Local structure investigation of transition metal doped ZnO and TiO_2 thin films by X-ray absorption spectroscopy

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Spintronics is an emerging field where the spins of electrons of a material are used simultaneously with their charges for the realisation of more efficient and advanced devices. Dilute magnetic semiconductors which are formed by incorporating small amount of transition metals (TM) in semiconductor hosts are considered to be potentially important materials for spintronics applications. Following the theoretical prediction by Dietl et. al. about room temperature ferromagnetism (RTFM) in 5%Mn doped ZnO, (Dietl, Ohno et al., Science 287, (2000) 5455) not only TM doped ZnO but other doped oxide semiconductors (DMS) such as SnO_2, TiO_2 and HfO_2 were also explored both experimentally as well as theoretically for the RTFM. The origin of ferromagnetism in DMS is still an unresolved question with contradictory reports that it is intrinsic in nature due to substitution of transition metal at host site or presence of defects such as interstitial/vacancy or it is extrinsic in nature due to presence of separate magnetic phase or metallic cluster are available in the literature.

In the present work the origin of room temperature ferromagnetism in TM (Mn, Co, Fe and Ni) doped ZnO and TiO_2 thin films have been investigated extensively using X-ray Absorption Spectroscopy (XAS) studies, comprising of both XANES and EXAFS measurements. The samples have been deposited with different doping concentration (1-10%) using an in-house built magnetron sputtering system and the XAS measurements at O K edge, Zn K edge and TM K&L edges have been carried out at BL-01 (soft X-ray) and BL-09 (hard X-ray) EXAFS beamlines, Indus-2, RRCAT, Indore, India.

TM doped ZnO thin films show room temperature ferromagnetism (RTFM) with increasing saturation magnetization with increase in TM doping concentration for Mn, Co and Fe doped ZnO and decreasing saturation magnetization with increase in doping concentration for Ni doped ZnO thin films. XANES and EXAFS results show that for all doping variants, TM atoms replace Zn atoms in ZnO lattice for lower doping concentrations, however for higher doping concentrations metallic clustering is observed for Ni and Mn doped ZnO. Combining the results obtained from XAS studies with that obtained from magnetic measurements, it has been observed that the presence of ferromagnetism in TM doped ZnO is due to the presence of defect such as oxygen vacancy for Mn and Ni doped and Zn vacancy for Fe doped ZnO. The presences of oxygen vacancies are further confirmed by using photoluminescence studies and depositing the films using excess oxygen partial pressure. Unlike single phase TM doped ZnO, Mn and Co doped TiO_2 thin films shows mixture of anatase and rutile phases for doped samples even though the undoped TiO_2 is found to be present in pure anatase phase. These films show RTFM originated from the presence of oxygen vacancies which have been observed in O K-edge, Ti and Mn/Co K edge XAS measurements. In both the cases the presence of vacancies has also been confirmed by comparing the XANES data with simulated results using FEFF 9.0. The presence of defects such as oxygen vacancy or metal interstitials in both doped ZnO and TiO_2 films support the theory that ferromagnetism in DMS arises due to defect mediated exchange interaction between TM ions.

References: A.K. Yadav et. al., AIP Advances 5 (2015) 117138; RSC Adv. 6(2016) 74982; Chem. Select. 2 (2017) 11012-11024 and Thin Solid Films 647 (2018) 70.