ESRF	**Experiment title: Influence of point defects concentration on stress relaxation and optical properties of ZnO films deposited by magnetron sputtering.**	**Experiment number**: 21891
Beamline: BM02	**Date of experiment**: from: 12/10/2009 to: 12/13/2009	**Date of report**: 07/01/2010
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Report:

Scientific background and aim:

Zinc oxide belongs to the wide band gap semiconducting oxides class. It is a transparent conductive oxide material used, for example, in flat panel displays and thin film solar cells. The deposition process using this oxide can be prepared at high temperature. Residual stresses are induced both by the deposition technique and/or by the differences in thermal expansion coefficients between film and substrate. The residual stress relaxation effects combined to the presence of points defects such as antisite defects and oxygen vacancies induce modification of physical properties of these films. For this reason, a residual stress analysis is necessary to understand the evolution of the material conductivity, and its optical properties. The control of the stress is important and the evolution of the stoechiometry needs to be understood because those two parameters are related to each other.

Ex situ stress analysis has been performed, and the driving force of thermal stress relaxation is still a matter of controversy in this material. In situ diffraction patterns into a furnace have been collected onto ZnO (100nm thick) into laboratory diffractometer and, large stress relaxation seems to occur at relatively low temperature. But in situ stress analysis cannot be performed and the acquisition of one single θ-2θ diffractogram takes about 3 hours. Thus the kinetic and the stress evolution cannot be captured.

The aim of the present experiment was to perform in situ stress analysis in a furnace during increasing temperature up to 700°C. Two different kind of samples were used: bared Zn0 and encapsulated ZnO films into amorphous Si_3N_4 (50nm thick) deposited onto silicon single crystals (100) have been set into a furnace onto the diffractometer of BM02. The diffracted intensity was collected with a CCD detector (MAR133). The experimental set-up allows working with small incident angle (about 3°). Diffraction patterns have been recorded every 30 seconds during the increase of temperature, the plateau at 700°C and the cooling at room temperature (rate: 5°C/min.). The data are treated with fit2D to obtain standard Intensity-2θ patterns, and the peak position is obtained with a home made software in Scilab (i.e. fitting using Pearson VII, and polynomial background).

Results:

The first sample allowed evidencing a large displacement of the sample holder inside the furnace during heating (displacement of 0.5 mm!). Thus we changed the procedure of the experimental measurements for all the other samples. We tried to compensate the displacement of the sample surface by step by step z displacement during the heating and did the same thing for the cooling, we used the smaller displacement provided by the experiment set-up (i.e. 50µm). The same experiment has been also performed on a CeO_2 powder deposited onto similar substrates to verify the pertinence of the procedure.

The large number of diffraction patterns allows following precisely the evolution of the position of the Bragg peak. As the semi-automated procedure to fit the diffraction pattern has to be elaborated by ourself, the data are still under progress. We can not completely automate the fitting procedure because of the diffuse scattering induced by the silicon substrate and because of the texture of the ZnO. Indeed, even if we are not in Bragg position, the silicon single

crystal substrate induced in some region of the CCD detector a large diffuse scattering onto the diffraction patterns(Fig. 1). As the sample is moving during heating, this diffusion scattering evolves during the experiment.

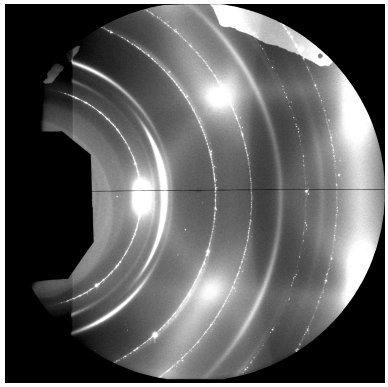

Fig. 1:Diffuse scattering of Silicon wafer (100) complicate the ZnO peak fitting.

The large sample displacement induces some changes in the diffraction patterns which have to be extracted from the whole data, and complexifies the analysis. We have to keep in mind that there are 600x136 diffratograms per sample. Anyway, the analysis procedure seems to work and we are starting to have interesting results:

- we obtain for each sample, each $\chi°$ and each temperature, the bragg position of the selected ZnO reflexion. We plotted, for the (002) direction (Fig. 2), the direct obtained evolution.

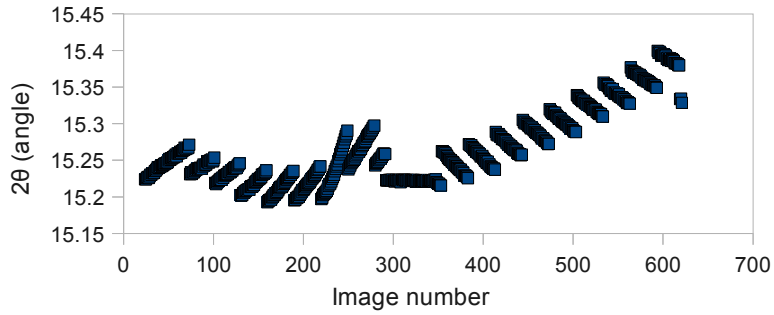

Fig. 2: Direct measure of peak position of ZnO (002) at χ=-21°. The movement of the sample (z direction) used to compensate the thermal drift of the sample holder is easily observable.

The 2θ jumps are directly linked to the mechanical movement (50µm) of the sample holder choosen for maintaining the diffraction geometry.

- CeO_2 powder allows for estimating the sample holder thermal drift influence on bragg position. After all provided corrections, the 2θ position evolution of the (002) reflexion of ZnO can be ploted vs temp (Fig. 3).

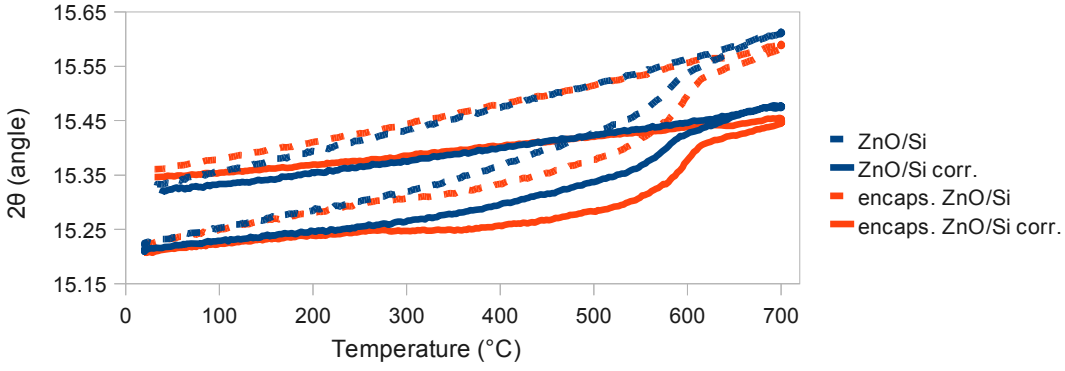

Fig.3: Evolution of the peak position versus temperature for ZnO/Si (002) [blue pointed] and encapsulated ZnO/Si [red pointed] at χ=-21° and the corrected evolution by taking into account the z-displacement (jumps, drift) (blue and red continued).

We can observe a clear difference of the evolution for both samples. During the heating, there is at about 280°C an unexpected change of the d-spacing in the ZnO layers, while the expected stress relaxation appears at temperature larger than 500°C. It seems that we begin to pointed out the stoechiometry modification during the heating between the bared ZnO film and the encapsulated one. These interesting first results have to be confirmed by the analysis (still under progress) of the whole diffraction peaks we recorded on the 2D detector (Fig. 1).