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


*CNR-Istituto Officina dei Materiali IOM, s.s. 14 km 163.5, 34149, Trieste, Italy
b University of Nova Gorica, Vipavska Cesta 11c, Ajdovščina, 5270, Slovenia
c Università degli Studi di Trieste, Via A. Valerio 2, 34127, Trieste, Italy.
d Elettra Sincrotrone di Trieste, s.s. 14 km 163.5, 34149, Trieste, Italy
e Università degli Studi di Parma, Parco Area delle Scienze 7/A, 43124, Parma, Italy.
*E-mail: roberta.ciprian@elettra.eu

Supplementary Information

Experimental Details

The system has been fabricated with a radiofrequency (RF) magnetron sputtering system, depositing simultaneously on polished polycrystalline Al₂O₃ (2 × 2 mm²) and thermally oxidised Si-(100) substrates (3 × 3 mm²). 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,\textsuperscript{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](image)

(a) Hysteresis loops measured in longitudinal geometry on S\textsubscript{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 SAl sample, acquired at the O K, Co and Zn L\textsubscript{2,3} edges are reported in Fig. SI2.

The spectra at the O K edge (Fig. SI2a) are characterised by two main features A\textsubscript{1} and A\textsubscript{2} in the 530-539 eV range, which stem from the hybridization of O 2p with dispersive Zn 4s and 4p states. The most intense A\textsubscript{2} peak is due to the transition of O 1s to more localised O 2p states.\textsuperscript{4-6} The A\textsubscript{1} pre-edge peak is sensitive to the formation and change in the amount of O vacancies (V\textsubscript{O}) as well as to the Co/ZnO interdiffusion, which induces unoccupied 3d states inside the ZnO energy band gap.\textsuperscript{7} Features A\textsubscript{3} and A\textsubscript{4} in the 539-545 eV range can be ascribed to the hybridization of O 2p – Zn and Co 4p states, while those above 545 eV are assigned to O 2p – Zn 4d states.\textsuperscript{8} The absence of sharp peak in the low energy region (below 530 eV), typical of 3d oxides, is due to the fully-occupied Zn d\textsuperscript{10} configuration in ZnO, and the consequent absence of O 2p and Zn 3d hybridised states.\textsuperscript{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 2s to hybridised O 2p – Co 3d states.\textsuperscript{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,\textsuperscript{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 S12. XANES spectra acquired in point $\alpha$ and $\beta$ 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 $\beta$ is clearly in the region where the ZnO are unaffected by the presence of Co, while the $\alpha$-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 B2 peak. This intense L3 edge peak is constituted by two spectral features indicated as B2 ’ and B2 ’’. The nanorods (position β) give rise to a shift of their positions towards slightly lower energy and to an inversion of the B2 ’ and B2 ’’ relative intensities.8

XANES spectra acquired at the Co L2,3 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 SAl acquired at (a) 300 and (b) 100 K.
References

(1) R. Ciprian, C. Baratto, A. Giglia, K. Koshmak, G. Vinai, M. Donarelli, M. Ferroni, M.,

(2) R. Ciprian, P. Torelli, A. Giglia, B. Gobaut, B. Ressel, G. Vinai, M. Stupar, A. Caretta,
G. De Ninno, T. Pincelli, B. Casarin, G. Adhikary, G. Sberveglieri, C. Baratto, M.
Malvestuto, RSC Adv. 2016, 6, 83399.


(4) S. Krishnamurthy, C. McGuinness, L. S. Dorneles, M. Venkatesan, J. M. D. Coey, J. G.
Lunney, C. H., Patterson, K. E., Smith, T. Learmonth, P.-A. Glans, T. Schmitt, J.-H. Guo,


(6) C. Guglieli, E. Céspedes, A. Espinosa, M. Á. Laguna-Marco, N. Carmona, Y. Takeda,
2014, 24, 2094.


(8) P. Sundara Venkatesh, C. L. Dong, C. L. Chen, W. F. Pong, K. Asokan, K. Jeganathan,

Lett. 2007, 91, 162503.

(10) S. Kumar, Y. J. Kim, B. H. Koo, H. Choi, C. G. Lee, S. K. Sharma, M. Knobel, S.

(11) N. Srinatha, B. Angadi, K. G. M. Nair, N. G. Deshpande, Y. C. Shao, W.-F. Pong, J.

