Properties of Thin Films: Focus on Nano-Layers

Enhanced hardness in ceramic coatings

Nano-layer stability

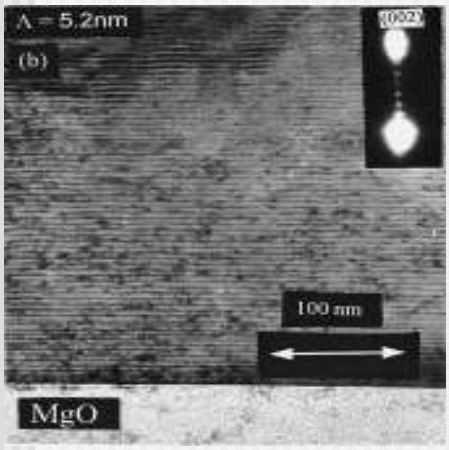
Other nano-effects

Hardness

Applications of Hard Coatings

- Hard wear-protective coatings
  - Protection of sliding contacts
  - Bearings
  - Al die casting
  - Cutting tools
    - Operation at elevated temperature
- Figures of merit
  - Adhesion
  - Surface flatness
  - Abrasive wear resistance - high hardness
  - Tool coatings
    - High hardness at elevated temperature
    - Chemical stability (workpiece solubility, oxidation)
    - Thermal expansion match with substrate
- Typical materials
  - TiN, (Ti,Al)N, Ti(C,N) - Hardnesses ~ 25 GPa

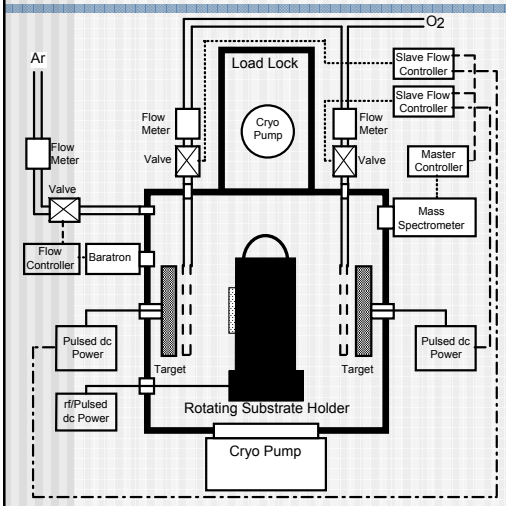
Nano-Layered Coatings



- Early focus was on miscible, iso-structural nanolayers, *e.g.*
  - TiN/VN, TiN/NbN, Cu/Ni
- Hardness enhancements
  - 2-3 times that of constituent materials
  - > 50 GPa hardness achieved

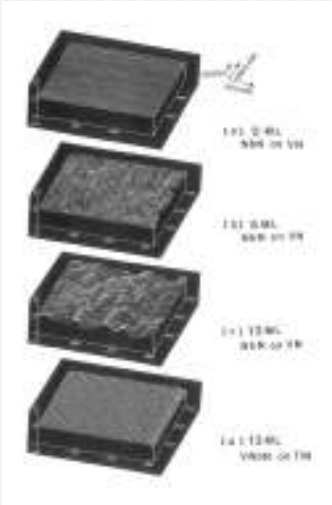
  S. A. Barnett, Physics of Thin Films, (Academic, New York, 1993) p.1
- Poor high temperature stability
  - TiN/NbN layers interdiffuse at elevated temperature

Nano-Layer Deposition



- Various nanolayers have been studied
  - Metal/metal
  - Nitride/nitride
  - Nitride/metal
  - Oxide/oxide, …..
- Readily deposited by conventional PVD methods
  - Reactive magnetron sputtering
    - E.g. for TiN, sputter Ti targets in Ar-N_2
  - Rotating substrate holder (as shown at left), or
  - Moving shutter

Nano-Layer Growth Limitations

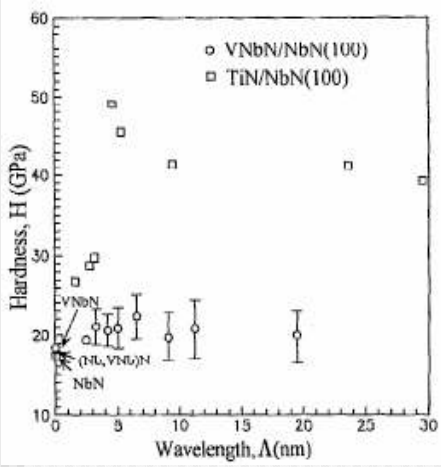


- AFM scans show morphologies of individual nitride layers
- From top to bottom
  - Starting VN surface - flat
  - 5 ML NbN on VN (5.7% mismatch)
    - Slight roughening
  - 13 ML NbN on VN
    - Large roughening
  - 13 ML VNbN on VN (3.6% mismatch)
    - No roughening
- Shows Stranski-Krastanov nucleation for large mismatch

Strength/Hardness Effects

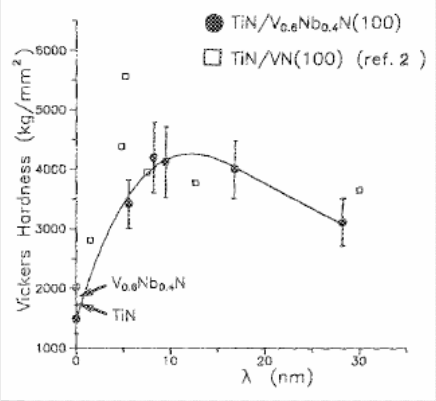
- Proposed nano-layer strengthening mechanisms:
  - Supermodulus effect
  - Effect of layers on grain size
    - Hall-Petch: $H = H_0 + Ct^{-0.5}$ (t = grain size)
  - Interfacial misfit dislocations blocking dislocation flow
  - <u>Lattice mismatch coherency strains</u>
  - <u>Shear modulus different</u>
  - <u>Incompatible dislocation slip systems</u>
    - Layers with different crystal structures

Shear Modulus Difference Effect



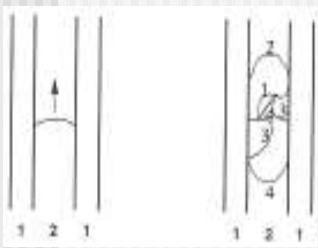
- Image force on dislocations attempting to cross interfaces
- Plot: hardness versus period
  - TiN/NbN
    - Large hardness increase
    - Large shear modulus difference ΔG
  - VN/NbN
    - No hardness increase
    - Small shear modulus difference ΔG
- Illustrates importance of modulus difference

Coherency Strain Effect



- Coherency strains can trap dislocations at interfaces
- Figure: nanoindenter hardness TiN/VN (strained) and TiN/VNbN (matched) multi-layers
  - Small periods: coherency strains expected
    - Slightly higher hardness
  - Larger periods: interfacial misfit dislocations expected
    - No hardness difference

Nano-Layer Strength Model



- Strength limited by one of two mechanisms (whichever gives lower strength)
  - Repulsion of dislocation from material with larger shear modulus
    - Stress on dislocation at distance *x* from interface with change in modulus *ΔG:*

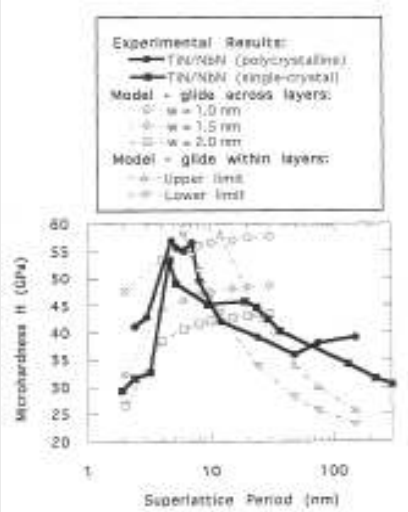
$$\tau = \frac{\alpha \Delta G b \cos\theta}{2x}$$

  - Stress to move a dislocation loop confined in a layer of thickness l_2:

$$\tau = \tau_0 + \frac{2\alpha \Delta G_2^0 b \cos\theta}{l_2} \ln\left(\frac{l_2}{b\cos\theta}\right)$$

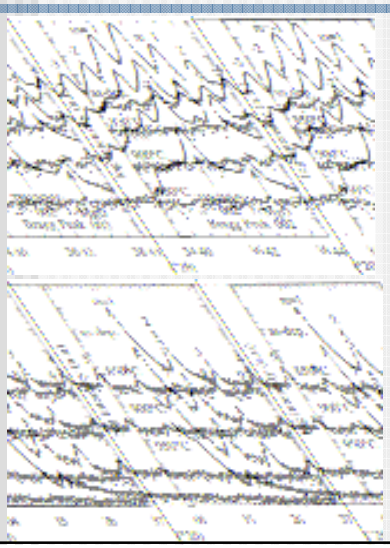
  - Or larger stress required to operate a dislocation source within a layer
    - Stress decreases as layers become thicker

Nano-Layer Hardness



- Hardness enhancements in TiN/NbN
- Model:
  - Limited dislocation glide across interfaces
  - Dislocation flow within layers
- Model predicts that hardness depends on:
  - Shear modulus difference:
    - High hardness for TiN/NbN, TiN/VN, but not VN/NbN
  - Degree of interface broadening
- *Chu, Wong, Sproul, Barnett, J. Materials Res.,* ***14****, 2500 (1999)*

Nano-Layer Instability



- TiN/NbN nanolayers (Λ = 4.4 nm)
  - x-ray diffraction superlattice reflections
- Represented by 1D composition wave

$$c(x) = \sum_{m=-\infty}^{m=\infty} A_m \sin(2\pi m x / \Lambda)$$

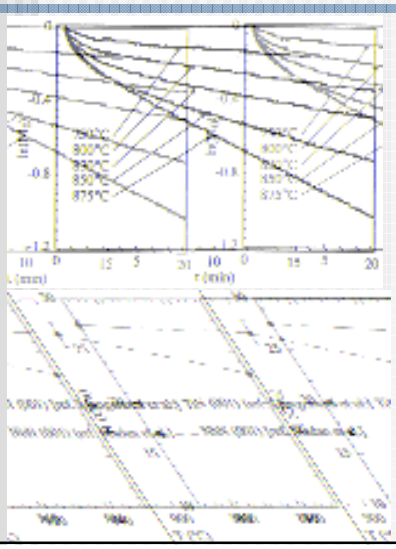
- Higher-order components decay faster

$$A_m(t) = A_m(t=0)\exp[-(2\pi m/\Lambda)^2 \tilde{D} t]$$

$$\tilde{D} = D[1 + \frac{2\kappa}{F''}(2\pi m/\Lambda)^2]$$

  - D = diffusion coefficient
  - Λ = period
  - F'' = curvature of free energy versus composition
  - κ = gradient energy coefficient
- Note: if F'' is negative (miscibility gap), diffusion against concentration gradient

Nitride/Nitride Interdiffusion



- TiN/NbN nanolayer, Λ = 4.4 nm
- Decay of first negative (m = 1) superlattice reflection intensity
- Increasingly rapid decay with increasing T

$$\frac{d}{dt}(\ln I_m) = -2\tilde{D}(2\pi m/\Lambda)^2$$

  - Yields T-dependent diffusivity
- Loss of distinct layers accompanied by decreased hardness

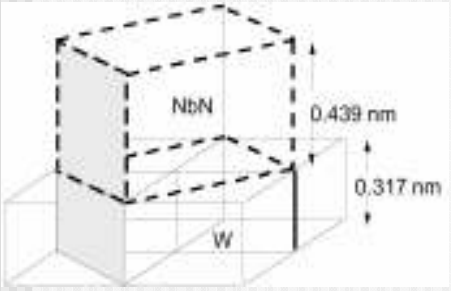
C. Engström et. al. JVST A 17 (1999) 2920.

High-Temperature-Stable Nano-Layered Coatings?

- Requirements:
  - Immiscible layers ($F'' << 0$)
  - No compound formation
  - Low-energy interfaces
  - Good adhesion, avoid high stresses
- Materials that satisfy these requirements:
  - Nitride/boride nano-layers: TiN/TiB_2, ZrN/ZrB_2
  - Metal/nitride nano-layers: W/ZrN, W/NbN, Mo/NbN

1. *A. Madan et al., J. Vac. Sci. Technol. A19, 952 (2001).*
2. *C. Engstrom et al., J. Materials Research 15, 554 (2000).*
3. *S. Barnett and A. Madan., Scripta Mat. 50, 739 (2004).*

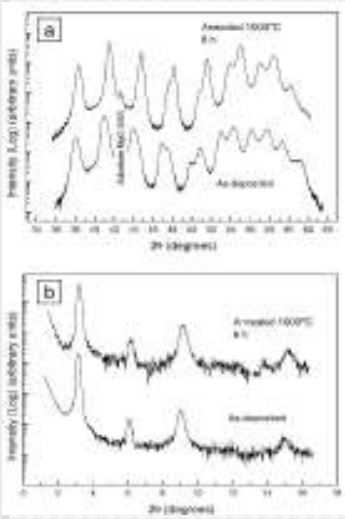
Metal/Nitride Nano-Layers



- No mutual solubility between bcc metals, e.g. W and transition-metal nitrides, e.g. NbN*
- Lattice mismatch between W and NbN is 2.1% (with a 45° rotation) - low energy coherent interfaces are possible
- Very high melting points
- Good thermal expansion match with cemented WC (5x10-6 K-1)

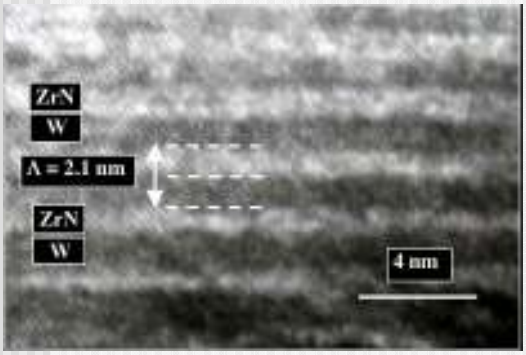
**P. Villars, A. Prince and H. Okamoto, Handbook of Ternary Alloy Phase Diagrams (ASM International, 1995).*

High Temperature Stability



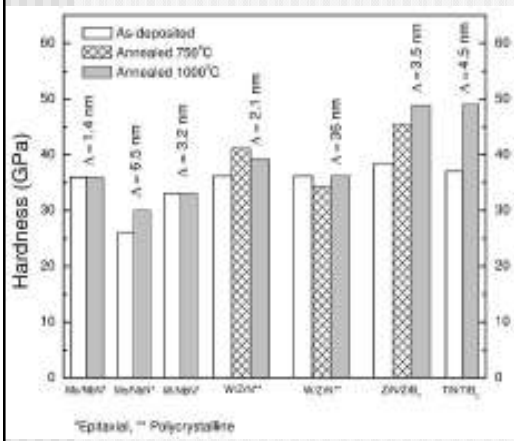
- W/ZrN, low-angle XRD
- Annealed at 750 -1050ºC for different times in a pure Ar ambient
- Peaks little effected by anneal
  - Indicates layers remain intact
- Much different than TiN/NbN shown above!

XTEM Image: W/ZrN



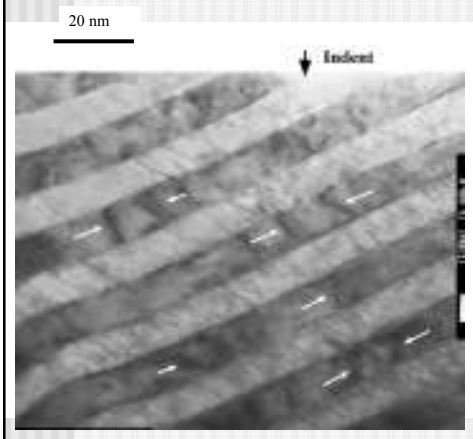
- Λ = 2.1 nm
- l_W/Λ = 0.5
- Annealed at 1000°C for 1 hour
- Well-defined layered structure retained

Nano-Layer Hardness: Various Systems



- Hardnesses of various nano-layers
  - Mo/NbN, W/NbN, W/ZrN
  - Hardness enhancement to 35-40 GPa
    - ~ 20 GPa rule of mixtures
- Annealed at 750 and 1000°C
  - Little effect of annealing on metal/nitride hardness
- Nitride/borides show large hardness increases!
  - See below

Nanolayer Deformation Mechanism in W/NbN



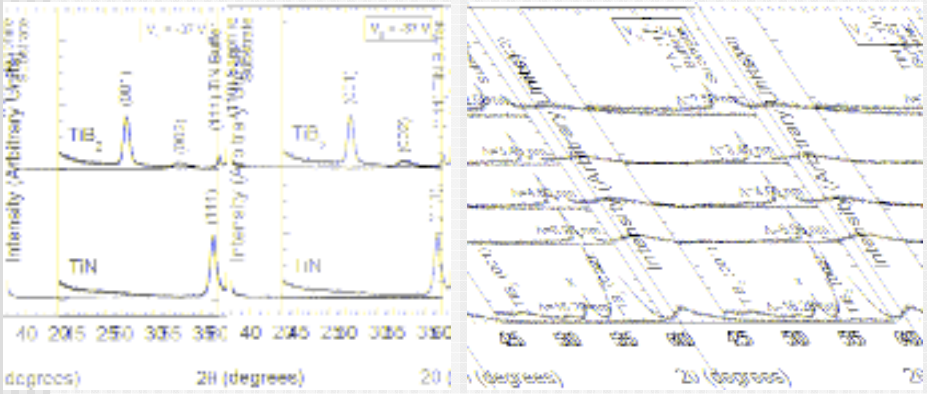
- Image under indented area
  - Defect contrast mainly due to indentation
- W layers (darker contrast) show dislocation loops (**b=a**/2<111>)
  - As in mechanisms discussed above
- NbN layers (ligher contrast) show planar faults on {111} planes
  - HRTEM: faults are not twins, and shear offsets seen at interfaces
  - **g•R** analysis: may be {111} stacking faults due to partial dislocation motion

Kramer et al. Scripta Mat. 50, 745 (2004).

Nitride/Boride Nano-Layers

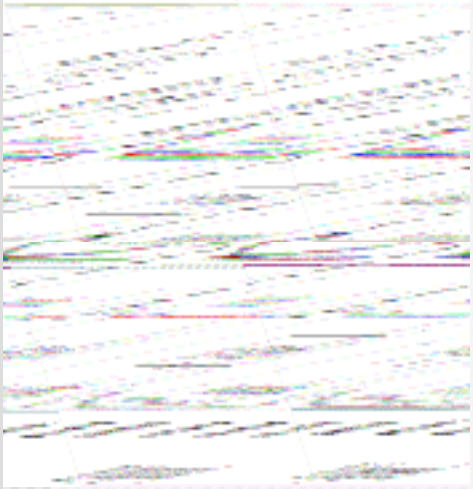
- Individual properties:
  - Boride harder and more wear-resistant
  - Boride more oxidation resistant
  - Boride has higher hot hardness ~ 5GPa at 1000°C
  - Nitride exhibits better adhesion
  - Both CTEs well matched to carbide substrates ($\alpha \approx 6 \times 10^{-6}$ K^{-1})
- Combined properties:
  - Immiscible and non-isostructural
  - Nitride (111) planes and boride (001) planes: ~1% lattice mismatch → Low energy interfaces

Nanolayer Effect On Structure



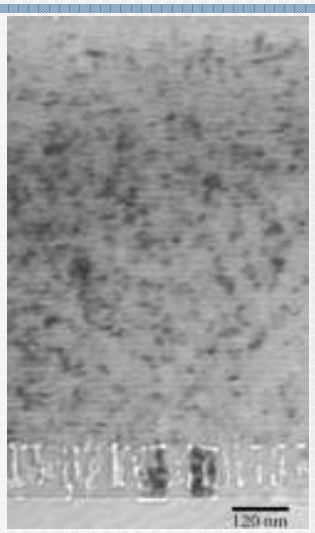
- LEFT: monolithic thin films
- RIGHT: nano-layered films
  - Lack of strong boride peaks
  - Very thin boride layers tend to be amorphous

TiN/TiB_2 XRD: Annealed



- Period = 3.5 nm
- TiN (111) preferential orientation and TiB_2 amorphous as deposited
- TiB_2 crystallizes with (001) orientation after annealing

TiN/TiB_2 XTEM: Annealed

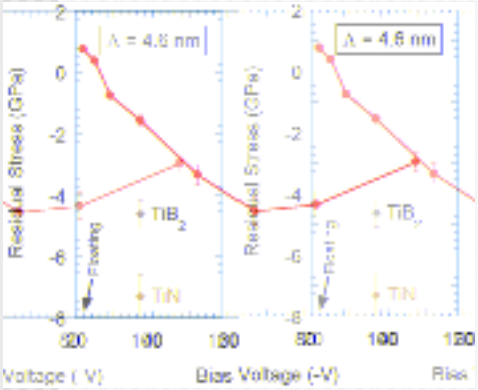


- 16 nm period
- Annealed at 1000°C for 1 hour in Ar
  - Sharpened electron diffraction peaks
  - Boride peak appears, indicating crystallization
- Layers still present
  - Difficult to see due to weak atomic number contrast

TiN/TiB_2 Hardness: Annealing Effect

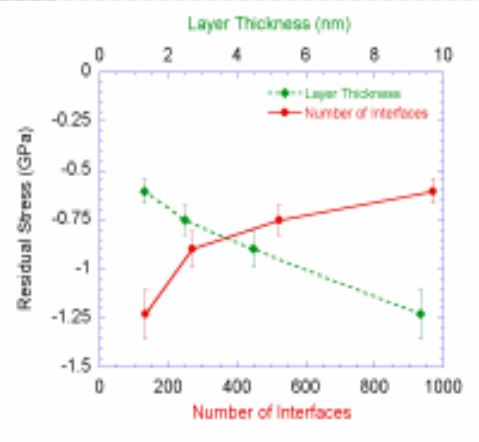
- As-deposited: no hardness enhancement
- Anneal: 1000°C, 1 h, Ar
- 10-15 GPa increase in hardness upon annealing (49 GPa max)
- Monolithic TiN hardness decreases upon annealing, while TiB_2 delaminates
  - As-deposited hardness enhanced by film compressive stress
  - Annealing removes stress
- Hardness maximum maintained to large periods
  - Different than nitride/nitride
  - May be related to nano-grain size preventing deformation within layers

Residual Stress: TiN/TiB_2



- Increase in compressive stress with increasing bias – ion-induced point defects (atomic peening)
- Stress relaxation at a higher bias – excessive damage leads to porosity
- Considerably less stress in nanolayers than monolithic films
  - Improved adhesion
  - Nano-layer interface effect

Effect of Interfaces on Stress



- 1 micron thick TiN/TiB_2
  - Period varied from 1 to 20 nm
  - Change in number of interfaces
- Un-biased TiN buffer layer substantially reduces stress
- Increasing interface density decreases compressive stress
  - Interfaces may act as sinks for point defects

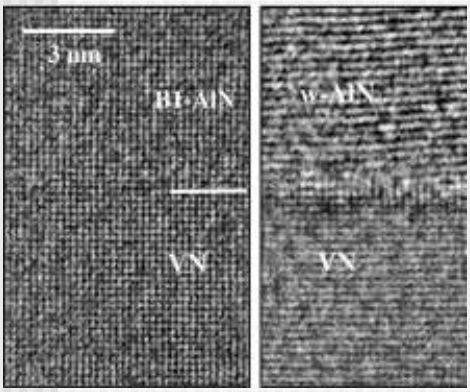
Fayeulle, Nastasi, J. Appl. Phys. ***81****, 6703 (1997)*

Anderson et al. Surf. Coat. Technol. ***123****, 219 (2000)*

Advantages of Nitride/Boride Nanolayers

- Reduced compressive stress
- Enhanced adhesion compared to boride
- Hardness increases substantially after annealing
  - Due to crystallization of boride layers
  - Homogeneous films either decrease in hardness (nitride) or delaminate (boride)
  - ~50GPa hardness for annealed films corresponds to ~100% enhancement over monolithic films

Epitaxial Stabilization



- AlN/VN nano-layers
- Equilibrium AlN is hexagonal wurtzite
- Cubic AlN stabilized in layers < 4 nm (LEFT IMAGE)
- Transforms to wurtzite structure for thicker layers (RIGHT IMAGE)
- Possible to realize new properties in stabilized layers
- Also observed in AlN/TiN, AlN/NbN

Li, Kim, Barnett, Marks, J. Mater. Res. ***17****, 1225 (2002).*

Summary and Conclusions

- Miscible nanolayers
  - Hardness enhancement due to dislocation confinement
  - Interdiffusion at elevated temperature
    - Loss of hardness enhancement
- Polycrystalline W/ZrN nano-layers stable upon annealing
  - 1-nm-thick layers stable at 1000°C
  - Hardness maintained constant
- Nitride/boride nanolayers show reduced stress, better adhesion than boride
  - Nanoindentation hardness stable or increases for temperatures anneals at 1000°C
    - Nano-layer hardness as high as 49 GPa (nitride/boride) due to boride crystallization
- Non-equilibrium phases via epitaxial stabilization