

Document made available under the Patent Cooperation Treaty (PCT)

International application number: PCT/JP05/004720

International filing date: 10 March 2005 (10.03.2005)

Document type: Certified copy of priority document

Document details: Country/Office: JP
Number: 2004-313350
Filing date: 28 October 2004 (28.10.2004)

Date of receipt at the International Bureau: 31 March 2005 (31.03.2005)

Remark: Priority document submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b)



World Intellectual Property Organization (WIPO) - Geneva, Switzerland
Organisation Mondiale de la Propriété Intellectuelle (OMPI) - Genève, Suisse

Japan Patent Office
JAPAN PATENT OFFICE

I certify that the matters set forth in the attached documents are the same as those set forth in the following application documents.

This is to certify that the annexed is a true copy of the following application as filed with this Office.

Date of Application	October 28, 2004
Date of Application:	
Japanese Patent Application	
Number	Japanese Patent Application 2004-313350
Application Number:	[JP2004-313350]
[ST. 10/C]:	
Applicant	Japan Science and Technology Agency
Applicant(s):	National Institute of Advanced Industrial Science and Technology

February 21, 2005

Commissioner, Japan Patent Office [signature]

Commissioner, Japan Patent Office

[stamp:] Commissioner,
Japan Patent Office Seal

[Document Title]	Japanese Patent Application
[Reference No.]	P04-1160
[Submission Date]	October 28, 2004
[Address]	To: Commissioner, Japan Patent Office
[International Patent Classification]	H01L 43/00
[Inventor]	
[Address or Location]	National Institute of Advanced Industrial Science and Technology, 1-1-1 Higashi, Tsukuba-shi, Ibaraki-ken
[Name]	Tsukuba Center
[Name]	Shinji Yuasa
[Patent Applicant]	
[Identification Number]	503360115
[Personal or Corporate Name]	
[Patent Applicant]	Japan Science and Technology Agency
[Identification Number]	301021533
[Personal or Corporate Name]	National Institute of Advanced Industrial Science and Technology
[Agent]	
[Identification Number]	100091096
[Patent Attorney]	
[Personal or Corporate Name]	Yusuke Hiraki
[Appointed Agent]	
[Identification Number]	100105463
[Patent Attorney]	
[Personal or Corporate Name]	Mitsuo Sekiya
[Appointed Agent]	
[Identification Number]	100102576
[Patent Attorney]	
[Personal or Corporate Name]	Toshiaki Watanabe
[Appointed Agent]	
[Identification Number]	100108394
[Patent Attorney]	
[Personal or Corporate Name]	Kenichi Imamura
[Contact Information]	Person in charge
[Priority Claim Based on Previous Application]	
[Application No.]	Japanese Patent Application 2004-71186
[Application Date]	March 12, 2004
[Indication of Fees]	
[Prepayment Ledger Number]	015244
[Payment Amount]	JPY 16,000
[Inventory of Submitted Items]	
[Name of Item]	Scope of Claims 1
[Name of Item]	Specification 1
[Name of Item]	Drawings 1
[Name of Item]	Abstract 1

[Document Title] Scope of Claims

[Claim 1]

A magnetoresistive element, characterized by a magnetic tunnel junction structure having a tunnel barrier layer, a first ferromagnetic layer having a BCC structure formed on the first surface side of the tunnel barrier layer, and a second ferromagnetic layer having a BCC structure formed on the second surface side of the tunnel barrier layer,

wherein the tunnel barrier layer is formed of a single crystal $\text{MgO}_x(100)$ or a polycrystalline MgO_x ($0 < x < 1$) layer with the (100) crystal plane preferentially oriented.

[Claim 2]

A magnetoresistive element, characterized by a magnetic tunnel junction structure having a tunnel barrier layer made of $\text{MgO}(100)$, a first ferromagnetic layer made of $\text{Fe}(100)$ formed on the first surface side of the tunnel barrier layer, and a second ferromagnetic layer made of $\text{Fe}(100)$ formed on the second surface side of the tunnel barrier layer,

wherein the MgO layer is formed of a single crystal $\text{MgO}_x(100)$ or a polycrystalline MgO_x ($0 < x < 1$) layer with the (100) crystal plane preferentially oriented.

[Claim 3]

A magnetoresistive element characterized by a magnetic tunnel junction structure having a tunnel barrier layer made of $\text{MgO}(100)$, a first ferromagnetic layer made of a single crystal (100) layer or a polycrystalline layer with a (100) crystal plane preferentially oriented of Fe or an Fe-based alloy having a BCC structure formed on the first surface side of the tunnel barrier layer, and a second ferromagnetic layer made of a single crystal (100) layer or a polycrystalline layer with a (100) crystal plane preferentially oriented of Fe or an Fe-based alloy having a BCC structure formed on the second surface side of the tunnel barrier layer,

wherein the discontinuous value (tunnel barrier height) between the conduction band bottom of the $\text{MgO}(100)$ layer and the Fermi level of the $\text{Fe}(100)$ layer is lower than the ideal value for a single crystal.

[Claim 4]

A magnetoresistive element according to Claim 3, characterized in that the discontinuous value is in the range of 0.2 to 0.5 eV.

[Claim 5]

A magnetoresistive element according to Claim 3, characterized in that the discontinuous value is in the range of 0.10 to 0.85 eV.

[Claim 6]

A memory element comprising a transistor and a magnetoresistive element according to any one of Claims 1 to 5 used as a load for the transistor.

[Claim 7]

A method for manufacturing a magnetoresistive element, characterized by comprising: a step of preparing a substrate,

a step of depositing a single crystal (100) layer of a first Fe or Fe-based alloy having a BCC structure or a polycrystalline layer with a (100) crystal plane preferentially oriented on the substrate,

a step of depositing a tunnel barrier layer made of single crystal MgO_x (100) or polycrystalline MgO_x ($0 < x < 1$) with a (100) crystal plane preferentially oriented on the (100) layer of the first Fe or Fe-based alloy having a BCC structure under high vacuum,

and a step of forming a single crystal (100) layer of a second Fe or Fe-based alloy having a BCC structure or a polycrystalline layer with a (100) crystal plane preferentially oriented on the tunnel barrier layer.

[Claim 8]

A method for manufacturing a magnetoresistive element, characterized by comprising: a first step of preparing a substrate made of single crystal $\text{MgO}_x(100)$ or polycrystalline MgO_x ($0 < x < 1$) with the (100) crystal plane preferentially oriented,

a second step of depositing a single crystal (100) layer or a polycrystalline layer with the (100) crystal plane preferentially oriented of a first Fe or Fe-based alloy having a BCC structure on the substrate, and then annealing for crystallization,

a third step of depositing a tunnel barrier layer made of single crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with a (100) crystal plane preferentially oriented on the (100) layer of the first Fe or Fe-based alloy having a BCC structure under high vacuum,

and a fourth step of forming a single crystal (100) layer of a second Fe or Fe-based alloy having a BCC structure or a polycrystalline layer with a (100) crystal plane preferentially oriented on the tunnel barrier layer.

[Claim 9]

A method of manufacturing a magnetoresistive element according to Claim 7 or 8, characterized in that it includes, between the first and second steps, a step of growing a seed layer made of single crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with (100) crystal plane preferentially oriented.

[Claim 10]

A method of manufacturing a magnetoresistive element according to Claim 7 or 8, characterized in that it includes a step of adjusting the x value of MgO_x during the step of forming a tunnel barrier layer made of the single crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with the (100) crystal plane preferentially oriented.

[Claim 11]

A method for manufacturing a magnetoresistive element, characterized by comprising: a step of preparing a substrate,

a step of depositing a single crystal (100) layer of a first Fe or Fe-based alloy having a BCC structure or a polycrystalline layer with a (100) crystal plane preferentially oriented on the substrate,

a step of forming an amorphous MgO layer on the (100) layer of the first Fe or Fe-based alloy having a BCC structure, and crystallizing the amorphous MgO layer by annealing to form a tunnel barrier layer made of single-crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with a (100) crystal plane preferentially oriented,

and a step of forming a single crystal (100) layer of a second Fe or Fe-based alloy having a BCC structure or a polycrystalline layer with a (100) crystal plane preferentially oriented on the tunnel barrier layer.

[Claim 12]

The method for manufacturing a magnetoresistive element according to Claim 11, characterized in that the amorphous MgO layer is deposited by a sputtering method using a target in which the x value of MgO_x has been adjusted.

[Claim 13]

The manufacturing method of the magnetoresistive element according to Claim 11, characterized in that the step of forming the amorphous MgO includes a step of adjusting the x value of MgO_x .

[Claim 14]

A magnetoresistive element, characterized by a magnetic tunnel junction structure having a tunnel barrier layer, a first ferromagnetic layer made of an amorphous magnetic alloy formed on the first surface side of the tunnel barrier layer, and a second ferromagnetic layer made of an amorphous magnetic alloy formed on the second surface side of the tunnel barrier layer,

wherein the tunnel barrier layer is formed of a single crystal $\text{MgO}_x(100)$ or a polycrystalline $\text{MgO}_x(0 < x < 1)$ layer with the (100) crystal plane preferentially oriented.

[Claim 15]

A magnetoresistive element, characterized by a magnetic tunnel junction structure having a tunnel barrier layer comprised of $\text{MgO}(100)$, a first ferromagnetic layer made of an amorphous magnetic alloy formed on the first surface side of the tunnel barrier layer, and a second ferromagnetic layer made of an amorphous magnetic alloy formed on the second surface side of the tunnel barrier layer,

wherein discontinuous value (tunnel barrier height) between the bottom of the conduction band of the $\text{MgO}(100)$ layer and the Fermi level of the first or second ferromagnetic layer made of the amorphous magnetic alloy is lower than the ideal value in a single crystal.

[Claim 16]

A magnetoresistive element according to Claim 14 or 15, characterized in that the discontinuous value is in the range of 0.2 to 0.5 eV.

[Claim 17]

A magnetoresistive element according to Claim 14 or 15, characterized in that the discontinuous value is in the range of 0.1 to 0.85 eV.

[Claim 18]

A memory element comprising a transistor and a magnetoresistive element according to any one of Claims 14 to 17 used as a load for the transistor.

[Claim 19]

A method for manufacturing a magnetoresistive element, characterized by comprising: a step of preparing a substrate,

a step of depositing a first ferromagnetic layer made of an amorphous magnetic alloy on the substrate, a step of forming an amorphous MgO layer on the first ferromagnetic layer, and crystallizing the amorphous MgO layer by annealing to form a tunnel barrier layer made of single-crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with a preferred orientation of the (100) crystal plane;

a step of depositing a second ferromagnetic layer made of an amorphous magnetic alloy on the tunnel barrier layer.

[Claim 20]

A method for manufacturing a magnetoresistive element, characterized in that during the step of forming a tunnel barrier layer made of single-crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with a (100) crystal plane preferentially oriented, deposition is performed by a sputtering method using a target in which the x value of MgO_x has been adjusted.

[Document Title] Specification

[Title of Invention] Magnetoresistive element and manufacturing method thereof

[Technical Field]

[0001]

The present invention relates to a magnetoresistive element and a manufacturing method thereof, and in particular to a magnetoresistive element having high magnetoresistance and a manufacturing method thereof.

[Prior Art]

[0002]

MRAM (Magnetoresistive Random Access Memory) is a high-capacity memory element that replaces DRAM, which is a memory element currently in wide use. It is also being widely researched and developed as a high-speed non-volatile memory. For example, a 4Mbit MRAM sample has been shipped.

[0003]

FIG. 8 is a diagram illustrating the structure of the TMR element, which is the heart of the MRAM, and its operating principle; As shown in FIG. 8(A), the TMR element has a tunnel structure in which a tunnel barrier made of an oxide is sandwiched between two electrodes made of a ferromagnetic metal, the first and second electrodes. Amorphous Al-O layer is used as the tunnel barrier layer (see Non-Patent Literature 1). As shown in FIG. 8(A), in the case of parallel magnetization in which the orientation of the magnetization of the first ferromagnetic electrode and the second ferromagnetic electrode is parallel, the electrical resistance of the element with respect to the normal direction at the interface of the tunnel structure is reduced. On the other hand, as shown in FIG. 8(B), in the case of anti-parallel magnetization in which the orientation of the magnetization of the first ferromagnetic electrode and the second ferromagnetic electrode is parallel, the electrical resistance of the element with respect to the normal direction at the interface of the tunnel structure is increased. This resistance value does not change under normal conditions, and is stored as information "1" or "0" depending on whether the resistance value is high or low. Parallel magnetization and anti-parallel magnetization are stored in non-volatile form and can be used as basic elements of non-volatile memory.

FIG. 9 is a diagram illustrating an example basic structure of MRAM, FIG. 9(A) is a perspective view of MRAM, FIG. 9(B) is a schematic circuit configuration diagram, and FIG. 9(C) is a cross-sectional view illustrating an example structure. As shown in FIG. 9(A), the MRAM is arranged such that the word lines WL and the bit lines BL intersect, and MRAM cells are arranged at the intersection. As shown in FIG. 9(B), MRAM cells disposed at the intersection of the word and bit lines have a TMR element and a MOSFET serially connected with this TMR element, and the memory information can be retrieved by reading the resistance value of the TMR element acting as a load resistance by the MOSFET. The rewriting of information can be done, for example, by applying a magnetic field to the TMR element. As shown in FIG. 9(C), the MRAM memory cell has a MOSFET 100 having a source region 103 formed in the p-type Si substrate 101, a drain region 105, and a gate electrode 111 formed relative to the channel region defined therebetween, and a TMR element 117. The source region 103 is grounded (GND) via the source electrode 113 and the drain region 105 is connected to the bit line BL via the drain electrode 115 and the TMR element. The word line WL is connected to the gate electrode 111 in a region not shown in the drawings.

[0004]

As described above, nonvolatile memory MRAM can be a memory element suitable for high integration because one MOSFET 100 and TMR element 117 can form one memory cell.

[0005]

[Non-Patent Literature 1] D. Wang, et al.: Science 294 (2001) 1488.

[Disclosure of Invention]

[Problem to be Solved by the Invention]

[0006]

With current technology, it is possible to realize a 64Mbit MRAM, but to achieve even higher integration, it is necessary to improve the characteristics of the TMR element, which is the heart of MRAM. In particular, to improve the output voltage of the TMR element, both an increase in magnetoresistance and an improvement in voltage characteristics are necessary. FIG. 10 is a diagram showing the change in magnetoresistance of a conventional TMR element with an amorphous Al-O tunnel barrier depending on the applied voltage (L1). As

shown in FIG. 10, the conventional TMR element has a small magnetoresistance, and in particular, the magnetoresistance tends to decrease rapidly when a voltage is applied. With such characteristics, the output voltage considering the operating margin is too small, making it difficult to use it in an actual memory element. More specifically, the magnetoresistance of the current TMR element is low at about 70%, and the output voltage is also low at 200mV or less, which is essentially half the output voltage of a DRAM, and there is a problem that as the integration density increases, the signal becomes buried in noise and cannot be read.

[0007]

The present invention is intended to increase the output voltage in the TMR element. Furthermore, the present invention aims to provide a memory device that operates stably due to its large magnetoresistance.

[Method for Solving the Problem]

[0008]

According to one aspect of the present invention, a magnetoresistive element is provided, characterized by a magnetic tunnel junction structure having a tunnel barrier layer, a first ferromagnetic layer having a BCC structure formed on a first surface side of the tunnel barrier layer, and a second ferromagnetic layer having a BCC structure formed on a second surface side of the tunnel barrier layer, wherein the tunnel barrier layer is formed of a single crystal $\text{MgO}_x(100)$ or a polycrystalline $\text{MgO}_x(0 < x < 1)$ layer with a (100) crystal plane preferentially oriented.

[0009]

In addition, a magnetoresistive element is provided, characterized by a magnetic tunnel junction structure having a tunnel barrier layer made of $\text{MgO}(100)$, a first ferromagnetic layer made of $\text{Fe}(100)$ formed on the first surface side of the tunnel barrier layer, and a second ferromagnetic layer made of $\text{Fe}(100)$ formed on the second surface side of the tunnel barrier layer, characterized in that the MgO layer is formed of a single crystal $\text{MgO}_x(100)$ or a polycrystalline $\text{MgO}_x(0 < x < 1)$ layer with a (100) crystal plane preferentially oriented. It is characterized in that the discontinuous value (tunnel barrier height) between the bottom of the conduction band of the $\text{MgO}(100)$ layer and the Fermi energy of the $\text{Fe}(100)$ layer is lower than that in a single crystal. By using the above configuration, the magnetoresistance is increased, and the output voltage of the TMR element can be increased. By using the above-mentioned magnetoresistive element as the load of one transistor, a nonvolatile memory element can be formed.

[0010]

According to another aspect of the present invention, there is provided a method for manufacturing a magnetoresistance element, comprising the steps of preparing a substrate, depositing a first $\text{Fe}(100)$ layer on the substrate, depositing a tunnel barrier layer made of single crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with a (100) crystal plane preferentially oriented on the first $\text{Fe}(100)$ layer under high vacuum by electron beam deposition, and forming a second $\text{Fe}(100)$ layer on the tunnel barrier layer.

[0011]

Also, a method for manufacturing a magnetoresistive element is provided, which comprises a first step of preparing a substrate made of single-crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with a (100) crystal plane preferentially oriented, a second step of depositing a first $\text{Fe}(100)$ layer on the substrate and then annealing the substrate for crystallization, a third step of depositing a tunnel barrier layer made of single-crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with a (100) crystal plane preferentially oriented on the first $\text{Fe}(100)$ layer under high vacuum by electron beam deposition, and a fourth step of forming a second $\text{Fe}(100)$ layer on the tunnel barrier layer. Incidentally, between the first and second steps, there may be a step of growing a seed layer made of single crystal $\text{MgO}_x(100)$ or polycrystalline $\text{MgO}_x(0 < x < 1)$ with a (100) crystal plane preferentially oriented. In addition, the amorphous MgO layer may be deposited using a target in which the x value of MgO_x has been adjusted. In this case, the x value of MgO_x may be adjusted during the step of forming the amorphous MgO .

[0012]

According to yet another aspect of the present invention, there is provided a magnetoresistive element characterized by magnetic tunnel junction structure having a tunnel barrier layer made of MgO(100), a first ferromagnetic layer made of an amorphous magnetic alloy formed on the first surface side of the tunnel barrier layer, and a second ferromagnetic layer made of an amorphous magnetic alloy formed on the second surface side of the tunnel barrier layer, characterized in that the discontinuous value (tunnel barrier height) between the Fermi level of the conduction band bottom of the MgO(100) layer and the first or second ferromagnetic layer made of the amorphous magnetic alloy is lower than the ideal value in a single crystal.

[Effects of Invention]

[0013]

According to the present invention, a larger magnetoresistance can be obtained than that of a conventional TMR element, and the output voltage of the TMR element can be increased. Therefore, there is an advantage that it is easy to achieve high integration of MRAM using TMR elements.

[Best Form for Implementing the Invention]

[0014]

The term "ideal value" for single crystals used in this specification is a value estimated from an experiment using ultraviolet photoelectron spectroscopy (Reference: W. Wulfhekkel, et al.: Appl. Phys. Lett. 78 (2001) 509.). In this state, it can be said that this is the upper limit of the tunnel barrier of ideal single crystal MgO with almost no oxygen vacancies or lattice defects, so the term "ideal value" is used.

[0015]

Before explaining the embodiment of the invention, the inventors' considerations will be explained. The magnetoresistance (MR) ratio of MTJ is expressed by the following formula:

$$\Delta R/R_p = (R_{ap} - R_p)/R_p$$

Here, R_p and R_{ap} are the tunnel junction resistances when the magnetizations of the two electrodes are parallel and anti-parallel. According to Jullire's formula, the MR ratio at low bias voltage is expressed as follows:

$$\text{MR ratio} = (R_{ap} - R_p)/R_p = 2P_1P_2/(1 - P_1P_2);$$

$$P\alpha = (D\alpha \uparrow(E_F) - D\alpha \downarrow(E_F))/(D\alpha \uparrow(E_F) + D\alpha \downarrow(E_F)), \alpha = 1, 2(1).$$

[0016]

Here, $P\alpha$ is the spin polarization rate of electrons, and $D\alpha \uparrow(E_F)$ and $D\alpha \downarrow(E_F)$ are the densities of state (DOS) in the Fermi energy (E_F) of the majority spin band and minority spin band, respectively. Since the spin polarization of ferromagnetic transition metals and alloys is less than 0.5, Jullire's formula predicts a maximum MR ratio of 70%.

When an MTJ element is fabricated using an amorphous Al-O tunnel barrier and polycrystalline electrodes, an MR ratio of about 70% is obtained at room temperature. However, it is difficult to obtain an output voltage of 200 mV, which is comparable to that of a DRAM, and this is a problem for the realization of MRAM, as mentioned above.

[0017]

The inventors are attempting an approach to grow MTJs using magnesium oxide single crystal (100) or polycrystalline MgO with a (100) crystal plane preferentially oriented as the tunnel barrier. Unlike conventional amorphous alumina barriers, magnesium oxide is a crystal (a substance in which atoms are regularly arranged), so it is expected that the electrons will not be scattered and the coherent state of electrons is preserved during the tunneling process. FIG. 1 is a diagram showing the MTJ element structure (FIG. 1(B)) in accordance with the present embodiment and the energy band structure of the ferromagnetic metal Fe(100) and showing the relationship of $E-E_F$ TO THE [100] DIRECTION of the wavenumber space (FIG. 1(A)). As shown in FIG. 1(B), the MTJ element structure according to this embodiment is composed of a first Fe(100) layer 1, a second Fe(100) layer 5, and a single-crystal $\text{MgO}_x(100)$ layer or a polycrystalline $\text{MgO}_x(0 < x < 1)$ layer with a (100) crystal plane preferentially oriented 3 sandwiched between them. According to the Jullire model, if the momentum of the conduction electrons is preserved during the tunneling process, the tunneling current through MgO is dominated by electrons with wave vector k_z in a direction perpendicular to the tunneling barrier (normal direction to the

junction interface). According to the energy band diagram of Fe in the $[100](\Gamma-H)$ direction shown in FIG. 1(A), the density of state (DOS) at Fermi level E_F does not exhibit such a high polarization rate because the sub-bands of the multiple and small spins have states at Fermi level E_F . However, if the coherent state of the electrons is preserved during the tunneling process, only conduction electrons with a total symmetric wave function about an axis perpendicular to the barrier will be associated with states in the barrier region and have a certain tunneling probability. As shown in FIG. 1(A), the majority spin $\Delta 1$ band (solid line) has a state in Fermi level E_F , but the minority spin $\Delta 1$ band (dashed line) has no state in Fermi level E_F . These half-metallic characteristics of the $Fe\Delta_1$ band may lead to a very high MR ratio in coherent spin-polarized tunneling. Epitaxial (single crystal or (100) oriented polycrystal) MTJs are considered ideal for realizing the above-mentioned coherent tunneling because electron scattering during the tunneling process is suppressed.

[0018]

The magnetoresistive element according to the first embodiment of the present invention and its manufacturing method will be described below with reference to the drawings. FIG. 2(A) to FIG. 2(D) are diagrams showing the manufacturing steps of a magnetoresistive element having a Fe (100)/MgO (100)/Fe (100) structure (hereinafter referred to as "Fe (100)/MgO (100)/Fe (100) MTJ") according to an embodiment of the present invention. Fe (100) is a ferromagnetic material having a BCC structure. First, a single crystal MgO (100) substrate 11 is prepared, and a MgO (100) seed layer 15 is grown by the MBE method (molecular beam epitaxy method) to improve the morphology of the surface of the single crystal MgO (100) substrate 11. Continuing, as shown in FIG. 1(B), a 50 nm thick epitaxial Fe(100) lower electrode (first electrode) 17 is grown on the MgO (100) seed layer 15 at room temperature and then annealed at 350°C under ultra-high vacuum (2×10^{-8} Pa). It should be noted that the conditions for electron beam deposition are: the acceleration voltage is 8 kV, the growth rate is 0.02 nm/s, the growth temperature is room temperature (293 K), the source is MgO with a stoichiometric composition (Mg to O ratio is 1:1), the distance between the source and the substrate is 40 cm, the background vacuum is 1×10^{-8} Pa, and the O_2 partial pressure is 1×10^{-6} Pa. Furthermore, it is also possible to use a source with an O deficiency in place of the stoichiometric composition MgO (Mg to O ratio 1:1).

[0019]

FIG. 3(A) is a diagram illustrating the RHEED image of the Fe (100) lower electrode (first electrode) 17 in this case. As shown in FIG. 3(A), the Fe (100) lower electrode (first electrode) 17 is shown to have good crystallinity and flatness. Next, the 2 nm thick MgO (100) barrier layer 21 is epitaxially grown on the Fe (100) lower electrode (first electrode) 17 at room temperature, as shown in FIG. 2 (C). In this case, the electron beam evaporation method of MgO was used. FIG. 3(B) is a diagram illustrating an RHEED image of the MgO (100) barrier layer 21 in this case. As shown in FIG. 3(B), the MgO (100) barrier layer 21 also shows good crystallinity and flatness.

[0020]

As shown in FIG. 2 (D), a Fe (100) upper electrode (second electrode) 23 with a thickness of 10 nm at room temperature was formed on the MgO (100) barrier layer 21. Subsequently, a 10 nm thick Co layer 25 was deposited on the Fe (100) upper electrode (second electrode) 23. The Co layer 25 is for realizing an anti-parallel magnetization arrangement by increasing the holding force of the upper electrode 23. Next, the above-mentioned sample was microfabricated to form an Fe (100)/MgO (100)/Fe (100) MTJ element.

[0021]

The above-mentioned EB deposition of MgO was performed under ultra-high vacuum conditions of 10^{-9} Torr. With this method, even when a 300 nm film is formed on a glass substrate, it is colorless and transparent, and it is clear that a good single crystal film is formed. FIG. 4 is a diagram illustrating the observations of the quadrupole mass spectrum during MgO growth. As shown in FIG. 4, it can be seen that the partial pressure for spectra P1 of 0 and P2 of O_2 is high. FIG. 5 is a diagram illustrating film deposition rate dependence of oxygen partial pressure during MgO deposition; As shown in FIG. 5, the oxygen partial pressure is quite high, and the oxygen partial pressure increases with the deposition rate. These facts suggest that oxygen is being removed from the MgO single crystal during deposition, and there is a possibility that oxygen vacancies such as MgO_x ($0.9 < x < 1$) are occurring. When oxygen vacancies occur, the MgO tunnel barrier height is thought to be lowered (for example, within the range of 0.10-0.85 eV, more specifically, 0.2-0.5 eV), which is thought to increase the tunnel current. Furthermore, in the case of a general Al-O tunnel barrier, the tunnel barrier height between Fe (100) is thought to be 0.7-2.5 eV. In contrast, the ideal tunnel barrier height for MgO crystals is 3.6 eV, and experimental values of 0.9-3.7 eV have been obtained. When the method according to the present embodiment is used, the tunnel barrier height is estimated to be about 0.3 eV, and it is found that the resistance of the tunnel barrier can be reduced. However, other factors, such as the effect of the coherent tunnel described above, may also be involved. It should be noted that the value of x of MgO_x based on oxygen deficiency is $0.98 < x < 1$, and more preferably $0.99 < x < 1$, and does not include those such as simple Mg, and is basically within the range in which the characteristics of MgO are maintained.

[0022]

FIG. 6 is a diagram illustrating a typical magnetoresistance curve of an Fe (100) / MgO (100) / Fe (100) MTJ element manufactured by the above method. The MR ratio was 146% at the measurement temperature 20K and 88% at the measurement temperature 293K. This value is the highest MR ratio obtained to date at room temperature. Such a high MR ratio cannot be explained by the spin polarization of the Fe (100) electrode, but rather is considered to be related to coherent spin polarized tunneling. As a result of prototyping 160 MTJ elements, the variation in MR ratio and tunnel resistance values was within 20%. MTJ yield was also more than 90% at the laboratory stage. These high values suggest the effectiveness of this approach. The resistance-area product (RA) of the MTJ is several $k\Omega\mu m^2$, which is a value suitable for: MRAM.

[0023]

FIG. 7(a) is a diagram showing the bias voltage dependency of MR ratio at room temperature. As shown in FIG. 7(a), it can be seen that the bias voltage dependency of the MR ratio is quite low. Although the characteristics are asymmetric, the voltage V_{half} at which the MR ratio is reduced to half is very high at 1250 mV. It should be noted that the voltage V_{half} at which the MR ratio is reduced to half in the conventional Al-O system is 300 to 600 mV. The output voltage V_{out} of the MTJ (= bias voltage $\times$ (Rap-Rp)/Rap) is shown in FIG. 7(B). The maximum output voltage V is 380 mV in forward bias. This value is about twice the value for the Al-O barrier (200 mV). Thus, the fact that high values were obtained for both the MR ratio and the output voltage shows the effectiveness of the technology according to this embodiment.

[0024]

It should be noted that, in the above embodiment, BCC Fe (100) was used, but BCC Fe alloys, such as Fe-Co alloys, Fe-Ni alloys, and Fe-Pt alloys, can be used instead. Alternatively, Co, Ni, etc., may be inserted between the Fe(100) layer and the MgO(100) layer to a thickness of about one atomic layer or several atomic layers.

[0025]

Next, a magnetoresistive element and a manufacturing method thereof according to a second embodiment of the present invention will be described. The manufacturing method of the Fe (100)/MgO (100)/Fe (100) TMR element according to this embodiment is characterized in that MgO (100) is first deposited in a polycrystalline or amorphous state by a sputtering method or the like, and then annealed to form polycrystalline or single-crystalline structures with the (100) crystal plane oriented. The sputtering conditions are, for example: The

temperature was room temperature (293K), and sputtering was performed in an Ar atmosphere using a 2-inch ϕ MgO as the target. The acceleration power is 200 W and the growth rate is 0.008 nm/s. Since the MgO deposited under this condition is in an amorphous state, crystallized MgO can be obtained by increasing the temperature from room temperature to 300 °C and holding at 300 °C for a period of time.

[0026]

It should be noted that the method of introducing O vacancies can be any of the following: a method where growth is performed under conditions that generate O vacancies during growth, a method where O vacancies are introduced later, or a method of adjusting the amount of O defects to a certain degree by oxidizing the O-deficiency state, for example, by oxygen plasma treatment or natural oxidation.

[0027]

As described above, the magnetoresistive element technology according to the present embodiment has the advantage that it does not require a large-scale device because amorphous MgO is deposited by sputtering and then crystallized by annealing.

[0028]

Next, a magnetoresistive element according to a modified embodiment of the present invention will be described with reference to the drawings. FIG. 11 is a diagram showing the element structure of an MTJ according to a modified embodiment of the present invention, and corresponds to FIG. 1(B). As shown in FIG. 11, the magnetoresistive element according to this embodiment is characterized in that it uses an amorphous ferromagnetic alloy, for example, CoFeB layers 501, 505, as electrodes provided on a single crystal MgO_x (100) or oxygen-deficient polycrystalline MgO_x ($0 < x < 1$) layer 503 with a (100) crystal plane preferentially oriented. The amorphous ferromagnetic alloy can be formed, for example, by a deposition method or a sputtering method. The obtained characteristics, etc. are generally the same as in the first embodiment.

[0029]

It should be noted that, for amorphous magnetic alloys, for example, FeCoB, FeCoBSi, FeCoBP, FeZr, CoZr, and the like can also be used.

[0030]

Although the magnetoresistive elements according to the present embodiments have been described above, the present invention is not limited to these. It will be obvious to those skilled in the art that various other modifications, improvements, and combinations are possible. For example, instead of introducing oxygen vacancies into the MgO layer, a method of adjusting the tunnel barrier height by doping with, for example, Ca or Sr may be used. In addition, as the deposition method of the MgO layer, the electron beam evaporation method or the sputtering method has been described as an example, but it goes without saying that other deposition methods are also applicable. In addition, the term "high vacuum" refers to a value of approximately 10^{-6} Pa or less when oxygen is not introduced, for example, and to a value of about 10^{-4} Pa when oxygen is actively introduced.

[Industrial Applicability]

[0031]

The output voltage value of the MRAM is improved to about twice that of the conventional one, and the structure is suitable for ultra-high integration MRAM of gigabit class.

[Brief Description of the Drawings]

[0032]

[FIG. 1] A diagram showing the MTJ element structure according to the first embodiment of the invention (FIG. 1(B)) and the energy band structure of ferromagnetic metal Fe (100), and a diagram showing the relationship of $E-E_F$ to the [100] direction of the wavenumber space (FIG. 1(A)).

[FIG. 2] Fig. 2(A) to Fig. 2(D) are diagrams showing the manufacturing steps of a magnetoresistive element having a Fe(100)/MgO(100)/Fe(100) structure according to an embodiment of the present invention (hereinafter referred to as "Fe(100)/MgO(100)/Fe(100) MTJ").

[FIG. 3] FIG. 3(A) is a diagram showing the RHEED image of the Fe (100) lower electrode (first electrode), and FIG. 3(B) is a diagram showing the RHEED image of the MgO (100) barrier layer in this case.

[FIG. 4] A diagram showing the results of observations of the quadrupole mass spectrum during MgO growth.

[FIG. 5] A diagram showing the film deposition rate dependence of partial pressure of oxygen during MgO deposition.

[FIG. 6] A diagram showing a typical magnetoresistive curve of a Fe (100)/MgO (100)/Fe (100) MTJ element.

[FIG. 7] FIG. 7(A) is a diagram showing the bias voltage dependency of MR ratio at room temperature. FIG. 7 (B) is a diagram showing the output voltage V_{out} of the MTJ ($= \text{bias voltage} \times (\text{Rap}-\text{Rp})/\text{Rap}$).

[FIG. 8] A diagram showing the structure of the TMR element and its operating principle.

[FIG. 9] A diagram showing an example basic structure of MRAM, where FIG. 9(A) is a perspective view of MRAM, FIG. 9(B) is a schematic circuit configuration diagram, and FIG. 9(C) is a cross-sectional view showing an example structure.

[FIG. 10] A diagram showing the change in magnetoresistance due to applied voltage in a conventional TMR element using amorphous Al-O as the tunnel barrier.

[FIG. 11] A diagram showing the element structure of the MTJ according to a variation of the embodiment of the present invention, corresponding to Figure 1(B).

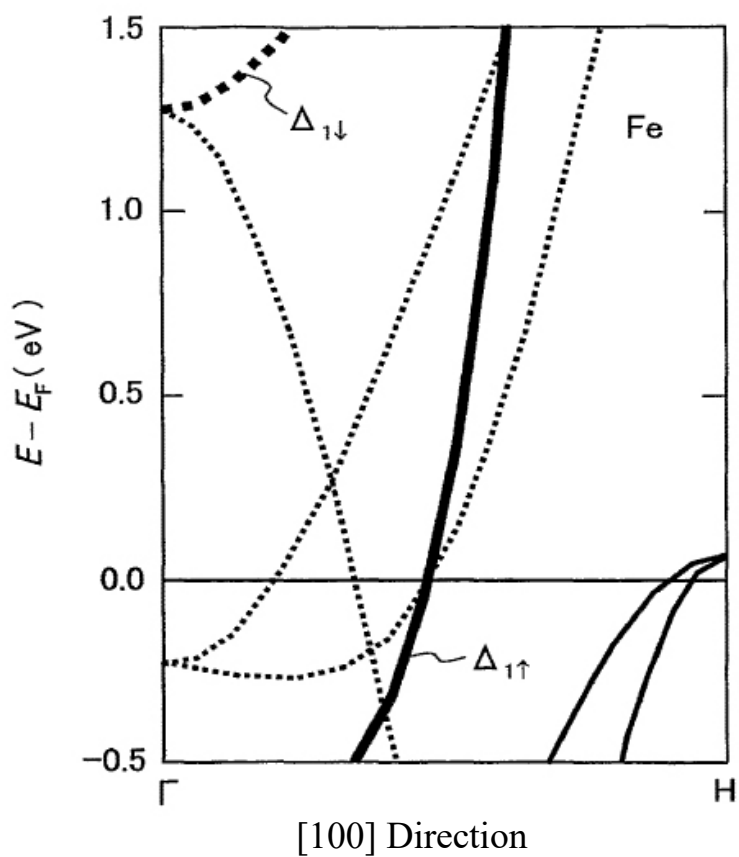
[Explanation of References]

[0033]

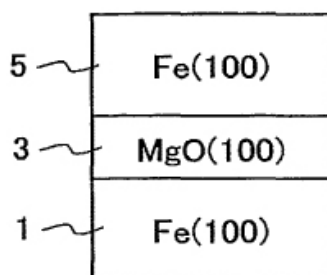
1: First Fe(100) layer, 3: Single crystal MgO_x (100) or polycrystalline MgO_x layer ($0 < x < 1$) with the (100) crystal plane preferentially oriented, 5: Second Fe(100) layer, 11: Single crystal MgO_x (100) or polycrystalline MgO_x substrate ($0 < x < 1$) with the (100) crystal plane preferentially oriented, 15: MgO(100) seed layer, 17: Epitaxial Fe(100) lower electrode (first electrode), 21: MgO barrier layer (100), 23: Epitaxial Fe(100) upper electrode (second electrode), 503: Single crystal MgO_x (001) or polycrystalline MgO_x layer ($0 < x < 1$) with the (001) crystal plane preferentially oriented, 501: Lower electrode made of amorphous ferromagnetic material (first electrode), 503: MgO barrier layer, 505: Upper electrode made of amorphous ferromagnetic material (second electrode).

[Document Title] Drawings
[Figure 1]

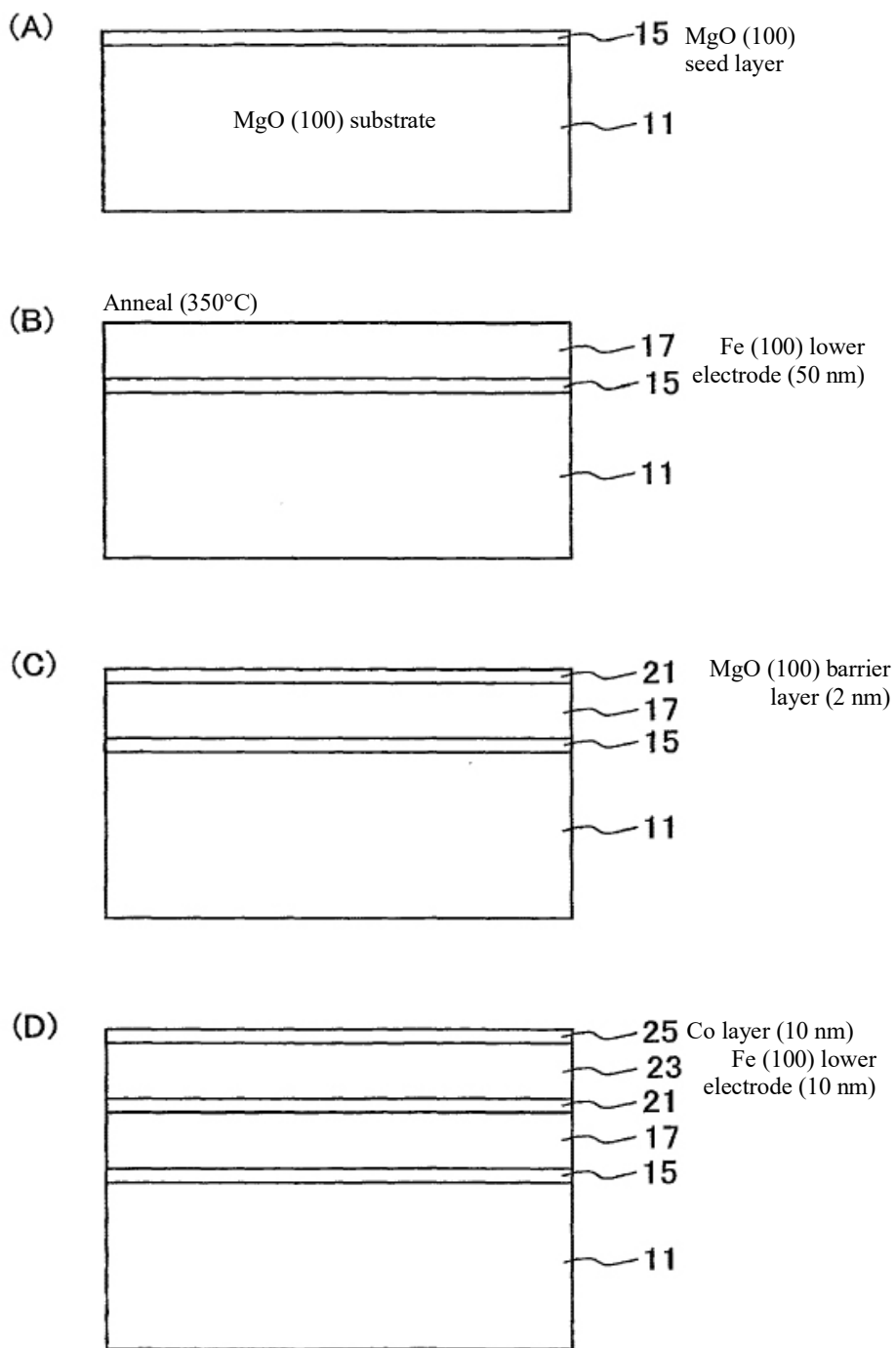
(A)



(B)

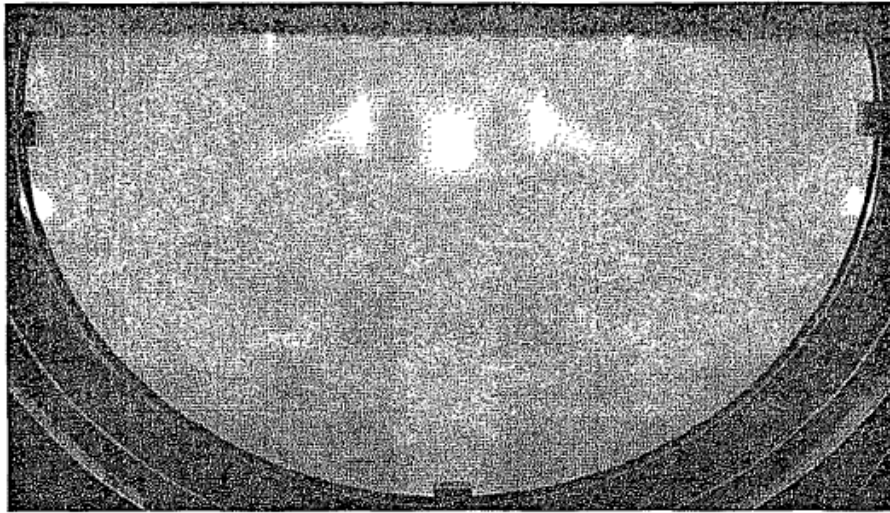


[Figure 2]

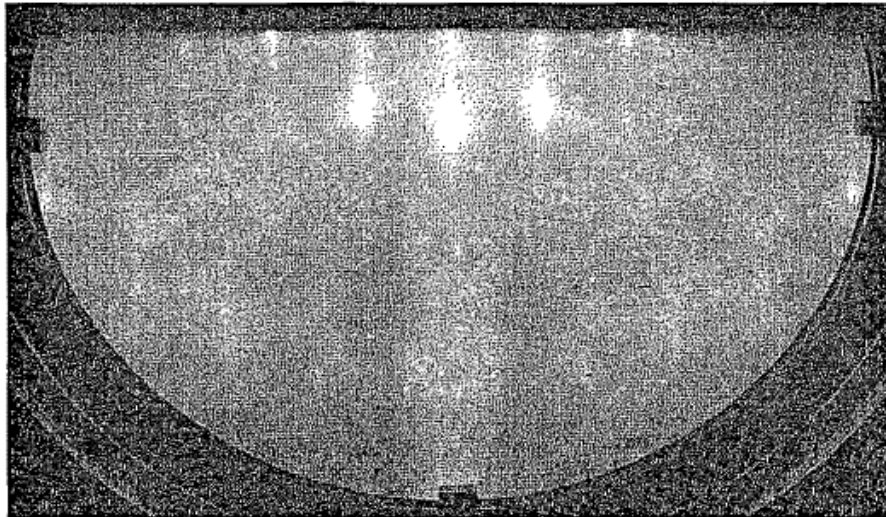


[Figure 3]

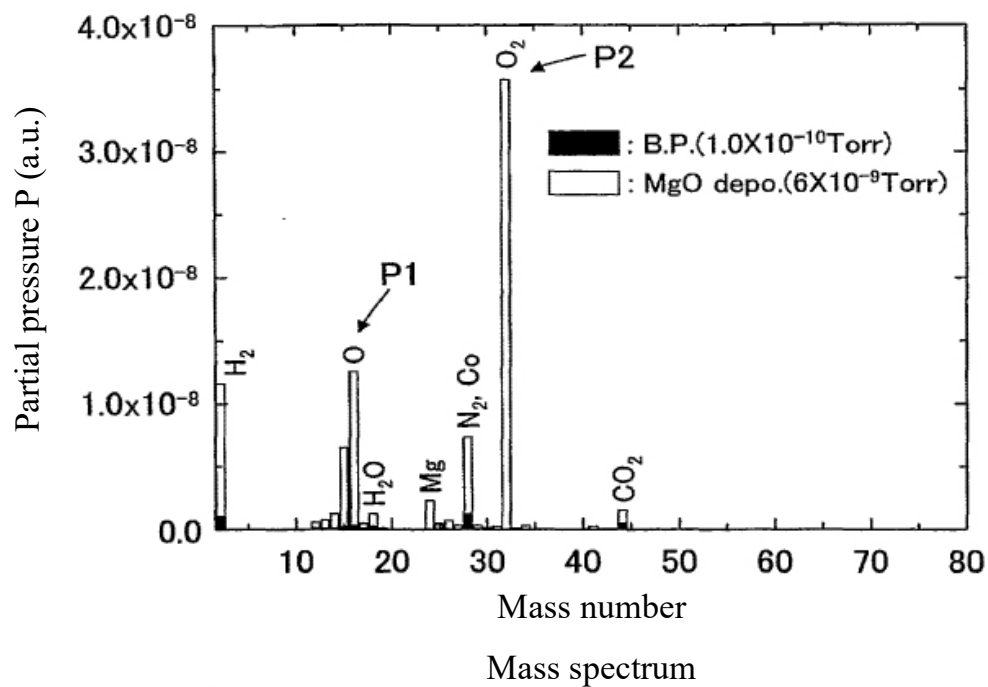
(a)



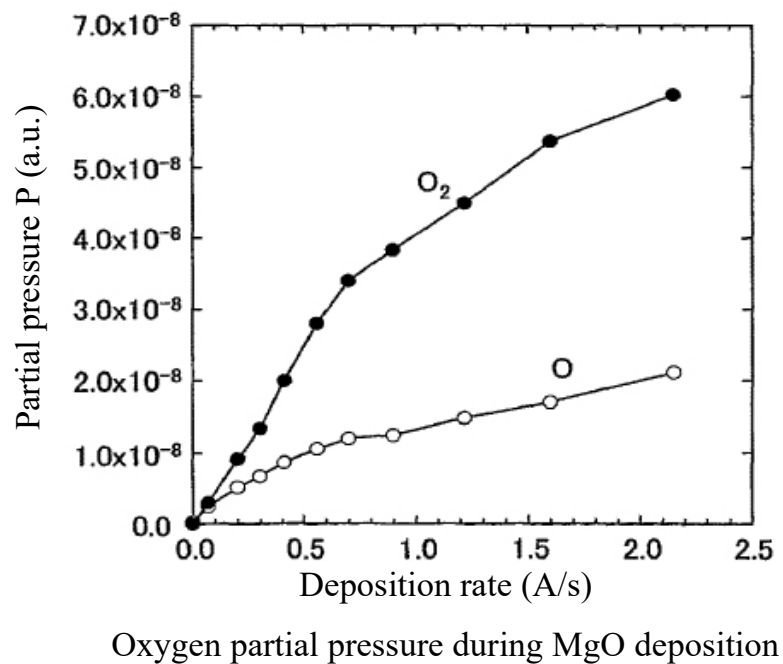
(b)



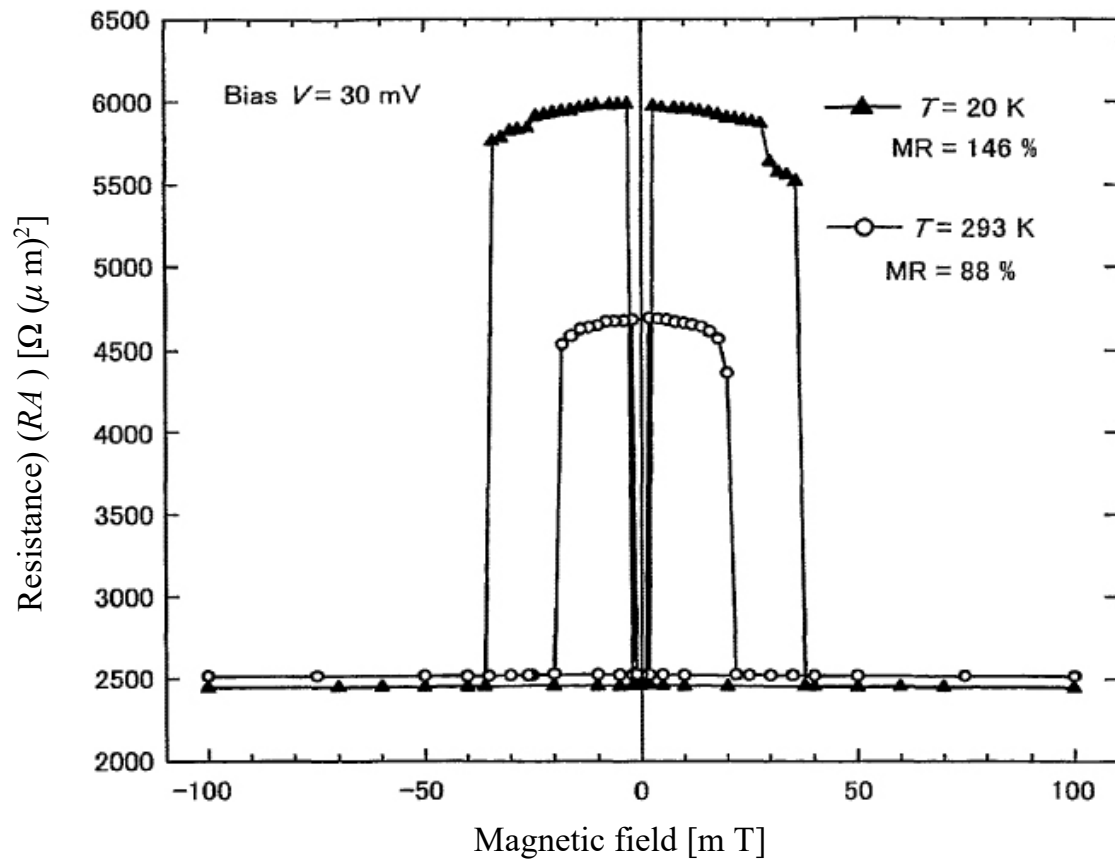
[Figure 4]



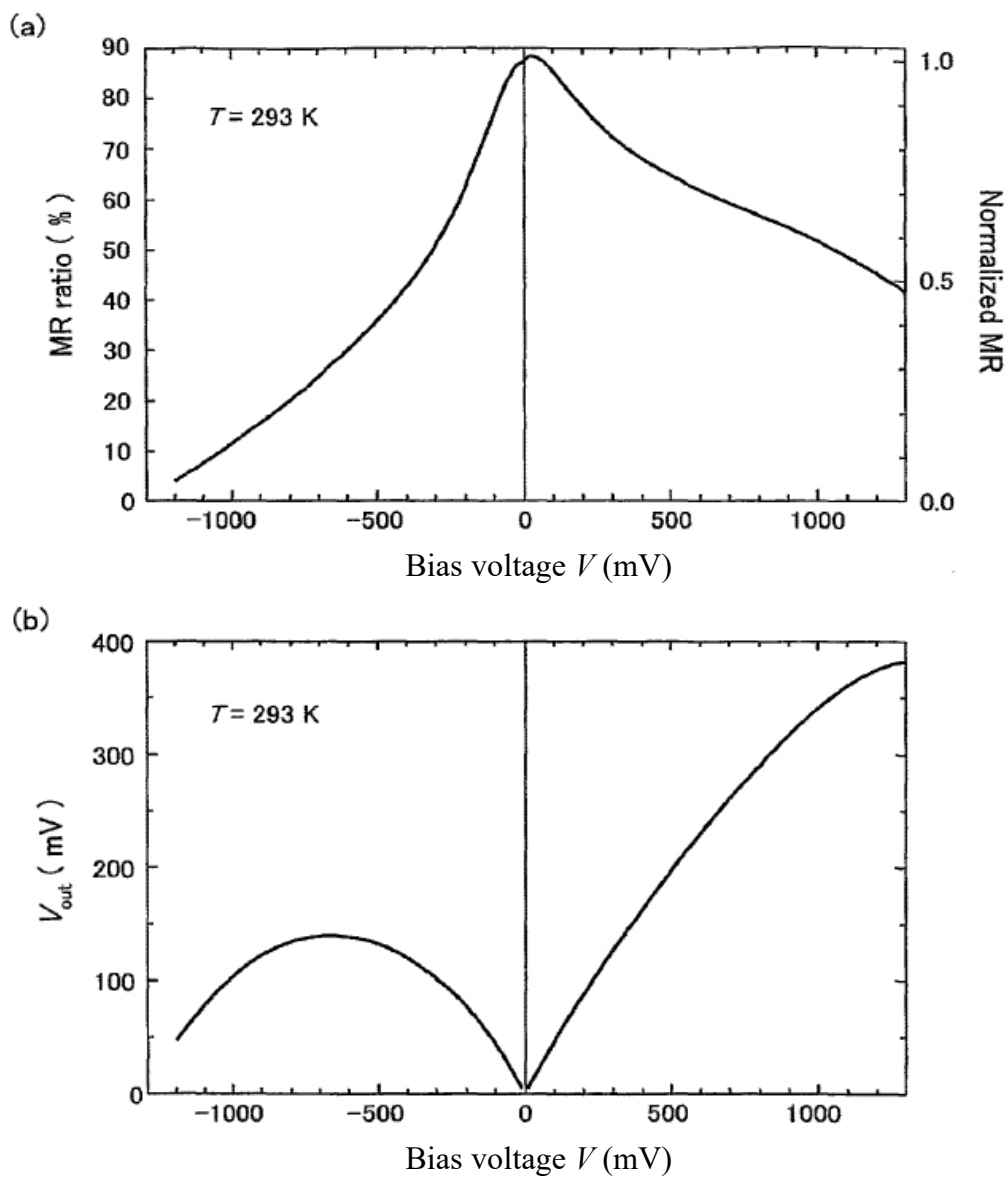
[FIG. 5]



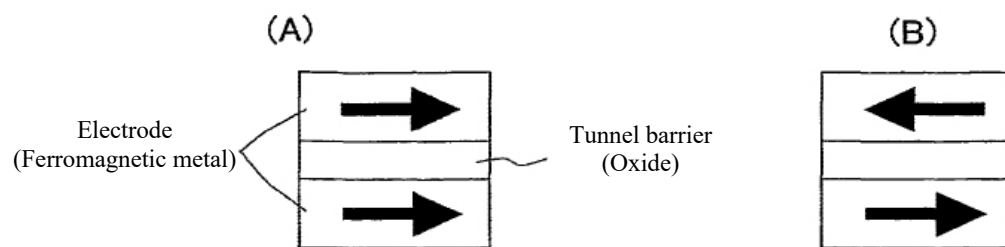
[FIG. 6]



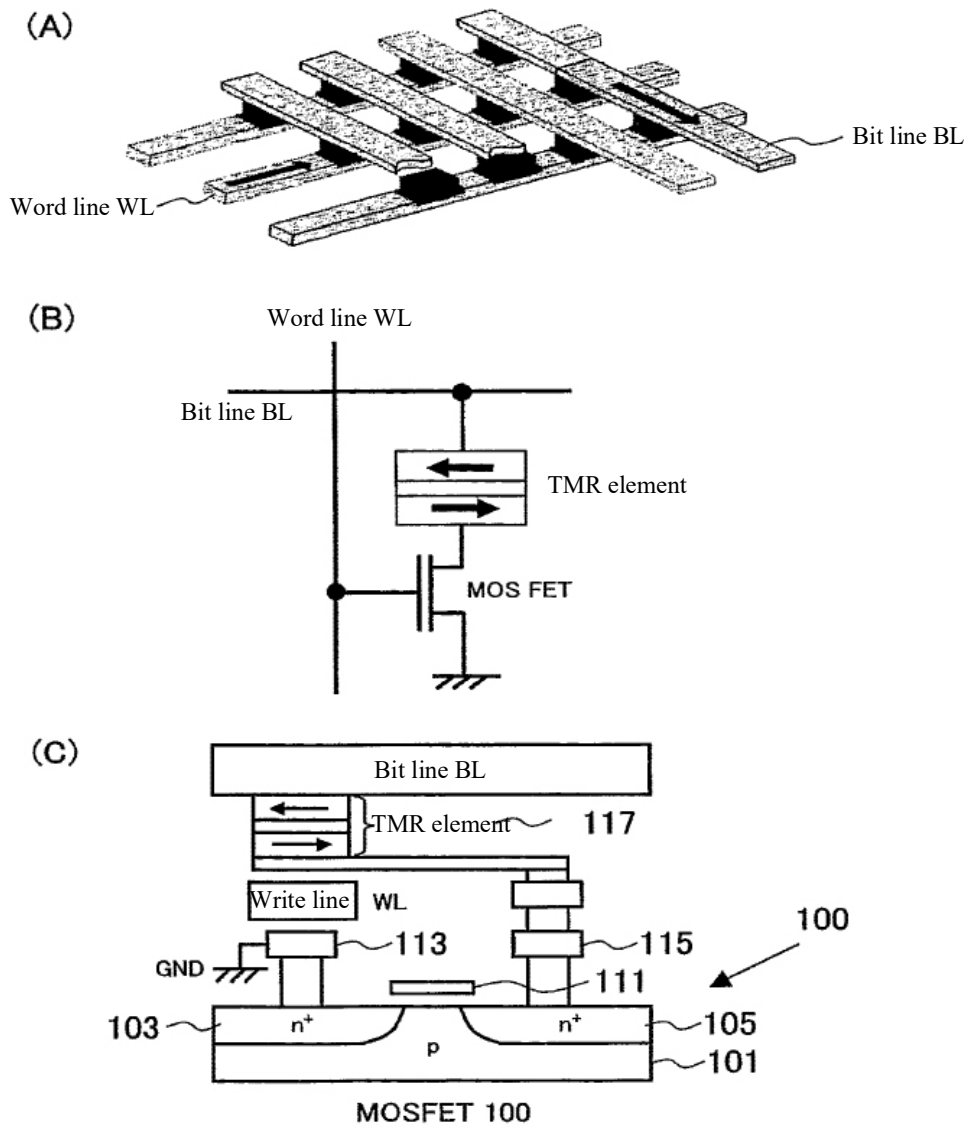
[FIG. 7]



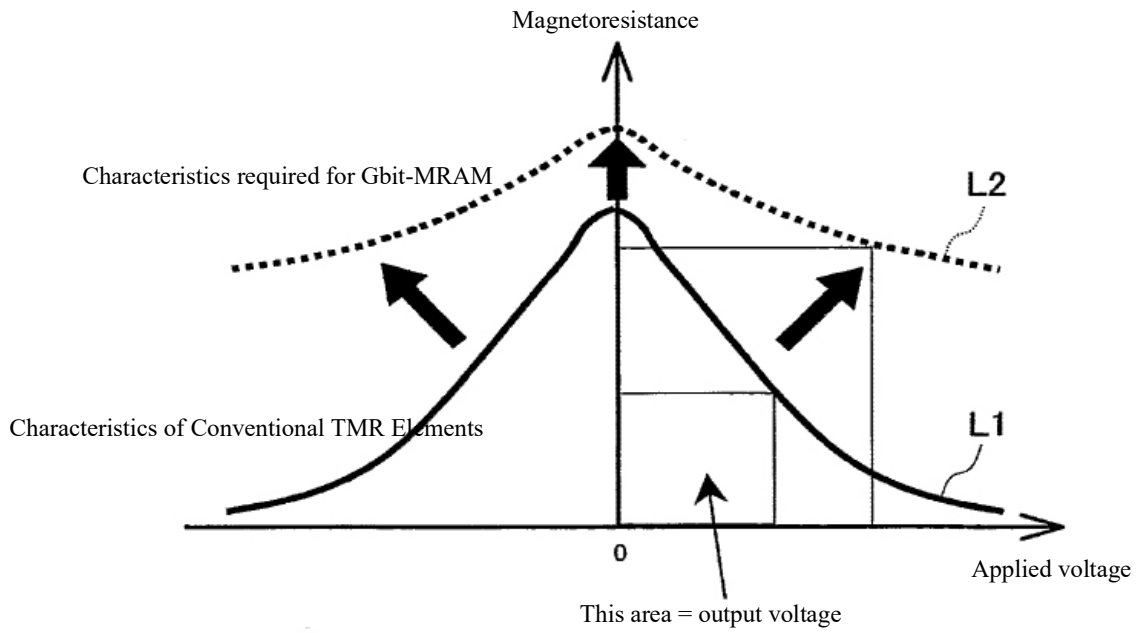
[FIG. 8]



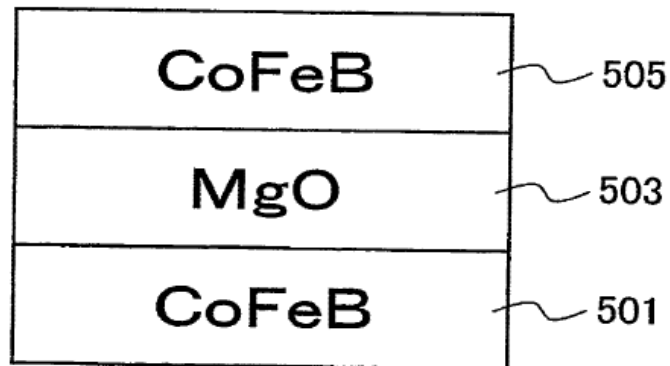
[FIG. 9]



[FIG. 10]



[FIG. 11]



[Document Title] Abstract

[Abstract]

[Problem] To increase the output voltage value of MRAM.

[Means for Solving] A single crystal MgO(100) substrate 11 is prepared, and a 50 nm thick epitaxial Fe(100) lower electrode (first electrode) 17 is grown on an MgO(100) seed layer 15 at room temperature, and then annealed at 350°C in ultra-high vacuum (2×10^{-8} Pa). The 2 nm thick MgO (100) barrier layer 21 is epitaxially grown on the Fe (100) lower electrode (first electrode) 17 at room temperature. In this case, electron beam evaporation of MgO is used. A Fe (100) upper electrode (second electrode) 23 with a thickness of 10 nm at room temperature was formed on the MgO (100) barrier layer 21. Subsequently, a 10 nm thick Co layer 21 was deposited on the Fe (100) upper electrode (second electrode) 23. The Co layer 21 is for realizing an anti-parallel magnetization arrangement to enhance the forced magnetic field of the upper electrode 23. Next, the above-mentioned sample was microfabricated to form an Fe (100)/MgO (100)/Fe (100) MTJ element.

[Representative Drawing] FIG. 2

Certification/Additional information

Japanese Patent Application Number JP2004-313350
 Receipt number 50401841490
 Document Title Japanese Patent Application
 Officer in charge Makoto Kusumoto 2169
 Creation Date December 15, 2004

< Certification information/Additional information>

[Patent Applicant]

[Identification Number] 503360115
 [Address or Location] 4-1-8 Honcho, Kawaguchi-shi, Saitama-ken
 [Personal or Corporate Name] Japan Science and Technology Agency

[Patent Applicant]

[Identification Number] 301021533
 [Address or Location] Kasumigaseki 1-3-1, Chiyoda-ku, Tokyo-to
 [Personal or Corporate Name] National Institute of Advanced Industrial
Science and Technology

[Agent]

Applicant
 [Identification Number] 100091096
 [Address or Location] Toranomon 4-3-20, Minato-ku, Tokyo-to Kamiyacho MT
Building
19th Floor Hiraki International Patent Office
 [Personal or Corporate Name] Yusuke Hiraki

[Appointed Agent]

[Identification Number] 100105463
 [Address or Location] Toranomon 4-3-20, Minato-ku, Tokyo-to Kamiyacho MT
Building
19th Floor Hiraki International Patent Office
 [Personal or Corporate Name] Mitsuo Sekiya

[Appointed Agent]

[Identification Number] 100102576
 [Address or Location] Toranomon 4-3-20, Minato-ku, Tokyo-to Kamiyacho MT
Building
19th Floor Hiraki International Patent Office
 [Personal or Corporate Name] Toshiaki Watanabe

[Appointed Agent]

[Identification Number] 100108394
 [Address or Location] Toranomon 4-3-20, Minato-ku, Tokyo-to Kamiyacho MT
Building
19th Floor Hiraki International Patent Office
 [Personal or Corporate Name] Kenichi Imamura

Applicant History Information

Identification number	[503360115]
1. Date of change	April 1, 2004
[Reason for change]	Name change
Address	4-1-8 Honcho, Kawaguchi-shi, Saitama-ken
Name	Japan Science and Technology Agency

Applicant History Information

Identification number [301021533]

1. Date of change April 2, 2001

 [Reason for change] New registration

 Address Kasumigaseki 1-3-1, Chiyoda-ku, Tokyo-to

 Name National Institute of Advanced Industrial Science and Technology

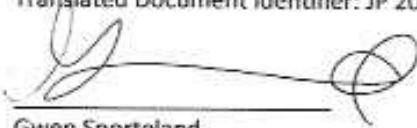
I, Gwen Snorteland, hereby declare:

- a) TransPerfect Translations, a Delaware corporation, with its principal office at 1250 Broadway 32nd Floor, New York, NY 10001, is a professional translation company of multiple languages, including English and Japanese;
- b) I am a translator that handles translations for TransPerfect Translations;
- c) I am fluent in the Japanese and English languages;
- d) I have translated from the original document to the translated document identified below, and to the best of my knowledge, information, and belief the translation of that document is accurate; and

I declare under the penalty of perjury under the laws of the United States that the foregoing is true and correct; and further declare that I am aware that willful false statements and the like so made are punishable by fine and imprisonment, or both, under 1001 of Title 19 of the United States Code.

Original Document Identifier: JP 2004-313350

Translated Document Identifier: JP 2004-313350_EN

A handwritten signature in black ink, appearing to be 'Gwen Snorteland', written over a horizontal line.

Gwen Snorteland

Signed: July 11, 2024