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Fifty shades of TiN:

How deposition conditions influence growth morphology and structure, and thereby hardness and especially fracture toughness

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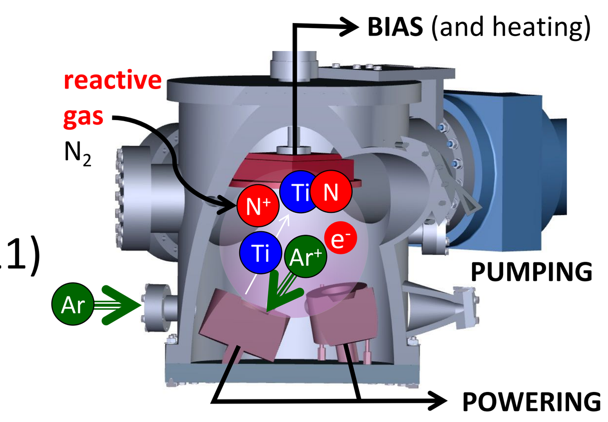
1. Introduction

The outstanding properties and property-combinations of transition metal nitrides (TMNs) – such as high strength, good wear resistance, high temperature stability, combined with chemical resistance – lend them their wide range of applications spanning from structural to protective functional materials. These include protective coatings for machining tools, or corrosion- and abrasion-resistant coatings for applications in the aerospace and automotive industries. In addition, TMNs are used as diffusion barriers, for example in microelectronics, or simply as decorative coatings (especially TiN). For many investigations and characterizations, TiN is a welcome benchmark. Here, about fifty different TiN coatings were prepared by reactive as well as non-reactive magnetron sputtering – and investigated for their microstructure and mechanical properties.

2. Synthesis

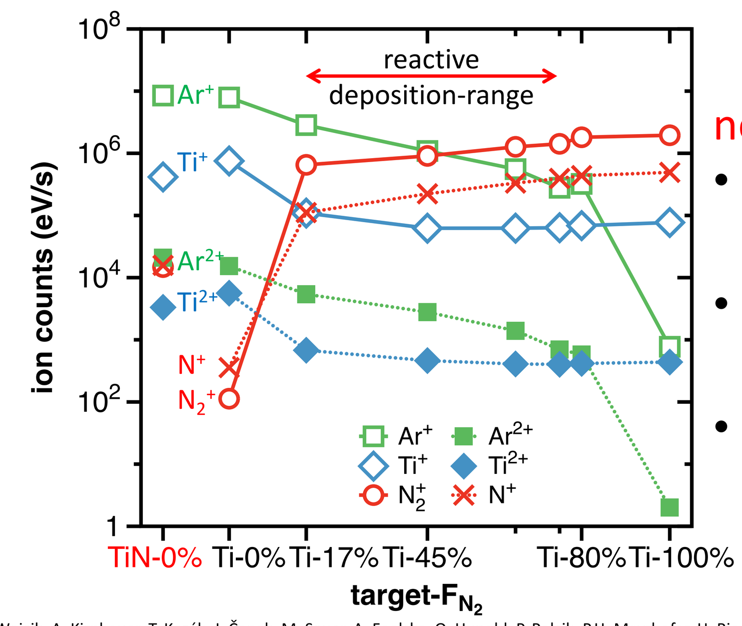
Deposition parameter variations (for ~50 different TiN's)

- substrate-to-target distance **ST: 4 x** (40 – 130 mm)
- deposition pressure **p_t: 2 x** (0.4 and 0.7 Pa)
- bias potential **U_b: 5 x** (-20, -40, -50, -60, -80 V)
- substrate temperature **T_s: 7 x** (150 – 700 °C)
- N_2 gas volume fraction **F_{N2}: 5 x** (0, 12.5, 30, 45, 70 %)
- sputtering power density **P_m: 5 x** (3, 7.5, 9, 11, 13 W/cm²)
- **targets: 2 x (Ti and TiN)**
- substrates: Si(100), MgO(100)-(110)-(111) Al_2O_3, austenite



Mass spectroscopy measurements

during reactive (Ti-target) or non-reactive (TiN-target) magnetron sputtering of TiN (P_m: ~7.5 W/cm²) [1].

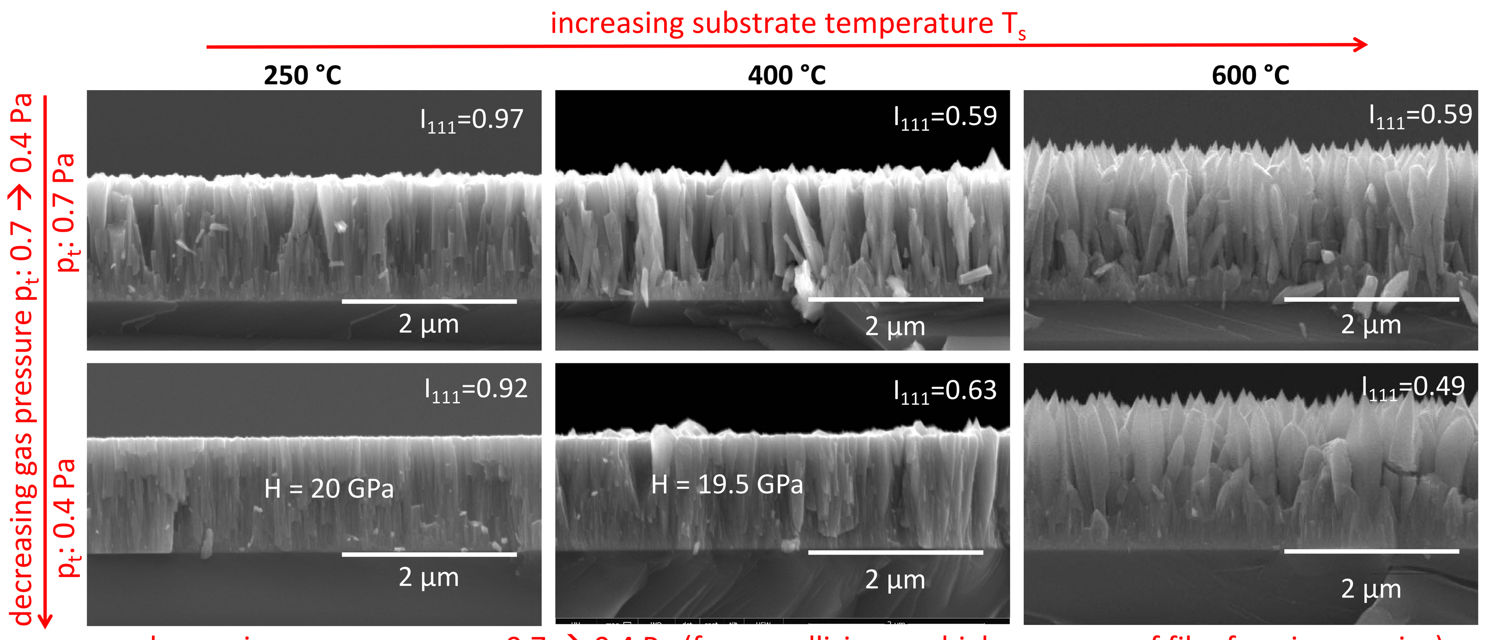


non-reactive:
- ~10x higher Ti^+ and Ti^{2+}
- ~10^2x lower N^+ and N_2^+
- no N_2

1) R. Hahn, A. Tymoszuk, T. Wojcik, A. Kirnbauer, T. Kozák, J. Čapek, M. Sauer, A. Foelske, O. Hunold, P. Polcik, P.H. Mayrhofer, H. Riedl, Surf. Coat. Technol. 420 (2021) 127327

3. Growth morphologies and microstructures

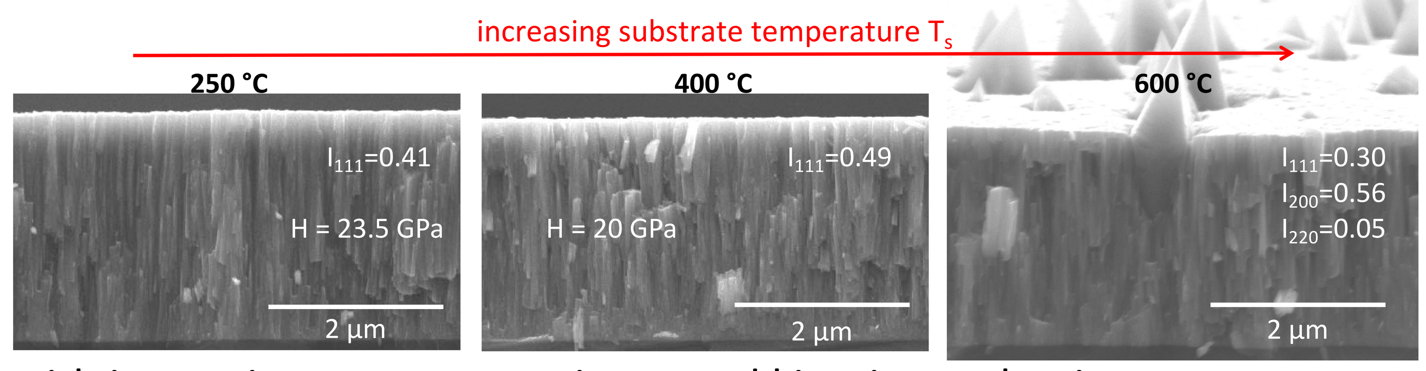
- **Non-reactive deposition (U_b = -40 V, P_m = 7.5 W/cm²)**



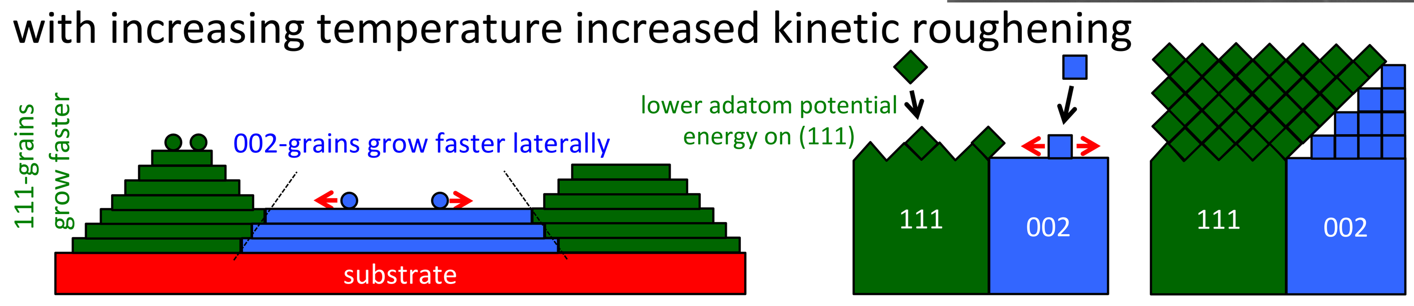
decreasing gas pressure p_t: 0.7 → 0.4 Pa (fewer collisions ⇒ higher energy of film forming species)

column tops are faceted due to kinetic roughening

- **Non-reactive deposition (p_t = 0.4 Pa, U_b = -40 V, P_m = 13 W/cm²)**

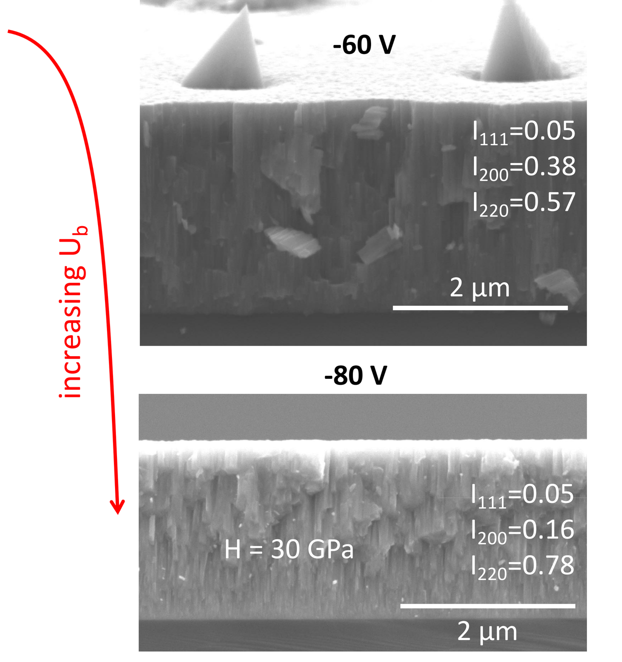


with increasing temperature increased kinetic roughening



For low temperature: Polar 111-surfaces (with three backbonds) result in a higher adatom incorporation probability on 111-grains, which finally over-grow the non-polar 002-grains.

- **T_s = 600 °C**

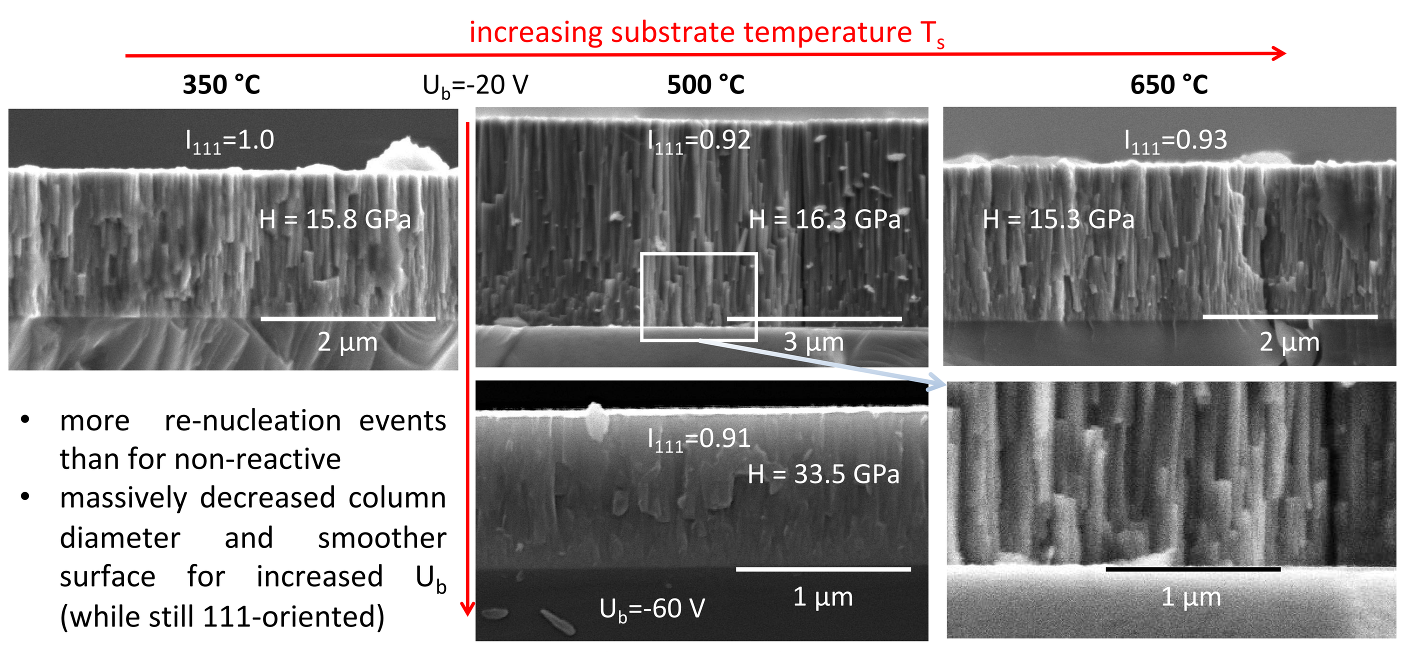


low ion density: (220) for E_i: 60–90 eV in agreement with earlier studies [2]

increased sputtering power P_m: 7.5 → 13 W/cm² (higher energy of film-forming species)

2) P.H. Mayrhofer, M. Geier, C. Löcker, L. Chen, Int. J. Mat. Res. (2009)

- **Reactive deposition (p_t = 0.4 Pa, F_{N2} = 30 %, ST = 11 cm, P_m = 11 W/cm²)**



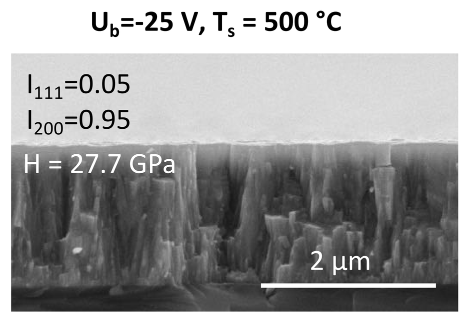
increasing bias potential

- more re-nucleation events than for non-reactive
- massively decreased column diameter and smoother surface for increased U_b (while still 111-oriented)

column tops are faceted, when U_b is low

- **reduced substrate–target distance (ST = 4 cm)**

U_b=-25 V, T_s = 500 °C



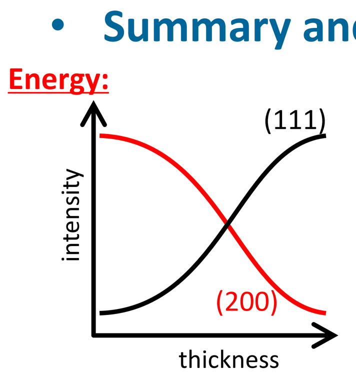
With increased plasma density, even at low dep. temperatures (T_s = 150 °C), dense growth morphologies are possible, and high hardness.

Rule of thumb for 1 collision: p(Pa)·Λ(cm) ≈ 1

Thus, the mean free path Λ at 0.4 Pa is 2.5 cm.

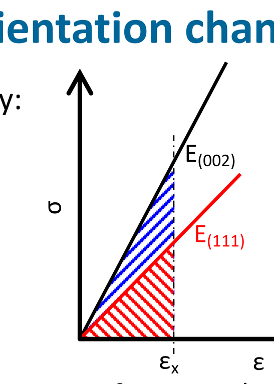
- **Summary and conclusions on orientation changes**

Energy:



Anisotropy in surface energy: $\gamma_{(111)}>\gamma_{(022)}>\gamma_{(002)}$

and strain energy: $\varepsilon_{(002)}>\varepsilon_{(022)}>\varepsilon_{(111)}$, $E_{(002)}>E_{(022)}>E_{(111)}$

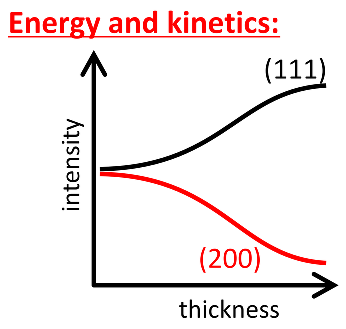


For the same strain, lower stress and lower stored energy for (111) than (002).

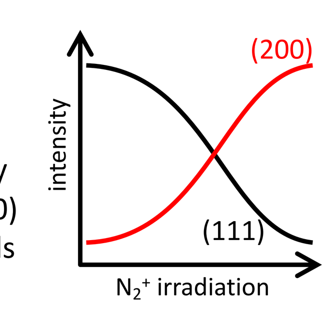
Probably overrated as easily overruled by other energetic and kinetic effects.

For small thicknesses, the surface energy is the dominating factor. ⇒ (200)-orientation for TiN, as the (200)-surface has the lowest energy! With increasing thickness the (111) will be preferred.

Energy and kinetics:



(111) wins (at low T) by overgrowing (200), due to the higher adatom incorporation (lower adatom potential energy at 111). At higher T, (200) is preferred, but depends on sputter conditions.

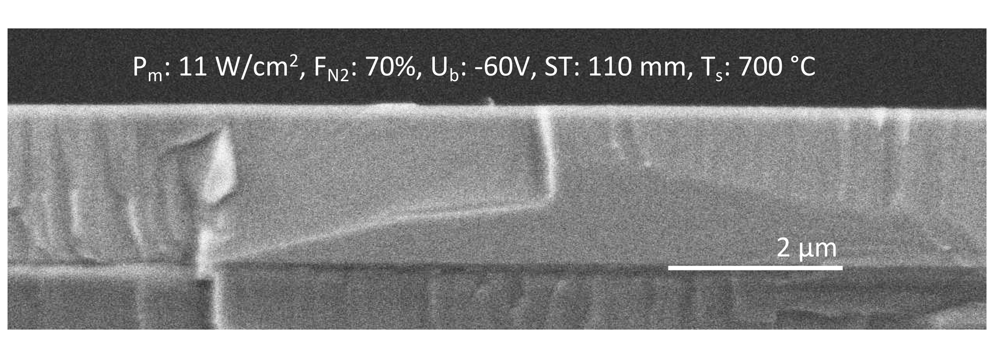


The (002) columns win by overgrowing the (111) columns for high N_2^+ irradiation! N chemisorbs easier on (001) than on (111). (Difficult for non-reactive, as lower N_2^+)

based on: D. Gall, S. Kodambaka, M.A. Wall, I. Petrov, J.E. Greene, J. Appl. Phys. 93 (2003) 9086–9094

4. Mechanical properties

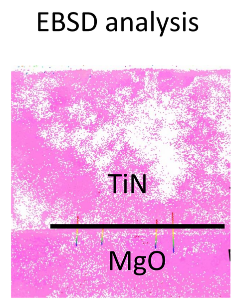
- **Epitaxial growth on MgO**



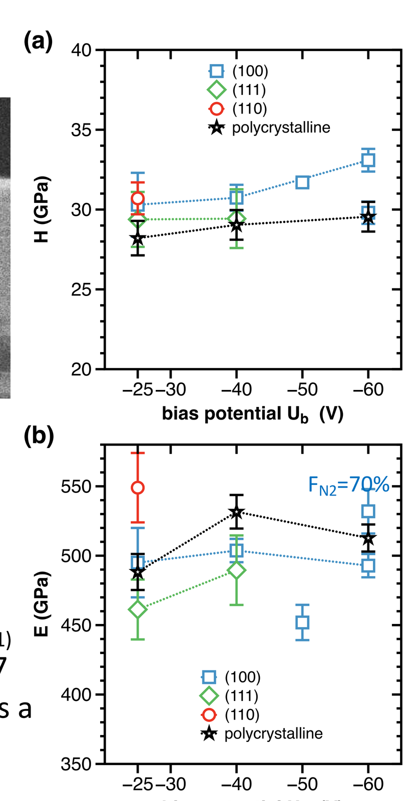
epitaxial growth works also for:

P_m (W/cm²)	F_{N2} (%)	U_b (V)	ST (mm)	T_s (°C)
11	70	-60	110	700
9	47	-50	110	500
3	12.5	-60	40	650
3	12.5	-40	40	650
3	12.5	-25	40	650

EBSD analysis

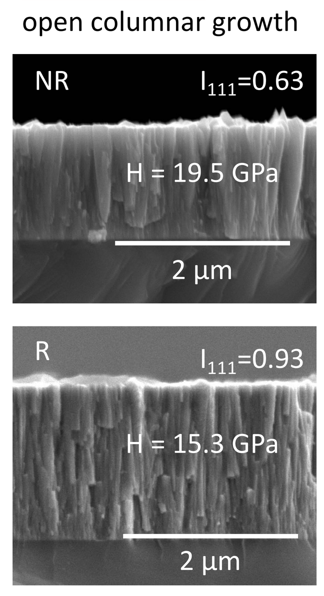


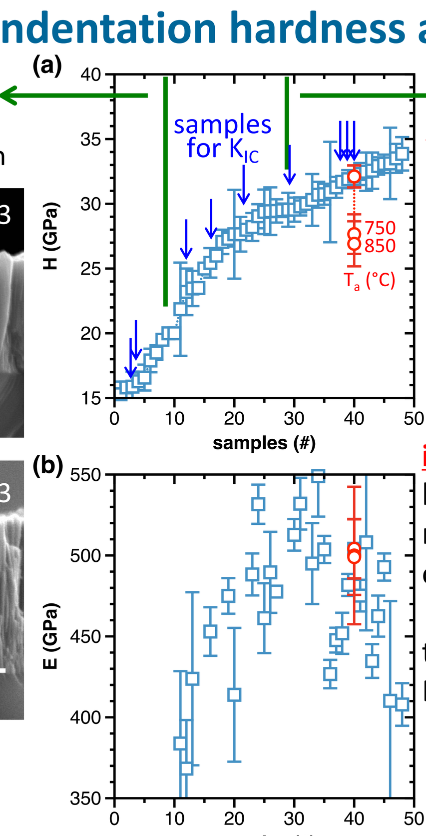
theoretically: $E_{(100)}>E_{(110)}>E_{(111)}$ 524 > 431 > 407 but res. stress has a huge impact



- **Overview on indentation hardness and residual stresses**

H ≤ 20 GPa for: open columnar growth



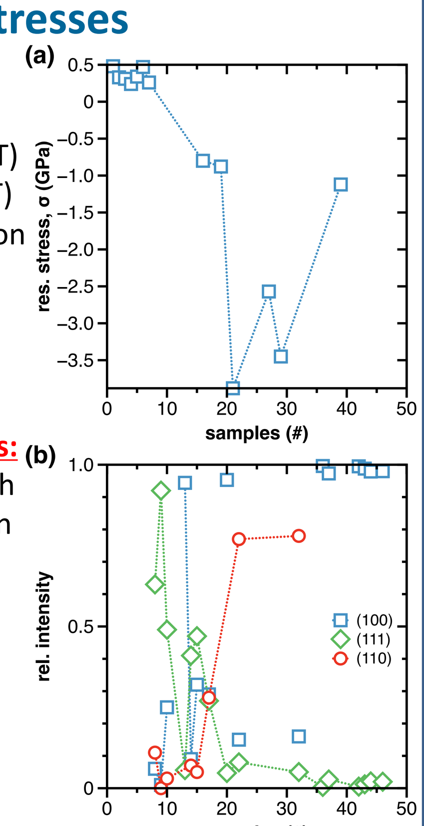


H ≥ 30 GPa for:
- high bias (large ST)
- low bias (small ST)
- epitaxial growth on MgO(100) & MgO(110)

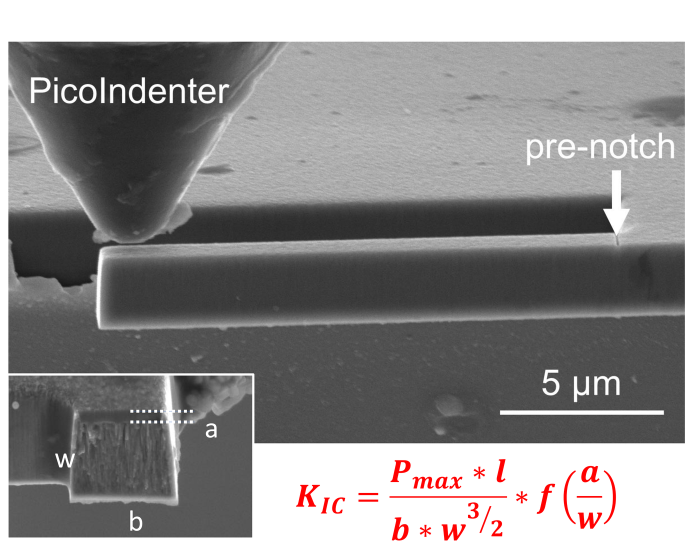
indentation modulus: better correlates with residual stresses than orientation

σ↑⇒E↑

theoretically: $E_{(002)}>E_{(022)}>E_{(111)}$

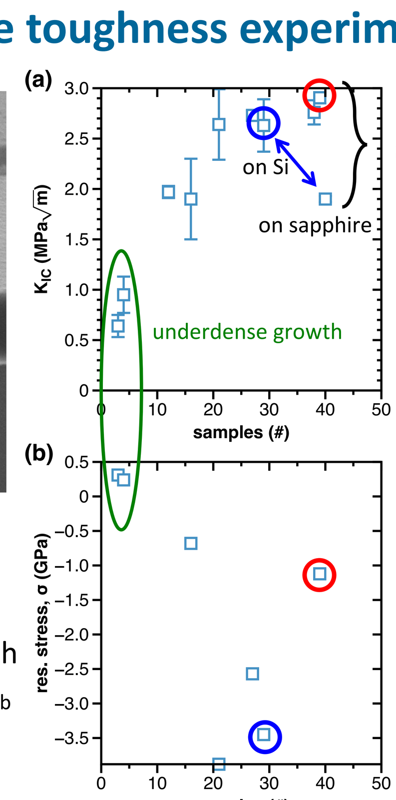


- **In-situ micromechanics for fracture toughness experiments**



$$K_{IC} = \frac{P_{max} * l}{b * w^{3/2}} * f\left(\frac{a}{w}\right)$$

A correlation between stresses and K_{IC} was found with ~1 MPa√m per -1 GPa stress (when using only bias U_b to densify the coatings). This can be overcome by "clever" deposition parameters!



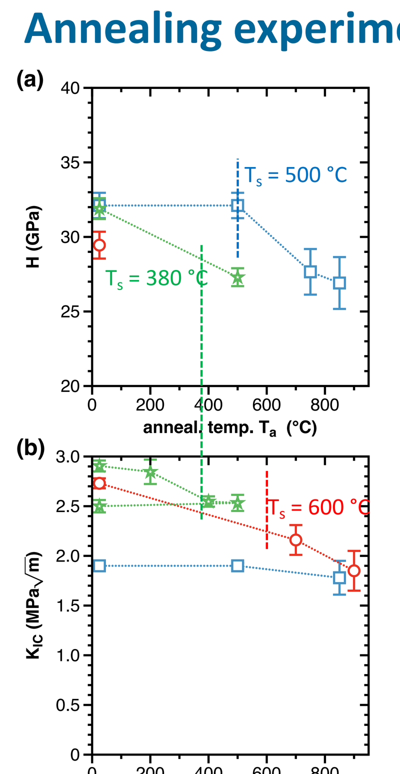
annealing experiments

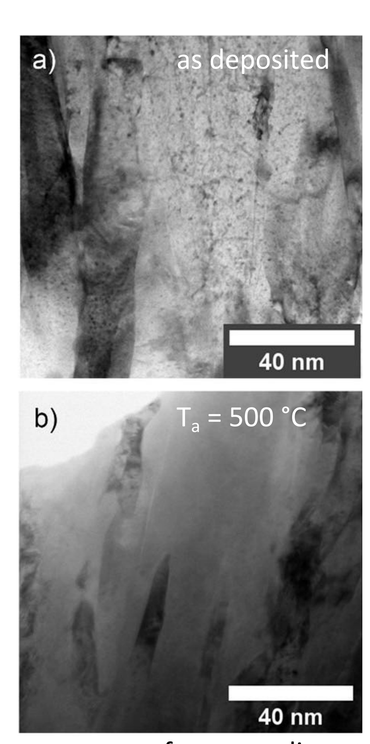
highest K_{IC} combined with moderate stresses
- U_b = -40 V
- ST = 40 mm
- P_m = 9 W/cm²
- T_s = 380 °C
- polycrystalline on Si
- highly 200-oriented

2nd-highest K_{IC}: epitaxial on MgO(100)

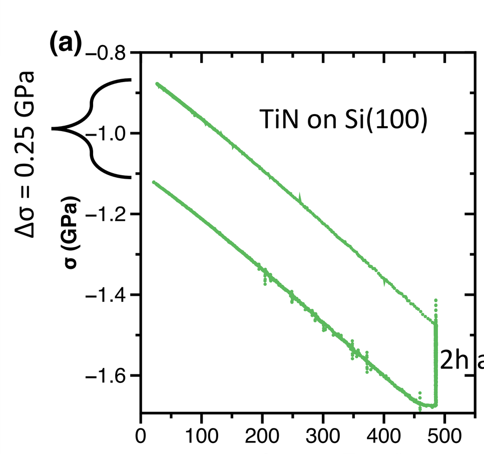
otherwise the polycrystalline ones have K_{IC} ≤ 2 MPa√m

- **Annealing experiments of selected TiN coatings**





as deposited, high defect density (P_m = 9 W/cm², U_b = -40 V, F_{N2} = 30%, T_s = 380 °C, ST = 40 mm, highly 200-oriented)



J. Buchinger,...P.H. Mayrhofer, ... Materials and Design 194 (2020) 108885

after annealing at T_a = 500 °C, pronounced recovery effects

J. Buchinger, L. Löfler, J. Ast, A. Wagner, Z. Chen, J. Michler, Z.L. Zhang, P.H. Mayrhofer, D. Holec, M. Bartosik, Materials and Design 194 (2020) 108885

4. Conclusions

- Plasma conditions are extremely important for proper coating development and reproducibility.
- Low ion energies but high intensity is preferred.
- Rougher films for non-reactive deposition when using similar P_m, T_s, U_b, ST
- Densification obtained by high energy (≥ 80 eV) ion bombardment comes at a steep price: Significant Lattice defects; Compressive stresses; Discharge gas incorporation
- The plasma influences, morphology, chemistry, structure and hence material properties.
- Highest *H (32 GPa)* and K_{IC} *(2.9 MPa√m)* combination for 200-oriented film, obtained by low U_b and intense plasma.