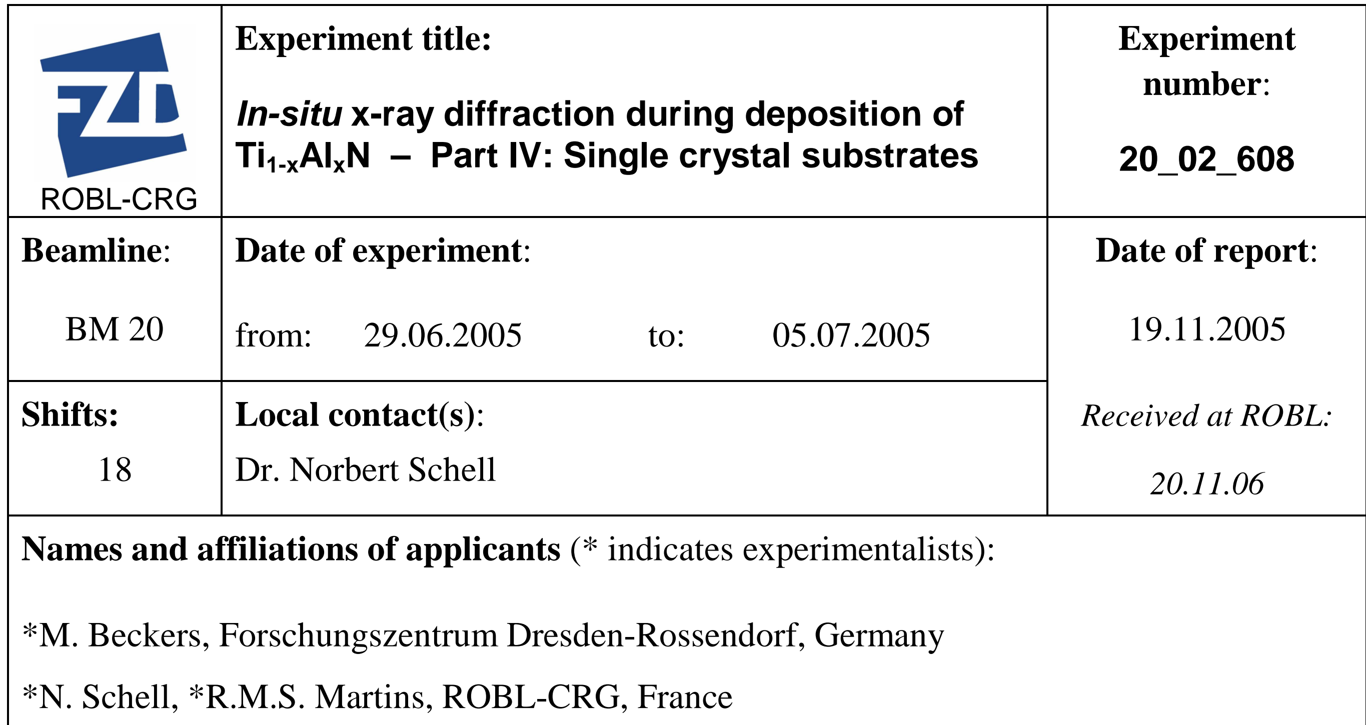

ROBL-CRG	**Experiment title:** *In-situ* **x-ray diffraction during deposition of $Ti_{1-x}Al_xN$ – Part IV: Single crystal substrates**	**Experiment number:** **20_02_608**
Beamline: BM 20	**Date of experiment:** from: 29.06.2005 to: 05.07.2005	**Date of report:** 19.11.2005
Shifts: 18	**Local contact(s):** Dr. Norbert Schell	*Received at ROBL:* *20.11.06*

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Report

AIM:

The meta-stable nitride $Ti_{1-x}Al_xN$ finds widespread use as wear-protective hard coating in metal forming industries. Previous studies comprised the influence of growth rate, temperature and Al-content on the development of $Ti_{1-x}Al_xN$ preferred orientation for deposition on amorphous substrates [1, 2], which crucially effects the coating's performance. Also the heteroepitaxial $M_{n+1}AX_n$ phase Ti_2AlN growth on a $Ti_{0.63}Al_{0.37}N$ seed layer on MgO single crystal substrates at substrate temperatures of ~700°C was reported [3]. The epitaxial Ti_2AlN growth mode and hence its microstructure was found to depend on the substrate temperature. To conclude for the role of the seed layer, during the present experiment we investigated the growth mode of $Ti_{1-x}Al_xN$ on MgO, varying its orientation as wells as the Al-content x, and substrate temperature.

EXPERIMENTAL:

A total of ***six $Ti_{1-x}Al_xN$ samples*** were deposited onto single crystal MgO(111) and MgO(100) substrates by reactive magnetron **co-*sputtering from Ti and Al targets*** in an Ar/N_2 atmosphere at substrate temperatures of 300 and 700°C. Prior to deposition, all substrates were degassed and reconstructed by holding 700°C for one hour. All samples were deposited at a working pressure of 0.35 Pa with Ar and N_2 fluxes of 2.76 and 1.38 sccm, respectively. To keep the deposition rate constant at ~0.5 Å/s, the total output of the Ti plus Al magnetrons were kept at 85 W, with the Ti/Al power ratios changing from 80/5 W to 60/25 W, in order to change the Al concentration from x = 0.05 to 0.37. The total film thickness of up to 400 nm was achieved in four to five deposition steps of approximately 100 nm each. Each sequential deposition step was characterized in two different scattering geometries: (1) low angle specular reflectivity (XRR), either time-resolved at a fixed angle to monitor each layer's growth mode by the corresponding x-ray intensity oscillations, or angle-resolved for thickness and roughness determination. (2) Large angle x-ray diffraction (XRD) to determine phase formation and off-plane lattice parameters. The energy of the incident x-rays was monochromatized to $\lambda = 0.961$ Å.

THEORY:

The x-ray intensity oscillations observed during growth are associated with diffraction from alternating monolayer coverages θ_n, running from 0 to 1, with $\theta_{n+1} < \theta_n$. The intensity for an ideal layer-by-layer growth of n monolayers, disregarding absorption, roughening, and substrate, can be written as $I = (F \cdot \sum_n \theta_n e^{-iqdn})^2$, with F being the structure amplitude, q the momentum transfer during measurement, and d the layer spacing. Roughness can be included by interlayer diffusion rates or Gaussian height distributions. Lu *et al.* [4] demon-

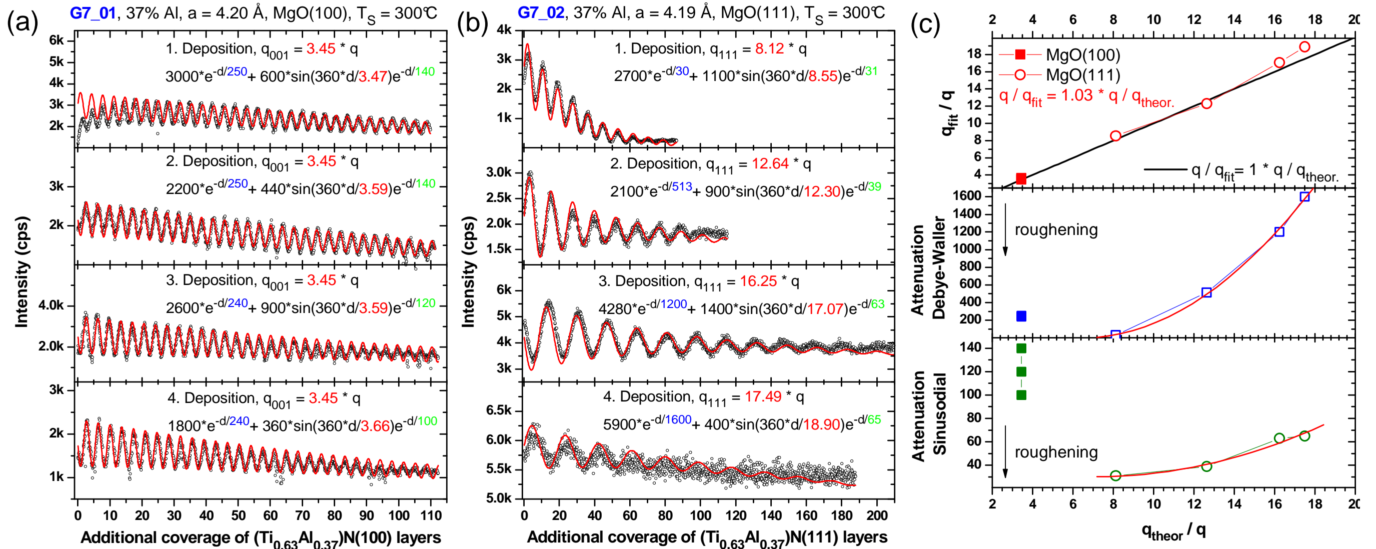

Fig. 1: *In situ* growth oscillation results with fittings for $(Ti_{0.63}Al_{0.37})N$ deposited onto (a) MgO(100) and (b) MgO(111). (c) shows the individual fit paramters plotted over the ratio of theoretical and measured q values.

-strated that in case of roughening the intensity curve can be parameterized by a combination of oscillatory and exponential decay terms.

RESULTS:

Figure 1 shows exemplary results and fittings to *in situ* data with the above parameterization, as displayed in the legends of Figs 1(a) and 1(b), with the individual fitting parameters highlighted. The data were obtained during the growth of $Ti_{0.63}Al_{0.37}N$ films, deposited at 300°C onto (a) MgO(100) and (b) MgO(111), respectively. The measured data are plotted over the nominal additional $Ti_{0.63}Al_{0.37}N(100)$ and $Ti_{0.63}Al_{0.37}N(111)$ monolayers, calculated from XRR thicknesses and XRD lattice constants obtained after each of the four sequential deposition steps.

In general, oscillation measurements are carried out at the anti-Bragg ½*q_d position, with *d* being the film lattice spacing along the <hkl> direction of the measured crystal truncation rod. This means every intensity oscillation represents the completion of another monolayer. However, when substantial surface roughening is involved only very few oscillations can usually be observed under these conditions. Therefore, all data here were taken at a q_{exp} value off the anti-Bragg position, at corresponding incidence angles where the initial intensity is high enough to detect several oscillations during growth. Hence, at a constant growth rate the number of oscillations per completed monolayer changes for each measurement, as can be seen in Fig. 1(b). Yet, the ratio between fitted and measured q value q_{fit}/q plotted over the ratio between theoretical and measured q value q_{theor}/q yield a straight line, as illustrated in the top layer of Fig. 1(c). Therefore, also measurements at different q_{exp} values can still be fitted with the same single layer-by-layer growth model.

Furthermore, the decay of the oscillation amplitudes in Figs 1(a) and 1(b) clearly indicate surface roughening, which are accounted for by exponential attenuation of the sinusoidal oscillation and the overall intensity, whose factors are shown in the middle and bottom layers of Fig. 1(c). Following Lu *et al.* [4] these can also be deduced back to any q value position, with a q^2-dependence as illustrated by the fitted curves. Comparing the different attenuation factors, the $Ti_{0.63}Al_{0.37}N$ surface roughening is by far more pronounced for the MgO(111) than for the MgO(100). Data for low Al-content $Ti_{0.92}Al_{0.08}N$ not shown here reveals an even more pronounced difference in roughening. This can be understood by the difference in Ti adatom binding energies on the TiN surface being 10.09 eV for (111) and 3.3 eV for (100), respectively. The difference in adatom mobilities is attenuated at a deposition temperature of 700°C. Hence the exponential decay for (111) and (100) orientation is of the same low order, as has been shown also in previous experiments [3].

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