ROBL-CRG	**Experiment title:** ***In-situ* x-ray diffraction during sputter deposition of Ti-Al-N MAX-phase thin films**	**Experiment number:** **20_02_640**
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Report

AIM:

The ternary nitrides and carbides advertised under the name ***$M_{n+1}AX_n$ phases*** – with M being a transition metal, A an A group element and X nitrogen or carbon – show a unique combination of metallic and ceramic properties including good electrical conductivity, high temperature stability and machinability [1]. Due to these properties $M_{n+1}AX_n$ phase bulk samples as well as thin films have been extensively studied during the past years. Carbides have been deposited by DC sputtering from compound targets, from individual M and A targets with co-evaporated $C_{60,}$ and from three elemental targets at temperatures around 900°C. For the nitrides the only published thin film results so far concern Ti_2AlN, deposited ***by reactive sputtering*** in an Ar/N_2 gas mixture from a compound 2Ti:Al target at 830°C or ***from Ti and Al elemental targets at 670°C*** [2]. An alternative route of $M_{n+1}AX_n$ phase thin film growth could be by self-organized topotaxial solid-state-reaction between MX and A, alternatively between AX and M. Hence, during this experiment we investigated the possible ***formation of Ti_2AlN during annealing of TiN/Al and AlN/Ti multilayer stacks.***

EXPERIMENTAL:

A total of ***nine multilayer stacks*** were deposited onto single crystal MgO(111) and Al_2O_3(0001) substrates by reactive and non-reactive magnetron ***sputtering from Ti and Al targets*** in an Ar/N_2 atmosphere at substrate temperatures between 200 and 500°C. The deposition parameters for the Ti and Al metal layers were set to target powers of Ti and Al = 20 W with an Ar flux of 3.4 sccm and a working pressure of 0.5 Pa, leading to Ti and Al deposition rates of 0.21 and 0.32 Å/s, respectively. The deposition parameters for the TiN and AlN layers were set to target powers of Ti = 80W and Al = 27 W with an Ar/N_2 flux ratio of 2.16/0.66 sccm and a working pressure of 0.35 Pa, leading to Ti and Al deposition rates of 0.21 and 0.32 Å/s, respectively. 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, or angular-resolved for thickness and roughness determination. (2) Large angle x-ray diffraction (XRD) to determine phase formation and off-plane lattice parameters. Subsequent to deposition, some layers were ***annealed up to 650°C substrate temperature*** to check for ***possible Ti_2AlN formation***. The energy of the incident x-rays was monochromatized to λ = 1.053 Å, i.e. 11774 ± 20 eV as estimated from single-crystal substrate peak shifts.

RESULTS

Fig. 1 shows the *in-situ* data obtained for a 26 nm AlN / 10 nm TiN / 11 nm AlN / 20 nm Ti / 11 nm AlN stack on Al_2O_3 deposited at 200°C substrate temperature and subsequently annealed for about 2 h at 500°C. The XRD data in Fig. 1(a) reveal basal-plane heteroepitaxial growth of AlN(0001) and Ti(0001) onto

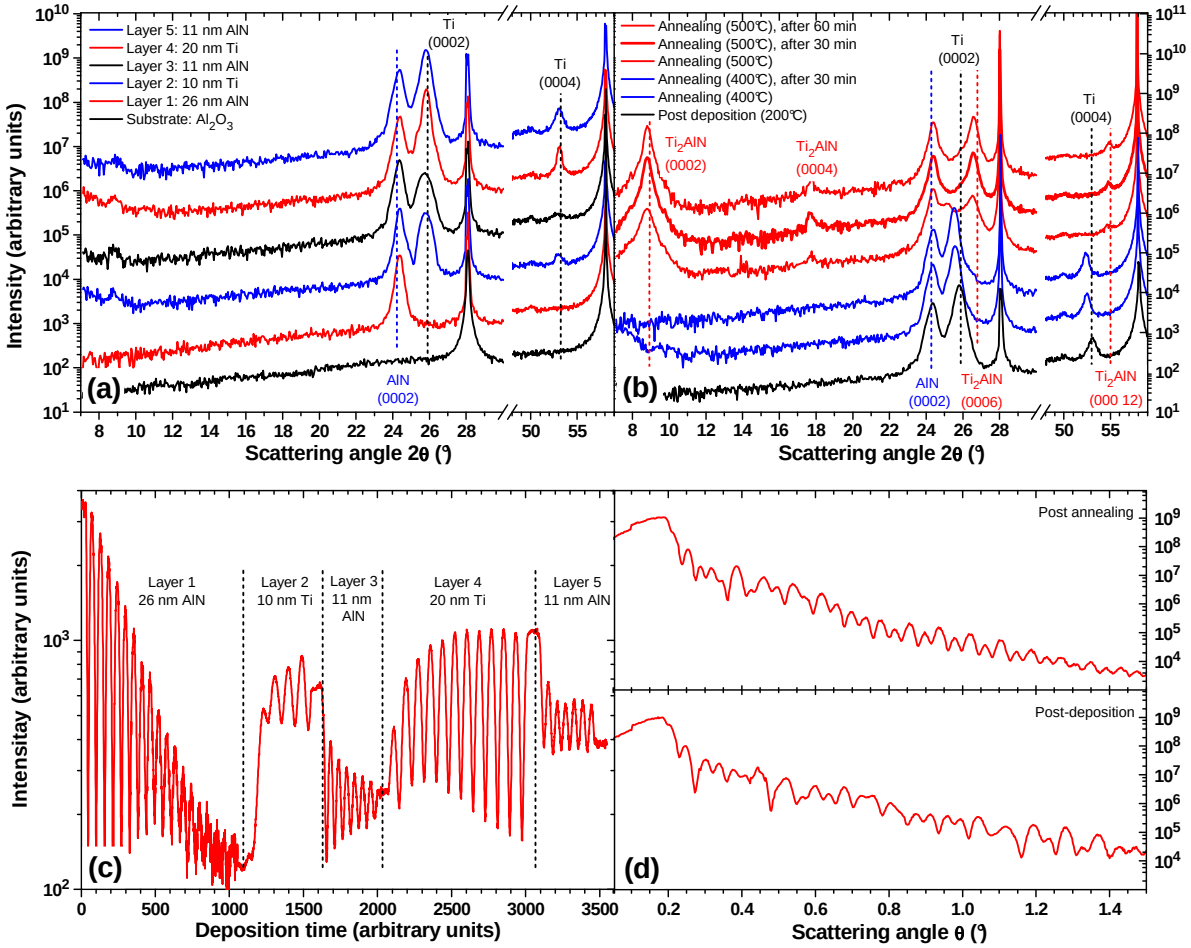

Fig. 1: *In-situ* results of a AlN/Ti multilayer stack. (a) sequential XRD results during deposition at 200°C, (b) XRD data during annealing up to 500°C, (c) time-resolved reflecivity of each deposition step (d) angular-resolved XRR data of the sample in the as-deposited and post-annealed state.

Al_2O_3(0001). The AlN(0002) signal shows lower intensity when compared to the yet thinner Ti layer, which can be understood by the growth oscillations in Fig. 1(c). Since the adatom mobility on AlN at 200°C is relatively low, the growth surface roughens and correspondingly the intensity oscillations for each AlN deposition show rapid exponential decay. Ti on the contrary has a higher electron density than AlN plus an increased adatom mobility, hence already during initial growth stages the reflectivity signal is increased, amplified by a significant surface smoothing, as can be deduced from the exponential growth of the intensity oscillations. In accordance to the smoother growth front a lower mosaicity of the Ti can be expected, and hence also an increased XRD signal. The oscillations were not recorded at the anti-bragg ½*Q_d value, but could easily be fitted with a layer-by-layer growth model when taking the Q_{meas}/Q_d value into account, where Q_d denores the Q value corresponding to the c-axis value of Ti and AlN, respectively. During annealing, shown in Fig. 1(b), at 400°C the first stage of interfacial reaction seems to be AlN decomposition and nitrogen diffusion into Ti to form a TiN_x compond as can be deduced from the shifting Ti peak, pointing towards lattice expansion. No further reaction takes place after holding 400°C for another 30 minutes. When increasing the temperature to 500°C, however, 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 diminishes beyond the detection limit after a holding time of 60 minutes. The interfacial reaction can also be deduced from the XRR data shown in Fig. 1(c), where the single layer beating after annealing has vanished. The basal plane-oriented Ti_2AlN formation occuring at 500°C reported is 170°C lower than temperatures reported in [2] and may open up low temperature Ti_2AlN applications as well as $M_{n+1}AX_n$ phase formation by other AlN / M diffusion couples.
No Ti_2AlN formation at temperature up to 650°C has been found for TiN/Al couples (data not shown here).

REFERENCES

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