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Self-Formed Exchange Bias of Switchable Conducting Filaments in NiO Resistive Random Access Memory Capacitors

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ABSTRACT We report on the ferromagnetism of conducting filaments formed in a NiO thin film, which exhibited a typical bistable resistive switching characteristic. The NiO thin film showed an antiferromagnetic hysteresis loop for a high resistive state (R_{OFF}). However, for a low resistive state (R_{ON}), the conducting filaments exhibited a ferromagnetic hysteresis loop for the field cooling. The ferromagnetic hysteresis behavior of the R_{ON} state reveals switchable exchange coupling between the ferromagnetic Ni conducting filaments and the antiferromagnetic NiO layer.

KEYWORDS: NiO · conducting filaments · exchange coupling · resistive switching

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Resistive random access memory (RRAM) has been researched for next-generation nonvolatile memory due to its simple structure, high-density integration, and fast operation.[1,2] RRAM is one of the memristive systems that show hysteretic loops consisting of two constructive variables which are current−voltage for memristor, charge−voltage for memcapacitor, and current−flux for meminductor.[3] Various switching has been reported, including a conducting filament model, a multilevel switching model, a Schottky barrier model, electrochemical migration at the interface, and trap charging/discharging.[4−7] Among these switching models, the conducting filament model defined a low resistivity state (LRS) and a high resistivity state (HRS) by the formation and removal of conducting filaments.[1,8−10] The existence of conducting filaments in RRAM devices was demonstrated by conducting atomic probe microscopy studies on Nb-doped $SrTiO_3$ and NiO thin films.[10,11] For the LRS states of NiO thin films, Ni conducting filaments were observed by transmission electron microscopy, indicating that, as a possible RRAM switching mechanism, conducting filaments can be formed by oxygen decomposition from NiO during the switching.[12−15] Interestingly, there is a possibility of exchange coupling between Ni conducting filaments and NiO layers that surround Ni conducting filaments because Ni is ferromagnetic while NiO is antiferromagnetic.[16,17]

Meanwhile, many researchers have widely studied the phenomenon of exchange bias, which enables a nanosized ferromagnetic domain smaller than the superparamagnetic domain size to overcome thermal fluctuation.[16−25] Generally, in the bilayers of ferromagnetic and antiferromagnetic materials, exchange bias causes a shift in the magnetic hysteresis loop with a larger coercive magnetic field. Without an exchange bias, the hard magnetization behavior of the antiferromagnetic material causes this shift of the soft magnetization curve of a ferromagnetic material.[16] Thus, a high ferromagnetic domain stability generated from the exchange bias makes it possible to decrease the thermal fluctuations and to form small ferromagnetic dots in a radius of less than a few nanometers at relatively high temperatures, above which superparamagnetism has been observed to be stable.[26] Therefore, the superparamagnetic limit in a hard disk drive can be solved by forming an exchange bias in the ferromagnetic nanostructures, such as nanowires and nanodots, which are wrapped by antiferromagnetic materials.[17−19,21] Since Ni conducting filaments have small diameters, less than a few nanometers, and are wrapped with antiferromagnetic NiO, the filaments in a NiO RRAM capacitor provide an opportunity for the formation of self-formed exchange bias of ferromagnetic nanowires.[8,10,12−15] In this work, we investigate the magnetism of conducting filaments formed in a NiO thin film which exhibit a typical bistable resistive switching characteristic. For conducting filaments formed at a low resistive state (R_{ON}) of the

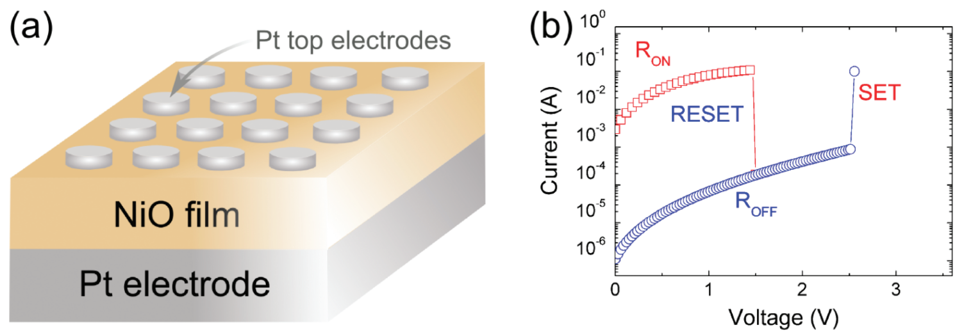

Figure 1. (a) Illustration of an array of Pt/NiO/Pt capacitors. (b) Bistable resistive switching of the NiO thin film.

NiO RRAM capacitor, exchange coupling between the ferromagnetic conducting filaments and the antiferromagnetic NiO layers wrapping the conducting filaments was observed.

We fabricated polycrystalline NiO thin films with 100 nm thicknesses on Pt/TiO_2/SiO_2/Si substrates using a radio frequency sputtering method. A commercially available 2 in. NiO target was used for the deposition of thin films at a base pressure of $\sim10^{-7}$ Torr prior to the deposition. During the deposition, the substrate temperature was set to 750 °C, and the working pressure of the mixed gas (argon and oxygen) was maintained at 10 mTorr. The structure of the NiO thin film was investigated by X-ray diffraction (XRD, Cu Kα radiation 1.542 Å), in which the NiO thin film exhibited a polycrystalline structure with (111), (220), and (222) XRD peaks. The thickness of the NiO thin film (100 nm) was measured in the cross-sectional view of a scanning electron microscope (SEM). The surface morphology and the roughness of the NiO thin film were observed by SEM and atomic force microscopy (AFM). For the preparation of a RRAM capacitor, an array of Pt top electrodes with a diameter of 100 μm and a thickness of 100 nm was deposited onto a NiO thin film by RF magnetron sputtering, as shown in Figure 1a. For the investigation of ferromagnetic properties, magnetic hysteresis loops were obtained by a SQUID magnetometer (Quantum Design, MPMS).

To confirm a typical resistive switching characteristic as a memristor (a current−voltage hysteresis loop) of the Pt/NiO/Pt capacitor, the current−voltage characteristics of the material were measured and showed a bistable resistive switching behavior, as shown in Figure 1b. In a voltage sweep, a R_{ON} state changes to a R_{OFF} state above the RESET bias of approximately 1.5 V. This R_{OFF} state also changes to the R_{ON} state above the SET bias of approximately 2.6 V. To check the reproducible switching behavior of the Pt/NiO/Pt capacitor, bistable resistivities were obtained as a function of switching cycle, up to 500 cycles. Typical retention and endurance properties of the Pt/NiO/Pt capacitor were observed.[7] Therefore, conducting filaments in the Pt/NiO/Pt capacitor are switchable as SET or RESET states.

Before measuring the magnetic properties, two samples were prepared with two different states of R_{ON} and R_{OFF} for all of the Pt/NiO/Pt capacitors arranged on the Pt/TiO_2/SiO_2/Si substrate. One hundred switching cycles were sufficient to establish a stable switching state because resistivities of the R_{OFF} and R_{ON} states fluctuate in lower switching cycles.[10] To form stable R_{ON} and R_{OFF} states of the Pt/NiO/Pt capacitor, R_{OFF} and R_{ON} states were selected corresponding to 100 switching cycles for the Pt/NiO/Pt capacitor, and this capacitor showed a good switching property as a typical RRAM capacitor. To enlarge the magnetic signal measured by the SQUID magnetometer, all capacitors covering the Pt/TiO_2/SiO_2/Si substrate were switched. After switching, the magnetization was measured as a function of the magnetic field.

Figure 2a,b shows a pictorial view of the filament model as a resistive switching mechanism. For the R_{OFF} state (Figure 2a), filaments were not formed, while conducting filaments were formed for the R_{ON} state (Figure 2b). The conducting filaments in the NiO thin film consist of metallic Ni atoms with a ferromagnetic property, as confirmed by experiments and theoretical results.[12,14,15,18,27] In these studies, TEM studies showed the evidence of Ni filaments, and theoretical results exhibited that an oxygen vacancy induces metallic states as well as ferromagnetic states in insulating and antiferromagnetic NiO.[11] Thus, there is a possibility of exchange coupling between Ni conducting filaments and NiO layers which wrap the Ni conducting filaments.[13−15,17,18] Therefore, Ni conducting filaments could exhibit ferromagnetic properties or superparamagnetic behaviors because the smaller diameters of the Ni conducting filaments cannot endure thermal fluctuations.[13,16] To confirm the exchange coupling between the Ni conducting filaments and the antiferromagnetic NiO layers, we compared the magnetic properties of the Pt/NiO/Pt capacitor in the two states of R_{OFF} and R_{ON}.

For the magnetic measurements, we applied a magnetic field normal to the NiO thin film surface, as conducting Ni filaments are normal to the Pt bottom electrode. For a magnetic field parallel to the NiO thin film, the NiO thin film exhibited a typical antiferromagnetic hysteresis loop for the R_{OFF} and R_{ON} states. Figure 2c,d shows the magnetizations as a function of the magnetic field ($M-H$ curves) for the R_{OFF} and R_{ON} states of the

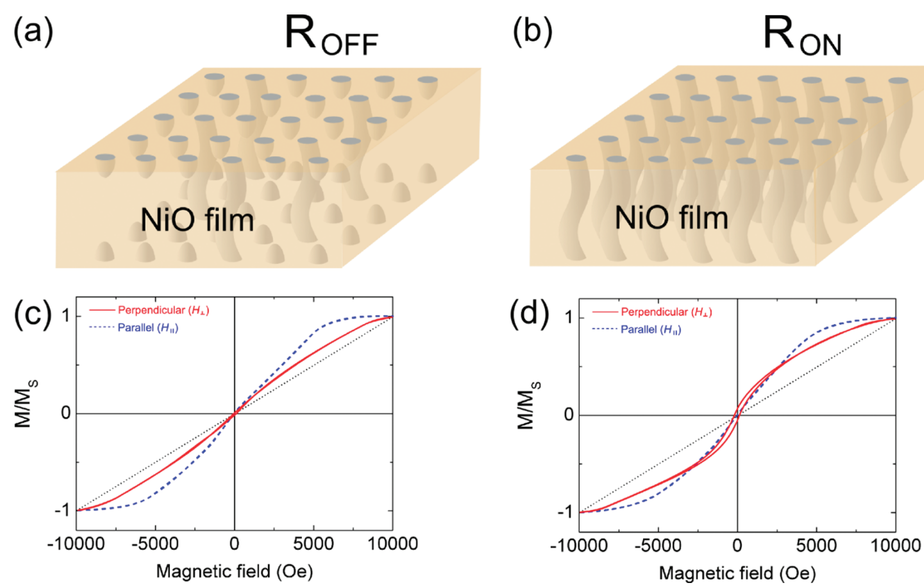

Figure 2. Pictorial view of the filament model as a resistive switching mechanism, when (a) filaments are disconnected (R_{OFF} state) and (b) filaments are formed (R_{ON} state). (c) $M-H$ curves for a R_{OFF} state. (d) $M-H$ curves for a R_{ON} state. A magnetic field is applied perpendicular to the NiO thin film. The R_{ON} state exhibits a ferromagnetic hysteresis loop with a remanent magnetic moment resulting from the formation of conducting filaments.

NiO thin film, respectively, that were measured by a SQUID magnetometer with a magnetic field normal to the NiO thin film at room temperature. For the case of the R_{OFF} state, the NiO thin film exhibits an antiferromagnetic $M-H$ curve. Magnetic anisotropy of the antiferromagnetic NiO thin film is observed with magnetic fields parallel and normal to the NiO thin film surface, resulting from the structural anisotropy of the 100 nm NiO thin film.[28] Alternatively, the R_{ON} state showed a ferromagnetic hysteresis loop with a remanent magnetization for a magnetic field normal to the NiO thin film surface. In the $M-H$ curve of the R_{ON} state for the perpendicular magnetic field, a remanent magnetic moment with a considerable coercive field was observed, indicating that the R_{ON} state had a ferromagnetic state along the direction of the conducting filaments. Thus, the R_{OFF} and R_{ON} states well support that there is exchange coupling occurring between the Ni conducting filaments and the NiO layers.

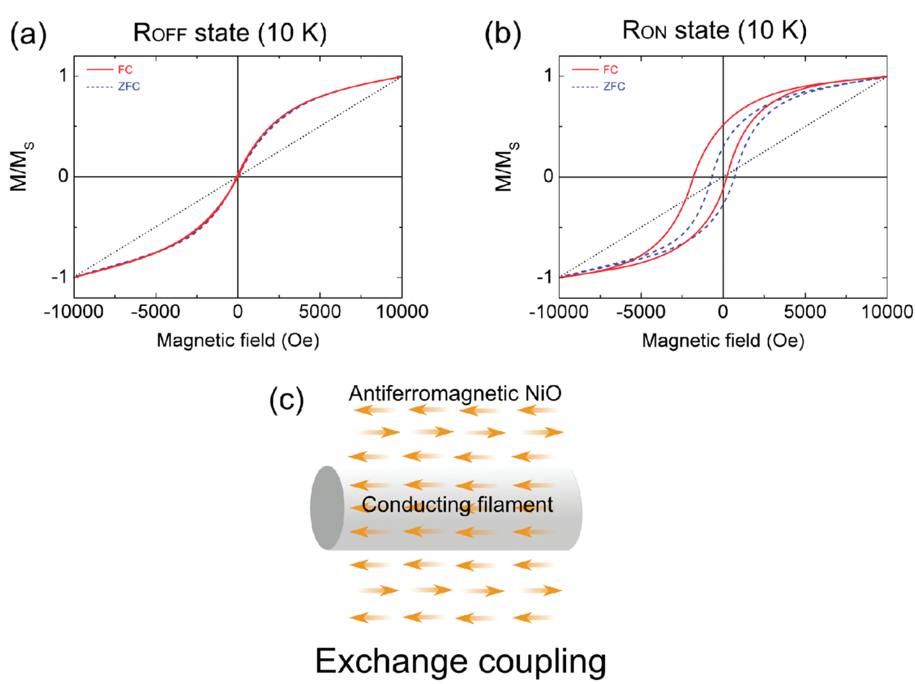

Figure 3. (a) $M-H$ curves for a R_{OFF} state measured at 10 K. (b) $M-H$ curves for a R_{ON} state measured at 10 K. A magnetic field is applied perpendicular to the NiO thin film. (c) Schematic drawing of the spin configurations of the exchange coupling between the conducting filaments and the NiO layer.

Generally, exchange coupling can be confirmed by comparing $M-H$ curves for zero field cooling (ZFC) and field cooling (FC). The $M-H$ curve for FC shows a shift in position from a zero field, and it also has a larger hysteresis than that for ZFC.[17] Thus, to establish the exchange coupling between the Ni conducting filaments and the NiO layers, the $M-H$ curves of the R_{OFF} and R_{ON} states were measured for ZFC and FC at 10 K, as shown in Figure 3a,b, respectively. Here, we used an applied magnetic field normal to the NiO thin film surface because conducting filaments can be formed in this direction. For the R_{OFF} state, the NiO thin film exhibited typical antiferromagnetic hysteresis loops for ZFC and FC, as shown in Figure 3a. In particular, the coercive field is almost zero, and there is no remanent magnetic moment. For the R_{ON} state, a ferromagnetic hysteresis loop for a ZFC was observed (Figure 3b), and there was no significant shift in the ferromagnetic hysteresis loop. The ferromagnetic hysteresis loop has a coercive magnetic field of approximately 670 Oe. As opposed to the hysteresis loop for the ZFC, a significant shift in the ferromagnetic hysteresis loop was observed for the FC, indicating that there was an exchange coupling between the Ni conducting filaments and the NiO layer.[18−26] This exchange coupling in the ferromagnetic hysteresis loop prompts the change in a coercive magnetic field. The two coercive magnetic fields were 210 and 1830 Oe for the right and left-hand sides, respectively. As shown in the schematic drawing, the spin configurations of the exchange coupling between the conducting filaments and the NiO layer were constructed (Figure 3b).[17] The estimated bias magnetic field of approximately 1050 Oe was greater than the coercive magnetic field of the ZFC hysteresis loop. This result is similar to the exchange bias phenomenon in ferromagnetic nanostructures wrapped by antiferromagnetic materials.[17−19,21] The phenomenon of exchange bias in NiO RRAM capacitors was formed simultaneously with the formation of Ni conducting filaments, different from that of magnetic nanostructures. Specifically, the phenomenon of exchange bias was switchable according to the R_{OFF} and R_{ON} states of the NiO RRAM capacitors.

In summary, anisotropic ferromagnetism of Ni conducting filaments formed in a NiO thin film was demonstrated. The NiO RRAM capacitor exhibited a typical bistable resistive switching characteristic. The magnetizations of the R_{OFF} and R_{ON} states were measured as a function of the applied magnetic field. For the R_{OFF} state, the NiO thin film showed an antiferromagnetic hysteresis loop. However, for the R_{ON} state, the conducting filaments exhibited a ferromagnetic hysteresis loop. The ferromagnetic hysteresis loop of the R_{ON} state for the FC showed switchable exchange coupling between the ferromagnetic Ni conducting filaments and the antiferromagnetic NiO layer.

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