

Research Update: Magnetoionic control of magnetization and anisotropy in layered oxide/metal heterostructures

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Research Update: Magnetoionic control of magnetization and anisotropy in layered oxide/metal heterostructures

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Electric field control of magnetization and anisotropy in layered structures with perpendicular magnetic anisotropy is expected to increase the versatility of spintronic devices. As a model system for reversible voltage induced changes of magnetism by magnetoionic effects, we present several oxide/metal heterostructures polarized in an electrolyte. Room temperature magnetization of Fe-O/Fe layers can be changed by 64% when applying only a few volts in 1M KOH. In a next step, the bottom interface of the in-plane magnetized Fe layer is functionalized by an L1₀ FePt(001) underlayer exhibiting perpendicular magnetic anisotropy. During subsequent electrocrystallization and electrooxidation, well defined epitaxial Fe₃O₄/Fe/FePt heterostructures evolve. The application of different voltages leads to a thickness change of the Fe layer sandwiched between Fe-O and FePt. At the point of transition between rigid magnet and exchange spring magnet regime for the Fe/FePt bilayer, this induces a large variation of magnetic anisotropy. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4942636>]

The perspective of electrically controlled, integrable functional magnetic nanostructures motivates intense research in the field of spintronics.^{1–4} Current-driven magnetization switching and domain wall motion have been achieved by the use of spin polarized currents inducing spin transfer torques (STT) or spin orbit torques.^{3,4} In these current-based mechanisms, Joule heating occurs, causing undesirable energy dissipation. As an alternative, electric field (E) control of magnetism is strongly pursued, promising significantly lower energy loss.⁵ In this emerging field of E -controlled spintronics, E -based switching of magnetization,^{6,7} as well as E -induced modulations of magnetic properties facilitating current-induced switching of magnetization,^{2,8} is highly discussed.⁹ Recent exciting device proposals include, e.g., E -assisted STT-magnetic random access memories² as well as E -controlled magnetic skyrmion transistors.¹⁰

E -effects in metals, in comparison to magnetic semiconductors and multiferroic systems,^{5,11} promise large magnetization combined with applicability at room temperature. Due to the short screening length, reasonable E -effects in metals are only expected at large interface/volume ratio. Theoretical predictions^{12,13} and experimental studies on E -effects on magnetism in Co,^{14,15} Fe,^{16–18} FeRh,¹⁹ and (Fe,Co)Pt^{20–22} films strongly triggered research efforts. Since for spintronics, the functionality of ferromagnetic metallic layers strongly depends on magnetization and magnetic anisotropy,²³ an E -induced modulation of these properties is anticipated. On one hand, similar to magnetic data storage, strong perpendicular magnetic anisotropy (PMA) is beneficial in order to overcome thermal fluctuations at the nanoscale. On the other hand, as the threshold current increases with the effective anisotropy field, lowering PMA during current-induced switching of magnetization would be favourable. E -controlled modulation of interfacial PMA has been proposed as one

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approach to overcome this obstacle.⁸ Meanwhile, *E*-modulated magnetic anisotropy^{8,16,17,20,21} and magnetization^{20,22,24} have been achieved in ultrathin metallic films. In order to apply the electric field, various architectures have been utilized: dielectric layers^{14,16,17} as well as solid^{25,26} or liquid^{20–22,24,27} electrolytes.

Different interfacial mechanisms are discussed to explain the observed *E*-induced modulations of magnetism in metallic layers. Changes of the electronic band filling in the uppermost atomic layers, obtained by capacitive electronic charging via dielectric layers or electrolytic double layers, have been suggested as origin for *E*-induced variations of interface and/or magnetocrystalline anisotropy.^{16,19,21} Recently, an increasing number of reports points towards an influence of interfacial chemistry.^{15,18,20,22,25–29} The background is that the applied electric field, besides capacitive charging, can induce charge-transfer reactions leading to a reversible change of the oxidation state of, e.g., Fe or Co species.^{20,26,29} Magnetic changes based on such electrochemical reactions have recently been denominated magnetoionic (MI) effect.²⁶ In contrast to capacitive electronic charging, MI effects are not restricted to the uppermost atomic layers but depend on the reaction layer thickness of the electrochemical reaction. In principle, composition, phases, structure, and microstructure can be changed, promising tremendously larger magnetic property changes achievable by MI effects than by sole electronic charging. In our previous work, that initially aimed for magnetoelectric effects in FePt and CoPt films by double layer charging, nonaqueous Li-based electrolytes were used.^{20,22,30} Voltage-induced changes of anisotropy and magnetization were observed that exceeded those expected for electronic charging and could only be explained by charge transfer processes in a surface iron oxide. An increase of the functional iron oxide layer thickness led to an enhanced voltage-induced change of magnetization of 13%, however, not in films with PMA.²⁰

The present work demonstrates that strong MI effects in combination with PMA can be obtained in well-defined oxide/metal heterostructures when exploiting suitable reversible electrochemical reactions and taking advantage of additional interface effects. We benefit from supercapacitor research here: In pseudocapacitors, in analogy to the MI effect, large charge storage densities based on charge-transfer reactions are aimed at. The search for MI effects from such electrochemically well studied systems allows a direct correlation between charge-transfer reactions and magnetic property changes. We chose the system Fe-O/Fe in aqueous KOH where a reversible change of the oxidation state of Fe has been reported.^{31,32} Additionally, the bottom interface of the Fe layer is functionalized by an L1₀ FePt underlayer exhibiting PMA. This allows to exploit magnetic exchange coupling at the Fe/L1₀ FePt interface.³³ This way, simultaneous control of both, magnetization and anisotropy, in a well-defined trilayered heterostructure with dominating PMA is achieved.

Fe films are prepared by magnetron sputtering (base pressure = 2×10^{-9} mbar, working pressure = 8×10^{-3} mbar, room temperature). To ensure adherence and conductivity, 3 nm Cr and 50 nm Pt buffer layers are first sputter deposited on a Si(111) substrate, followed by 10 nm of Fe. For 5 and 2 nm thick Fe films, the Pt buffer thickness is reduced to 10 nm for a better signal to noise ratio during anomalous Hall effect (AHE) measurements.³⁴ The Fe films are sputtered without cap layer and undergo natural oxidation after removal from the vacuum chamber. For Fe-O/Fe/FePt composite films, in a first step continuous 3 nm thick (001) textured L1₀-FePt films with perpendicular anisotropy are prepared on Pt/MgO(001) by pulsed laser deposition (PLD) as described in previous work.²⁰ On top of FePt, 3 nm Fe is sputter deposited with identical conditions as described above. Sputtering is chosen here, in contrast to PLD, in order not to destroy the L1₀ order by the high kinetic energy of the deposited ions.^{20,34}

For microstructural, structural, and compositional characterization, high resolution transmission electron microscopy (HRTEM), fast Fourier transforms (FFT), scanning transmission electron microscopy (STEM), as well as electron energy loss spectroscopy (EELS) are performed at 300 kV accelerating voltage on an aberration-corrected FEI Titan³ 80-300 microscope, equipped with a Gatan Tridiem 863ER spectrometer. Sample preparation has been performed by focused ion beam (FIB) using 30 kV Ga⁺ ions (FEI Helios 600i).

The Fe-O/Fe and Fe-O/Fe/FePt films are polarized as working electrodes in a 1M KOH aqueous electrolyte. A Pt wire serves as counter electrode. The open circuit potential lies at -0.3 V vs. saturated calomel electrode (SCE). The upper and lower potentials of -1.26 and -0.18 V vs.

SCE, respectively, were determined in preceding electrochemical experiments in a three electrode cell in order to achieve oxidation and reduction of Fe species while avoiding Fe dissolution and electrolyte side reactions. The influence of electrooxidation and electroreduction on the magnetism is probed by *in situ* AHE measurements. During AHE measurements, a current between 10 and 100 mA is applied along one in-plane direction and the Hall voltage is measured along the other in-plane direction. Hysteresis is corrected for the normal Hall effect. As the magnetic field is applied perpendicular to the film plane, the anomalous Hall resistance R_{AH} is a measure for the perpendicular component of magnetization. The electrochemical cell for *in situ* AHE is a two electrode cell, described in further detail in previous work.³⁰ The ratio of cell diameter versus AHE press contact spacing is 0.65. For this geometry, the difference in geometry correction factor should be below 25%.³⁵ In the following, we neglect this contribution of the area outside the cell to the measured AHE signal. Thus, the electrochemically induced changes reported later on are underestimated by a small extent. In order to define the appropriate cell voltages, reference measurements have been carried out in the three electrode setup. The voltages quoted in this work represent the actual potential of the working electrode vs. SCE.

First, the properties of as deposited Fe-O/Fe films and the effect of polarization in KOH on their properties are presented. HRTEM and STEM investigations of the as deposited Fe-O/Fe film with 10 nm nominal Fe thickness in Figs. 1(a) and 1(c) show that a stable, about 3 nm thick, native iron oxide layer has formed on top of the Fe layer. The roughness is defined by the columnar growth of the Pt buffer.

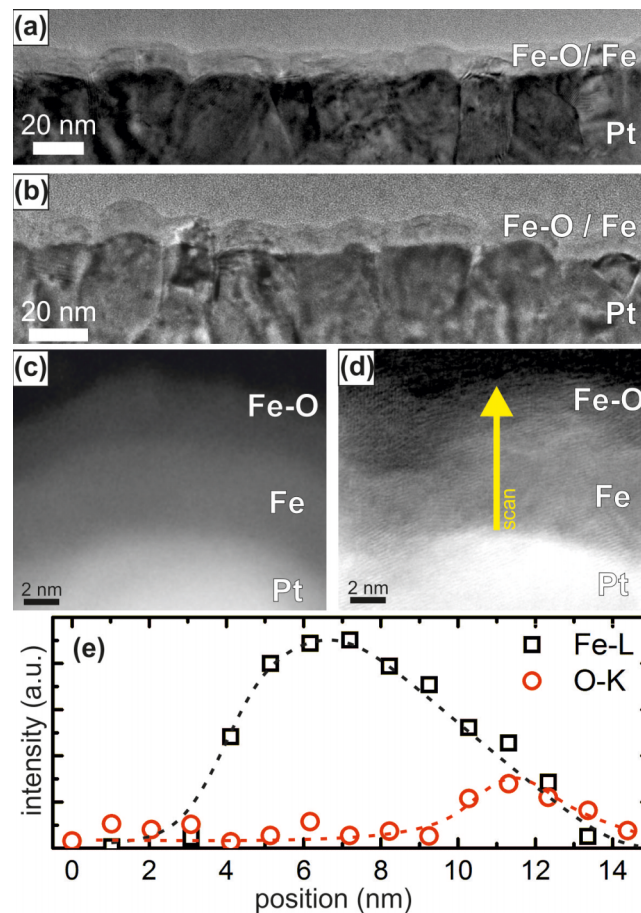


FIG. 1. (a) and (b) TEM overview and (c) and (d) STEM images of the Fe-O/Fe film with 10 nm nominal Fe thickness (a) and (c) before and (b) and (d) after the electrochemical treatment. (e) Intensity of the Fe-L and the O-K edge across the Fe-O/Fe structure. The scan direction of the performed EELS measurement is marked in (d).

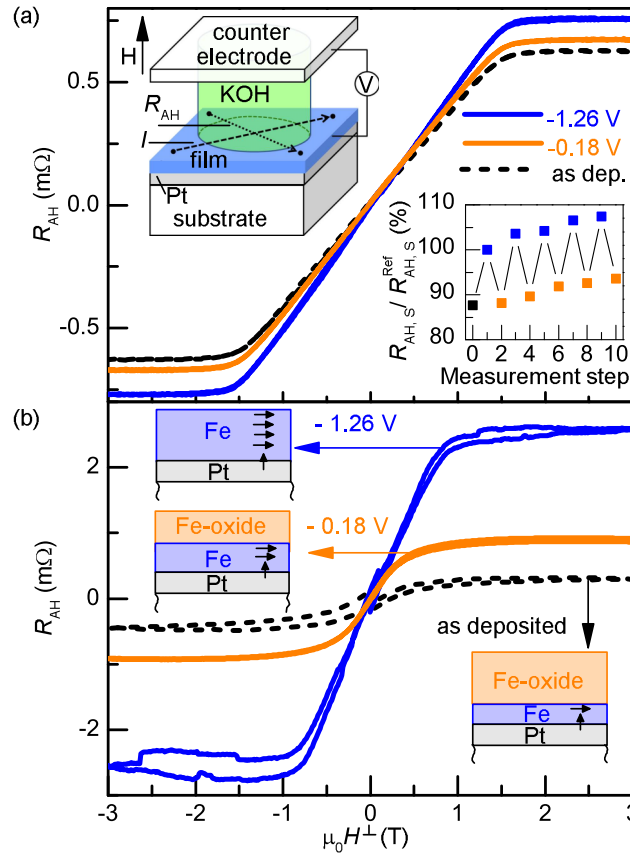


FIG. 2. Magnetization curves as measured by AHE of Fe-O/Fe films with nominal Fe thickness of (a) 10 nm and (b) 2 nm in as deposited state and polarized in 1M KOH at -1.26 V and -0.18 V. The left inset in (a) sketches the *in situ* AHE measurement geometry with applied current I and measured R_{AH} in the film plane, and simultaneous polarization of the film via the KOH electrolyte. The right inset in (a) depicts the relative changes of $R_{AH,S}$ as measure for J_S for the 10 nm thick Fe films for 10 subsequent switching experiments. The state after reducing the film for the first time at -1.26 V is used as reference value $R_{AH,S}^{Ref}$. Sketches in (b) visualize the different film architectures with arrows indicating the expected local spin orientation.

The magnetic properties of as deposited Fe-O/Fe films with 10 and 2 nm nominal Fe thickness as measured by AHE are exemplarily displayed in Fig. 2 as black dashed curves. A linear increase of magnetization with increasing external magnetic field is observed for the most part, pointing at rotational magnetization processes. This is as expected for a thin film, where shape anisotropy dominates and the film plane is the magnetically easy plane. In the ideal case of a flat continuous Fe film, the field $\mu_0 H_S$ required for saturation in perpendicular direction should equal the saturation polarization J_S of 2.1 T. Fig. 3(a) shows that $\mu_0 H_S$ only amounts up to 1.4 T for the 10 nm film and is decreased further with decreasing film thickness. A deviation from shape anisotropy has already been reported for various Fe films.^{36–39} As origin, a decreased J_S and/or additional anisotropy contributions are discussed. In the present Fe-O/Fe films, a decreased J_S may result from the presence of ferrimagnetic γ -Fe₂O₃ ($J_S = 0.48$ T) and Fe₃O₄ ($J_S = 0.6$ T) in the native oxide layer.^{39,40} In addition, roughness induced anisotropy contributions³⁶ and a perpendicular interface anisotropy at the Fe/Pt interface^{37,38} can compete with shape anisotropy in the present films and lead to the reduction of H_S . All three origins are expected to be more dominant in thinner films, being consistent with the observed reduction of H_S when decreasing the film thickness (Fig. 3(a)).

Aiming at voltage-induced magnetic changes by the MI effect, the Fe-O/Fe films are used as working electrode subsequently polarized at -1.26 V and -0.18 V in the KOH electrolyte. The setup is schematically displayed in the left inset in Fig. 2(a). The *in situ* AHE curves obtained for 10 and 2 nm films are exemplarily shown in Figs. 2(a) and 2(b), respectively. Remarkable

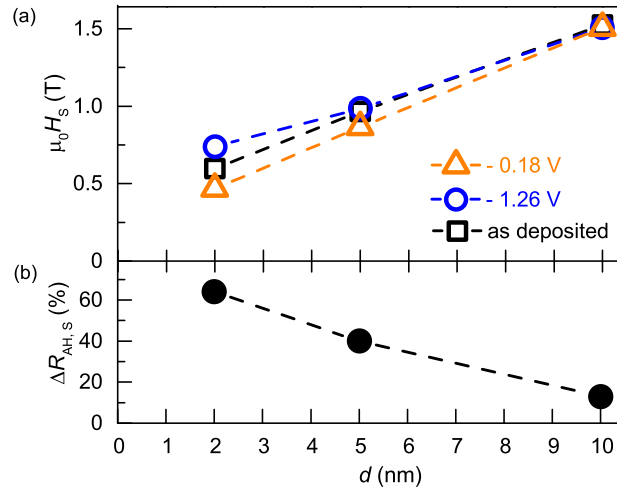


FIG. 3. (a) $\mu_0 H_s$ in dependence on the nominal Fe film thickness d and on the voltage during polarization in 1M KOH. $\mu_0 H_s$ has been approximated by extrapolation of the linear portion of the magnetization curve to the saturation value. (b) depicts $\Delta R_{AH,S} = [(R_{AH,S}(1.26 \text{ V}) - R_{AH,S}(0.18 \text{ V})) / (R_{AH,S}(1.26 \text{ V}))]$ as a measure for ΔJ_s in dependence on d .

voltage-induced changes of the magnetic properties are evident. The strongest change is observed for the value of the maximum anomalous Hall resistance $R_{AH,S}$. As $R_{AH,S}$ is proportional to J_s , changes in $R_{AH,S}$ are discussed as changes in J_s in the following. In comparison to the as deposited state, J_s is strongly increased when applying a voltage of -1.26 V. The voltage is subsequently switched to a more anodic potential of -0.18 V, resulting in a decrease of J_s . However, J_s still remains higher than in the as deposited state. The inset on the right in Fig. 2(a) shows that the significant change of J_s can be repeated for at least 10 times by switching between the two voltages. The voltage-induced change of J_s , given as $\Delta R_{AH,S}$ in Figure 3(b), strongly increases with decreasing film thickness. For 2 nm thick films, ΔJ_s amounts up to 64%. From Fig. 3(a) it becomes clear that for the 5 and 2 nm thick films also H_s is affected by the voltage. For -1.26 V, H_s is enhanced and for -0.18 V it is lowered in comparison to the as deposited state, and the effect is the strongest for the thinnest film of 2 nm.

In Figs. 1(b), 1(d), and 1(e), HRTEM, STEM, and EELS investigations of the 10 nm film after the electrochemical treatment are presented. The samples have been taken out of the electrolyte without an external potential applied. Thus, information on the oxidized (-0.18 V), rather than reduced state (-1.26 V), is obtained after removal from the electrolyte. The TEM overview and STEM images (Figs. 1(b) and 1(d)) resemble those of the as deposited state (Figs. 1(a) and 1(c)) and prove that the film has not deteriorated during repeated electrochemical polarization. In particular, the Fe-O layer is still continuous and not granular. In combination with the EELS line scan (Fig. 1(e)), the metallic Fe layer and a top iron oxide of about 3 nm thickness are identified.

In the following, the observed magnetic changes are discussed in relation to the expected electrochemical reactions. The strong voltage-induced ΔJ_s is consistent with a reversible reduction to ferromagnetic metallic Fe at -1.26 V and oxidation to a non- or weakly magnetic oxide film at -0.18 V in 1M KOH.^{41,42} Thus, when first polarizing the films at -1.26 V, electroreduction of the Fe-O layer to metallic Fe explains the large increase of J_s in comparison to the as deposited state. During the subsequent oxidation step at -0.18 V, the significant decrease of J_s is consistent with the expected formation of a passivating Fe-O layer composed of a mixture of Fe_3O_4 , Fe_2O_3 , and FeOOH .^{43,44} Schematically, the resulting film architectures for both voltages are visualized in Fig. 2(b). From the achieved ΔJ_s , it can be concluded that the metallic Fe layer undergoing electrooxidation exhibits a thickness of about 1.5 nm. Considering the volume expansion during oxidation, this corresponds to an Fe-O layer thickness of about 3-4 nm,^{43,44} in good agreement with the oxide layer thickness observed by HRTEM (Figs. 1(d) and 1(e)). This large reaction zone explains the enormous ΔJ_s achieved when the film thickness is reduced to few nanometers. Considering the Fe layer thickness dependence of H_s discussed earlier, the observed increase (decrease)

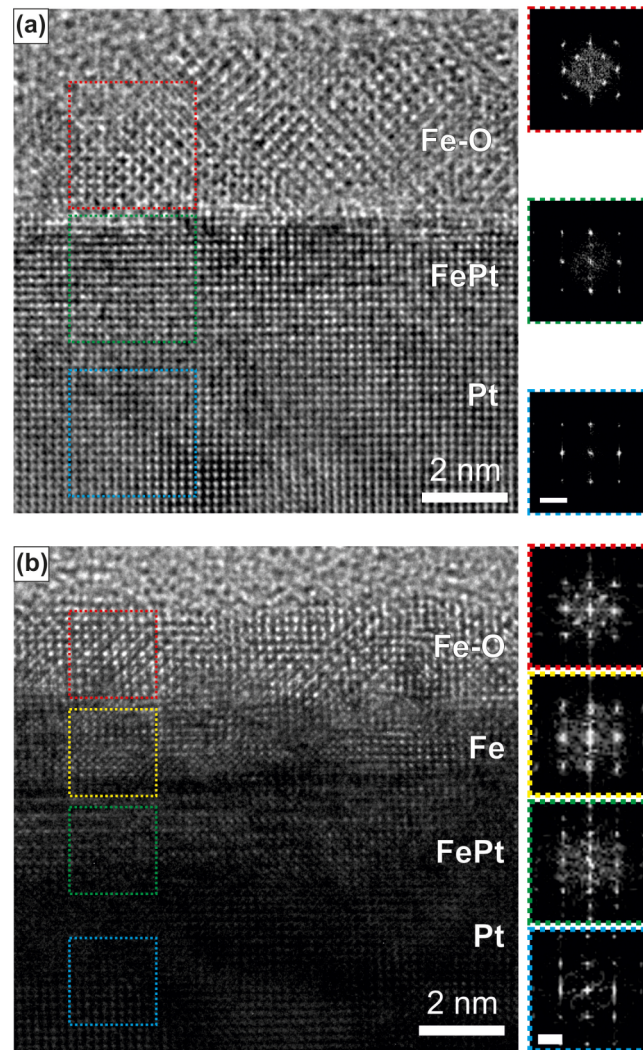


FIG. 4. HRTEM investigations of the Fe-O/Fe/FePt heterostructure (a) before and (b) after the electrochemical treatment. In (b) the selected FFT of the layers shows the growth of Fe and Fe₃O₄ with the epitaxial relation Pt[100](002)//FePt[100](002)//Fe[100](011)//Fe₃O₄ [100](004). The scale bar in the FFTs is 5/nm.

of H_S at -1.26 V (-0.18 V) (Fig. 3(a)) is consistent with the increase (decrease) of the Fe layer thickness by reduction (oxidation).

J_S after electrooxidation is decreased, but still remains higher than J_S of the as deposited state (Fig. 2). This as well as the observed drift towards higher J_S during subsequent reduction/oxidation steps (right inset in Figure 2(a)) might be related to an increasing remaining amount of metallic Fe when a more stable passive layer is formed during repeated electroreduction and electrooxidation (see discussion and Fig. 4(b) on Fe-O/Fe/FePt heterostructures below).

Up to now, large voltage-induced magnetization changes based on MI effects within several nanometers of the Fe-O/Fe surface in KOH have been proven. As a next step we in addition manipulate the bottom interface of the Fe film to adjust the magnetic anisotropy. We chose 3 nm thick, epitaxially grown, (001) oriented and L1₀ ordered FePt films with PMA as underlayer.²⁰ As expected for continuous L1₀ FePt(001) films,^{20,45} these films exhibit a rectangular magnetization curve and a remanence/saturation ratio close to one for a magnetic field applied perpendicular to the substrate. In comparison to thicker epitaxial FePt films on Pt buffer layers,⁴⁶ the present ultrathin FePt films exhibit a very low coercivity (0.06 T), which is consistent with the lower number of misfit dislocations observed.³⁴ Magnetization reversal occurs by switching of magnetization here, in

contrast to rotation of magnetization as observed in the Fe films. On top of the FePt layer, 3 nm Fe is sputter deposited. The composite Fe/FePt films are removed from the vacuum chamber which again leads to natural oxidation of Fe. The HRTEM image in Fig. 4(a) reveals that a virtually complete oxidation of the Fe layer occurred and an about 4–5 nm thick Fe-O layer is present on top of FePt. From the HRTEM and selected area FFTs, it can be concluded that the oxide layer is composed of Fe_3O_4 for the most part. FFT of the FePt layer only gives weak indications of $L1_0$ order, which is, however, most probably related to the destruction of chemical order by the FIB preparation of the TEM sample.

The AHE curve of the as deposited Fe-O/(Fe)/FePt heterostructure exhibits a slightly reduced coercivity and enhanced J_S in comparison to the FePt film (Fig. 5 and Ref. 34). The curve shape remains close to rectangular and the remanence/saturation ratio $R_{\text{AH,R}}/R_{\text{AH,S}}$ is still close to one. In agreement with the HRTEM investigations, this small change can be explained by only marginal metallic Fe remaining on top of FePt, as most of the iron is present in oxidized state. In this case, the properties are consistent with the film being in the rigid magnet regime⁴⁷ where due to exchange coupling the spin orientation in a soft magnetic Fe layer does not deviate from the FePt spin direction.³³ Schematically, this is illustrated in the respective sketch in Fig. 7. In experiments and calculations, the critical thickness of the Fe layer for the transition from rigid magnet to exchange spring magnet regime in Fe/FePt composites is reported to be around 2–3 nm.^{33,47}

After immersion of the Fe-O/Fe/FePt composite film in 1M KOH and application of -1.26 V and -0.18 V, strong voltage-induced changes of the magnetic hysteresis are observed (Fig. 5). Fig. 6(a) summarizes the relative change of J_S and the remanence/saturation ratio extracted from the hysteresis for several subsequent switching steps. At -1.26 V, J_S is always increased whereas the remanence/saturation ratio is significantly decreased. Applying -0.18 V leads to a decrease of J_S and at the same time to an increase of the remanence/saturation ratio. Similar to the case of Fe films, J_S at -0.18 V still remains higher than that of the as deposited state.

The inset in Fig. 5 displays the normalized AHE curves to better illustrate the additional significant voltage induced changes in curve shape. In comparison to the as deposited state, for -0.18 V the hysteresis exhibits a rounded part that points towards rotational processes in addition to switching of magnetization. The deviation from the rectangular shape is even more pronounced at -1.26 V, where a significant part of the hysteresis exhibits a continuous increase of magnetization. Here, rotation of magnetization dominates over switching of magnetization, proving that the magnetic easy axis of the composite film is no longer fully perpendicular to the substrate. The conventional approach to quantify PMA by comparing in-plane and out-of-plane magnetization curves is

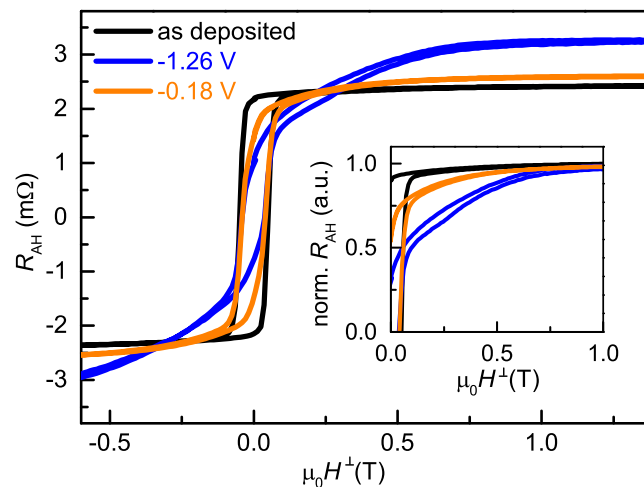


FIG. 5. Magnetization curves as measured by AHE of Fe-O/Fe/FePt composite films in as deposited state and during polarization at -1.26 V and -0.18 V in 1M KOH. The inset shows corresponding normalized first quadrant magnetization curves.

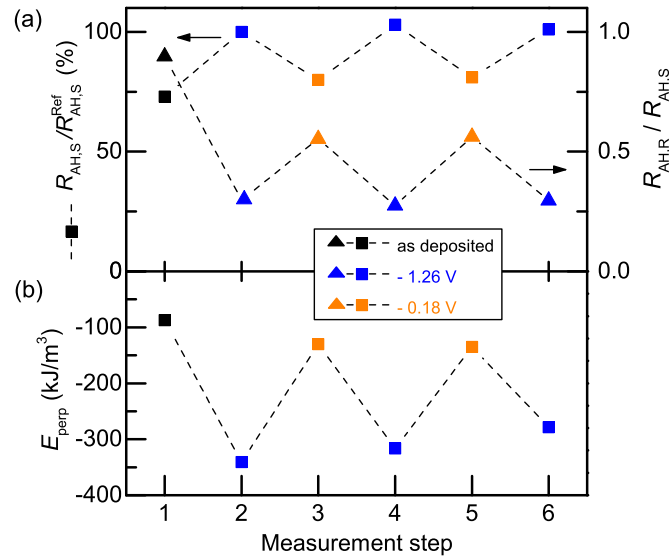


FIG. 6. Magnetic properties of Fe-O/Fe/FePt composite films in as deposited state and for 5 subsequent switching experiments in 1M KOH at -1.26 V and -0.18 V: (a) Relative change of $R_{AH,S}$ as measure for J_S (left axis) and remanence/saturation ratio $R_{AH,R}/R_{AH,S}$ (right axis), (b) E_{perp} . In (a), the value of $R_{AH,S}$ during first time polarizing at -1.26 V is taken as reference value $R_{AH,S}^{Ref}$.

not possible here, as curves with the magnetic field applied parallel to the substrate are not measurable with AHE. Alternatively, the energy required for saturation when magnetizing in perpendicular direction can be calculated from the area between the AHE curve and the y-axis according to $E_{perp} = -\frac{J_S}{R_{AH,S}} \int_0^{R_{AH,S}} H dR_{AH,S}$.¹⁷ A step-like AHE curve and negligible E_{perp} are expected for full perpendicular alignment of the spins. Due to the negative sign in the formula, deviations from fully perpendicular anisotropy result in a decrease of E_{perp} , allowing to evaluate changes in E_{perp} as changes in PMA. The ratio $\frac{J_S}{R_{AH,S}}$ has been derived from the curve at -1.26 V, assuming that at this potential the composite is close to the fully reduced state.⁴² In Fig. 6(b), E_{perp} is plotted for the subsequent polarizing steps. For -1.26 V, E_{perp} is always decreased, indicating a lower PMA. In contrast, E_{perp} is increased at -0.18 V, pointing towards higher PMA. By application of the different voltages, E_{perp} can be switched from about -100 kJ/m³ to about -350 kJ/m³. Evaluating the ratio of magnetic anisotropy energy change following the proposal of Maruyama *et al.*,¹⁷ we achieve 55% change of magnetic anisotropy energy. This anisotropy change, achieved for a voltage change of only a few volts, is higher than the anisotropy change of 39% achieved in Fe monolayers charged via a dielectric layer and for much higher voltage difference of 400 V.¹⁷

HRTEM investigations after the electrochemical treatment (Fig. 4(b)) reveal a layered Fe₃O₄/Fe/L1₀-FePt/Pt heterostructure. As discussed with the Fe-O/Fe films, information gained here represents the oxidized state. It is remarkable that, even though samples have had contact to air after removal from the electrolyte, a well-defined trilayered heterostructure is observed (Fig. 4(b)) that is clearly different from the Fe-O/FePt bilayer present after natural oxidation (Fig. 4(a)). A metallic

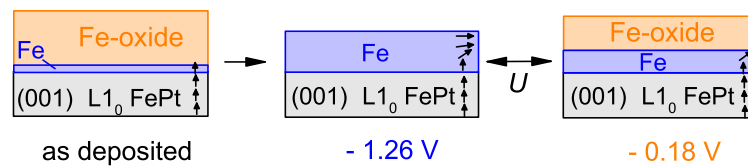


FIG. 7. Idealized drawings of the film architectures present in as deposited state and during polarization at -1.26 V and -0.18 V in 1M KOH. Arrows indicate the expected local spin direction.

Fe layer with a thickness of about 2 nm is sandwiched between Fe-O and FePt. This is backed up by supplementary EELS measurements.³⁴ The fact that metallic Fe is observed after repeated electroreduction and electrooxidation suggests that a more stable and protective passive iron oxide layer forms during electrochemical treatment in KOH than by oxidation in air. The structural data obtained by FFT allow to identify the iron oxide as Fe₃O₄. The FePt, Fe, and Fe₃O₄ layers all exhibit an epitaxial relationship: Pt[100](002)//FePt[100](002)//Fe[100](011)//Fe₃O₄[100](004). Thus, on the epitaxial L1₀ FePt underlayer epitaxial growth of metallic Fe and Fe₃O₄ takes place during repeated electroreduction and electrooxidation, respectively.

The oxidized state, exhibiting an Fe/FePt bilayer with 2 nm Fe layer thickness, is at the critical point for the transition from rigid magnet to exchange spring magnet behaviour.^{33,47} This allows to discuss the observed large voltage-induced changes in anisotropy by a combination of MI effects at the Fe-O/Fe surface with exchange coupling at the Fe/FePt interface. As discussed for single Fe-O/Fe films, voltage-induced reduction and oxidation will cause a variation of the metallic Fe layer thickness. The observed voltage dependent J_S is a straightforward consequence of this. In addition, the Fe layer thickness defines the average spin orientation in the Fe layer in Fe/FePt composites: With increasing distance from the Fe/FePt interface, Fe spins will gradually deviate from perpendicular direction towards the film plane.³³ The change in film architecture and the expected resulting local spin orientations are visualized for both voltages in the sketches in Fig. 7. For the reduction step, a large Fe layer thickness results in a great share of Fe spins deviating from the perpendicular direction. This explains the observed dominant rotational magnetization processes, lower PMA and low remanence/saturation ratio at -1.26 V. Electrooxidizing the Fe layer at -0.18 V in turn leads to a decrease of Fe film thickness and thus increased fraction of perpendicularly oriented spins. As a result, the remanence/saturation ratio and PMA strongly increase. This process is reversible as evident from the six measurement steps summarized in Fig. 6. Still, both values are lower than the respective values of the as deposited Fe/FePt composite with native oxide layer. In agreement with HRTEM, this is due to the higher amount of metallic Fe remaining after electrooxidation in comparison to oxidation in ambient air.

To summarize, strong voltage-induced changes of both saturation magnetization and anisotropy are demonstrated in Fe-O/Fe heterostructures with tailored top and bottom interfaces by exploiting MI effects. It is especially remarkable that naturally oxidized Fe surfaces are sufficient and neither protection atmosphere nor cap layers are required. For a few nanometer thick Fe-O/Fe films, most of the magnetic volume can be converted by an external voltage. Reduction and oxidation of Fe species in 1M KOH readily take place in a reaction layer thickness of several nanometers and allow for large magnetization changes when merely 1.1 V is applied at room temperature. This is advantageous in comparison to E -effects obtained with solid electrolytes, where heating or significantly higher voltages are required for reasonable magnetic property changes.^{14,15,17,25,26} For device implementation of a liquid electrolyte, concepts from batteries and supercapacitors may be adopted. In contrast to E -effects obtained by capacitive charging, which can only control the topmost metallic atomic layers, here several nanometers are affected. This allows to control a volume appropriate for most nanoscale applications. In the present work, the reversibility of the magnetoionic changes was proven for up to 10 cycles. With regard to application, the longevity of the changes must be further investigated. Recent work on supercapacitors,⁴⁸ exploiting similar oxidation and reduction reactions in Fe/alkaline electrolyte systems, showed reversibility for at least several hundreds of cycles.

Combining the variable Fe-O/Fe film with a permanent L1₀ FePt(001) underlayer enables E -induced changes of the average magnetization orientation and switching from rigid magnet to exchange spring magnet regime. The mechanism is based on the MI-induced variation of the Fe layer thickness in a well defined and epitaxial Fe₃O₄/Fe/FePt heterostructure evolving during electrooxidation and electroreduction. As consequence, magnetization, remanence ratio, and PMA can be reversibly manipulated by an applied electric field. The proposed concept of combining a top surface utilizing MI effects with a tailored bottom interface controlled by magnetic exchange coupling allows to achieve E -control of magnetization and PMA at the same time. This approach

is promising for novel low-power spintronic devices and expandable to a variety of functional nanostructures.

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