EXPERIMENTAL REPORT: EXPERIMENT HE-3161

The main objective of our project HE-3161 was to provide experimental evidence for the conduction mechanism in ZnO thin films upon low-level doping with Al, using hard x-ray photoelectron spectroscopy (HAXPES). Two aspects of the proposal HE-3161 made it a challenging experiment. First, the aim was to study of application-oriented materials, second, it required the use of high energy photons in photoemission implying the use of a specially developed experimental installation. Both of these experimental objectives have been successfully attained. As stated in the proposal, three Al-doped ZnO films and one undoped ZnO film have been measured with 7000 eV photons on beamline ID16, using the VOLPE analysis chamber, demonstrating the excellent operation of the experimental set-up. It must be said that one essential element was the improved geometrical set-up of the VOLPE spectrometer: working at grazing incidence and normal emission increased the measured intensity of more than one order of magnitude.

Valence band and core emission lines have been recorded in order to find the electronic states that doping introduces into the band-gap of this oxide semiconductor and to provide an independent assessment of the sample composition, respectively. Due to the fact that these samples are not prepared in the usual clean conditions of surface physics, high energy photoemission (HAXPES) will provide a more exact composition of these films, since it has a bigger probing depth than standard surface XPS. Thus, core level lines are not affected by surface effects and contaminant contributions are minimized.

We have proven the huge relative enhancement of the s levels at high excitation energy which has made possible to determine precisely the exact energy location of the doping states within the valence band. The detected density of states of states (DOS), however, has a very weak absolute signal, even in the most heavily doped film Al:ZnO 45, as it is evident in the figure, showing the valence band region of the four measured samples. A shift to higher binding energies in the valence band features is evident for the more doped samples, Al:ZnO 30 and Al:ZnO 45, probably due to band bending.

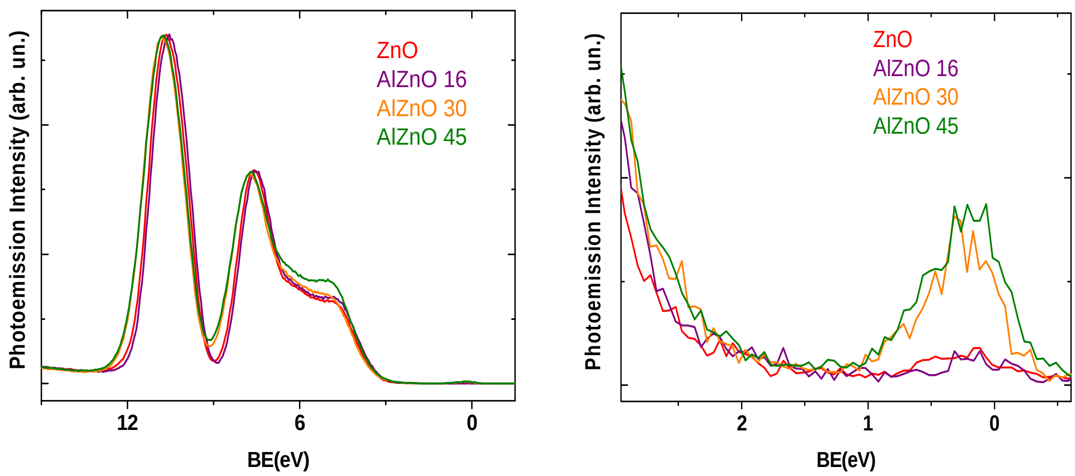
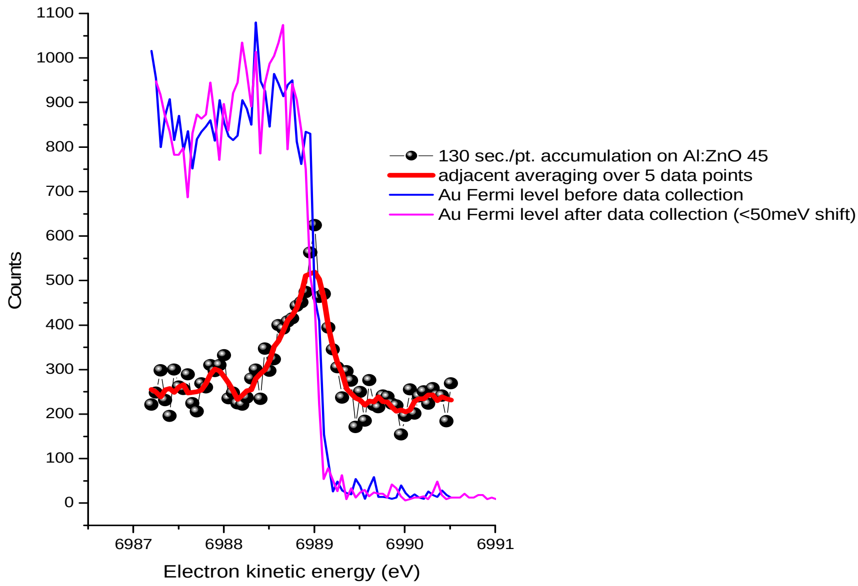


Figure: Photoemission spectra of the valence band of ZnO films with different Al doping levels (left panel) and the corresponding Fermi level region (right panel).

Due to the weakness of DOS signal at the Fermi level, measurements in the band-gap region had to be made using a moderate resolution experimental configuration, in order to maximize the number of incoming photons and thus the intensity of the signal. As a consequence of that, the real width of the density of states peak due to doping is masked by experimental resolution (~ 400 meV). In the right panel of the above figure, experimental signals obtained in the Fermi level region corresponding to the four measured samples, are presented. The signal intensities have been normalized to the Zn 3d peaks. As it is evident in the figure, the more doped samples show a bigger feature in the Fermi level region, but it is worth mentioning here that even the undoped sample evidences the presence of intermediate states in the band-gap, probably due to intrinsic defects in the film or to air exposure induced surface contamination. The analysis concerning the width and shape of the peaks, as well as the band alignments and of its correlation with electric measurements, are currently under analysis.

For one sample, we tried also higher resolution measurements (~150meV). The bottom figure compares the Fermi level of the more Al doped ZnO film with that of a gold reference, taken just before and after in order to assess the stability of the energy scale over the long data acquisition (6 hours).



In the near future we would like to extent our studies to Ga-doped ZnO samples. In that sense, a new proposal P24860, has been submitted for the next beam-time allocation period, starting on next month of July. After the results obtained for the Al-doped ZnO films, we feel that higher energy resolution will be essential to describe in detail the doping related states at the Fermi level and their influence on the overall electronic structure.