Nitridation Process of Al Layer by Microwave-Excited Plasma and Large Magnetoresistance in Co-Fe/Al-N/Co-Fe Tunnel Junctions—As a Comparison With Oxidization Process

Satoru Yoshimura, Toshihiro Shoyama, Toshiharu Nozawa, Masakiyo Tsunoda, and Migaku Takahashi, *Member, IEEE*

***Abstract*—Nitridation and oxidization processes of metal Al film to form very thin insulating layer in magnetic tunnel junctions (MTJs) are investigated, using microwave-excited plasma. The plasma nitridation process provides wider controllability than the plasma oxidization for the formation of ultrathin insulating layer in MTJs, because of the slow nitriding rate of metal Al films, comparing with the oxidizing rate of them. As a result, high tunnel magnetoresistance (TMR) ratios of 49% and 44% with respective resistance-area product ($R \times A$) of 3×10^4 $\Omega\mu m^2$ and 6×10^3 $\Omega\mu m^2$ are obtained in the Co-Fe/Al-N/Co-Fe MTJs. These values are comparable to those of MTJs with Al-O barriers. The remarkable feature of the nitridation process is its larger amount of plasma exposure, needed to obtain similar resistance in MTJs, comparing with the oxidization process. It means wider controllability of the plasma nitridation for the formation process of very thin tunnel barriers. We conclude that Al-N is a hopeful barrier material to realize MTJs with high TMR ratio and low $R \times A$ for high-performance MRAM cells.**

***Index Terms*—Al-N barrier, low-reactivity, magnetic tunnel junction (MTJ), microwave-excited plasma, nitridation and oxidization processes.**

I. Introduction

SINCE the discovery of large tunnel magnetoresistance (TMR) over 10% at room temperature [1], [2], magnetic tunnel junctions (MTJs) have been strong candidates for several applications, such as magnetic random access memories (MRAMs). High TMR ratios and low resistance-area products ($R \times A$) of MTJs are important to realize MRAMs with low error rate and fast operation speed [3], [4]. In order to achieve these properties, the formation process of a very thin insulating layer should be precisely controled. Although, the plasma oxidization of metal Al films is generally accepted to be a suitable method to obtain high TMR ratio in MTJs, its high reactivity makes it difficult to oxidize ultrathin Al layers precisely down to the interface to the lower ferromagnetic electrode. The nitridation process of metal Al films is expected to progress more mildly than the oxidization process of metal Al films, from the aspects of affinity of reactive gases for metals and the lower diffusion coefficient of nitrogen in the insulator than that of oxygen [5]. However, the highest TMR ratio, which has been reported for the MTJs with Al-N layer, is only 33% [6] and smaller than that for the MTJs with an Al-O barrier. This seems to be an obstacle to utilize the Al-N layer as a tunnel barrier of MTJs.

We already reported a very high TMR ratio of 59% on MTJs with a Co-Fe/Al-O/Co-Fe system by using microwave-excited plasma for the oxidation process of metal Al layer [7]. The microwave-excited plasma realizes high electron density ($\sim 10^{12}$ cm^{-3}) and low electron temperature ($\sim$1 eV), which is suitable for the formation of ultrathin insulating layer without introducing atomic bombardment damages [8].

In the present study, we investigated the formation process of Al-N layer in MTJs with the microwave-excited plasma nitridation method through the magnetotransport properties of MTJs, comparing with the plasma oxidation process. Since the change of inert gas mixed into oxygen for the plasma oxidization process is effective to improve the magnetotransport properties of MTJs with Al-O [7], we also discuss the effect of inert gas mixed into nitrogen on the magnetotransport properties of MTJs with Al-N.

II. Experimental Procedure

The MTJs of substrate/Ta 50 Å/Cu 200 Å/Ta 50 Å/$Ni_{76}Fe_{24}$ 20Å/Cu 50 Å/$Mn_{75}Ir_{25}$ 100 Å/$Co_{71}Fe_{29}$ 40 Å/Al-N or Al-O/$Co_{71}Fe_{29}$ 40 Å/$Ni_{76}Fe_{24}$ 200 Å/Ta 50 Å were prepared on thermally oxidizing Si wafers. All the metallic films were deposited by dc magnetron sputtering method. The barrier formation was performed by depositing a metal Al film with thickness $d_{Al} = 8, 10, 15$ Å and subsequent nitriding or oxidizing it in the chamber with a radial line slot microwave antenna (RLSA) [9]. The mixing concentration of nitrogen or oxygen into inert gas was 5% or 0.5% to 3%, respectively. The nitridation time or oxidation time was varied from 10–150 s or 1–40 s. The applied microwave power density was 1.1 W/cm^2.

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S. Yoshimura is with the Japan Society for the Promotion of Science, Tokyo 102-8471, Japan and also with the Takahashi Laboratory, Department of Electronic Engineering, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan (e-mail: syoshi@ecei.tohoku.ac.jp).

T. Shoyama, T. Nozawa, and M. Tsunoda are with the Takahashi Laboratory, Department of Electronic Engineering, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan (e-mail: shoyama@ecei.tohoku.ac.jp; nozawa@ecei.tohoku.ac.jp; tsunoda@ecei.tohoku.ac.jp).

M. Takahashi is with the New Industry Creation Hatchery Center, Tohoku University, Sendai 980-8579, Japan and also with the Takahashi Laboratory, Department of Electronic Engineering, Graduate School of Engineering, Tohoku University, Sendai 980-8579, Japan (e-mail: migaku@ecei.tohoku.ac.jp).

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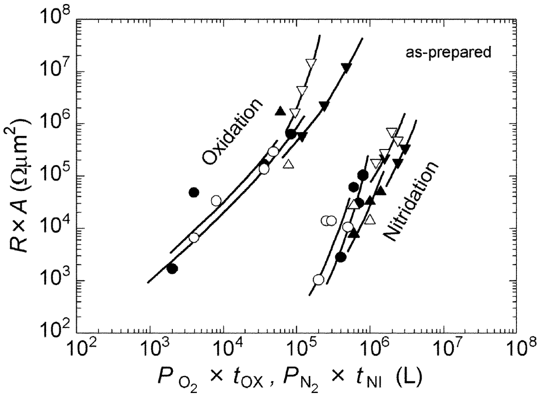

Fig. 1. Resistance-area product of as-prepared MTJs with the Al layer thickness of (circle) 8 Å, (triangle) 10 Å, (inverse triangle) 15 Å, fabricated with the various condition of nitridation or oxidation. The horizontal axis corresponds to the amount of plasma exposure. Mixed inert gas is (closed symbols) Ar and (open symbols) Kr, respectively.

A photolithographic process and ion milling were used to pattern the tunnel junctions in a normal area of 25–2500 μm^2. The TMR measurements were performed with a four-point probe method at a bias voltage of 5 mV. The scaling of the resistance inversely with the area of the junction and the constant TMR regardless of the size of the junction exclude the possibility of geometrical enhancement of the TMR. The thermal treatment consisted of consecutive 60-min vacuum annealing at each temperature, followed by furnace field cooling (1 kOe).

III. Results and Discussion

Fig. 1 shows resistance-area product $(R \times A)$ of as-prepared MTJs with $d_{\rm Al} = 8, 10.15$ Å, fabricated with the various condition of nitridation or oxidation using Ar + N_2, Kr + N_2, Ar + O_2, Kr + O_2 plasma. The horizontal axis corresponds to the amount of plasma exposure, represented by the product of the partial pressure of nitrogen/oxygen and the exposing time for nitridation/oxidation plasma, where 1 L (Langmuir) is defined as 1×10^{-6} Torr s. The needed amount of nitrogen exposure is one to two orders larger than that of oxygen exposure during the plasma nitridation/oxidation process, to obtain a same $R \times A$ value. It indicates that the nitriding rate of metal Al film is quite slow, compared to the oxidizing rate of metal Al film, as expected. When we attend to the effect of inert gas, the $R \times A$ of the MTJs with Al$(d_{\rm Al} = 15\,\text{Å}) - \text{O}$ (square symbols) fabricated with Kr + O_2 plasma is obviously higher than that of the MTJs fabricated with Ar + O_2 plasma under the same amount of plasma exposure. On the other hand, the $R \times A$ of MTJs with Al-N does not strongly depend on the inert gas kind and is slightly higher for the Kr + N_2 case than for the Ar + N_2 case. This is due to the difference of inert gas effect on excitation of reactive species in plasma between the oxidization process and the nitridation process. We otherwise confirmed through the optical emission spectroscopy that the reactive species in nitridation plasma does not change with changing the inert gas among Ar and Kr, in contrast to that highly reactive O^1D radicals are excited more effectively in the Kr + O_2 plasma than in the Ar + O_2 plasma [8].

Fig. 2 show the changes of the TMR ratio and the $R \times A$ of the MTJs with various metal Al layer thickness fabricated with Ar + N_2 or Kr + N_2 plasma, as a function of the annealing temperature, $T_{\rm a}$. The nitridation conditions of MTJs in Fig. 2 are summarized in Table I. The nitridation condition (in other words, the amount of nitridation plasma exposure) is optimized to maximize the achievable TMR ratio of MTJs during thermal annealing, for the respective metal Al layer thickness. The data plotted at 100 °C correspond to those for the as-prepared MTJs. Regardless of the Al layer thickness, TMR ratio increases with increasing $T_{\rm a}$ and takes the maximum at a certain temperature, then decreases. The annealing temperature at which the TMR ratio reaches its maximum shifts from 250 °C to 300 °C with decreasing $d_{\rm Al}$ from 15 Å to 8 Å. The 49% and 44% TMR ratio are obtained at $T_{\rm a} = 280$ °C and 300 °C for MTJs with $d_{\rm Al} = 10$ Å and 8 Å, respectively. These TMR ratios are larger than the values that have ever been reported for the CoFe/Al-N/CoFe tunnel junctions and are comparable to the CoFe/Al-O/CoFe junctions. Taking into account the 44% of TMR with 6×10^3 $\Omega\mu$m^2 of $R \times A$ and separately evaluated bias voltage of 450 mV, where the TMR ratio becomes half, one says that this MTJ satisfies the specification for 1-Gb MRAM cells: 25% of TMR at 400 mV bias with 6 k$\Omega\mu$m^2 of $R \times A$, assuming 0.15 μm^2 cell [10].

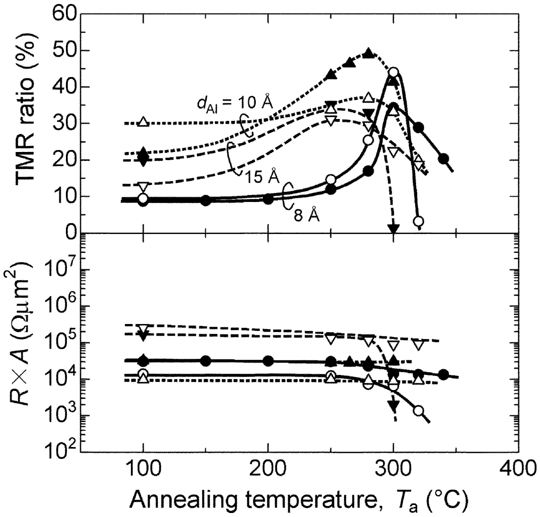

Fig. 2. Annealing temperature dependence of TMR ratio and resistance-area product for the MTJs with various metal Al layer thickness of (circle) 8 Å, (triangle) 10 Å, (inverse triangle) 15 Å, (closed symbols) fabricated with and Ar + N_2, and (open symbols) Kr + N_2 plasma.

TABLE I
Nitridation Conditions of MTJs With Various Metal Al Layer Thickness (8, 10, 15 Å) Fabricated With an Ar + N_2 and Kr + N_2 Plasma

Al thickness (Å)	Inert gas	Nitrogen concentration (%)	Plasma exposing time (s)	Nitrogen plasma exposure (L)
8	Ar	5	35	7.0×10^5
8	Kr	5	15	3.0×10^5
10	Ar	5	50	1.0×10^6
10	Kr	5	70	1.4×10^6
15	Ar	5	120	2.4×10^6
15	Kr	5	80	1.6×10^6

In Fig. 3, the changes of the TMR ratio and $R \times A$ of the MTJs with an Al-O barrier against $T_{\rm a}$ are shown as a reference. The $d_{\rm Al}$ are 8 and 15 Å. Kr + O_2 plasma was used. The oxidation conditions of MTJs in Fig. 3 are shown in Table II. For

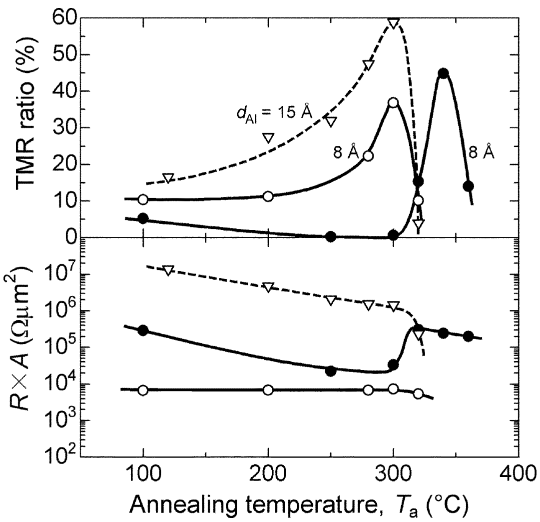

Fig. 3. Annealing temperature dependence of TMR ratio and resistance-area product for the MTJs with various metal Al layer thickness of (circle) 8 Å, (inverse triangle-symbols) 15 Å, fabricated with and Kr + O_2 plasma. Plasma oxidization condition is (circles) $P_{O2} \times t_{OX} = 4.0 \times 10^3$ L, (bullets) 4.8×10^4 L, (triangle) 1.6×10^5 L, respectively.

TABLE II

OXIDATION CONDITIONS OF MTJS WITH VARIOUS METAL Al LAYER THICKNESS (8 and 15 Å) FABRICATED WITH AN Kr + O_2 PLASMA

Al thickness (Å)	Inert gas	Oxygen concentration (%)	Plasma exposing time (s)	Oxygen plasma exposure (L)
8	Kr	0.5	2	4.0×10^3
8	Kr	3	4	4.8×10^4
15	Kr	3	13	1.6×10^5

the case of $d_{Al} = 8$ Å with 4.0×10^3 L and $d_{Al} = 15$ Å, the TMR ratio takes maximum at $T_a = 300$ °C, regardless of the Al layer thickness, and $R \times A$ slightly decreases with increasing T_a, similarly to the MTJ with Al-N shown in Fig. 2. On the other hand, in the case of $d_{Al} = 8$ Å with 4.8×10^4 L, the high TMR ratio of 45% is unexpectedly obtained at very high annealing temperature of 340 °C, whereas the TMR ratio is ~0% at T_a less than 300 °C. At the same time, $R \times A$ jumps up about one order above $T_a = 300$ °C. These behaviors are generally observed in the so-called "over-oxidized" MTJs [11] and in the MTJs with intentional oxide layer between barrier layer and pinned ferromagnetic layer [11], [12]. They are characterized with the sudden increase of TMR accompanied with the significant increase of $R \times A$. Taking into account this, we can say that MTJs with Al-N layer in Fig. 2 and MTJs with Al-O layer, indicated by open symbols in Fig. 3, are not "over-nitrided/oxidized" junctions and might be optimized to nitride/oxidize the metal Al layer precisely down to the interface to the lower ferromagnetic electrode for respective metal Al layer thickness.

In Fig. 4, the amount of nitrogen or oxygen exposure during the plasma process of metal Al film are replotted against d_{Al} from Fig. 1. The TMR ratio and $R \times A$ value obtained after annealing at 250 °C to 300 °C are attached for several MTJs. The shaded areas indicate the optimized nitridation/oxidization condition to obtain high TMR ratio for respective d_{Al}. With decreasing d_{Al} from 15 Å, the needed amount of oxygen exposure decreases fast, but that of nitrogen exposure decreases relatively slow. It means that the optimized nitridation condition is less sensitive to the metal Al layer thickness than that of oxidization. In other words, the plasma nitridation process provides wider controllability than the oxidization process for ultrathin barrier formation in MTJs.

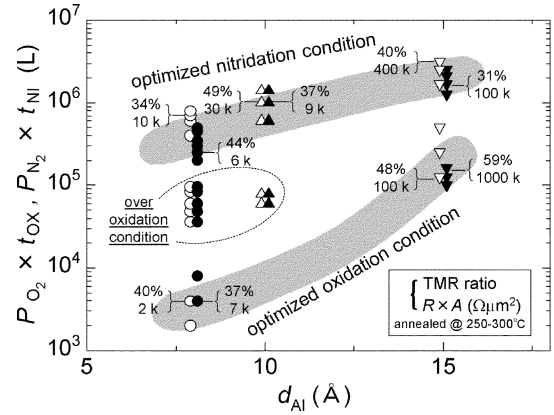

Fig. 4. Amount of nitrogen or oxygen exposure during the plasma process of metal Al film of MTJs. Mixed inert gas is (closed symbols) Ar and (open symbols) Kr, respectively.

In conclusion, we succeeded to induce large (49%) TMR ratio in MTJs with Al-N barrier, which is comparable to the MTJs with Al-O barrier, and found that the nitridation process of ultrathin Al layer has wider controllability than the oxidization process.

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