ROBL-CRG	**Experiment title:** ***In-situ* XRD during magnetron deposition and subsequent annealing for nc metals and two-component alloys**	**Experiment number:** **20_02_620**
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Report:

We studied the **growth of** magnetron-sputtered **$Ti_{1-x}Al_xN$** thin films on amorphous substrates. In expansion of previous results concerning the influence of deposition rate on texture, here the Al concentration x was tuned from 0 to 0.73 while keeping all other parameters (especially the deposition rate) constant. For **$x < 0.1$** the **texture is not affected** by Al incorporation. For **$0.15 < x < 0.48$** a complete **reversal of preferred orientation from (002) to (111)** can be induced. Increasing x towards the AlN segregation threshold at **$x = 0.60$** leads to extremely hard **nano-composite TiAlN/AlN**, and pushing x further to **0.73** leads to stressed **AlN** with an a-axis off-plane **(1000) preferred orientation.**

EXPERIMENTAL

All samples were deposited in the ROBL growth chamber [1]. Si(100) wafers with a 1400 Å amorphous oxide capping layer of size 15 x 15 mm have been used as substrates. By applying a liquid notrogen trap, the base pressure was reduced to appr. 1×10^{-4} Pa. A constant working pressure of 0.35 Pa was achieved by a sputter gas inlet of 2.82 sccm in the ***ratio** $Ar/N_2 = 2/1$*. The summed DC power of the Ti and Al targets (99.999 % purity) was kept constant at 80 W during all depositions, resulting in a growth rate of ~0.38 ± 0.02 Å/s. The ***substrate temperature was kept at 300°C***. A substrate ***bias voltage of -30 V*** was applied.

Three different scattering techniques have been used to characterize the growth process. First, specular reflectivity (XRR) for growth rate calculation. Second and third, large angle off-plane scattering in Bragg-Brentano geometry (XRD) and Grazing Incidence grazing exit large angle in-plane X-ray Scattering (GIXS). The fitted integrated peak intensities reveal information about texture and crystallinity, and the exact positions of the Bragg peaks yield information about lattice constants, off-plane and in-plane, repectively. The energy of the incident x-rays was monochromatized to 12.917 keV ($\lambda = 0.961$ Å).

	Power Ti (W)	Power Al (W)	Stoichiometry
G3_05	80	0	TiN
G4_01	67	13	$Ti_{0.77}Al_{0.23}N$
G3_03	48	32	$Ti_{0.43}Al_{0.57}N$
G4_03	46	34	$Ti_{0.37}Al_{0.63}N$
G3_06	44	36	$Ti_{0.33}Al_{0.67}N$
G3_04	38	42	$Ti_{0.27}Al_{0.73}N$

Deposition parameters for the various samples investigated.

RESULTS

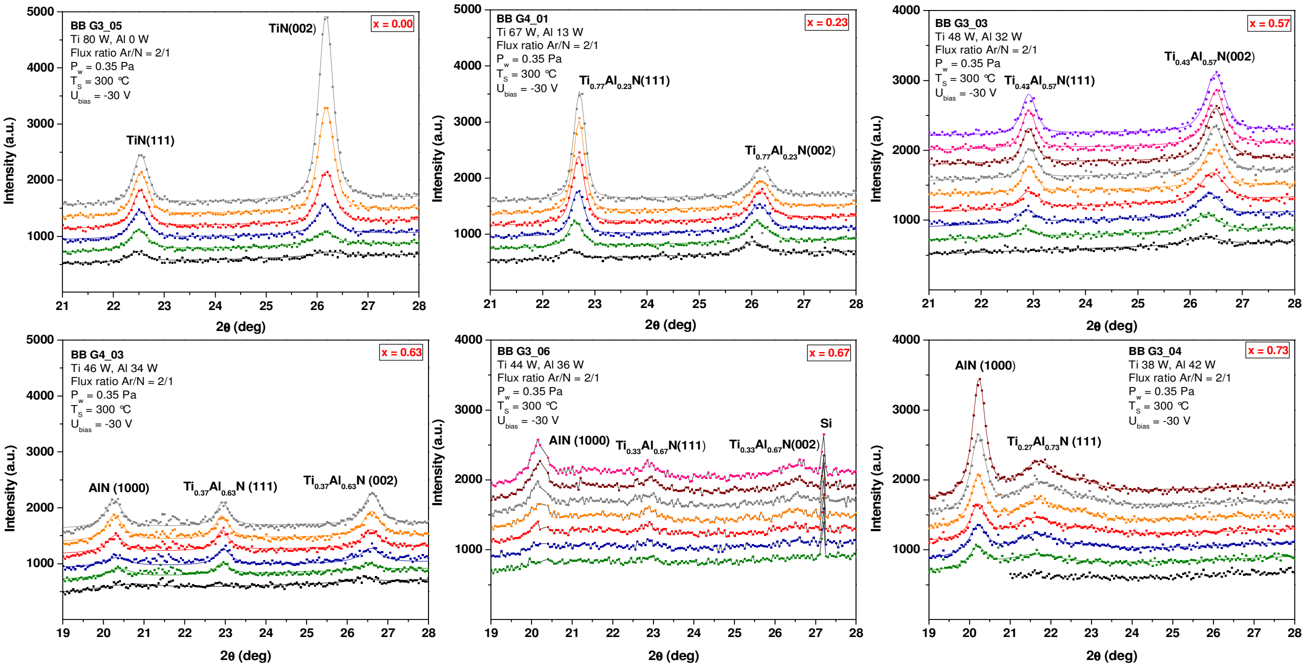

Fig. 1: The dotted curves show the observed Bragg-Brentano intensities with increasing sample thickness (final thickness around 200–300 nm) for various Al concentration x. The superposed straight lines show the fits obtained using a Pseudo-Voigt function for each single peak. The GIXS data show corresponding behaviour.

A deposition at a growth rate of 0.38 Å/s results in a (002) dominated preferred off-plane orientation even for higher thicknesses. Increasing x up to ~0.10 does not change this behaviour (Fig. 1, *top left*), which has been addressed to the high ion/neutral flux ratio to the substrate [2].

Contrary to expectatins, for 0.1 < x < 0.48 the samples show the typical cross-over behaviour from rather (002) oriented nucleation to a (111) preferred orientation at higher thicknesses (Fig. 1, *top middle*). This change of texture is attributed to the higher adatom mobility of Al (compared to Ti) giving rise to a higher concentration of Al in (111) grains, as can be seen from calculated lattice constants.

For x values near the segregation threshold of x ~ 0.6 this higher Al concentration leads to “disturbing” AlN precipitation mainly on (111) grains. Therefore, the (111) preferred orientation is reversed again to (002) (Fig. 1, *top right and bottom left*). For higher x values (yet still close to the segregation threshold), the crystal size dramatically decreases (Fig. 1, *bottom middle*). Due to the nanocrystalline structure of the $Ti_{1-x}Al_xN$ grains, each separated by a thin amorphous AlN matrix, increased hardnesses up to 35 GPa have been found.

For x values reasonably above the segregation threshold, the hexagonal wurtzite $Al_{1-y}T_{1-.y}N$ phase prevails. In contrast to pure AlN films which tend to grow with (0002) off-plane texture, here (1000) off-plane texture has been observed (Fig. 1, *bottom right*). This has been reported to be the energetically favoured orientation for highly stressed films [3]. Since the hexagonal $Al_{1-y}T_yN$ grains are still sorrounded by kind of “misfitting” fcc $Ti_{1-x}Al_xN$ grains we assume high stresses to be the origin of the observed (1000) orientation.

[1] W. Matz, N. Schell, W. Neumann, J. Bøttiger, and J. Chevallier, Rev. Sci. Instrum. **72** (2001) 3344
[2] M. Beckers, N. Schell, R.M.S. Martins, A. Mücklich, and W. Möller, *submitted* for publication
[3] M.M.M. Bilek, D.R. McKenzie, and W. Moeller, Surf. Coat. Technol. **186** (2004) 21