ROBL-CRG	**Experiment title:** ***In-situ x-ray scattering during formation of MAX phase (V,Cr)2AlN thin films by reactive co-sputtring and solid-state reaction***	**Experiment number**: **HS 3443**
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Report

AIM:

The family of ternary nitrides and carbides grouped 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 – exhibit 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 material as well as thin films have been extensively studied during the past years. Various carbide thin film $M_{n+1}AX_n$ phases have been deposited by DC magnetron sputtering. For the nitrides, only Ti_2AlN has been synthesized as thin film, either deposited **by reactive DC magnetron sputtering from compound or elemental Ti and Al elemental targets** [2] or by **self-organized topotaxial solid-state reaction between AlN(0001)/Ti(0001) stacks** [3]. During this experiment, the aim is a transfer from the Ti-Al-N system to the Cr-Al-N and V-Al-N systems, hence the **synthesis of Cr_2AlN and V_2AlN** either by reactive sputtering or by solid-strate-reaction between stacks of (Cr,V)N/Al or AlN/(Cr,V).

EXPERIMENTAL:

A total of **12 samples** was deposited onto Al_2O_3(0001) substrates by reactive and non-reactive magnetron sputtering from Cr, V and Al targets at temperatures between 200 and 700°C. The deposition parameters for the V, Cr and Al metal layers were target powers of 40 W, 20 W and 20 W, respectively, with an Ar flow of 3.4 sccm at a working pressure of 0.5 Pa, leading to V, Cr and Al deposition rates of 0.34, 0.53 and 0.42 Å/s, respectively. The deposition parameters for the VN, CrN and AlN layers were target powers of 60 W, 70 W and 27 W, respectively with an Ar/N_2 flow ratio of 2.16/0.66 sccm and a working pressure of 0.35 Pa, leading to VN, CrN and AlN deposition rates of 0.8, 1.2 and 0.21 Å/s, respectively. Each sequential deposition step was characterized by specular x-ray reflectivity (XRR) for thickness and roughness and symmetric x-ray diffraction (XRD) for phase determination and off-plane lattice parameters. During each deposition, the time-resolved specular reflectivity was measured at a fixed incident angle of 1°, to monitor each layer's growth mode. Subsequent to deposition, some layers were annealed up to 750 °C substrate temperature to **check for possible $(Cr,V)_2AlN$ formation**. The x-rays were monochromatized to a wavelength of λ=1.053 Å.

RESULTS

Fig. 1 shows the *in situ* data obtained for two series of AlN/Cr and CrN/Al stacks that were deposited onto Al_2O_3(0001) at 200°C substrate temperature and subsequently annealed to 750 °C.

The XRD data in Fig. 1(b) for a sequential deposition of ~20 nm AlN and ~10 nm Cr reveal heteroepitaxial growth of AlN(0001) and Cr(110) with low Cr peak intensity due to high mosaicity induced by the high 7% lattice mismatch. Accordingly, both peak signals do not increase significantly during subsequent depositions.

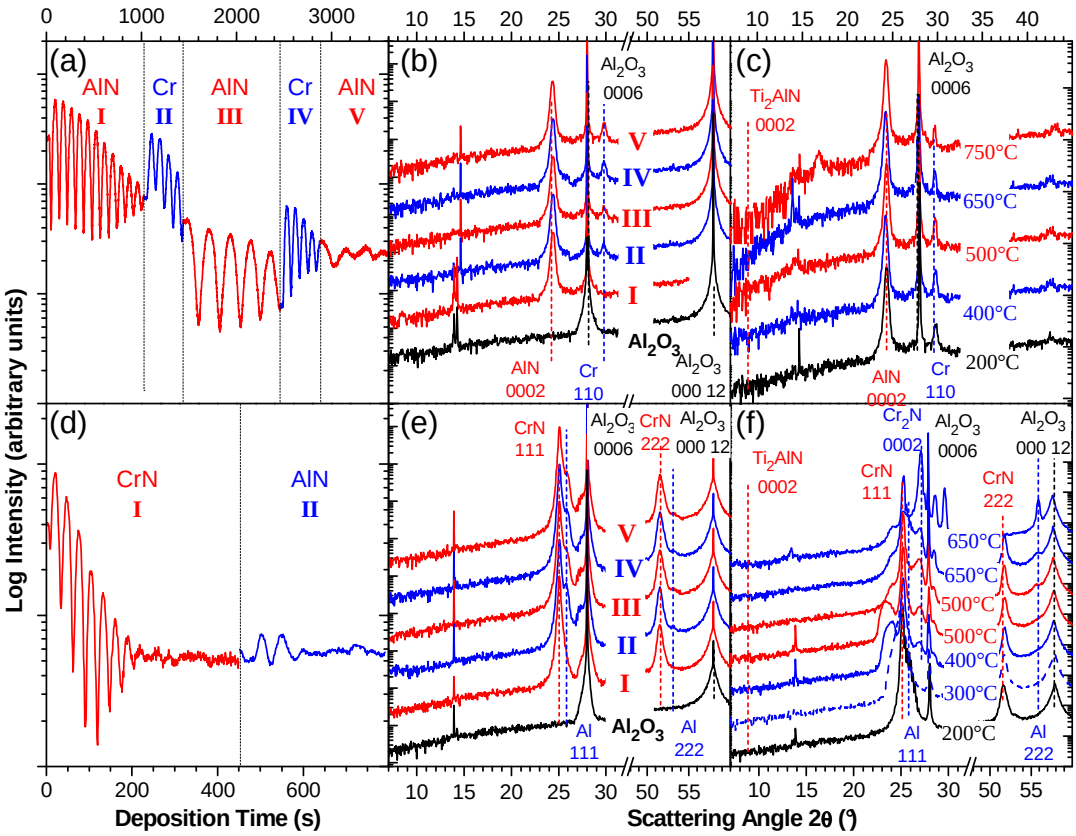

Fig. 1: *In situ* results of AlN/Cr and CrN/Al stacks: (a,d) time-resolved XRR during each deposition step (b,e) sequential XRD during deposition at 200°C, (d,f) XRD data during annealing

The lattice mismatch is also reflected in the time-resolved XRR data, where the growth oscillation amplitude decays with each deposition. During annealing, shown in Fig. 1(c), the system remains stable up to 750 °C, with sharp interfaces as detected by XRR and *ex situ* Rutherford backscattering spectroscopy (RBS). This is in contrast to AlN-Ti, where at 400 °C AlN decomposition is induced, with subsequent Ti_2AlN formation at 500 °C. This can be explained by the higher affinity of Ti towards N in comparision to Cr. Based on this low affinity of Cr towards N, also CrN/Al stacks were investigated. The XRD data in Fig. 1(e) for a sequential deposition of ~30 nm CrN and ~15 nm Al reveal cube-on-cube heteroepitaxial growth of CrN(111) and Al(111). The absence of the Al 222 peak points towards rather low crystalline quality, which can also be extracted from the time-resolved XRR data in Fig. 1(d). Growth on the high energy CrN(111) surface leads to quick roughening due to the low adatom mobility at the given substrate temperature. The roughening persists for Al growth, despite the higher mobility on the Al(111) surface. During annealing [Fig. 1(f)], already a temperature of 400 °C is sufficient to induce CrN decomposition and layer-by-layer topotaxial $Cr_2N(0001)$ formation, as is discernible by the appearing and shifting Laue fringes around the CrN(111) peak for a holding time at 400 °C and higher annealing temperatures. An annealing temperature of 650 °C is sufficient for an almost complete transformation of the intial CrN, as can be deduced from the lack of the CrN 222 peak and the appearance of the metallic Cr 110 signal. Obviously the initial CrN/Al stack loses a substantial amount of N into the vacuum, which was confirmed by *ex situ* RBS. These also revealed a substiantial loss of Al in comparison to the as-deposited state. In conclusion, neither annealing of CrN/Al and AlN/Cr stacks nor a direct deposition of 2CrAlN at higher temperatures (data not shown) yield Cr_2AlN formation. The same applies to VN/Al and AlN/V stacks, as well as to 2VAlN depositions (data not shown). Based on the the conducted experiments **we conclude that – in contrast to the Ti-Al-N system – no stable M_2AX phase exists in the ternary Cr-Al-N and V-Al-N systems.**

REFERENCES

[1]: M. W. Barsoum: Progr. Sol. State Chem. **28**, 201 (2000).
[2]: M. Beckers, *et al.:* Appl. Phys. Lett. **89**, 074101 (2006).
[3]: C. Höglund,. M. Beckers, *et al.:* Appl. Phys. Lett. **90**, 174106 (2007).