	Experiment title: Diffusion kinetics of the decomposition process in TiN/AlN multilayer thin films	Experiment number: SI-2551
Beamline: BM20	**Date of experiment**: from: 16/Nov/2012 to: 20/Nov/2012	**Date of report**: 29/Jan/2013
Shifts: 12	**Local contact(s)**: Dr. Carsten Bähtz	*Received at ESRF:*

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Preliminary Report:

The synchrotron experiments performed recently at BM20 are a substantial part of the microstructure study that is required to describe quantitatively the interplay between the lattice strains at the TiN/AlN interfaces and the intermixing of TiN and AlN in metastable fcc-$Ti_{1-x}Al_xN$ at high temperatures. The explanation of this interplay is a precondition for understanding the thermal stability and decomposition processes in metastable fcc-$Ti_{1-x}Al_xN$. As the elementary cell of fcc-TiN is larger than the elementary cell of fcc-AlN, a formation of lattice strain at the TiN/AlN interfaces is anticipated if fcc-TiN and fcc-AlN grow heteroepitaxially on each other. This lattice strain can be reduced via intermixing of thermodynamically immiscible phases TiN and AlN and via consequent formation of the metastable fcc-(Ti,Al)N. From the thermodynamic point of view, the formation and/or stabilization of the metastable phase would be facilitated by the reduction of the internal lattice strain. Within the experiment # SI-2551, periodic structures were deposited via magnetron sputtering from two independent targets (Ti and Al) in a reactive atmosphere containing nitrogen and argon, and in-situ investigated using a combination of X-ray reflectometry (XRR) and glancing-angle X-ray diffraction (GAXRD) at the high temperatures up to 950°C. The periodic structures consisted of repeated stacks of TiN/$Ti_{1-x}Al_xN$/AlN layers. The intended thickness of individual TiN and AlN layers was 5 nm. The intended thickness of the intermediate $Ti_{1-x}Al_xN$ layers was 3-4 nm. The growth rates needed for estimation of the sputter times were determined (as a function of the power on the Al and Ti cathodes) on an identical deposition apparatus located at the Helmholtz-Center Dresden Rossendorf (HZDR), s. Table 1.

power Ti target (W)	power Al target (W)	power ratio P_{Al}/P_{Total}	growth rate $Ti_{1-x}Al_xN$ (Å/s)	x_{Al} in $Ti_{1-x}Al_xN$
60	20	0.25	0.547	0.28
50	30	0.375	0.524	0.47
40	40	0.5	0.596	0.60
50	0	0	0.302	0
0	30	1	0.288	1

Tab. 1 Growth rates of TiN, AlN and $Ti_{1-x}Al_xN$, and the Al amount in $Ti_{1-x}Al_xN$ as functions of the target powers – data from the preliminary deposition experiments performed at HZDR.

The Al content in fcc-$Ti_{1-x}Al_xN$ was intended to be controlled via the power ratio P_{Al}/P_{Total}. The dependences of the normalized growth rate (growth rate/P_{Total}) and the Al concentration in $Ti_{1-x}Al_xN$ on P_{Al}/P_{Total} (Fig. 1) have shown that AlN is deposited faster than TiN (at the same power on the respective target). The XRR experiments performed at BM20 on the in-situ deposited periodic TiN/$Ti_{1-x}Al_xN$/AlN stacks revealed the thickness of the periodic motif, from which the mean growth rates were calculated (s. dashed lines in Fig. 1b). Unlike to the experiments at HZDR, the growth rates at BM20 decreased successively in the course of the sputtering processes (#2, #3, #4). This phenomenon, which is probably caused by the poisoning of the cathodes (mainly Al), did not allow the intended individual layer thicknesses to be adjusted with sufficient precision.

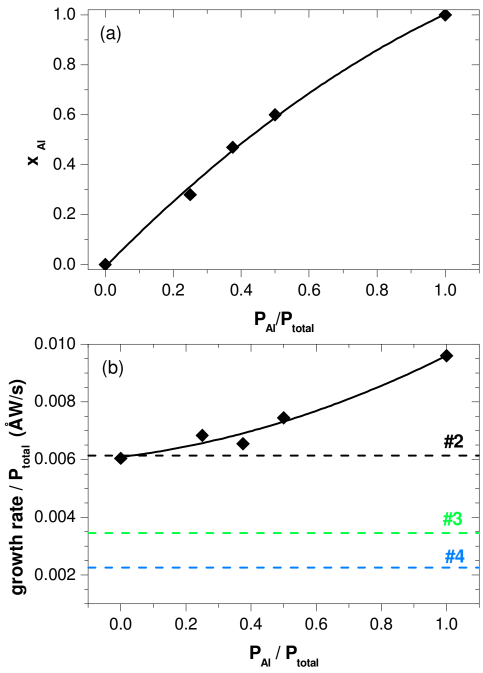

Fig. 1 *Al concentration (a) and growth rate (b) as functions of the sputter power on the Al cathode. Dots are for the samples from HZDR, dashed lines for the samples from BM20.*

Still, the in-situ high-temperature GAXRD experiments (Fig. 2) confirmed that the samples remain cubic even if they were annealed for 45 min at 950°C. According to the first results, no wurtzitic AlN (w-AlN) was formed. Still, this result must be confirmed by transmission electron microscopy on annealed samples. Furthermore, a shift of the diffraction lines 111 and 200 toward higher diffraction angles was observed in the GAXRD patterns of the annealed samples (Fig. 2). This shift indicates a decrease of the lattice parameter in the out-of-plane direction (the inclination of the diffraction vector from the sample surface perpendicular direction is below 14°), which is related either to a decrease of the stress-free lattice parameter or to a decrease of the (compressive) residual stress in $Ti_{1-x}Al_xN$.

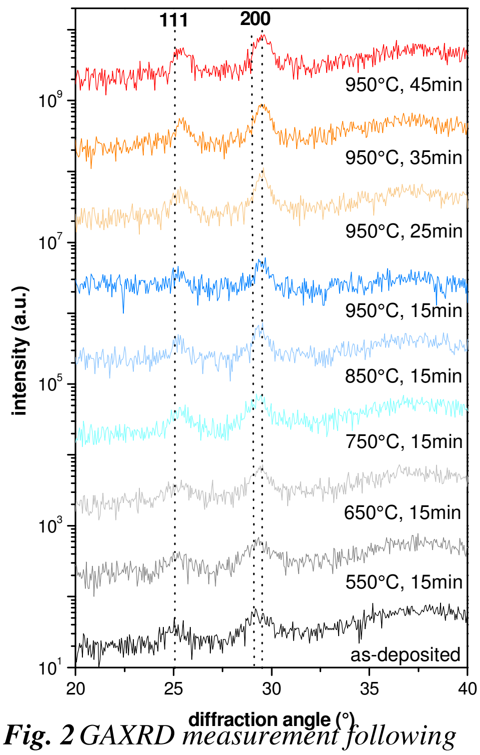

Fig. 2 *GAXRD measurement following annealing experiments of TiN/(Ti, Al)N/AlN multilayer coatings which were deposited at the target powers P_{Ti} = 65W and P_{Al} = 20W.*

Both phenomena would be facilitated by the intermixing of TiN and AlN within the TiN/(Ti,Al)N/AlN stack. It is worth noting that the decrease of the lattice parameter due to the intermixing of TiN and AlN overbalances even the expected increase of the lattice parameter due to the thermal expansion. The observed decrease of the lattice parameter also endorses the claim that no w-AlN was formed. The formation of w-AlN would be accompanied by the segregation of AlN from $Ti_{1-x}Al_xN$ and by an increase of the lattice parameter of $Ti_{1-x}Al_xN$. Another indicator of the intermixing of TiN and AlN is the observed change in the width of the diffraction lines 111 and 200, which get narrower with increasing annealing temperature. As the line broadening in the (Ti,Al)N films is a measure of the local concentration fluctuations [Ch. Wüstefeld, D. Rafaja, M. Dopita, M. Motylenko, C. Baehtz, C. Michotte, M. Kathrein, Surf. Coat. Technol. 206 (2011) 1727-1734], the decreasing line broadening can be interpreted as an equalization of the artificial concentration gradients produced during the deposition of the periodic TiN/(Ti,Al)N/AlN stacks through the intermixing of TiN and AlN. However, this stabilisation of the metastable $Ti_{1-x}Al_xN$ is possibly enabled by the small thicknesses of the TiN and AlN layers in the stacks achieved in this experiment. Therefore, additional in-situ experiments at BM20 are proposed, in which periodic stacks with wider individual layers should be deposited and investigated in-situ. One series should contain no w-AlN in the as deposited state. In another series, the w-AlN should grow. The presence or absence of w-AlN is in the stacks will be controlled by the Al concentration in $Ti_{1-x}Al_xN$.