ESRF	**Experiment title:** Initial stages of the ZnO - Al_2O_3 solid state reaction: a micro-XANES study	**Experiment number**: CH-2852
Beamline: ID24	**Date of experiment**: from:10/06/2009 to:16/06/2009	**Date of report**: 24/08/2009
Shifts: 18	**Local contact(s)**: Dr. Mark Newton	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Sonia Pin*, Paolo Ghigna*, Giorgio Spinolo*

Dipartimento di Chimica Fisica "M. Rolla", Università di Pavia, V.le Taramelli 16, I-27100, Pavia, Italy

Report:

A 20 nm thick ZnO thin film has been obtained by RF-magnetron sputtering of ZnO (Aldrich, 99.99 %) onto Al_2O_3 (1 1 $\bar{2}$ 0) oriented single crystals (MaTecK) at room temperature. After the deposition the film has been treated in sequence at 800 °C for 20 minutes. According to previous work by our group [1], at this temperature and after this firing time, for a film 20 nm thick, the solid state reaction forming the $ZnAl_2O_4$ spinel is fired up and it is just in the very early stages. To expose the reactive interface, the sample was polished with 0.1 μm diamond paste. The polishing has been made with an angle of about 0.01 ° with respect to the surface, as sketched schematically in Fig. 1. This procedure ensures the "spreading" of the coordinate perpendicular to the surface along those that are parallel: in this case the 20 nm thickness of the film is spread over a lateral length of ca. 100 μm. The sample has then been mounted on the ID24 beamline, with the sample surface perpendicular to the incoming beam. A silicon diode detector, mounted close to the sample at an angle of 45 ° degrees, was used to collect the XANES in fluorescence mode. The beam was focused with a horizontal (vertical) FWHM of 7 (150) μm. Zn-K edge spectra have been the acquired across the sample, after calibration in energy by the acquisition of a spectrum of a Zn foil. It should be noted that a large part of the beamtime awarded was used for the beamline set up and in trying different sample preparation procedures, before the one described above demonstrated successful.

The results are summarised in Fig. 2, 3 and 4. In particular, in Fig. 2 the fluorescence signal at 9680 eV (*i.e.* above the Zn-K edge) is plotted vs. the horizontal coordinate. It is clearly seen that the fluorescence signal increases over a distance of *ca.* 100 μm, thus indicating that the approach used for the sample preparation procedure worked in a very satisfactory way. Fig. 3 reports the XANES spectra acquired along the horizontal coordinate of Fig. 2. The information that can be obtained from Fig. 3 is twofold.

First, the edge jump is proportional to the Zn amount. Thus, Fig. 3 is equivalent in some way to a concentration depth profile, as obtained, for example, by SIMS. However, it may be worth noting that, owing to the very gentle method of sample preparation, such a profile is not affected by artefacts due to the sputtering process such as atomic mixing. To make the concentration depth profile clearer, the edge jump has been mapped in Fig. 4.

Second, the XANES manifolds change in shape as the beam is moved far from the interface. A comparison with the inset of Fig. 3 demonstrate that far from the interface the spectra are almost identical to that of pure ZnO. On the contrary, close to the interface, the edge region is characterised by a more complicated shape: in

particular, in the white line a three peak structure, reminiscent of that of the $ZnAl_2O_4$ spinel may be recognised.

In conclusion, with this experiment we have demonstrated the feasibility of a microXANES mapping of a buried interface. Owing to our sample preparation procedure, a nano-metric resolution has been obtained even with a probe with micrometric dimension. In addition, with this kind of approach, the possibility of having both compositional and structural information about a buried interface in one shot has been established as possible. It may be worth to point out that, while a number of well established techniques exist for the study of surfaces (i.e. the interface between a condensed phase and a vacuum), the study of buried interfaces is much more difficult. The results described in this report can possibly open the way to a new method for the study of buried interfaces.

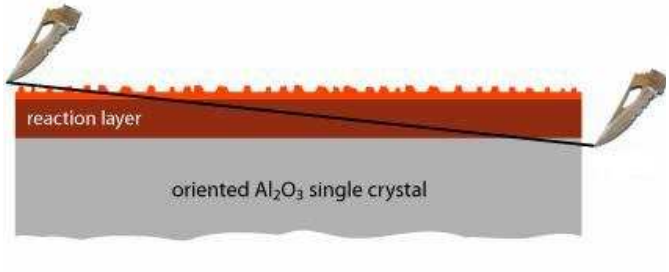

Fig.1: Scheme of the polishing procedure

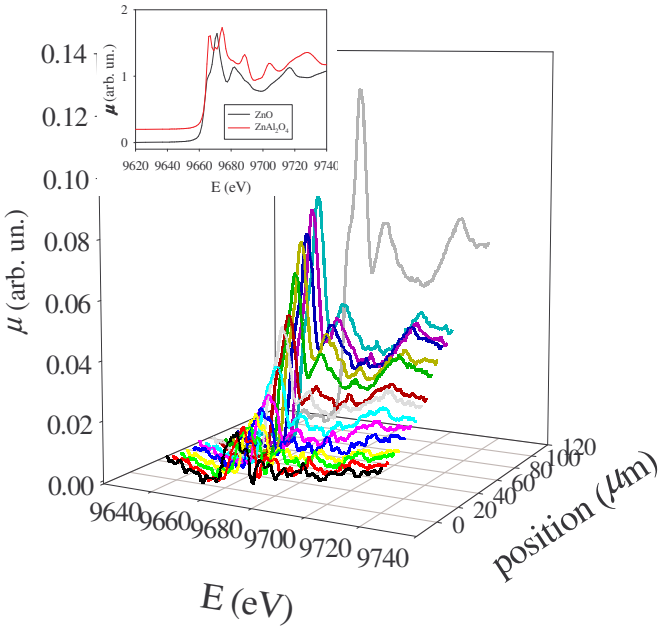

Fig.3: XANES spectra at the Zn-K edge along the horizontal coordinate. For comparison the ZnO and $ZnAl_2O_4$ spectra are reported in the inset.

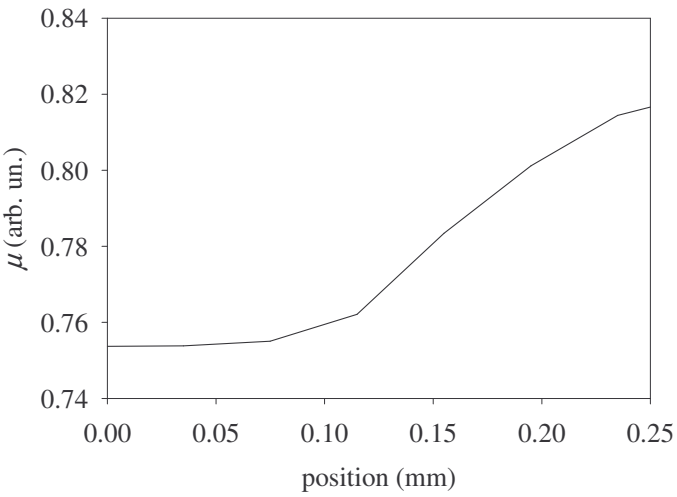

Fig.2: Fluorescence signal at 9680 eV (*i.e.* above the Zn-K edge) plotted vs. the horizontal coordinate.

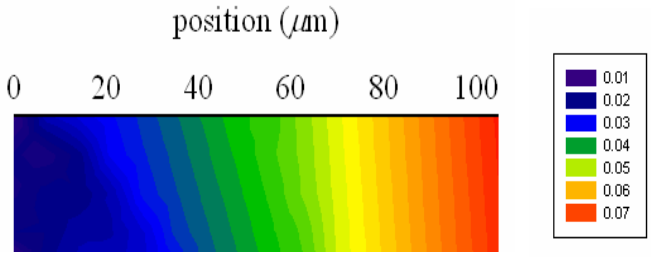

Fig.4: Edge jump at the Zn-K edge

References

[1] - S. Pin, P. Ghigna, G. Spinolo, E. Quartarone, P. Mustarelli, F. D'Acapito, A. Migliori, G. Calestani, Journal of Solid State Chemistry 182, 1291 (2009).