ROBL-CRG	**Experiment title:** GISAXS study of the secondary phase morphology in transparent conductive oxide thin films	**Experiment number**: 20-02-698
Beamline: BM 20	**Date of experiment**: from: 17-11-2010 to: 20-11-2010	**Date of report**: 08-02-2011
Shifts: 9	**Local contact(s)**: Dr. Carsten Baehtz	*Received at ROBL:*

Names and affiliations of applicants (* indicates experimentalists):

G. Abrasonis*[1], M. Vinnichenko*[1], S. Brunken*[2], K. Ellmer[2]

[1] *Institute of Ion Beam Physics and Materials Research, Helmholtz Zentrum Dresden-Rossendorf (HZDR), P .O. Box 510119, 01314 Dresden, Germany*
[2] *Institute Solar Fuels, Helmholtz Zentrum Berlin (HZB), Hahn-Meitner-Platz 1, 14109 Berlin, Germany*

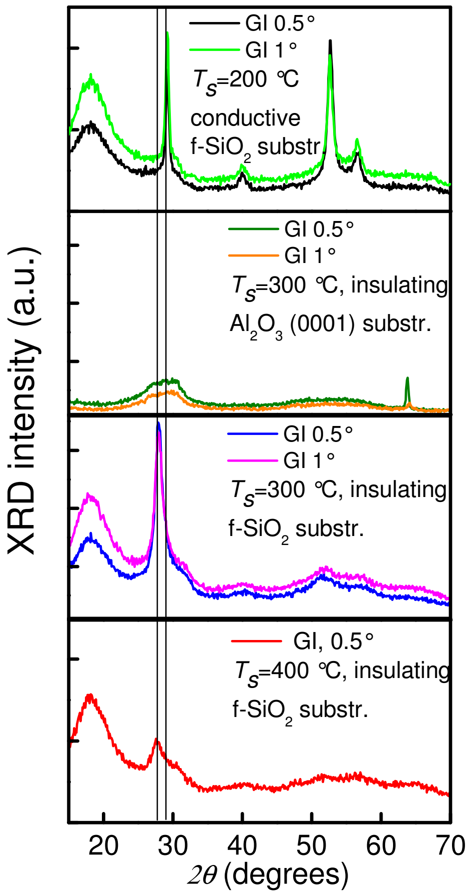
Report:

A proper understanding of secondary phase formation and their influence on the free electron generation and transport is of crucial importance for establishing performance limits of transparent conductive oxides (TCOs). Therefore, these experiments were aimed at checking the applicability of synchrotron based x-ray diffraction (XRD) and grazing-incidence small-angle x-ray scattering (GISAX) for this purpose. The focus was on Al-doped ZnO (AZO) and Nb-doped TiO_2 (TNO), while certain experiments were carried out for Ga-doped ZnO (GZO).

The AZO films were deposited in HZDR by reactive pulsed magnetron sputtering using metallic Zn-Al targets (Al concentration of 4.7 and 8.7 at. %.) at different temperatures (T_S=200-400 °C). Film grown on amorphous fused silica substrates were compared to those grown on single crystal Al_2O_3 (0001) substrates. The GZO films were grown at HZB epitaxially on ZnO (0001) substrates at elevated temperatures using DC sputtering of ceramic ZnO-Ga_2O_3 targets. The TNO samples (HZB) were grown on glass substrates at RT using reactive magnetron sputtering.

Electrically insulating and high-resistivity AZO films with the thickness in the range of 200-400 nm were selected for these experiments. The films deposited at T_S>300 °C exhibit Al concentration 16-20 at. % and are electrically insulating. The film grown at

T_S=200 °C had Al concentration of 8 at. % and relatively high electrical resistivity. The GZO films had Ga concentration in the range of 3 at.% and had lower electrical resistivity compared to AZO.



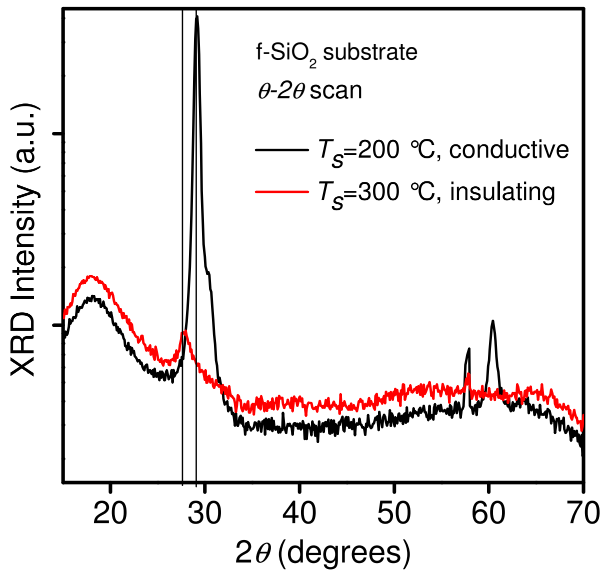


Figure 1. XRD patterns of AZO films grown at different conditions measured in grazing incidence (left, linear scale) and θ-2θ (right, logarithmic scale) geometry.

In the case of the AZO films, it is clearly observed that the insulating samples with a high aluminum concentration (16-20 at.%) have much broader and weaker XRD peaks compared to a conductive film (8 at. % of Al) (see Fig. 1). The broad peak below ~20° is attributed to the amorhous fused silica substrate. Preliminary analysis shows that the line at 28.97° observed for the conductive sample is associated with the ZnO (0002) diffraction. The distinct line at 27.68° is observed only in insulating films and is interpreted as a diffraction from the new $(ZnO)_3Al_2O_3$ secondary phase in agreement with previous study where θ-2θ scans using Cu $K\alpha$ wavelength were performed for similar AZO films (*Vinnichenko et al, APL 96, 141907 (2010)*). In addition to the earlier measurements, it has been found that:

1) intensity of this diffraction line drops dramaticall while changing from GI to θ-2θ geometry that points to a strongly disordered nano-crystalline structure of these films;
2) the films grown on sapphire show much weaker diffraction from this phase even in GI compared to AZO film grown on fused silica at identical conditions;

3) deposition of AZO films at the epitaxial substrate does not prevent formation of this phase, but its amount seems to be comparable with amount of nanocrystaline ZnO in this case.

XRD of GZO and TNO shows only ZnO and TiO_2-related peaks, respectively.

GISAX measurements even of the smoothest (rughness of 2 nm) insulating AZO films showed that the contribution from the surface roughness is dominating the signal. This means that the contribution from inhomogneities is much smaller than from the surface roughness.

Finally, it is shown that synchrotron-based XRD of AZO films is a useful tool for determination of secondary phase formation, however, GISAX measurements of this system does not provide additional information in this case.