

Voltage-induced reversible changes in the magnetic coercivity of Fe/ZnO heterostructures

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(Received 2 December 2013; accepted 31 January 2014; published online 12 February 2014)

In this study, the magnetic coercivity (H_c) of Fe/ZnO heterostructure monotonically decreased as voltage was applied. The reversibility of this effect was demonstrated by cyclically changing the bias voltage from 0 to 6–9 V; the H_c decreased 15%–20%. The H_c value exhibited the same variation whether the applied voltage was positive or negative. As thick Fe-oxide gradually formed at the interface by using direct current heating, the H_c increased and the Fe/ZnO heterostructure demonstrated a similar voltage-induced reduction of H_c . © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4865591>]

The electric-field-induced reversible modulation of magnetism in nanoscale thin-films has been widely studied, exhibiting strong potential for use in technical applications and particularly in magnetic data storage devices.¹ Because conventional magnetic field or spin-torque-triggered magnetization switching methods yield high power consumption and energy dissipation, electric-field-controlled or assisted switching methods have been explored for use with voltage-controlled magnetic materials, which are applicable in spintronic devices.^{1–4} In the previous decade, researchers attained the voltage-control of magnetism by using single magnetic layers, magnetic semiconductors,^{5–9} multiferroic materials,¹⁰ and other hybrid systems.^{4,10} Voltage-controlled magnetism can involve various possible physical origins such as the modulation of carrier density, d-state electron occupation-induced changes of interface magnetic anisotropy,¹¹ the coupling between ferroelectricity and ferromagnetism. In magnetic semiconductors, the local electric field can substantially change the carrier density because of the limited number of conducting electrons; this severely modulates the magnetic properties. In previous studies, the electric-field-effect has significantly influenced magnetic semiconductors, but the voltage-control is not typically applicable in ambient conditions because of the low Curie temperature. Numerous recent studies have focused on ferromagnetic transition metals combined with MgO, in which the perpendicular anisotropy is stable and the voltage-control of magnetism is practicable.^{3,4,12–20} Until recently, few groups have reported other material systems.^{10,16,21,22} Seki *et al.* observed no remarkable change in the magnetic coercivity (H_c) of an FePt/ AlO_x system, in contrast to the pronounced H_c change observed in an FePt/MgO system.¹⁶ Furthermore, multiferroics and magnetoelectrics provide another mechanism for the voltage-control of magnetism. In addition, numerous perovskite-type oxides have been exploited to control magnetism by using electric field, because of the strain-induced coupling at the interface.¹⁰ Most of the studies have used oxide-based ferromagnets, instead of ferromagnetic transition metal films because it is difficult to attain the coupling between ferromagnetic metal and ferroelectric oxide.

Based on the aforementioned mechanisms for the voltage-control of magnetism, this study explored the Fe/ZnO hybrid system. ZnO has been widely studied as an essential semiconducting material for use in technical applications. The Curie temperature of transition-metal-doped ZnO has been predicted to be higher than room temperature (RT), and therefore, it could be feasible for application as a magnetic semiconductor in spintronics.²³ ZnO also exhibits large electromechanical responses, which are useful in microelectromechanical and communication devices.²⁴ Our previous study of Fe/ZnO demonstrated that Fe-oxidation can be triggered by annealing at 400–500 K, using direct current heating. This interface oxidation irreversibly modulates the magnetism of Fe layer.²⁶ In this study a reversible, voltage-controlled change in H_c was observed when the ZnO thickness was increased to hundreds of nanometers. The H_c of the Fe overlayer reduced by approximately 15%–20% after applying a voltage of 6–9 V. The interface effect on the voltage-controlled H_c is also discussed.

As shown in Fig. 1, Au/Fe/ZnO/Au multilayer structures were prepared on $\text{Al}_2\text{O}_3(0001)$ substrates to detect how voltage affected magnetism. The top and bottom Au layers were used as the electrodes when applying the voltage. The Au over-layer protects the Fe film from oxidation and contamination. A 320-nm ZnO thin film was deposited at 600 K in oxygen at an ambient pressure of 8×10^{-2} millibars by using a pulsed laser deposition (PLD) technique.²⁶ The laser wavelength was 266 nm; it was generated using an Nd:YAG Q-switch laser that exhibited an energy density of approximately 4 J/cm². To characterize the semiconducting properties of ZnO films, photoluminescence (PL) spectroscopy was conducted at RT, using an He-Cd laser that generated an excitation wavelength of 325 nm. After growing the ZnO layer in an ultra-high vacuum chamber (base pressure 3×10^{-9} Torr), the Au and Fe layers were deposited on the ZnO by using e-beam heated evaporators.²⁷ The magnetic hysteresis loops were investigated in an ambient air environment (approximately 300 K) by using the in-plane magneto-optical Kerr effect (MOKE) and various bias voltages.²⁷

Previous studies have reported high quality (0001)-oriented ZnO thin films on $\text{Al}_2\text{O}_3(0001)$ by using PLD-deposition. Fig. 1(b) shows the PL spectra of the as-deposited 2 nm Au/2 nm Fe/320 nm ZnO/20 nm Au/ $\text{Al}_2\text{O}_3(0001)$. These PL

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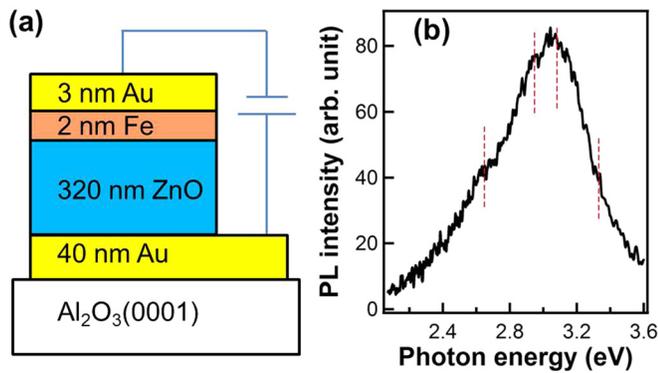


FIG. 1. (a) Schematic illustration of the Au/Fe/ZnO/Au/Al₂O₃(0001) heterostructure. (b) PL spectra of the as-deposited 2 nm-Fe/320 nm-ZnO heterostructure.

spectra exhibited peaks at 2.65, 2.95, 3.08, and 3.35 eV, representing oxygen-defect related, donor-acceptor pair, bound exciton, and free exciton emission lines, respectively.

The MOKE measurement was executed at RT using a magnetic field along the in-plane direction, while the applied bias voltage was gradually increased from 0 to 6 V. As shown in Fig. 2(a), the magnetic coercivity (H_c) of the MOKE hysteresis loops decreased as the bias voltage increased; hysteresis shape was invariant and the ratio of remanence to saturated magnetization remained at approximately 0.9. The H_c was plotted as a function of the bias

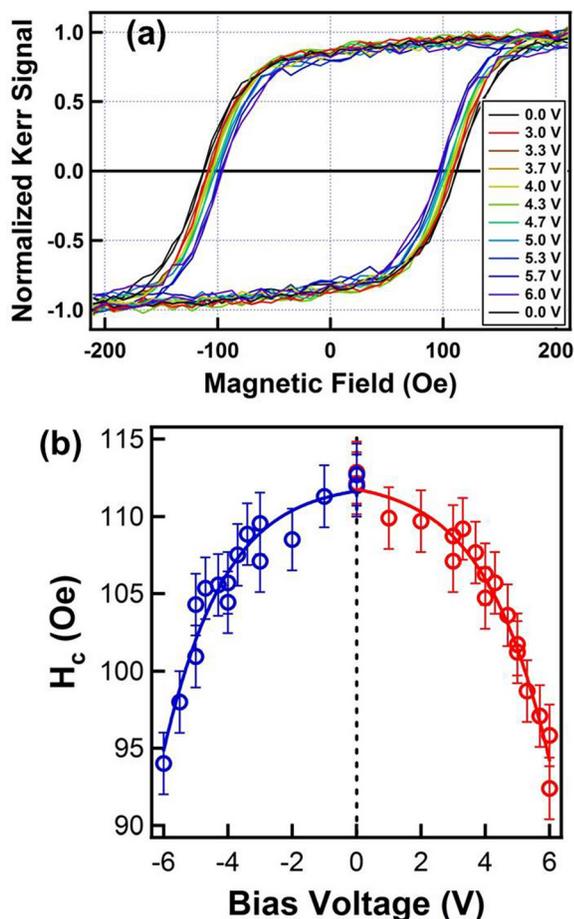


FIG. 2. (a) MOKE hysteresis loops measured at RT, and various bias voltages. (b) Summarized H_c values plotted as a function of bias voltage. The solid lines are guides for the eye.

voltage from -6 V to $+6$ V in Fig. 2(b). Before applying the bias voltage ($V=0$), the H_c was 112 ± 2 Oe. As the biased increased from 0 to 3 V, the H_c slightly decreased to 109 ± 2 Oe. When the voltage was greater than 3 V, the H_c drastically reduced, attaining a minimal H_c value of 93 ± 2 Oe at 6 V. The H_c exhibited the same variation, whether the applied voltage was positive or negative, indicating that the H_c reduction is not related to the electric field direction.

Fig. 3 shows the reversibility of the voltage-induced H_c reduction. The bias voltage was cyclically switched between 0 and 6 V and the MOKE hysteresis loops were recorded, as shown in Fig. 3(a). 6 V bias voltage application always causes the same deformation. As plotted in Fig. 3(b), the H_c reversibly switched between 112 ± 2 Oe and 93 ± 2 Oe, corresponding to the applied voltages of 0 and 6 V, respectively. A maximal voltage of 6 V was chosen because our previous studies have shown that applying a high voltage generates a large current, which can heat the Fe/Zn junction to 400–500 K, yielding further Fe-oxidation at the Fe/ZnO interface. Thus, we set a maximal voltage of 6 V to avoid further oxidation (Figs. 2 and 3).

Because an inevitable oxide layer exists at Fe/ZnO interface, the magnetic behavior of Fe/ZnO heterostructure might be strongly affected by this interfacial layer. Many studies have focused on the interface properties using X-ray photoemission spectroscopy (XPS). In the study of Wett *et al.* on the Fe/ZnO(0001) system at ambient temperature, FeO was formed at the interface.²⁵ Further annealing led to a stepwise

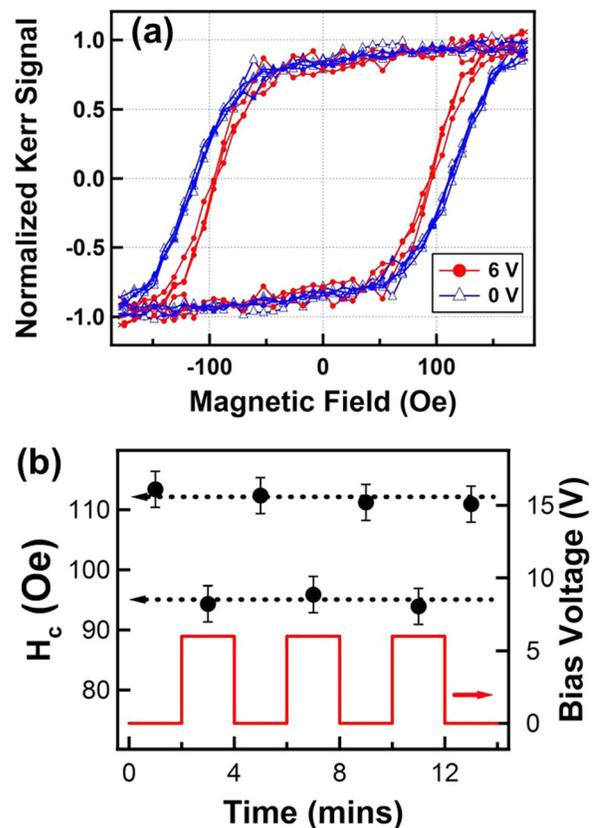


FIG. 3. (a) MOKE hysteresis loops measured when the bias voltage was cyclically switched between 0 V (blue, triangle) and 6 V (red, circle). (b) The analyzed H_c (left axis) and switched bias voltage (right axis) were plotted as a function of time.

oxidation of Fe to FeO (670 K) and Fe₂O₃ (820 K). Their experiment was mostly performed on 2.4 nm Fe/ZnO(0001) and the XPS measurement monitored the surface top layers. Our latest study explored the depth-profiling Fe-oxide formation close to the interface.²⁶ The H_c of Fe/ZnO heterostructure was significantly enhanced by 2–3 times after applying a suitable direct heating current. This H_c enhancement is irreversible and originates from the Fe-oxidation at the Fe/ZnO interface induced by direct current heating while the bias voltage is applied. Depth-profiling XPS analysis confirmed the formation of FeO, Fe₃O₄, and Fe₂O₃ close to the interface region, depending on the Fe thickness and annealing process. To investigate whether interface conditions changed how voltage reversibly affected on H_c , we applied large voltages of 10 and 12 V to generate more Fe-oxide at the interface. Fig. 4 shows that after applying 10 V for 10 min, the H_c value irreversibly increased from 112 ± 2 eV to 147 ± 4 Oe (measured when $V=0$). After the 10 V-annealing, not only the H_c was enhanced but also the resistance of Fe/ZnO junction was decreased.²⁶ Thus, the sample became durable up to a higher voltage of at least 8 V, without any further irreversible Fe-oxidation. The voltage-induced change of H_c was plotted as a function of bias voltage. After the sample was annealed by 10 V for 10 min, the H_c reversibly decreased from 147 ± 4 Oe to 112 ± 4 Oe as the bias voltage was increased from 0 V to 8 V. After applying a higher voltage of 12 V to the sample for 10 min, the H_c irreversibly increased again to 189 ± 4 Oe (measured when $V=0$), and the sample became durable up to at least 9 V. For this 12 V-annealed sample, as shown in Fig. 4, the H_c reversibly decreased from 189 ± 4 Oe to 147 ± 4 Oe as the bias voltage was increased from 0 V to 9 V.

We summarize the above experimental observations as following. (1) When the applying voltage is larger than certain threshold values, the interfacial oxidation will be triggered and lead to the irreversible H_c enhancement. (2) If the applied voltage is small and insufficient to heat up the

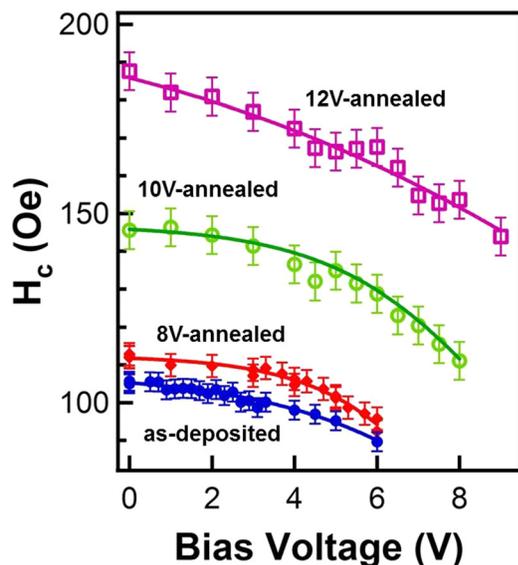


FIG. 4. The summarized H_c values were plotted as a function of bias voltage for as-deposited sample and the samples after applying 8 V, 10 V, and 12 V to the Fe/ZnO junction for 10 min. The solid lines are guides for the eye.

sample, further interfacial oxidation will not be triggered and the reversible H_c variation is observed within the small voltage region. The H_c value always symmetrically reduces based on the polarity of bias voltage, indicating that the mechanism of voltage-effect on magnetism is not changed by thick Fe-oxide at the interface. The naturally formed interfacial Fe-oxide layer may play important role in the possible strain transfer which is reversibly controlled by bias voltage, because the crystalline structure continuously evolves from Fe to Fe-O to ZnO. On the other hand, for the purpose of application, we need a high resistive interface of Fe/ZnO, because only the voltage is required for inducing strain variation. We hope to reduce the current as small as possible in order to decrease the energy dissipation. That is also why we purposely applied a large voltage to increase the Fe-oxide interfacial layer and then check the reversible H_c effect, as shown in Fig. 4.

In the aforementioned MOKE measurement with applied voltage, because ZnO is a semiconducting thin film, not an insulating layer, unavoidably the samples were slightly heated by the applied voltage and current during the measurement. For an applied voltage of 6 V, the conducting current is smaller than 0.08 A/mm², and the maximum raise of temperature is less than 50 K under the air cooling. It means that the sample temperature is actually within 300–350 K during MOKE measurement. If the Curie temperature (T_c) of Fe film is close to this temperature region, the heating effect can be one possible reason for the H_c reduction. However, in our Fe/ZnO heterostructure, the Fe thickness is 2 nm, which equals to ≈ 13 mono-atomic layers (ML). Previous studies have shown that the T_c of 3 ML Fe on Au(100) or Ag(111) reaches 600–700 K, respectively.^{28,29} Moreover, T_c of 9.5 ML Fe/Ag(100) is up to 1160 ± 200 K, close to the bulk T_c .³⁰ T_c of the 2 nm Fe layer used in our experiment must be at least up to 700 K or even higher, which is far above the temperature variation during MOKE measurement. Thus, the temperature-induced H_c reduction is supposed to be negligible and unlikely to dominate the change of H_c in our measurement.

Previous studies on the voltage-control of H_c in MgO-based systems have shown that modulating the d-band electron filling induced asymmetric variation in the positive and negative bias. In addition, because of strain-induced interface coupling, perovskite-type oxides have been successfully exploited to control magnetism by using electric field.¹⁰ In relevant studies, the H_c has exhibited a symmetric variation as a function of the positive and negative bias voltage, because magnetoelectrics provide an additional mechanism for the voltage-control of magnetism. Sahoo *et al.* reported that for a Fe thin film in proximity of a BaTiO₃ single crystal, up to 20% coercivity change was achieved via electrical control at room temperature.¹⁰ In the proposed Fe/ZnO heterostructure, the interface exhibited Ohmic conduction behavior (i.e., the electric current was proportional to the bias voltage).²⁶ The ZnO layer can provide a charged interface modulating the interface magnetic anisotropy of the Fe layer. In addition, because of the large electromechanical response of ZnO, the voltage-induced H_c reduction might result from coupling between the ferromagnetic metal and ferroelectric oxide. Luo *et al.* have reported that a

1.2%-Fe-doped ZnO films showed a typical symmetric displacement-voltage butterfly loop with a displacement maximum of 1.25 nm at -8.9 V, indicating a strain as high as 0.45% and the ferroelectric behavior of the ZnO film.²⁴ In our previous study of 2–5 nm Fe/2–10 nm ZnO, the H_c value exhibited no changes after applying a bias voltage of 0–6 V, although a thin ZnO layer might yield a correspondingly large electric field (=bias voltage divided by thickness). In this study, compared with using a thin layer, using a thick ZnO layer (320 nm) more substantially influenced how the voltage affected the magnetism. This observation supports that strain coupling existed between Fe and ferroelectric ZnO; thus, the ZnO must be sufficiently thick to modulate the strain of Fe film. However, we need to agree that other than strain transfer, the possibilities of reversible chemical changes or interface charge cannot be fully excluded and need further experiment for clarification.

In this experiment, the level of magnetic coercivity substantially decreased when a bias voltage was applied to the Fe/ZnO heterostructure. The H_c value decreased 15%–20% at a maximal bias voltage of 6–9 V. The voltage-induced modulation of magnetism was reversible and indicated that the H_c value symmetrically varied based on the polarity of the bias voltage. Subsequent Fe-oxidation at the Fe/ZnO interface caused by direct heating did not affect the mechanism of voltage-controlled magnetism. The strain coupling between the ferromagnetic Fe layer and electromechanical response of ZnO is proposed as a possible mechanism for this voltage-induced change of H_c . The findings demonstrate the reversible voltage-control of magnetism in an Fe/ZnO heterostructure; thus, ZnO is proposed as an efficient material for providing electromechanical coupling to a magnetic overlayer. These observations should be valuable in future studies and for reference when using magnetic metal/ZnO systems.

This work was financially supported by the National Science Council of Taiwan (Grant Nos. NSC 102-2923-M-003-002-MY3, NSC 102-2112-M-003-003-MY3, and NSC 100-2112-M-003-007-MY3).

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