Valence-change-induced Fano resonance: RPES of Yb implanted ZnO

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INTRODUCTION

Rare Earth (RE) doped wide-band gap semiconductors like ZnO are recognized for their diverse structural, physical, and chemical properties useful for optoelectronic applications. They can be used as optical fibers, in lasers, optically pumped glass fibers and phosphors. Zinc oxide doped with ytterbium is also seriously considered to be utilized as a down-converter material in silicon-based solar cells. Usage of Yb^{3+} ions is promising in this field because of perfect matching between the wavelength of the $^2F_{5/2} - {}^2F_{7/2}$ transition in Yb^{3+} ion (980 nm) and the silicon band gap. It has been demonstrated that the process of transfer of one higher-energy photon into two infra-red photons may lead to the considerable reduction of energy loss in solar cells [1]. Due to this fact, the basic knowledge on the valence band (VB) as well as the electronic structure of ytterbium with respect to the electronic structure of the host ZnO matrix is of a great importance as it can influence the transfer process.

Resonant photoemission spectroscopy (RPES) is a method that is able to provide this kind of information identifying contribution of the Yb 4*f* states to the electronic structure of a ZnO:Yb system. This could be achieved by tuning the photon energy to the N_5 absorption edge of Yb. If the photon energy is slightly lower than the energy needed to excite a core level electron into the conduction band (i.e. slightly below the absorption edge) only the direct photoelectron process is possible. In contrast, at the absorption edge an additional, indirect channel with the same initial and final states is opened. Within the single particle model, this can be described as the two-step process [2]. In the first step, a 4*d* electron is excited into an empty state in the conduction band leaving behind a 4*d* core hole. In the second step, this core hole decays via a Super-Coster-Kroning process, which transfers the energy to a valence band electron. Both the direct photoemission process as well as the indirect decay have the same initial and final states, so they can interfere constructively. Consequently, one is able to observe an enhancement of the photoemission intensity from the Yb 4*f* shell and consequently extract this photoemission response from the overall photoemission signal. The purpose of this poster is to show how RPES can be used to study the electronic structure of zinc oxide doped with ytterbium, as well as to discuss a possible application of the RPES in theoretical studies of the electronic structure of the ZnO:Yb system.

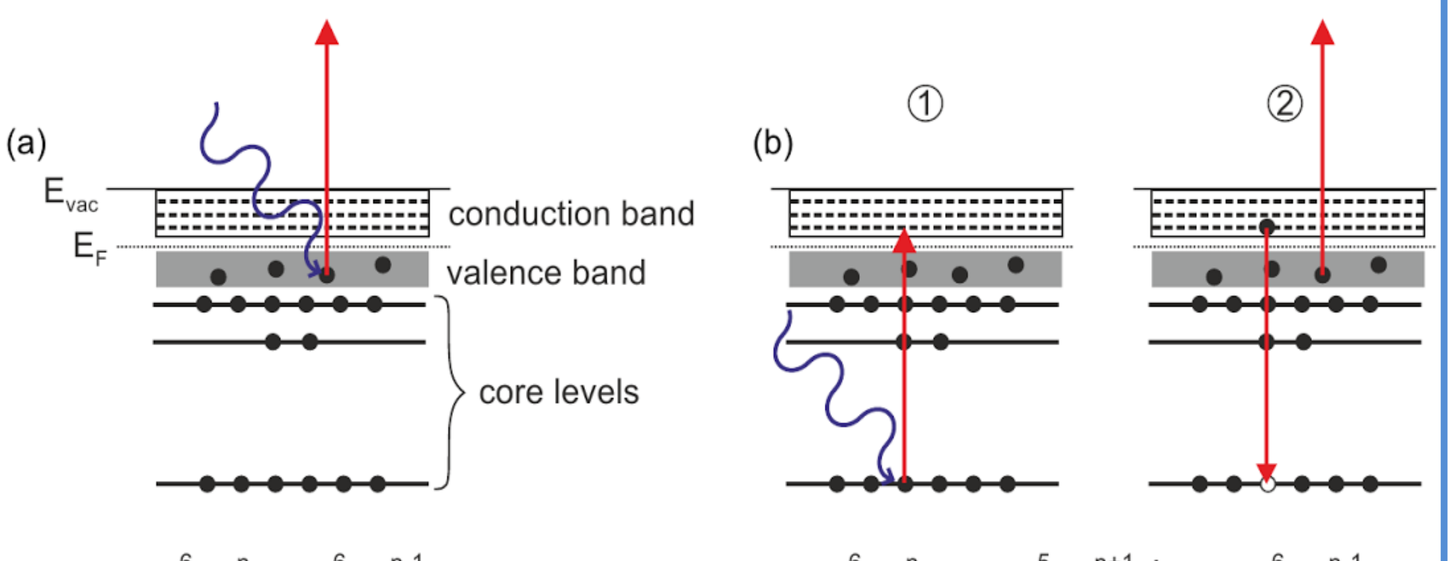
[1] B.M. van der Ende, L. Aarts, A. Meijerink, *Adv. Mat.* **21**, 3073 (2009). [2] F. de Groot, A. Kotani, *Core Level Spectroscopy of Solids*, CRC Press, 2008.

SAMPLE PREPARATION AND EXPERIMENTAL DETAILS

The RPES spectra were collected for zinc oxide films grown by Atomic Layer Deposition (ALD). Ytterbium ions were incorporated into the ZnO matrix via implantation (at the level of 10^{15} at./cm^2) with subsequent annealing at 800^{0}C for 5 min. ALD is a promising method to be used in solar batteries production due to its low cost, good quality of obtained films, and ability to cover very large substrates, even up to a meter size. In turn, ion implantation is a convenient method for introducing Yb ions into the ZnO lattice due to the fact that ion concentration and its depth profile can be easily controlled.

X-ray photoelectron spectroscopy (XPS) and RPES experiments were carried out at the Materials Science Beamline (MSB) at the Elettra Synchrotron Light Source in Trieste, Italy. The MSB is a bending magnet beamline with a plane grating monochromator that provides light in the energy range of 21–1000 eV. The UHV end station, with a base pressure of 1×10^{-8} Pa, is equipped with a 'Specs Phoibos 150' electron energy analyzer and a dual Mg/Al X-ray source. High-resolution RPES measurements were performed across the 4*d*→4*f* resonance of Yb. Complementary XPS spectra of Yb 4*d* core level were recorded at the same end station using the excitation energy of 630 eV. The binding energies of VB spectra were calibrated to the Fermi edge of the molybdenum sample holder.

Resonant X-ray photoelectron spectroscopy (RPES) vs XPS

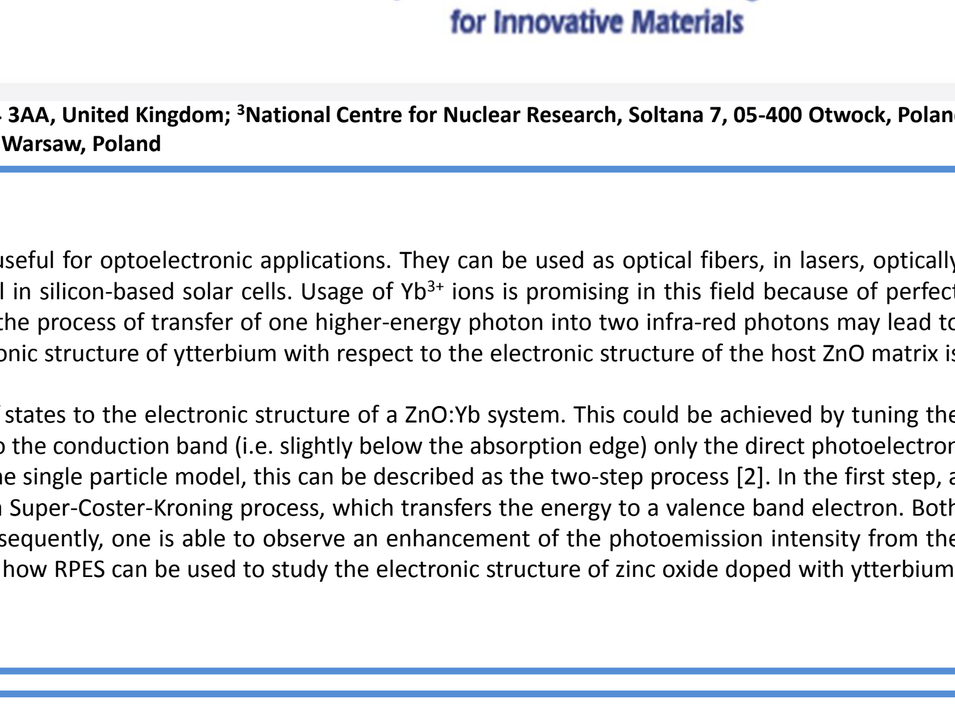


$$2p^6 3d^n \rightarrow 2p^6 3d^{n-1} + e^- \qquad 2p^6 3d^n \rightarrow (2p^5 3d^{n+1})^* \rightarrow 2p^6 3d^{n-1} + e^-$$

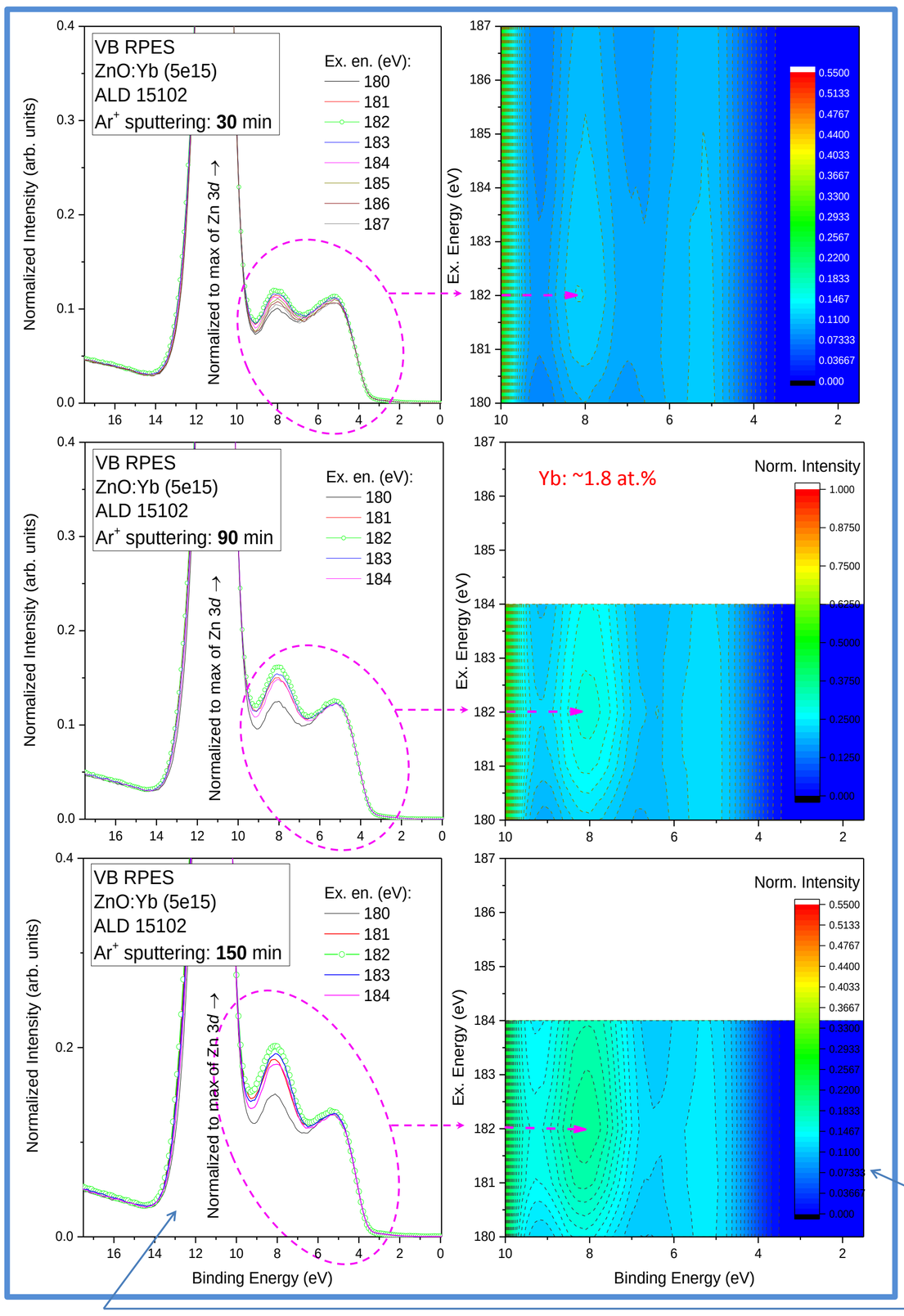
(a) Direct photoemission process of a valence band electron. (b) Two-step model of the additional, resonant excitation channel at the L-edge [A. Köhl, Micro-spectroscopic investigation of valence change processes in resistive switching $SrTiO_3$ thin films, 39, D82, p. 28, 2014].

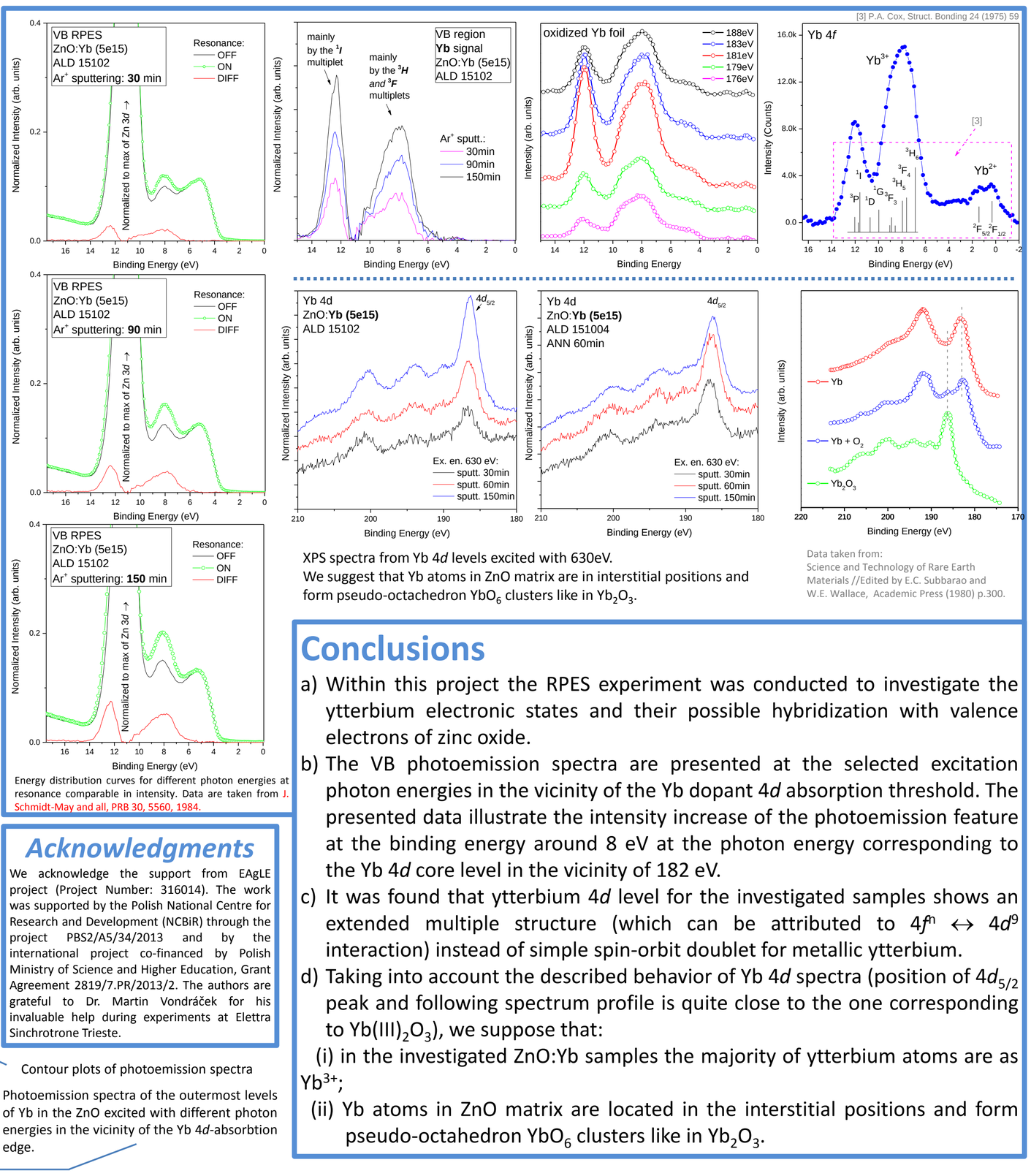
$$Yb\ 4d^{10}4f^{13} + h\nu \rightarrow [Yb\ 4d^9 4f^{14}]^* \rightarrow Yb4d^{10}4f^{12} + e^-$$
$$Yb\ 4d^{10}4f^{13} + h\nu \rightarrow Yb4d^{10}4f^{12} + e^-$$

Rutherford Backscattering Spectrometry (RBS)



The RBS random (open symbols) and aligned (solid symbols) spectra obtained for virgin ZnO films and after implantation with 150keV Yb ions at fluence 5x10^{15} at/cm^2 (before and after annealing).





XPS spectra from Yb 4*d* levels excited with 630eV.
We suggest that Yb atoms in ZnO matrix are in interstitial positions and form pseudo-octahedron YbO_6 clusters like in Yb_2O_3.

Data taken from:
Science and Technology of Rare Earth Materials //Edited by E.C. Subbarao and W.E. Wallace, Academic Press (1980) p.300.

Contour plots of photoemission spectra

Photoemission spectra of the outermost levels of Yb in the ZnO excited with different photon energies in the vicinity of the Yb 4*d*-absorbtion edge.

Energy distribution curves for different photon energies at resonance comparable in intensity. Data are taken from J. Schmidt-May and all, PRB 30, 5560, 1984.

Acknowledgments

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Conclusions

a) Within this project the RPES experiment was conducted to investigate the ytterbium electronic states and their possible hybridization with valence electrons of zinc oxide.

b) The VB photoemission spectra are presented at the selected excitation photon energies in the vicinity of the Yb dopant 4*d* absorption threshold. The presented data illustrate the intensity increase of the photoemission feature at the binding energy around 8 eV at the photon energy corresponding to the Yb 4*d* core level in the vicinity of 182 eV.

c) It was found that ytterbium 4*d* level for the investigated samples shows an extended multiple structure (which can be attributed to $4f^n \leftrightarrow 4d^9$ interaction) instead of simple spin-orbit doublet for metallic ytterbium.

d) Taking into account the described behavior of Yb 4*d* spectra (position of $4d_{5/2}$ peak and following spectrum profile is quite close to the one corresponding to $Yb(III)_2O_3$), we suppose that:

(i) in the investigated ZnO:Yb samples the majority of ytterbium atoms are as Yb^{3+};

(ii) Yb atoms in ZnO matrix are located in the interstitial positions and form pseudo-octahedron YbO_6 clusters like in Yb_2O_3.