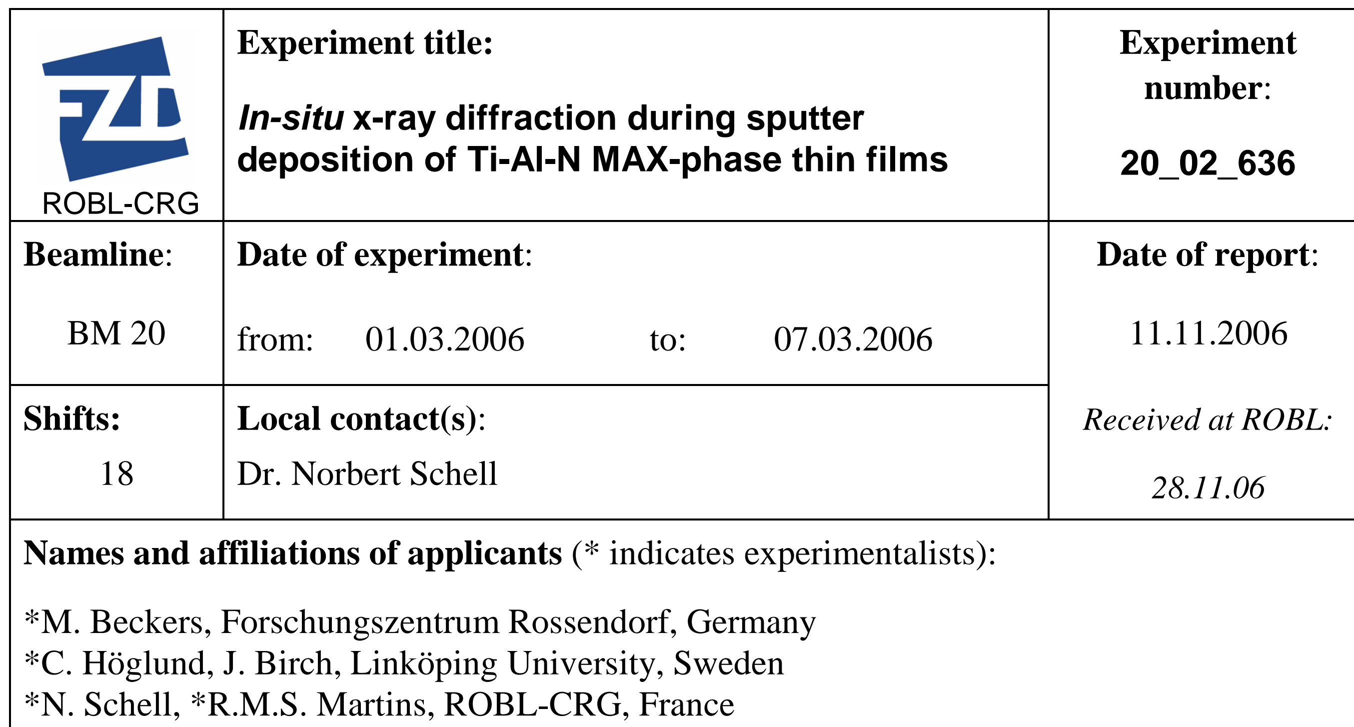

ROBL-CRG	**Experiment title:** *In-situ* **x-ray diffraction during sputter deposition of Ti-Al-N MAX-phase thin films**	**Experiment number**: **20_02_636**
Beamline: BM 20	**Date of experiment**: from: 01.03.2006 to: 07.03.2006	**Date of report**: 11.11.2006
Shifts: 18	**Local contact(s)**: Dr. Norbert Schell	*Received at ROBL: 28.11.06*

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Report

AIM:
Due to their combination of metallic and ceramic properties, the ***$M_{n+1}AX_n$ phases*** – ternary nitrides and carbides with M being a transition metal, A an A group element and X nitrogen or carbon – are subject of numerous studies. Also thin films of the $M_{n+1}AX_n$ carbides have been extensively studied, but only ***very recently*** the first results on nitride deposition in form of ***Ti_2AlN*** have been published [1, 2; compare Reports 20_02_608, part III + IV]. However, for ***Ti_4AlN_3*** and the proposed meta-stable modification ***Ti_3AlN_2*, *no experimental work*** on thin films has been reported up to now. Hence, during this experiment the **growth of $Ti_{n+1}AlN_n$ $M_{n+1}AX_n$ phase** compounds with n = 2 and 3 was studied ***in-situ***.

EXPERIMENTAL:
A total of nine samples were deposited onto single crystal MgO(111) and Al_2O_3(0001) substrates by reactive magnetron co-sputtering from Ti and Al targets in an Ar/N_2 atmosphere at temperatures between 600 and 725°C. According to previous experiments [3] the Ti_4AlN_3 deposition parameters were set to target powers of Ti 83 W and Al 14 W with Ar/N_2 flux ratios of 7.82/0.6 sccm, leading to a working pressure of 0.8 Pa. Thin $(Ti_{0.63}Al_{0.37})N$ or Ti_2AlN were used as seed layers, in order to improve Ti_4AlN_3 nucleation and prevent interfacial diffusion processes to the MgO substrate. A constant bias voltage of -30 V was applied for all depositions. Each sequential deposition step of seed layer and Ti_4AlN_3 was characterized in two different scattering geometries: (1) low angle specular reflectivity for thickness determination and (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 11.554 keV ($\lambda = 1.073$ Å). Additional ex-situ techniques used were Rutherford backscattering spectrometry (RBS) to obtain the final film composition and high resolution transmission electron microscopy (HRTEM) to cross-check for local $M_{n+1}AX_n$ phase formation.

RESULTS

Fig. 1 shows the XRD results for samples deposited onto Al_2O_3 at 600°C, 675°C, and 725°C substrate surface temperature. For 725°C and 625°C, prior to the Ti_4AlN_3, a thin Ti_2AlN seed layer was deposited at 675°C, showing basal plane growth as displayed by the multiple (000ℓ) diffraction peaks (see also [1]). Similar results as in Figure 1 have been obtained for Ti_4AlN_3 growth onto MgO(111) and/or using $(Ti_{0.63}Al_{0.37})N$ as a seed layer. For 675°C substrate temperature, as depicted in Figure 1(a), the deposition of 700 Å nominal Ti_4AlN_3 does not induce this phase, but an Ti_2AlN growth with segregation of surplus Ti into cubic $(Ti_{1-x}Al_x)N$ with unknown Al concentration. This may be ascribed to an insufficient Al adatom mobility, which consistent

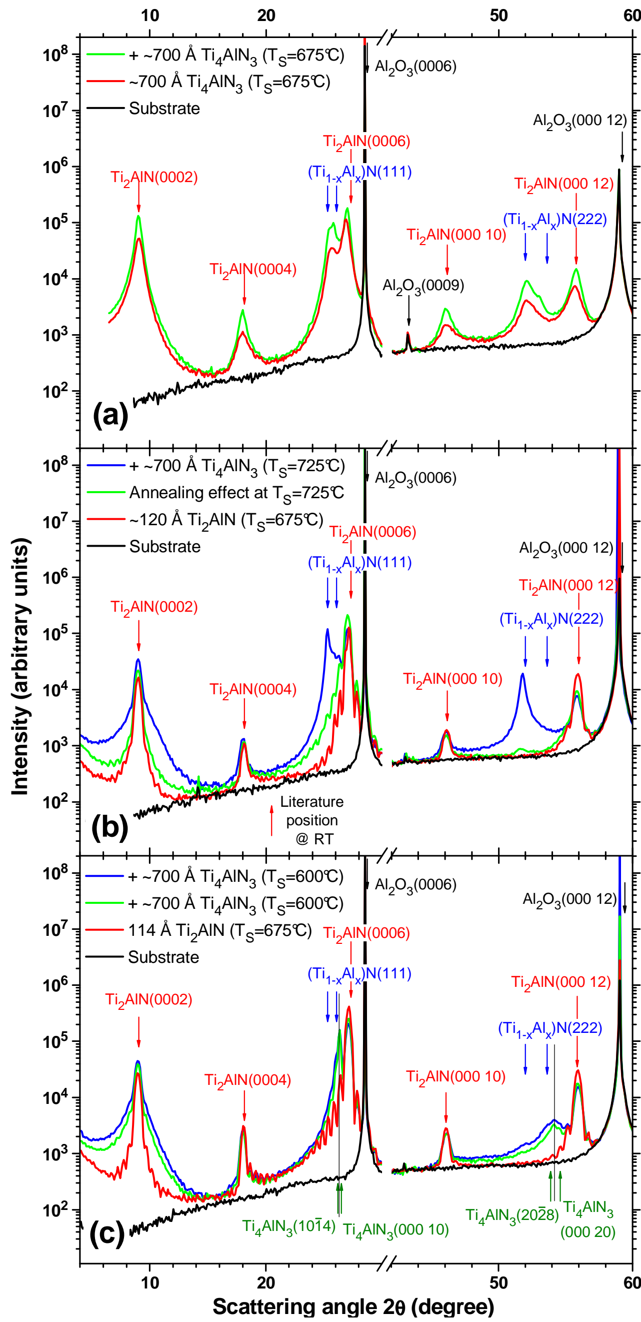

Fig. 1: *In-situ* XRD of nominal Ti_4AlN_3 deposition at different temperatures

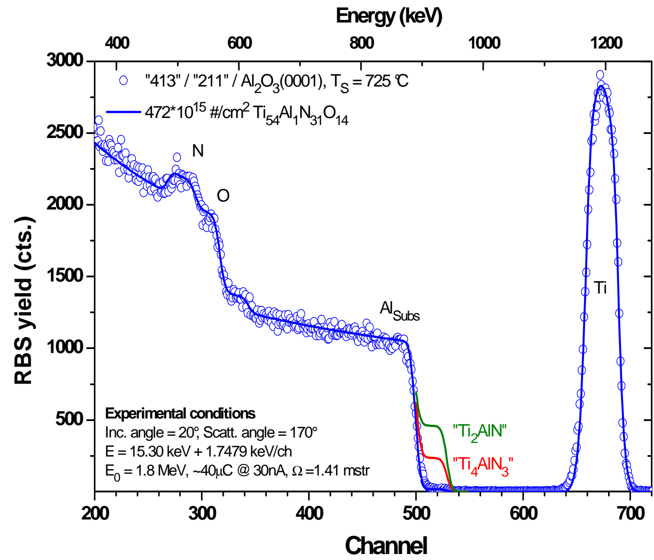

Fig. 2: *Ex-situ* RBS of nominal Ti_4AlN_3 deposited at 725°C, showing Al loss

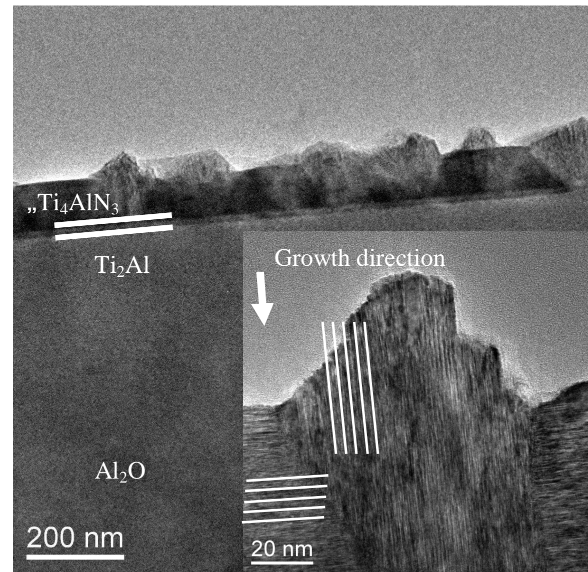

Fig. 3: *Ex-situ* HR-TEM micrograph of nominal Ti_4AlN_3 deposited at 600°C

with [2] should be overcome by higher temperature. However, when heating to 725°C the previously deposited Ti_2AlN shows first traces of decomposition, as depicted in Fig. 1(b). Accordingly, nominal Ti_4AlN_3 deposition induces nucleation of a very low-mosaicity TiN, with no Al incorporation at all, as proven by ex-situ RBS shown in Fig. 2. Hence, the Al seems to act as a surfactant for TiN growth before desorption from the growth surface and evaporation into the vacuum. When depositing the nominal Ti_4AlN_3 at 600°C, the stoichiometry as proven by RBS (not shown here) is 4Ti:Al:3N, and the XRD shows peaks that may be attributed to a tilted Ti_4AlN_3 growth, as observed also for diffusion-limited Ti_2AlN growth [1]. However, the HRTEM results depicted in Fig. 3 reveal hillocks and two competing alledged basal plane orientations with no evidence of a disctinct Ti_4AlN_3 phase, but a irregularly twinned structure stil that needs further investigations.

References

[1]: M. Beckers, N. Schell, *et al.:* Journal of Applied Physics **99**, 34902 (2006).

[2]: M. Beckers, N. Schell, *et al.:* Applied physics letters **89**, 074101 (2006).