ESRF	**Experiment title:** Stability of ternary and quaternary oxynitride coatings by in-situ annealing and XRD / HAXPES combination	**Experiment number**: HC 3515
Beamline: BM25B	**Date of experiment**: from: 27 jun 2018 to: 03 jul 2018	**Date of report**:
Shifts: 18	**Local contact(s)**: Juan Rubio Zuazo (email: rubio@esrf.fr)	*Received at ESRF:*

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Report:

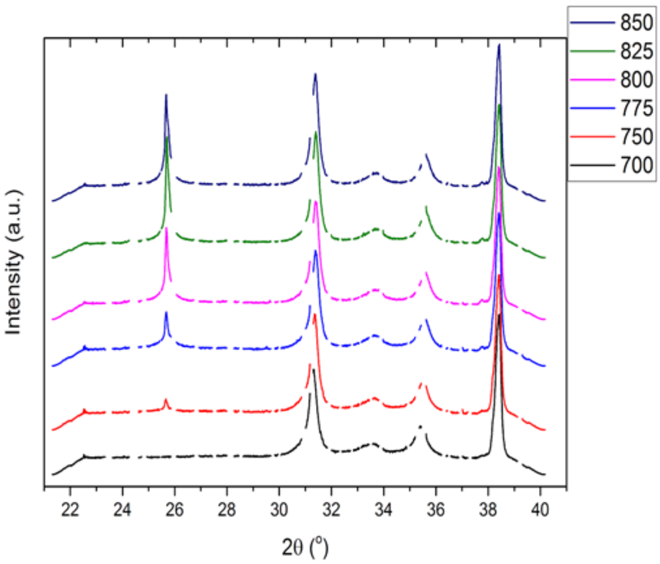
During the allocated beamtime of 18 shifts, annealing experiments were performed in the experiment chamber of BM25B on a total of four thin film samples. Samples were characterised *in-vacuoo* after each annealing step by simultaneous measurements of both grazing incidence X-ray diffraction (GIXRD) and hard X-ray photoelectron spectroscopy (HAXPES), using a photon energy of 8524 eV ($\lambda = 1.455$ Å). Annealing experiments were conducted from temperatures of 350 to 875°C. The use of hard X-rays allowed us to probe the bulk of the thin film samples, without the need for Ar^+ ion etching which is known to create artefacts on the studied samples.[1] Additionally some of the annealing experiments were followed by mass spectrometry (MS) to observe gaseous decomposition products.

During the beamtime, the decomposition of ternary Al-Ge-N thin films was primarily studied (two of four samples). These coatings contain a metastable solid solution phase based on wurzite AlN, w-$(Al_{1-x}Ge_x)N_y$, see previous work.[2] This metastable solid solution phase is expected to decompose by segregation of Ge, and the release of N_2:

$$\text{w-}(Al_{1-x}Ge_x)N_y \rightarrow \text{w-}Al_{1-x}N_{y-x} + x\text{Ge} + {}^{x}\!/_{2}N_2 \qquad \text{(equation 1)}$$

This decomposition has previously been demonstrated by ion beam bombardment, showing the formation of metallic Ge.[1] In the present experiments we have been able to follow the decomposition in more detail and *in-situ* by annealing and the combination of HAXPES and XRD.

Preliminary results are shown in Fig 1 to 3. The decomposition product (Ge) is observed by X-ray diffractograms (Fig 1) which show the growth of a crystalline Ge-phase (peak at 2θ~25.5°) as a result of annealing above 750°C. Also shown in Fig 1 are the corresponding HAXPES spectra of the Ge 2p core levels (Fig 2), showing a change in the chemical state of Ge, consistent with a partial decomposition of the wurzite $(Al_{1-x}Ge_x)N_y$ phase according to equation 1. The mass spectrometry data (see example in Fig 3) also confirms the decomposition process, showing the release of N_2 from the sample upon annealing.



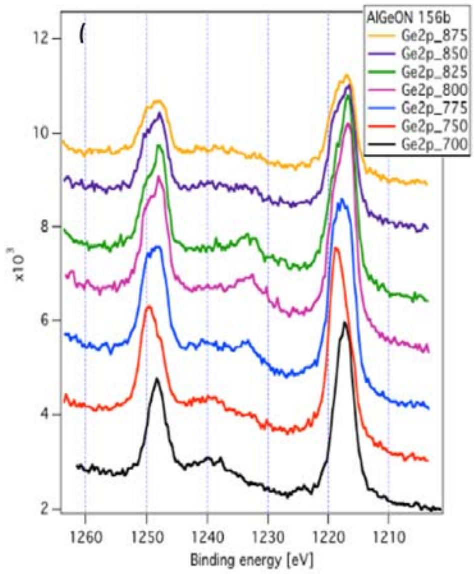


Figure 1 – X-ray diffractograms of AlGeN-sample after 10 min annealing at temperatures between 700 and 850°C.

Figure 2 – Ge 2p core levels of AlGeN-sample, observed with HAXPES after 10 min annealing at temperatures 700 and 875°C.

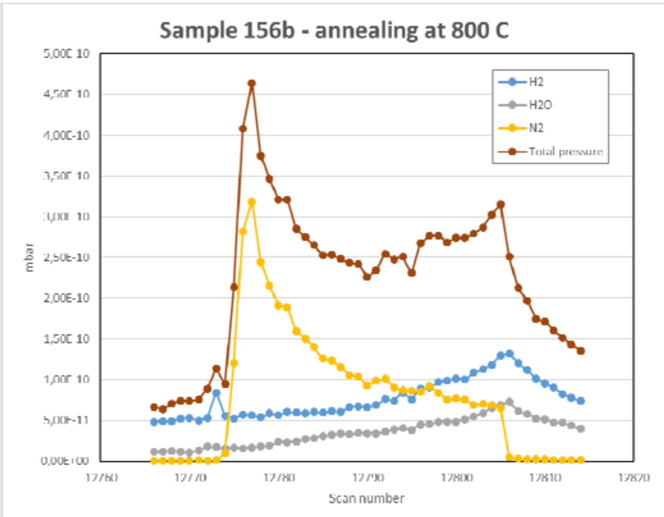


Figure 3 – Mass spectrometry data for N_2, H_2O and H_2 taken during annealing of AlGeN-sample at 800°C, showing the release of nitrogen gas in the annealing step (and outgassing of the sample holder slightly later in time.

These results are now being complemented by ex-situ techniques at Uppsala university in preparation of a scientific paper. Additional analysis include scanning and transmission electron microscopy (SEM and TEM), as well as ex-situ X-ray photoelectron spectroscopy (XPS) with high spatial resolution to differentiate between different areas of the same sample. A manuscript is presently under preparation, and we expect a paper based on the HC3515 experiments to be published within a year of the beamtime.

References:

[1] E. Lewin, M. Parlinska, J. Patscheider, *Nanocomposite Al-Ge-N thin films and their mechanical and optical properties*, **Journal of Materials Chemistry** 22, 16761-16773 (2012) [doi:10.1039/C2JM32815A]

[2] E. Lewin, J. Counsell, J. Patscheider, *Spectral artefacts post sputter-etching and how to cope with them – a case study of XPS on nitride-based coatings using monoatomic and cluster ion beams*, **Applied Surface Science**, 442, 487 (2018) [doi:10.1016/j.apsusc.2018.02.191]