ROBL-CRG, BM20
Materials Research

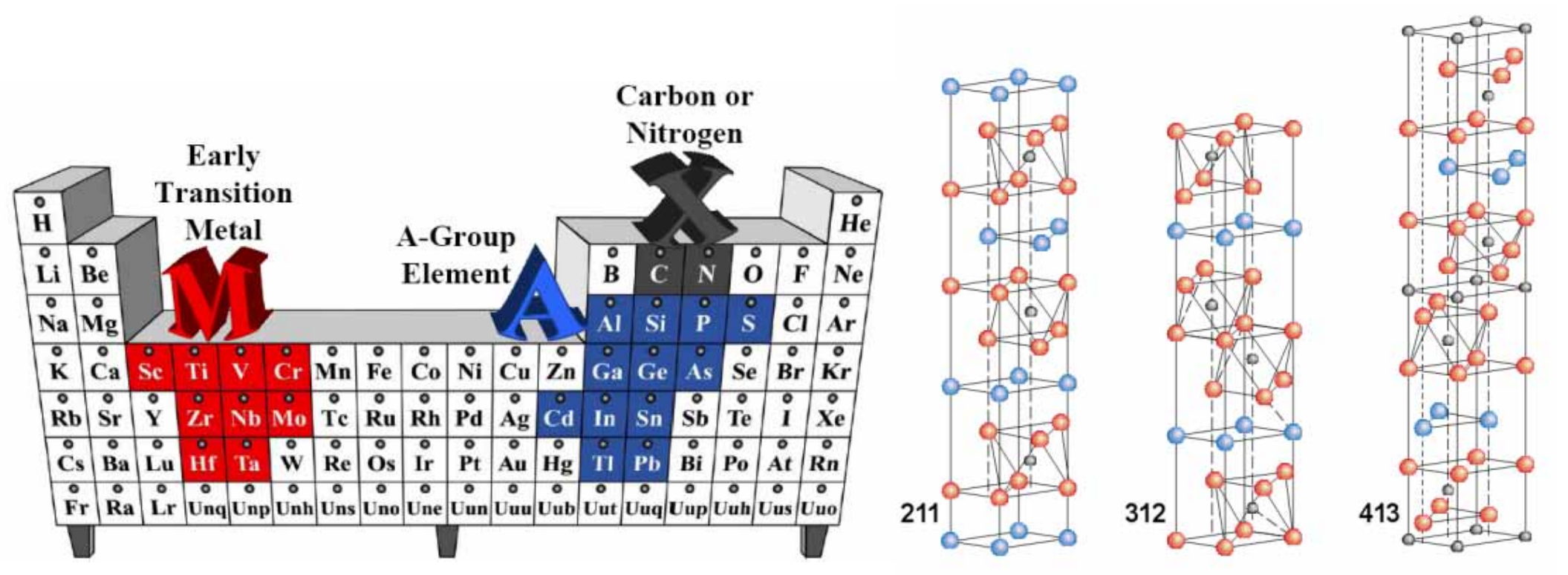
Institute of Ion-Beam Physics
and Materials Research

Forschungszentrum
Rossendorf
www.fz-rossendorf.de

Growth and microstructure of Ti_2AlN MAX phase thin films characterized by *in situ/ex situ* x-ray diffraction and transmission electron microscopy

M. Beckers, N. Schell, R.M.S. Martins, A. Mücklich, W. Möller

Motivation



Nano-laminated $M_{n+1}AX_n$ phases

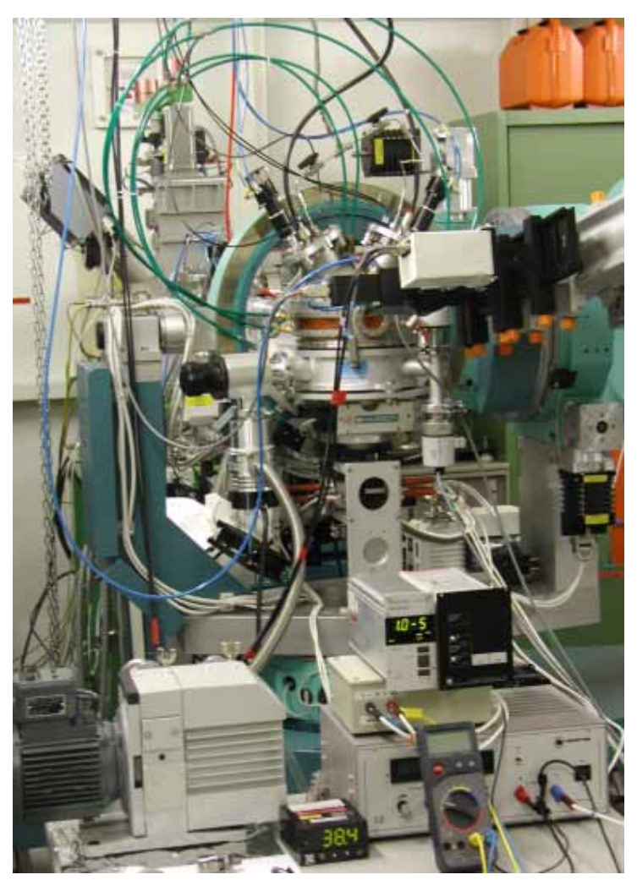
Properties of Ti_3SiC_2	Value	Ceramic	Metal
Hardess	5 GPa		👍
Young Moduls	346 GPa	👍	
Resistivity	22 µWcm		👍
Thermal conductivity	37 $Wm^{-1}K^{-1}$		👍
Decomposition temperature	> 1800 K	👍	
Oxidation Resistance	excellent	👍	
Machinability	excellent		👍

Unique combination of metallic and ceramic properties

> 50 bulk phases synthesized

Only carbidic thin films explored

Thin film deposition

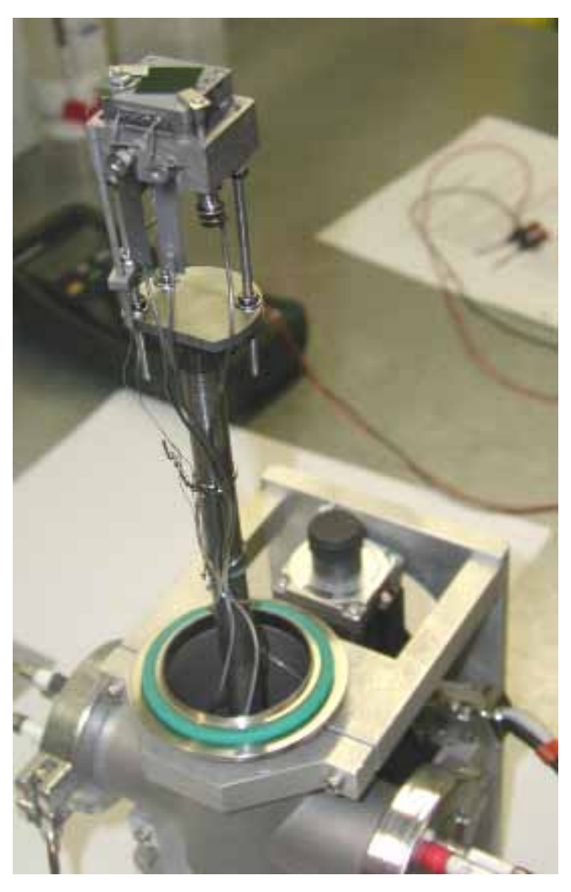


Sputter chamber

Magnetron

Sample positioning

W. Matz, et al.: Rev. Sci. Instrum. 72 (2001) 3344



Substrate holder

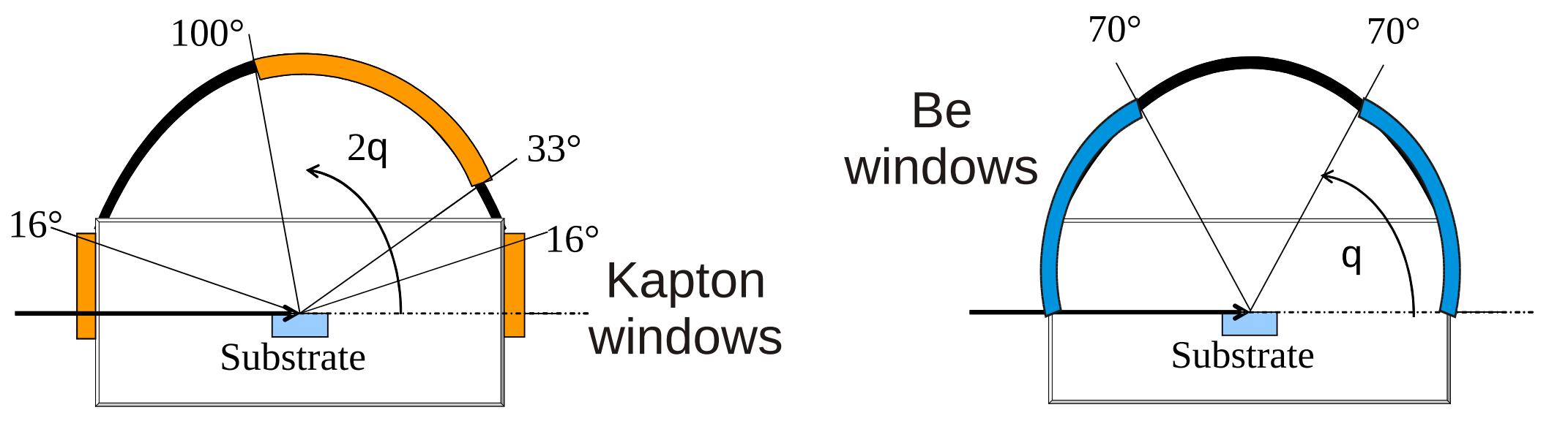
Base pressure: < 3 x 10^{-6} mbar
Targets: 1 inch 5N Al + 5N Ti
Sputter gases: 5N Ar + 5N N_2
Target-Substrate distance 100 mm
Substrates: MgO, Al_2O_3
T = RT - 1000 °C
U_{bias} = 0 - 1000 V

$(Ti_{0.63}Al_{0.37})N$
Ar/N2 = 2.76/1.38 sccm -> 0.35 Pa
Ti / Al = 60 W / 20 W

Ti_2AlN
Ar/N2 = 7.94/0.48 sccm -> 0.80 Pa
Ti / Al = 80 W / 27 W

Compound mode

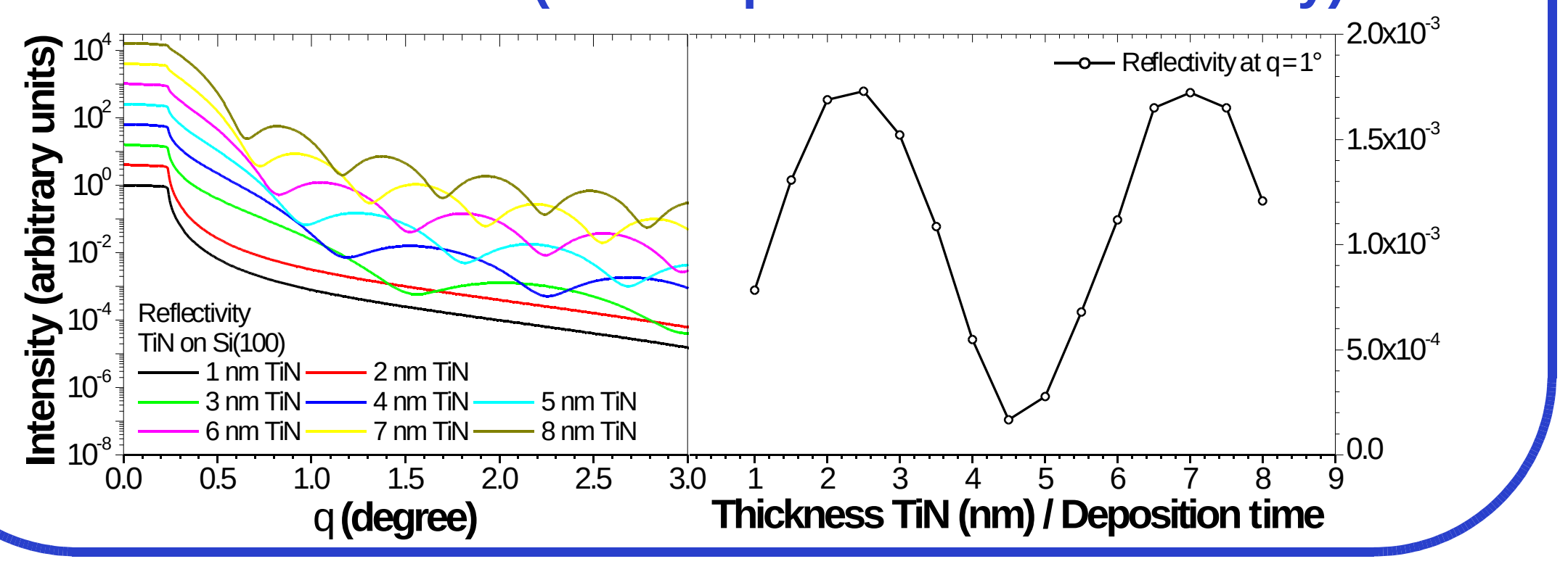
In-situ x-ray techniques



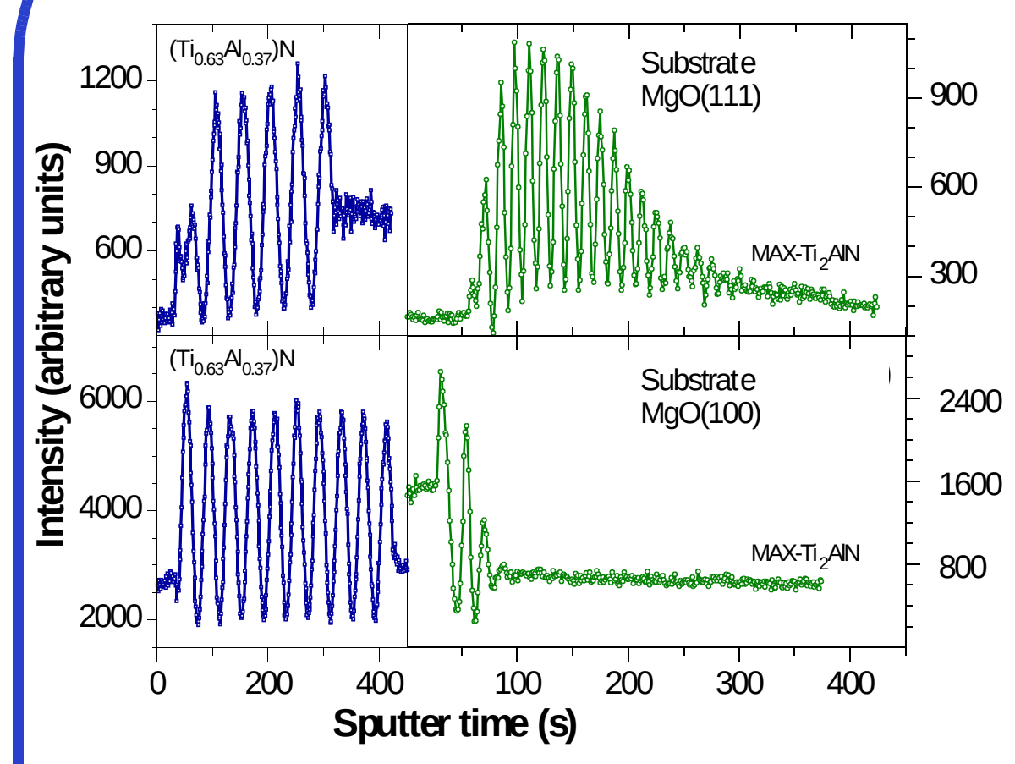
Old setup

New setup

Obtainable information
Film thickness, roughness, density (XRR)
Phases, lattice constants, texture (XRD)
Growth mode (time dependent XRR intensity)



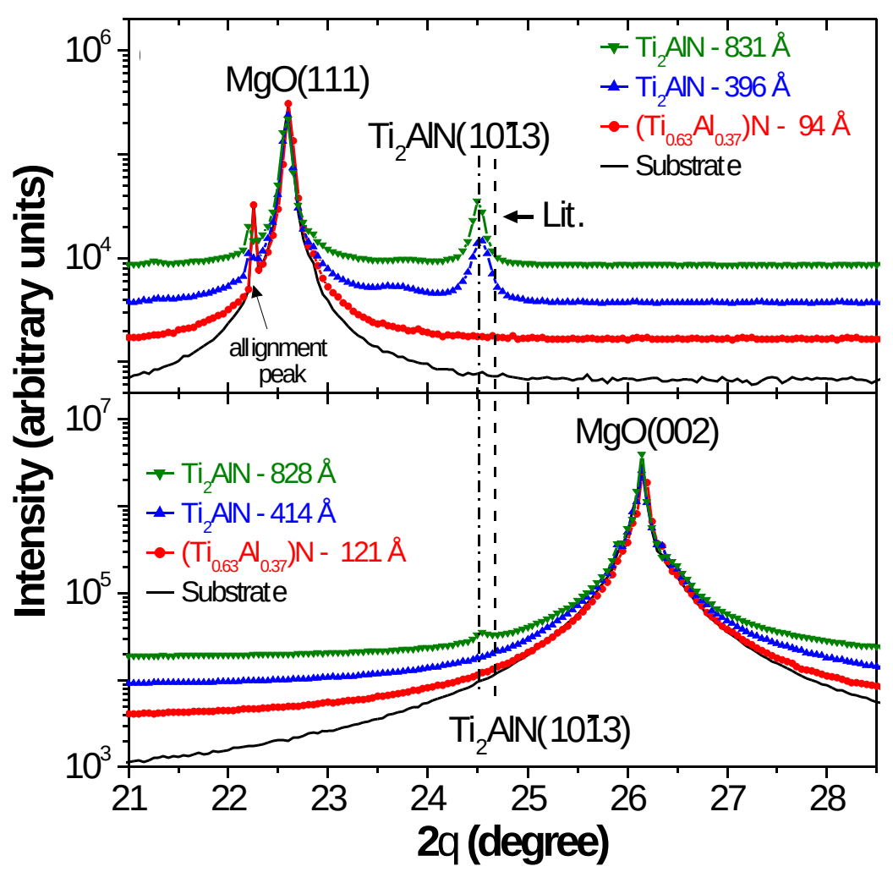
Growth onto MgO(111) and MgO(100) at $T_{Substrate}$ = 690°C with 10 nm cubic $(Ti_{0.63}Al_{0.37})N$ seed layer



Oscillatory behaviour is fingerprint for layer-by-layer growth

No roughness increase for $(Ti_{0.63}Al_{0.37})N$ for both substrate orientations

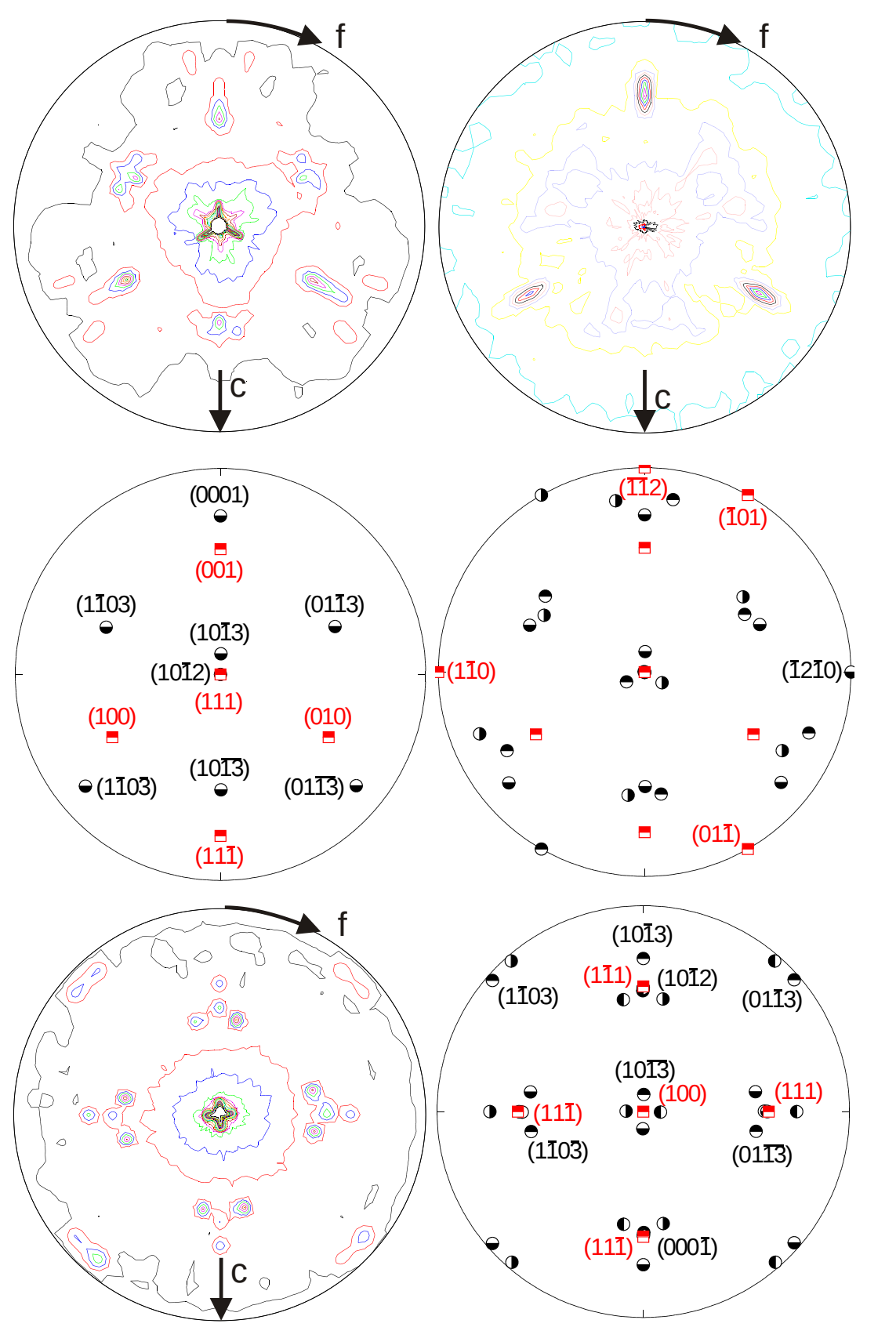
Roughening for Ti_2AlN,
more pronounced
for MgO(100) substrate
-> Stranski-Krastanov-like growth



Only $Ti_2AlN(10\bar{1}3)$ peak visible for both substrate orientations

Close vicinity to $Ti_2AlN(0006)$, yet excludable due to lack of multiplicity (000l) peaks

$Ti_2AlN(10\bar{1}2)$ suppressed due to selection rules



Pole figures of Ti_2AlN on MgO(111)

Left: $Ti_2AlN(10\bar{1}3)$ [+ $Ti_2AlN(0006)$ + MgO(111) + MgO(100)]

Right: $Ti_2AlN(0002)$

Theoretical pole figures

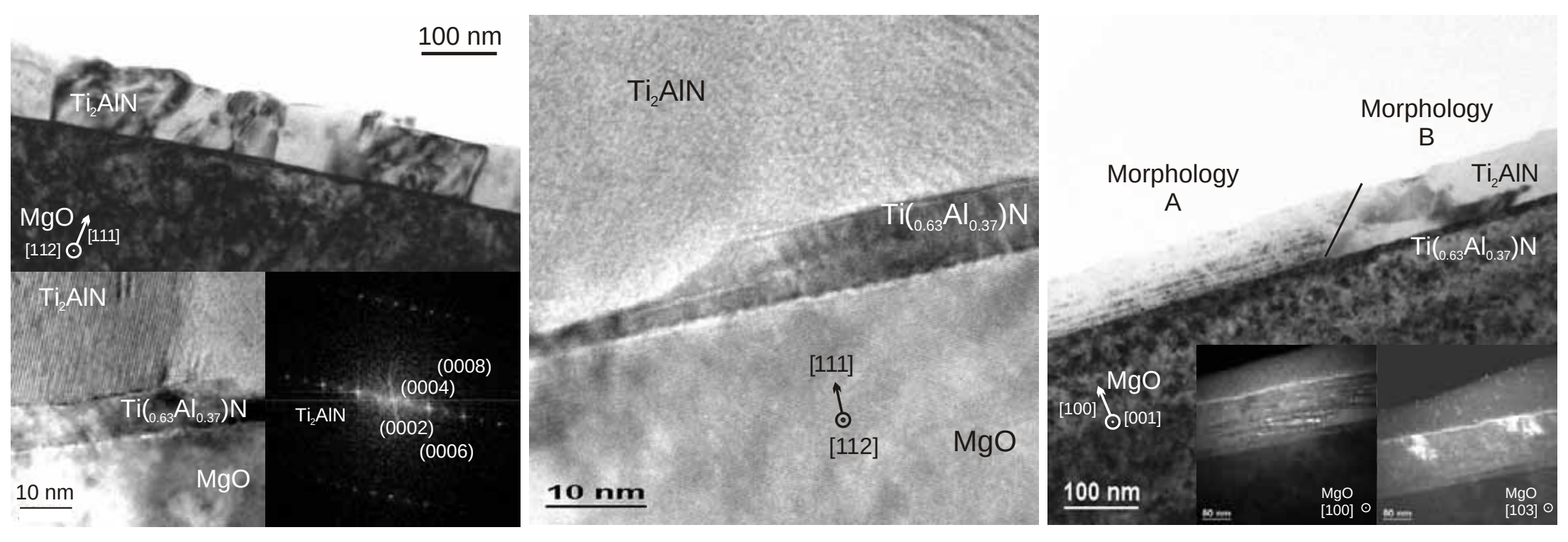
Azimuthal rotation for 0 (◒), 120 (◑) and 240 (◓) degrees

"Obvious" orientational relationship
MgO{111}<110> // $Ti_2AlN(10\bar{1}2)<\bar{1}2\bar{1}0>$

Pole figures for Ti_2AlN on MgO(100)

Azimuthal rotation for 0 (◓),90 (◑), 180 (◒) and 270 (◐) degrees

Persistent orientational relationship
MgO{111}<110> // $Ti_2AlN(10\bar{1}2)<\bar{1}2\bar{1}0>$



XTEM of Ti_2AlN on MgO(111)

No single crystal morphology, equi-axed grains with vertical size comparable to layer thickness

High surface roughness, resembling to time-resolved XRR data

Individual grains comprised of tilted (000l) basal plane layers as proven by image FFT

Interfacial topotaxial solid-state reaction between $(Ti_{0.63}Al_{0.37})N$ and Ti_2AlN proven by HR-XTEM

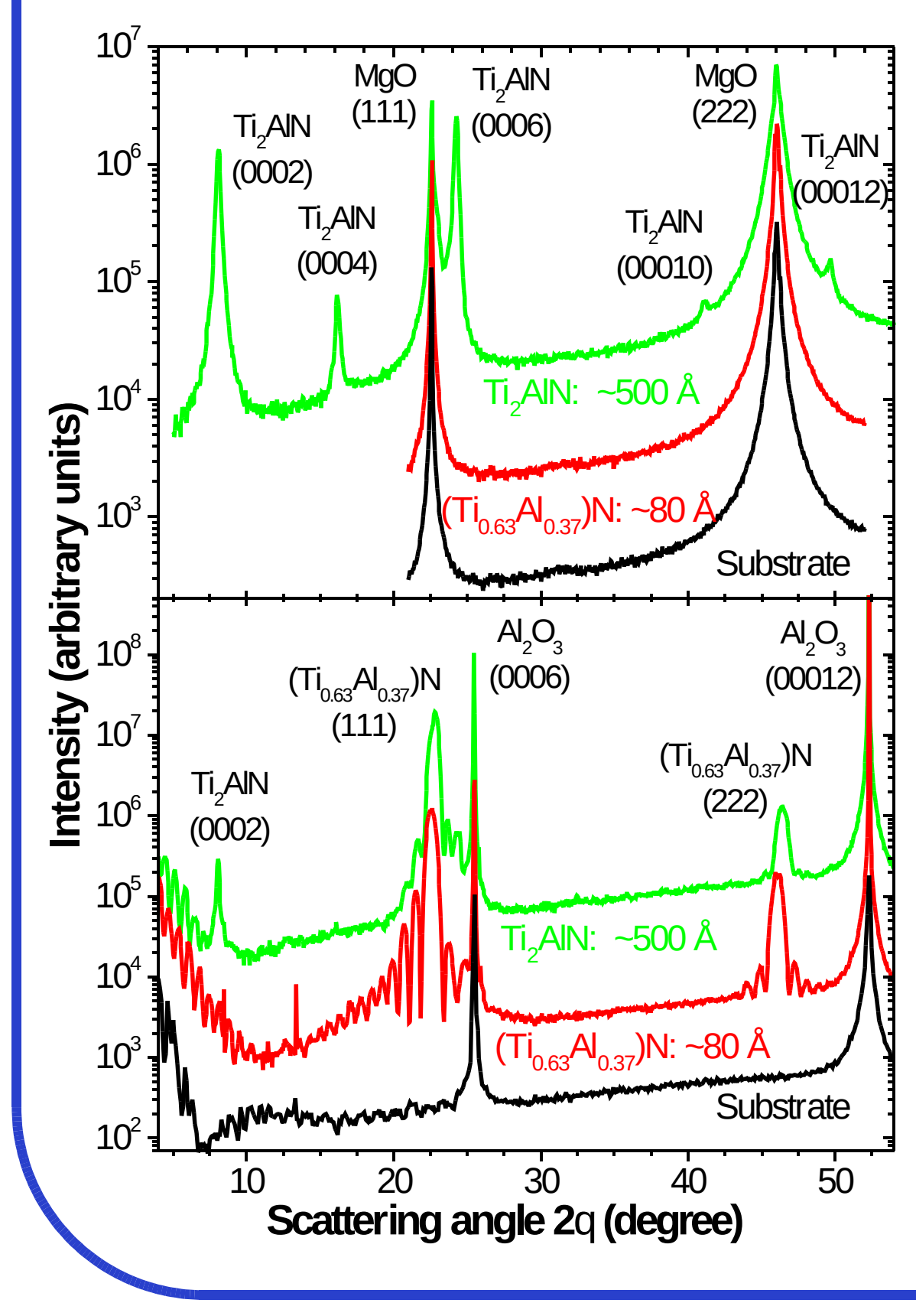
XTEM of Ti_2AlN on MgO(100)

Complete morphology change due to multiple tilted substrate adaptation

Lateral morphology variation due to additional multiple in-plane orientations

Growth at $T_{Substrate}$ ~ 800°C

***In-situ* XRD - new chamber setup**



Deposition onto MgO(111)

$(Ti_{0.63}Al_{0.37})N$ seed layer not resolvable from MgO{111} peaks

Multiple $Ti_2AlN(000l)$ peaks and minor traces of $Ti_2AlN(10\bar{1}4)$ visible
-> Predominant basal plane growth

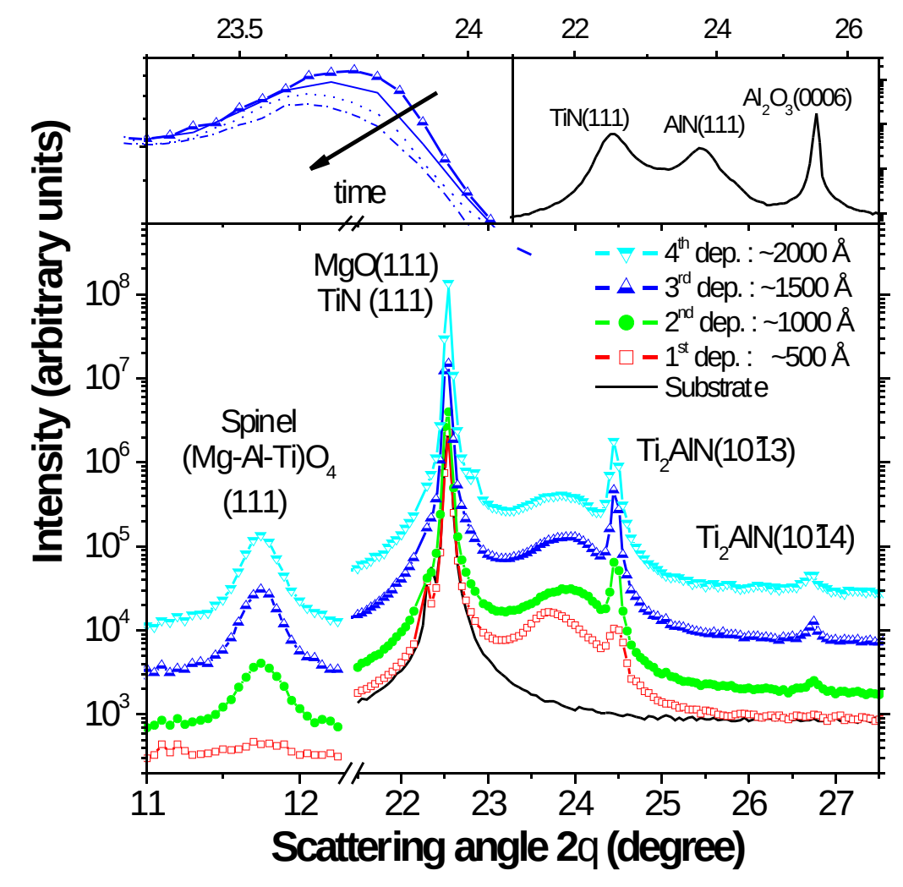
Deposition onto $Al_2O_3(0001)$

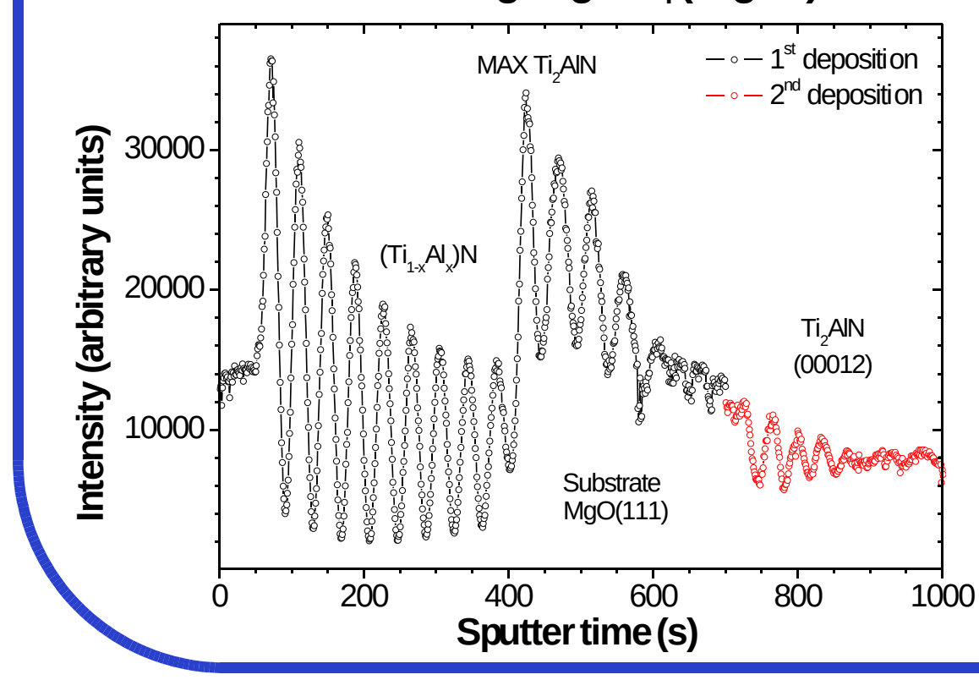
Epitaxial growth of $(Ti_{0.63}Al_{0.37})N$ seed layer (Laue fringes, slight compressive stress)

Only $Ti_2AlN(0002)$ detectable
-> Basal plane growth

Interfacial solid-state reaction detectable from shift of Laue fringes

Growth onto MgO(111) at $T_{Substrate}$ = 690°C without seed layer





***In-situ* XRD - old chamber setup**

Formation of self-organized N-understoichiometric cubic $(Ti_{1-x}Al_x)N$ thin layer at nominal 2Ti-A-N gas composition

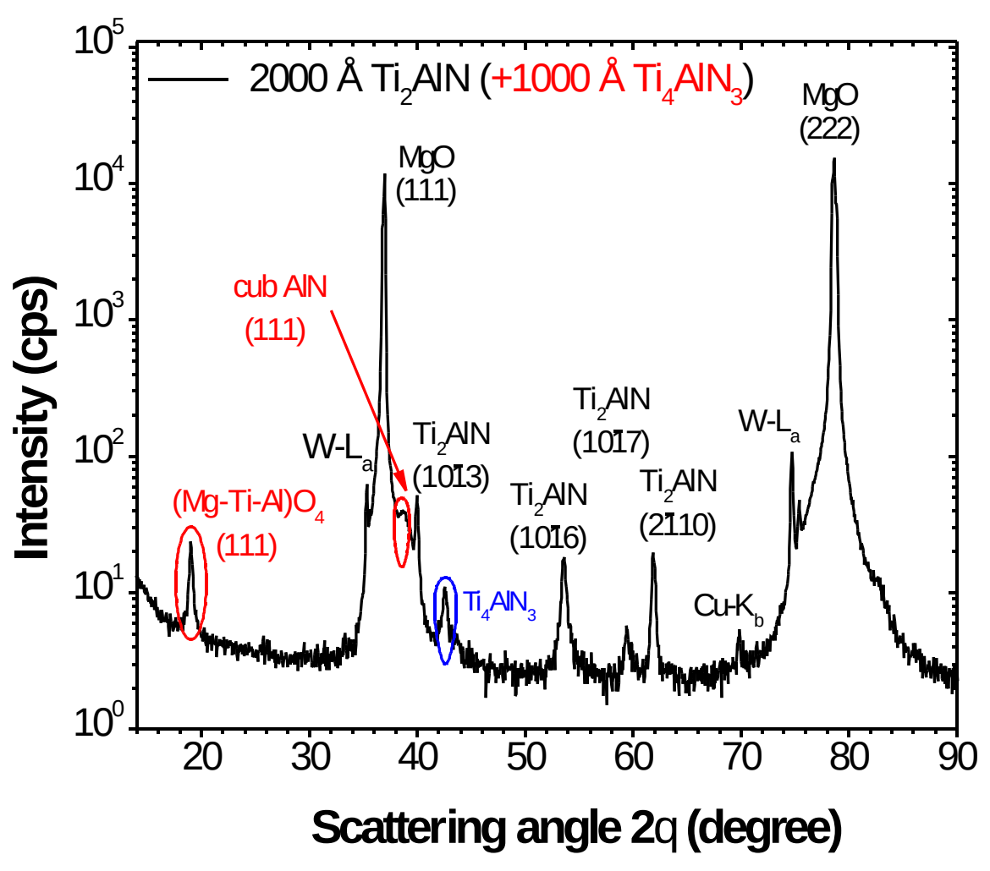
Spinodal decomposition into TiN + cubic AlN, concurrent topotaxial $(Mg\text{-}Ti\text{-}Al)O_4$ formation

Only $Ti_2AlN(10\bar{1}3)$ peak detectable
-> Tilted basal plane growth !?

Time-dependent XRR

Layer-by-layer growth of $(Ti_{1-x}Al_x)N$ layer with increased roughening than for deliberate $(Ti_{0.63}Al_{0.37})N$

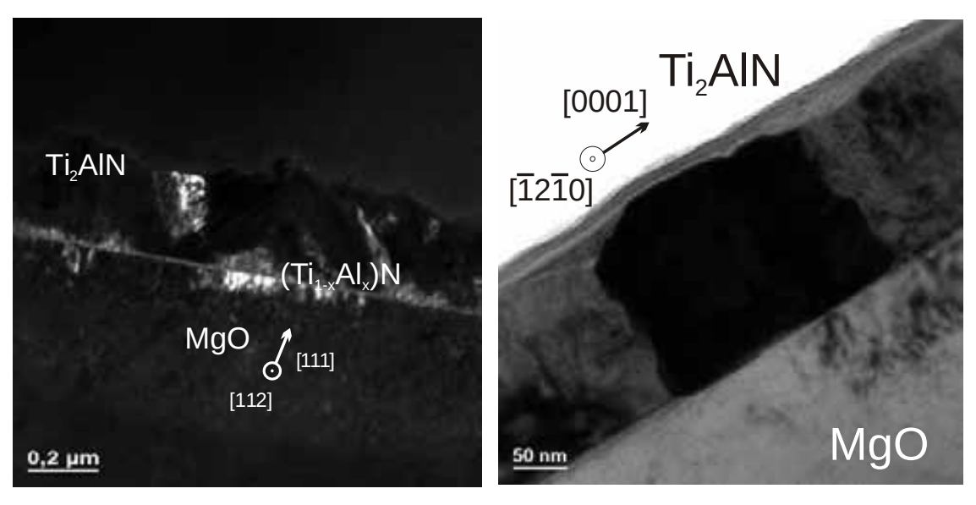
Onset of Ti_2AlN nucleation during ongoing growth clearly visible



***Ex-situ* lab source XRD**

Cubic AlN layer still detectable
-> stable cubic interfacial layer

Multiple Ti_2AlN peaks detectable with only slight deviation from powder intensity distribution
-> No epitaxial relationship between film and substrate
-> Ti_2AlN layer is non-textured, proven by pole figures

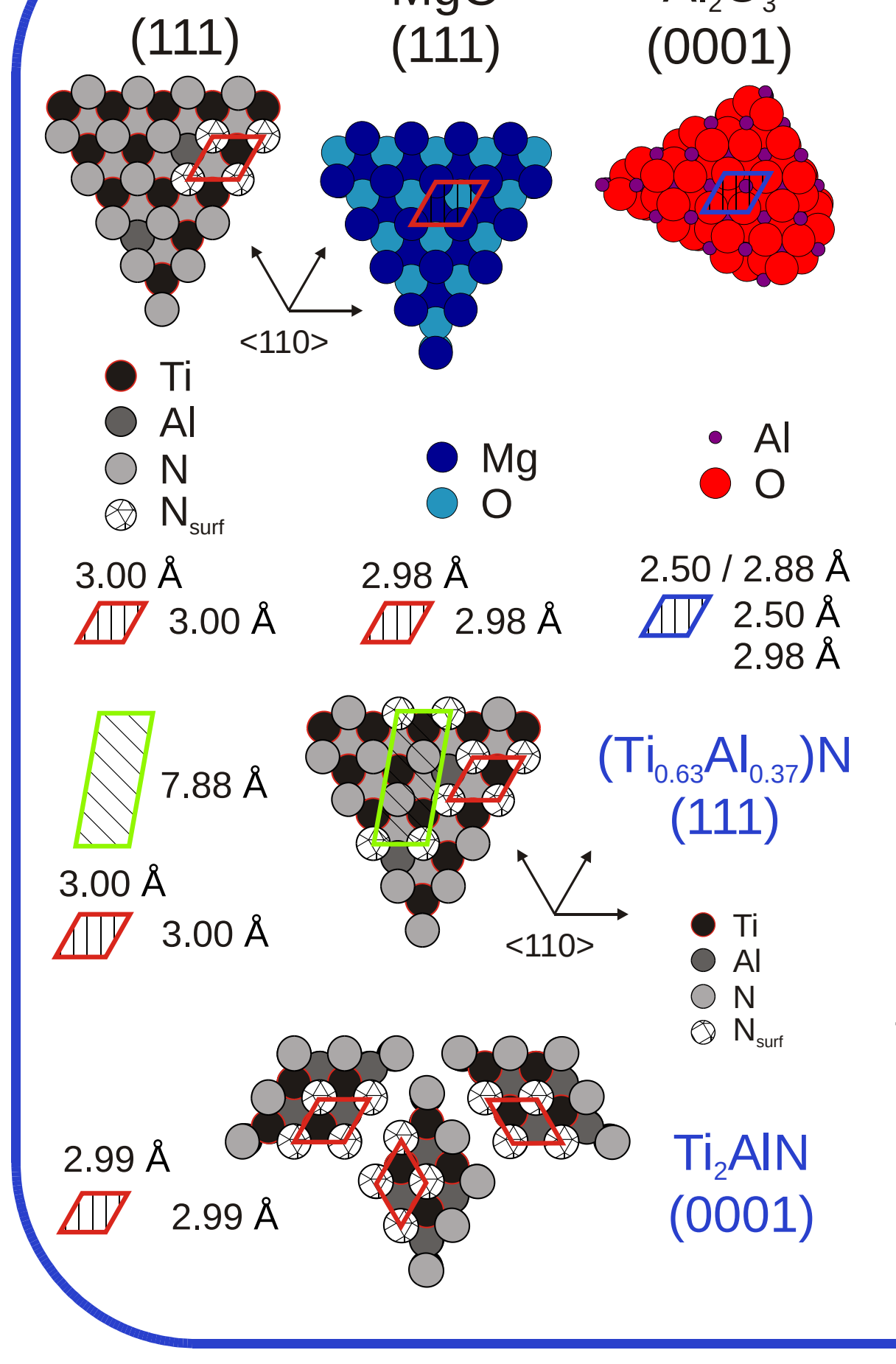


XTEM investigation

Cubic TiN/AlN interfacial layer clearly detectable from dark field images

Ti_2AlN layer still consists of grains with sizes up to layer thickness
Local epitaxy of individual grain is possible, however rare

Theoretical model, discussion and conclusion



Both MgO(111) and $Al_2O_3(0001)$ offer epitaxial adaptation for cubic Ti-Al-N(111) growth

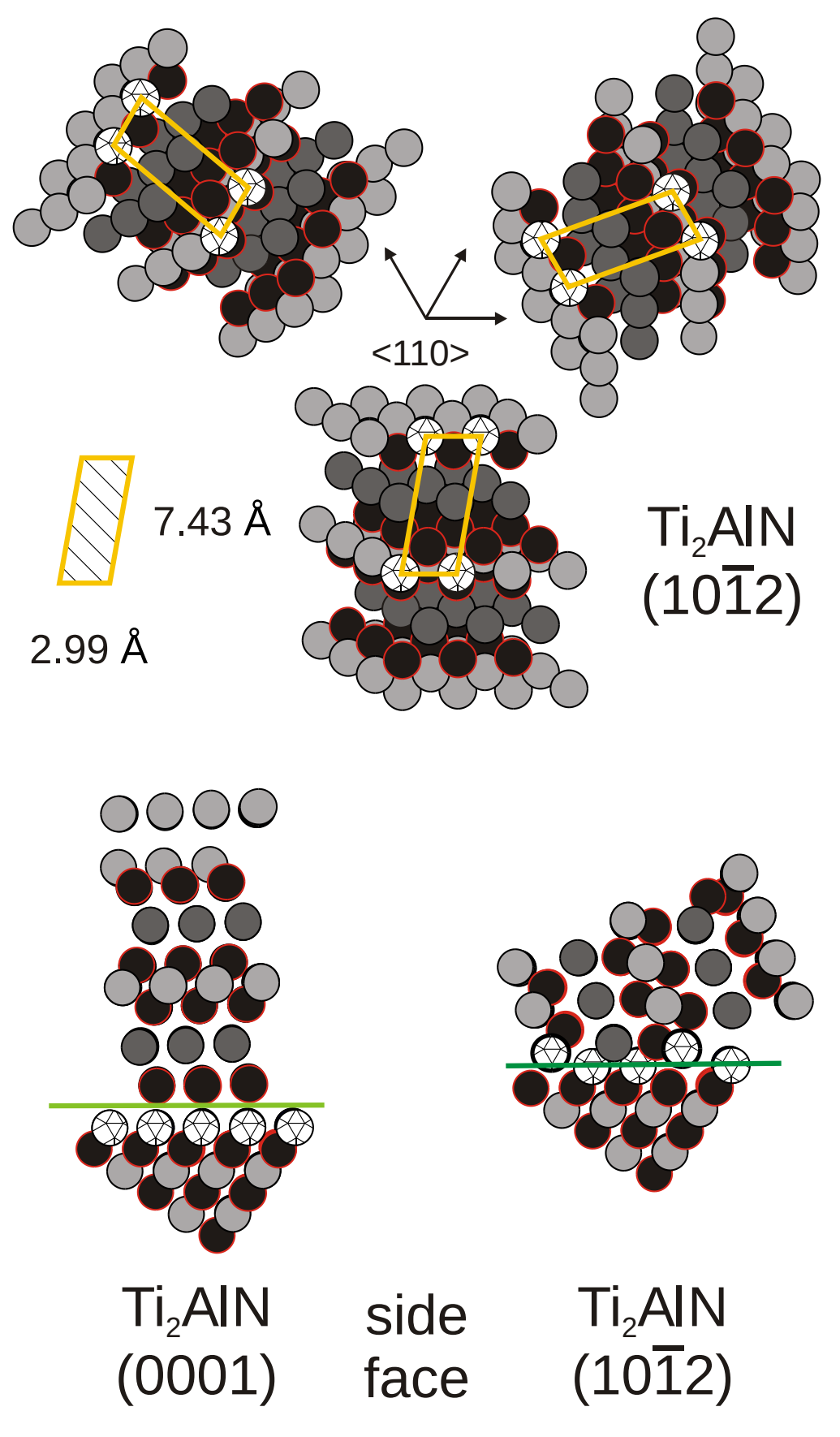
MgO(111) ~ 0.7 % mismatch

$Al_2O_3(0001)$ ~ 4 and 17 % mismatch

$(Ti_{0.63}Al_{0.37})N(111)$ surface offers epitaxial adaptation to Ti_2AlN basal plane (0.33 % mismatch)

Three <110> directions on $(Ti_{0.63}Al_{0.37})N(111)$ plane allow threefold orientation of Ti_2AlN during nucleation

During coalescence adjacent grains can adjoin without grain boundaries
-> single crystal film



$Ti_2AlN(10\bar{1}2)$ offers adaptation to one $(Ti_{0.63}Al_{0.37})N$<110> direction (mismatch 0.33 %)

Other <110> directions need over next atom binding and show high lattice mismatch (6%)

Threefold in-plane orientation does not allow grain-boundary-free coalescence
-> equi-axed morphology

Initial atomic Ti layer needed for nucleation of $Ti_2AlN(0001)$ onto $(Ti_{0.63}Al_{0.37})N(111)$
Co-sputtering process provides flux of both **Ti *AND* Al**

Higher substrate temperature or high low-energy ion flux to substrate
-> Element partitioning

Low substrate temperature
-> Changed interfacial adaptation

Conclusions

- Successful deposition of Ti_2AlN MAX phase thin films (Second experiment world-wide)
- Growth and microstructure can be influenced by seed layer deposition and substrate temperature during growth
- A $(Ti_{0.63}Al_{0.37})N$ seed layer and low substrate temperature leads to tilted basal plane growth, irrespectible of substrate orientation due to kinetical restriction during nucleation, which asks for specific interfacial adaptation
- A $(Ti_{0.63}Al_{0.37})N$ seed layer and high substrate temperature leads to upright basal plane growth due to sufficient adatom mobility during nucleation to allow elemental partitioning both for MgO(111) and $Al_2O_3(001)$ substrates
- Deposition without deliberate $(Ti_{1-x}Al_x)N$ seed layer still leads to formation of cubic interfacial layer, with subsequent spinodal decomposition into TiN and AlN. The rough surface of the self-organized cubic seed layer leads to non-epitaxial growth of Ti_2AlN

Financial support from the Deutsche Forschungsgemeinschaft under contract SCHE 682 is gratefully achknowledged.

Corresponding authors:
Dipl.-Phys. Manfred Beckers Tel.: +49 351 260 3389 M.Beckers@fz-rossendorf.de
Forschungszentrum Rossendorf, P.O. Box 510119, D-01314, Germany
Dr. Norbert Schell Tel.: +33 47688 2367 Schell@esrf.fr
ROBL-CRG (BM20), ESRF

Member of the Leibniz-Association