ROBL-CRG	**Experiment title:** ***In-situ*** **x-ray diffraction during sputter deposition of Ti$_{1-x}$Al$_x$N – Part III: MAX Phases**	**Experiment number**: **20_02_608**
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Report:

The heteroepitaxial growth of ***MAX phase*** ***Ti$_2$AlN*** ($M_{n+1}AX_n$ with M = Ti, A = Al, X = N and n = 1) ***on*** single crystal substrates ***MgO(001) and MgO(111)***, deposited by reactive magnetron co-sputtering from Ti and Al targets in an Ar/N$_2$ atmosphere at a temperature of ***690 °C***, has been studied *in situ*. Using real-time specular x-ray reflectivity, ***layer-by-layer growth*** first of an approximately 10 nm thick epitaxial fcc Ti$_{0.63}$Al$_{0.37}$N seed layer, then, after changing the deposition parameters, of the MAX phase itself was observed, with an increased surface-roughening on MgO(001) substrate. Using off-plane Bragg-Brentano x-ray scattering, the pseudomorphic growth of Ti$_2$AlN to the underlying seed-layer as well as MgO was established with lattice parameters of c = 1.3463 nm and a = 0.2976 nm. From *ex-situ* pole figures at a laboratory source the epitaxial relationship between film and substrate lattice was determined to be ***MgO {111}<110> // Ti$_2$AlN {1012}<1210>***, regardless of choice of substrate orientation during deposition. They furthermore reveal “pseudo-twinning” of the Ti$_2$AlN thin films along MgO<110>, leading to a threefold grain orientation as also seen in cross-sectional transmission electron microscopy.

EXPERIMENTAL

A constant bias voltage of -30 V was applied for all depositions. The base pressure at the deposition temperature of 690 °C was ~8 x 10^{-5} Pa. For the fcc Ti$_{1-x}$Al$_x$N seed layer an Ar/N$_2$ flux of 13.8/6.9 sccm was chosen leading to a working pressure of 0.35 Pa. The Ti and Al magnetron powers were 60 W and 20 W, respectively, leading to a composition of Ti$_{0.63}$Al$_{0.37}$N as near as possible to the nominal corresponding MAX ratio. In order to achieve stable growth conditions for the Ti$_2$AlN MAX phase layer the deposition pressure was increased to 0.8 Pa at an Ar/N$_2$ flux of 39.7/2.4 sccm. The Ti and Al magnetron powers were 80 W and 26 W, respectively, leading to the Ti/Al ratio of 2/1 as required and calculated from preceding work.

The energy of the incident x-rays was monochromatized to 12.917 keV (λ = 0.961 Å).

Two different scattering geometries were employed: (1) low angle specular reflectivity either at a fixed incidence angle to determine the growth mode or scanned for the determination of the thickness; (2) large angle x-ray diffraction (XRD) in Bragg-Brentano geometry in order to determine the off-plane lattice parameter. (Pole figures were measured at a laboratory source with CuK$_\alpha$ radiation. The final film composition was derived from Rutherford back-scattering (RBS). Cross sectional transmission electron microscopy (TEM) measurements were carried out using a CM300 microscope at 300 keV.)

RESULTS

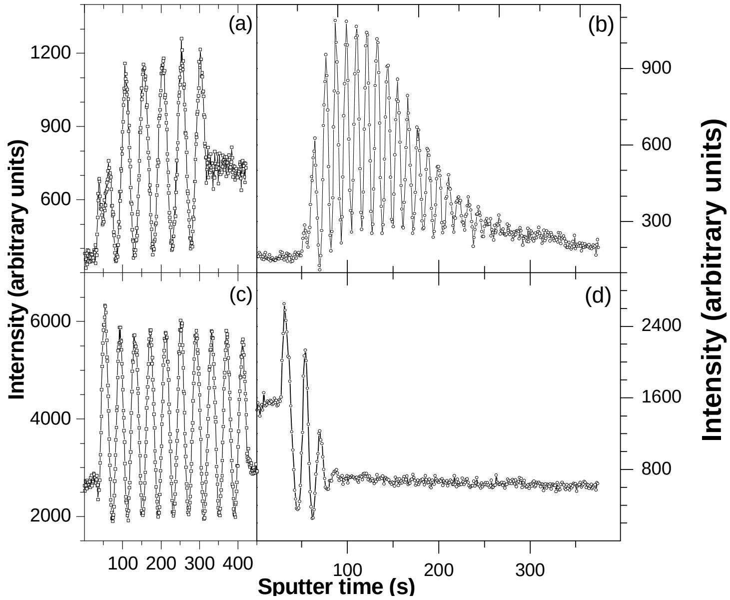


FIG. 1: Time dependent *in-situ* **XRR** of fcc $Ti_{0.63}Al_{0.37}N$ seed layers (a, c) and MAX phases Ti_2AlN (b, d) on the substrates MgO(111) (a, b) and MgO(001) (c, d) under fixed incidence & scattering angles. The oscilatory behaviour for the deposited seed layers as well as the films on top are a fingerprint of *layer-by-layer* growth. The decreasing amplitudes of the oscillations reveal increasing roughness or island growth which is more pronounced for the film on MgO(001).

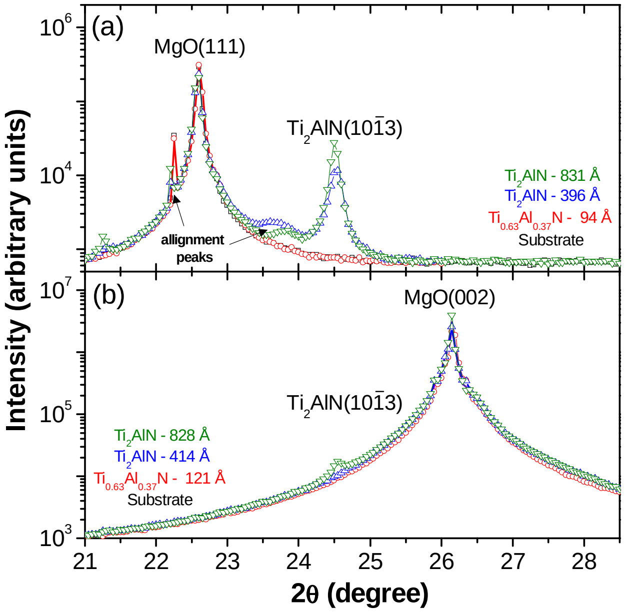


FIG. 2: *In-situ* **x-ray diffractograms** recorded in vertical Bragg-Brentano geometry on the substrates MgO(111) (a) and MgO(001) (b) after deposition of the seed layer and two MAX film layers of approximately 40 nm each.

FIG. 3: Cross sectional TEM micrograph of Ti_2AlN grown on MgO(111) along the [112] zone axis. (a) shows an overview over the film morphology consisting of large crystal regions, (b) a high resolution micrograph at the interface with the typical MAX phase layered structure of (000l) planes as confirmed from d-spacing calculation by FFT (c). →

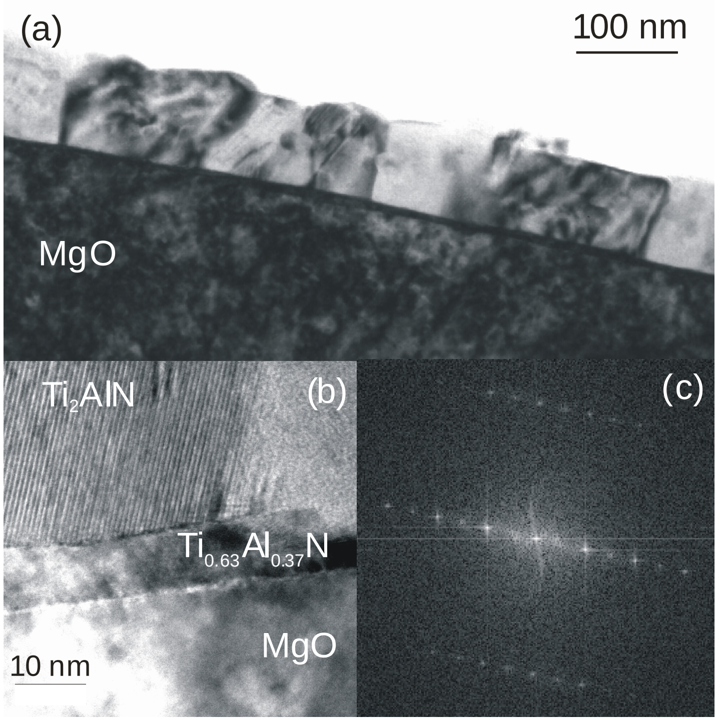
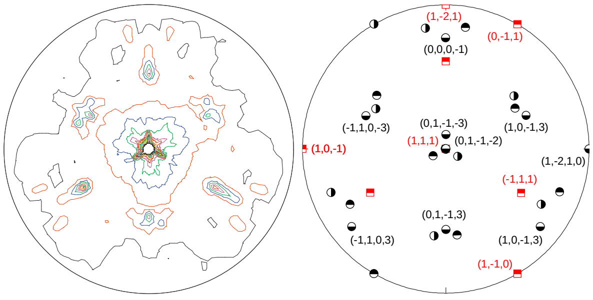


FIG. 4: Pole figure of MAX phase Ti_2AlN grown on MgO(111) substrate, measured in the Bragg peak $Ti_2AlN(10\bar{1}3)$ (left) with theoretical poles, including $Ti_2AlN\{10\bar{1}3\}$, $\{10\bar{1}2\}$, {0006} and MgO{111}, {110}, $(1\bar{2}1)$, calculated from a stereographic projection (right).



Beckers, M., Schell, N. Martins, R., Mücklich, A., and Möller, W., *The growth and microstructure of epitaxial MAX phase Ti_2AlN thin films characterized by in-situ x-ray diffraction*, submitted to JAP.