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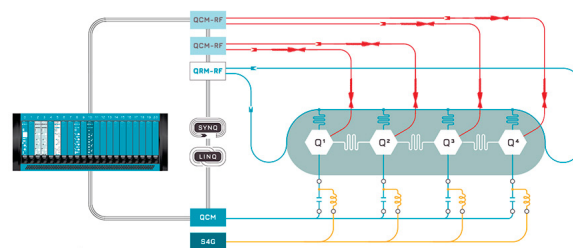
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Ultra-low voltage control of magnetic properties in amorphous MgO

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We report ultra-low voltage controlled magnetic properties in an amorphous MgO (a-MgO) thin film. The intrinsic magnetization of MgO can be decreased by about 57.5% by the application of a positive bias voltage while increased by about 56.7% by a negative bias, at an ultralow voltage of just 0.2 V. More interestingly, this ultralow voltage also induces a strong magnetic anisotropy in the a-MgO film. Further analysis indicates that the migration of O²⁻ ions under an electric field results in a change in the Mg/O ratio and the redistribution of Mg vacancies, thus leading to the change in the magnetic properties of the film. The control of room temperature magnetic properties at ultralow voltages may find applications in multifunctional memory and ultralow-power consumption spintronics. *Published by AIP Publishing.* <https://doi.org/10.1063/1.5000129>

The electrical control of magnetic properties is of significant importance for both basic science and low-power-consumption spintronics.^{1,2} Significant progress in this area has been made in many materials, such as magnetic semiconductors,³ multiferroic materials,⁴ and magnetic tunnel junctions (MTJs).⁵ However, most magnetoelectric effects in these materials lack the property of nonvolatility.^{3–5} Recently, the electrical control of nonvolatile magnetization through the resistive switching (RS) effect has been observed in doped and undoped crystallized oxide films, such as Mn:TiO₂,⁶ Co:ZnO,⁷ Fe:ZnO,⁸ Mn:ZnO,⁹ TiO₂,¹⁰ ZnO,¹¹ and HfO₂.¹² The migration of O²⁻ ions under an applied electric field is commonly used to explain this phenomenon. However, the magnetic modulation in amorphous oxides through the RS effect is only beginning to be explored. Compared to crystallized films, the amorphous oxide film offers many merits such as higher oxygen ion mobility, lower process temperature, and good cell-to-cell uniformity.^{13–15} Thus, it is natural to expect that a high-performance magnetoelectric device could be developed by utilizing amorphous films as functional materials.

As a classical simple metal oxide, MgO has a wide band-gap rocksalt structure, with applications ranging from MTJs¹⁶ to ac-type plasma display panels¹⁷ to heterogeneous catalysis.¹⁸ On the one hand, the RS effect was observed in ultrathin MgO-based tunnel barriers^{19,20} and relatively thick MgO films.^{21,22} The random barrier double-well model²³ and conductive filament mechanism²⁴ have been proposed to explain these phenomena, respectively. On the other hand, the undoped MgO film with defects has been found to demonstrate room-temperature ferromagnetism.^{25–27} Theoretical calculations^{28,29} and experimental results^{25,26} show that the magnetism in MgO is induced by Mg vacancies. The majority of the magnetic moments arises from the spin polarization

of the 2p electrons of O atoms surrounding the Mg vacancies.²⁸ Nevertheless, a few reports suggest that the ferromagnetism in MgO might originate from O vacancies.³⁰ The origin of ferromagnetism in pure MgO is still controversial. Furthermore, even though the RS characteristics in the magnetic MgO film have been reported previously,³¹ the electrical control of magnetic properties in the MgO film has not been investigated yet. Here, we show that nonvolatile ferromagnetism in the amorphous MgO (a-MgO) film can be reversibly controlled by means of a very low programming voltage of 0.2 V. Interestingly, electric-field-induced anisotropic magnetization in a-MgO films was also observed. The physical mechanism of the change in the Mg/O ratio under applied bias voltage and hence magnetism with low-resistance state (LRS) and high-resistance state (HRS) was discussed.

The MgO film was deposited on a Pt/Ti/SiO₂/Si substrate by the pulsed laser deposition (PLD) method from a magnesium oxide target. During the deposition, KrF pulse laser ($\lambda = 248$ nm) energy was controlled to be 300 mJ at 1 Hz with a substrate temperature of 600 °C in a vacuum of 10 Pa. Then, the subsequent *in situ* annealing was performed in an oxygen atmosphere at 600 °C for 30 min. Circular Ti top electrodes with a diameter of 200 μ m were deposited on the film with a shadow mask via direct current (DC) magnetron sputtering. X-ray diffraction (XRD, X'pert PRO MPD) was employed to characterize the crystal structure of the MgO film, and no any peak related to the crystalline phase of the MgO was observed. The photoluminescence (PL) spectrum was measured using a spectrofluorophotometer (SHIMADZU, RF-5301PC). The thickness of the film was studied using a field-emission scanning electron microscope (FE-SEM, Hitachi, S-4800). The current-voltage (*I-V*) characteristics were carried out by a two probe configuration using a Keithley 2612A source meter. Hysteresis loops were measured using a physical property measurement system (PPMS, Quantum Design). The elemental compositional and

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chemical state analysis was performed using X-ray photo-emission spectroscopy (XPS) measurements (PHI5000 Versa Probe).

Figure 1(a) shows the PL spectrum of the as-grown a-MgO film excited at a wavelength of 225 nm. A broad peak centered at 370 nm is evident, indicating the existence of Mg vacancies in the a-MgO film.^{26,27,32} Figure 1(b) shows a cross-sectional scanning electron microscopy (SEM) image of the as-deposited a-MgO film. The thickness of the film was estimated to be approximately 35 nm. From the wide-scan XPS spectrum of the a-MgO film [Fig. 1(c)], the only elements present in the film were Mg, O, and C; thus, the incorporation of any additional magnetic impurities could be ruled out.

The inset of Fig. 2(a) shows the schematic configuration of the a-MgO memory cell. The bias voltages were applied to the Ti top electrode (TE) with the Pt bottom electrode (BE) grounded. Figure 2(a) shows typical I - V characteristics of the Ti/a-MgO/Pt memory cell. The device exhibits bipolar switching behavior without the electroforming process. It is worth noting that the magnitudes of both SET and RESET voltages are only 0.2 V. The corresponding electric field (given by the voltage divided by the active layer thickness) in the SET/RESET process is only 57 kV/cm, which is much lower than that in the crystallized MgO film (for example, 430 kV/cm and 595 kV/cm in SET and RESET processes³³). Such a low operating voltage and electric field mean that the device requires less energy. The endurance property of the memory cell is shown in the inset of Fig. 2(a). The switching operations almost follow the same trace during more than 800 cycles, suggesting the good endurance and consistent performance of the memory cell. Figure 2(b) shows the

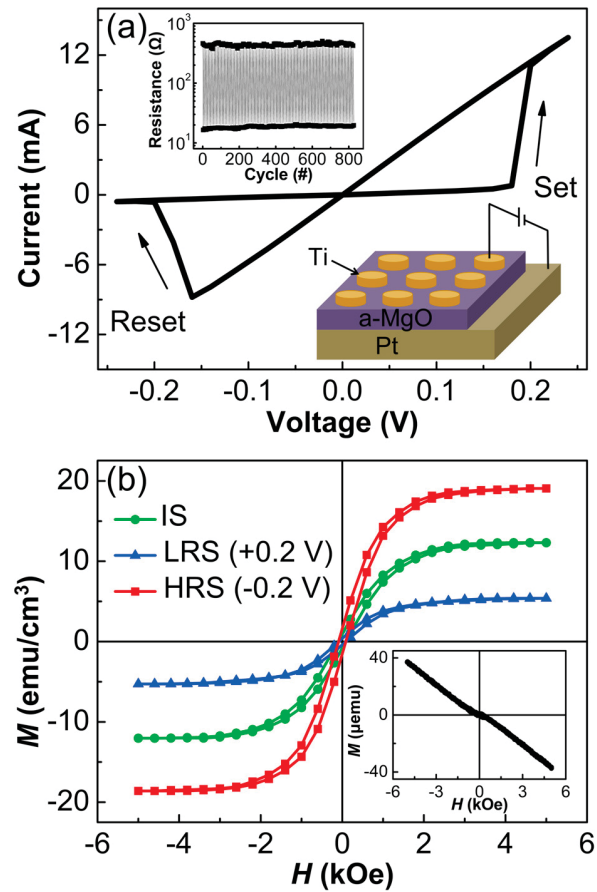


FIG. 2. (a) Typical switching loop of the Ti/a-MgO/Pt memory cell. The inset shows the endurance property read at 0.1 V and schematic configuration of the Ti/a-MgO/Pt memory cell. (b) The in-plane magnetic hysteresis loops of the a-MgO film in the IS, LRS, and HRS at room temperature. The inset shows the signal of the Pt/Ti/SiO₂/Si substrate.

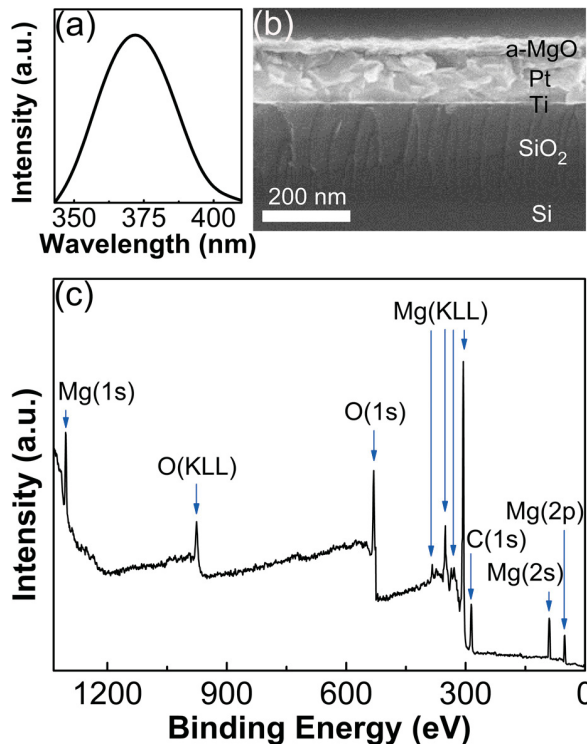


FIG. 1. (a) PL spectrum, (b) cross-sectional SEM image, and (c) wide-scan XPS spectrum of the as-grown a-MgO film.

hysteresis loops of the a-MgO film at room temperature in different resistive states (the signal from the commercially obtained Pt/Ti/SiO₂/Si substrate is shown in the bottom-right of Fig. 2(b) and has been subtracted using the method similar to that described in Refs. 7, 9, and 34). Ferromagnetism with different saturation magnetization (M_s) levels was observed in the initial state (IS), low-resistance state (LRS), and high-resistance state (HRS). The M_s of the a-MgO film in the IS was approximately 12 emu/cm³, which is comparable to the values previously reported for pristine MgO materials.^{26,35} After each cell was simultaneously triggered into the LRS using a voltage of 0.2 V, the value of M_s decreased to 5.1 emu/cm³. When the device was switched to the HRS by applying a reset voltage of -0.2 V, the value of M_s significantly increased to 18.8 emu/cm³, which is approximately four times greater than that in the LRS. The variation of the magnetization in the a-MgO film was quite different from that of most metal oxide materials, such as ZnO and TiO₂, in which the value of M_s reaches the maximum in the LRS.^{10,11} This difference may arise from the different magnetism origin in MgO compared to that of other metal oxides (for example, the magnetism of ZnO and TiO₂ originates from O vacancies^{36,37}). More interestingly, unlike the isotropic magnetization in the IS and LRS, the magnetization in the HRS was found to be remarkably anisotropic, as shown in Fig. 3. The value of M_s was found to be much greater when the

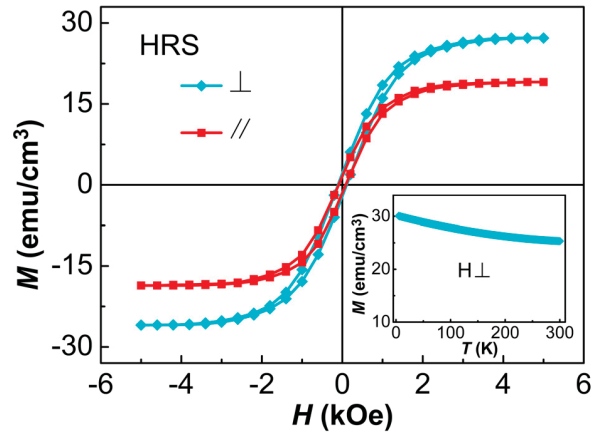


FIG. 3. The hysteresis loops in the HRS with the field parallel (//) and perpendicular ($\perp$) to the film. The inset shows the temperature dependence of the magnetization taken at 5000 Oe field perpendicular to the film.

magnetic field was applied perpendicular to the film than when it was applied parallel to the film. Furthermore, the temperature dependence of the magnetization (M - T) curve exhibited pronounced ferromagnetic behavior with Curie temperature (T_c) above 300 K under the field perpendicular to the film (inset of Fig. 3).

To investigate the mechanism of electrical control of magnetic properties through the RS effect in the a-MgO, we performed XPS depth profiling analyses of the Ti/a-MgO/Pt device. The Mg 1s photoelectron emission signal was continuously monitored during the Ar ion etching process to allow the position of the interface to be determined. The depth profiles show that the Mg 1s signal appeared at an etching time of 6 s (Ti/a-MgO interface) and then disappeared after 54 s (a-MgO/Pt interface). In the LRS, the Mg 1s spectra of the a-MgO film show that the positions of Mg 1s peaks at the various depths located at 1303.6 eV. We fitted the Mg 1s spectrum at 24 s as a representative, as shown in Fig. 4(a). The fitting result reveals the coexistence of primary Mg^{2+} (1304 eV)²⁷ and small amount of metallic Mg (1303 eV)³⁸ in the a-MgO. This result indicates that metallic Mg conducting filaments formed in the a-MgO film in LRS. This phenomenon is quite similar to the electric-field-induced formation of metallic Ni filaments in NiO films.³⁹ However, as seen from Fig. 4(b), the O 1s peak in the LRS is located at 530.2 eV (we choose 24 s curve as a representative), which is assigned to the lattice oxygen ions in the MgO.^{26,27} The O vacancy peak at approximately 531.6 eV (Ref. 21) was not observed. The existence of metallic Mg in an MgO film without O vacancies has also been reported in a previous study.²⁴ Figure 4(c) shows the ratios of Mg to O in the a-MgO film in different states as obtained from the XPS depth profiles. The Mg/O ratio was clearly less than 1 at different depths in the IS, indicating the existence of Mg vacancies in the film, as confirmed by the PL spectrum [Fig. 1(a)]. When the film was driven into the LRS by a positive bias, the Mg/O ratio became much higher than those in the IS at the various depths. The Mg/O ratio is almost a constant at different depths in both the IS and LRS. However, when the film was driven into the HRS by a negative bias, the Mg/O ratio decreased with the increasing depth as shown in Fig. 4(c). It

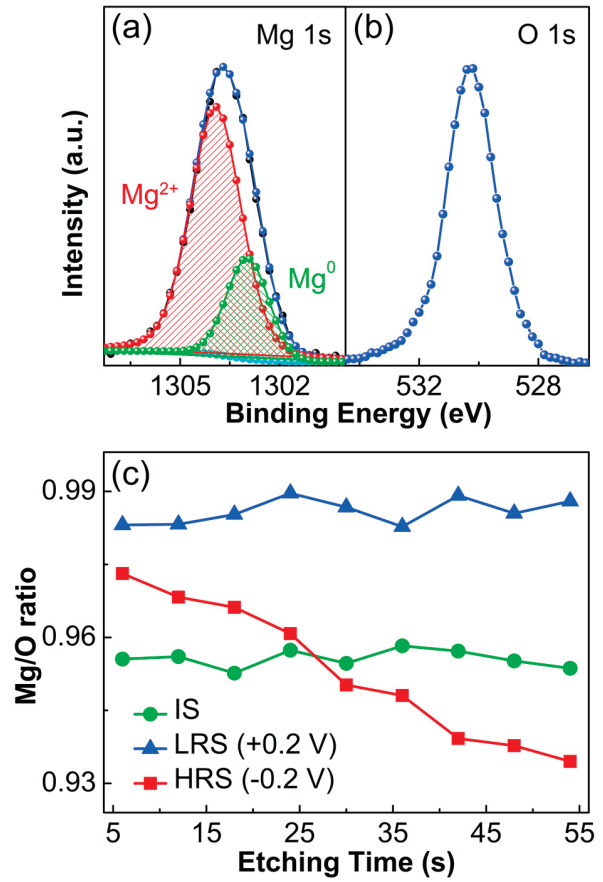


FIG. 4. (a) Fitting results for the Mg 1s spectrum at 24 s in the LRS. (b) O 1s spectrum at 24 s in the LRS. (c) Variation in the ratio of Mg to O with the etching time in the a-MgO film in the IS, LRS, and HRS.

shows that the Mg/O ratio was lower than that in the IS near the BE (decreases from 0.954 in the IS to 0.934 in the HRS at the same etching time of 54 s), whereas it was higher than that in the IS near the TE (increases from 0.957 in the IS to 0.973 in the HRS at the same etching time of 6 s).

Based on the above results and discussion, we propose a mechanism of the simultaneous change in the resistance and magnetization in this system. As the O vacancy was not observed in all state O 1s XPS spectrum (not shown here), the ferromagnetism observed in this Mg deficiency a-MgO film should be related to Mg vacancy defects. When a positive electric field is applied to the TE, negatively charged O^{2-} ions in the a-MgO film move toward the Ti TE and are adsorbed by the chemically active Ti.⁴⁰ The escaping of the O^{2-} ions in the MgO film reduces partly Mg^{2+} ions into metallic Mg and ultimately forms conductive filaments between the TE and BE, thus driving the device into the LRS. At the same time, the decrease in the O^{2-} ions causes an increase in the Mg/O ratio in the a-MgO film in the LRS. It is known that the peroxy defects, O^{2-} , are associated with Mg^{2+} vacancies.⁴¹ Remind that the number of the Mg ions in the film is fixed. Thus, the application of bias voltage reduces the concentration of Mg vacancies in the LRS compared with that in the IS. Previous works show that the magnetism in the MgO film correlated directly with Mg vacancies.^{26,27} In this work, the decrease in the Mg vacancy concentration leads to a weaker M_s in the LRS. When a

negative electric field is applied to the TE during the RESET process, the O^{2-} ions that were held in the Ti TE move back into the a-MgO film. These O^{2-} ions oxidize the metallic Mg in the film into Mg^{2+} ions again under the action of both thermal and electric field effects.⁴² This causes the rupture of the metallic Mg conducting filaments and drives the device into the HRS. At the same time, a redistribution of Mg vacancies occurred under the negative electric field. We noted that the Mg/O ratio near the BE is much lower than that near the TE as shown in Fig. 4(c). This means that most of the surplus O^{2-} ions were aggregated near the Pt BE in the HRS, i.e., the concentration of Mg vacancies near the BE is much higher than that near the TE. These concentrated Mg vacancies result in a stronger magnetism in the HRS. Seike *et al.* proposed that self-organized ferromagnetic nanowires of Mg vacancies can be formed in MgO-based MTJs.⁴³ In this work, the Mg vacancies are redistributed and arranged perpendicular to the film (along the direction of the electric field) in the HRS, and thus, the ferromagnetic nanowires of magnesium vacancies may be formed near the BE and results in a magnetic anisotropy.

In summary, room temperature ferromagnetism in amorphous MgO (a-MgO) thin films can be reversibly decreased (increased) more than 50% by application of an ultralow positive (negative) voltage of 0.2 V. In addition, this ultralow voltage also induces a strong magnetic anisotropy in the a-MgO film. The magnetic modulation is attributed to the redistribution of the Mg vacancies under the electric field. Our findings offer a new pathway for the electrical manipulation of magnetic properties and show promise for applications in low-power spintronics and multifunctional memory devices.

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