Photo-ESR and spin-echo photo-ESR investigations of ZnO:Co

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Semiconducting materials showing a room temperature ferromagnetic (RT FM) response are required for spintronics applications. This fact explains a concentrated research of ZnCoO, for which carriers mediated RT FM was theoretically predicted. To realize this Co should stay in 2+ charge state (expected when Co substitutes zinc in ZnO) in heavily doped samples. Recharging to 1+ or 3+ should be excluded for electrons or holes mediated FM. This explains motivation of the present work.

For ZnCoO alloys a strong absorption band appears with onset at about 2.4 – 2.6 eV. Origin of this absorption in ZnCoO was discussed in several works. The broad absorption band was related either to Co charge transfer transitions (Co photo-ionization) or to excitation of surface plasmons resonances in nanometer size metallic Co inclusions. The first interpretation is in line with the results of photo-conductivity measurements. It was proposed that the broad absorption band is the result of competition of two photo-ionization processes – Co 2+ to 3+ (at a lower energy) and 2+ to 1+ (close to the band-to-band transition), the latter overlapping with a process of photo-generation of Co localized excitons.

The origin of the absorption band is cleared out in the present work, based on the results of electron spin resonance (ESR), spin-echo ESR and photo-ESR investigations. ESR investigations were performed for bulk samples with a relatively low Co concentration – less than 10^{17} cm^{-3}. Only in this case we could detect a photo-sensitive ESR signal of Co^{2+} ions. Conventional photo-ESR experiment is supported by the results of pulsed ESR (spin-echo) study. Photo-sensitivity of spin echo Co^{2+} ESR signal is studied. In parallel to photo-sensitivity of Co^{2+} ESR signal light sensitivity of ESR signal of shallow donors was also examined. This allowed to determine which carriers are photo-generated upon Co photo-ionization.

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