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Structural and Electronic Properties of Ti Doped ZnO: XRD, TEM, EELS and Ab-initio Simulations

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ZnO is a wide used ferroelectric material with a variety of applications. When ZnO is doped by the appropriate transition metal elements, physical properties of the material can be significantly modified [1,2]. Here we present a comprehensive study based on a combination of XRD, optical properties, HRTEM and EELS to investigate the structural and electronic properties of Ti-doped ZnO.

ZnO:Ti thin films were prepared by RF reactive magnetron co-sputtering in Ar/O_2 atmosphere from pure Zinc and Titanium targets (99.99%). Changes of amount of Ti in films were documented by EDS. Structural changes were measured by XRD using two scattering geometries. High-resolution transmission electron microscopy (HRTEM) was carried out on a thin film cross-section samples (XTEM) by Transmission Electron Microscope JEOL JEM 2200FS operated at 200 kV (autoemission Shottky gun, point resolution 0.19 nm) with an in-column energy Ω-filter for EELS/EFTEM.

Pure ZnO wurtzite structure showed strong texture. In this case it is more appropriate to use Seemann-Bohlin asymmetric XRD geometry instead of Bragg-Brentano symmetrical geometry. HRTEM of cross-section thin film sample for 2.4 at% of Ti in ZnO is shown in Figure 1a. As it can be seen from XRD measurements shown in Figure 1b, with increasing Ti content the structure of thin films changes step by step from ZnO to $Zn_xTi_{1-x}O_y$ with corresponding change from more crystalline to less crystalline structure. All quantities show noticeable gap between the films with lower and higher titanium concentration.

The local electronic structure around O and Ti atoms has been studied by the Electron Energy Loss spectroscopy (EELS). In order to understand oxygen K and Ti L2,3 edges we performed ab-initio calculations based on the density functional theory. EELS spectra of O atoms were calculated using full potential linearized augmented plane wave method as implemented in WIEN2k program [3]. For the element specific EELS, we made a 2x2x2 supercell of 42 atoms. It turned out to be important to include core hole effect in the calculations using the final state rule. Direct comparison between theoretical and experimental spectra is shown in Figure 2a. Very good agreement between theory and experiment allows us to analyze various spectral features. Example of two spectra for O_1 and O_2 are shown in Figure 2a with marked oxygen atom positions in Figure 2b. O_1 is sitting close to Ti atoms and leads to the main asymmetric peak in the measured spectra. In addition, the shoulder at 10eV above the Fermi level can be attributed to the O_2 which also is seen by the experiment and it can be attributed to the O-atoms with binding to the Zn. All optical quantities show noticeable change in optical band-gap between the films with lower and higher titanium concentration. This could be considered as some transition from ZnO-like to $ZnTiO_3$-like phase.

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[4] The result was developed within the CENTEM project no. CZ.1.05/2.1.00/03.0088, CENTEM PLUS (LO1402), CEDAMNF reg. no. CZ.02.1.01/0.0/0.0/15_003/0000358, co-funded by the ERDF and COST CZ LD15147.

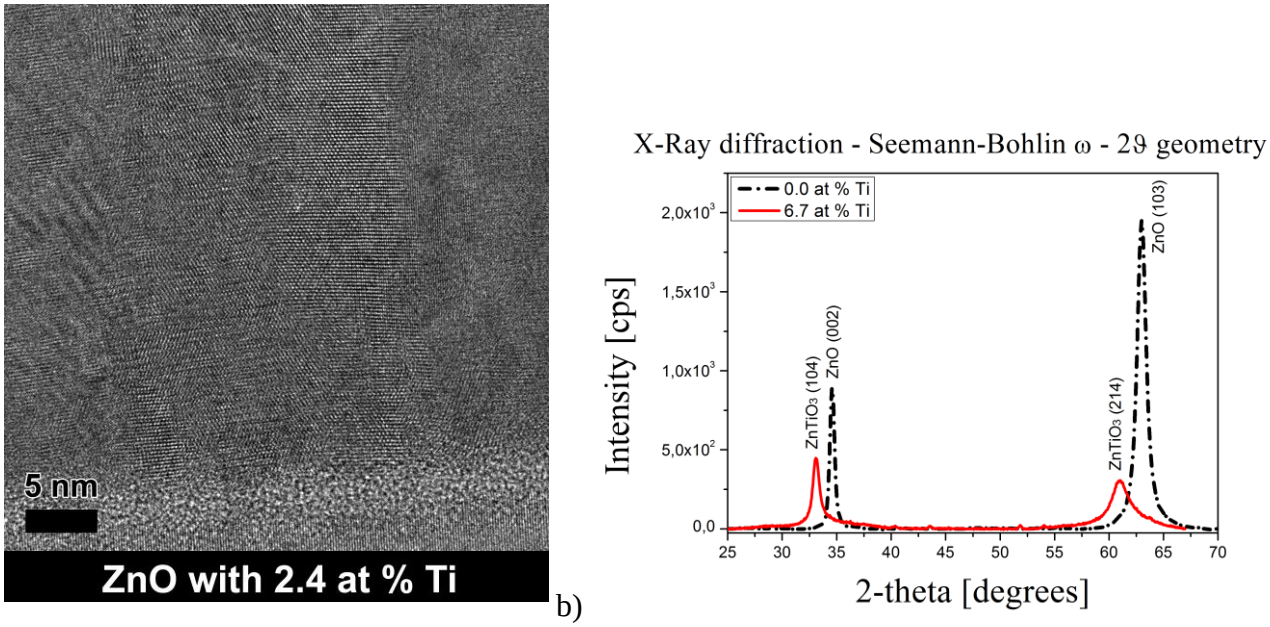

Figure 1. HR-TEM from XTEM ZnO:Ti thin film on Si substrate (a) and XRD measurement of ZnO thin films with 0.1 or 4.2 at % Ti respectively (b).

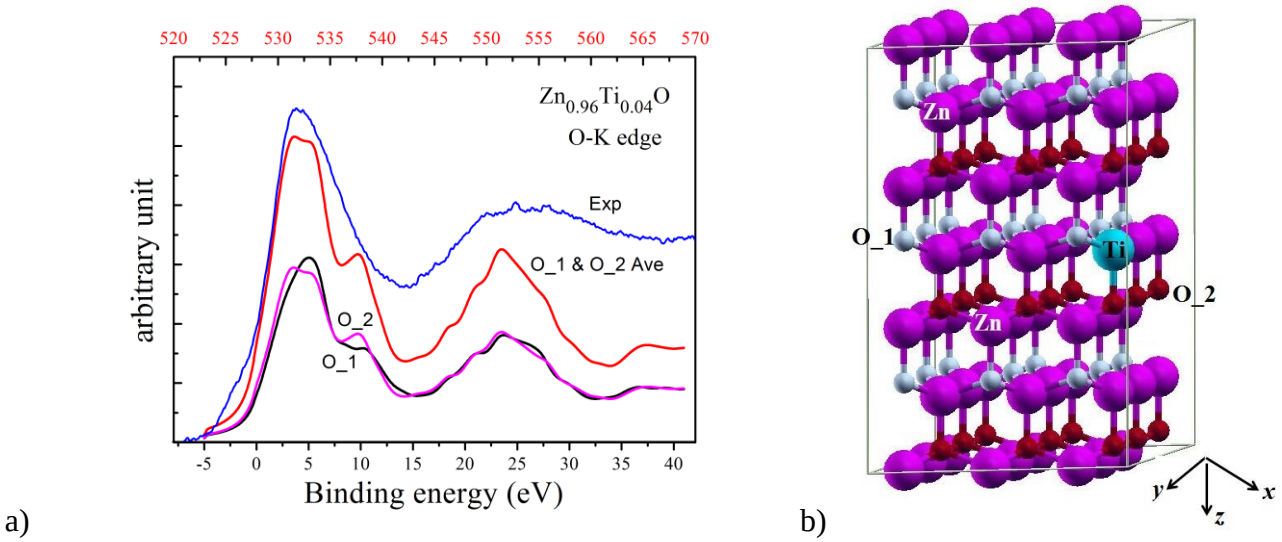

Figure 2. EELS Ab-initio calculations of O-edge from ZnO with 2.4 at % Ti together with measured experimental data (a). Sketch of the supercell used for EELS calculation (b).

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