Voltage-induced Interface Reconstruction and Electrical Instability of the Ferromagnet-Semiconductor Device

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Using x-ray magnetic spectroscopy with in-situ electrical characterizations, we investigated the effects of external voltage on the spin-electronic and transport properties at the interface of a Fe/ZnO device. Layer-, element-, and spin-resolved information of the device was obtained by cross-tuning of the x-ray mode and photon energy, when voltage was applied. At the early stage of the operation, the device exhibited a low-resistance state featuring robust Fe-O bonds. However, the Fe-O bonds were broken with increasing voltage. Breaking of the Fe-O bonds caused the formation of oxygen vacancies and resulted in a high-resistance state. Such interface reconstruction was coupled to a charge-transfer effect via Fe-O hybridization, which suppressed/enhanced the magnetization/coercivity of Fe electronically. Nevertheless, the interface became stabilized with the metallic phase if the device was continuously polarized. During this stage, the spin-polarization of Fe was enhanced whereas the coercivity was lowered by voltage, but changes of both characteristics were reversible. This stage is desirable for spintronic device applications, owing to a different voltage-induced electronic transition compared to the first stage. The study enabled a straightforward detection of the spin-electronic state at the ferromagnet-semiconductor interface in relation to the transport and reversal properties during operation process of the device.

Ferromagnetic materials have a non-volatile nature at room temperature, but their magnetization can be switched reversibly with unlimited times. On the other hand, the electrical properties of semiconductors can be effectively altered by doping photons and electric fields, which provide amplification and transistor actions. Due to the impressive technological advantages of these two materials, their combination, called spintronics, emerges with an exploding technological impact. To make the control of magnetization fully compatible with current semiconductor devices, using external voltage has become a desirable means to control magnetization¹,². Extensive studies have demonstrated that voltage can manipulate magnetic phase transformation³–⁵, exchange bias⁶,⁷, spin polarization⁸–⁹, and magnetic anisotropy¹⁰–¹². These findings demonstrate the advance in spintronics because of the possibility of devices operating with reduced power consumption, and the compatibility of voltage-controlled devices with semiconductor integrated circuits. Although these findings have been recognized with great excitement, the underlying physics is an important yet unsolved problem, especially from the viewpoint of electronic interactions that regulate the magnetic ordering. A general explanation for the phenomena is the change in the occupation of ferromagnetic (FM) 3d orbital, due to the band-filling effect¹⁶,¹³,¹¹. Despite many interpretations have been provided, evidence for the voltage-induced change in the spin-polarized electronic state is rarely reported due to experimental difficulty¹⁴–¹⁸. We hereby demonstrate the use of a technique on a ferromagnet/semiconductor device that is sensitive to the real-time change of the electronic state of FM with respect to the magnetic and transport properties of the device. By simultaneously operating x-ray magnetic spectroscopy and the voltage-control characterizations upon a Fe/ZnO device, we independently probed the behaviors of the ferromagnetic layer (Fe) out from the whole device during voltage application (including the spin electronic state, etc.)
hysteresis, and anisotropy magneto-resistance). Such an element-resolved approach enabled a straightforward understanding of the phenomenon from the viewpoint of electronic states, thus making this work unique from previous studies that mainly approach the subject from a macroscopic setting. Of particular importance, the measurements were carried out in an ultra-high vacuum (UHV) condition (<10^{-9} Torr). Thus, we can rule out the possibility that the ambient condition may contribute to interfacial hybridization during voltage application. Hence, the observed modification of interfacial hybridization, along with the magnetic evolution, can be exclusively ascribed to the voltage effect alone. We observed, on a straightforward fashion, a Fe oxidation $\rightarrow$ metallic transition arising from 3$d$ electronic redistribution with increasing voltage. The electronic transition resulted from a Fe-O charge-transfer effect is responsible for the change of Fe's magnetization and coercivity ($H_c$), both of which appeared reversible below a certain threshold voltage. Taking advantage of the helicity-dependent x-ray, the occupations of the majority- and minority-spin states of Fe, in conjunction with voltage-induced hybridization, were also explored. In an effort to rationalize and predict the behavior of voltage-controlled magnetism, this work delivers a close understanding of the local moments and electronic interactions from which this phenomenon is derived.

**Results and Discussions**

Figure 1(a) shows a high resolution transmission electron microscopy (TEM) image of the Au (2 nm)/Fe (3 nm)/ZnO (300 nm) hetero-structure device. Figure 1(b) shows the x-ray diffraction (XRD) pattern of the sample with ZnO (002), Fe (110) and Al$_2$O$_3$ (006) indices. Figure 1(c) shows the time-dependent resistance of the device with varying applied voltages (30, 70, 90 and 110 V). Figure 1(d) shows the ex-situ- and in-situ treatment-dependent $H_c$ with varying voltages (MOKE). Inset of (b) shows zoom-in information of the Fe index.

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Figure 1. Structural, magnetic and electrical properties of the device. (a) Cross-sectional HRTEM image and (b) XRD pattern of the Au/Fe/ZnO hetero-structure device. (c) Time-dependent resistance of the device with 30, 70, 90, and 110 V treatments. (d) Ex-situ- and in-situ treatment-dependent $H_c$ with varying voltages (MOKE). Inset of (b) shows zoom-in information of the Fe index.
The resultant magnetic properties were first examined by magneto-optic Kerr effect (MOKE). For ex-situ treatment, the voltage was applied on the device for 5 min, and data were collected after the removal of the applied voltage. Ex-situ treatment reflects the change of magnetic state of the device at the early stage of operation, during which the device underwent an irreversible, electrically unstable transition. In contrast, for in-situ treatment, data were collected after an 8-min operation, and the voltage was continuously supplied during data collection. In-situ treatment refers to the real-time change of magnetic state of the device for constant operation. During this process, the device entered into an electrically stable state. Figure 1(d) presents the ex-situ and in-situ treatment-MOKE results with voltage-dependency, where coercivity ($H_c$) in ex-situ treatment is found to increase with the applied voltage. However, the in-situ treated sample displays an opposite voltage dependency in $H_c$. The details of the ex-situ- and in-situ treatment- hysteresis loops are demonstrated in Fig. S1 (ESI). Apparently the two states correspond to two different magnetic behaviors in response to the applied voltage.

We then focus on the x-ray characterizations with in-situ electrical measurements in order to explore the mechanism responsible for the observed phenomenon. Figure 2(a) illustrates the geometric layout of the Hall bar device with respect to x-ray measurements (XAS/XMCD) under the applied voltage (polarity is shown). For x-ray measurements, voltage was applied along vertical direction of the device (CPP). While for AMR measurements, voltage was applied along horizontal direction of the device (CIP). (b) The real configuration of employed circuits on the device and the x-ray sample holder. (c) Illustration for the tuning of x-ray collection mode in relation to sample profiling (i.e., TEY and TFY are surface and bulk sensitive, respectively). The zoom-in figure of (b) shows the details (pattern linewidth, connection, and x-ray hitting spot) of the device layout on the x-ray holder.

Figure 2. In-situ x-ray setup and device layout. (a) Illustration for the geometric layout of the Hall bar device with respect to x-ray measurements (XAS/XMCD) under the applied voltage (polarity is shown). For x-ray measurements, voltage was applied along vertical direction of the device (CPP). While for AMR measurements, voltage was applied along horizontal direction of the device (CIP). (b) The real configuration of employed circuits on the device and the x-ray sample holder. (c) Illustration for the tuning of x-ray collection mode in relation to sample profiling (i.e., TEY and TFY are surface and bulk sensitive, respectively). The zoom-in figure of (b) shows the details (pattern linewidth, connection, and x-ray hitting spot) of the device layout on the x-ray holder.
Figure 3. Voltage-dependent x-ray results. (a) Voltage-dependent Fe $L_3$ XAS with ex-situ treatment, collected by TEY mode. XAS peaks corresponding to Fe-metallic and Fe-O features are marked. (b) Voltage dependent O $K$-edge XAS with ex-situ treatment, collected by TEY (solid lines) and TFY (dashed lines) modes. Arrow indicates Fe-O hybridization with an O termination of the ZnO layer adjacent to the Fe layer. All the XAS spectra have been normalized to the absorption jump.

We find that the charge transfer is accompanied by the change of spin-electronic states of the Fe layer. Figure 4(a) provides the x-ray magnetic circular dichroism (XMCD) spectra before and after the 110-V ex-situ treatment. The XMCD signal appears to decrease upon voltage treatment. This is indicative of the suppression of Fe atomic moment. We collected helicity-dependent Fe $L_3$-edge XAS for both 0- and 110-V ex-situ treatments. We define $\mu(\uparrow)$ and $\mu(\downarrow)$ as the XAS spectra with positive and negative helicities generated from circularly polarized x-rays, respectively. Therefore, $\mu(\uparrow)$ and $\mu(\downarrow)$ intensities are inversely proportional to the occupations of majority- and minority-spin states of Fe 3d orbital, respectively. The minority spin states (as shown by $\mu(\downarrow)$ intensity in Fig. 4(b)) of Fe appear to decrease upon ex-situ treatment. However, the majority spin states (as shown by $\mu(\uparrow)$ intensity in Fig. 4(c)) are independent of the applied voltage (the shoulder feature of 110-V ex-situ treatment $\mu(\uparrow)$ around 710 eV is associated with the oxidation $\rightarrow$ metallic transition, while this feature is independent of magnetic as it appears in both with and without 110-V ex-situ treatment $\mu(\uparrow)$ XAS). The discrepancy between minority and majority states of Fe, therefore, is the origin of the change of Fe atomic moment in response to interface reconstruction. We correlate this with TEY O K-edge XAS (Fig. 3(b)) which provides information...
of Fe-O hybridization at the Fe/ZnO interface. The pre-peaks of TEY O K-edge XAS are split by octahedral ligand-fields with $t_{2g}$ and $e_g$ states for the $3d$ metals. Upon ex-situ treatment, the double-peak feature turns to a single-peak feature at ~530 eV, whereas the major peak (marked as E) at ~537 eV appears more prominent. This is a clear evidence for the change of Fe $4s$-$O 2p$ hybridization $^{21-23}$, and this electronic transition is responsible for the decrease of the Fe atomic moment by interface reconstruction. Moreover, when correlating with helicity (spin)-dependent Fe $L_3$-edge XAS, we find that the Fe-O electronic transition involves the change of minority states via the charge-transfer mechanism; i.e., electrons only follow from the ZnO to Fe’s minority state through Fe $4s$-$O 2p$ hybridization. The spin-dependent electronic diagram of the Fe layer, with respect to interface reconstruction (i.e., ex-situ treatment), is summarized in Fig. 4(d). The spin polarization of the Fe layer is only influenced by the minority spin state. Upon interface reconstruction, the occupation of the Fe minority state increases due to the charge donated by the ZnO. This leads to a decrease of the Fe spin polarization as the band-splitting is reduced. We notice that the charge transfer suppressed the Fe magnetization mainly by lowering its orbital moment ($L_z$). This is implied by the noticeable changes of both $L_2$ XAS and XMCD spectrum, whereas $L_3$ XAS and XMCD remain nearly unchanged with the applied voltage. According to the XMCD sum rules $^{24}$, the $L_2$-edge is corresponsive to $L_z$ change, whereas the $L_3$-edge is responsible for $S_z$ variation for $3d$ metals. It is well known that $L_z$ is far more sensitive than $S_z$ to structural transition. Unlike $S_z$, which can freely switch upon field reversal, $L_z$ is often bound to lattice and structural coordination. Therefore, the voltage-induced interface reconstruction is expected to result in broken-symmetry effects reflected by $L_z$ modification.

We then take a further look at the correlation between charge transfer and interface reconstruction. We took photoluminescence (PL) spectra for the samples with and without 110 V ex-situ treatment, as shown in Fig. 5(a) and (b), respectively. Without ex-situ treatment, the band edge emission at 380 eV is attributed to free excitonic emission of ZnO, whereas the broad peak is attributed to extrinsic defect sites due to the recombination of photo-generated holes with electrons occupying the singly ionized oxygen vacancies ($O_\text{v}$) $^{25-28}$. Upon ex-situ treatment, $O_\text{v}$ becomes the dominant characteristic. $O_\text{v}$ must be present at the Fe/ZnO interface that caused Fe-O bond-breaking. One can imagine that $O_\text{v}$ serve as a hub for electrons that are readily available to follow from ZnO to Fe when an electric field (i.e., the applied voltage) is given. The formation of $O_\text{v}$ also explains the increase in resistance by interface reconstruction. We then take the element-specific hysteresis curves on the Fe layer by fixing photon energy at the Fe $L_3$-edge upon the magnetic field reversal. Figure 5(c) shows the voltage-dependent hysteresis curves of the Fe layer. We observe a voltage-induced increase of switching field with increasing ex-situ treatment.

![Figure 4](image-url)

**Figure 4.** Helicity/spin-resolved x-ray results. (a) Fe $L_2/L_3$ XMCD spectra with and without 110 V ex-situ treatment. (b) Helicity-dependent ($\mu(+) \text{ and } \mu(-)$) Fe $L_3$ XAS spectra with and without 110 V ex-situ treatment. Inset of (b) illustrates the x-ray measurements with two x-ray helicities. (d) Illustration for the spin-dependent electronic diagram of the Fe layer in relation to the charge transfer effect upon ex-situ treatment. $\mu(+)$ and $\mu(-)$ correspond to the different x-ray helicities associated with majority and minority state, respectively. The charge transfer only involves the change in Fe’s minority state.
treatment. Independently we also collected AMR data of ex-situ treatment –110 V (Fig. 5(d)). The increase of switching field in AMR is consistent with Hc enhancement. From the viewpoint of magnetic reversal, Ov could act as domain-wall pinning centers. As shown in many previous studies, crystal defects tend to pin the domain wall during magnetic reversal. This caused increase in both Hc and AMR switching field.

Next, we discuss the in-situ treatment results. Lower figure of Fig. 6(a) shows the results of Fe L2/L3-edge XMCD for a prolonged supply of a 110-V on the device (>8 minutes), followed by a temporary removal of the voltage, and then a re-application of the 110-V on the device. For in-situ treatment, the device has passed the interface reconstruction period and entered into an electrically stable state. Contrary to ex-situ treatment, the

Figure 5. Magnetic properties with ex-situ treatment. PL spectra for the device (a) with and (b) without 110 V-ex-situ treatment. Inset figures of (a) and (b) illustrate the Fe-ZnO bond-broken and bond-formed situations for with and without 110V-ex-situ treatment, respectively. (c) Voltage-dependent hysteresis curves of the Fe layer with ex-situ treatment. (d) AMR measurement of the device with (red curve, units on right y-axis) and without (black curve, units on left y-axis) 110 V-ex-situ treatment. Magnetic field direction with respect to the patterned sample is shown in inset figures.

Figure 6. Reversibility test of in-situ treatment by x-ray. (a) Lower figure: Fe L2/L3 XMCD spectra with application (pink), removal (blue), and reapplication (green) of 110 V-in-situ treatment; upper figure: helicity-dependent (μ(+) and μ(−)) Fe L3 XAS spectra with and without 110 V-in-situ treatment. (b) Hysteresis curves of the Fe layer with application (pink), removal (blue), and reapplication (green) of 110 V-in-situ treatment.
XMCD signal is enhanced with in-situ treatment. We find that the XMCD returns to original magnitude upon the removal of in-situ treatment, and it can be re-enhanced by re-applying in-situ treatment. This means a reversible control of the transition with the applied voltage. As shown by helicity-dependent XAS (upper figure of Fig. 6(a)), we find that the moment increase involves the change of both majority and minority states. Besides, both the \( L_z \)-edge (\( L_z \)-related) and \( L_s \)-edge (\( S_z \)-related) XMCD signals are promoted with the applied voltage, which implies an intrinsic increase of the Fe atomic moment. This indicates a distinct voltage-induced electronic transition compared to the ex-situ treatment, because of the completion of the interface reconstruction. For this type of electronic transition, the spin-polarization (i.e., XMCD) of the FM layer is enhanced, due to the change of both majority and minority states by electronic filling. Interestingly, the enhanced spin-polarization is accompanied by the decrease of \( H_c \) (Fig. 6(b)) in which the reversibility is also observed. We find that 110 V is the maximum voltage that can allow the reversible behavior. The spin-electronic transition will become permanent if the voltage exceeds this value. This indicates the operation limit of the device.

Conclusion
In summary, we have extensively investigated the voltage effects on the Fe/ZnO device by directly probing the Fe/ZnO spin-electronic state, with a strong attempt to capture the spirit of the voltage-controlled magnetism that has been emerging in recent years. Our results are important in several aspects. First, the Fe/ZnO interface was reconstructed by the applied voltage at the early stage of device operation. In this stage, the resistance was raised up due to Fe-O bond breaking, and \( O_2 \) was formed at the interface. With a continuous supply of voltage, the metallic phase of the Fe layer was stabilized, thus turning the device into an electrically stable state. In this state, the external voltage drove a different electronic transition from the first state, in which the spin-polarization was enhanced along with a reduction of the switching field. In this state we found that both characteristics were reversible, as long as the applied voltage was kept below a threshold value. This finding offers an optimistic view for the FM/SM design: (i) the spin-polarization enhancement suggests a probable increase of spin current that could be injected into the semiconductor; (ii) the decrease of \( H_c \) infers a lower switching current for device operation. Both characteristics are desirable for spintronics applications. However, there is a serious concern about how to remove the negative impacts of interface reconstruction that occur at the early operation stage (i.e., causing electrically unstable state and \( H_c \) increase). This stage causes considerable power-consumption for the device as a result of the increase in resistance and lowering in switching speed. This problem might be solved by having a Zn-rich, instead of O-rich surface prior to depositing the Fe layer, or inserting a non-magnetic, highly conductive interlayer between the Fe and ZnO. Second, ZnO is a good candidate for spin pumping owing to its Rashba-type spin-orbital interaction that may give rise to a long-distance spin transport\(^{41-42}\). If the interface-reconstruction effect could be mitigated to some extent, a longer spin-relaxation time might be achieved for ZnO in combination with 3d metals. This will allow a better control of the spin electrons in ZnO. This work is supported by the Ministry of Science & Technology, Taiwan, under Grant No. MOST 104-2633-M-009-001.

Methods
Device fabrication. Multi-layers of Au/Fe/ZnO/Au were sequentially deposited on an Al\(_2\)O\(_3\)(0001) substrate. The Au and Fe layers were deposited using e-beam-heated evaporators while the ZnO thin films were prepared using a pulsed laser deposition technique\(^{35,34}\). A Hall bar structure of Au/Fe/ZnO/Au/Al\(_2\)O\(_3\) was fabricated using the lithography technique for transport measurement.

Structural characterizations. XRD was performed at BL17B1, National Synchrotron Radiation Research Center (NSRRC), Taiwan, with a photon energy of 8 keV. TEM was used to examine the interface microstructure.

Magnetic and photoluminescence measurements. Magnetic properties (hysteresis curves) of the device were measured using a MOKE system, equipped with an electromagnet that provides a magnetic field range of ±1000 Oe. PL spectra were collected using a Kimmon IK3001R-G system equipped with a He-Cd laser (720 W).

X-ray magnetic spectroscopy and transport measurements. X-ray magnetic spectroscopy was operated at BL11A (Dragon beamline, NSRRC). This beamline was incorporated with an electrical control system allowing simultaneous measurements of XAS, XMCD, and electrical transport. More details about the setup can be found in ref. 35. Resistance in the CPP geometry and element-specific hysteresis curve measurements were operated on the Fe layer by tuning the photon energy to the Fe \( L_3 \) absorption edge upon the magnetic field reversal at the same beamline. An independent four-point probe AMR measurement in the current-in-plane geometry and magnetization hysteresis loop were performed along horizontal direction of the device, using a magnetoresistance (MR) and a longitudinal micro-MOKE technique\(^{46}\). The detection of x-ray absorption spectra was taken via a TEY mode and a TFY mode to probe the surface- and bulk-sensitive information of the device, all in an UHV condition (<10\(^{-9}\) Torr). Two voltage treatments were carried out in this study, as described in the content of results and discussion. A sample CPP resistance of 3.5 kohm was independently measured prior to the x-ray measurement. The same sample resistance was obtained by the electrical control system incorporated to the x-ray setup. During measurements, the sample was maintained at 200 K using a temperature controller in order to prevent voltage-induced heating and thermal gradient on the device. Device breakdown occurred at 130 V, at which TEY/TFY signal cannot be obtained anymore. Therefore, the maximum applied voltage to the device was set to be 110 V.
References

1. Miron, I. M. et al. Perpendicular switching of a single ferromagnetic layer induced by in-plane current injection. Nature 476, 189 (2011).
2. Katine, J. A., Albert, F. J., Buhrman, R. A., Myers, E. B. & Ralph, D. C. Current-driven magnetization reversal and spin-wave excitations in Co/Cu/Co pillars. Phys. Rev. Lett. 84, 3149 (2000).
3. Chiba, D. et al. Electrical control of the ferromagnetic phase transition in cobalt at room temperature. Nat Mater. 10, 853 (2011).
4. Zhou, S., Guo, Y., Zhao, J., He, L. & Shi, L. Site-induced Griffiths phase and second-order ferromagnetic transition in Sr3MnO4 nanofilms. J. Phys. Chem. C 115, 1535 (2011).
5. Binek, C. et al. Electrically controlled exchange bias for spintronic applications. J. Appl. Phys. 97, 10CS14 (2005).
6. van den Brink, A. et al. Field-free magnetization reversal by spin-Hall effect and exchange bias. Nat. Commun. 7, 10854 (2016).
7. Matsukura, F., Tokura, Y. & Ohno, H. Control of magnetism by electric fields. Nat. Nanotechnol. 10, 209 (2015).
8. Sapkota, K. R., Chen, W., Maloney, S. F., Poudyal, U. & Wang, W. Magnetoresistance manipulation and sign reversal in Mn-doped ZnO nanowires. Sci. Rep. 6, 35036 (2016).
9. Swartz, A. G. et al. Spin-dependent transport across Co/LaAlO3/SrTiO3 heterojunctions. Appl. Phys. Lett. 105, 032406 (2014).
10. Weisheit, M. et al. Electric field-induced modification of magnetism in thin-film ferromagnets. Science 319, 349 (2007).
11. Endo, M., Kanai, S., Ikeda, S., Matsukura, F. & Ohno, H. Electric-field effects on thickness dependent magnetic anisotropy of sputtered MgO/CoFe2O4/Ta/MgO/CoFe2O4/Ta structures. Appl. Phys. Lett. 96, 212503 (2010).
12. Maruyama, T. et al. Large voltage-induced magnetic anisotropy change in a few atomic layers of iron. Nat. Nanotechnol. 4, 158 (2009).
13. Niranjan, M. K., Duan, C. G., Jaswal, S. S. & Tsymbal, E. Y. Electric field effect on magnetization at the Fe/MgO(001) interface. Phys. Rev. Lett. 113, 267202 (2014).
14. Leitner, K. et al. Electric-field control of magnetism by reversible surface reduction and oxidation reactions. Phys. Rev. B 87, 244411 (2013).
15. Radaelli, G. et al. Electric control of magnetism at the Fe/BaTiO3 interface. Nat. Commun. 5, 3404 (2014).
16. Bonell, E. et al. Reversible change in the oxidation state and magnetic circular dichroism of Fe driven by an electric field at the FeCo/MgO interface. Appl. Phys. Lett. 102, 152401 (2013).
17. Miwa, S. et al. Voltage-controlled magnetic anisotropy in Fe/MgO tunnel junctions studied by x-ray absorption spectroscopy. Appl. Phys. Lett. 107, 162402 (2015).
18. Mosquera, A. A. et al. Exciton and core-level electron confinement effects in transparent ZnO thin films. Sci. Rep. 3, 1714 (2013).
19. Satyarthi, P. et al. Coexistence of intrinsic and extrinsic origins of room temperature ferromagnetism in as implanted and thermally annealed ZnO films probed by x-ray absorption spectroscopy. J. Appl. Phys. 113, 183708 (2013).
20. Cao, C. Y. et al. Low-cost synthesis of flowerlike α-Fe2O3 nanostructures for heavy metal ion removal: adsorption property and mechanism. Langmuir 28, 4573 (2012).
21. Schedel-Niedrig, Th & Weiss, W. & Schlögl R. Electronic structure of ultrathin ordered iron oxide films grown onto Pt(111). Phys. Rev. B 52, 17449 (1995).
22. Wu, Z. Y. et al. Characterization of iron oxides by x-ray absorption at the oxygen K edge using a multiple-scattering approach. Phys. Rev. B. 55, 2570 (1997).
23. Chen, C. T. et al. Experimental confirmation of the x-ray magnetic circular dichroism sum rules for iron and cobalt. Phys. Rev. Lett. 75, 152 (1995).
24. Das, A. K. & Srinivasan, A. Evidence of oxygen defect induced ferromagnetism in heat treated electrodeposited ZnO nanowires. J. Magn. Magn. Mater. 404, 190 (2016).
25. Ghosh, A. et al. Tuning the work function of ordered ZnO nanostructures by capping with faceted Au nanostructure and oxygen defects: enhanced field emission experiments and DFT studies. Nanotechnology 27, 125701 (2016).
26. Illiberi, A., Roozeboom, F. & Poodt, P. Spatial atomic layer deposition of zinc oxide thin films. ACS Appl. Mater. Interfaces 4, 268 (2012).
27. Faber, H. et al. Impact of oxygen plasma treatment on the device performance of zinc oxide nanoparticle-based thin-film Transistors. ACS Appl. Mater. Interfaces 4, 1693 (2012).
28. Hsiao, C. H., Yao, Y. D., Lo, S. C., Chang, H. W. & Ouyang, C. Domain wall pinning on strain relaxation defects (stacking faults) in nanoscale FePd (001)/MgO thin Films. Appl. Phys. Lett. 107, 142407 (2015).
29. Li, W., Chen, A., Lu, X. & Zhu, J. Collective domain-wall pinning of oxygen vacancies in bismuth titanate ceramics. J. Appl. Phys. 98, 024109 (2005).
30. Chen, C. T. et al. Experimental confirmation of the x-ray magnetic circular dichroism sum rules for iron and cobalt. Phys. Rev. Lett. 75, 152 (1995).
31. Lee, J. C. et al. Reverse spin Hall effect induced by spin pumping into semiconducting ZnO. Appl. Phys. Lett. 104, 052401 (2014).
32. D’Ambrosio, S. et al. Ferromagnetic resonance of Py deposited on ZnO grown by molecular beam epitaxy. J. Appl. Phys. 54, 093001 (2015).
33. Lin, W. C., Chang, P. C., Tsai, C. J., Hsieh, T. C. & Lo, F. Y. Magnetism modulation of Fe/ZnO heterostructure by interface oxidation. Appl. Phys. Lett. 103, 212405 (2013).
34. Lin, W. C., Chang, P. C., Tsai, C. J., Shieh, T. C. & Lo, F. Y. Voltage-induced reversible changes in the magnetic coercivity of Fe/ZnO heterostructures. Appl. Phys. Lett. 104, 062411 (2014).
35. Huang, C. C., Chang, S. J., Yang, C. Y., Chou, H. & Tseng, Y. C. Instrument for x-ray absorption spectroscopy with in situ electrical control characterizations. Rev. Sci. Instrum. 84, 123904 (2013).
36. Chang, L. J., Yao, Y. D., Lin, P. & Lee, S. F. Magnetic interaction in domain wall depinning at square notch and antinotch traps. IEEE Trans. Magn. 47, 2519 (2011).

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Author Contributions

The scientific idea of this work was initiated by S.J. Chang (1st author), who also wrote the first version of the manuscript. P.-C. Chang (2nd author) and W.-C. Lin (3rd author) helped on sample preparation. Transport measurements were done by S.-H. Lo (4th author) and L.-J. Chang (5th author). Y.-C. Tseng (7th and corresponding author) did most of the manuscript revision. S.-F. Lee (6th author) did partial manuscript revision. All authors reviewed and commented on the manuscript.
