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Large voltage-induced magnetic anisotropy change in a few atomic layers of iron

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In the field of spintronics, researchers have manipulated magnetization using spin-polarized currents[1-3]. Another option is to use a voltage-induced symmetry change in a ferromagnetic material to cause changes in magnetization or in magnetic anisotropy[4-14]. However, a significant improvement in efficiency is needed before this approach can be used in memory devices with ultralow power consumption. Here, we show that a relatively small electric field (less than 100 mV nm^{-1}) can cause a large change (~40%) in the magnetic anisotropy of a bcc Fe(001)/MgO(001) junction. The effect is tentatively attributed to the change in the relative occupation of 3*d* orbitals of Fe atoms adjacent to the MgO barrier. Simulations confirm that voltage-controlled magnetization switching in magnetic tunnel junctions is possible using the anisotropy change demonstrated here, which could be of use in the development of low-power logic devices and non-volatile memory cells.

To develop voltage-driven spintronic devices, several areas of investigation have been suggested, including voltage control of magnetic anisotropy[4,7], ferromagnetism in ferromagnetic semiconductors[8,9], magnetoelectric switching of exchange bias[10,11] and anisotropy[12], magnetoelectric interface effects[5,6], multiferroic properties[13] and magnetostriction in a hybrid system with piezoelectric materials[14]. Most work to date has been carried out only at low temperatures, using GaMnAs or perovskite systems, or needed piezoelectric distortions, which may limit the endurance of any devices. Weisheit and colleagues[7] observed up to 4.5% coercivity change in FePt(Pd) films with the application of voltage. However, they required the use of a liquid electrolyte to apply a high electric field at the surface. In this study, we have overcome these difficulties by using ultrathin Fe/MgO junctions. The system is built from all-solid-state and distortion-free materials that have controllable perpendicular surface anisotropy[15–20].

As shown in Fig. 1, the sample structure stack layers comprised a MgO substrate/MgO(10 nm)/Cr(10 nm)/Au(50 nm)/Fe(2–4 ML)/MgO(10 nm)/polyimide(1,500 nm)/ITO(100 nm) (ML, monatomic layer; see Methods). Because the influence of the electric field on the perpendicular anisotropy is effective only at the interface, the ferromagnetic layer had to be composed of only a few monatomic layers. In addition, to control the perpendicular anisotropy, the film had to have a moderate crystalline and surface anisotropy in the absence of the bias voltage. In this regard, we used an ultrathin Fe layer for the anisotropy change. Because the Fe grew almost in a layer-by-layer mode onto the Au(001) surface at room temperature, we were able to precisely control the layer thickness[21]. The ultrathin epitaxial Fe layer deposited on the Au(001) buffer layer exhibited a transition in magnetic anisotropy from in-plane to perpendicular, depending on the film thickness[20]. Such features are ideal for the observation of the anisotropy change in response to the electric field, because we could systematically control the strength of the perpendicular anisotropy. The insulating layers comprised MgO and polyimide. MgO was used because it can be epitaxially grown onto an Fe(001) surface and exhibits a high breakdown voltage as a barrier material in magnetic tunnel junctions[22]. The polyimide layer was used to ensure a pinhole-free barrier over an extended area.

Figure 2 shows representative magnetic hysteresis loops in a 0.48-nm-thick Fe layer under the application of a bias voltage, obtained from Kerr ellipticity, η_K, measurements. Under two different bias voltages, $U = +200$ and -200 V, a significant change in perpendicular anisotropy was observed. The perpendicular magnetic anisotropy energy per unit volume of the film, E_{perp}, was calculated from the η_K–H curve, assuming a linear relation between η_K and magnetization:

$$E_{perp} = -\mu_0 \frac{M_s}{\eta_s} \int_0^{\eta_s} H \mathrm{d}\eta_K, \qquad (1)$$

where μ_0, M_S, H, η_K and η_s are permeability of free space, saturation magnetization, external magnetic field, Kerr ellipticity and saturation Kerr ellipticity, respectively. If the film possesses uniaxial crystalline anisotropy K_u, and surface anisotropy K_s, the E_{perp} is expressed as

$$E_{perp}d = \left(-\frac{1}{2}\mu_0 M_s^2 + K_u\right)d + K_{S,MgO/Fe} + K_{S,Fe/Au} + \Delta K_S(V) \qquad (2)$$

where d is the film thickness. $\Delta K_S(V)$ is a surface anisotropy, induced by application of a voltage. When a positive voltage $U = +200$ V was applied, then decreased to $U = -200$ V, perpendicular anisotropy was induced and the magnetic anisotropy energy was changed from -31.3 to -13.7 kJ m^{-3}. The ratio of the magnetic anisotropy energy change, defined as $\Delta E_{perp}/(2E_{perp,ave}) = (E_{perp,200V} - E_{perp,-200V})/(E_{perp,200V} + E_{perp,-200V})$, was 39%. If we count this change as a change in the surface anisotropy energy, that is, $\Delta K_s(V)$ in equation (2), it corresponds to 8.4 μJ m^{-2}.

To precisely measure the thickness dependence of the effect, we used a modulation technique (see Methods). The inset in Fig. 2 shows the external field dependence of the $\mathrm{d}\eta_K/\mathrm{d}V$ signal that was obtained for the same sample. The $\mathrm{d}\eta_K/\mathrm{d}V$ signal displays a maximum value, $(\mathrm{d}\eta_K/\mathrm{d}V)_{max}$, where the η_K hysteresis curves, obtained for positive (B) and negative (A) bias voltages, show a

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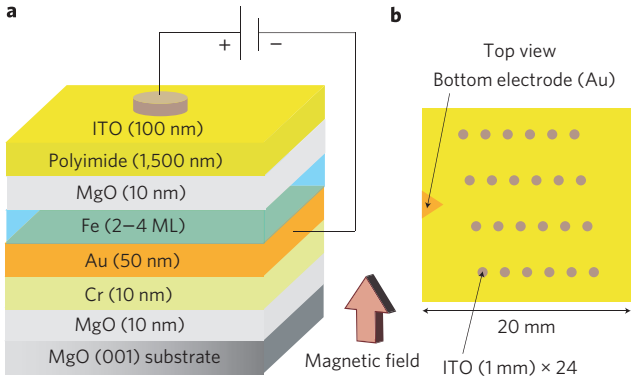

Figure 1 | Schematic of the sample used for a voltage-induced magnetic anisotropy change. a, A positive voltage is defined as a positive voltage on the top electrode with respect to the bottom electrode. A perpendicular magnetic anisotropy was induced by a negative voltage. The magnetic field was applied perpendicular to the film plane for Kerr ellipticity measurements. **b**, We fabricated the wedge-shaped Fe layer, incorporating 24 samples on the substrate, to investigate the dependence of the effect on Fe thickness.

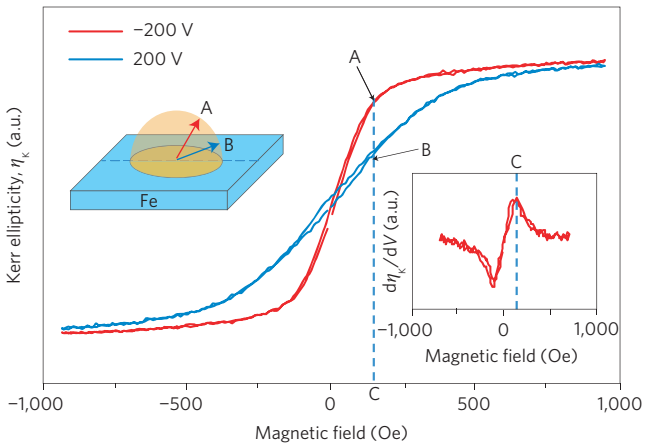

Figure 2 | Magneto-optical Kerr ellipticity η_k for different applied voltages as a function of applied field. The thickness of the Fe film was 0.48 nm. A significant change in the hysteresis curve indicated a large change in perpendicular anisotropy following application of the bias voltage. The right inset shows the voltage modulation response of the Kerr ellipticity, $d\eta_K/dV$. The left inset illustrates the magnetization direction at points A and B in the hysteresis curves.

maximum difference (C point in Fig. 2, inset). Figure 3a shows $(d\eta_K/dV)_{max}$ as a function of film thickness. The effect was largest for an Fe film with a thickness of 0.48 nm, and was smaller for both thinner and thicker films. Because the influence of the electric field is effective only at the metal/insulator interface, it is natural to observe a smaller effect for the thicker Fe films. Figure 3b shows the dependence of the saturation Kerr ellipticity, η_s, on Fe thickness. The linear dependence of η_s down to 0.25 nm (1.8 ML on average) proves that continuous films had been grown, even if they were only a few atomic layers in thickness. In addition, this behaviour also proves that the film was uniform across the thickness. In Fig. 3c, $E_{perp}d$ is plotted as a function of Fe layer thickness d at zero bias voltage, together with a linear fit using equation (2). The fit indicates that $K_{s,MgO/Fe} + K_{s,Fe/Au} = 580\ \mu J\ m^{-2}$ and $M_s = 1.5\ MA\ m^{-1}$, neglecting a contribution from K_u. M_s is about 83% that of the bulk value. The reduction in the apparent M_s could be caused by a contribution from a positive K_u, produced by a lattice mismatch between Fe and Au (1.6%). The value of $K_{s,MgO/Fe} + K_{s,Fe/Au}$ observed here was a little higher than previous observations made on a Au/Fe(001) interface[23], $K_{s,Fe/Au} = 470$, 400, 540 $\mu J\ m^{-2}$. This suggests that the MgO/Fe interface also has a positive contribution to K_s. The experimental data deviate from the linear fit line below 0.48 nm. This is well-documented behaviour for ultrathin films and may have many origins[24]. The thickness at which the linear fit, using equation (2), starts to deviate corresponds to the thickness where the maximum of $(d\eta_K/dV)_{max}$ is obtained. One of the possible reasons for this is a deterioration of the film quality in this ultrathin thickness region. Clarification of the mechanism of the deviation requires further investigation.

One possible origin of the effect is in the influence of an electric field on electron filling of the Fe layer, which should affect the magnetic anisotropy (see Supplementary Information). Kyuno and colleagues pointed out that surface magnetic anisotropies in 3*d* ferromagnetic metal/noble metal interfaces were very sensitive to the electron filling of 3*d* orbitals[25]. In our case, from the capacitance of the junction, we estimate that we could change electron filling by 2×10^{-3} electrons per Fe surface atom by the application of 200 V. From the density of states, this corresponds to about 1 meV change in chemical potential (see Supplementary Information). This small change, however, may produce a non-negligible change in the surface anisotropy energy. From our experiment, we could change anisotropy energy by 4 μeV per surface Fe atom. This magnitude of change can be reproduced from Kyuno's calculation using 1 meV change in the chemical potential. Kyuno also noted that the effect originates mainly from the large density of states (DOS) of a d_{xy} and $d_{x^2-y^2}$ character ($|m_z| = 2$) in the Fermi energy in the Fe/Au (001) system, in which Au has a large spin–orbit coupling[26–29]. In our case, because the Fe has two interfaces, with Au(001) and MgO(001), the situation is not completely the same, but a similar mechanism may occur. As schematically shown in Fig. 3d, the application of a negative voltage, for example, may cause an increase in the energy of the $d_{3z^2-r^2}$ ($m_z = 0$) states, because of higher electron density at the barrier/Fe interface, leading to a reduction in the electron occupancy in those states. Therefore, the electron occupancy in the d_{xy} and $d_{x^2-y^2}$ states could be changed relative to one another, leading to a modulation of the magnetic anisotropy. Further discussion requires first principles calculations.

In our experiment, we needed to apply a large voltage because of the thickness of the polyimide layer. The estimated voltage drop across the MgO layer, however, was ~45 mV nm^{-1} if we can neglect charge accumulation in the barrier (see Supplementary Information). As we know that more than 2 V can be applied to a 2-nm-thick MgO barrier, a much larger effect can be expected for conventional tunnel magnetoresistance junctions with a MgO barrier.

In the latter part of this letter, we suggest a novel magnetization switching technique, using the voltage-induced magnetic anisotropy change explored in this work (see Supplementary Information). Figure 4 shows a result of macro-spin model simulation of voltage-controlled magnetization switching for a 0.48-nm Fe film. Here, we used parameters obtained from the above described experiments and an additional ferromagnetic resonance (FMR) experiment (see Fig. 4 caption). An external magnetic field of 8 kA m^{-1} was applied normal to the film plane to tilt the magnetization towards the perpendicular direction. Initially, the bias voltage was held off (point A in Fig. 4). If we then apply a bias voltage with a slow rise time, the perpendicular anisotropy field changes and the magnetization changes its direction to point B. However, if the rise time of the pulse is short enough (less than 1 ns), a dynamic precession and switching to another energetically stable point is achieved (point C in Fig. 4). When the voltage pulse is switched off with a slow fall time, the magnetization stabilizes at point D (Fig. 4) after the relaxation process. This simulation clearly shows that if we

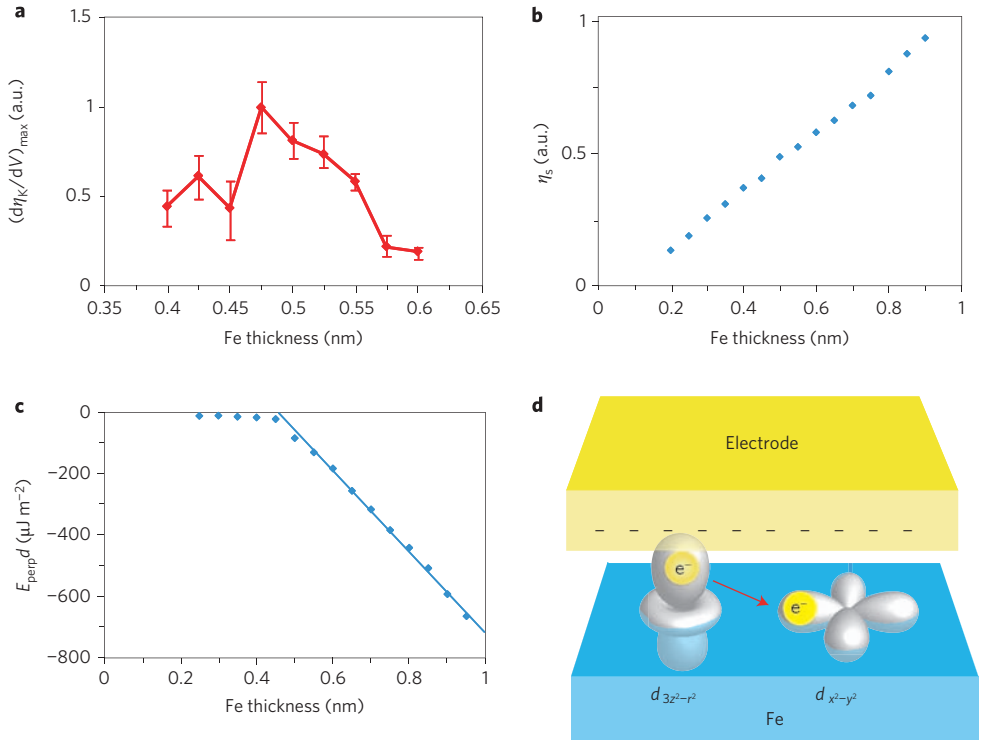

Figure 3 | Fe layer thickness dependencies of the voltage modulation response of η_K, saturation Kerr ellipticity η_s, and $E_{perp}d$. a, Maximum $d\eta_K/dV$ signal as a function of Fe layer thickness. The lock-in modulation technique was used for the precise measurement of the voltage response. The line through the data is a visual aid. **b**, Fe layer thickness dependence of the saturation Kerr ellipticity η_s. **c**, Plot to calculate surface anisotropy energy and bulk anisotropy energy. The Y-cut corresponds to the surface anisotropy energy. The slope corresponds to the bulk anisotropy (see text). **d**, Schematic of the effect of the electric field on electron filling of the 3*d* orbitals in the ultrathin Fe layer. Application of a negative voltage, for example, may suppress the number of electrons in the $m_z = 0$ states, because of the quadrupole effect.

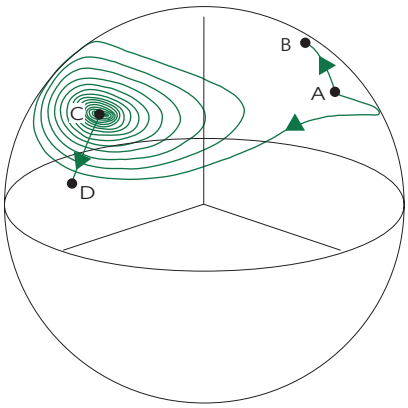

Figure 4 | A macro spin model simulation of voltage-controlled magnetization switching. The green line indicates the trajectory of the spin. The parameters used for the calculation include a damping constant $\alpha = 0.025$, perpendicular anisotropy fields of 12 kA m^{-1} for the on state and 22 kA m^{-1} for the off state. An external perpendicular field of 8 kA m^{-1} is also applied to tilt the magnetization. The magnetic cell is assumed to have a rectangular shape, with a 1.6 kA m^{-1} in-plane hard axis demagnetization field.

fabricate a Fe/MgO/Fe/Au junction with radio-frequency signal access, successful magnetization switching by the application of high-speed, low-voltage pulse should be possible. We believe that this novel magnetization switching will be demonstrated in the near future and, by combining it with magnetoresistive structures, could prove to be a highly successful technique.

Our results show that it is possible to control magnetic anisotropy by the application of an electric field in Fe/MgO junctions, which can be combined with high-quality Fe/MgO/Fe magnetic tunnel junctions. This approach provides a technique for voltage-controlled magnetization switching and could lead to innovations in ultra-low-power spintronic devices.

Methods

In this study, we focused on a structure comprising a solid insulator and an ultrathin epitaxial ferromagnetic layer with moderate perpendicular surface anisotropy[15–20]. The sample structure consisted of MgO substrate/MgO(10 nm)/Cr(10 nm)/Au(50 nm)/Fe(2–4 ML)/MgO(10 nm)/polyimide(1,500 nm)/ITO(100 nm) layers. All layers, except for the top thick polyimide and ITO layers, were grown epitaxially by a molecular beam epitaxy method, using electron beam evaporators in an ultra-high vacuum. The Au buffer layer was annealed at 250 °C, after deposition at room temperature, to obtain an atomically flat surface. The ultrathin Fe layer and insulating MgO layer were grown on the Au(001) surface at room temperature. The sample was coated with polyimide using a spin coater, and annealed at 200 °C. ITO was used for the top electrodes, 1 mm in diameter, and was deposited using a metal mask. A bias voltage was applied between the top ITO and the bottom Au electrode.

Magnetic hysteresis loops of ultrathin Fe films were measured using the magneto optical Kerr effect (MOKE) in a polar configuration[30]. The voltage dependence of the hysteresis was detected either by a direct observation of Kerr ellipticity, η_K, signals for different bias voltages, or by a lock-in detection of the small change in Kerr ellipticity with respect to an applied bias voltage modulation, $d\eta_K/dV$. The modulation amplitude and frequency were 160 V (peak-to-peak) and 37 Hz, respectively.

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Author contributions

Y.S. conceived and designed the experiments and performed micro magnetic calculation. T.M. and Y.S. performed the experiments and analysis. T.N. and A.A.T. led experiments and physical discussions. K.O., N.T. and M.M. established experimental techniques. S.M. and Y.A. performed FMR measurements. M.S. and T.S. contributed to general discussions. T.M. wrote the paper with review and input from Y.S., T.N. and A.A.T.

Additional information

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