Nanofabrication of magnetic tunnel junctions by using side-edge thin film deposition

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Abstract

Nanostructured double ferromagnetic tunnel junctions (MTJs) are indispensable for investigation of spin-dependent single-electron transport at low temperature. A new fabrication process that enables us to reduce the size of MTJs down to nanometer scale by using the side edge of a patterned film were developed. The multilayers of MTJ partially replaced by thick Al₂O₃/Cu double layer were prepared by using electron beam lithography and lift-off, then Pt film was vacuum-evaporated onto the side edge of Al₂O₃/Cu film, which masked MTJ during following Ar ion milling. As a result, the double MTJs with the dimension of 10 nm × 10 μm were formed beneath the Pt film. The large tunnel magnetoresistive ratio of 35% and symmetrical I–V characteristics were obtained at room temperature.

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1. Introduction

Nanometer-sized ferromagnetic tunnel junction (MTJ) shows both charge quantization [1] and spin-dependent transport of the electron [2]. The former is known as single-electron tunneling (SET) observed first by Fulton and Dolan [3] in a tiny double Al/Al-oxide/Al junction structure, and the latter as tunnel magnetoresistive effect (TMR), which was discovered by Julliere [4] and progressed by Miyazaki and Tezuka [5] and Moodera et al. [6]. Nowadays, novel phenomena due to interplay of SET and TMR effect are predicted to occur in these system. Especially, phenomena such as a strong enhancement of the TMR ratio [7–9] or the oscillatory bias dependence [10–12] are much attractive since they can achieve the highly functional devices such as the switchable MTJs for the future advanced architecture of magnetic random access memory. Nevertheless, only a few experimental studies have been reported up to now [13–17], due to the difficulties in fabricating well defined tiny and highly optimized MTJs, which are comparable with the theories.

In order to perform these studies, we need so called ferromagnetic single-electron transistors (F-SETs), which consist of triple electrodes called ‘Source’, ‘Island’, and ‘Drain’ connected via tiny MTJs. The chemical potential of the island is capacitively controlled by the external gate structure. Since Coulomb blockade effect, the principle of SET, appears on the condition of $E_c(= e^2/2 C) \gg k_B T$, where $E_c$ is the electrostatic energy of the island, $C$ is the capacitance of the junctions, and $k_B$ is the Boltzmann constant, the area of the junctions must be extremely minimized to reduce their capacitances. Even in the case of the operation at the liquid He temperature ($\sim 4.2$ K), tunneling area of F-SETs has to be less than 100 nm², which is hardly achieved with the use of the current microfabrication techniques such as electron beam lithography. Therefore, these experimental studies have been so far performed by using special techniques, such as double angle evaporation method [13,14] or self-assembled ferromagnetic metal particle array [15–17] (Table 1). However, these methods have some drawbacks instead of overcoming the processing limit of the junction area. For instance, the deposition technique is restricted to the vacuum evaporation in Refs. [13,14] and self-formation makes it very difficult to optimize the junction properties such as the TMR ratio or...
In this work, we developed a unique method of microfabricating MTJs in place of previous one, and successfully fabricated tiny double MTJ structure, which is the basic component of F-SET. The developed method enables us to reduce the junction size down to the order of thin film thickness and to control the junction properties precisely beforehand. Therefore, F-SETs fabricated by using this method would fulfill the requirement of both higher electrostatic energy of the island and sufficiently large TMR ratio, which are important to the future quantitative studies of spin-dependent single-electron transport in MTJs.

2. Experiment

The stacked structure consisting of Ni$_{80}$Fe$_{20}$ (10 nm)/Co$_{75}$Fe$_{25}$ (10 nm)/Al–O (1.3 nm)/Co$_{75}$Fe$_{25}$ (10 nm)/Ta (5 nm) was prepared onto a (100)-oriented thermally oxidized Si substrate (Fig. 1(c)). The deposition was performed by using inductively coupled plasma (ICP) assisted RF magnetron sputtering system ($<3 \times 10^{-6}$ Pa), which has the three chambers of load-lock, oxidation and main with six magnetron cathodes (Fig. 1(a)). The bottom layer of the Ni$_{80}$Fe$_{20}$/Co$_{75}$Fe$_{25}$ is a soft magnetic layer, and the top Co$_{75}$Fe$_{25}$ is a hard one. The magnetization of both layer was oriented to the same direction during the deposition process by an internal permanent magnet with the field of 100 Oe. Al-oxide layer was formed by the sputtering of Al and followed by ICP plasma oxidation for 3 min in the oxidation chamber (Fig. 1(b)). All the process of the deposition was performed in low pressure of Ar (<7 $\times$ $10^{-2}$ Pa) and done without breaking vacuum on the way. Fig. 1(d) shows cross-sectional transmission electron microscopy (TEM) image of Ni$_{80}$Fe$_{20}$ (15 nm)/Co$_{75}$Fe$_{25}$ (5 nm)/Al-oxide (1.3 nm)/Co$_{75}$Fe$_{25}$ (15 nm) structure. From this image, an ultra thin Al-oxide layer was confirmed forming homogeneously at the junction interface.

![Diagram](image_url)

Fig. 1. Sample preparation at the first stage of the side-edge deposition process. (a) Soft and hard magnetic layers were continuously deposited onto the substrate by using ICP assisted RF magnetron sputtering system. (b) ICP plasma oxidation was performed on the condition of Ar:O$_2$ = 4:10, target: 15 W, coil: 100 W, where LCR circuit was freely terminated for reducing plasma damage to the substrate. (c) The multilayers of Ni$_{80}$Fe$_{20}$ (10 nm)/Co$_{75}$Fe$_{25}$ (10 nm)/Al–O (1.3 nm)/Co$_{75}$Fe$_{25}$ (10 nm)/Ta (5 nm). (d) The cross-sectional transmission electron micrograph (TEM) of the junction interface.
Next, the stacked structure was covered with Pt (20 nm) by using e-gun type vacuum evaporator, and Ti (10 nm) was also deposited through a stainless-steel metal shadow mask, which had 81 patterns of a bridge with 100 nm width between a pair of the large pads (Fig. 2(a)). Ar ion milling was performed to define the structure, where Ti of 10 nm was used as an etching mask. Then, the substrate was spin coated by 500 nm positive e-beam resist (Nippon Zeon, ZEP-520) and baked at 150°C for 5 min.1 By performing electron beam lithography with 20 kV field emission type e-beam writer (ELIONIX, ERA-8000FE), cross pattern was formed across the bridge. The revealed area of the MTJ was etched away by using Ar ion milling, and filled with thick Al2O3 (100 nm)/Cu (100 nm) film by using both magnetron sputtering and lift-off (Fig. 2(b)). Accordingly, the cross structure of Al2O3/Cu was formed in the middle of the bridge. The dimension of the cross structure was 200 μm × 10 μm for the long bar, and 10 μm × 30 μm for the short one. Thereafter, the sample was held in a vacuum evaporation system with the angle of 45° to the line from the substrate to the source, and Pt of 10 nm thick was vacuum evaporated obliquely on the side edge of the cross structure (Fig. 2(c)). The deposition process was monitored with a quartz crystal oscillator, which was calibrated by a surface profilometer. Finally, Ar ion milling was performed to define the area of the junctions until the surface of bottom Co75Fe25 layer appeared. Here, the Pt film on the side edge was ‘thick’ enough, so we could use it as an etching mask of the junctions. The area of the junctions can be, thus, defined by the thickness of Pt film and lateral dimension of Al2O3/Cu film, denoted as the product of $l \times w$; where $l$ is the size of the projection part of Al2O3/Cu film and $w$ is the thickness of the Pt film (Fig. 2(d)). We chose the area of 10 μm × 10 nm in this study. In the completed structure, an electron flows through the path described with a black arrow in Fig. 2(e), which means the current flows through double MTJs with nanometer scale. Electrical measurements were performed by using DC four-point probe method at room temperature. Bias voltage ranging from 10 to 100 mV was applied to the sample, where TMR ratio showed no apparent decrease. The magnetic field up to 1.2 kOe was applied to the same direction as $l$, which also corresponded to an easy axis out of the induced magnetic anisotropy.

3. Results and discussion

3.1. Side-edge profile of resist pattern

As we mentioned in Section 2, the cross structure of Al2O3/Cu was shaped by sputtering deposition and lift-off. Therefore, it is quite important to control the profiles of the resist pattern since the side edges of the Al2O3/Cu films must be steep enough to prevent the Pt film on the side edge from being exhausted immediately by following Ar ion milling. Fig. 3(a) shows the surface profile of the line and space pattern of the e-beam resist with the thickness of 1 μm observed by using atomic force microscopy (AFM). The surface of the MTJ structure was quite flat (peak to valley value $R_{p-v} < 5$ Å) due to O2 plasma ashing, which was employed for de-scum. The spacing between the resist was uniform all over the pattern, and the sidewall of the resist seemed not to be tapered at least in this image. Fig. 3(b) shows the scanning ion microscopy (SIM) image of the resist pattern (tilted at 60°), which was covered with Cu (300 nm)/Carbon

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1 180–200°C is recommended, but MTJs are so sensitive to the thermal treatment that all the process is to be performed at relatively low temperature.
(500 nm) and cross-sectioned by focused ion beam (FIB) etching. Optimizing the condition of electron irradiation, we found that dose of 50 μC/cm² was suitable for producing the most steep side wall. The completed double MTJ structure observed by scanning electron microscopy (SEM) is shown in Fig. 4. The MTJs were formed at the projection parts of the Al₂O₃/Cu structure, which was indicated with the white arrow in the micrograph. Ultimately, l can be reduced down to about 100 nm that corresponds to the critical temperature \( T_c \) of the order of 10 K, although we chose the area of \( 10 \mu m \times 10 \mu m \) in this study. In order to operate this structure as F-SETs in future, however, the long bars of the cross structure (island) is to be cut off since such large electrode has a capacitance out of their own size. Local milling method such as FIB would be employed for shaping the island. Simultaneously, a part of Al₂O₃/Cu films can be used as the gate electrode by connecting them to the external pad.

Fig. 3. (a) Surface profile of the e-beam resist measured by AFM. (b) SIM image of the cross-section of the line and space, where the e-beam resist was coated on Si substrate. (c) The side edge of Al₂O₃/Cu film reflects the shape of the resist pattern.

Fig. 4. SEM image of bird point view of the completed MTJ structure. The triple electrodes will be used as source, island, and drain of F-SETs structure, respectively.

3.2. Magnetic properties

Fig. 5(a) shows the MR hysteresis of the double MTJ structure with the junction area of \( 10 \mu m \times 10 \mu m \). The resistance increased sharply at the magnetic field of 50 Oe, and slightly decreased in the anti-parallel alignment, then rapidly dropped down to the initial value at about 700 Oe. The TMR ratio as large as 35% was obtained, which was comparable to that of a standard spin valve type MTJ as deposited (not annealed) state. For comparison, the same multilayers of the MTJ were microfabricated to the shape of a square by using a conventional photo lithographic process. Fig. 5(b) shows the MR curve of the single MTJ with the dimension of \( 30 \mu m \times 30 \mu m \). There are some discrepancies in their properties: the switching field of the hard magnetic layer is about 100 Oe and the MR ratio is only 15%. These disagreements seem to be out of their dimensions, since the hard magnetic layer of the double MTJ structure became a wire in shape which had the dimension of \( 10 \mu m \times 10 \mu m \times 10 \mu m \) at the final step. Some experimental studies of the ferromagnetic nanowire show both single domain behavior and the increasing switching field as decreasing the width of the wire [18,19]. This increase of the switching field can be explained from the analysis by Stoner and Wohlfarth [20], where the coercive field of ferromagnetic wires are inversely

\(^2\) Since the intensity of a FIB is distributed like Gaussian, the object must be covered with a hard mask during FIB etching in order to cover the edge of the object. Our equipment can easily produce a diamond like carbon layer by means of FIB assisted chemical vapor deposition. The Cu layer of \( 300 \mu m \) was employed to avoid charging-up and to clearly distinguish the region of the e-beam resist from the carbon layer.

\(^3\) \( l = \text{a few 10 nm} \) is achievable by using an e-beam writer with higher acceleration voltage or thinner e-beam resist (a few 10 nm), but we focused on a typical facility for e-beam lithography procedure in this paper.
The fact of the increase, therefore, strongly suggested that our double MTJs were in the shape of a narrow wire. On the other hand, the difference in the TMR ratio could be caused by the configuration of the magnetization in both magnetic layers. In our double MTJs, the single domain behavior and the large switching field of the hard layer could induce an ideal anti-parallel alignment, hence showed such large TMR ratio as 35%, while the anti-parallel state in the single MTJ seems to be imperfect due to the relatively low coercivity of Co75Fe25 layer.

3.3. Current–voltage characteristics

Fig. 6(a) shows $I–V$ curve of the double MTJ structure with the dimension of $10 \mu m \times 10 \, \text{nm}$. A nonlinear characteristic was observed up to 1 V. Using a model of tunneling current across the double tunnel junctions proposed by Simmons [21], we estimated the barrier width $d$ and the barrier height $\phi$ to be 1.27 nm and 1.0 eV, respectively. Obtained $d$ showed good agreement with the thickness of Al-oxide, which was designed to be 1.3 nm as deposited of Al. Fig. 6(b) shows the $I–V$ of the single MTJ with the area of $30 \mu m \times 30 \, \text{nm}$. It turned out that zero point of the voltage was slightly shifted to the negative region by 7.4 mV, while the wire structure exhibited no shift. Simmons’ model is not suitable for such asymmetrical $I–V$ characteristics. Therefore, we performed the curve fitting using the model of tunneling current extended by Brinkman et al. [22]. The difference of the barrier height $\Delta \phi$ was estimated to be 0.2 eV, and the barrier height of the top $\phi_1$ and bottom $\phi_2$ were 1.1 and 0.9 eV, respectively. This existence of the asymmetrical barrier potential caused asymmetrical behavior of the bias dependence. Although the single MTJ structure had such asymmetrical barrier property, the completed structure did not show any symmetry. This is due to the two serial connection of the same asymmetrical MTJ structure by facing each other, which builds the symmetrical structure as shown in Fig. 6(c).

4. Summary

We have developed a unique microfabrication procedure of double MTJs with nanometer scale. Two serial Ni80Fe20-Co75Fe25/Al-oxide/Co75Fe25 junctions were fabricated by using lift-off and the side-edge thin film deposition technique. The completed structure showed the large TMR ratio of 35% and the rectangle shape of the hysteresis curve. The large switching field of the hard magnetic layer supported that...
the tunneling area was wire in shape. The barrier parameter obtained by the fitting of the $I-V$ characteristics exhibited the symmetrical barrier potential, and showed good agreement with the designed barrier thickness.

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References

[1] H. Grabert, M.H. Devoret (Eds.), Single Charge Tunneling, Nato ASI Series, vol. 294, Plenum Press, New York, 1992.
[2] R. Meservey, P.M. Tedrow, Spin-polarized electron tunneling, Phys. Rep. 238 (1994) 173–243.
[3] T.A. Fulton, G.J. Dolan, Observation of single-electron charging effects in small tunnel junctions, Phys. Rev. Lett. 59 (1987) 109–112.
[4] M. Julliere, Tunneling between ferromagnetic films, Phys. Lett. 54A (1975) 225–226.
[5] T. Miyazaki, N. Tezuka, Giant magnetic tunneling effect in Fe/Al$_2$O$_3$/Fe junction, J. Magn. Magn. Mater. 139 (1994) L231–L234.
[6] J.S. Moodera, L.R. Kinder, T.M. Wong, R. Meservey, Large magnetoresistance at room temperature in ferromagnetic thin film tunnel junctions, Phys. Rev. Lett. 74 (1995) 3273–3276.
[7] S. Takahashi, S. Maekawa, Effect of Coulomb blockade on magnetoresistance in ferromagnetic tunnel junctions, Phys. Rev. Lett. 80 (1998) 1758–1761.
[8] X.H. Wang, A. Brataas, Large magnetoresistance ratio in ferromagnetic single-electron transistors in the strong tunneling regime, Phys. Rev. Lett. 83 (1999) 5138–5141.
[9] C. Karlsson, X.H. Wang, Magnetoresistance of ferromagnetic single-electron transistors, Appl. Phys. Lett. 77 (2000) 3618–3620.
[10] J. Barnaś, A. Fert, Magnetoresistance oscillations due to charging effects in double ferromagnetic tunnel junctions, Phys. Rev. Lett. 80 (1998) 1058–1061.
[11] K. Majumder, S. Hershfield, Magnetoresistance of the double-tunnel junction Coulomb blockade with magnetic metals, Phys. Rev. B 57 (1998) 11521–11526.
[12] A. Brataas, Yu.V. Nazarov, J. Inoue, G.E. Bauer, Spin accumulation in small ferromagnetic double-barrier junctions, Phys. Rev. B 59 (1999) 93–96.
[13] K. Ono, H. Shimada, S. Kobayashi, Y. Ootuka, Enhanced magnetic valve effect and magneto-Coulomb oscillations in ferromagnetic single-electron transistor, J. Phys. Soc. Jpn 66 (1997) 1261–1264.
[14] H. Brükel, G. Reiss, H. Vinzelberg, M. Bertram, I. Mönch, J. Schumann, Enhanced magnetoresistance of permalloy/Al-oxide/cobalt tunnel junctions in the Coulomb blockade regime, Phys. Rev. B 58 (1998) R8893–R8896.
[15] L.F. Schelp, A. Fert, F. Fettar, P. Holody, S.F. Lee, J.L. Maurice, F. Petroff, A. Vaurès, Spin-dependent tunneling with Coulomb blockade, Phys. Rev. B 56 (1997) R5747–R5750.
[16] K. Nakajima, Y. Saito, S. Nakamura, K. Inomata, Magnetoresistance oscillations in double ferromagnetic tunnel junctions with layered ferromagnetic nanoparticles, IEEE Trans. Magn. 36 (2000) 2806–2808.
[17] K. Yakushiji, S. Mitani, K. Takenashi, S. Takahashi, S. Maekawa, Enhanced tunnel magnetoresistance in granular nanobridges, Appl. Phys. Lett. 78 (2001) 515–517.
[18] K.J. Kirk, J.N. Chapman, C.D.W. Wilkinson, Lorentz microscopy of small magnetic structures (invited), J. Appl. Phys. 85 (1999) 5237–5242.
[19] K. Matsuyama, S. Komatsu, Y. Nozaki, Magnetic properties of nanostructured wires deposited on the side edge of patterned thin film, J. Appl. Phys. 87 (2000) 4724–4726.
[20] E.C. Stoner, E.P. Wohlfarth, A mechanism of magnetic hysteresis in heterogeneous alloys, Philos. Trans. R. Soc. Lond. A-240 (1948) 590–642.
[21] J.G. Simmons, Generalized formula for the electric tunnel effect between similar electrodes separated by a thin insulating film, J. Appl. Phys. 34 (1963) 1793–1803.
[22] W.F. Brinkman, R.C. Dynes, J.M. Rowell, Tunneling conductance of asymmetrical barriers, J. Appl. Phys. 41 (1970) 1915–1921.