Karlsruhe Institute of Technology

ANKA

Combined XRD and EXAFS study of Cr-Al-N gradient samples

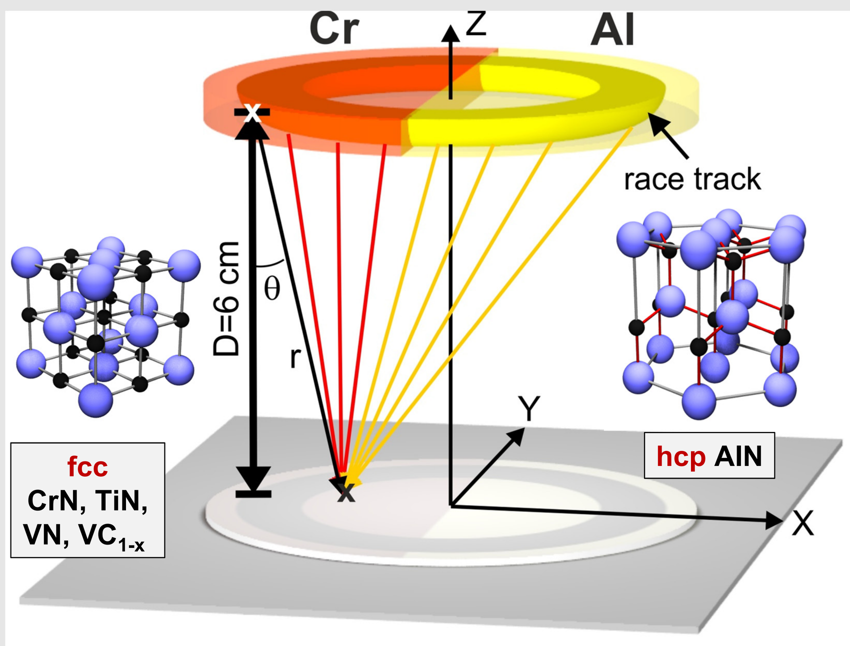
Bärbel Krause*, Michael Stüber, Anna Zimina, Mareike Trappen, Ralph Steininger, Sven Ulrich, S. Kotapati, S. Mangold, Jian Ye, Tilo Baumbach

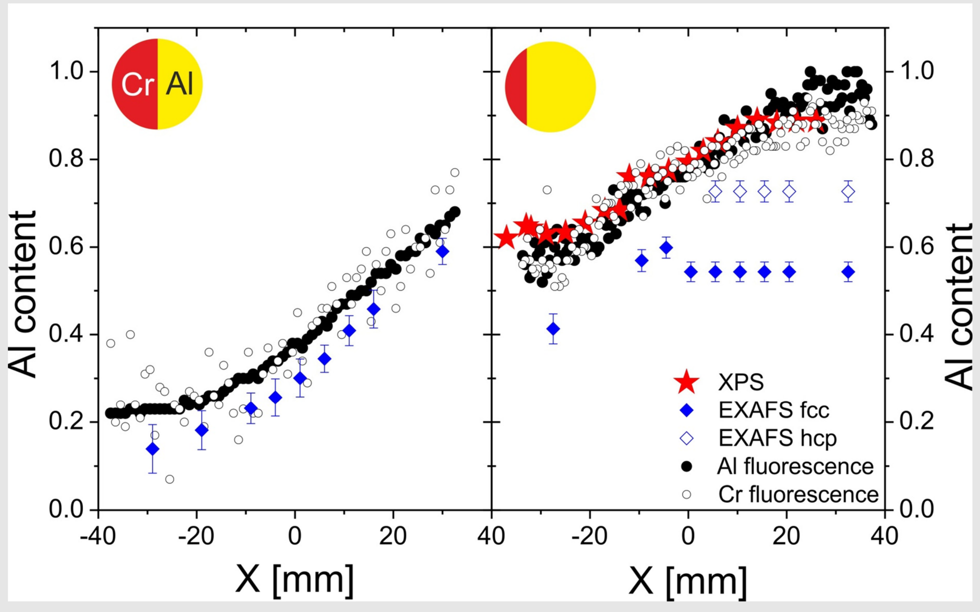
Karlsruhe Institute of Technology (KIT), Germany

Introduction

Ternary hard coating materials such as CrAlN and TiAlN are widely used in industry. The hardness of the coatings is directly influenced by coexisting crystalline phases, crystallite size, and texture [1-5]. These are mainly controlled by the Al content and the growth conditions. Here we report a systematic XRD and EXAFS study of Cr-Al-N gradient thin films deposited by reactive magnetron sputtering from a segmented target. The influence of the sputter geometry and the chemical composition on the microstructure will be analyzed.

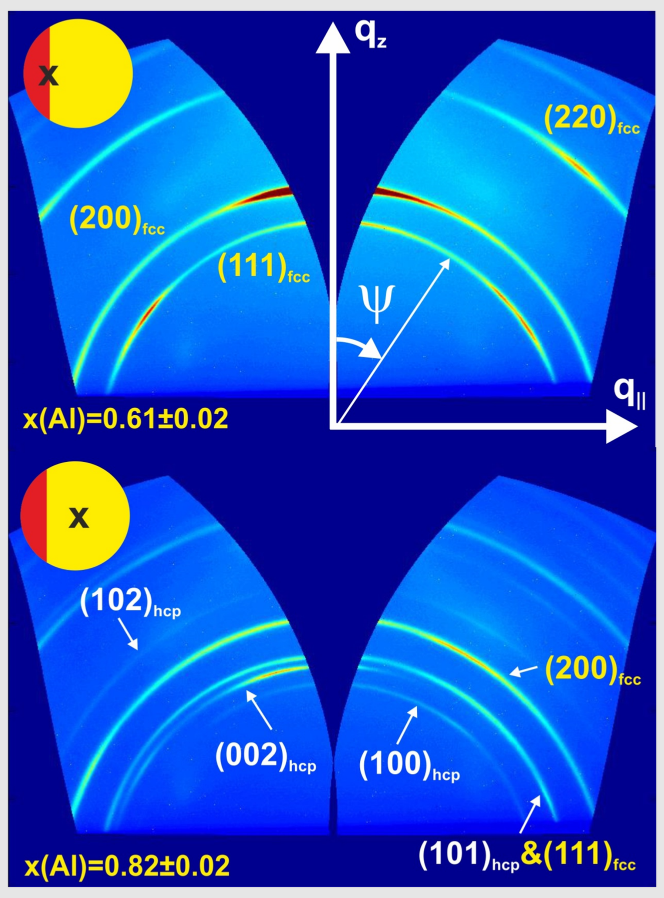
Cr-Al-N Gradient Samples



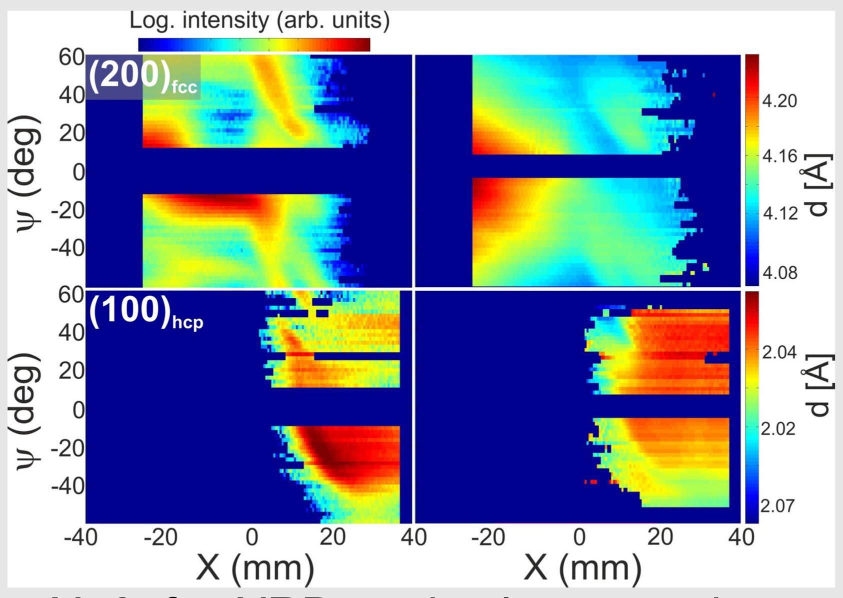


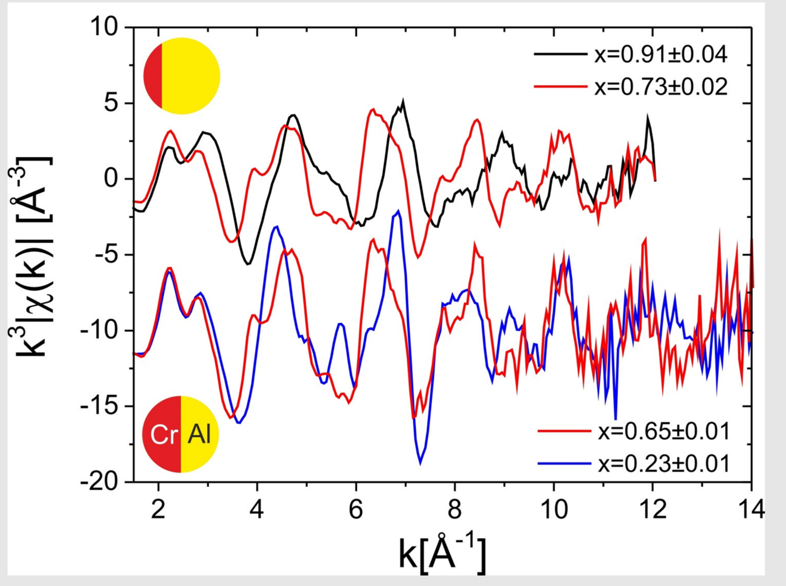
- Reactive RF magnetron sputtering
- Sputter gas N2, 72 sccm, pressure 0.6 Pa
- 2 segmented targets with different Cr:Al ratio
- Large composition range, verified by fluorescence analysis and XPS
- fcc/hcp transition expected at c=0.75 [2]

fcc / hcp transition: EXAFS, XANES, and XRD



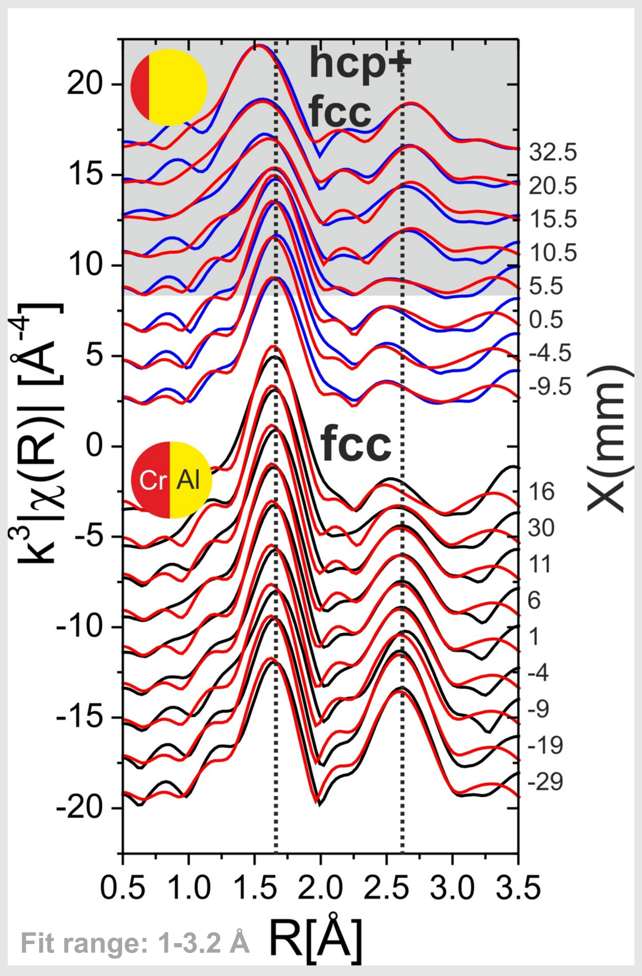
XAS + XRD: SUL beamline (ANKA)

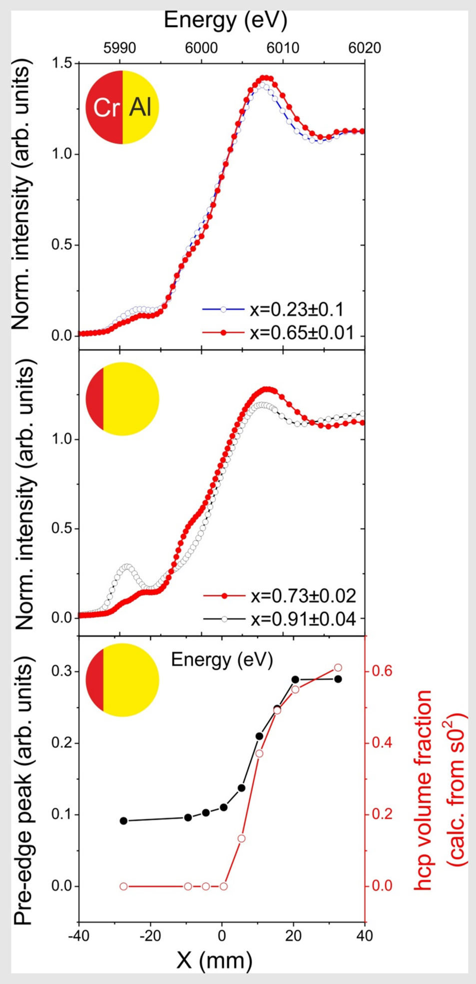




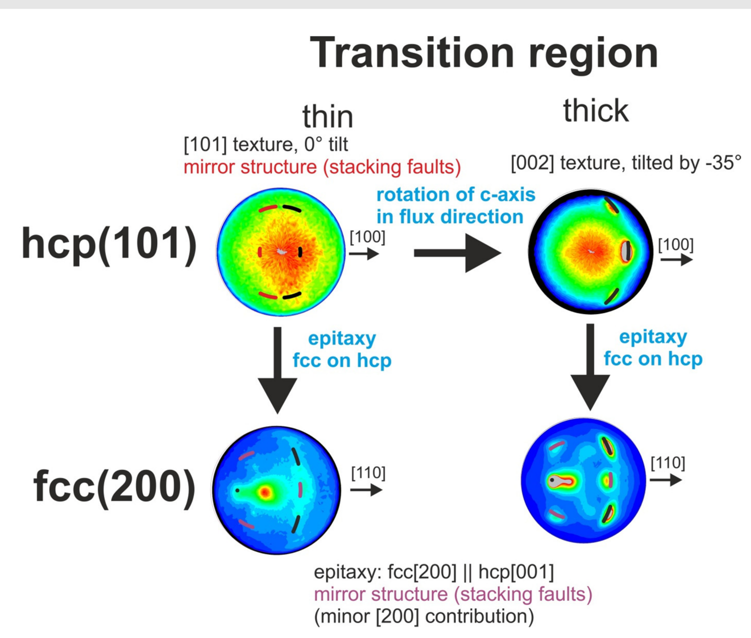
- X<0: fcc XRD peaks, low pre-edge peak → Model: fcc single scattering paths
- X>0, fcc & hcp XRD peaks, lattice parameter does not change significantly, pre-edge peak increases → Model: fcc + hcp, single scattering paths
- Model similar to [3,4] for TiAlN and [1] for VAlCN

x(Al)<0.75: fcc with variable composition, x(Al)>0.75 phase separation in fcc+hcp (constant composition)





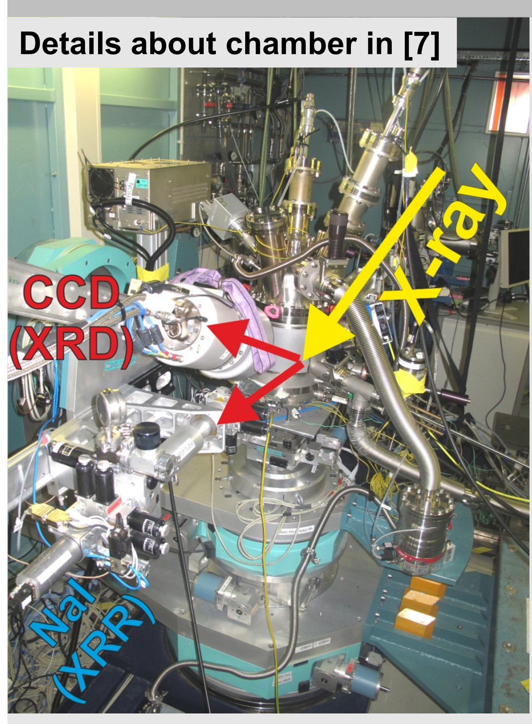
Local Epitaxy

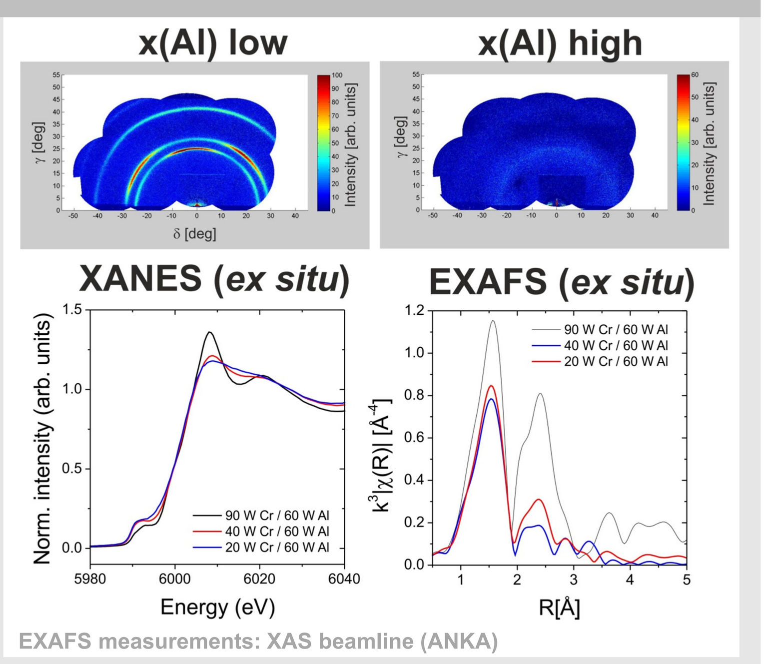


- Similar to known AlN textures (001), (101) [5]
- Expected [2] and observed: $(001)_{hcp}||(111)_{fcc}$ large tilt but [111] along surf. norm.
- Similar to typical CrN textures (111), (200)

- biaxial orientation (→ target symmetry)
- texture changes with film thickness
- fcc and hcp orientations related

In situ Codeposition





- Al: RF, 129 mm target-substr.
- Cr: DC, 229 mm target-substr.
- Ar+N2 (0.5/1.2 sccm), p=0.4 Pa
- Composition varied by power

- low Al content: fcc
- high Al content: amorphous

Conclusions

- EXAFS model based on XRD and XANES observations
- → Composition dependent occupation of second shell for fcc and hcp phase
- Interesting: c(Al)>0.75 → fcc+hcp (equilibrium: fcc → hcp transition expected [2])
- Epitaxy and stacking faults might play a role in stabilizing coexisting phases

References

[1] D. Rafaja et al., Surf. Coat. technol. 257 (2014), 26-37
[2] P. Mayrhofer et al., Act. Mater. 56 (2008), 2469-2475
[3] B. Krause, et al, J. Appl. Cryst. **46**, 1064 – 1075 (2013)
[4] M.-H. Tuilier et al., Surf. Coat. Technol. **201**, 4536–4541 (2007)
[5] M.-H. Tuilier, et al., J. Appl. Phys. **103**, 083524 (2008)
[6] A. Rodriguez-Navarro et al., J. Mat. Res. **12**, 1850-1855 (1997)
[7] B. Krause et al., J. Synchrotron Rad. **19** 2012, 216–222

Acknowledgements

We thank ANKA for the provision of beam time, A. Weißhardt and H. Gräfe for the help in the UHV lab, and S. Stankov for the support at the Smartlab Diffractometer. Special thanks also to the beamline scientists of the MPI beamline, P. Wochner and S. Ibrahimkutti, and to the technical staff at ANKA. Without them, such a complex experiment would not have been possible.