Hydrogen lithography for nanomagnetic domain on Co-doped ZnO using an anodic aluminum oxide template

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Based on hydrogen-mediated ferromagnetism and a selective hydrogen exposure technique, i.e., hydrogen lithography, we attempted to produce magnetic domains in a paramagnetic host. Hydrogen lithography on Co-doped ZnO with an anodic aluminum oxide template was used to produce nanomagnetic domains in paramagnetic Co-doped ZnO. The domains showed in-plane magnetization with a head-to-tail configuration at room temperature, which is consistent with the object-oriented micro-magnetic framework simulations. © *2014 AIP Publishing LLC*.
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Research trends in recent spintronics studies have focused mainly on two types of materials: magnetic semiconductors and ferromagnetic metals.[1–3] Since the discovery of giant magnetoresistance spintronics based on ferromagnetic metals, there has been considerable progress in the development of highly efficient, low-power-consumption spin-current, and logic devices, using nanoscale ferromagnetic elements.[4,5] Ferromagnetic semiconductors possess both ferromagnetic and semiconducting properties. They are produced by doping a semiconductor, commonly a compound semiconductor (e.g., GaAs), with a transition metal. Electrical conduction in a magnetic semiconductor can be manipulated by controlling the movement and/or spin of the charge carriers.[6,7] Control of the ferromagnetism using carrier-mediated mechanisms has attracted significant interest; however, the low Curie temperature (T_C) limits the optimal performance of room-temperature spintronic devices.[8] This has led to an extensive search for transition metal-doped wide-bandgap semiconductors (e.g., ZnO and TiO_2) to enhance the ferromagnetic properties of spin devices.[9,10] Among these materials, Co-doped ZnO (ZnCoO) has demonstrated its considerable potential applicability.[11,12] However, the reproducibility and reliability of its ferromagnetism is still debated.[13–18]

In previous studies, we presented theoretical and experimental evidence for the Co–H–Co complex, with a preferable parallel spin state in paramagnetic ZnCoO.[19,20] The reversible ferromagnetic-to-paramagnetic switching, as well as its higher T_C value (which exceeds room temperature), suggested its potential for use in spin devices.[21–27] We speculated that the design of the ferromagnetic semiconducting pattern embedded in the ZnCoO semiconductor could be used as an integrated opto-spintronic device, thereby serving not only its main purpose as a magnetic semiconductor but also providing the means for rewritable information and display device operation manipulated by hydrogen.[28–30]

In this study, we confirmed highly stable and reversible ferromagnetism controlled by hydrogen content and introduced a technique for designing localized ferromagnetic ordering in a paramagnetic ZnCoO semiconductor using hydrogen exposure of selected areas.

ZnCoO thin films were fabricated on an $Al_2O_3(0001)$ by radio frequency (RF)-sputtering deposition. The hydrogen exposure process was carried out using hot isostatic pressing (HIP: QIH-3, Flow Autoclave System, Inc.) under the following conditions: Ar:H_2 (90:10 vol. %) mixed gas, 100 bars, 300 °C, and 10 h. An anodic aluminum oxide (AAO, Whatman, Inc.) template was used as a mask for selective hydrogen injection into the ZnCoO sample. Magnetic field-dependent magnetization was measured using a vibrating sample magnetometer (VSM) equipped with a physical property measurement system (PPMS: Model 6000, Quantum Design, Inc.). Atomic and magnetic force microscopy was carried out with a commercial atomic force microscopy system (XE-100, Park Systems, Inc.) under ambient conditions at room temperature.

Figure 1(a) shows changes in the remnant magnetization (i.e., the magnitude of ferromagnetism) of ZnCoO thin films as a function of hydrogen exposure and ejection processes, which were picked up from the hysteresis curves measured over a year. The remnant magnetization was reversibly measured by repetitive hydrogen injection and ejection processes over five cycles and can be adjusted by varying the hydrogen exposure conditions.

Figure 1(b) shows a three dimensional (3D) atomic force microscopy (AFM) image and magnetic force microscopy (MFM) images obtained from the ZnCoO sample exposed to hydrogen using HIP, respectively. The AFM image shows the same surface quality (rms = 1.414 nm) as that before

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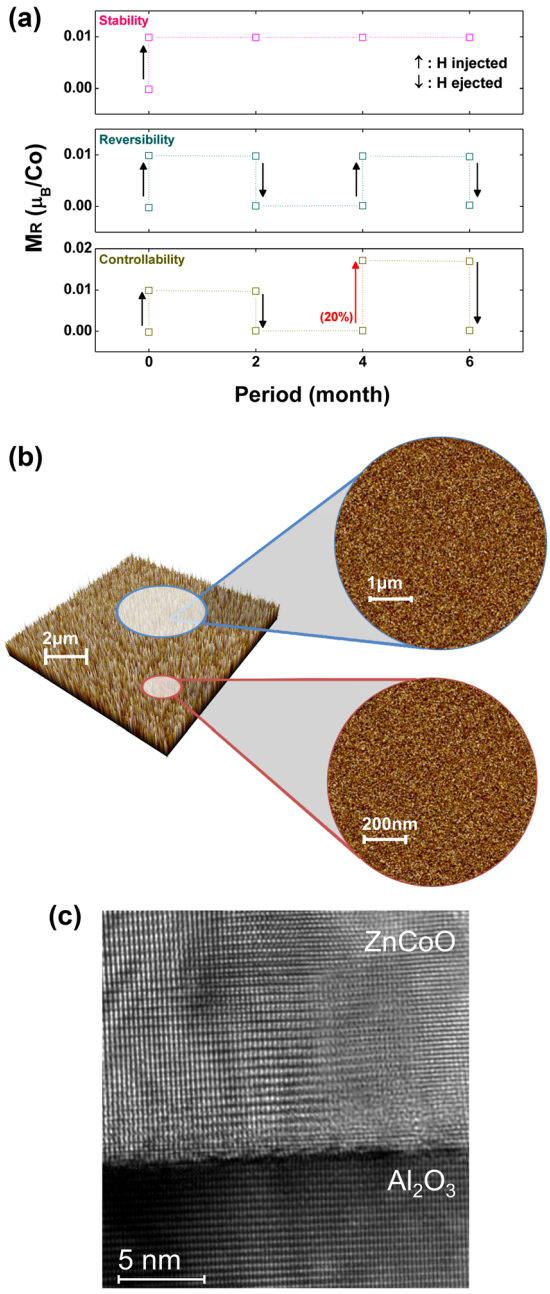

FIG. 1. (a) The stability, reversibility, and controllability of magnetization in Co-doped ZnO (ZnCoO) by hydrogen. The arrows pointing up and down refer to hydrogen injection and hydrogen ejection, respectively. (b) Atomic force microscopy (AFM) three dimensional (3D) image, magnetic force microscopy (MFM, circle images) images, and (c) cross-sectional high-resolution transmission electron microscopy (HRTEM) images of ZnCoO thin films exposed to hydrogen.

hydrogen treatment. However, information on the individual magnetic domains (e.g., the easy axis) could not be obtained because the whole sample was hydrogenated equally; it was not possible to observe the relative difference between different areas of the sample. MFM images using a scale of a few hundred nanometers did not indicate evidence of any strongly magnetized spots (assumed to be caused by magnetic cluster). In typical cross-sectional high-resolution transmission electron microscopy (HRTEM) images (Fig. 1(c)), no evidence of extra phases, such as columnar structures, due to the presence of Co-metal clusters or Co-rich wurtzite clusters were observed in the films.[31,32]

To demonstrate magnetic patterning by hydrogen, we performed hydrogen treatment using a mask with selective exposure, as shown in Fig. 2. We expected that uncovered areas of ZnCoO exposed to hydrogen would become ferromagnetic, whereas covered areas would remain paramagnetic. First, we attempted to design the mask employing conventional ultraviolet (UV) lithography technique.[33] Through a patterned photoresist (PR) layer using an UV lithography process, the sample was exposed to hydrogen. We obtained a magnetic contrast image corresponding to the edge of the PR structure, but it was determined to be a false image induced by sudden morphological changes associated with the edge of the PR residual.[33] Because the heat treatment accompanying the hydrogen exposure hardened the PR, neither dry- nor wet-etching was able to remove the hardened PR layer without damaging the ZnCoO thin film. These experiments provided information on the masking layer requirements under selective hydrogen exposure: the mask should demonstrate high heat durability and should be able to be removed easily. Thus, we carried out selective hydrogen exposure using AAO template. The AAO template satisfies the requirements specified. The AAO template does not require complicated lithographic processes, and it can be used for patterning magnetic domains according to its porous structure. The AAO template was affixed to the ZnCoO thin film by silver paste, to minimize the gap between the two materials.[33] Care was taken to avoid covering the apertures with the paste.

The AFM images in Figs. 3(a) and 3(b) show no evidence of sample deformation from hydrogen treatment. The MFM images in Figs. 3(c) and 3(d), corresponding to the AFM images of Figs. 3(a) and 3(b), respectively, reveal randomly distributed black and white spots that were not observed in the AFM images. These spots are not clearly

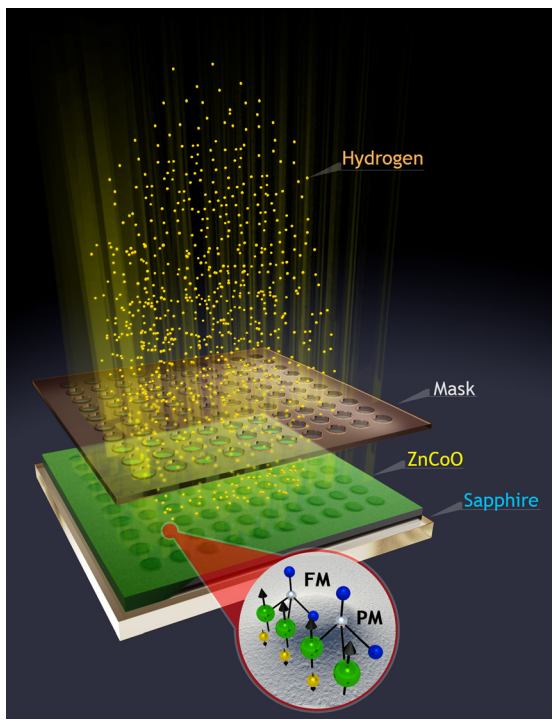

FIG. 2. Schematic diagram of the magnetic pattern designed by hydrogen exposure.

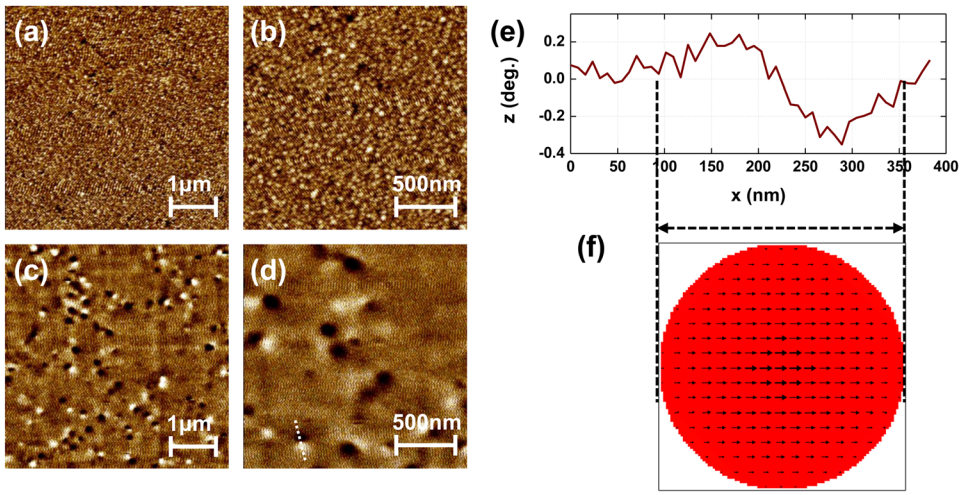

FIG. 3. (a) AFM topography image of ZnCoO film after hydrogen exposure through the anodic aluminum oxide (AAO) template and (b) a magnified image of (a). (c) and (d) MFM phase images corresponding to (a) and (b), respectively. (e) Line profile of the magnetic phase for the white-dotted line in (d). (f) The object-oriented micro-magnetic framework (OOMMF) simulation results for the circular structure.

periodic; however, the magnetic contrasts are quite distinguishable. Interestingly, the black and white spots appear to be almost paired, with a distinct magnetic phase difference of ~0.5°. The magnetic phase profile in Fig. 3(e) shows the change in the magnetic forces along the white-dotted line crossing the black-and-white spot in Fig. 3(d). The black and white spots appear to be associated with the head and tail of a magnetic domain lying in the plane, which reflects the fact that the in-planar magnetic domain was formed by hydrogen injection.

To confirm the in-plane magnetization for the hydrogenated area, we obtained a simulated image based on the object-oriented micro-magnetic framework (OOMMF). Figure 3(f) shows the results of the OOMMF simulation for hydrogenated ZnCoO; the simulation was performed under the following conditions: saturation magnetization $= 3 \times 10^3$ A m^{-1}; anisotropy constant $= 52$ J m^{-3}; these values were obtained from an independent experiment. The exchange stiffness for ZnCoO has not been reported to date; thus, we estimated an exchange stiffness of 1×10^{-13} J m^{-1} for the simulation, which is similar to the value reported for GaMnAs.[34] Simulated results did not vary within the range 1×10^{-14} to 1×10^{-12} J m^{-1}. The OOMMF simulation exhibited clear in-plane magnetization with an applied magnetic field, which was consistent with the MFM results.

Most of the magnetic domains did not precisely follow the direction of the applied H-field; the slight misorientation is assumed to be due to the interaction between magnetic domains built into the paramagnetic ZnCoO layer. To obtain a more periodic dot array with clear magnetic ordering, we attempted to grow an AAO template directly on ZnCoO, in the hope that the close contact would provide high-quality periodicity. However, the acidic environment produced during the wet-etching process for AAO fabrication damaged the ZnCoO. We have since attempted to find alternative materials for masking hydrogen exposure. If an effective method for using hydrogen exposure without heat treatment can be developed, then conventional lithography techniques could be applied to make periodic magnetic patterns.

We realized highly stable ferromagnetism in ZnCoO with hydrogen exposure, and the ferromagnetism was reversible with hydrogen injection and ejection. The magnitude of the magnetism depended on hydrogen exposure conditions, which determined the hydrogen content of the sample. Utilizing an HIP system, we fabricated nanosized magnetic patterns in localized areas of a ZnCoO thin film, using so-called hydrogen lithography with a commercially available AAO template. MFM provided the evidence of head-to-tail in-plane magnetization. This technique allows the sizes of the domains to be adjusted arbitrarily, the magnetization to be reversed as ferro-to-para according to hydrogen injection and ejection, and the magnetic intensity to be controlled. Thus, hydrogen lithography is a promising technique for spin-display, nanologic device fabrication, and spintronics applications based on ZnCoO.

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