Room-temperature ferromagnetism of Cu-doped ZnO fims probed by soft X-ray magnetic circular dichroism

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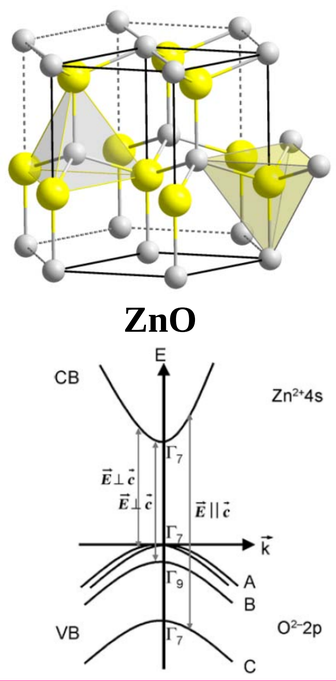
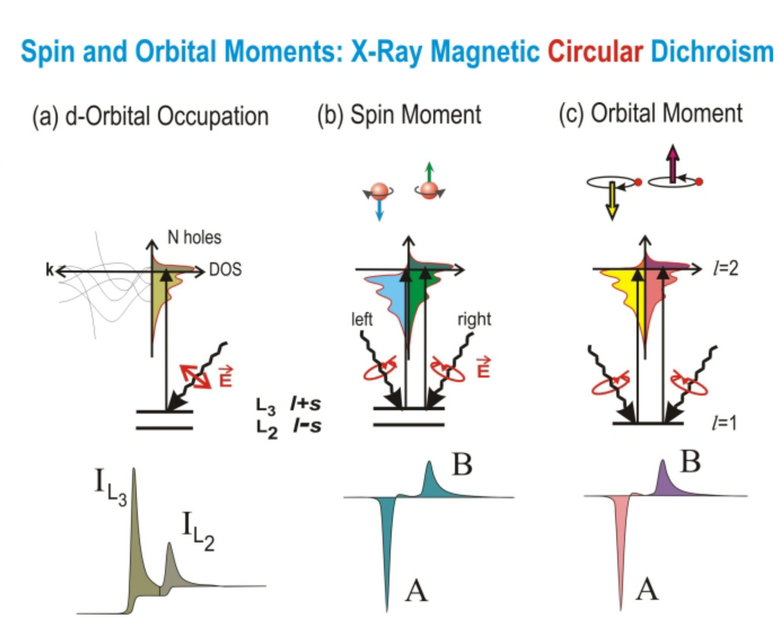
Introduction

Spintronics, which exploits the spin property of electrons, is an emerging paradigm for the next-generation electronic devices. Diluted magnetic semiconductors (DMSs) combine the electronic functionality of conventional semiconductors and the non-volatility of ferromagnetism, representing one of the most promising route to the realization of room-temperature spintronic devices. However, the lack of direct experimental evidence for the intrinsic ferromagnetism in DMS to date has rendered the nature of the observed magnetic phenomenon highly controversial. The element-specific softy x-ray magnetic circular dichroism (SXMCD) is regarded as the litmus test for any intrinsic ferromagnetism.



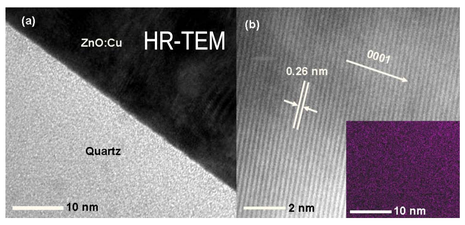


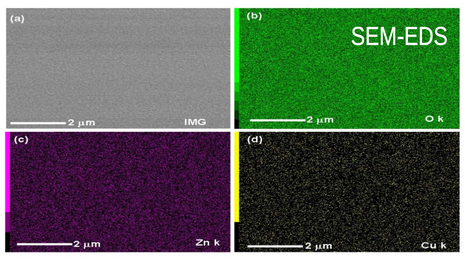
I. Experimental

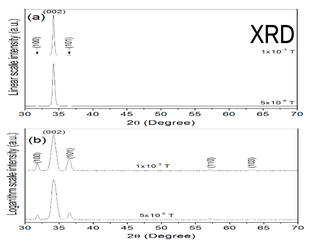
- Samples:
  Cu doped ZnO thin films (50 nm) were grown by PLD using mixed ZnO and CuO powder (99.99%)
  Sample 1: undoped ZnO (reference)
  Sample 2: 2%at ZnO:Cu at O rich pressure (1×10^{-3} torr)
  Sample 3: 2%at ZnO:Cu at O poor pressure (5×10^{-6} torr)

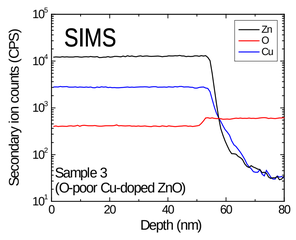
- Characterizations:
  - ➢ Crystal Structure and morphology: XRD, TEM, SEM, EDS, SIMS
  - ➢ Electronic Structures: XPS, XAS, PL, Raman
  - ➢ Magnetic Properties: SQUID, SXMCD

II. Film Structure and Morphology



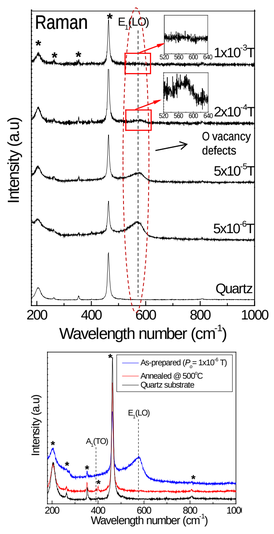


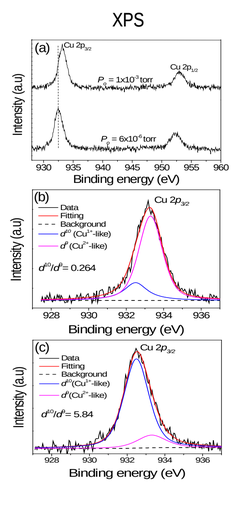


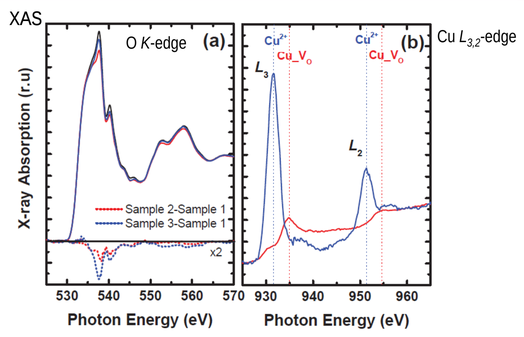


Good film crystallinity and homogeneous distribution of all elements.

III. Characterization of Defects

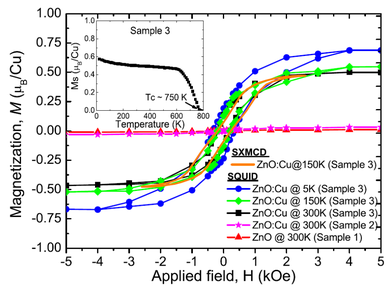


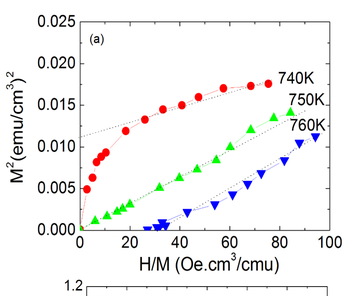


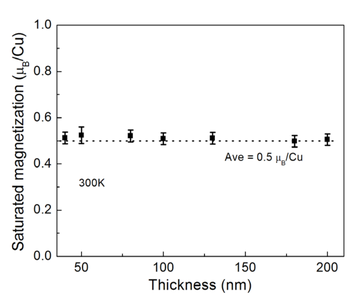


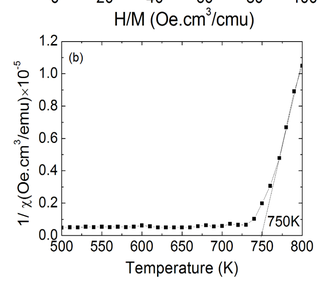
- ➢ Significant amount of oxygen vacancies (V_O) present in sample 3 (O-poor).
- ➢ Regular Cu^{2+} ($3d^9$) is dominant in sample 2 (O-rich), while Cu_V_O (mixed $3d^9+3d^{10}$) is dominant in sample 3 (O-poor) due to the doping effect of V_O.

III. Magnetic Properties (SQUID)



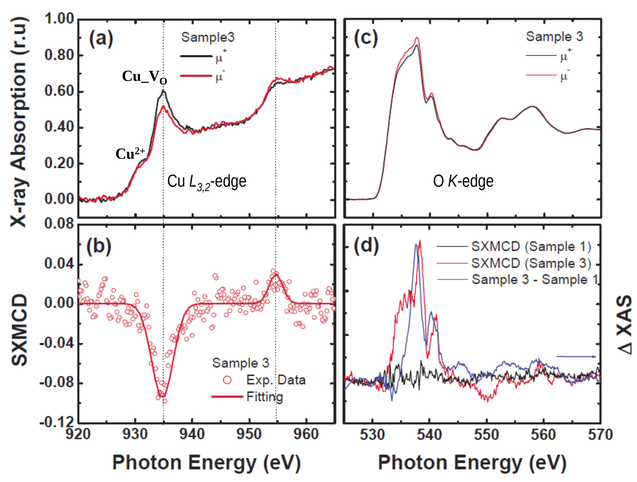






- ➢ Undoped (sample 1) and Cu-doped @ O rich condition (sample 2) are non-magnetic.
- ➢ Cu-doped @ O poor condition (sample 3) shows strong room-temperature ferromagnetism with Currie temperature of 750 K.

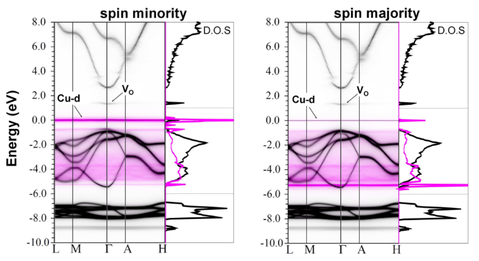
IV. SXMCD



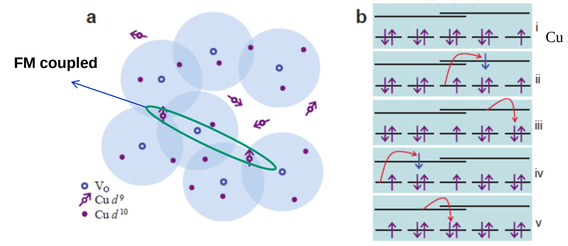
- ➢ Strong XMCD signals occur at both Cu *L*-edge and O *K*-edge only for the FM sample 3—consistent with SQUID.
- ➢ The XMCD at Cu *L*-edge centralized only at the 935 eV peak (Cu_O_V), while at the *regular* Cu^{2+} site is negligible
- ➢ Antiparallel alignment of the magnetic moments between Cu and O sites.
- ➢ The XMCD signal at O K-edge closely resemble the shape of ΔXAS, indicating close correlation of magnetism and O_V orbital.

V. Theoretical Calculations & Model

Band structures calculation (LDA+*U* with Wannier Function)



Indirect "double-exchange" model



- ➢ Innovated First-principle calculations with disorder visualize the large sized V_O orbital residing within the host band gap and reveal incomplete spin polarization in the Cu 3*d* bands.
- ➢ The local magnetic moments of Cu in the vicinity of the V_O orbital are ferromagnetically coupled through a "double-exchange" like effect mediated by the overlapping vacancy orbitals.

Conclusions

- ➢ **Cu (2%) doped ZnO under O-deficient condition displays ferromagnetism with T_c of 750 K.**
- ➢ **The intrinsic band polarization in Cu-doped ZnO is successfully probed by the SXMCD at both Cu and O states.**
- ➢ **The observed FM is proposed to originate from the alignment of the localized large moments of Cu in the vicinity of oxygen vacancies mediated by the large-sized vacancy orbitals through an indirect "double-exchange" like effect.**

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