Zinc Oxide Films Implanted with Rare Earth (RE) for Optoelectronic Applications

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RE-ion doped semiconductor materials are particularly interesting for infrared (IR) emitting optoelectronic devices due to their intra-4*f* shell transitions in the 1.4-1.7 μm range [1-2]. In addition, with visible emission from higher excited levels (green for Er, Yb), they potentially can be used in devices such as optical amplifiers, lasers and optically pumped glass fibers [3]. For this, it is important to understand the RE ions fundamental properties in wide band gap semiconductors, such as their lattice site locations and surroundings, and the optical ion activation mechanisms and emission properties.

The resonant photoemission (ResPES) experiment was used in this project to investigate the ytterbium electronic states and their hybridization with valence electrons of zinc oxide. The measurements were performed at Elettra synchrotron facility (Trieste, Italy). The obtained data were used to establish the correlation between the optical properties and the electronic structure. Both commercial single ZnO crystals and epitaxial ZnO films grown at IP PAS by Atomic Layer Deposition (ALD) technique were under investigations. Ytterbium ions were incorporated into the ZnO matrix via ion implantation and subsequent annealing. We investigated samples containing different quantity of (co-)doped RE atoms (implantation of Yb at the level of 10^{15} and 10^{16} cm^{-2}). Prior to photoemission experiments, Ar^+ sputtering and annealing of the investigated samples up to ~573 K were performed. Photoemission spectra were taken for the photon energy range 180-190 eV i.e. across the ***Yb4d*** – ***Yb4f*** photoionization threshold which allows observation the Fano resonance enhancement from the ***Yb4f*** electron shell.

In ResPES the photon energy is tuned to the inter-ion absorption resonance (in our case Yb $N_{5,4}$) providing an interfering channel for a classical photoelectron excitation. As a result, the photoemission intensity dramatically increases or decreases, depending on the relative amplitudes and phases of the interfering channels. This effect is applied to derive the contributions of the ***Yb4f*** electron states to the valence band of the measured system. We found a inconsiderable but clear resonant enhancement of ***Yb4f*** states to the ZnO:Yb valence band at binding energy about 7.5 eV below the Fermi level. A weak Fano resonance is consistent with a large $4f^{14-\delta}$ occupancy. It was also found that ytterbium 4*d* level shows an extended multiple structure instead of a simple spin-orbit doublet for metallic ytterbium, which allows concluding that majority of ytterbium atoms are bonded to oxygen and indicates that one of the $4f^{14}$ electrons has been promoted to the valence level. This multiple structure can be attributed to $4f^n \leftrightarrow 4d^9$ interaction.

The obtained results enhance our general understanding of RE ions fundamental properties and are of great importance to the development of optical devices as well as devices used in short-range high speed networks operating in the IR.

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