Giant magneto-electric coupling in 100 nm thick Co capped by ZnO nanorods

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Supplementary Information

Experimental Details

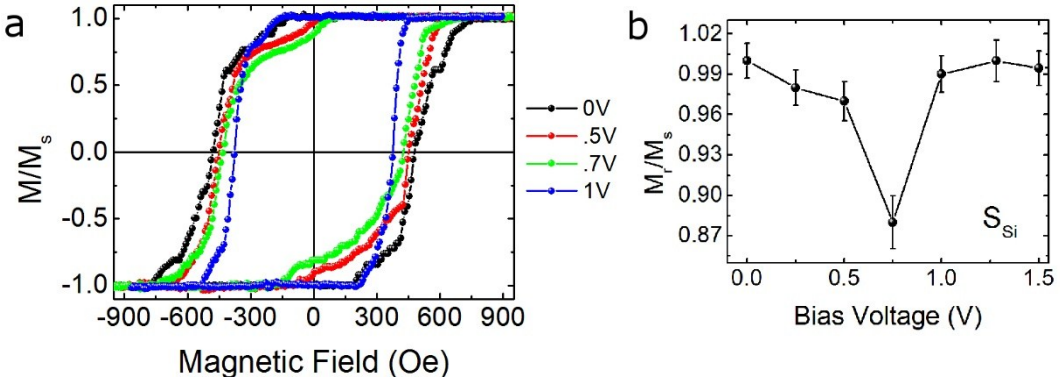
The system has been fabricated with a radiofrequency (RF) magnetron sputtering system, depositing simultaneously on polished polycrystalline Al_2O_3 (2 × 2 mm^2) and thermally oxidised Si-(100) substrates (3 × 3 mm^2). A Co layer, 100 nm thick, has been directly deposited on the substrates at room temperature (RT). Subsequently, a very thin and non-continuous Sn layer (a few angstroms thick) has been deposited. Sn acts as a catalyst for the growth of the ZnO NRs. The NRs have been fabricated at 400°C, via a self-assembly process, with a RF power of 150 W at 10^{-2} mbar and a growing time of 300 s.[1-3] A schematic picture of the layer stack is reported in Fig. 1a of the main text. On top of Co, a layer of ZnO forms having a columnar/granular structure.[2] From this ZnO layer, the nanorods spontaneously develop, with the length and width determined by the sputtering deposition time. X-

ray diffraction data indicate that Co grew in its hcp structure, while ZnO shows a hexagonal wurtzite structure,[1] textured along the (001) direction.

The morphology of the multilayer has been investigated in cross section by a ZEISS Supra 40 field emission gun (FEG) scanning electron microscope (SEM) equipped with a Gemini column and an In-lens detector yielding an increased signal-to-noise ratio. Images were recorded collecting either secondary or backscattered electrons generated at 5 keV accelerating voltage.

Superconducting quantum interference device (SQUID) measurements have been carried out at 100 and 300 K in order to study the magnetic properties of the system with bulk sensitiveness.

Figure SI1



(a) Hysteresis loops measured in longitudinal geometry on S_{Si} sample and (b) the corresponding M_r/M_s ratio as a function of the applied voltages in the range 0 – 1 V. The error bars have been evaluated from 15 hysteresis loops acquired at each voltage step.

X-ray Absorption Near Edge Spectroscopy (XANES) - Unpoled Sample

XANES spectra of the unpoled S_{Al} sample, acquired at the O *K*, Co and Zn $L_{2,3}$ edges are reported in Fig. SI2.

The spectra at the O *K* edge (Fig. SI2a) are characterised by two main features A_1 and A_2 in the 530-539 eV range, which stem from the hybridization of O 2*p* with dispersive Zn 4*s* and 4*p* states. The most intense A_2 peak is due to the transition of O 1*s* to more localised O 2*p* states.[4-6] The A_1 pre-edge peak is sensitive to the formation and change in the amount of O vacancies (V_O) as well as to the Co/ZnO interdiffusion, which induces unoccupied 3*d* states inside the ZnO energy band gap.[7] Features A_3 and A_4 in the 539-545 eV range can be ascribed to the hybridization of O 2*p* – Zn and Co 4*p* states, while those above 545 eV are assigned to O 2*p* – Zn 4*d* states.[8] The absence of sharp peak in the low energy region (below 530 eV), typical of 3*d* oxides, is due to the fully-occupied Zn d^{10} configuration in ZnO, and the consequent absence of O 2*p* and Zn 3*d* hybridised states.[9] In Co-doped ZnO compounds, this low-energy peak can also arise as a consequence of Co/ZnO intermixing which allows transitions from O 2*s* to hybridised O 2*p* – Co 3*d* states.[7,10-11] The absence of this feature, in particular in the spectra corresponding to α position (defined in Fig. 5a of the main text), suggests that the Co/ZnO interdiffusion is below the detection limit already at the Co/ZnO interface.

The O *K* spectrum acquired in α-point differs from that in β-point, characterised by the presence of ZnO nanorods. Indeed, the spectra for β have well defined and narrower spectral features, probably due to the contributions which arise from the nanorod tips and sidewalls,[12] contributions that are totally absent in point α. This is also in agreement with the increase in point β of the relative intensity of the most

intense peak A_2 with respect to A_1, A_3 and A_4 features, an increase that is normally ascribed to ZnO nanostructures.[8,13-14]

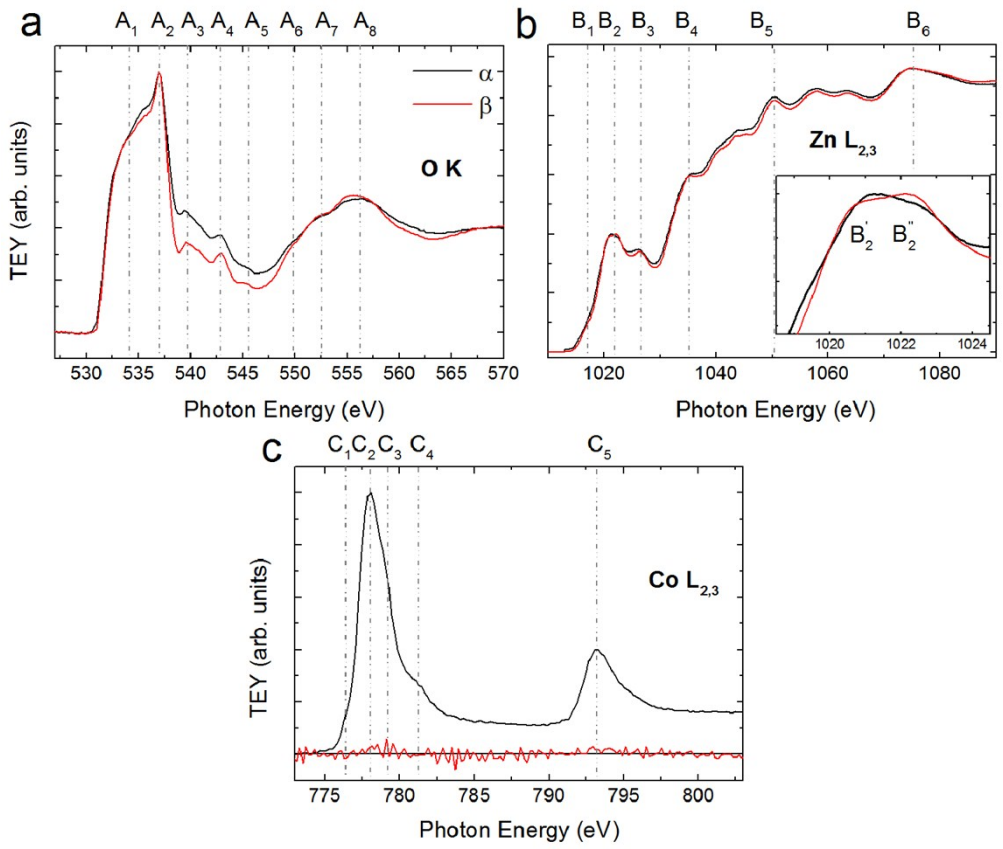


Figure SI2. XANES spectra acquired in point α and β indicated in Fig. 5a of the main text at (a) O *K* edge, (b) and (c) $L_{2,3}$ edges of Zn and Co, respectively.

Considering the difference in the image intensity scale in Fig. 5a of the main text, position β is clearly in the region where the ZnO are unaffected by the presence of Co, while the α-spectrum represents the Co/ZnO interface, affected by a huge strain due to the lattice mismatch.

Figure SI2b represents Zn $L_{2,3}$-edge XANES spectra in the different sample positions. The Zn 3*d* orbital is fully occupied, and the lowest unoccupied state is Zn 4*s*. Therefore, the spectral features between 1020 and 1035 (B_1-B_3) are associated to transition from Zn 2*p* to 4*s* state as well as to antibonding 3*d* state.[12-15] The spectrum

acquired for β differs from the α-spectrum. The inset shows the enlargement of the B_2 peak. This intense L_3 edge peak is constituted by two spectral features indicated as B_2' and B_2''. The nanorods (position β) give rise to a shift of their positions towards slightly lower energy and to an inversion of the B_2' and B_2'' relative intensities.[8]

XANES spectra acquired at the Co $L_{2,3}$ edges (Fig. SI2c) are ascribed to metallic Co. The ZnO nanorods in point β prevented the detection of the Co signal. Indeed, as measurements were performed in total electron yield (TEY) mode, penetration depth was of few nm; thus, the Co/ZnO interface was too buried to be detected. On the contrary, in α point the absence of ZnO nanorods allows measuring the Co edges.

Figure SI3

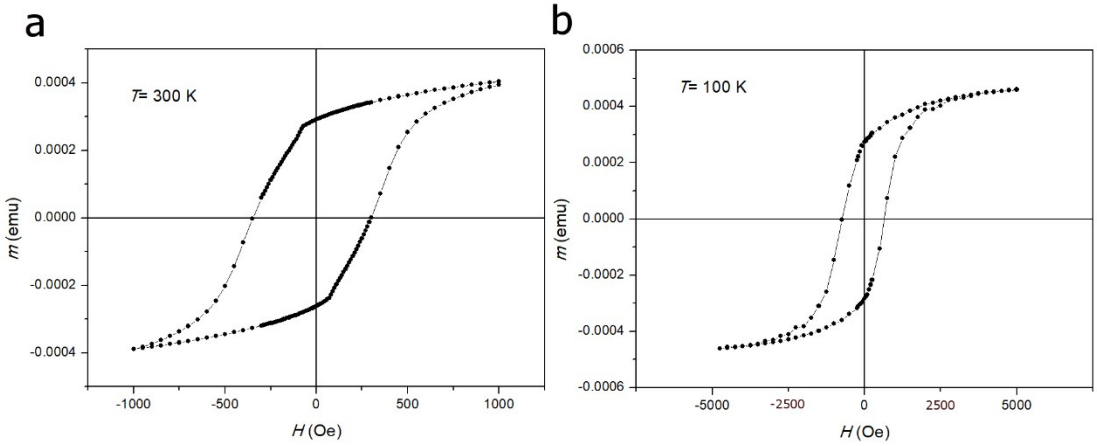


Figure SI3. SQUID hysteresis loops for S_{Al} acquired at (a) 300 and (b) 100 K.

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