ESRF	**Experiment title:** Nano-line beam diffraction of thin polycrystalline films	**Experiment number**: Mi1046
Beamline: ID11	**Date of experiment**: from: 26October2011 to: 1November2011	**Date of report**:
Shifts: 18	**Local contact(s)**: Gavin Vaughan	*Received at ESRF:*

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Report:

Summary

The aim of this proposal was to perform combined analysis (phase, texture, stress, fluorescence, absorption) through z-scan measurements along the film thickness using a nano line beam in cross section. The hard X-beam has a high aspect ratio (100nm x 5 µm). A high energy (42keV) was chosen to have a deep penetration. The samples were previously prepared to obtain a 100µm thick sample in beam direction. Based on such a configuration, the irradiated surface was higher than 10^4 µm², compatible with powder diffraction method, for grain size from few nms to few µms.

Experimental method

The experiment was carry out on second experiment hutch on ID11. The beam was monochromatized at E = 42.033KeV and silicium nano-lenses were used. But only vertical nano-lenses were used to obtain the nano-line beam [1]. The sample was installed on piezo nano-stages.

The samples were previously prepared using equipments available in Leti. Specific sample shape preparation (parallelepiped 0.2 x 0.7 x 5 mm) was perform using a specific wafer micro-saw. Samples was then fixed on a Si wafer and installed on the stages.

Two additional cradles installed below the translation stages were used to adjust x and y tilt. A telescope was installed slightly parallel to the beam to roughly adjust the sample surface parallel to the beam. Additional optic camera was mounted above the sample to adjust the sample position in the lenses focus plane.

A diode was used to perform absorption scan before installing 2048 x 2048 Frelon CCD camera. An energy dispersive detector was mounted above the sample to collect fluorescence signal during the z-scan.

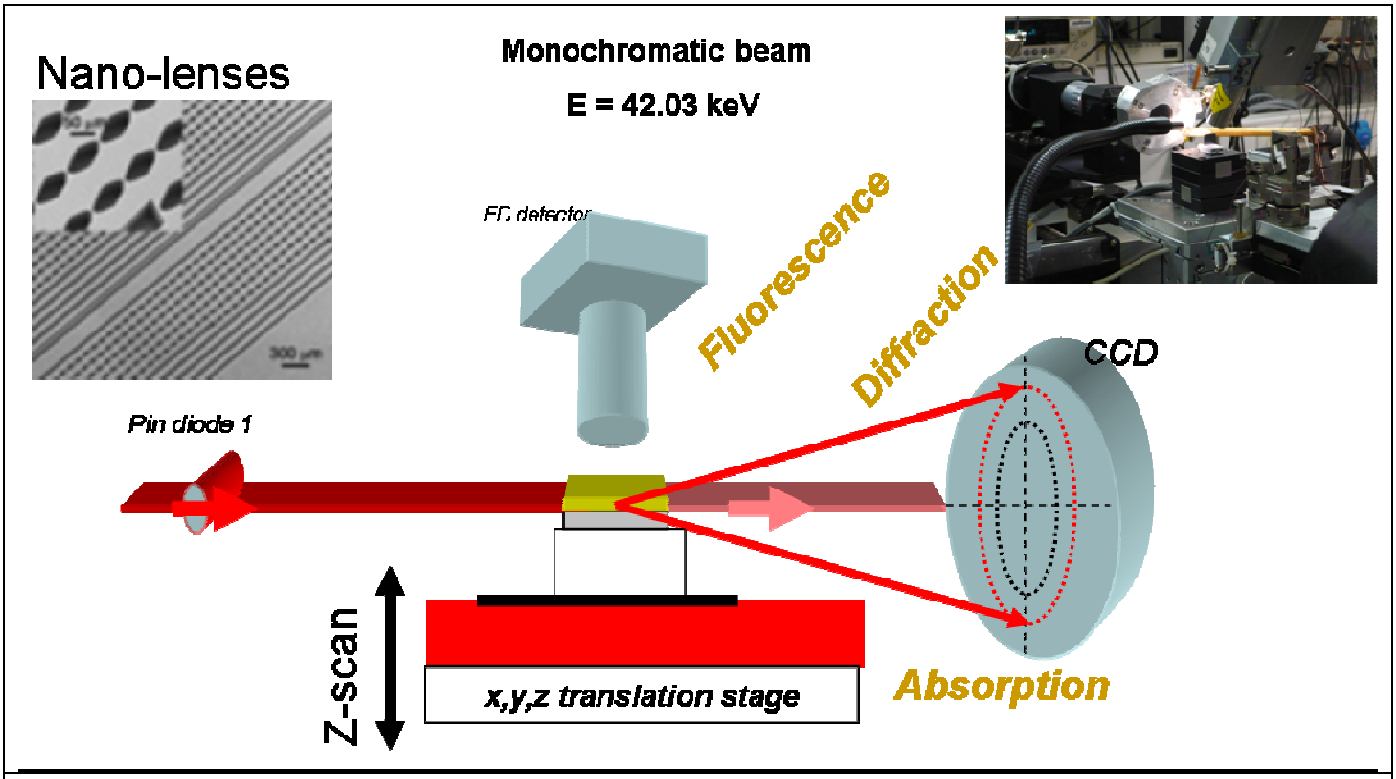


Fig. 1: Schematic of the nano-line beam diffraction set-up on ID11.

Alignment procedure

A specific approach was implemented to align the sample. Iteratively the two rotations (parallel and perpendicular to the beam) were adjusted to obtain smaller edge as possible. After some iterations (~ 2hours), we were confident to have a Z-resolution around 150nm.

A thin layer (Ta/TaN 25 nm) was deposited above the region of interest (Fig.2). This layer was used to make easier sample alignment.

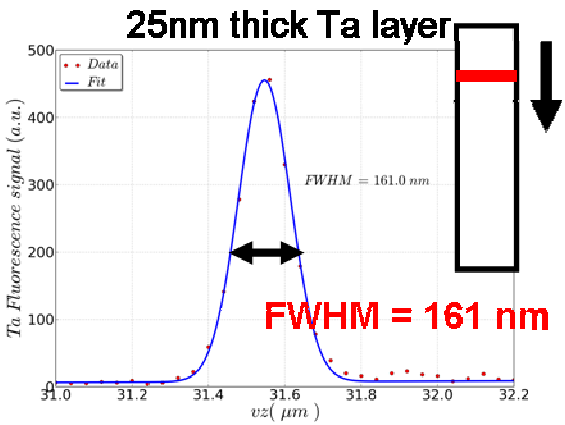


Fig. 2: Beam size convoluted to 25nm tick Ta layer (Ta fluorescence signal)

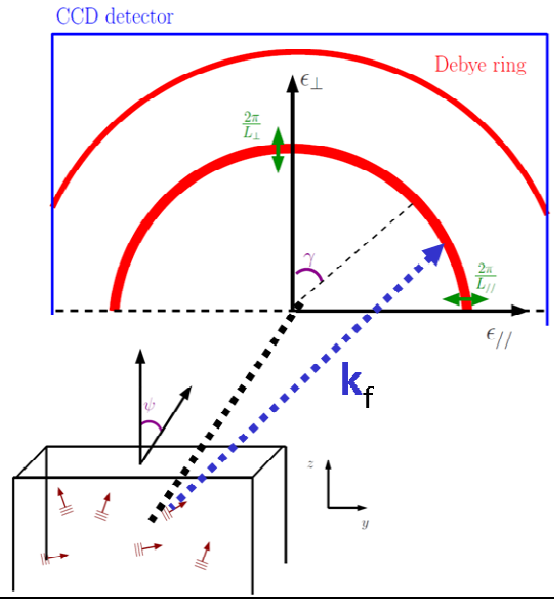


Fig. 3: Strain analysis principle

CCD calibration and Data treatment

The CCD calibration is made through fit2d calibration routine. First a median image is created as the sum along the z-scan. This image is representative from the whole thin film and could be compared with lab-source X-ray measurements. Lab-source measurements are made for different Ψ tilt and averaged. This <dhkl> list is put into fit2d calibration routine. This procedure has been tested on different samples and is robust to adjust the distance and camera tilt. Very similar dspacing(Ψ) are obtained between lab-measurement and z-averaged image from ID11 measurement.

These calibration parameters were used into fit2d macro to perform 2D signal azimuthal integration. Dark and flat field contributions were also corrected. First the 360° integrated spectrum is used to identify the phase present in the sample for each z-position.

To go further, 10° sections of Debye ring were integrated to obtain θ/2θ for different Ψ directions (Fig.3). Several python code has been developed to batch the Debye ring section fitting along the z-scan. As an output a text file is created including z position, peak position, Ψ, dspacing, integrated intensity, and width. Then in-plane and out-of-plane strain has been deduced. The intensity against Ψangle gives also information about texture.

Results

Several kinds of sample have been measured during the experiment. The goal was to identify the most appropriate ones to validate this new experimental approach.

1. SOFC sample

A SOFC (Solid oxide Fuel Cell) was tested first. The sample is a 1 mm film composed of three layers: the electrolyte (dense ZrO2 layer), a functional anode and an anode. This stack is obtained by sintering and the anode is porous. An oxidation has also been performed. So the Ni is transformed into NiO (huge volume variation).

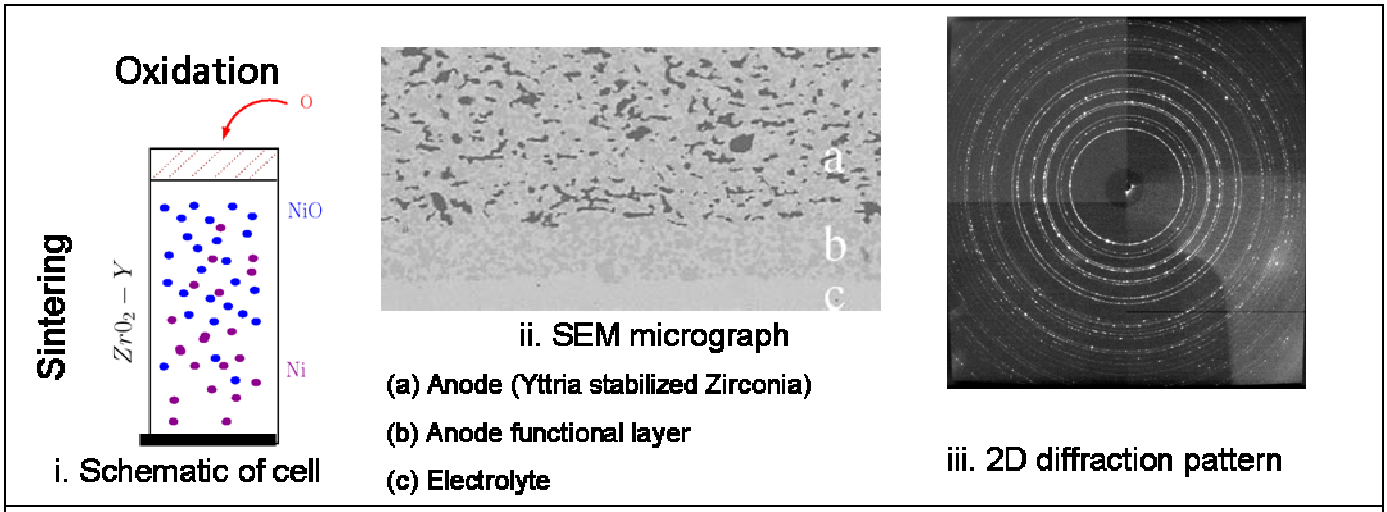


Fig. 4: *i. The solid oxide fuel cell is manufactured by sintering ii. SEM image from [2] iii. Typical 2D diffraction pattern obtain on Frelon CCD*

We wish to measure this sample to evaluate the oxidation profile in the anode. The z-resolution was not fundamental for this sample. We perform 5µm z steps. First absorption and fluorescence profiles give us some information about the porosity (Fig. 5c.d). A significant evolution has been evidence. Moreover θ/2θ scan evolution provides the oxidation profile (Fig. 5a.b).

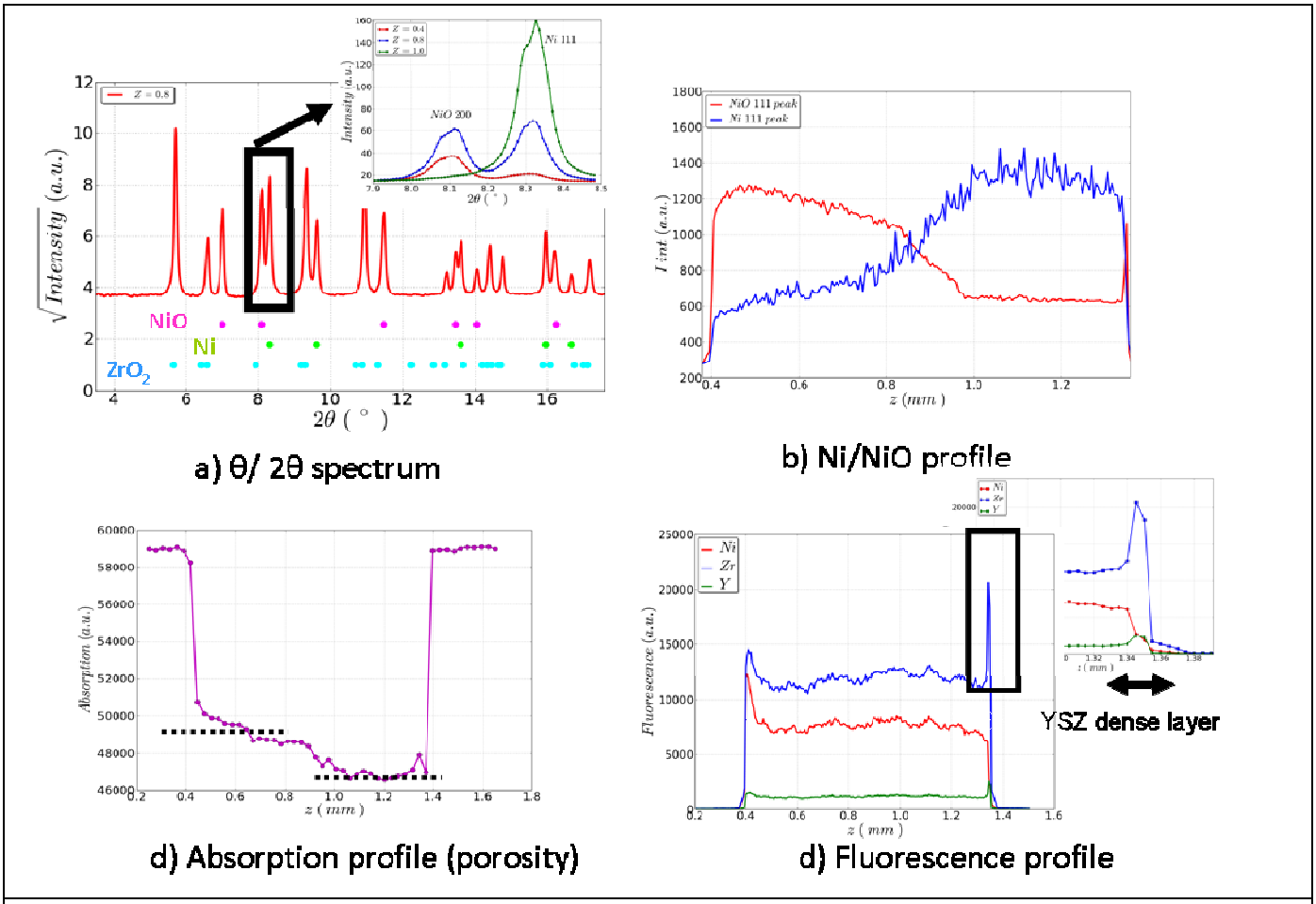


Fig. 5: Density, fluorescence and phase profiles has been obtained on the SOFC sample

2. Fe thin film oxidation

Magnetite Fe_3O_4 is of great interst thanks to its notable dielectric and magnetic properties. This oxide is a key of many tehcnologies. For specific applications, complete or partial oxidation of magnetite is essential. In spite of strong differences in functional properties, structural similarities make the distinction between these two phases tactful and quantification analysis of the oxidation is difficult, particularly with nanostructures using classical characterisation techniques [3].

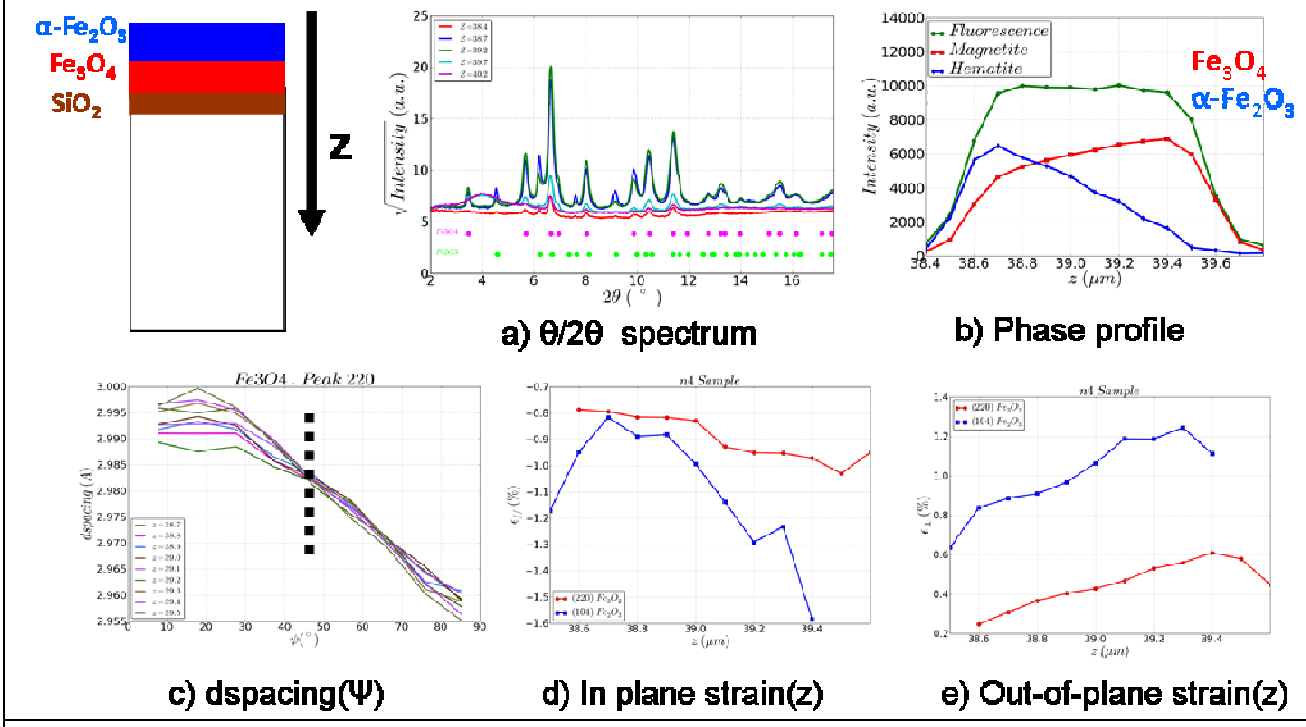


Fig. 6: Oxidation and strain profile has been evaluated in the film thickness.

The analysis shows the presence of hematite (α-Fe_2O_3) and magnetite (Fe_3O_4). No maghemetite (γ-Fe_2O_3 intermediate oxidation state) has been observed. Besides strain and texture gradient have been observed in the thickness. Strain can be monitored by fitting the Debye ring distorsions. Hence in-plane and out-of-plane strain could be evaluated in the thickness with a 150 nm in-depth resolution (Fig.2d.e.).

3. Cu/Cu direct bonding

3D technology will be the next step for the development of microelectronic devices. Vertical interconnection is one of the challenging issues. Cu/SiO_2 patterned surface might be one of the possible techniques to address it. Direct patterned Cu/SiO_2 surfaces bonding at room temperature, atmospheric pressure and ambient air has been demonstrated [4]. Some question about the texture, strain are still opened. That is why we measure this sample on ID11.

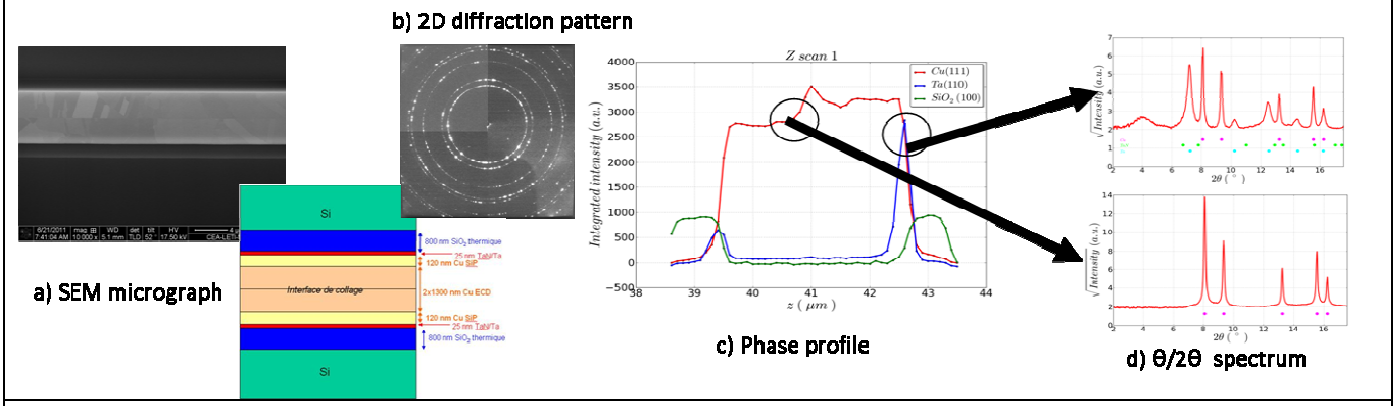
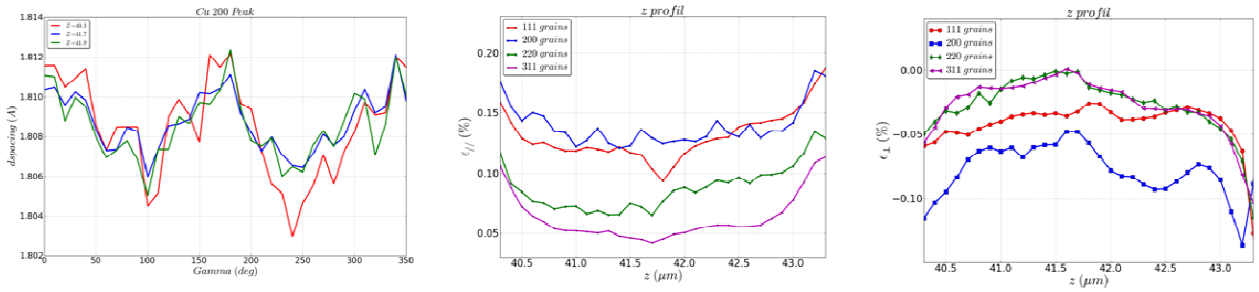


Fig. 7: (a) SEM cross section image. Phase profile (c) is deduced from θ/2θ scan (d) evolution against z.

We perform Z-scan measurements to observe gradients in the film. We find the SiO2/Ta/Cu/Cu/Ta/SiO2 stack in the θ/2θ scan (Fig. 7c). Besides strain has been evaluated in Cu in the thickness with 150nm in-depth resolution (Fig. 8).



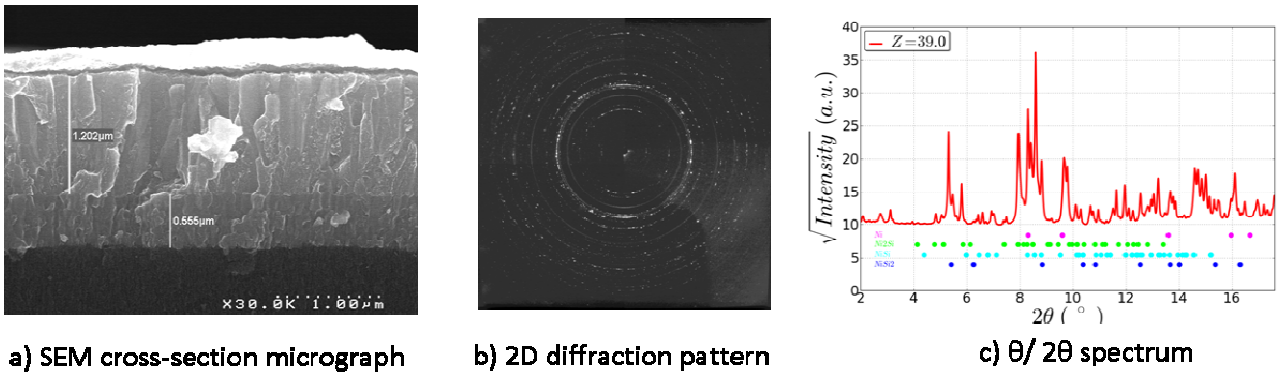
a) Debye ring distortions b) In plane strain(z) c) Out-of-plane strain(z)

Fig. 8: Strain analysis in the two 1.5 µm Cu layers.

4. Ni/ Mesoporous Si sample

In context of CMOS integration Ni silicide processes are very important [5-6]. We wish to study the silicidation behaviour in new kind of sample: a mesoporous Si thin film. A 10µm porous silicon layer was elaborated on the top of (100) Si wafer thanks to a specific HF preparation. A 1µm Ni layer was then deposited by ion sputtering. Finally the sample was annealing during few hours at 425°C to activate the solid reaction between Si and Ni.

We measured this ex-situ annealed sample on ID11. We wish quantify the diffusion of the metal into pores. This setup is particularly convenient for this measure.



a) SEM cross-section micrograph b) 2D diffraction pattern c) θ/ 2θ spectrum

Fig. 9: A SEM cross-section image shows two different layers after annealing. .Phase identification (c) has been performed thanks to 2D pattern (b).

We succeed to localize the θ-Ni_2Si and NiSi phases in the thickness. Absorption and Ni fluorescence profile show a diffusion in porous matrix of around 3 µm.

5. PZT thin film

PZT ($PbZrTiO_3$) is a ceramic perovskite material that shows a marked piezoelectric effect. Our sample was 350 nm thick. We measure this sample to show an eventual gradient ratio in the thickness between Zr and Ti. A error occurs during the z-scan. We only obtain good data in the middle of the film. Nevertheless this sample show a strong 111 texture (cf fig.10c). We observe also a important number of 111 twins (additional peak tilted 39° from 111 direction).

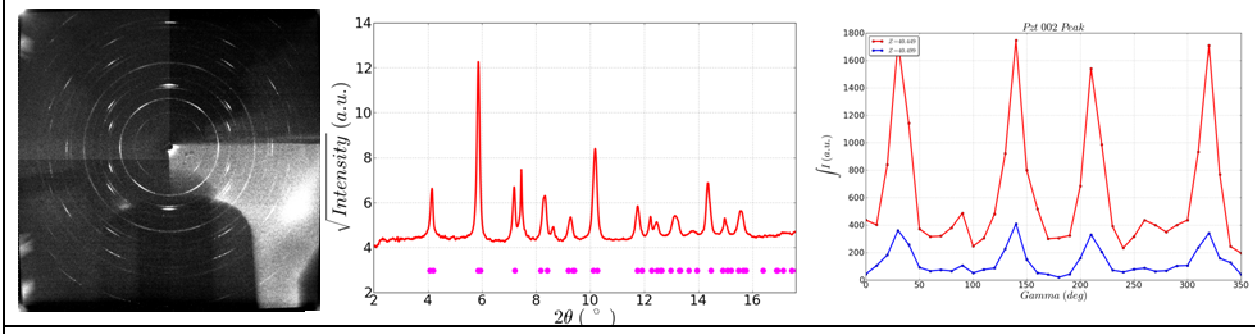


Fig. 10: A strong 111 texture has been observed on a 350 nm PZT film.

This specific sample proves texture technique sensitivity.

Conclusion

The main goal of this first proposal was be to develop an experimental setup combining X-ray diffraction, X-ray fluorescence and X-ray absorption (Fig. 1). **This experiment was a full success**. Optimization procedures, sample alignment, CCD calibration have also been defined and tested during this first experiment.

The results show that this approach is efficient and powerful. It is a unique tool to perform in depth chemical and structural analysis [7]. We believe important progresses could be made in the understanding of polycrystalline thin film complex behaviours. In-situ experiment is the next development step. In-situ could provide precious information to understand basic behaviours of polycrystalline thin films.

References:

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