All-Solid-State Magnetic Properties Tuning Device Achieved by Redox Reaction of Fe₃O₄ Thin Film

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Abstract

An all-solid-state magnetic properties tuning device composed of Fe₃O₄ thin film and Li⁺ ion conducting solid electrolyte was fabricated for use in tuning magnetization and magnetoresistance (MR), which are key factors in the creation of high-density magnetic storage devices. Magnetization, and MR were reversibly controlled by redox (electrochemical reduction and oxidation) reaction due to Li⁺ insertion and removal. Various Fe₃O₄ thin film properties was tuned by donation of an electron to the Fe³⁺ ions in Fe₃O₄ thin film. This technique should lead to the development of spintronics devices based on the reversible tuning of magnetization and spin polarization (*P*).

1. Introduction

High-density magnetic storage devices (*e.g.*, hard disk, magneto-optical disk, and MRAM) have become even more important due to the information explosion now underway. Since these devices operate on the basis of the tuning of magnetic properties including magnetization, MR, and Kerr rotation angle, development of a technique for the tuning in thin film devices should lead to generate technological innovations in high-density storage, low power consumption, high operating speed, and so on. One promising approach to such tuning is electrostatic carrier doping into magnetic materials because the magnetic properties originate from the density of states (DOS) near the Fermi level, which are closely related to the electronic carrier density.

While this approach is effective in principle and thus has been tried, it is not straight forward because the carrier density achieved by electrostatic carrier doping with dielectric thin films is quite low compared to that for typical ferromagnetic materials (10^{22} cm⁻³).

Here, we report *in situ* tuning of the magnetic properties of ferromagnetic oxide thin film based on electrochemical carrier doping achieved using an all-solid-state redox device. Magnetite (Fe₃O₄) was used as the ferromagnetic oxide. It has been predicted to be a half-metal at room temperature and has been intensively investigated for application to MRAM devices. Extremely high carrier density doping of Fe₃O₄ by electrochemical Li⁺ insertion (*e.g.*, 3.2×10^{21} cm⁻³) enables various magnetic properties including magnetization and MR to be tuned to an extent unachievable with conventional electrostatic carrier doping using dielectric thin films [1].

2. Experimental

Experiment procedure of MOKE measurement

Magneto Optical Kerr effect (MOKE) measurement was performed to observe a magnetic property modulation in Fe₃O₄ caused by Li⁺ insertion and removal achieved by an all-solid-state magnetic property tuning device. Setup for MOKE measurement is illustrated in Fig. 1(a). The device was prepared by pulse laser deposition and RF sputtering. Thickness of the top Pt, Fe₃O₄, Li₄SiO₄ (LSO), LiCoO₂ (LCO), and bottom Pt films are 10, 30, 800, 200, 60 nm, respectively. The measurement was performed in polar Kerr configuration, where the magnetic field is normal to the thin film surface. The measurement was performed in air at room temperature. Detail of the experimental setup is described elsewhere [1].

Experiment procedure of magnetoresistance tuning in the allsolid-state redox transistor

Variation of MR in the all-solid-state redox device shown in Fig. 1(b) was measured using Physical Property Measurement System (PPMS, Quantum Design, USA). The measurement was performed in helium gas. DC voltage was applied for 1000 s, followed by the MR measurement in the magnetic field from -70 kOe to 70 kOe. The cycle was repeated with increasing DC voltage from 0 to 4 V by 0.5 V step. Variation in magnetization (M) was estimated using that in Kerr rotation angle observed in the experiment. Detail of the estimation is described elsewhere [1].

3. Results and discussion

MOKE measurement

Figure 2(a) shows MOKE *M*-*H* (magnetic field) loops obtained at various DC voltage. Typical ferromagnetic hysteresis of Fe₃O₄ was observed for all voltage conditions. The device exhibited a gradual decrease in *M* above 10 kOe with an increasing positive voltage to LCO, *i.e.*, Li⁺ insert into Fe₃O₄. A similar decrease in *M* was reported for electrostatic carrier doping into Fe₃O₄ using solid dielectric though the decrease extent was smaller (4%). Furthermore, such a decrease in *M* was also reported for Fe₃O₄ powder that had been lithiated by liquid reagents. The decrease in *M* for our device agrees well with those in previous reports. The DC voltage dependence of *M* in the saturation region (*H* above 10 kOe) is shown in Fig. 2(b), where *M* is plotted as a value normalized by the initial M (V = 0 V). The normalized *M* was tuned from unity to 0.64 at 2 V, and the variation from 0 to 2 V was repeatable [1], indicating that the *M* tuning in the voltage region was due to reversible Li⁺ insertion and removal. In contrast, the decrease in *M* above 2.5 V was irreversible (shown in blue arrow). This was due to irreversible generation of a paramagnetic rocksalt phase [1].

MR measurement

Figure 3 (a) shows the voltage dependence of MR in Fe_3O_4 thin film in the transistor device shown in Fig. 1(b). MR is defined as R(H)-R(0)/R(0), where R(H) and R(0) are the resistance with a magnetic field, H, and the resistance without a magnetic field, respectively. The observed negative MR was similar to that of polycrystalline Fe₃O₄ film, and the MR curves showed significant variation with respect to the applied DC voltage. The voltage dependence of MR at 70 kOe is shown in Fig. 3(b). The negative MR value increased from 2.0 to 3.0% in the voltage range from 0 to 1.5 V, indicating that P in the vicinity of the Fe₃O₄ grain boundaries increased due to Li⁺ insertion. It then started to decrease at above 2.0 V since P decreased due to the occurrence of electron donation to Fe³⁺ ions not only at the B sites (down spin causing increase in P) but also at the A sites (up spin causing decrease in P).

4. Conclusions

The all-solid-state redox device for *in situ* tuning of the magnetic properties of the Fe₃O₄ was fabricated. Satu ration *M* was reversibly tuned to 64% by electrochemical Li⁺ ion insertion and removal. Furthermore, the observed MR was enhanced from 2.0 to 3.0%. These tuning properties are



Fig. 1 (a) Illustration of setup for MOKE measurement. (b) Schematic illustration of all-solid-state redox transistor.

much better than those achieved by electrostatic carrier doping with solid dielectric and can be used to develop a novel class of high-density magnetic storage devices. Controlling ionic motion near the magnetic material/solid electrolyte interface makes nanoionics-based devices an exciting field for exploring next-generation information technology devices.

Reference

[1] T. Tsuchiya and K. Terabe et al., ACS Nano 10 (2016) 1655.



Fig. 2 (a) MOKE *M*-*H* loops of device. (b) DC voltage dependence of *M* in saturation region (*H* above 10 kOe).



Fig. 3 (a) DC voltage dependence of MR in Fe₃O₄ thin film in device.(b) DC voltage dependence of MR at 70 kOe obtained from Fig. 3 (a).