Zinc oxide films grown at low temperature – electrical properties and hydrogen contamination

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The origin of the commonly observed high background donor conductivity of zinc oxide has been a subject of extensive research. Theoretical calculations supported by electron paramagnetic resonance experiments show that native points defects alone cannot be responsible for a high electron conductivity, because V_o is a deep donor while the energy formation of Zn_i is relatively high [1]. Based on both theoretical and experimental studies hydrogen is widely regarded as a dominant donor in this material [2-3].

However, this model does not work for zinc oxide films deposited at the low temperature range (200^{o}C and below) [4-5]. For such films the scaling of electron concentration with deposition temperature is observed [4-5], i.e. electron concentration in ZnO films deposited at 100^{o}C is at the level of 10^{16} cm^{-3} and is 3 orders of magnitude lower than electron concentration observed when the growth temperature achieves 200^{o}C. On the other hand, electron concentration is accompanied by a high hydrogen content as measured by SIMS and both this quantities anti-correlate [4]. Moreover, hydrogen content considerably exceeds electron concentration.

In the presented work we investigated a series of thin ZnO films deposited at temperature between 100 and 200^{o}C by Atomic Layer Deposition with diethylzinc and deionized water precursors. Our detailed X-ray Photoelectron Spectroscopy studies show the increase of the oxygen to zinc ratio when deposition temperature drops from 200 to 100^{o}C. The Rutherford Backscattering (RBS) measurements confirm this result. Rapid Thermal Annealing (RTA) performed in an oxygen atmosphere leads to the slight lowering of the hydrogen content, but it still remains at a very high level of 10^{20} cm^{-3}.
In temperature dependent photoluminescence (PL) spectra taken in the range of 10 – 300K we observe a big difference between *as grown* and annealed samples. In both cases the peak related to the donor bound exciton D^{o}X at energy 3.367 eV (with FWHM = 8 meV) is observed at 10K. However, the dominant emission appears at 3.322 eV. Phonon repetition have been observed as well. After 3 min. RTA process all PL features become considerable sharper and the intensity of the D^{o}X related emission considerably increases. The origin of PL peaks has been analyzed.

The presented data suggest that low deposition temperature provides oxygen-rich conditions in which lower concentration of oxygen vacancies is created. The oxygen vacancies decorated with hydrogen seem to act as shallow donors in this material, while a main part of hydrogen remains electrically inactive.

Acknowledgements. The work was supported by the Polish National Science Centre (NCN) Project based on the decision No. DEC-2012/07/B/ST3/03567. The Author EP was supported by the NCN Project based on the decision No. DEC-2013/09/D/ST3/03750.

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