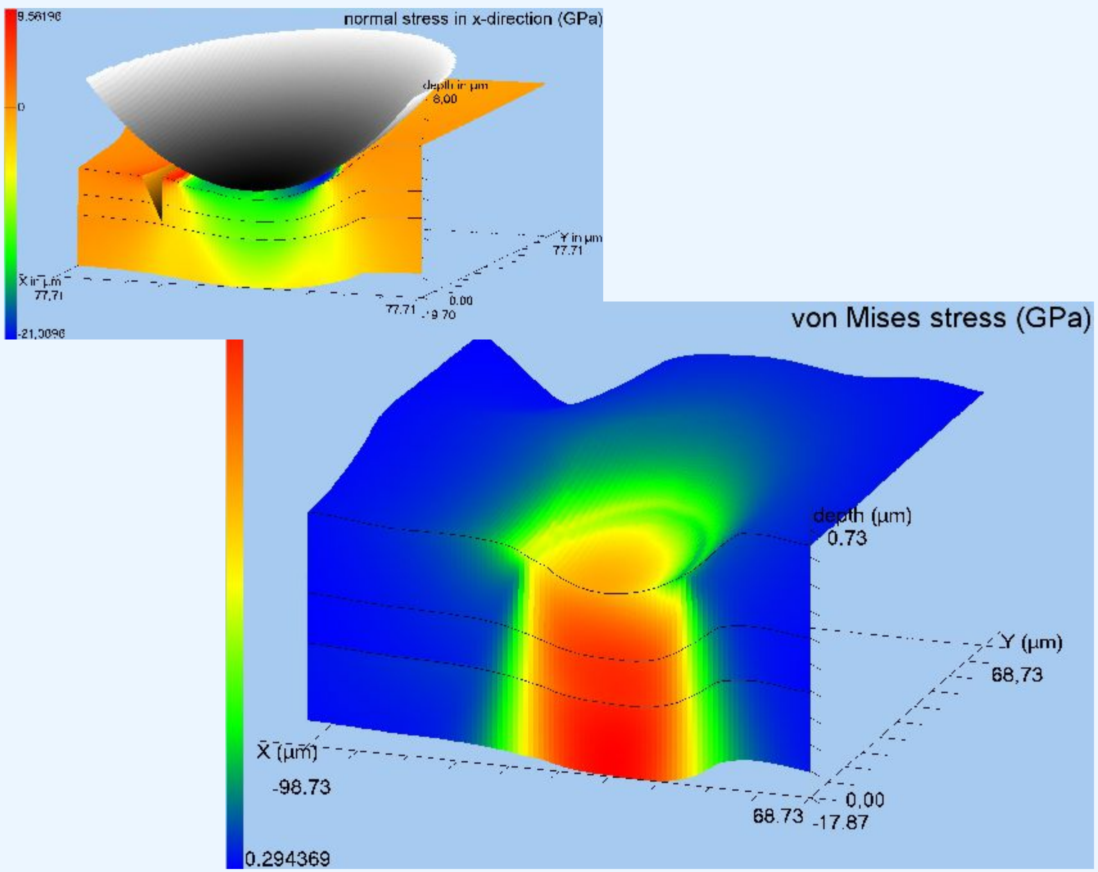
- surface/interface roughness
- porosity
- intergrain interaction
- homogeneity
- morphology
- composition
- etc.



A. Anders, Thin Solid Films 518 (2010) 4087 – 4090

Introduction



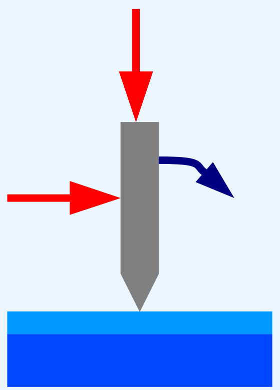


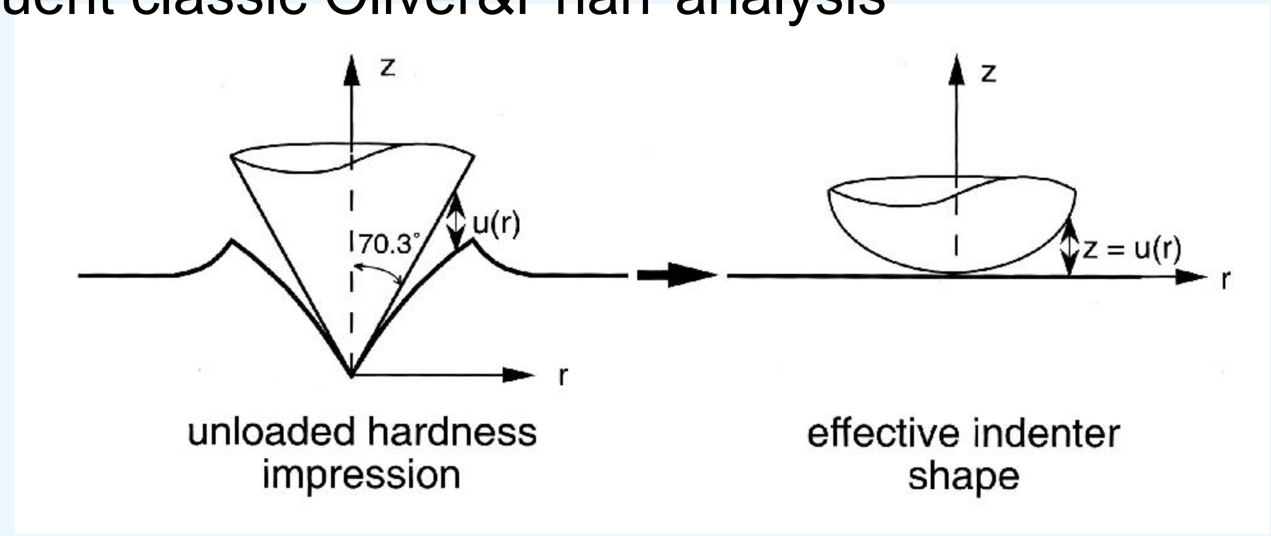
(Apparently) affected mechanical properties:

- elastic modulus *E*
- yield strength *Y* (hardness *H*)
- critical stresses of all fracture modes

How can film structures distort seeming mechanical properties?

- usual method for properties determination:
  - contact measurements
    - load-depth sensing indentation
    - (physicalized[1]) scratch/tribology test
  - subsequent classic Oliver&Pharr analysis[2]





1 N. Schwarzer et al., Surface & Coatings Technology 206 (2011) 1327–1335

2 G.M. Pharr, A. Bolshakov, J. Mater. Res., Vol. 17, No. 10, 2002

How can film structures distort seeming mechanical properties?

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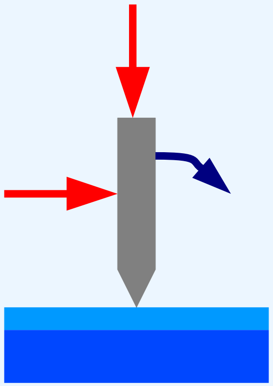
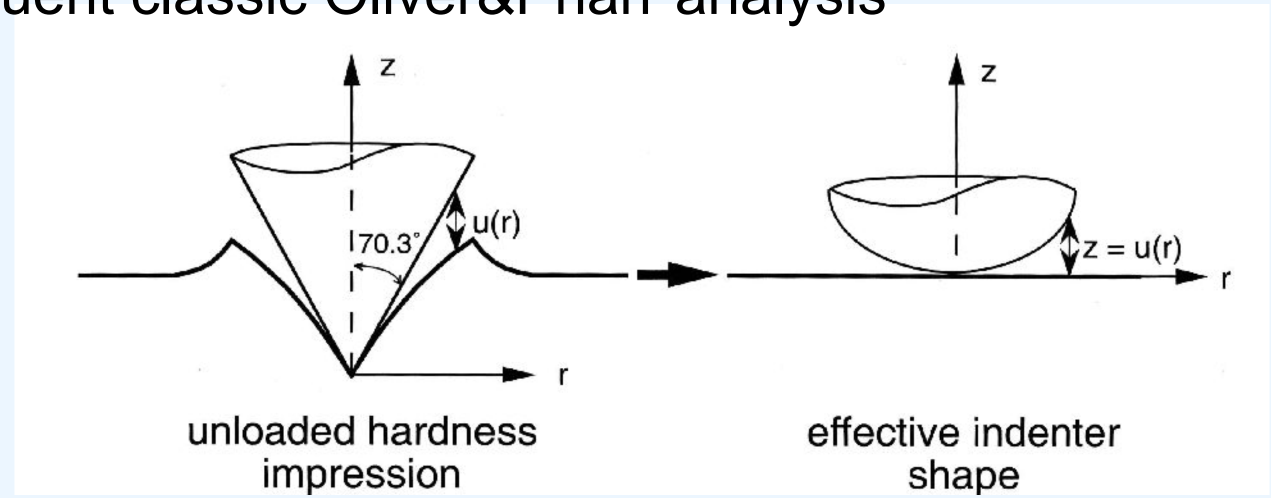




BUT: Originally intended for plain bulk samples!

Most surfaces structures are not considered!

e.g.: layers, gradients, surface roughness, ...

Example No. 1: influence of surface roughness

- Oliver&Pharr method **extended for surface roughness** by Schwarzer [3]

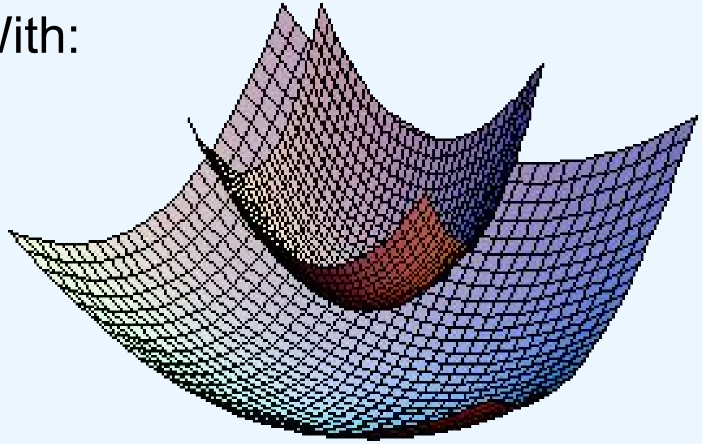
solution in paraboloidal (for curved space model) — cylindrical coordinates (for half space model)

$$\phi(\xi,\eta) = J_0(c*\xi) * Y_0(-i*c*\eta) \quad \& \quad \phi(r,z) = J_0(c*r) * \exp(c*z)$$

$$r = \sqrt{x^2 + y^2}$$

With:

$$x = \xi * \eta * \cos\varphi; \quad y = \xi * \eta * \sin\varphi; \quad z = (\xi^2 - \eta^2)/2$$

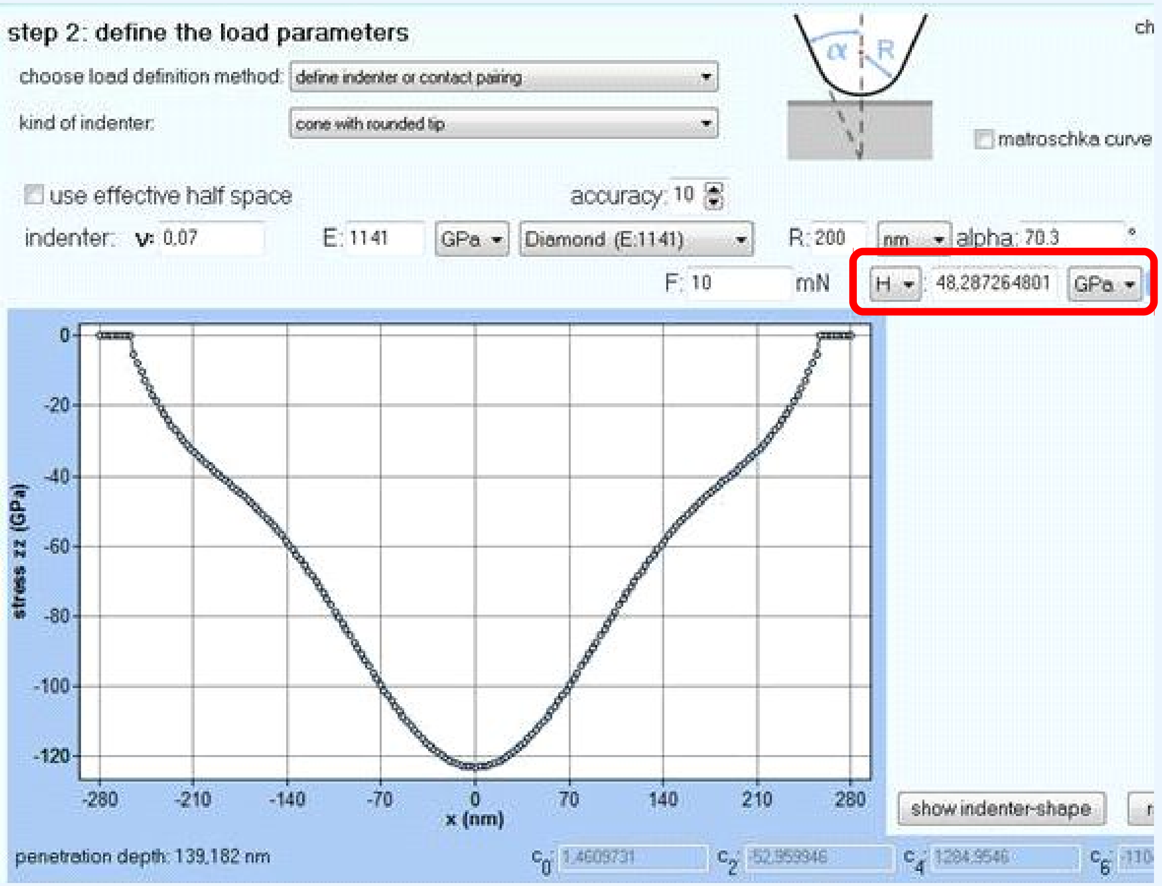


constant η gives surface of paraboloid

[3] More: **Poster EP-1** on Thursday or **booth #205**

Example No. 1: influence of surface roughness

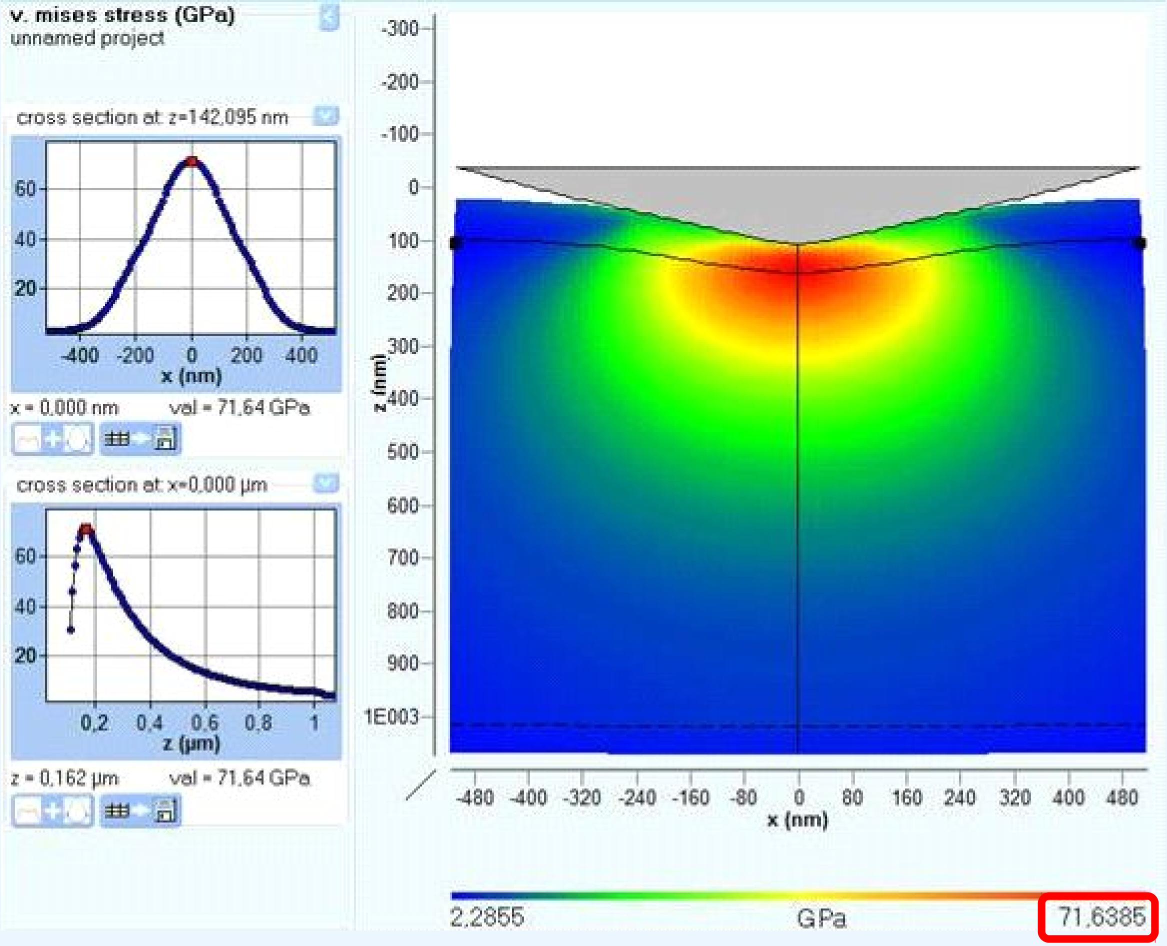
- For a ta-C coating we apparently obtain impressive *H* = 48 GPa.



But ...

Example No. 1: influence of surface roughness

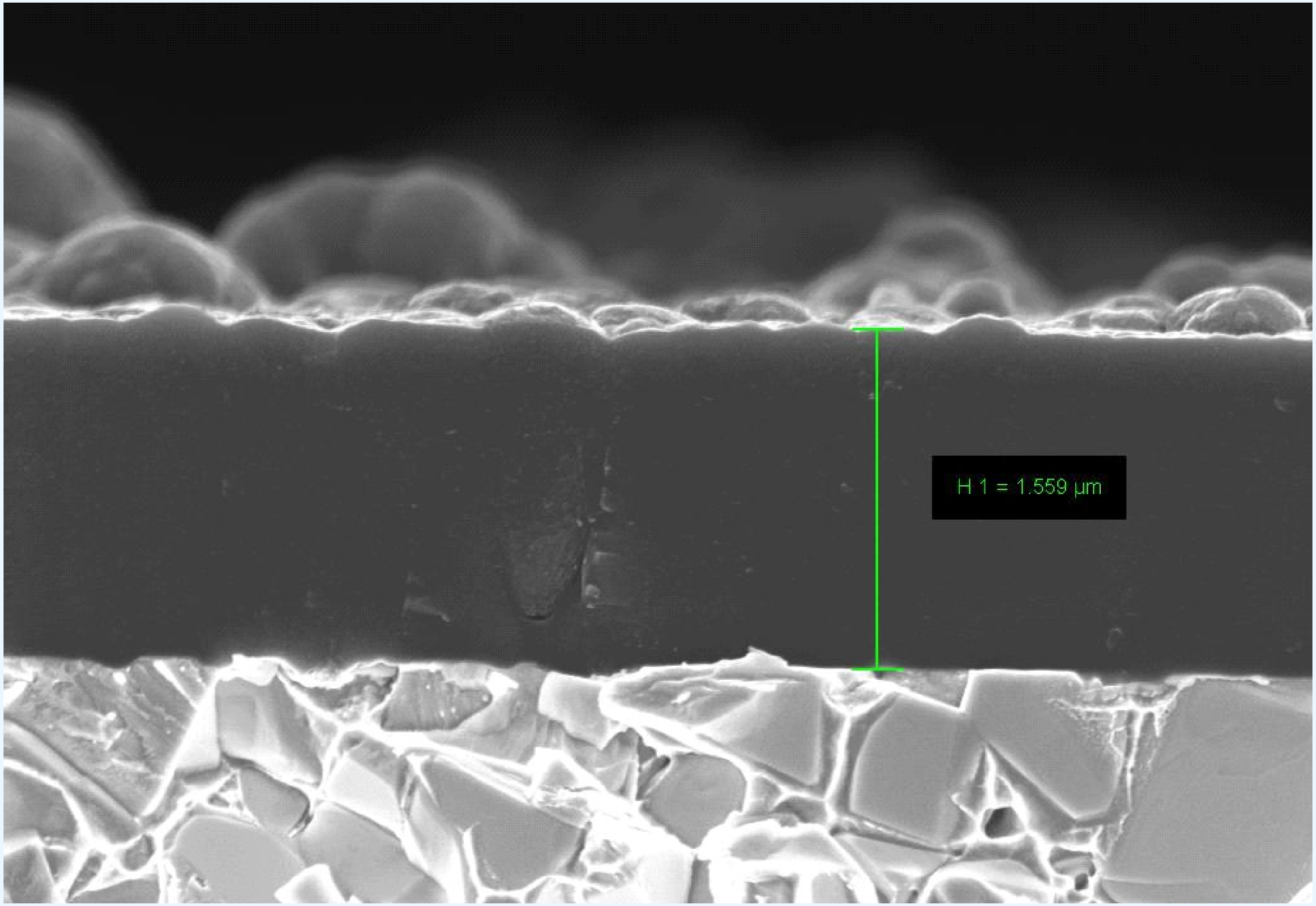
- … von Mises stress far too high for this material ($Y < 30$ GPa)



What is wrong?

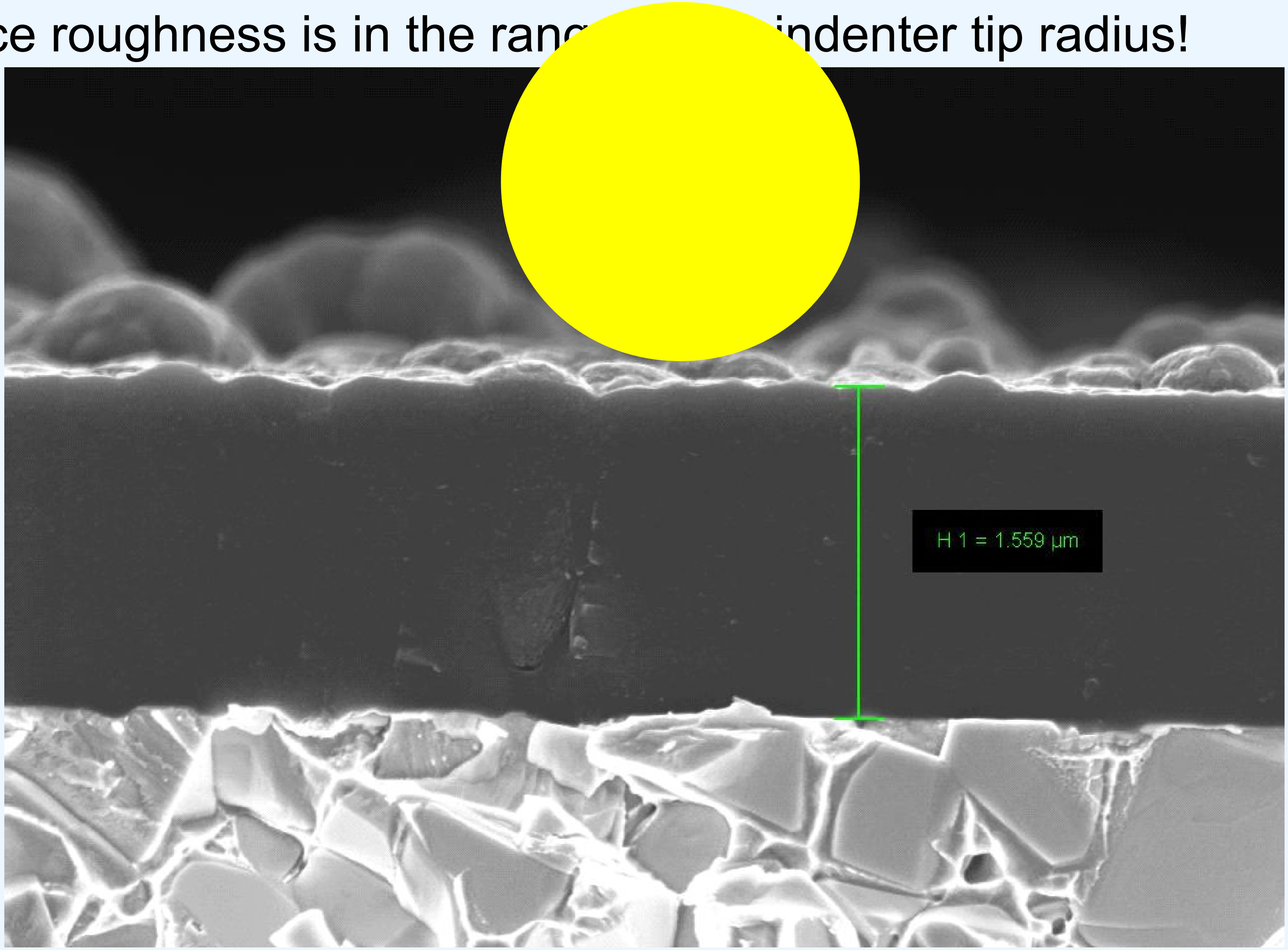
Example No. 1: influence of surface roughness

- Surface roughness is in the range of the indenter tip radius!



Example No. 1: influence of surface roughness

- Surface roughness is in the rang[...] indenter tip radius!

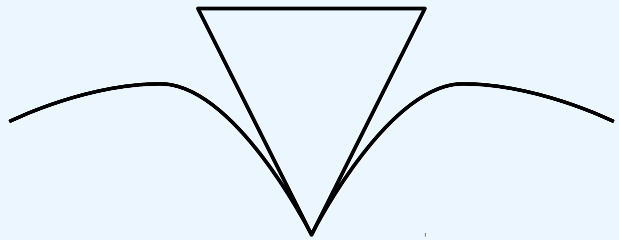


→ conforming contact

Example No. 1: influence of surface roughness

$$\rightarrow A_{actual} > A_{assumed} \Rightarrow H_{measured} > H_{actual}$$

$$H = \frac{F_{max}}{A_c}$$



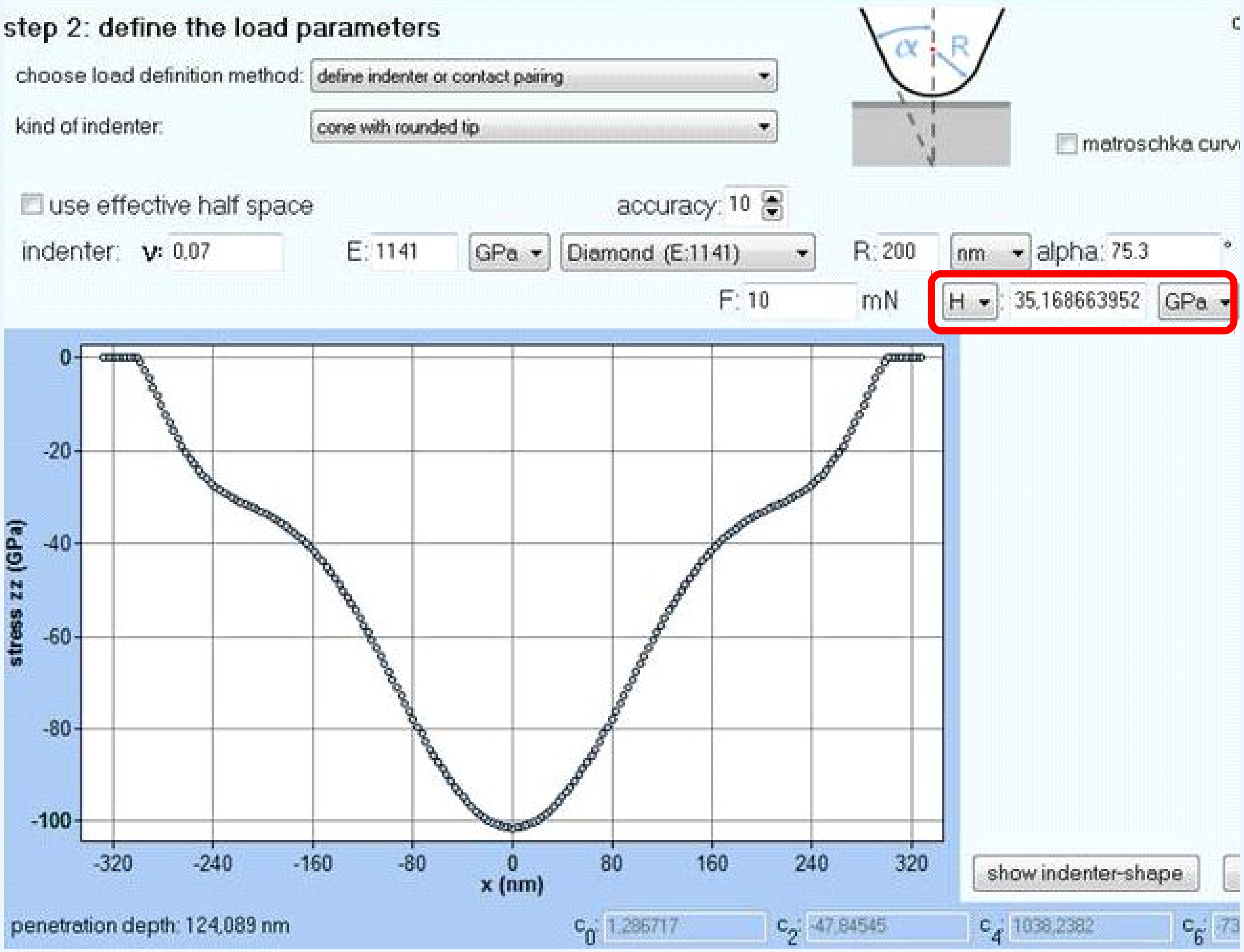
unloaded indentation impression

effetive indenter shape

If we take this into account during analysis, ...

Example No. 1: influence of surface roughness

… hardness decreases to more reasonable 35 GPa.



Hardness was overrated by 37%!

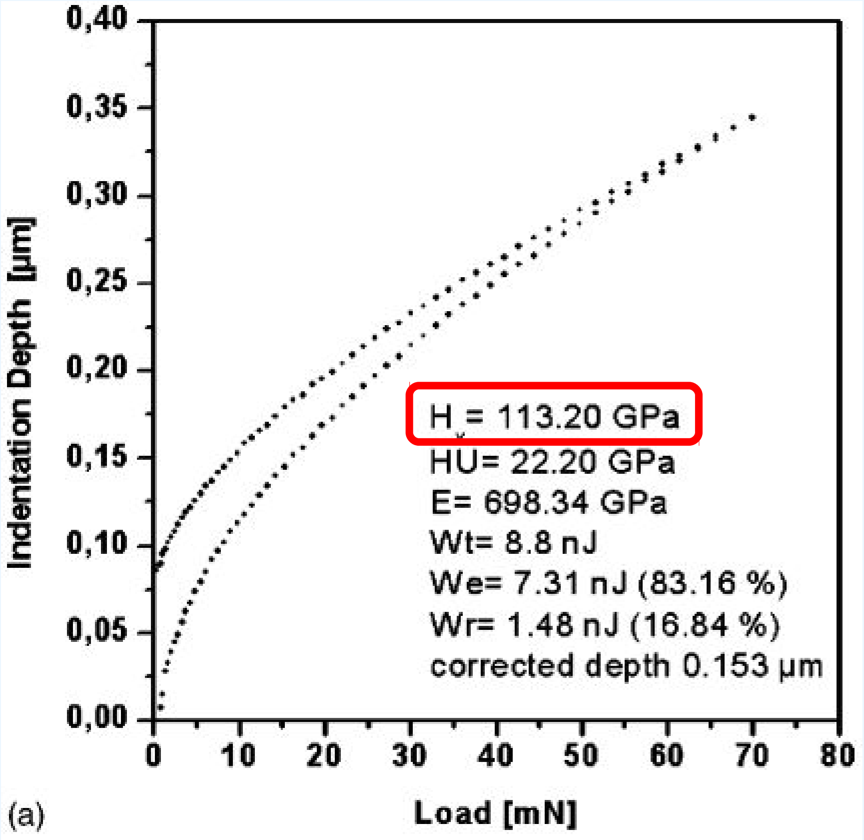
Example No. 1: Conclusions

- Deposition parameters can have a **significant influence** on mechanical material properties
- As it is not possible to derive such effects on mechanical properties solely from deposition parameters due to the dynamic nature of any deposition process, **material structures can be used as proxy and must be measured after processing.**

→ Never neglect the surface structure!

(Due to recent events) Example No. 2: „Ultra-Hardness“

- Veprek et al. claim to have processed so called “**ultra-hard**” nano-composite coatings with **hardness exceeding 100 GPa**.
- In 2006, Fischer-Cripps showed that Veprek's **analysis was severely flawed**[5]

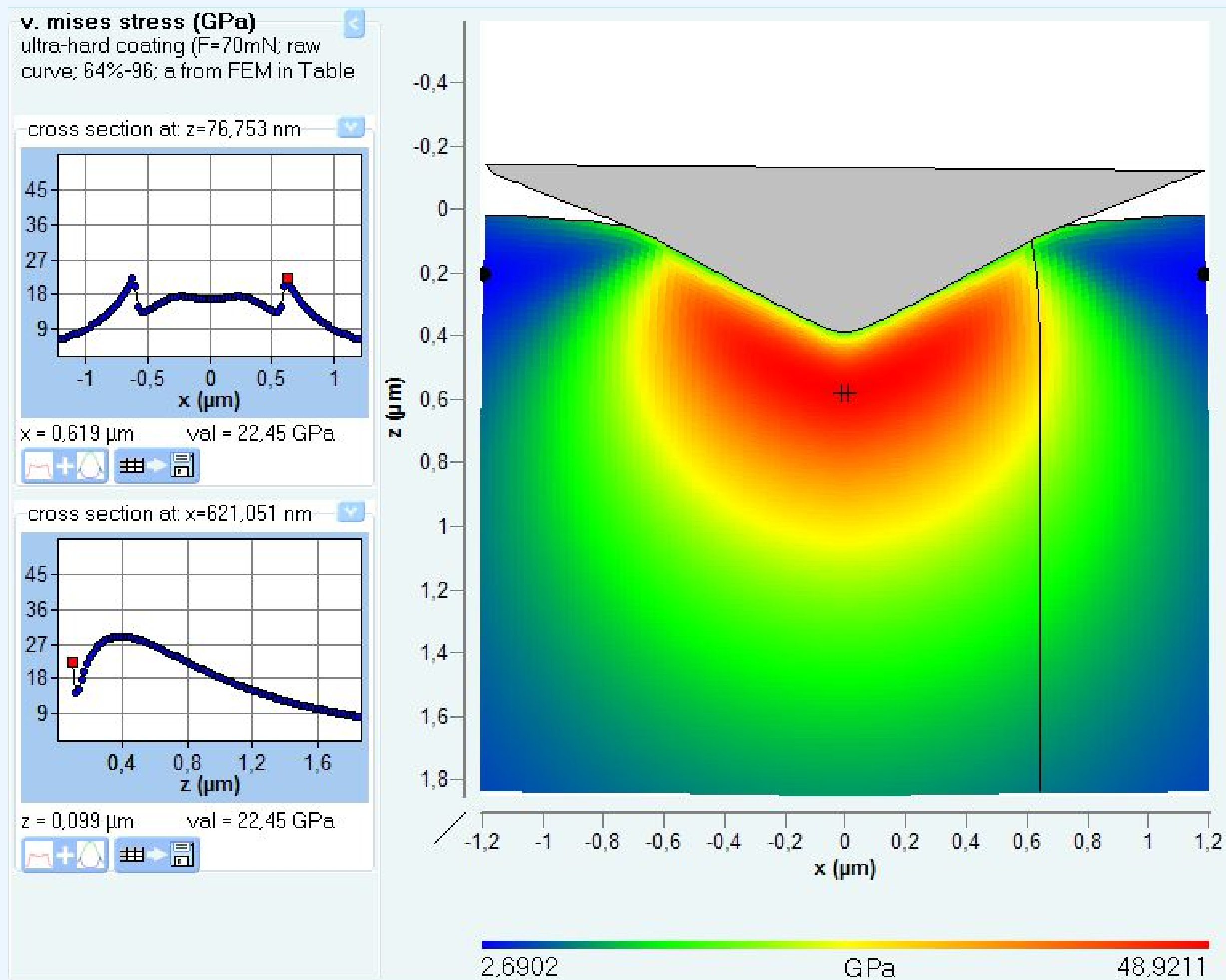


Veprek et al., J. Vac. Sci. Technol. A, Vol. 21, No. 3, 2003

5 Fischer-Cripps et al., Surface & Coatings Technology 200 (2006) 5645 – 5654

(Due to recent events) Example No. 2: „Ultra-Hardness“

- A proper analysis reveals[6]:
  E = 449.3 GPa
  Y = 48.9 GPa
  H = 57.8 GPa
- **Only** about **half as much** as Veprek claims (113 GPa or even more)!



6 Fuchs: “The Saga of Ultra-Hard Nano-Composite Coatings”, 2012.

(Due to recent events) Example No. 2: Conclusions

- **Do not worry if your coatings do not achieve "ultra-hardness"** results after proper analysis, because **Veprek's "ultra-hardness" is nothing but a saga**. C.f.:
  - Scharzer: **talk E2-1-9**, Thursday, 10:40 am
  - Fischer-Cripps: **talk E2-1-10**, Thursday, 11:00 am
  - www.siomec.de/The-Saga-of-Ultra-Hard-Coatings
  - **booth #205**
  - Fischer-Cripps et al., Philosophical Magazine, 2012.
  - Schwarzer, Philosophical Magazine, 2012.
  - Fuchs: "The Saga of Ultra-Hard Nano-Composite Coatings", 2012.

Example No. 3: Stoichiometry

- Veprek et al.: “Plasma chemical vapor deposition and properties of hard C_3N_4 thin films”, J. Vac. Sci. Technol. A 13(6), 1995:

  “**Compact thin films of** stoichiometric, amorphous **C_3N_4 have been prepared** by means of chemical transport of carbon in intense nitrogen glow discharge at relatively high deposition temperature of about 800°C. Their hardness reached 2500 Vickers (kg/mm^2).”

V. CONCLUSIONS

The results reported in the present article show that compact, uniform films of the composition of C_3N_4 can be prepared by plasma CVD in an intense nitrogen discharge if a sufficient excess of atomic nitrogen as compared with the concentration of CN radicals is present in the deposition zone. Energetic ion bombardment and a high temperatures of

[39] J. Weidmann, Diploma thesis, Technical University Munich (1995).

BUT ...

Example No. 3: Stoichiometry

- … within Weidmann's diploma thesis
  - **not the slightest lead to true C_3N_4!**
  - On the contrary a clear statement has been made there, that the stiochiometric finding is **just a coincidence one cannot automatically interpret as true C_3N_4!**
  - When visiting the TUC later in the 90ies, Weidmann even reported that the paper was **published without his knowledge and authorization!**

And a few years later Veprek cooked up the “ultra-hardness” myth.

Conclusions

- Do you know the **constraints** of the applied methodology?
- Always **challenge your results**!
- **Do not hesitate to ask very reasonable questions even though they are very basic!**

  (Any sound scientist will answer them properly.)