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60% magnetoresistance at room temperature in Co-Fe/Al-O/Co-Fe tunnel junctions oxidized with Kr-O₂ plasma

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The influence of the mixed inert gas species for plasma oxidization process of a metallic Al layer on the tunnel magnetoresistance (TMR) was investigated for a magnetic tunnel junction (MTJ), Ta 50 Å/Cu 200 Å/Ta 200 Å/Ni-Fe 50 Å/Cu 50 Å/Mn₇₅Ir₂₅ 100 Å/Co₇₀Fe₃₀ 25 Å/Al-O/Co₇₀Fe₃₀ 25 Å/Ni-Fe 100 Å/Cu 200 Å/Ta 50 Å. Using Kr-O₂ plasma, a 58.8% of TMR ratio was obtained at room temperature after annealing the junction at 300 °C, while the achieved TMR ratio of the MTJ fabricated with usual Ar-O₂ plasma remained 48.6%. A faster oxidization rate of the Al layer by using Kr-O₂ plasma is a possible cause to prevent the over oxidization of the Al layer, which depolarizes the surface of the underlaid ferromagnetic electrode, and to realize a large magnetoresistance. © 2002 American Institute of Physics. [DOI: 10.1063/1.1475363]

Since the discovery of a large tunnel magnetoresistance (TMR) over 10% at room temperature,^{1,2} the magnetic tunnel junction (MTJ) has been a strong candidate for applications such as a reproducing element of a hard disk head, and magnetic random access memories. A large TMR is one of the most important properties for MTJs to apply them to possible devices. Up to the present, MTJs with TMR in excess of 40% at room temperature have been demonstrated by several groups in a Co-Fe/Al-O/Co-Fe system,³⁻⁷ and the maximum TMR reported is almost 50%.^{6,7} These MTJs with large TMR are fabricated with a plasma oxidization process after the deposition of an ultrathin metallic Al layer. This method seems to be most favorable to provide a high quality tunnel barrier among the various fabrication methods for the Al-O layer. In the plasma oxidization process for MTJs, Ar and O₂ molecule mixture gas is usually used. The experimental parameters, generally varied to optimize the oxidization condition for the metallic Al layer, are such as the mixing ratio of Ar and O₂, the applied power to discharge plasma, and the oxidization time. However, particular attention has not been paid to the role of the inert gas. In the field of metal-oxide-semiconductor fabrication, it is known that the electric properties of a thin gate insulating layer, fabricated by plasma oxidization of Si, are strongly affected by the inert gases mixed in the oxygen plasma. Kr as a mixed inert gas provides excellent electric properties of the gate oxidization layer, such as lower interface trap density at the SiO₂/Si interface, compared to the case in which Ar gas is used.^{8,9} Kr-O₂ plasma also realizes a very uniform gate oxidization layer even on a shallow trench isolation edge, since a homogeneous oxidization rate is obtained irrespective of the crystallographic orientation of the Si surface.^{10,11}

In the present study, we thus investigate the influence of the inert gas species mixed in the plasma for oxidization of metallic Al films on TMR of MTJs. One can expect the

changes of TMR through the change of the quality of the Al-O barrier, by using inert gases other than the normally used Ar. Furthermore, we investigate the changes of the magnetotransport properties by a postthermal annealing procedure.

Tunnel junctions with the structure of sub/Ta 50 Å/Cu 200 Å/Ta 200 Å/Ni-Fe 50 Å/Cu 50 Å/Mn₇₅Ir₂₅ 100 Å/Co₇₀Fe₃₀ 25 Å/Al-O/Co₇₀Fe₃₀ 25 Å/Ni-Fe 100 Å/Cu 200 Å/Ta 50 Å were prepared on thermally oxidized Si wafers using a cluster tool constructed by Tsukishima Kikai Co. Ltd. All the metallic films were deposited by a dc magnetron sputtering method in the chamber having the base pressure of 3×10^{-9} Torr using highly purified (9N) Ar gas. The barrier formation is performed by depositing a 15-Å-thick metallic Al film and subsequently oxidizing it in the oxidization chamber having a radial line slot antenna (RLSA)¹²⁻¹⁴ for 2.45 GHz-microwave. The RLSA-plasma source produces a high density ($\sim 10^{12}$ cm⁻³) and low electron temperature (~ 1 eV) plasma.^{15,16} The details of this plasma oxidization technique are explained elsewhere.¹⁷ He, Ar, and Kr were used as the inert gases mixed with O₂ molecule gas for the plasma oxidization, respectively. The operating pressure of the mixed gas and the O₂ content in it were 1 Torr and 3%, respectively. The applied microwave power density was 1.1 W/cm². The oxidization time was varied from 3.5 to 40 s. The junctions were patterned by photolithography technique in normal area of 6×6 up to 60×60 μm². The transport measurements are performed with a four-point probe method at room temperature. The scaling of the resistance inversely with the area of the junction, the almost constant TMR regardless the size of the junction, and the low sheet resistivity of the Cu electrode exclude the possibility of geometrical enhancement of the TMR.¹⁸ The thermal treatment consists of 30 min of consecutive vacuum annealing at each temperature, followed by furnace field cooling (1 kOe).

Figure 1 shows the changes of the resistance-area products ($R \times A$) of as-prepared junctions as a function of the plasma oxidization time. In the cases of the junctions fabricated with He-O₂ and Kr-O₂ plasma, $R \times A$ increases more

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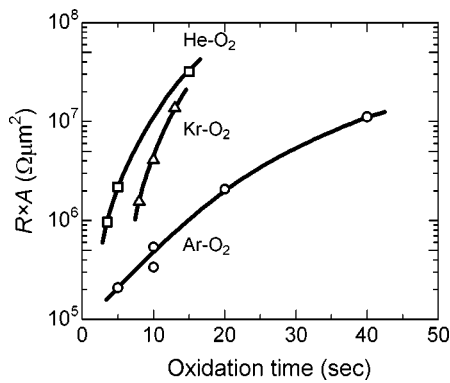


FIG. 1. Resistance-area product of the as-prepared tunnel junctions, fabricated with He-O₂, Kr-O₂, and Ar-O₂ plasma, as a function of the plasma oxidation time.

rapidly than in the case of the junctions fabricated with Ar-O₂ plasma, as the oxidation time increases. It means that the mixing inert gas species affects the oxidation rate of the metallic Al layer. Taking into account the highly efficient generation of O(2p⁴)¹D radical by using inert He or Kr rather than Ar,^{9,19} one can see that the high oxidation rate of metallic Al in He-O₂ and Kr-O₂ plasma are due to O¹D, which is known as a very active radical.

Figure 2 shows the changes of TMR, $R \times A$, and barrier characteristics of the MTJs as a function of the annealing temperature (T_a). The data plotted at 120 °C correspond to those for the as-prepared MTJs. The barrier height (ϕ) and the barrier width (d) were obtained by fitting the current-voltage curves with the Simmons model. The ϕ and d are plotted only in the annealing temperature range where the barrier parameters for both the positive and the negative branches of the current-voltage characteristics are not significantly deviated. In the case of MTJs fabricated with Ar-O₂ plasma (left-hand side column), the as-prepared samples show 15%–27% of TMR respective of the oxidation time. The TMR increases to 35%–50% after annealing up to 250 °C, then turns to decrease at above 250 °C, irrespective of the oxidation time. $R \times A$, which is 5×10^5 – $1 \times 10^7 \Omega \mu\text{m}^2$ for the as-prepared samples with respective

oxidization time, monotonously decreases by a factor of 5–10, after annealing at 250 °C. These changes of TMR and $R \times A$ roughly correspond to the changes of the barrier characteristics. Namely, the barrier height increases from an initial level of 1.7–2.4 eV to 2.7–3.5 eV, and the barrier width decreases from 11–15 Å to 9–11 Å, after annealing at 250 °C. This behavior is attributed to the change of oxygen distribution in the barrier layer during the annealing process as reported by several groups.^{20–23} An interesting feature that should be pointed out here is the remarkable decrease of the $R \times A$ value in coincidence with the decrease of the barrier width. It is a peculiar feature of the present plasma source and is advantageous in forming low resistance MTJs. Details of this effect will be published elsewhere.¹⁷

In the cases of He-O₂ (center column) and Kr-O₂ plasmas (right-hand side column), the MTJs fabricated with the shortest oxidation times (3.5 s for He-O₂ and 8 s for Kr-O₂) show a similar behavior as in the Ar-O₂ case, in which a maximum TMR of almost 50% is obtained around $T_a = 250$ °C. However, the MTJs fabricated with longer oxidation times show different behaviors. When the oxidation time increases, the annealing temperature where the TMR takes maximum shifts to the higher temperature and the achieved TMR exceeds 50%. Related to this TMR behavior, the barrier parameters for the respective oxidation time show different trends in their changes against T_a . In general, the barrier height increases with increasing T_a . However, as the oxidation time increases, the annealing temperature at which the barrier height starts to rise clearly shifts to a higher temperature. This phenomenon seems to be caused by diffusion controlled permeation of oxygen in the barrier layer during the thermal annealing process. Namely, some amount of oxygen in the barrier layer of the as-prepared samples may loosely bond with Al atoms and migrate within the barrier layer to form a more stable oxide having a large barrier height, such as Al₂O₃. The thicker the Al-O layer becomes, as in the as-prepared state fabricated with longer oxidation time, the greater the required activation energy for the oxygen to diffuse across the barrier layer. Thus, the MTJs with longer oxidation times need a higher temperature to form

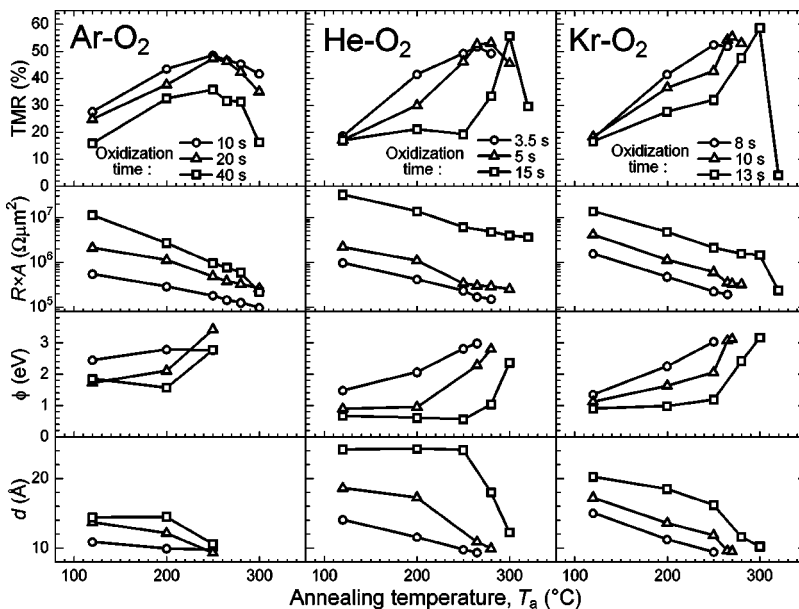


FIG. 2. Annealing temperature dependence of the TMR ratio, resistance-area product ($R \times A$), and effective barrier height (ϕ) and width (d), for Ta 50 Å / Cu 200 Å / Ta 200 Å / Ni-Fe 50 Å / Cu 50 Å / Mn₇₅Ir₂₅ 100 Å / Co₇₀Fe₃₀ 25 Å / Al-O / Co₇₀Fe₃₀ 25 Å / Ni-Fe 100 Å / Cu 200 Å / Ta 50 Å junctions, fabricated with He-O₂, Kr-O₂, and Ar-O₂ plasma, respectively.

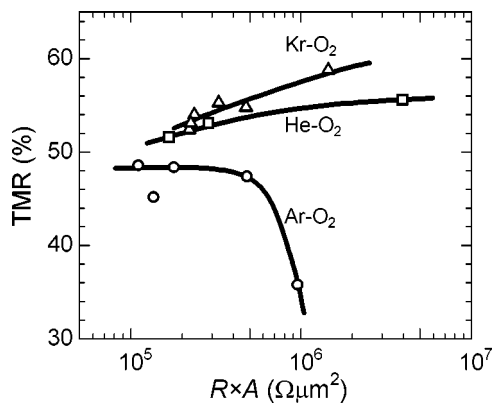


FIG. 3. Plots of the maximum TMR ratio obtained during the annealing process vs the corresponding resistance-area product, for the tunnel junction oxidized with He-O₂, Kr-O₂, and Ar-O₂ plasma, respectively.

the barrier layer with a large barrier height. Anyway, in the cases of He-O₂ and Kr-O₂ plasma, one can obtain a large TMR in excess of 50% for MTJs fabricated with a longer oxidation time after thermal annealing at 270 °C–300 °C. The maximum value of TMR in the present study is 58.8%, obtained in the MTJ fabricated with 13 s oxidation time in Kr-O₂ plasma and annealed at $T_a = 300$ °C. This is an extremely large value reported for a Co-Fe/Al-O/Co-Fe tunnel junction system.

In order to know the origin of the larger achievable TMR for the cases of Kr-O₂ and He-O₂ compared with the case of Ar-O₂, the maximum TMR of each case, fabricated with various oxidation times and treated with the thermal annealing process, is plotted in Fig. 3 as a function of the corresponding $R \times A$ value. A contrasted behavior of TMR is found between the Ar-O₂ case and the other two cases. The TMR of MTJs fabricated with Ar-O₂ plasma maintains a value of about 48% when the $R \times A$ is less than $5 \times 10^5 \Omega \mu\text{m}^2$, then decreases to 36% for $R \times A = 10^6 \Omega \mu\text{m}^2$. On the other hand, for MTJs fabricated with Kr-O₂ or He-O₂, TMR in excess of 50% is obtained at $R \times A \sim 2 \times 10^5 \Omega \mu\text{m}^2$ and still increases up to $R \times A > 10^6 \Omega \mu\text{m}^2$. The cause of the decreasing TMR in a higher resistance region, found for the Ar-O₂ case, is generally elucidated by the over oxidation mechanism.^{20,22,24} Namely, the oxidation condition is so strong that the surface of the underlaid ferromagnetic layer is also oxidized and results in the decreasing TMR owing to the reduction of the polarization of the ferromagnetic electrode. However, the MTJs fabricated with Kr-O₂ or He-O₂ show larger TMR even though they have higher resistance than the over oxidized MTJ with Ar-O₂. It means that the over oxidation mechanism was not significant in these MTJs. This result can be explained if we consider the difference of the oxidation process of a metallic Al layer by using various mixing inert

gases. The oxygen will permeate to the underlayer surface through the grain boundaries rather than the inner grain of the metallic Al layer, because the diffusing mobility of oxygen is generally larger at the grain boundaries than the inner grain. Thus, the distribution of the oxygen in MTJs along the film thickness direction will spread as the oxidation time increases, and the underlaid ferromagnetic electrode surface will be easily oxidized. Taking into account the oxidation rate shown in Fig. 1, one says that a faster oxidation rate for the Kr-O₂ or He-O₂ cases than the Ar-O₂ case was favorable to prevent the oxidation of the underlaid ferromagnetic electrode surface and resulted in the large TMR even in the high resistance MTJs.

- ¹ T. Miyazaki and N. Tezuka, *J. Magn. Magn. Mater.* **139**, L231 (1995).
- ² J. S. Moodera, L. R. Kinder, T. M. Wong, and R. Meservey, *Phys. Rev. Lett.* **74**, 3273 (1995).
- ³ S. S. P. Parkin, K. P. Roche, M. G. Samant, P. M. Rice, R. B. Beyers, R. E. Scheuerlein, E. J. O'Sullivan, S. L. Brown, J. Bucchigano, D. W. Abraham, Y. Lu, M. Rooks, P. L. Trouilloud, R. A. Wanner, and W. J. Gallagher, *J. Appl. Phys.* **85**, 5828 (1999).
- ⁴ H. Kikuchi, M. Sato, and K. Kobayashi, *J. Appl. Phys.* **87**, 6055 (2000).
- ⁵ S. Cardoso, P. P. Freitas, C. de Jesus, P. Wei, and J. C. Soares, *Appl. Phys. Lett.* **76**, 610 (2000).
- ⁶ X. F. Han, M. Oogane, H. Kubota, Y. Ando, and T. Miyazaki, *Appl. Phys. Lett.* **77**, 283 (2000).
- ⁷ E. Nakashio, J. Sugawara, S. Onoe, and S. Kumagai, *IEEE Trans. Magn.* **36**, 2812 (2000).
- ⁸ T. Ueno, A. Morioka, S. Chikamura, and Y. Iwasaki, *Jpn. J. Appl. Phys., Part 2* **39**, L327 (2000).
- ⁹ K. Sekine, Y. Saito, M. Hirayama, and T. Ohmi, *IEEE Trans. Electron Devices* **48**, 1550 (2001).
- ¹⁰ N. Ueda, Y. Saito, M. Hirayama, Y. Yamauchi, S. Sugawa, and T. Ohmi, *Extended Abstracts of the 2001 International Conference on Solid State Devices Materials* (Japan Society of Applied Physics, Tokyo, 2001), p. 164.
- ¹¹ T. Hamada, Y. Saito, M. Hirayama, H. Aharoni, and T. Ohmi, *IEEE Trans. Electron Devices* **22**, 423 (2001).
- ¹² N. Goto and M. Yamamoto, *Inst. Electr. Commun. Eng. Tech. Rep.* **80**, 43 (1980) [in Japanese].
- ¹³ M. Ando, K. Sakurai, N. Goto, K. Arimura, and Y. Ito, *IEEE Trans. Antennas Propag.* **33**, 1347 (1985).
- ¹⁴ J. Hirokawa, M. Ando, and N. Goto, *IEE Proc. Part H* **137**, 249 (1990).
- ¹⁵ M. Hirayama and T. Ohmi, *Extended Abstracts 1996 International Conference of the American Vacuum Symposium (AVS, New York, 1996)*, p. 199.
- ¹⁶ T. Yamamoto, N. T. Chien, M. Ando, N. Goto, M. Hirayama, and T. Ohmi, *Jpn. J. Appl. Phys., Part 1* **38**, 2082 (1999).
- ¹⁷ K. Nishikawa, M. Tsunoda, S. Ogata, and M. Takahashi, *IEEE Trans. Magn.* (submitted).
- ¹⁸ J. S. Moodera, L. R. Kinder, J. Nowak, P. LeClair, and R. Meservey, *Appl. Phys. Lett.* **69**, 708 (1996).
- ¹⁹ T. Ueno, T. Akiyama, K. Kuroiwa, and Y. Tarui, *Appl. Surf. Sci.* **79**, 502 (1994).
- ²⁰ M. Sato, H. Kikuchi, and K. Kobayashi, *J. Appl. Phys.* **83**, 6691 (1998).
- ²¹ H. Kikuchi, K. Kobayashi, and M. Sato, *J. Magn. Soc. Jpn.* **23**, 49 (1999).
- ²² J. J. Sun, V. Soares, and P. P. Freitas, *Appl. Phys. Lett.* **74**, 448 (1999).
- ²³ Y. Ando, H. Kubota, M. Hayashi, M. Kamijo, K. Yaoita, A. C. C. Yu, X. F. Han, and T. Miyazaki, *Jpn. J. Appl. Phys., Part 1* **39**, 5832 (2000).
- ²⁴ D. Song, J. Nowak, and M. Covington, *J. Appl. Phys.* **87**, 5197 (2000).