ROBL-CRG	**Experiment title:** *In-situ x-ray diffraction during sputter deposition of Ti-Al-N MAX-phase thin films*	**Experiment number**: **20_02_649**
Beamline: BM 20	**Date of experiment**: from: 05.04.2007 to: 10.04.2007	**Date of report**: 13.03.2009
Shifts: 15	**Local contact(s)**: Carsten Baehtz	*Received at ROBL: 13.03.09*

Names and affiliations of applicants (* indicates experimentalists):

M. Beckers*, F. Eriksson*, Linköping University, Sweden
C. Baehtz, Forschungszentrum Rossendorf, Germany & ROBL-CRG, France

Report

AIM:

The $M_{n+1}AX_n$ phases (n=1, 2 or 3, MAX) are a class of ternary nanolaminates, consisting of a transition metal M, an A-group element A and either nitrogen and/or carbon as X. They are subject of scientific interest due to their unusual combination of both metallic and high-performance ceramic properties [1]. Over the last years MAX phases have also been investigated in thin film form, and their synthesis by DC magnetron sputtering has been demonstrated for several carbide systems. For the nitrides, however, to date only the Ti_2AlN phase was synthesized, e.g. using reactive sputtering from either a compound 2Ti:Al target [2] or elemental Ti and Al targets [3,4]. Basal-plane oriented $Ti_2AlN(0001)$ films are usually achieved by epitaxial deposition onto lattice-matched MgO(111) or $Al_2O_3(0001)$, with a required deposition temperature of at least 675 °C [4]. It was previously demonstrated that this temperature to achieve basal-plane oriented epitaxial $Ti_2AlN(0001)$ films can be lowered down to 500 °C by making use of solid-state-reaction between already c-axis oriented AlN(0001)/Ti(0001) multilayer templates that were deposited at 200 °C and later on annealed [5]. Since the material properties of Ti_2AlN are highly anisotropic, and single-crystal substrates pose a high cost factor, the aim of the current experiment is to investigate the possibility of basal-plane oriented $Ti_2AlN(0001)$ formation by solid-state-reaction from self-organized epitaxial Ti/AlN layers deposited onto amorphous SiO_2.

EXPERIMENTAL:

8 samples were deposited onto Si(001) with a 1 µm thick amorphous SiO_2 capping layer, using reactive and non-reactive magnetron sputtering from Ti and Al targets at temperatures between 200 and 375 °C. The Ti metal layers were deposited at a target power of 40 W and with an Ar flux of 3.4 sccm at a working pressure of 0.5 Pa, leading to a deposition rate of 0.59 Å/s. The deposition parameters for the AlN layers were a target power 27 W, at Ar/N_2 fluxes of 2.16/0.66 sccm and a working pressure of 0.35 Pa, leading to a deposition rate of 0.25 Å/s. After each sequential deposition step, the films were characterized by specular x-ray reflectivity (XRR) for thickness and roughness, symmetric x-ray diffraction (XRD) for phase determination and lattice parameters, as well as rocking curves and pole figures to check for eventual preferred out-of-plane orientation and texture. During each deposition, the time-resolved specular reflectivity was measured at fixed angles of $\theta/2\theta$=1.4°/2.8°, to monitor each layer's growth mode. Subsequent to deposition, some layers were annealed up to 600°C to check for Ti_2AlN formation. The incident x rays were monochromatized to λ=1.053 Å.

RESULTS

Fig. 1 shows the *in situ* data obtained for a AlN/Ti stack deposited at a substrate temperature of 275 °C.
The XRD data in Fig. 1(a) show that a sequential deposition of Ti and AlN onto SiO_2 at T_S=275 °C

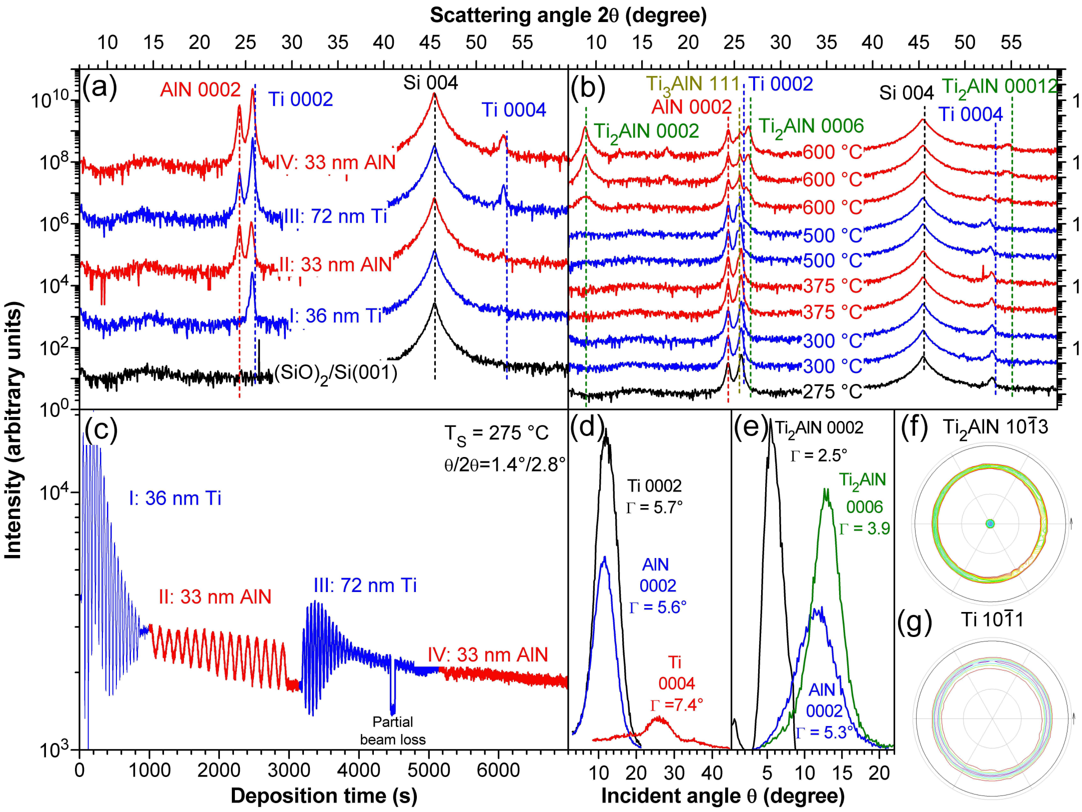

Fig. 1: *In situ* results of an AlN/Ti stack: (a) sequential XRD during deposition, (b) XRD during annealing, (c) time-resolved XRR for each deposition step (d,e) rocking curves (f,g,) pole figures for as-deposited and annealed films.

(T_S/T_M=0.28) yields a smooth Ti nucleation layer with a preferred low surface energy (0001) out-of-plane orientation. This basal plane orientation is maintained for subsequent AlN and Ti layers, with a final 0002 peak rocking curve full width at half maximum (FWHM) of ~5.7° as shown in Fig. 1(d). The substantial rocking cuve broadening for the Ti 0004 peak points towards mosaicity rather than a limited in-plane coherence length as reason for the rather large FWHM. A Ti deposition at 200°C leads to a rough non-textured Ti nucleation layer due to insufficient adatom mobility (T_S/T_M=0.24) with competitive growth, despite the ion bombardment from the unbalanced magnetron. At a deposition temperature of 350°C (T_S/T_M = 0.32), Ti-SiO_2 interfacial reactions are induced, as demonstrated by *ex situ* Rutherford backscattering spectroscopy (RBS), which result in a comparably non-textured Ti nucleation layer, and hence a non-textured AlN/Ti stack. The time-resolved XRR data in Fig. 1(c) display decaying and increasing oscillation amplitudes for Ti and AlN deposition, respectively. In contrast to previous experiments [5], the Ti deposition rate was doubled in the present case, leading to a more pronounced roughening and hence faster amplitude decay during Ti deposition. During annealing, shown in Fig. 1(b), at 375°C the first stage of AlN/Ti interfacial reaction seems to be AlN decomposition and nitrogen diffusion into Ti to form a TiN_x compound, as can be deduced from the shifting Ti peaks. Annealing to 500°C yields diffusion of both released Al and N into the Ti, with consecutive phase transformation into Ti_3AlN with lattice-matching 111 orientation. When increasing the temperature to 600°C, already after the ramping period of approx. 5 minutes Ti_2AlN formation is evident by a Ti_2AlN 0002 peak. Accordingly, the Ti 0002 intensity vanishes after a holding time of 60 minutes. The AlN 0002 peak is still discernible due to AlN residuals, whereas all Ti has been transformed into Ti_2AlN, exept a thin Ti-SiO_2 interfacial layer as proven by *ex situ* RBS. Both, the Ti_2AlN and the residual AlN exhibit a narrow out-of-plane orientation distribution, with a rocking curve FWHM of 2.5° and 5.3°, respectively [Fig(1(e)]. Pole figures on Ti{10$\bar{1}$1} and Ti_2AlN{10$\bar{1}$3}, displayed in Fig. 1 (f,g), show, however, that only the out-of-plane Ti and Ti_2AlN orientation has a preferred and narrow distribution, while the in-plane distribution is fully random, as can be expected from the self organized pseudo-epitaxial growth of the Ti nucleation layer.

References

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