MAGNETIC PROPERTIES OF Co, Al AND Mn, AL Co-DOPED ZnO FILMS

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ZnO films, co-doped with Co and Al or Mn, Al, were grown from $Zn_{0.945}Mn_{0.05}Al_{0.005}O$ or $Zn_{0.945}Co_{0.05}Al_{0.005}O$ ceramic targets, respectively, on a-plane sapphire substrates by means of pulsed laser deposition (PLD) using a KrF excimer laser. The growth and sample parameters are given in the table.

Sample	Target composition	$p(O_2)$ [mbar]	Substrate T [ºC]	No. of pulses	t [nm]	n (5 K) [cm^{-3}]
TF1	$Zn_{0.945}Mn_{0.05}Al_{0.005}O$	4×10^{-5}	343	1500	36	2.13×10^{20}
TF2	$Zn_{0.945}Mn_{0.05}Al_{0.005}O$	0.005	726	30300	782	9.96×10^{18}
TF3	$Zn_{0.945}Co_{0.05}Al_{0.005}O$	4×10^{-5}	450	1800	43	1.42×10^{20}
TF4	$Zn_{0.945}Co_{0.05}Al_{0.005}O$	0.001	726	30300	685	4.35×10^{18}

The composition of the films was measured by combined Rutherford backscattering spectrometry (RBS) and particle induced X-ray emission (PIXE). The Al content in the films could not be determined, due to the underlying Al_2O_3 substrate. The Co and Mn contents in the films turned out to be larger than in the corresponding PLD targets and amounted to about 9 at.%. The crystal structure of the films was characterized by X-ray diffraction (XRD) and reciprocal space mapping (RSM), which indicated the highly c-axis-oriented ZnO films. No second phases, especially, no Co nanocrystals were detected even for a very long signal accumulation. No magnetic resonance trace of Co nanocrystals [2] was detected, either.

The critical electron concentration, at which the metal to insulator transition occurs, was estimated for a Co doped film to be $n_c = 4\times10^{19}$ cm^{-3} [1]. Thus, we have a film with $n < n_c$ and another one with $n > n_c$ for each type of doping. A possible ferromagnetic response of charge carriers in ferromagnetic semiconductors is the anomalous Hall effect (AHE). The Mn doped films and the Co doped film with the larger n show no AHE. However, TF4 shows an AHE at 5 K. TF4 also exhibits weak ferromagnetism at 5 K in SQUID measurements.

The magnetic resonance (EPR and FMR) and SQUID magnetization measurements revealed that the Mn doped ZnO samples were clearly paramagnetic, the Mn ions being substitutional on Zn sites. On the other hand, the EPR signature of substitutional Co^{2+} on Zn sites was not found in the Co doped samples. Instead, a broad resonance signal with $g_{eff} > 2$ was recorded, which behaves as FMR of a magnetic film in the case of non-aligned magnetization. Also, the magnetoresistivity (MR), Hall effect, and SQUID measurements point to some kind of ferromagnetic order in the Co doped samples. However, there is no evidence of carrier mediated ferromagnetism, since the sample exhibiting larger magnetic order (TF4) is the one with lower carrier concentration and the Co is not mainly incorporated as substitutional Co^{2+} in the ZnO lattice. We believe that the formation of small precipates or spinodal decomposition is more likely to be the origin of the observed weak ferromagnetism.

[1] Q. Xu et al., Phys. Rev. B **73**, 205342 (2006).

[2] H.J. von Bardeleben et al., Appl. Phys. Lett. **93**, 142505 (2008).