Resonant Photoemission Spectroscopy Study on the Contribution of the Yb 4f States to the Electronic Structure of ZnO

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The electronic structure of Yb implanted ZnO has been studied by the resonant photoemission spectroscopy. The contribution of the Yb 4f partial density of states is predominant at binding energy about 7.5 and ≈11.7 eV below the VB maximum. At photon energy about 182 eV the multiplet structure around 11.7 eV shows the strongest resonance that corresponds to the 1F multiplet which is almost exclusively responsible for this resonance, while 3H and 3F states are responsible for the resonance around 7.5 eV. It was also found that the Yb 4f partial density of states distribution shows some similarity to Yb2O3.

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1. 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 an interesting system because of its possible application as a down-converter material in silicon-based solar cells. The Yb3+ ions are promising in this field because of perfect matching between the wavelength of the 2F5/2–2F7/2 transition in Yb3+ 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, which is able to provide this kind of information identifying contribution of the Yb 4f states to the electronic structure of a ZnO:Yb system. This could be achieved by tuning the photon energy to the N5 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 4d electron is excited into an empty state in the conduction band leaving behind a 4d core hole. In the second step, this core hole decays via a super-Coster-Kronig 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 4f shell and consequently extract this photoemission response from the overall photoemission signal. The purpose of this paper 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.

2. Experimental

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^{16} at./cm^{2}) with subsequent annealing at 800°C for 5 min. Real concentration of Yb atoms in ZnO matrix was estimated through the analysis of RBS/c data using SIMRA program and is equal to 9.98 × 10^{20} at./cm^{2} in the top 150 nm. 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.

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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 $1 \times 10^{-8}$ Pa, is equipped with an Specs Phoibos 150 electron energy analyzer and a dual Mg/Al X-ray source. High-resolution RPES measurements were performed across the $4d \rightarrow 4f$ resonance of Yb. Complementary XPS spectra of Yb $4d$ 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.

3. Results and discussion

During the RPES experiment, VB spectra were measured using several photon energies tuned across a narrow energy range 180–187 eV. An enhancement of the photoemission intensity of an Yb $4f$ electronic state is observed at a 182 eV photon energy (on resonance) and compared to all the other energies (off resonance). The described effect is shown in Fig. 1a where RPES spectra are presented.

Fig. 1. (a) RPES spectra of the ZnO:Yb film implanted with a fluence of $1 \times 10^{16}$ ion/cm$^2$ taken across the Ybd→Ybf photoionization threshold and the difference of energy dispersive curves (ΔEDC) showing the PDOS of the Yb$4f$ contribution to the VB of ZnO:Yb. (b) Digitized EDC of oxidized Yb recorded across the Ybd→Ybf resonance (data taken from [3]) together with the bar diagram showing the multiplet structures of Yb$^{3+}$ (calculated by Cox [4]).

The difference between VB spectra measured on and off resonance (green open circles (excitation energy 182 eV) and black line (excitation energy 180 eV)) was used to extract the resonantly enhanced Yb $4f$ contributions to the total density of states in the VB region of the investigated sample. A direct comparison of the off- and on resonance spectra shows the most significant intensity differences at about 7.5 and 11.7 eV, which is visualized in the bottom curves in Fig. 1a. These features reached a maximum when the VB spectrum is recorded at 182 eV photon energy.

Estimated in such a way PDOS of the Yb $4f$ states were compared to the literature data that corresponds to an oxidized ytterbium foil [3] (see Fig. 1b). As was presented by Schmidt-May et al. [3], at photon energy of 182 eV the multiplet structure with the highest binding energy, around 11.7 eV, shows the strongest resonance (see Fig. 1b). According to the bar diagram showing the multiplet structure of Yb$^{3+}$ calculated by Cox [4] and presented in the middle part of Fig. 1b, it is the $1^1I$ multiplet that is almost exclusively responsible for this resonance, while the $3P$ and $1D$ only slightly contribute to the overall photoemission intensity. In contrast, the $3H$ and $3F$ multiplets are responsible for the resonance appearing in the binding energy around 7.5 eV. At that point, it could be concluded that the $4f$ photoemission response gives a direct evidence that Yb ions in the examined sample have an oxidation state of 3+. Additionally, it was found that ytterbium $4d$ levels for the investigated samples show an extended multiple structure instead of a simple spin–orbit doublet of metallic ytterbium (Fig. 2). As was shown in [5], for pure ytterbium the $4d$ spectrum exhibits a simple doublet (see Fig. 2b). In general, the effect of oxidation is reflected by broadening and shifting of the main structure of the $4d$ spectra to higher binding energy (see Fig. 2b). Namely, with the beginning of oxidation two weak structures appear in the $4d$ spectrum of metal at binding energies of 186 and 201 eV (the former, at 186 eV, is observed between the two components of the $4d$ doublet). The longer duration of oxidation is, the higher intensity of the peaks is observed. Additional structure appears in the $4d$ spectra for complete oxidation.

Fig. 2. (a) Photoelectron spectra from Yb $4d$ levels of ZnO:Yb excited with 630 eV radiation after sputtering treatment for 10 and 20 min. (b) Digitized photoelectron spectra corresponding to Yb $4d$ levels of pure and oxidized Yb foil and Yb$_2$O$_3$ excited with Al Ka radiation (data taken from [5]).

In case of Yb$_2$O$_3$, these peaks become prominent and no trace of the $4d$ doublet of the pure metal is detectable. Rao and Sarma [5] found that no attempt has been made to characterize the various components of the $4d$ multi-
culation. Difficulties arise from the requirements of intermediate coupling consideration in order to properly describe the 4d^9 4f^n configuration. Thus, taking into account an influence of oxidation on the 4d spectrum profile and similarity of spectrum profile examined in this work to the Yb_2O_3 (see Fig. 2), the following can be proposed regarding the investigated ZnO:Yb sample. Firstly, the majority of ytterbium atoms (Yb^{3+}) are bonded to oxygen and show an extended multiple structure indicating that one of the 4f^{14} electrons has been promoted to the valence level. This multiple structure can be attributed to 4f^{13} ↔ 4d^9 interaction.

Secondly, Yb^{3+} ions in the ZnO host matrix are located in the interstitial positions and according to investigations presented in [6] form presumably pseudo-octahedral YbO_6 clusters. Let us note that generally there are two distinct types of interstitial sites in the wurtzite structure: tetrahedral and octahedral sites. The tetrahedral site is out of our interest here. Janotti et al. [7] performed a comprehensive first-principles investigation of native point defects in ZnO based on density functional theory within the local density approximation (LDA) as well as the LDA+U approach and found that the octahedral site is the stable site for interstitial metal atom as opposed to the tetrahedral one. The octahedral site is in the interstitial channel along the c-axis. It is positioned at 1.9947 Å (R_Yb–Zn) and 2.2774 Å (R_Yb–O1) from three zinc and three oxygen atoms, respectively. Additionally, one can note that there are extra three atoms of oxygen at 2.2893 Å (R_Yb–O2), thus, 3×O1 and 3×O2 atoms form octahedron around Yb ion. All above confirms preliminary suggestion that YbO_6 order appears around implanted Yb atoms in the ZnO host matrix. A subsequent, more detailed theoretical investigations of the ZnO:Yb system accompanied with a comparison with experimental data are necessary to confirm this working hypothesis. This is an ongoing task with the results to be published elsewhere.

4. Summary

The RPES experiment was conducted to investigate the ytterbium electronic states and their position in respect of the valence electrons of zinc oxide. The VB photoemission spectra are presented for the selected excitation photon energies in the vicinity of the Yb dopant N_5 (4d_{5/2}) absorption threshold. The presented data illustrate the resonant enhancement of the photoemission feature at BE around 7.5 and 11.7 eV, which is observed for the photon energy corresponding to the Yb 4d–4f absorption threshold (182 eV). This weak photoemission resonance effect indicates a large 4f^{14}–4d occupancy. It was found that ytterbium 4d level for the investigated samples shows an extended multiple structure (which can be attributed to 4f^{13} ↔ 4d^9 interaction) instead of a simple spin–orbit doublet for metallic ytterbium. Taking into account the described behavior of the Yb 4d spectra (position of 4d_{5/2} peak and following spectrum profile is quite close to the one corresponding to Yb(III)O_3), we propose that: (i) in the investigated ZnO:Yb samples the majority of ytterbium atoms are Yb^{3+}; (ii) Yb atoms in ZnO matrix are located in the interstitial positions and form near local range YbO_6 clusters like in Yb_2O_3.

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