HZDR HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF ROBL-CRG	**Experiment title:** Nanocomposite formation in the system Cr-Zr-O	**Experiment number:** 20-02-727
Beamline: BM 20	**Date of experiment:** from: 05.03.14 to: 11.03.14	**Date of report:** 24.03.15
Shifts: 18	**Local contact(s):** Carsten Baehtz	*Received at ROBL:*
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Report:

The crystallization of amorphous Cr-Zr-O layers was studied by *in situ* high-temperature glancing angle X-ray diffraction (HT-GAXRD), high-temperature small-angle X-ray scattering (HT-SAXS) and high-temperature grazing incidence X-ray scattering (HT-GISAXS). The layers were deposited by using the ion beam sputtering on thermally oxidized (001)-oriented Si wafers and had the chemical compositions $Cr_{1.83}Zr_{0.17}O_{3.56}$ (sample CrZrO-5), $Cr_{1.60}Zr_{0.40}O_{3.71}$ (sample CrZrO-10), and $Cr_{1.20}Zr_{0.80}O_{3.71}$ (sample CrZrO-15). The deposition was done at room temperature and resulted in amorphous Cr-Zr-O layers with a thickness of approx. 400 nm. The synchrotron experiments were carried out at ROBL BM 20 using a constant energy of E=11.5 keV. The *in situ* HT-GAXRD was performed at the incident angle of 0.7°. The HT-SAXS experiments included the recording of the X-ray reflectivity curves and selected omega scans. For the HT-GAXRD and HT-SAXS experiments, a 1D detector (Mythen) was used. The HT-GISAXS patterns were recorded by a 2D detector (Pilatus) for ten incident angles in the range of 0.1 to 1° ($\Delta = 0.1°$). The microstructure evolution of the coatings was studied in vacuum in the temperature range between 500°C and 1100°C. The annealing time at each temperature step was 60 min. After each annealing step, the samples were cooled to 100°C and measured again.

The HT-GAXRD patterns were analyzed by using the Rietveld analysis (MAUD, TOPAS, Fullprof) in order to determine the phase composition, the stress-free lattice parameters, the residual stresses, the microstrain and the size of the crystallites in the crystalline phases present

in the respective sample. With increasing Zr content in the coatings, the crystallization of amorphous Cr-Zr-O was retarded. Sample CrZrO-5 crystallized already at 600°C, whereas the samples CrZrO-10 and CrZrO-15 crystallized first at 1000°C (Fig. 1). The dominant crystalline phase in all samples under study was α-Cr_2O_3 (SG: *R-3c*). In samples CrZrO-10 and CrZrO-15, α-Cr_2O_3 was complemented by ZrO_2 (SG: $P4_2/nmc$). Even after the annealing at the highest temperature, α-Cr_2O_3 contained a small amount of Zr. This was concluded mainly from the increase of the stress-free lattice parameters of α-Cr_2O_3. The Rietveld analysis of the GAXRD patterns measured at 100°C revealed that Zr occupies preferentially the interstitial positions in the crystal structure of α-Cr_2O_3 in analogy to Sn, Ti and Mg, when they are employed as doping elements [1]. Vice versa, ZrO_2 contained some Cr, which stabilized the tetragonal structure down to room temperature. The nanocomposite nature of samples CrZrO-10 and CrZrO-15 suppressed the growth of crystallites. Enhanced microstrain in the nanocomposites indicated that the doping elements (Zr in α-Cr_2O_3 and Cr in tetragonal ZrO_2) were non-uniformly distributed in samples with higher Zr content.

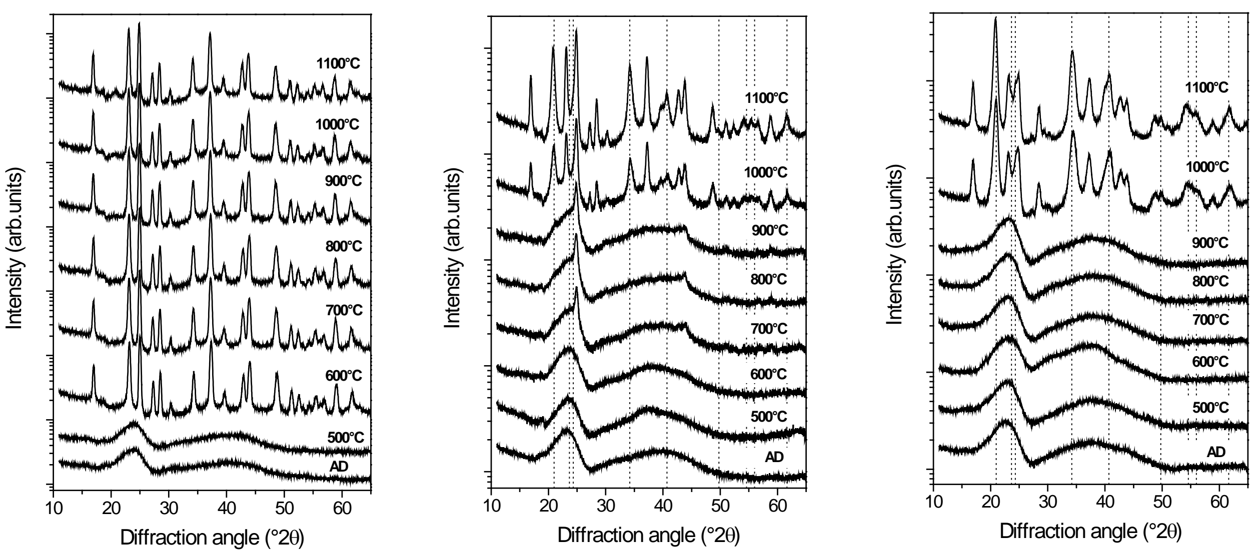

Figure 1: Diffraction patterns of samples CrZrO-5 (left), CrZrO-10 (middle) and CrZrO-15 (right) measured using HT-GAXRD at the temperatures up to 1100°C. The dashed vertical lines indicate the positions of the diffraction lines of tetragonal ZrO_2.

The analyses of SAXS and GISAXS patterns are still in progress.

[1] I. Ayub et al., Solid State Communications 123 (2002) 141.