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(54) **Title:** FERROMAGNETIC PREFERRED GRAIN GROWTH PROMOTION SEED LAYER FOR AMORPHOUS OR MICROCRYSTALLINE MgO TUNNEL BARRIER

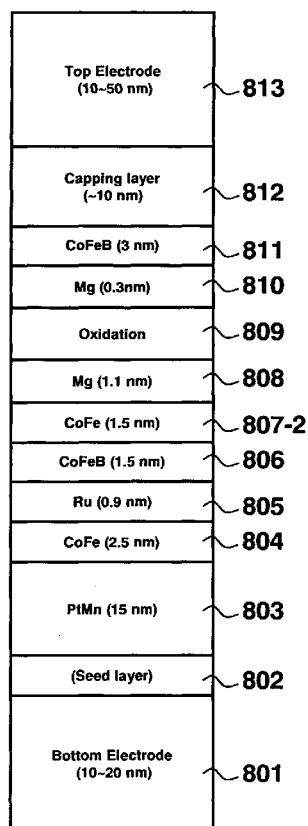


Fig.8A

(57) **Abstract:** MgO-based magnetic tunnel junction (MTJ) device includes in essence a ferromagnetic reference layer, a MgO tunnel barrier and a ferromagnetic free layer. The microstructure of MgO tunnel barrier, which is prepared by the metallic Mg deposition followed by the oxidation process or reactive sputtering, is amorphous or microcrystalline with poor (001) out-of-plane texture. In the present invention at least only the ferromagnetic reference layer or both of the ferromagnetic reference and free layer is proposed to be bi-layer structure having a crystalline preferred grain growth promotion (PGGP) seed layer adjacent to the tunnel barrier. This crystalline PGGP seed layer induces the crystallization and the preferred grain growth of the MgO tunnel barrier upon post-deposition annealing.



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DESCRIPTION

TITLE OF INVENTION

5 Ferromagnetic Preferred Grain Growth Promotion Seed Layer for Amorphous or Microcrystalline MgO Tunnel Barrier

BACKGROUND ART

10 [0001]

1. Field of the Invention

The present invention is related to the field of magnetic tunnel junction (MTJ) devices with particular reference to the magnetic random access
15 memory (MRAM) and the magnetic sensors including the recording read head in hard disk drive and so on, which employ tunneling magnetoresistance. More particularly, this invention relates to the MTJ devices with MgO tunnel barrier prepared by oxidation
20 methods or reactive sputtering method, microstructure of which is amorphous or microcrystalline with poor (001) out-of-plane texture. More particularly, this invention relates to the MTJ devices with the insertion of the crystalline ferromagnetic layers,
25 which is the PGGP seed layers, adjacent to the MgO tunnel barrier in order to enhance the crystallinity of the MgO tunnel barrier during post-deposition

annealing.

[0002]

2. Related Arts

Core element in the magnetic tunnel junction (MTJ)
5 device is "ferromagnetic layer / tunnel barrier /
ferromagnetic layer" tri-layer structure. The change
of resistance of the MTJ device is attributed to the
difference in the tunneling probability of the spin
polarized electrons through the tunnel barrier on the
10 bias voltage across the device in accordance with the
relative orientation of magnetizations of the two
ferromagnetic layers.

[0003]

The relative orientation of the magnetizations of the
15 two ferromagnetic layers sandwiching the tunnel
barrier is realized by the different nature of the
magnetization reversal of the two ferromagnetic
layers, in that the magnetization of one
ferromagnetic layer is not reversed by the external
20 magnetic field in operation, whereas that of the
other ferromagnetic layer responds to the external
magnetic field. Thus parallel or antiparallel
alignment of the magnetizations of the two
ferromagnetic layers sandwiching the tunnel barrier
25 in device operation is realized.

[0004]

Tunnel barrier is commonly a dielectric material and

must be ultra thin and extremely uniform in thickness as well as composition. Any inconsistency in terms of chemical stoichiometry or thickness degrades the device performance significantly.

5 [0005]

Most typically employed structure of MTJ device is schematically illustrated in Fig. 1, which consists of an antiferromagnetic pinning layer 103, a synthetic antiferromagnetic (SAF) pinned layer 110, a
10 tunnel barrier 107 and a ferromagnetic free layer 108. The synthetic antiferromagnetic (SAF) pinned layer includes a ferromagnetic pinned layer 104, a non-magnetic spacer 105 and a ferromagnetic reference layer 106.

15 [0006]

Ever since its discovery, high TMR at room temperature has been one of hot topics of industries due to its spintronics application, such as non-volatile magnetoresistive random access memory (MRAM)
20 and magnetic sensors such as the recording read-head in hard disk drive. For conventional field switching MRAM application, 1 Mbit MRAM with the bit size of $300 \times 600 \text{ nm}^2$ requires the MTJ to provide the magnetoresistance (MR) ratio of 40% at the
25 resistance-area ($R \times A$) product of about $1\text{k}-2\text{k} \ \Omega \mu\text{m}^2$. At the higher density of 250 Mbits, the bit size scales down to $200 \times 400 \text{ nm}^2$ and requires MR ratio of

higher than 40% at the $R \times A$ product of about $0.5 \text{ k } \Omega \mu\text{m}^2$. Further scaling can be achieved in MRAM by application of magnetization reversal by the spin transfer torque, however, it is required for the MTJ
5 to provide MR ratio higher than 150% at the $R \times A$ product range of $10\text{-}30 \text{ } \Omega \mu\text{m}^2$. For the recording read-head in hard disk drive, it is required for the MTJ to provide MR ratio higher than 50% at the $R \times A$ product range of $1\text{-}2 \text{ } \Omega \mu\text{m}^2$ in order to pick up
10 reliable signals from the media with areal density of 250 Gbit/in².

[0007]

Early efforts made on amorphous AlO_x tunnel barrier and ferromagnetic electrodes with high spin
15 polarization were not satisfactory for the requirements mentioned above. Recently single crystal Fe/MgO/Fe has been suggested by theoretical calculation, (Butler et al., Phys. Rev. B 63, (2001) p054416) and it is predicted that as high as 6000 %
20 room temperature-TMR can be obtained due to a superior spin filtering effect of MgO . This spin filtering effect, that is a total reflection of minority spin down electrons in antiparallel magnetization alignment of the two ferromagnetic
25 layers sandwiching MgO tunnel barrier of MTJ, is inherent from the absence of Bloch eigenstates in minority spin-down spin channel with Δ_1 symmetry at

the Fermi surface. This allows a coherent tunneling, and furthermore enables a giant TMR ratio. There is a microstructural requirement to allow this coherent tunneling, which is the epitaxial growth of Fe

5 (001)/MgO (001)/Fe (001), in that the tunneling electron passes through the (001) atomic planes of Fe and MgO. Experimental attempts to achieve this giant TMR based on single crystal (Fe/MgO/CoFe) growth using molecular beam epitaxy demonstrated room

10 temperature TMR up to 180%. (Yuasa et al. Appl. Phys. Lett. 87 (2005) p222508) Using MgO tunnel barrier with polycrystalline CoFe ferromagnetic electrodes, 220% room temperature TMR was reported, (Parkin et al. Nat. Mater. 3 (2004) p862) and even higher TMR

15 reported in MTJ prepared by practical magnetron sputtering on thermally oxidized Si wafer using amorphous CoFeB ferromagnetic electrodes. (Djayaprawira et al. Appl. Phys. Lett. 86 (2005) p092502)

20 [0008]

Great deal of efforts have been made to form the MgO tunnel barrier in the MTJ, which is ultra thin and extremely uniform in thickness as well as composition. Furthermore, similar amount of efforts have been

25 exerted to achieve the crystallinity of MgO tunnel barrier with (001) out-of-plane texture in order to satisfy the microstructural requirement, (001) out-of-

plane epitaxy together with bcc-structured sandwiching ferromagnetic layers, given by the theoretical calculation and confirmed by microstructural and thin film chemistry studies. (Y.

- 5 S. Choi et al. Appl. Phys. Lett. 90 (2007) p012505, Y. S. Choi et al. J. Appl. Phys. 101 (2007) p013907) [0009]

In general method of preparing MTJ devices for the mass production of MRAM or recording read-head, the deposition of MgO tunnel barrier is divided into the direct deposition and the metal deposition followed by oxidation process. Deposition of tunnel barrier using ceramic target by rf-sputtering or reactive sputtering of metal target in the ambience of gas mixture of oxygen and inert gas falls into the first group of direct deposition. Metal deposition followed by various kinds of oxidation processes, such as natural oxidation, plasma oxidation, radical oxidation or ozone oxidation, falls into the second group.

[0010]

One of critical bottlenecks for MTJ development is the uniform thickness control of tunnel barrier at the extremely thin thickness. If the thickness of the tunnel barrier is too thin, it is highly possible to contain pinholes, where leak current passes through without spin-dependent tunneling. This degrades

signal to noise ratio (S/N) significantly. Another bottleneck is chemical inhomogeneity of tunnel barrier, result in over- or under-oxidation, and the oxidation of underlying ferromagnetic layer. These
5 lead to asymmetric electrical properties with respect to signs of applied bias and abnormal increase of $R \times A$ product and decrease of TMR ratio due to the additional tunnel barrier thickness with spin scattering in the surface-oxidized underlying
10 ferromagnetic layer. (Park et al. J. Magn. Magn. Mat., 226-230 (2001) p926)
[0011]

Besides the issues of the uniform thickness control of ultra-thin MgO tunnel barrier and the chemical
15 homogeneity across the MgO tunnel barrier, most imminent issue to achieve the giant TMR ratio with low $R \times A$ product of MgO-based MTJ is the (001) out-of-plane texture of the ferromagnetic reference layer, MgO tunnel barrier and the ferromagnetic free layer,
20 and the high crystallinity of MgO tunnel barrier. Fig. 2 shows the relationship of MgO texture and crystallinity and the magnetotransport property in CoFeB/MgO/CoFeB MTJ, where MgO is deposited by rf sputtering. It is clearly shown in the Fig. 2A and
25 Fig. 2B that the MTJ prepared with highly crystalline and (001) textured MgO tunnel barrier induces the corresponding (001) texture of CoFe through

crystallization of CoFeB amorphous layers by annealing, thus overall (001) texture of CoFeB/MgO/CoFeB is realized. Therefore, it is possible to obtain significantly enhanced MR ratio at low $R \times A$ product, as shown in Fig. 2C. However, MTJ with MgO tunnel barrier with poor crystallinity shows very low MR ratio with extremely high $R \times A$ product, as also seen in Fig. 2C.

[0012]

Despite MgO tunnel barrier prepared by rf sputtering has shown great advances by process optimization, there are serious issues, which are hard to overcome for the mass-production, in that MR ratio and $R \times A$ product change very sensitively depending on the chamber condition and particle generation inherent from rf-sputtering. (Oh et al. IEEE Trans. Magn., 42 (2006) p2642) Furthermore, it has been reported that the final $R \times A$ product uniformity (1σ) of MTJ devices with MgO tunnel barrier prepared by rf-sputtering is more than 10%, whereas that of MgO tunnel barrier prepared by Mg deposition followed by oxidation process is less than 3%. (Zhao et al. US Patent Application, US 2007/0111332)

[0013]

Alternative methods of MgO tunnel barrier preparation are the metallic Mg deposition followed by the various oxidation processes or reactive Mg sputtering

in the ambience of gas mixture of oxygen and inert gas. Plasma oxidation has been employed in the preparation for AlOx tunnel barrier, however, its high reactivity makes it exceptionally difficult to oxidize ultra-thin metal layer, especially very fast oxidation rate of Mg for MgO formation, precisely down to the interface with the underlying ferromagnetic layer. Thus $R \times A$ product and MR ratio of $10000 \Omega \mu\text{m}^2$ / 45% are obtained by plasma oxidation process, (Tehrani et al. IEEE Trans. Magn., 91 (2003) p703) whereas those of $1000 \Omega \mu\text{m}^2$ / 30% by ozone oxidation from MTJ with AlOx tunnel barrier. (Park et al. J. Magn. Magn. Mat., 226-230 (2001) p926)

[0014]

Therefore, less energetic oxidation processes have been suggested, which are radical oxidation and natural oxidation to form MgO tunnel barrier. Also reactive sputtering of Mg metal target to form MgO tunnel barrier in the ambience of Ar and O₂. Fig. 3 shows the magnetotransport property measurement results obtained from MTJs with MgO tunnel barrier prepared by various methods of MgO tunnel barrier deposition. The MTJ structure is identical except the MgO tunnel barrier part, which is bottom layers/PtMn (15)/CoFe (2.5)/Ru (0.9)/CoFeB (3)/MgO (x)/CoFeB (3)/capping layer. Thickness in parenthesis is in nanometer scale. With reference to the MR ratio and R

×A product obtained from the MTJ with MgO prepared by rf sputtering, it is clearly shown that the MR ratio of the MTJ with MgO tunnel barrier prepared by oxidation methods and reactive sputtering is significantly lower. At given R×A product of $10 \Omega \mu\text{m}^2$, MTJ with MgO prepared by rf sputtering provides MR ratio of 180%, whereas MgO deposited by radical oxidation method provides 100%, natural oxidation provides 60%, and MgO prepared by reactive sputtering provides 135%.

[0015]

The microstructure analyses were carried out with high-resolution transmission microscopy (HREM) and x-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). As shown in Fig. 4A and Fig. 4B, it is clearly compared that the difference in the magnetotransport property results from the difference in the crystallinity of MgO tunnel barrier and the lack of epitaxy in CoFeB/MgO/CoFeB layers. Fig. 4A and Fig. 4B are cross-section HREM images taken from the MTJs with MgO tunnel barrier prepared by rf-sputtering and radical oxidation, respectively. As reported by Choi et al. in J. Appl. Phys. 101 (2007) p013907, CoFeB/MgO/CoFeB-based MTJ prepared by rf sputtering satisfies the microstructural requirement given by the theoretical calculations by Butler et al., in that MgO is highly crystalline and in good

grain-to-grain epitaxy with CoFe layers. The CoFe layers are crystallized by post-deposition annealing based on the crystalline MgO as a crystallization template, thus the grain-to-grain epitaxy is realized
5 in CoFe/MgO/CoFe layers. However, MgO tunnel barrier prepared by radical oxidation shows the poor crystallinity mixed with amorphous and it is hard to confirm the pseudo-epitaxy at the interface with CoFe layers.

10 [0016]

Fig. 4C shows the clear comparison of the MgO crystallinity and texture with respect to its deposition method, rf-sputtering and natural oxidation. Out-of-plane theta-2 theta scan confirms
15 that MgO tunnel barrier deposited on the amorphous CoFeB layer by rf-sputtering is highly crystalline in as-grown state and highly textured with (001) out-of-plane preferred orientation by pronounced MgO (002) peak at $2\theta = 42.4^\circ$. However, MgO prepared by
20 metal deposition followed by natural oxidation shows no pronounced peak, which indicates that the MgO layer is almost amorphous.

[0017]

Fig. 4D and Fig. 4E are XPS spectra obtained from the
25 MTJs with MgO tunnel barrier prepared by rf-sputtering and reactive sputtering, respectively. As reported by Choi et al. in Appl. Phys. Lett. 90

(2007) p012505, it is critical to have the dominant population of oxygen ions in the lattice point of NaCl-structured MgO for the crystallinity of MgO and higher MR ratio of the MTJ and lower RxA product. It is clear, as shown in Fig. 4D, that the population of oxygen ions (whose binding energy is around 531 eV) occupying lattice point of NaCl-structured MgO is very high in the MgO deposited by rf sputtering, however, there is considerable population of impurity oxygen ion (whose binding energy is around 533.3 eV), as shown in Fig. 4B, which is almost a third of that of oxygen ion in the lattice point in the MgO deposited by reactive sputtering. Thus it can be inferred that this high density of impurity oxygen ions in the MgO barrier is related to the poor crystallinity of MgO and is responsible for the poor MR ratio.

[0018]

In order to achieve good crystallinity of MgO tunnel barrier prepared by oxidation method, crystalline ferromagnetic reference layer, not bi-layer but single layer, has been employed, in that the structure of MTJ is bottom layers/PtMn (15)/CoFe (2.5)/Ru (0.9)/CoFe (3)/MgO (x)/CoFeB (3)/capping layer. As shown in Fig. 5A, MTJ with fully crystalline CoFe single reference layer provides noticeable drop of MR ratio to 35% from 130% by CoFeB

amorphous reference layer. And the shape of full hysteresis loop, Fig. 5B, from MTJ with fully crystalline CoFe single reference layer after as-deposition annealing at 360°C for 2 hrs under 10kOe magnetic field indicates that the poor or destroyed SAF structure, whereas that of MTJ, as shown in Fig. 5C, with amorphous CoFeB single reference layer after same condition of post-deposition annealing shows clear SAF coupling in the circle mark. Body-centered-cubic CoFe tends to grow (110) atomic planes parallel to the interface with Ru in order for the lattice match with hexagonal-close-packed Ru (0001) basal plane. (110) out-of-plane texture of ferromagnetic reference layer is not preferable for the giant TMR from the theoretical calculation by Butler et al. in MgO-based MTJ. Furthermore, the thermal stability of SAF(CoFeB/Ru/CoFe) is much worse than that of SAF(CoFeB/Ru/CoFeB), thus clearly distinctive magnetization separation between constituent ferromagnetic layers cannot be secured if the MTJ is composed of CoFeB/Ru/CoFe SAF structure after high temperature post-deposition annealing. Thus the crystalline CoFe single reference layer is proven to be not effective to achieve the good crystallinity of MgO tunnel barrier.

[0019]

Consequently, it can be understood that the poor

crystallinity of MgO tunnel barrier deposited by oxidation method or reactive sputtering cannot play a role of crystallization template to crystallize amorphous CoFeB into CoFe at the CoFeB/MgO interface.

- 5 Thus no grain-to-grain pseudo-epitaxy can be expected in CoFe/MgO/CoFe layers, which results in the poor magnetotransport property.

[0020]

[Citation List]

- 10 [Patent Literature]

[Patent Literature 1] T. Zhao et al., US Patent Application, US2007/0111332

[Patent Literature 2] S. Miura et al., US Patent Application, US2007/0111332

- 15 [Patent Literature 3] K. Nishimura et al., Japan Patent Application, 2008-103661

[Non Patent Literature]

[Non Patent Literature 1] W. H. Butler et al., Phys. Rev. B 63, 054416 (2001).

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- [Non Patent Literature 4] D. Djayaprawira et al.,
25 Appl. Phys. Lett. 86, 092502 (2005).

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[Non Patent Literature 7] B. Park et al., J. Magn. Magn. Mat., 226-230, 926 (2001).

5 [Non Patent Literature 8] S. C. Oh et al., IEEE Trans. Magn., 42, 2642 (2006).

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10 SUMMARY OF INVENTION

[0021]

The objective of the present invention is to provide satisfactory high MR ratio at low $R \times A$ product for the application to the spin transfer torque MRAM and the
15 recording read-head from the MTJ with MgO tunnel barrier, which is prepared by the metal deposition followed by the various oxidation methods or prepared by the reactive sputtering and the microstructure of which is amorphous or microcrystalline tunnel barrier
20 with poor (001) out-of-plane texture.

[0022]

According to a first aspect of the present invention, it is critical to crystallize or induce the preferred grain growth in the MgO tunnel barrier prepared by
25 the metal deposition followed by the various oxidation methods or prepared by the reactive sputtering.

[0023]

According to a second aspect of the present invention, the crystallization or the preferred grain growth of the MgO tunnel barrier, which is amorphous or
5 microcrystalline with poor (001) out-of-plane texture in as-grown state, can be achieved during the post-deposition annealing by use of crystalline ferromagnetic PGGP seed layer with body-centered-cubic structure under or sandwiching the MgO tunnel
10 barrier.

[0024]

According to a third aspect of the present invention, the microstructure of MTJ with MgO tunnel barrier after post-deposition annealing is eventually overall
15 (001) out-of-plane texture of the ferromagnetic reference layer, MgO tunnel barrier and the ferromagnetic free layer.

[0025]

According to a forth aspect of the present invention,
20 the MTJ device includes an antiferromagnetic pinning layer, a synthetic antiferromagnetic pinned layer, a tunnel barrier and a ferromagnetic free layer. The synthetic antiferromagnetic pinned layer includes a ferromagnetic pinned layer, a non-magnetic spacer and
25 a ferromagnetic reference layer.

[0026]

It is preferred that the ferromagnetic reference

layer is formed in bi-layer structure, in that the first amorphous ferromagnetic reference layer deposited on the non-magnetic spacer and the second crystalline ferromagnetic reference layer, which is
5 PGGP seed layer, deposited on the said first amorphous ferromagnetic reference layer.

[0027]

It is preferred that the first amorphous ferromagnetic reference layer in the bi-layer-
10 structured ferromagnetic reference layer is the ternary alloy containing Co, Fe and B, in which the content of boron is higher than 12 atomic %.

[0028]

It is preferred that the thickness of the first
15 amorphous ferromagnetic reference layer in the bi-layer-structured ferromagnetic reference layer is between 1 nm to 4 nm.

[0029]

It is preferred that the second crystalline
20 ferromagnetic reference layer, which is PGGP seed layer, in the bi-layer-structured ferromagnetic reference layer is the binary alloy of $\text{Co}_x\text{Fe}_{100-x}$, in which $0 < x < 80$.

[0030]

25 It is preferred that the second crystalline ferromagnetic reference layer, which is PGGP seed layer, in the bi-layer-structured ferromagnetic

reference layer can also be formed by single Fe element.

[0031]

It is preferred that the second crystalline
5 ferromagnetic reference layer, which is PGGP seed layer, in the bi-layer-structured ferromagnetic reference layer can also be the ternary alloy containing Co, Fe and B, in which the content of boron is less than 12 atomic %, thus crystalline
10 ternary alloy whose content of boron is less than 12 atomic %.

[0032]

It is preferred that the thickness of the second crystalline ferromagnetic reference layer in the bi-
15 layer-structured ferromagnetic reference layer is between 0.5 nm to 2 nm.

[0033]

It is preferred that the thickness of the second crystalline ferromagnetic reference layer in the bi-
20 layer-structured ferromagnetic reference layer is equal to or less than the thickness of the said first amorphous ferromagnetic reference layer in the bi-layer-structured ferromagnetic reference layer.

[0034]

25 It is preferred that the MgO tunnel barrier, which is amorphous or microcrystalline with poor (001) out-of-plane texture, is prepared by the deposition of

metallic Mg layer, the oxidation of the said metallic Mg layer by radical oxidation, plasma oxidation, natural oxidation or ozone oxidation, then finally deposition of the metallic Mg cap layer after
5 oxidation.

[0035]

It is preferred that the MgO tunnel barrier, which is amorphous or microcrystalline with poor (001) out-of-plane texture, can also be prepared by the deposition
10 of partially or fully oxidized Mg-oxide layer using reactive sputtering, the oxidation of the said partially or fully oxidized Mg-Oxide layer by radical oxidation, plasma oxidation, natural oxidation or ozone oxidation, then finally metallic Mg cap layer
15 after oxidation.

[0036]

It is preferred that the ferromagnetic free layer also can be formed in bi-layer structure, in that the first crystalline ferromagnetic free layer, which is
20 PGGP seed layer, deposited on the MgO tunnel barrier and the second amorphous ferromagnetic free layer deposited on the said first crystalline ferromagnetic free layer.

[0037]

25 It is preferred that the first crystalline ferromagnetic free layer, which is PGGP seed layer, in the bi-layer-structured ferromagnetic free layer

is the binary alloy of $\text{Co}_x\text{Fe}_{100-x}$, in which $0 < x < 80$.

[0038]

It is preferred that the first crystalline ferromagnetic free layer, which is PGGP seed layer, in the bi-layer-structured ferromagnetic free layer can also be formed by single Fe element.

[0039]

It is preferred that the first crystalline ferromagnetic free layer, which is PGGP seed layer, in the bi-layer-structured ferromagnetic free layer can also be the ternary alloy containing Co, Fe and B, in which the content of boron is less than 12 atomic %, thus crystalline ternary alloy whose content of boron is less than 12 atomic %.

[0040]

It is preferred that the thickness of the first crystalline ferromagnetic free layer, which is PGGP seed layer, in the bi-layer-structured ferromagnetic free layer is between 0.5 nm to 2 nm.

[0041]

It is preferred that the second amorphous ferromagnetic free layer in the bi-layer-structured ferromagnetic free layer is the ternary alloy containing Co, Fe and B, in which the content of boron is higher than 12 atomic %.

[0042]

It is preferred that the thickness of the second

amorphous ferromagnetic free layer in the bi-layer-structured ferromagnetic free layer is between 1 nm to 4 nm.

It is preferred that the magnetic tunnel junction
5 device with crystalline ferromagnetic layer inserted between the amorphous ferromagnetic layer and the amorphous or microcrystalline MgO tunnel barrier with poor (001) out-of-plane texture shows significantly reduced resistance-area product and noticeably
10 increased magnetoresistance ratio compared to the magnetic tunnel junction device without the insertion of the crystalline ferromagnetic layer, which is the PGGP seed layer, inserted between the amorphous ferromagnetic layer and the amorphous or
15 microcrystalline MgO tunnel barrier with poor (001) out-of-plane texture.

It is preferred that the resistance-area product and the magnetoresistance ratio of the magnetic tunnel junction device with crystalline ferromagnetic layer,
20 which is the PGGP seed layer, inserted between the amorphous ferromagnetic layer and the amorphous or microcrystalline MgO tunnel barrier with poor (001) out-of-plane texture are less than $5\Omega\mu\text{m}^2$ and higher than 170%, respectively.

25 [0043]

The existence of the second crystalline ferromagnetic reference layer and/or the said first crystalline

ferromagnetic free layer, which are PGGP seed layers, induce the crystallization and the preferred grain growth of the MgO tunnel barrier, which is amorphous or microcrystalline tunnel barrier with poor (001) out-of-plane texture in as-deposited state, after post-deposition annealing, as schematically described in Fig. 6A.

[0044]

Also the existence of the second crystalline ferromagnetic reference layer and/or the said first crystalline ferromagnetic free layer, which are PGGP seed layers, induce the crystallization and the preferred grain growth of the said first ferromagnetic amorphous reference layer and/or the said second ferromagnetic amorphous free layer, which are amorphous in as-deposited state, after post-deposition annealing, as schematically described in Fig. 6A.

[0045]

Therefore, the microstructure of MTJ after post-deposition annealing is eventually overall (001) out-of-plane texture of the ferromagnetic reference layer, MgO tunnel barrier and the ferromagnetic free layer. With this obtained microstructure of MTJ of the present invention, it is possible to achieve the significant increase of MR ratio as well as the noticeable reduction of $R \times A$ product, as shown in Fig.

6A. However, optimum annealing temperature of MTJ with bi-layer-structured ferromagnetic reference layer and/or bi-layer-structured ferromagnetic reference layer of the present invention cannot be lower than that of MTJ with rf-sputtered crystalline MgO and the single-layered amorphous ferromagnetic reference layer and free layer. It is easy to explain this increase of optimum annealing temperature by the difference of crystallization object. The layers to be crystallized in the MTJ of the present invention are the MgO tunnel barrier and the amorphous ferromagnetic layers, as shown in Fig. 6A, whereas the layers to be crystallized in the MTJ with rf-sputtered crystalline MgO are the amorphous ferromagnetic layers only, as shown in Fig. 6B. As the melting point of CoFe is much lower than that of MgO (thus the recrystallization temperature would correspond accordingly), it can be intuitively known that the temperature required to crystallize the CoFe would be lower than that for MgO.

[0046]

Similar structure of bi-layered ferromagnetic reference layer has been suggested by Miura et al. in Japanese patent application JP 2008-135432, which suggests the insertion of the amorphous or microcrystalline CoFe layer between the amorphous ferromagnetic CoFeB layer and the crystalline MgO

tunnel barrier. It is claimed that the insertion of amorphous or microcrystalline CoFe layer effectively lowers the annealing temperature down to 300°C by the crystallization template effect of the crystalline
5 MgO tunnel barrier. However, this is not applicable to the MTJ with MgO tunnel barrier prepared by oxidation methods or the reactive sputtering as the MgO tunnel barrier is amorphous or microcrystalline with poor (001) out-of-plane texture in as-deposited
10 state.

[0047]

Also Nishimura et al. (Patent Reference 3) has suggested the identical bi-layered ferromagnetic layer, which is the insertion of the amorphous or
15 microcrystalline CoFe layer between the amorphous ferromagnetic CoFeB layer and the crystalline MgO tunnel barrier under the MgO tunnel barrier in the Japanese patent application JP 2008-103661. Despite this patent application covers the MgO preparation
20 methods including rf sputtering and oxidation methods, only rf-sputtered MgO tunnel barrier, which is highly probable to be good crystalline, is suggested in the preferred embodiment and the MgO tunnel barrier deposited by reactive sputtering is not included. As
25 mentioned above, it is hard to apply same argument of using the crystalline MgO as a crystallization template for high MR ratio to the MTJ with MgO tunnel

barrier which is amorphous or microcrystalline with poor (001) out-of-plane texture in as-deposited state.

BRIEF DESCRIPTION OF DRAWINGS

5 [0048]

Fig. 1 is a schematic of a typical structure of the magnetic tunnel junction.

Fig. 2A, 2B and 2C show the relationships between the microstructure of MgO-based MTJ and the magnetotransport properties: (Fig. 2A) XRD theta-2 theta scan from MgO thin film, (Fig. 2B) XRD theta-2 theta scan from MgO-based MTJ (evolution of crystalline CoFe with annealing temperature), (Fig. 2C) comparison of MR ratio vs. $R \times A$ product from MTJs with MgO with or without (002) texture.

[0049]

Fig. 3 shows the comparison of MR ratio vs. $R \times A$ product from MTJs with MgO prepared by various methods.

20 Fig. 4A, 4B, 4C, 4D and 4E show the results of microstructure and the thin film chemistry analyses from MgO prepared by various methods: (Fig. 4A) a photograph of cross-section HREM image from MTJ with MgO prepared by rf-sputtering, (Fig. 4B) a photograph of cross-section HREM image from MTJ with MgO prepared by radical oxidation, (Fig. 4C) XRD theta-2 theta scan comparing the crystallinity and texture of

MgO tunnel barrier prepared by rf-sputtering and natural oxidation, (Fig. 4D) XPS O 1s spectrum obtained from MgO prepared by rf-sputtering, and (Fig. 4E) XPS O 1s spectrum obtained from MgO prepared by reactive sputtering.

[0050]

Fig. 5A, 5B and 5C show the comparison of magnetotransport property and the hysteresis loops of MTJs with ferromagnetic single reference layer of CoFe or CoFeB: (Fig. 5A) MR ratio vs. $R \times A$ product from MTJs with CoFe or CoFeB reference layer, and full hysteresis loops from MTJ with (Fig. 5B) CoFe reference layer and (Fig. 5C) CoFeB reference layer.

[0051]

Fig. 6A and Fig. 6B are the schematic comparison of crystallization and preferred grain growth process of MTJ after post-deposition annealing: (Fig. 6A) MTJ in the present invention with crystalline ferromagnetic PGGP seed layers sandwiching amorphous or microcrystalline MgO with poor (001) out-of-plane texture and (Fig. 6B) MTJ with amorphous ferromagnetic CoFeB layers sandwiching highly crystalline MgO.

[0052]

Fig. 7 exemplifies a MTJ device manufacturing apparatus.

Fig. 8A and Fig. 8B show schematics of MTJs in the

first and second embodiments of the invention with CoFe PGGP seed layer (Fig. 8A) only in reference layer and (Fig. 8B) in both of reference and free layer .

- 5 Fig. 8C shows schematic of MTJ in the third embodiment of the invention.

Fig. 8D shows schematic of MTJ in the forth embodiment of the invention.

[0053]

- 10 Fig. 9A shows the magnetotransport property comparison of A and B MTJ stacks of the first embodiment of the present invention compared to that of MTJs with MgO prepared by rf-sputtering and radical oxidation without PGGP seed layer and Fig. 9B
15 shows MR ratio and $R \times A$ product comparison of A and B MTJ stacks of the first embodiment with respect to the reference identical MTJ stack only without PGGP seed layer.

[0054]

- 20 Fig. 10A shows the magnetotransport property comparison of A and B MTJ stacks of the second embodiment of the present invention compared to that of MTJs with MgO prepared by rf-sputtering and radical oxidation without PGGP seed layer and Fig.
25 10B shows MR ratio and $R \times A$ product comparison of A and B MTJ stacks of the second embodiment with respect to the reference identical MTJ stack only

without PGGP seed layer.

[0055]

Fig. 11 shows MR ratio and $R \times A$ product comparison of
A MTJ stack of the second embodiment, of which the
5 thickness of the first amorphous CoFeB ferromagnetic
reference layer is fixed at 1.5 nm, whereas the
thickness of the second crystalline CoFe
ferromagnetic reference layer, which is PGGP seed
layer, varies.

10 [0056]

Fig. 12 shows MR ratio and $R \times A$ product comparison of
A MTJ stack of the third embodiment with respect to
the reference identical MTJ stack only without PGGP
seed layer.

15 Fig. 13 shows MR ratio and $R \times A$ product comparison of
A MTJ stack of the forth embodiment with respect to
the reference identical MTJ stack only without PGGP
seed layer.

[0057]

20 Fig. 14 shows schematic of MTJ of the fifth
embodiment in the present invention with CoFeB PGGP
seed layer in both of reference layer and free layer.
Fig. 15A and Fig. 15B show the XRD theta- 2 theta
scan obtained from CoFeB single layers, whose boron
25 contents are 20 atomic %, 5.1 atomic % and 2.9
atomic %. Peak position, full width at half maximum
and the resistivity from each of single layers are

shown in the table.

[0058]

Fig. 16A shows the magnetotransport property comparison of A and B MTJ stacks of the fifth
5 embodiment of the present invention compared to that of MTJs with MgO prepared by rf-sputtering and radical oxidation without PGGP seed layer.

Fig. 16B shows MR ratio and $R \times A$ product comparison of A and B MTJ stacks of the second embodiment with
10 respect to the reference identical MTJ stack only without PGGP seed layer.

[0059]

Fig. 17 shows schematic of MTJ of the sixth embodiment in the present invention with Fe PGGP seed
15 layer in both of reference layer and free layer.

Fig. 18 shows schematic of MTJ of the seventh embodiment in the present invention with CoFe PGGP seed layer in both of reference layer and free layer. Also bi-layer structured ferromagnetic pinned layer
20 is employed.

[0060]

Fig. 19 shows the magnetotransport property comparison of A MTJ stack of the seventh embodiment of the present invention compared to that of MTJ with
25 MgO prepared by natural oxidation without PGGP seed layer.

Fig. 20A, 20B and 20C show the schematic diagrams to

analyze the cross-section image obtained by high-resolution transmission electron microscope (HRTEM) and cross-section HRTEM images from as-grown MTJ of the second embodiment, respectively: (Fig. 20A) CoFe PGGP seed layer sandwiched by MgO tunnel barrier and CoFeB layer, (Fig. 20B) growth of CoFe PGGP seed layer with (001) out-of plane, and (Fig. 20C) growth of CoFe PGGP seed layer with (011) out-of-plane.

Fig. 21 is a photograph of overall crystallinity of the second CoFe ferromagnetic reference layer.

Fig. 22A is a photograph of cross-section HRTEM image from annealed MTJ of the second embodiment.

Fig. 22B is a photograph of the selected area diffraction patterns from the boxed-area of the HRTEM image.

Fig. 23A to Fig. 23F are graphs which show the comparison of TMR, RA and Hey of magnetic tunnel junctions with different stack structure.

Fig. 24 shows the evolution of hysteresis loop of 'No PGGP magnetic tunnel junction at annealing temperatures of 400°C, 300°C and "as grown"'. Fig. 25A to Fig. 25C shows the evolution of hysteresis loop of 'PGGP & bi-PL' magnetic tunnel junction at annealing temperatures of 380°C, 400°C and 420°C.

Fig. 26 schematically shows enhanced thermal stability.

DETAILED DESCRIPTION OF THE INVENTION

[0061]

Fig. 7 exemplifies a MTJ device manufacturing apparatus in the preferred embodiment. Fig. 7 is a schematic plan view of a vacuum processing system 700 for fabricating a magnetic tunnel junction device. A vacuum processing system shown in Fig. 7 is a cluster type system providing a plurality of thin film deposition chambers using physical vapor deposition technique. Plurality of deposition chambers in the said vacuum processing system is attached to the vacuum transfer chamber 701 provided with robot loaders at the center position (not shown). The said vacuum processing system 700 is equipped with two load-lock chambers 702 and 703 to load/unload substrates. The said vacuum processing system is equipped with degas chamber 704 and pre-etch/etch chamber 705. The vacuum processing system is equipped with oxidation chamber 706 and plurality of metal deposition chambers 707, 708, and 709. Each of chambers in the vacuum processing system is connected through a gate valve in order to open/close the passage between the chambers. Note that each of chambers in the vacuum processing system is equipped with pumping system, gas introduction system, and power supply system. Moreover, the gas introduction

system comprises flow-regulating means, the pumping system comprises pressure regulating means. Each operation of the flow regulating means and the pressure regulating means can control a certain pressure in the chamber during a certain period of time. Moreover, operations based on combination of the flow regulating means and the pressure regulating means can control the certain pressure in the chamber during the certain period of time.

10 [0062]

In each of the metal deposition chambers 707, 708, and 709 of the said vacuum processing system 700, each of the magnetic layers and the non-magnetic metal layers is deposited on the substrate one by one by the sputtering method. In the metal deposition chambers 707, 708, and 709, for example, a material of a target is "CoFe", a material of a target is "Ru", a material of a target is "CoFeB", and a material of a target is "Mg". And a material of a target is "antiferromagnetic material", a material of a target is "seed material", a material of a target is "capping material". Furthermore, a material of a target is "top electrode material" and a material of a target is "bottom electrode material". Pre-etching and etching are carried out in the pre-etch/etch chamber. Oxidation is carried out in the oxidation chamber 706. Moreover, each metal deposition chamber

comprises a sputtering apparatus which can perform dc-sputtering. Procedures, such as gas introduction into each chamber, switching the valve, power supply ON/OFF, an exhaust gas, and a substrate transfer, is
5 carried out by a system controller (not shown).

[0063]

Fig. 1 shows a typical stack structure 100 of MTJ for tunneling magnetoresistance (TMR) sensor or memory cell. Most advantageously, on an under layer 102 and
10 Si wafer 101 MTJ is composed of an antiferromagnetic pinning layer 103, a synthetic antiferromagnetic (SAF) pinned layer 110, a tunnel barrier 107 and a ferromagnetic free layer 108. A capping layer 109 on which top electrode 110 is attached is formed on the
15 free layer 108. In the stack structure shown in Fig.1, a synthetic antiferromagnetic pinned layer 110 is formed by including a ferromagnetic pinned layer 104, a non-magnetic spacer 105 and a ferromagnetic reference layer 106.

20 [0064]

The MTJ devices of the present invention are formed by preparation of the core element in the MTJ device, the core comprising "ferromagnetic pinned layer 104 / non-magnetic spacer 105 / ferromagnetic reference
25 layer 106 / tunnel barrier 107 / ferromagnetic free layer 108" multilayer structure, using the combinations of materials selected from the following

groups for the preferred embodiments.

[0065]

Group 1: materials selection for the preferred grain growth promotion (PGGP) layer

- 5 a. $\text{Co}_x\text{Fe}_{100-x}$, where $0 < x$ atomic % < 80
- b. $(\text{Co}_x\text{Fe}_{100-x})\text{yB}_{100-y}$, where $0 < x$ atomic % < 80
 and $88 < y$ atomic % < 100
- c. Fe

- 10 Group 2: Method of MgO tunnel barrier deposition
- d. $\text{Mg } x\text{\AA}/\text{oxidation process}^*/\text{Mg } y\text{\AA}$
- e. $\text{Mg } x\text{\AA}/\text{oxygen surfactant}/\text{Mg } x\text{\AA} / \text{oxidation process}^*/\text{Mg } y\text{\AA}$
- f. $\text{Mg } x\text{\AA}/\text{oxidation process}^*/\text{Mg } y\text{\AA} / \text{oxidation process}^*/\text{Mg } z\text{\AA}$
- 15 g. Reactive sputtering MgOx/Oxidation process^{*}/Mg yÅ
- h. $\text{Mg } x\text{\AA}/\text{Reactive sputtering MgOx/oxidation process}^*/\text{Mg } y\text{\AA}$
- 20 Oxidation process^{*} includes plasma, natural, radical and ozone oxidation.

Group 3: Position of the PGGP layer

- i. Reference layer only
- 25 j. Reference and free layers

Group 4: Selection of pinned layer

k. CoFeB single layer

l. CoFeB/CoFe bi-layer

(FIRST EMBODIMENT)

5 [0066]

The first embodiment is a method of forming the tunnel barrier of MTJ devices by radical oxidation method and the employment of CoFe as the preferred grain growth promotion seed layer, in that the core
10 element of the MTJ is formed by the combination of (a+d+i+k) or (a+d+j+k) of the group 1, 2, 3 and 4 mentioned above.

[0067]

Two different configurations of MTJ stacks, as
15 illustrated in Fig. 8A and Fig. 8B are used in the first embodiment as follows;

A stack (see Fig. 8A) : Bottom layers (801, 802)
/PtMn15 (803) /CoFe2.5 (804) /Ru0.9 (805) /CoFeB1.5
(806) /CoFe1.5 (807-2) /Mg1.1(808) /R-Ox x seconds
20 (809) /Mg0.3 (810) /CoFeB3 (811) /Capping layers
(812) / Top electrode (813),

B stack (see Fig. 8B) : Bottom layers (801', 802')
/PtMn15 (803') /CoFe2.5 (804') /Ru0.9 (805')
/CoFeB1.5 (806') /CoFe1.5 (807-2') /Mg1.1 (808') /R-
25 Ox x seconds (809') /Mg0.3 (810') /CoFe1.5 (807-1')
/CoFeB1.5 (811')/Capping layers (812') / Top
electrode (813'),

where unbracketed numbers are thickness in nanometer scale and the PGGP seed layer is indicated by underline.

[0068]

- 5 Referring to Fig. 8A and Fig. 8B, one of important aspect of the first embodiment is the insertion of the preferred grain growth promotion (PGGP) seed layer, which is the second crystalline CoFe ferromagnetic reference layer 807-2, 807-2' and/or
- 10 the first crystalline CoFe ferromagnetic free layer 807-1', under or sandwiching the MgO tunnel barrier.

[0069]

- The first amorphous Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic reference layer 806, 806' with
- 15 thickness of 1.5 nm is deposited on the non-magnetic Ru spacer layer 805, 805'. The second crystalline ferromagnetic Co(70at.%)Fe(30at.%) reference layer 807-2, 807-2', which is the preferred grain growth promotion seed layer, is deposited with thickness of
- 20 1.5 nm on the first amorphous ferromagnetic reference layer 806, 806'.

[0070]

The method of forming the MgO tunnel barrier is as follows;

- 25 deposition of first metallic Mg layer 808, 808' on the second crystalline ferromagnetic reference layer 807-2, 807-2', which is the preferred grain growth

promotion seed layer, with thickness of 1.1 nm,

[0071]

oxidation of the first metallic layer 808, 808' by
radical oxidation carried out in the oxidation
5 chamber, in which electrically-ground "shower plate"
is placed between an upper ionizing electrode and the
substrate. Oxygen plasma is generated by applying
300W of rf power to the ionizing electrode with
oxygen flow of 700 sccm. Oxygen radical shower flows
10 through the shower plate, whereas particles with
electric charge, such as ionized species and
electrons, cannot pass through due to the electric
grounding of shower plate, and deposition of the
metallic Mg cap layer 810, 810' with thickness of 0.3
15 nm on the first metallic Mg layer oxidized by radical
oxidation.

[0072]

With reference to Fig. 8A, the amorphous
Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic single
20 free layer 811 with thickness of 3 nm is deposited on
the metallic Mg cap layer 810.

[0073]

Also with reference to Fig. 8B, the first crystalline
ferromagnetic Co(70at.%)Fe(30at.%) free layer 807-1',
25 which is the preferred grain growth promotion seed
layer, is deposited with thickness of 1.5 nm on the
metallic Mg cap layer 810'. Then the second amorphous

Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic free layer 811' with thickness of 1.5 nm is deposited on the first crystalline ferromagnetic free layer 807-1'. [0074]

5 Post-deposition magnetic field annealing is carried out at 360°C for 2 hour under 10 kOe magnetic field. The purposed of post-deposition annealing is the crystallization of the first amorphous ferromagnetic reference layer 806, 806' and/or the second amorphous
10 ferromagnetic free layer 811, 811' and the preferred grain growth of the said amorphous or microcrystalline MgO tunnel barrier with poor (001) out-of-plane texture. This crystallization and the preferred grain growth are realized using the second
15 crystalline CoFe ferromagnetic reference layer 807-2, 807-2' and/or the first crystalline CoFe ferromagnetic free layer 807-1' as adjacent crystallization or preferred grain growth seed layer during annealing, thus eventually overall (001) out-
20 of-plane texture of the ferromagnetic reference layer, MgO tunnel barrier and the ferromagnetic free layer. [0075]

With reference to Fig. 9A and Fig. 9B, the magnetotransport properties of the MTJ prepared by
25 the method of the present invention were measured using CIPT method. In order for comparison, the MTJ with MgO tunnel barrier prepared by rf sputtering and

the MTJ with MgO tunnel barrier prepared by same oxidation method, in both of which crystalline CoFe PGGP seed layer is not employed, are shown as reference. As shown in Fig. 9A, with reference to the

5 MR ratio and $R \times A$ product obtained from the MTJ with MgO prepared by same oxidation method but without the insertion of the crystalline PGGP seed layer, it is apparent that the MTJ which employs the crystalline PGGP layer shows much improved magnetotransport

10 properties, in that noticeable increase of MR ratio is obtained with significant reduction of $R \times A$ product, which is comparable to or even better than those from MTJ with MgO tunnel barrier prepared by rf sputtering. At given $R \times A$ product of about $9 \Omega \mu\text{m}^2$, MTJ with MgO

15 prepared by radical oxidation without the crystalline CoFe PGGP seed layer provides MR ratio of 103%, whereas the MTJs with MgO deposited by radical oxidation with the crystalline CoFe PGGP seed layer, A stack and B stack, provide 200% and 190%,

20 respectively, which are comparable to or even higher than 185% obtained from the MTJ with MgO tunnel barrier prepared by rf sputtering without the crystalline PGGP seed layer. Clear evidence of $R \times A$ product reduction and MR ratio increase is shown in

25 Fig. 9B. Only difference between reference and A and B is whether the MTJ employs the crystalline PGGP seed layer or not. The radical oxidation condition

for all samples are identical; 300W, 700 sccm and 10 seconds. By use of the crystalline PGGP seed layer, R
×A product drops from 14 $\text{O}\mu\text{m}^2$ to 7.5 $\text{O}\mu\text{m}^2$, which
roughly drops by half, and MR ratio increases from
5 110% to 180%.

[0076]

Based on the previous studies correlating
magnetotransport property and the crystallinity and
pseudo-epitaxy in MTJ, it can be intuitively inferred
10 that the insertion of the crystalline CoFe PGGP seed
layer adjacent the MgO tunnel barrier, which is
amorphous or microcrystalline with poor (001) out-of-
plane texture, induces the crystallization and the
preferred grain growth of the MgO tunnel barrier
15 during the post-deposition annealing.

(SECOND EMBODIMENT)

[0077]

The second embodiment is a method of forming the
20 tunnel barrier of MTJ devices by natural oxidation
method and the employment of CoFe as the preferred
grain growth promotion seed layer, in that the core
element of the MTJ is formed by the combination of
(a+d+i+k) or (a+d+j+k) of the group 1, 2, 3 and 4
25 mentioned above.

[0078]

Two different configurations of MTJ stacks, as

illustrated in Fig. 8A and Fig. 8B, are used in the second embodiment as follows;

A stack (see Fig. 8A) : Bottom layers (801, 802)
/PtMn15 (803) /CoFe2.5 (804) /Ru0.9 (805) /CoFeB1.5
5 (806) /CoFe1.5 (807-2) /Mg1.1(808) /N-Ox x seconds
(809) /Mg0.3 (810) /CoFeB3 (811) /Capping layers
(812) / Top electrode (813),

B stack (see Fig. 8B) : Bottom layers (801', 802')
/PtMn15 (803') /CoFe2.5 (804') /Ru0.9 (805')
10 /CoFeB1.5 (806') /CoFe1.5 (807-2') /Mg1.1 (808') /N-
Ox x seconds (809') /Mg0.3 (810') /CoFe1.5 (807-1')
/CoFeB1.5 (811')/Capping layers (812') / Top
electrode (813'),

where unbracketed numbers are thickness in nanometer
15 scale and the PGGP seed layers are indicated by
underline. Except for the natural oxidation, the
stack configurations are same as those of the first
embodiment.

[0079]

20 Referring to Fig. 8A and Fig. 8B, which also
illustrate configurations of the stacks A and B of
the second embodiment, one of important aspect of the
second embodiment is the insertion of the preferred
grain growth promotion seed layer, which is the
25 second crystalline CoFe ferromagnetic reference layer
807-2, 807-2' and/or the first crystalline CoFe
ferromagnetic free layer 807-1', under or sandwiching

the MgO tunnel barrier.

[0080]

The first amorphous Co(60at.%)Fe(20at.%)B(20at.%)
ferromagnetic reference layer 806, 806' with
5 thickness of 1.5 nm is deposited on the non-magnetic
Ru spacer layer 805, 805'. The second crystalline
ferromagnetic Co(70at.%)Fe(30at.%) reference layer
807-2, 807-2', which is the preferred grain growth
promotion seed layer, is deposited with thickness of
10 1.5 nm on the first amorphous ferromagnetic reference
layer 806, 806'.

[0081]

The method of forming the MgO tunnel barrier is as
follows;

15 deposition of first metallic Mg layer 808, 808' on
the second crystalline ferromagnetic reference layer
807-2, 807-2', which is the preferred grain growth
promotion seed layer, with thickness of 1.1 nm,

[0082]

20 oxidation of the first metallic layer 808, 808' by
natural oxidation carried out in the oxidation
chamber. The natural oxidation process, which is
advantageously applied to the thinly formed metallic
Mg layer, requires purging the oxidation chamber with
25 oxygen gas at a pressure of approximately 6.5×10^{-1} Pa
and flowing the oxygen gas at the flow rate of 700
sccm, then leaving the as-deposited metallic Mg layer

in contact with the oxygen gas flow for given exposure time, and deposition of the metallic Mg cap layer 810, 810' with thickness of 0.3 nm on the first metallic Mg layer 809, 809' oxidized by natural
5 oxidation.

[0083]

With reference to Fig. 8A, the amorphous Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic single free layer 811 with thickness of 3 nm is deposited on
10 the metallic Mg cap layer 810.

[0084]

Also with reference to Fig. 8B, the first crystalline ferromagnetic Co(70at.%)Fe(30at.%) free layer 807-1', which is the preferred grain growth promotion seed
15 layer, is deposited with thickness of 1.5 nm on the metallic Mg cap layer 810'. Then the second amorphous Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic free layer 811' with thickness of 1.5 nm is deposited on the first crystalline ferromagnetic free layer 807-1'.

20 [0085]

With reference to Figs. 20A to 20C and Fig. 21, it is clear that the microstructure of the as-grown second CoFe ferromagnetic reference layer 807-2, 807-2', which is the preferred grain growth promotion seed
25 layer, on the first amorphous CoFeB ferromagnetic reference layer 806, 806' is crystalline with body-centered-cubic structure and with (001) out-of-plane

texture. Figs. 20A to 20C show the method of analysis of cross-section image obtained by the high-resolution transmission electron microscope to confirm whether CoFe PGGP seed layer 807-2, 807-2' grows with (001) out-of-plane or (011) out-of-plane. Inter-atomic spacing (d) of CoFe PGGP seed layer 807-2, 807-2' sandwiched by the MgO tunnel barrier and the first amorphous CoFeB ferromagnetic reference layer 806, 806' in Fig. 20A is d_{110} when the CoFe PGGP seed layer 807-2, 807-2' deposited on the first amorphous CoFeB ferromagnetic reference layer 806, 806' grows with (001) out-of-plane as shown in Fig. 20B, whereas the inter-atomic spacing (d) is d_{200} when the CoFe PGGP seed layer 807-2, 807-2' deposited on the first amorphous CoFeB ferromagnetic reference layer 806, 806' grows with (011) out-of-plane as shown in Fig. 20C. Inter-atomic spacing of (110) atomic planes (d_{110}) of the CoFe with body-centered-cubic structure is 2.02 Å and d_{200} is 1.41 Å. With respect to Fig. 21, overall crystallinity of the second CoFe ferromagnetic reference layer 807-2, 807-2', which is the preferred grain growth promotion seed layer, is confirmed. Inter-atomic spacing of CoFe PGGP seed layer 807-2, 807-2' is measured using d_{111} of Cu layer as a reference, where d_{111} is 2.08 Å, for the length reference (not shown here). Using this reference, the inter-atomic spacing of CoFe PGGP seed

layer 807-2, 807-2' was measured by averaging 6 atomic planes, which provides the inter-atomic spacing is 2.02 Å. Therefore, it can be confirmed that the crystalline CoFe PGGP seed layer 807-2, 807-
5 2' on the first amorphous CoFeB ferromagnetic reference layer 806, 806' grows with (001) out-of-plane. Furthermore, it also can be confirmed that the thickness of MgO tunnel barrier is 5 mono-layers, which is 10.5 Å correspondingly, and clear partition
10 of the first amorphous CoFeB ferromagnetic reference layer 806, 806' and the second crystalline CoFe ferromagnetic reference layer 807-2, 807-2'.

[0086]

Post-deposition magnetic field annealing is carried
15 out at 360°C for 2 hour under 10 kOe magnetic field. The purposed of post-deposition annealing is the crystallization of the first amorphous ferromagnetic reference layer 806, 806' and/or the second amorphous ferromagnetic free layer 811, 811' and the preferred
20 grain growth of the said amorphous or microcrystalline MgO tunnel barrier with poor (001) out-of-plane texture. This crystallization and the preferred grain growth are realized using the second crystalline CoFe ferromagnetic reference layer 807-2,
25 807-2' and/or the first crystalline CoFe ferromagnetic free layer 807-1' as adjacent crystallization or preferred grain growth seed layer

during annealing, thus eventually overall (001) out-of-plane texture of the ferromagnetic reference layer, MgO tunnel barrier and the ferromagnetic free layer. [0087]

5 With reference to Fig. 22A and Fig. 22B, it is clear that the microstructure of the second CoFe ferromagnetic reference layer 807-2, 807-2', which is the preferred grain growth promotion seed layer, and the first CoFeB ferromagnetic reference layer 806, 10 806' form a single-layer-structured fully crystalline CoFe reference layer with body-centered-cubic structure and with (001) out-of-plane texture. The same argument to analyze the cross-section image (Figs. 20A to 20C) obtained by the high-resolution 15 transmission electron microscope is applied to confirm whether single-layer-structured CoFe reference layer after annealing is crystalline with (001) out-of-plane or (011) out-of-plane. With respect to Fig. 22A, the single-layered structure of 20 reference layer is confirmed to be formed by merging the second CoFe ferromagnetic reference layer 807-2, 807-2', which is the preferred grain growth promotion seed layer, and the first CoFeB ferromagnetic reference layer 806, 806'. This formation of single- 25 layer-structured reference layer is explained by the crystallization of the first CoFeB ferromagnetic reference layer 806, 806' based on the second CoFe

ferromagnetic reference layer 807-2, 807-2' as the preferred grain growth promotion seed layer. Using the same length reference used in Fig. 21, the inter-atomic spacing of single-layer-structured CoFe

5 reference layer after annealing was measured by averaging 7 atomic planes from the boxed-area in Fig. 22B, which provides the inter-atomic spacing is 2.0 Å. Also the inter-atomic spacing of MgO tunnel barrier was measured to be 2.13 Å by the length reference.

10 Those inter-atomic spacings from the single-layer-structured CoFe reference layer and the MgO tunnel barrier after annealing confirm that both of MgO tunnel barrier and CoFe reference layer are fully crystalline with (001) out-of-plane texture.

15 Furthermore, Selected-area diffraction pattern shown in Fig. 22B from boxed-area in Fig. 22A by fast Fourier transformation using Gatan Digitalmicrograph confirms the grain-to-grain pseudo-epitaxy, which is 45° rotational epitaxy, between the MgO tunnel barrier

20 and the CoFe reference layer in that the [001] crystalline axis of single-layered CoFe reference layer is parallel to [011] crystalline axis of MgO tunnel barrier. Note that the diffraction patterns indexed with underline are from single-layer-

25 structured CoFe reference layer and the diffraction patterns without underline are from MgO tunnel barrier. This grain-to-grain pseudo-epitaxy in

CoFe/MgO/CoFe-based magnetic tunnel junction is critical pre-requisite to obtain the giant TMR as explained by Choi et al. in J. Appl. Phys. 101, 013907 (2007).

5 [0088]

With reference to Fig. 10A and Fig. 10B, the magnetotransport properties of the MTJ prepared by the method of the present invention were measured using CIPT method. In order for comparison, the MTJ
10 with MgO tunnel barrier prepared by rf sputtering and the MTJ with MgO tunnel barrier prepared by same oxidation method, in both of which crystalline CoFe PGGP seed layer is not employed, are shown as reference. As shown in Fig. 10A, with reference to
15 the MR ratio and $R \times A$ product obtained from the MTJ with MgO prepared by same oxidation method but without the insertion of the crystalline PGGP seed layer, it is apparent that the MTJ which employs the crystalline PGGP layer shows much improved
20 magnetotransport properties, in that noticeable increase of MR ratio is obtained with significant reduction of $R \times A$ product, which is comparable to or even better than those from MTJ with MgO tunnel barrier prepared by rf sputtering. At given $R \times A$
25 product of about $6 \Omega \mu\text{m}^2$, MTJ with MgO prepared by natural oxidation without the crystalline PGGP seed layer provides MR ratio of 74%, whereas the MTJs with

MgO deposited by natural oxidation with the crystalline CoFe PGGP seed layer, A stack and B stack, provide 170% and 183%, respectively, which are comparable to or even higher than 170% obtained from the MTJ with MgO tunnel barrier prepared by rf sputtering without the crystalline PGGP seed layer. Clear evidence of $R \times A$ product reduction and MR ratio increase is shown in Fig. 10B. Only difference between reference and A and B is whether the MTJ employs the crystalline CoFe PGGP seed layer or not. The natural oxidation condition for all samples are identical; oxygen flow rate 700 sccm and exposure time 30 seconds. By use of the crystalline PGGP seed layer, $R \times A$ product drops from $7 \text{ O}\mu\text{m}^2$ to $4.8 \text{ O}\mu\text{m}^2$, which roughly drops by two thirds, and MR ratio increases from 74.4% to 169%.

[0089]

Furthermore, another set of MTJs with A stack, of which thickness of the said second crystalline ferromagnetic CoFe reference layer varies, to optimize the thickness ratio between the first amorphous ferromagnetic CoFeB reference layer and the second crystalline CoFe reference layer in the bi-layer-structured ferromagnetic reference layer. Thickness of the first amorphous CoFeB ferromagnetic reference layer in the bi-layer-structured ferromagnetic reference layer is fixed at 1.5 nm. As

shown in Fig. 11, it is clearly shown that MR ratio drops sharply and $R \times A$ product increases when the thickness of the second crystalline CoFe ferromagnetic reference layer is 2.0 nm and over.

5 Thus it can be concluded that when the thickness of the first amorphous CoFeB ferromagnetic reference layer of the bi-layer-structured ferromagnetic reference layer is fixed at 1.5 nm, the thickness of the second crystalline CoFe ferromagnetic reference
10 layer cannot exceed 1.5 nm to obtain higher MR ratio at lower $R \times A$ product.

[0090]

Again, based on the previous studies correlating magnetotransport property and the crystallinity and
15 pseudo-epitaxy in MTJ, it can be intuitively inferred that the insertion of the crystalline CoFe PGGP seed layer adjacent the MgO tunnel barrier, which is amorphous or microcrystalline with poor (001) out-of-plane texture, induces the crystallization and the
20 preferred grain growth of the MgO tunnel barrier during the post-deposition annealing.

(THIRD EMBODIMENT)

[0091]

25 The third embodiment is a method of forming the tunnel barrier of MTJ devices by use of surfactant layer and followed by radical oxidation method and

the employment of CoFe as the preferred grain growth promotion seed layer, in that the core element of the MTJ is formed by the combination of (a+e+i+k) of the group 1, 2, 3 and 4 mentioned above.

5 [0092]

The following configuration of MTJ stack, as illustrated in Fig. 8C, is used in the third embodiment;

A stack (see Fig. 8C) : Bottom layers (801") /PtMn15
10 (803") /CoFe2.5 (804") /Ru0.9 (805") /CoFeB1.5 (806")
/CoFe1.5 (807-2") /Mg 0.43 (808") /Oxygen surfactant
layer 30 Langmuir (814")/Mg 0.67 (815")/R-Ox x
seconds (809")/Mg0.3 (810") /CoFeB3 (811") /Capping
layers (812") / Top electrode (813"),

15 where unbracketed numbers are thickness in nanometer scale and the PGGP seed layer is indicated by underline.

[0093]

Referring to Fig. 8C, one of important aspect of the
20 third embodiment is the insertion of the preferred grain growth promotion (PGGP) seed layer, which is the second crystalline ferromagnetic reference layer 807-2", under the MgO tunnel barrier.

[0094]

25 The first amorphous Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic reference layer 806" with thickness of 1.5 nm is deposited on the non-magnetic Ru spacer

layer 805". The second crystalline ferromagnetic
Co(70at.%)Fe(30at.%) reference layer 807-2", which is
the preferred grain growth promotion seed layer, is
deposited with thickness of 1.5 nm on the first
5 amorphous ferromagnetic reference layer 806".

[0095]

The method of forming the MgO tunnel barrier is as
follows;

deposition of first metallic Mg layer 808" on the
10 second crystalline ferromagnetic reference layer 807-
2", which is the preferred grain growth promotion
seed layer, with thickness of 0.43 nm,
formation of the oxygen surfactant layer 814" within
the vacuum chamber by exposing the 0.43 nm of
15 metallic Mg layer 808" to the oxygen ambience,
wherein the exposure is controlled to be 30 Langmuir
by the exposure time and the oxygen flow through the
chamber,

[0096]

20 deposition of second metallic Mg layer 815" on the
oxygen surfactant layer with thickness of 0.67 nm,
oxidation of the first and second metallic layers
808" and 815" by radical oxidation carried out in the
oxidation chamber, in which electrically-ground
25 "shower plate" is placed between an upper ionizing
electrode and the substrate. Oxygen plasma is
generated by applying 300W of rf power to the

ionizing electrode with oxygen flow of 700 sccm.

Oxygen radical shower flows through the shower plate, whereas particles with electric charge, such as

ionized species and electrons, cannot pass through

5 due to the electric grounding of shower plate, and

[0097]

deposition of the metallic Mg cap layer 810" with

thickness of 0.3 nm on the first and the second

metallic Mg layers 808" and 815" oxidized by radical
10 oxidation.

[0098]

With reference to Fig. 8C, the amorphous

Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic single

free layer 811" with thickness of 3 nm is deposited

15 on the metallic Mg cap layer 810".

[0099]

Post-deposition magnetic field annealing is carried out at 360°C for 2 hour under 10 kOe magnetic field.

The purposed of post-deposition annealing is the

20 crystallization of the first amorphous ferromagnetic

reference layer 806" and the amorphous ferromagnetic

free layer 811" and the preferred grain growth of the

said amorphous or microcrystalline MgO tunnel barrier

with poor (001) out-of-plane texture. This

25 crystallization and the preferred grain growth are

realized using the second crystalline CoFe

ferromagnetic reference layer as adjacent

crystallization or preferred grain growth seed layer during annealing, thus eventually overall (001) out-of-plane texture of the ferromagnetic reference layer, MgO tunnel barrier and the ferromagnetic free layer.

5 [0100]

With reference to Fig. 12, clear evidence of $R \times A$ product reduction and MR ratio increase is confirmed. Only difference between reference and A is whether the MTJ employs the crystalline PGGP seed layer or
10 not. The radical oxidation condition for all samples are identical; 300W, 700 sccm and 10 seconds. By use of the crystalline PGGP seed layer, $R \times A$ product drops from $22.5 \text{ O}\mu\text{m}^2$ to $8.3 \text{ O}\mu\text{m}^2$, which roughly drops by a third, and MR ratio increases from 120% to 170%.

15 [0101]

Again, based on the previous studies correlating magnetotransport property and the crystallinity and pseudo-epitaxy in MTJ, it can be intuitively inferred that the insertion of the crystalline CoFe PGGP seed
20 layer adjacent the MgO tunnel barrier, which is amorphous or microcrystalline with poor (001) out-of-plane texture, induces the crystallization and the preferred grain growth of the MgO tunnel barrier during the post-deposition annealing.

25

(FORTH EMBODIMENT)

[0102]

The forth embodiment is a method of forming the tunnel barrier of MTJ devices by reactive sputtering and the employment of CoFe as the preferred grain growth promotion seed layer, in that the core element
5 of the MTJ is formed by the combination of (a+h+i+k) of the group 1, 2, 3 and 4 mentioned above.

[0103]

The following configuration of MTJ stacks, as illustrated in Fig. 8D, is used in the forth
10 embodiment;

A stack : Bottom layers (801''' and 802''') /PtMn15 (803''') /CoFe2.5 (804''') /Ru0.9 (805''') /CoFeB1.5 (806''') /CoFe1.5 (807-2''') /Mg 0.6 (808''') /MgOx reactive sputtering 0.6 (816''') /N-Ox x seconds
15 (809''')/Mg 0.35 (810''') /CoFeB3 (811''') /Capping layers (812''') / Top electrode (813'''),
where unbracketed numbers are thickness in nanometer scale and the PGGP seed layer is indicated by underline.

20 [0104]

Referring to Fig. 8D, one of important aspect of the forth embodiment is the insertion of the preferred grain growth promotion seed layer, which is the second crystalline CoFe ferromagnetic reference layer
25 807-2''', under the MgO tunnel barrier.

[0105]

The first amorphous Co(60at.%)Fe(20at.%)B(20at.%)

ferromagnetic reference layer 806''' with thickness of 1.5 nm is deposited on the non-magnetic Ru spacer layer 805''. The second crystalline ferromagnetic Co(70at.%)Fe(30at.%) reference layer 807-2'', which
5 is the preferred grain growth promotion seed layer, is deposited with thickness of 1.5 nm on the first amorphous ferromagnetic reference layer 806''.

[0106]

The method of forming the MgO tunnel barrier is as
10 follows;

deposition of first metallic Mg layer 808''' on the second crystalline ferromagnetic reference layer 807-2'', which is the preferred grain growth promotion seed layer, with thickness of 0.6 nm,
15 formation of MgO layer 816''' through the reactive sputtering of Mg in the mixed gas of argon and oxygen by flowing argon at the flow rate of 40 sccm and the oxygen at the flow rate of 4 sccm with thickness of 0.6 nm on the first metallic Mg layer 808''',

20 [0107]

oxidation of the first metallic layer 808''' and the MgO layer 810''' by natural oxidation carried out in the oxidation chamber. The natural oxidation process, which is advantageously applied to the thinly formed
25 metallic Mg layer and the MgO layer, requires purging the oxidation chamber with oxygen gas at a pressure of approximately 6.5×10^{-1} Pa and flowing the oxygen

gas at the flow rate of 700 sccm, then leaving the as-deposited metallic Mg layer and the MgO layer in contact with the oxygen gas flow for given exposure time, and deposition of the metallic Mg cap layer
5 810''' with thickness of 0.3 nm on the MgO layer and the first metallic Mg layer oxidized by natural oxidation.

[0108]

With reference to Fig. 8D, the amorphous
10 Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic single free layer 811''' with thickness of 3 nm is deposited on the metallic Mg cap layer 810'''.

[0109]

Post-deposition magnetic field annealing is carried
15 out at 360°C for 2 hour under 10 kOe magnetic field. The purposed of post-deposition annealing is the crystallization of the first amorphous ferromagnetic reference layer 806''' and the amorphous ferromagnetic free layer 811''' and the preferred
20 grain growth of the said amorphous or microcrystalline MgO tunnel barrier with poor (001) out-of-plane texture. This crystallization and the preferred grain growth are realized using the second crystalline ferromagnetic reference layer 807-2''' as
25 adjacent crystallization or preferred grain growth seed layer during annealing, thus eventually overall (001) out-of-plane texture of the ferromagnetic

reference layer, MgO tunnel barrier and the ferromagnetic free layer.

[0110]

With reference to Fig. 13, clear evidence of $R \times A$ product reduction and MR ratio increase is confirmed. Only difference between reference and A is whether the MTJ employs the crystalline CoFe PGGP seed layer or not. The natural oxidation condition for all samples are identical; oxygen flow rate 700 sccm and exposure time 30 seconds. By use of the crystalline PGGP seed layer, $R \times A$ product drops from $16.5 \text{ O}\mu\text{m}^2$ to $10.2 \text{ O}\mu\text{m}^2$ and MR ratio increases from 135% to 185%.

[0111]

Again, based on the previous studies correlating magnetotransport property and the crystallinity and pseudo-epitaxy in MTJ, it can be intuitively inferred that the insertion of the crystalline CoFe PGGP seed layer adjacent the MgO tunnel barrier, which is amorphous or microcrystalline with poor (001) out-of-plane texture, induces the crystallization and the preferred grain growth of the MgO tunnel barrier during the post-deposition annealing.

(FIFTH EMBODIMENT)

[0112]

The fifth embodiment is a method of forming the tunnel barrier of MTJ devices by natural oxidation

method and the employment of CoFeB as the crystalline preferred grain growth promotion seed layer, in that the core element of the MTJ is formed by the combination of (b+d+j+k) of the group 1, 2, 3 and 4 mentioned above.

[0113]

Two identical configurations of MTJ stacks, as illustrated in Fig. 14, are used in the fifth embodiment with different boron content in the CoFeB PGGP seed layer as follows;

A stack : Bottom layers (1401, 1402) /PtMn15 (1403) /CoFe2.5 (1404) /Ru0.9 (1405) /CoFeB1.5 (1406) /CoFeB (Boron 2.9 atomic %) 1.5 (1407) /Mg1.1 (1408) /N-Ox x seconds (1409)/Mg0.3 (1410) /CoFeB (Boron 2.9 atomic %) 1.5 (1411) /CoFeB1.5 (1412) /Capping layers (1413) / Top electrode (1415),

B stack : Bottom layers (1401, 1402) /PtMn15 (1403) /CoFe2.5 (1404) /Ru0.9 (1405) /CoFeB1.5 (1406) /CoFeB (Boron 5.1 atomic %) 1.5 (1407)/Mg1.1 (1408) /N-Ox x seconds (1409)/Mg0.3(1410)/CoFeB (Boron 5.1 atomic %) 1.5 (1411)/CoFeB1.5 (1412) /Capping layers (1413) / Top electrode (1415),

where unbracketed numbers are thickness in nanometer scale and the PGGP seed layers are indicated by underline.

[0114]

Referring to Fig. 14, one of important aspect of the

fifth embodiment is the insertion of the preferred grain growth promotion seed layers, which are the second crystalline ferromagnetic reference layer and the first crystalline ferromagnetic free layer,
5 sandwiching the MgO tunnel barrier.

[0115]

With respect to Fig. 15A and Fig. 15B, it is clear that the microstructure of CoFeB with boron content of 5.1 atomic % and 2.9 atomic % is crystalline in
10 as-deposited state, whereas that of CoFeB with boron content of 20 atomic % is amorphous, which is confirmed by xRD theta - 2 theta scan from the CoFeB single layer deposited on the thermally oxidized Si wafer. Intensity is normalized by thickness of CoFeB
15 single film. Calculated grain size using Sherrer formula shows that the grain size of CoFeB (B: 2.9 atomic %) is larger than that of CoFeB (B: 5.1 atomic %), which can be reassured by the significant reduction of resistivity. Resistivity of the CoFeB
20 changes noticeably with its crystallinity corresponding to its boron contents. Furthermore, the shift of the XRD peak from 45.35° of CoFeB (B: 2.9 atomic %) to 45.02° of CoFeB (B: 5.1 atomic %) indicates the lattice expansion of CoFe with its
25 inclusion of boron at the interstitial sites of body-centered-cubic structure.

[0116]

The first amorphous Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic reference layer with thickness of 1.5 nm is deposited on the non-magnetic Ru spacer layer. [0117]

- 5 The second crystalline ferromagnetic reference layer in the stack A of the fifth embodiment, which is the preferred grain growth promotion seed layer, is deposited by co-sputtering of Co(70at.%)Fe(30at.%) target and Co(60at.%)Fe(20at.%)B(20at.%) target and
- 10 the composition ratio is controlled by the manipulation of the power ratio of co-sputtering. The composition of the second crystalline ferromagnetic reference layer, which is the PGGP seed layer, is Co(69.9at.%)Fe(27.2at.%)B(2.9at.%) with thickness of
- 15 1.5 nm on the first amorphous ferromagnetic reference layer. With reference to Fig. 15A and Fig. 15B, it is confirmed that the as-grown state of Co(69.9at.%)Fe(27.2at.%)B(2.9at.%) layer is crystalline. Also the crystallinity of
- 20 Co(69.9at.%)Fe(27.2at.%)B(2.9at.%) is confirmed by the reduction of resistivity to 20.6 $\mu\Omega$ -cm from 111 $\mu\Omega$ -cm of Co(60at.%)Fe(20at.%)B(20at.%) due to the better crystallinity compared to the amorphous phase. [0118]
- 25 The second crystalline ferromagnetic reference layer in the stack B of the fifth embodiment, which is the preferred grain growth promotion seed layer, is

deposited by co-sputtering of Co(70at.%)Fe(30at.%) target and Co(60at.%)Fe(20at.%)B(20at.%) target and the composition ratio is controlled by the manipulation of the power ratio of co-sputtering. The composition of the second crystalline ferromagnetic reference layer, which is the PGGP seed layer, is Co(69.3at.%)Fe(25.6at.%)B(5.1at.%) with thickness of 1.5 nm on the first amorphous ferromagnetic reference layer. With reference to Fig. 15, it is confirmed that the as-grown state of Co(69.3at.%)Fe(25.6at.%)B(5.1at.%) layer is crystalline. Also the crystallinity of Co(69.3at.%)Fe(25.6at.%)B(5.1at.%) is confirmed by the reduction of resistivity to 43.2 $\mu\Omega\cdot\text{cm}$ from 111 $\mu\Omega\cdot\text{cm}$ of Co(60at.%)Fe(20at.%)B(20at.%) due to the better crystallinity compared to the amorphous phase. [0119]

The method of forming the MgO tunnel barrier is as follows;

deposition of first metallic Mg layer on the second crystalline ferromagnetic reference layer, which is the preferred grain growth promotion seed layer, with thickness of 1.1 nm, [0120]

oxidation of the first metallic layer by natural oxidation carried out in the oxidation chamber. The natural oxidation process, which is advantageously

applied to the thinly formed metallic Mg layer,
requires purging the oxidation chamber with oxygen
gas at a pressure of approximately 6.5×10^{-1} Pa and
flowing the oxygen gas at the flow rate of 700 sccm,
5 then leaving the as-deposited metallic Mg layer in
contact with the oxygen gas flow for given exposure
time, and
deposition of the metallic Mg cap layer with
thickness of 0.3 nm on the first metallic Mg layer
10 oxidized by natural oxidation.

[0121]

The first crystalline ferromagnetic free layer in the
stack A of the fifth embodiment, which is the
preferred grain growth promotion seed layer, is
15 deposited by co-sputtering of Co(70at.%)Fe(30at.%)
target and Co(60at.%)Fe(20at.%)B(20at.%) target and
the composition ratio is controlled by the
manipulation of the power ratio of co-sputtering. The
composition of the second crystalline ferromagnetic
20 reference layer, which is the PGGP seed layer, is
Co(69.9at.%)Fe(27.2at.%)B(2.9at.%) with thickness of
1.5 nm on the metallic Mg cap layer.

[0122]

The first crystalline ferromagnetic free layer in the
25 stack B of the fifth embodiment, which is the
preferred grain growth promotion seed layer, is
deposited by co-sputtering of Co(70at.%)Fe(30at.%)

target and Co(60at.%)Fe(20at.%)B(20at.%) target and the composition ratio is controlled by the manipulation of the power ratio of co-sputtering. The composition of the second crystalline ferromagnetic
5 reference layer, which is the PGGP seed layer, is Co(69.3at.%)Fe(25.6at.%)B(5.1at.%) with thickness of 1.5 nm on the metallic Mg cap layer.

[0123]

Then the second amorphous

10 Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic free layer with thickness of 1.5 nm is deposited on the first crystalline ferromagnetic free layer, which is the preferred grain growth promotion seed layer.

[0124]

15 Post-deposition magnetic field annealing is carried out at 360°C for 2 hour under 10 kOe magnetic field. The purposed of post-deposition annealing is the crystallization of the first amorphous ferromagnetic reference layer and/or the second amorphous
20 ferromagnetic free layer and the preferred grain growth of the said amorphous or microcrystalline MgO tunnel barrier with poor (001) out-of-plane texture. This crystallization and the preferred grain growth are realized using the second crystalline
25 ferromagnetic reference layer and/or the first crystalline ferromagnetic free layer as adjacent crystallization or preferred grain growth seed layer

during annealing, thus eventually overall (001) out-of-plane texture of the ferromagnetic reference layer, MgO tunnel barrier and the ferromagnetic free layer. [0125]

5 With reference to Fig. 16A and Fig. 16B, the magnetotransport properties of the MTJ prepared by the method of the present invention were measured using CIPT method. In order for comparison, the MTJ with MgO tunnel barrier prepared by rf sputtering and
10 the MTJ with MgO tunnel barrier prepared by same oxidation method, in both of which crystalline PGGP seed layer is not employed, are shown as reference. As shown in Fig. 16A, with reference to the MR ratio and $R \times A$ product obtained from the MTJ with MgO
15 prepared by same oxidation method but without the insertion of the crystalline PGGP seed layer, it is apparent that the MTJ employs the crystalline CoFeB PGGP layer shows much improved magnetotransport properties, in that noticeable increase of MR ratio
20 is obtained with significant reduction of $R \times A$ product, which is comparable to or even better than those from MTJ with MgO tunnel barrier prepared by rf sputtering. At given $R \times A$ product of about $6 \Omega \mu\text{m}^2$, MTJ with MgO prepared by natural oxidation without the crystalline
25 PGGP seed layer provides MR ratio of 74%, whereas the MTJs with MgO deposited by natural oxidation with the crystalline CoFeB PGGP seed layer, A stack and B

stack, provide 178% and 170%, respectively, which are comparable to or even higher than 170% obtained from the MTJ with MgO tunnel barrier prepared by rf sputtering without the crystalline PGGP seed layer.

- 5 Clear evidence of R×A product reduction and MR ratio increase is shown in Fig. 16B. Only difference between reference and A and B is whether the MTJ employs the crystalline PGGP seed layer or not. The natural oxidation condition for all samples is
- 10 identical; oxygen flow rate 700 sccm and exposure time 30 seconds. By use of the crystalline PGGP seed layer, R×A product drops from 7 O μ m² to 4.2 O μ m² and MR ratio increases from 74.4% to 160%.

[0126]

- 15 Again, based on the previous studies correlating magnetotransport property and the crystallinity and pseudo-epitaxy in MTJ, it can be intuitively inferred that the insertion of the crystalline PGGP seed layer adjacent the MgO tunnel barrier, which is amorphous
- 20 or microcrystalline with poor (001) out-of-plane texture, induces the crystallization and the preferred grain growth of the MgO tunnel barrier during the post-deposition annealing.

25 **(SIXTH EMBODIMENT)**

[0127]

The sixth embodiment is a method of forming the

tunnel barrier of MTJ devices by natural oxidation method and the employment of Fe as the crystalline preferred grain growth promotion seed layer, in that the core element of the MTJ can be formed by the
5 combination of (c+d+j+k) of the group 1, 2, 3 and 4 mentioned above.

[0128]

The following configuration of MTJ stack, as illustrated in Fig. 17, can be used in the sixth
10 embodiment;

A stack : Bottom layers (1701, 1702) /PtMn15 (1703) /CoFe2.5 (1704) /Ru0.9 (1705) /CoFeB1.5 (1706) /Fe x (1707) /Mg1.1 (1708) /N-Ox x seconds (1709)/Mg0.3 (1710) /Fe x (1711)/CoFeB1.5 (1712) /Capping layers
15 (1713) / Top electrode (1714),

where unbracketed numbers are thickness in nanometer scale and the PGGP seed layers are indicated by underline.

[0129]

20 Referring to Fig. 17, one of important aspect of the sixth embodiment is the insertion of the preferred grain growth promotion seed layer, which is the second crystalline ferromagnetic Fe reference layer 1707 and the first crystalline ferromagnetic Fe free
25 layer 1711, sandwiching the MgO tunnel barrier (1708, 1709, 1710).

[0130]

The first amorphous Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic reference layer 1706 with thickness of 1 - 4 nm is deposited on the non-magnetic Ru spacer layer 1705.

5 [0131]

The second crystalline ferromagnetic Fe reference layer 1707 in the stack A of the sixth embodiment, which is the preferred grain growth promotion seed layer, is deposited with thickness of 0.5 - 2 nm on
10 the first amorphous ferromagnetic reference layer 1706.

[0132]

The method of forming the MgO tunnel barrier is as follows;

15 deposition of first metallic Mg layer 1708 on the second crystalline ferromagnetic reference layer 1707, which is the preferred grain growth promotion seed layer, with thickness of 1.1 nm,

[0133]

20 oxidation of the first metallic layer 1708 by natural oxidation carried out in the oxidation chamber. The natural oxidation process, which is advantageously applied to the thinly formed metallic Mg layer, requires purging the oxidation chamber with oxygen
25 gas and flowing the oxygen gas, then leaving the as-deposited metallic Mg layer in contact with the oxygen gas flow for given exposure time, and

deposition of the metallic Mg cap 1710 layer with thickness of 0.3 nm on the first metallic Mg layer 1709 oxidized by natural oxidation.

[0134]

- 5 The first crystalline ferromagnetic Fe free layer 1711 in the stack A of the sixth embodiment, which is the preferred grain growth promotion seed layer, is deposited with thickness of 0.5 - 2 nm on the metallic Mg cap layer 1710.

10 [0135]

Then the second amorphous

- Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic free layer 1712 with thickness of 1 - 4 nm is deposited on the first crystalline ferromagnetic free layer 1711, which is the preferred grain growth promotion seed layer.

(SEVENTH EMBODIMENT)

[0136]

- 20 The seventh embodiment is a method of forming the tunnel barrier of MTJ devices by natural oxidation method and the employment of CoFe as the preferred grain growth promotion seed layer and also the employment of bi-layer structured pinned layer, in that the core element of the MTJ is formed by the combination of (a+d+i+l) or (a+d+j+l) of the group 1, 2, 3 and 4 mentioned above.

[0137]

The configuration of MTJ stacks, as illustrated in Fig. 18, is used in the seventh embodiment as follows;

- 5 A stack : Bottom layers (1801, 1802) /PtMn15 (1803)
/CoFeB1.25 (1804)/CoFe1.25 (1805) /Ru0.9 (1806)
/CoFeB1.5 (1807) /CoFe1.5 (1808) /Mg0.7 (1809) /N-Ox
x seconds (1810)/Mg0.3 (1811) /CoFe1.5 (1812)
/CoFeB1.5 (1813) /Capping layers (1814) / Top
10 electrode (1815),

where unbracketed numbers are thickness in nanometer scale, the PGGP seed layers are indicated by underline, and the bi-layered pinned layers are indicated in bold font.

15 [0138]

- Referring to Fig. 18, one of important aspect of the seventh embodiment is the insertion of the preferred grain growth promotion seed layer, which is the second crystalline CoFe ferromagnetic reference layer
20 1805 and/or the first crystalline CoFe ferromagnetic free layer 1812, under or sandwiching the MgO tunnel barrier (1809, 1810, 1811). Another important aspect of the seventh embodiment is the employment of the bi-layer-structured ferromagnetic pinned layer, in
25 that the first amorphous CoFeB ferromagnetic pinned layer 1804 on the antiferromagnetic PtMn pinning layer 1803 and the second crystalline CoFe

ferromagnetic pinned layer 1805 on the first amorphous CoFeB ferromagnetic pinned layer 1804 are deposited with the thickness of 1.25nm and 1.25nm, respectively.

5 [0139]

The first amorphous Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic reference layer 1807 with thickness of 1.5 nm is deposited on the non-magnetic Ru spacer layer 1806. The second crystalline ferromagnetic
10 Co(70at.%)Fe(30at.%) reference layer, which is the preferred grain growth promotion seed layer, is deposited with thickness of 1.5 nm on the first amorphous ferromagnetic reference layer 1807.

[0140]

15 The method of forming the MgO tunnel barrier is as follows;

deposition of first metallic Mg layer 1809 on the second crystalline ferromagnetic reference layer 1808, which is the preferred grain growth promotion seed
20 layer, with thickness of 0.7 nm,

[0141]

oxidation of the first metallic layer 1809 by natural oxidation carried out in the oxidation chamber. The natural oxidation process, which is advantageously
25 applied to the thinly formed metallic Mg layer, requires purging the oxidation chamber with oxygen gas at a pressure of approximately 9.9×10^{-2} Pa and

flowing the oxygen gas at the flow rate of 100 sccm, then leaving the as-deposited metallic Mg layer in contact with the oxygen gas flow for given exposure time, and

- 5 deposition of the metallic Mg cap layer 1811 with thickness of 0.3 nm on the first metallic Mg layer 1810 oxidized by natural oxidation.

[0142]

- With reference to Fig. 18, the first crystalline
10 ferromagnetic Co(70at.%)Fe(30at.%) free layer 1812, which is the preferred grain growth promotion seed layer, is deposited with thickness of 1.5 nm on the metallic Mg cap layer 1811. Then the second amorphous Co(60at.%)Fe(20at.%)B(20at.%) ferromagnetic free
15 layer 1813 with thickness of 1.5 nm is deposited on the first crystalline ferromagnetic free layer 1812.

[0143]

Post-deposition magnetic field annealing is carried out at 380°C for 2 hour under 10 kOe magnetic field.

- 20 The purposed of post-deposition annealing is the crystallization of the first amorphous ferromagnetic reference layer 1807 and/or the second amorphous ferromagnetic free layer 1813 and the preferred grain growth of the amorphous or microcrystalline MgO
25 tunnel barrier with poor (001) out-of-plane texture. This crystallization and the preferred grain growth are realized using the second crystalline CoFe

ferromagnetic reference layer 1805 and/or the first crystalline CoFe ferromagnetic free layer 1812 as adjacent crystallization or preferred grain growth seed layer during annealing, thus eventually overall
5 (001) out-of-plane texture of the ferromagnetic reference layer, MgO tunnel barrier and the ferromagnetic free layer.

[0144]

With reference to Fig. 19, the magnetotransport
10 properties of the MTJ prepared by the method of the present invention were measured using CIPT method. In order for comparison, the MTJ with the structure of "Bottom layers /PtMn15 / CoFe2.5 /Ru0.9 /CoFeB3 /Mg1.1 /N-Ox x seconds/ Mg0.3 / CoFeB3 /Capping
15 layers", in which crystalline CoFe PGGP seed layer is not employed and the ferromagnetic pinned layer is CoFeB single layer, is shown as reference (marked ■). Also the reference MTJ is annealed at 360°C for 2 hours under 10 kOe magnetic field. As shown in Fig.
20 19, with reference to the MR ratio and $R \times A$ product obtained from the MTJ with MgO prepared by same oxidation method but without the insertion of the crystalline PGGP seed layer, it is apparent that the MTJ which employs the crystalline PGGP layer shows
25 much improved magnetotransport properties, in that noticeable increase of MR ratio is obtained with significant reduction of $R \times A$ product. At given $R \times A$

product of about $1.5 \Omega \mu\text{m}^2$, MTJ with MgO prepared by natural oxidation without the crystalline PGGP seed layer provides MR ratio of 25.8%, whereas the MTJ with MgO deposited by natural oxidation with the
5 crystalline CoFe PGGP seed layer, A stack, provides 168.8%.

[0145]

Again, based on the previous studies correlating magnetotransport property and the crystallinity and
10 pseudo-epitaxy in MTJ, it can be intuitively inferred that the insertion of the crystalline CoFe PGGP seed layer adjacent the MgO tunnel barrier, which is amorphous or microcrystalline with poor (001) out-of-plane texture, induces the crystallization and the
15 preferred grain growth of the MgO tunnel barrier during the post-deposition annealing.

[0146]

With reference to Fig. 23A to Fig. 23F, Fig. 24 and Fig. 25A to Fig. 25C, it is clear that the magnetic
20 tunnel junction with bi-layered ferromagnetic pinned layer as illustrated in Fig. 18 shows better thermal stability than the magnetic tunnel junction with single ferromagnetic pinned layer. Fig. 23A to Fig. 23F show the comparison of TMR, RA and Hex of
25 magnetic tunnel junctions with different stack structure. 'No PGGP' indicates the magnetic tunnel junction without PGGP seed layer and bi-layered

ferromagnetic pinned layer. 'PGGP only' indicates the magnetic tunnel junction only with PGGP seed layer but no bi-layered ferromagnetic pinned layer. 'PGGP & bi-PL' indicates the magnetic tunnel junction with

5 both of PGGP seed layer and bi-layered ferromagnetic pinned layer. Bi-layered ferromagnetic pinned layer is described above as Group 41. TMR of 'No PGGP' magnetic tunnel junction drops significantly at the temperature of 400°C, whereas that of 'PGGP only' and

10 'PGGP & bi-PL' magnetic tunnel junctions sustains upto 400°C. However, exchange-biasing (Hex) of both of 'No PGGP' and 'PGGP only' magnetic tunnel junctions shows noticeable drop from 380°C annealing and down to 500Oe at 400°C annealing, however, that of 'PGGP & bi-

15 PL' magnetic tunnel junction at 400°C is as high as 1500Oe, which shows strong thermal stability. Shape of hysteresis loops shows clear difference in Fig. 24 and Fig. 25A to Fig. 25C. Fig. 24 shows the evolution of hysteresis loop of 'No PGGP' magnetic tunnel

20 junction at annealing temperatures of 400°C, 360 °C and "as grown" and Fig. 25A to Fig. 25C show the evolution of hysteresis loop of 'PGGP & bi-PL' magnetic tunnel junction at annealing temperatures of 380°C, 400°C and 420°C. It is clear that 'No PGGP'

25 magnetic tunnel junction loses exchange-biasing (Hex) and SAF plateau at 400°C, whereas 'PGGP & bi-PL' magnetic tunnel junction sustains Hex and SAF plateau

at 400°C.

[0147]

This enhanced thermal stability of magnetic tunnel junction with 'bi-PL' can be explained by the boron segregation blocking manganese (Mn) diffusion from antiferromagnetic Mn-alloy. Fig. 26 shows the schematic explanation of enhanced thermal stability. During annealing, boron in CoFeB pinned layer diffuses out while CoFeB crystallizes based on CoFe pinned layer as crystallization template and segregates at the CoFeB/Mn-alloy interface. As Mn diffusion has been reported to be responsible for the reduction of Hex, Mn diffusion barrier, which is boron segregated at the interface, is attributed to achieving the better thermal stability. This thermal stability of magnetic tunnel junction enlarges the process window for MRAM production as it includes high temperature CMOS process.

The present invention includes an embodiment wherein only a ferromagnetic pinned layer deposition step comprises a crystalline ferromagnetic pinned layer formation step and an amorphous ferromagnetic pinned layer formation step. And the crystalline ferromagnetic pinned layer is nearer to a non-magnetic spacer layer than the amorphous ferromagnetic pinned layer.

CLAIMS

1. A method of manufacturing a magnetic tunnel junction device, the method comprising:
 - 5 a first layer deposition step of depositing a first layer which contains ferromagnetic material;
 - a tunnel barrier layer deposition step of depositing a tunnel barrier layer onto the ferromagnetic layer;
 - and
 - 10 a second layer deposition step of depositing a second layer which contains ferromagnetic material onto the tunnel barrier layer,wherein the first layer deposition step comprises a first amorphous ferromagnetic layer formation step
 - 15 of forming a first amorphous ferromagnetic layer, and a second crystalline ferromagnetic layer formation step of forming a second crystalline ferromagnetic layer, which is the preferred grain growth promotion (PGGP) seed layer, sandwiched by the first amorphous
 - 20 ferromagnetic layer and the tunnel barrier layer.
2. The method according to claim 1, wherein the first amorphous ferromagnetic layer of the said first layer is ternary alloy containing Co, Fe and B.
 - 25
 3. The method according to claim 1, wherein the first amorphous ferromagnetic layer of the said first layer

is formed with the thickness between 1 nm and 4 nm.

4. The method according to claim 1, wherein the second crystalline ferromagnetic layer, which is the
5 PGGP seed layer, of the first layer is formed using at least one of Co, Ni, Fe and B.

5. The method according to claim 1, wherein the second crystalline ferromagnetic layer, which is the
10 PGGP seed layer, of the first layer is crystalline with a body-centered-cubic structure.

6. The method according to claim 1, wherein the second crystalline ferromagnetic layer, which is the
15 PGGP seed layer, of the first layer is deposited with (001) out-of-plane texture.

7. The method according to claim 1, wherein the second crystalline ferromagnetic layer, which is the
20 PGGP seed layer, of the first layer is formed with the thickness between 0.5 nm and 2 nm.

8. The method according to claim 1, wherein the thickness of the second crystalline ferromagnetic
25 layer, which is the PGGP seed layer, of the first layer is equal to or less than the thickness of the thickness of the first amorphous ferromagnetic layer

of the first layer.

9. The method according to claim 1, wherein the tunnel barrier layer deposition step comprises:

- 5 a first metal layer formation step of forming a first metal layer on the said second crystalline ferromagnetic layer, which is the PGGP seed layer, and
- a process step of performing an oxidation process
- 10 through the said first metal layer to form a metal-oxide layer, and
- a step of depositing a second metal cap layer onto the metal-oxide layer.

- 15 10. The method according to claim 9, the oxidation process includes radical oxidation, plasma oxidation, ozone oxidation and natural oxidation.

11. The method according to claim 9, wherein the
- 20 tunnel barrier is amorphous or microcrystalline with poor (001) out-of-plane texture.

12. The method according to claim 1, wherein the tunnel barrier layer deposition step comprises:
- 25 a metal-oxide layer formation step of forming a partly or fully oxidized metal-oxide layer on the second crystalline ferromagnetic layer, which is the

PGGP seed layer,
a process step of performing an oxidation process
through the metal oxide layer to form a fully
oxidized metal-oxide layer, and
5 a step of depositing a metal cap layer onto the fully
oxidized metal-oxide layer.

13. The method according to claim 12, the metal-oxide
formation process is reactive sputtering and the
10 oxidation process includes radical oxidation, plasma
oxidation, ozone oxidation and natural oxidation.

14. The method according to claim 12, wherein the
tunnel barrier prepared by reactive sputtering is
15 amorphous or microcrystalline with poor (001) out-of-
plane texture.

15. The method according to claim 1, wherein the
second layer is an amorphous layer, which is ternary
20 alloy containing Co, Fe and B.

16. The method according to claim 1, wherein the
second layer can also be prepared by the deposition
step which comprises:
25 a third crystalline ferromagnetic layer, which is the
PGGP seed layer, formation step of forming a third
crystalline ferromagnetic layer deposited on the

tunnel barrier layer, and
a fourth amorphous ferromagnetic layer formation step
of forming a fourth amorphous ferromagnetic layer
deposited on the third crystalline ferromagnetic
5 layer, which is the PGGP seed layer.

17. The method according to claim 16, wherein the
third crystalline ferromagnetic layer, which is the
PGGP seed layer, of the second layer is formed using
10 at least one of Co, Ni, Fe and B.

18. The method according to claim 16, wherein the
third crystalline ferromagnetic layer, which is the
PGGP seed layer, of the second layer is crystalline
15 with a body-centered-cubic structure.

19. The method according to claim 16, wherein the
third crystalline ferromagnetic layer, which is the
PGGP seed layer, of the second layer is deposited
20 with (001) out-of-plane texture.

20. The method according to claim 16, wherein the
third crystalline ferromagnetic layer, which is the
PGGP seed layer, of the second layer is formed with
25 the thickness between 0.5 nm and 2 nm.

21. The method according to claim 16, wherein the

fourth amorphous ferromagnetic layer of the second layer is ternary alloy containing Co, Fe and B.

22. The method according to claim 16, wherein the
5 fourth amorphous ferromagnetic layer of the second layer is formed with the thickness between 1 nm and 4 nm.

23. The method according to claim 1, further
10 comprising:
a ferromagnetic pinned layer deposition step of depositing a ferromagnetic pinned layer; and
a non-magnetic spacer layer deposition step of depositing a non-magnetic spacer layer,
15 wherein the first layer is deposited as a ferromagnetic reference layer on the ferromagnetic pinned layer.

24. The method according to claim 23, wherein the
20 ferromagnetic pinned layer is amorphous ferromagnetic pinned layer, which is ternary alloy containing Co, Fe and B.

25. The method according to claim 23, wherein the
25 ferromagnetic pinned layer can also be prepared by the deposition step comprises:
a first amorphous ferromagnetic pinned layer

formation step of forming a first amorphous
ferromagnetic pinned layer, and
a second crystalline ferromagnetic pinned layer
formation step of forming a second crystalline
5 ferromagnetic pinned layer deposited on the first
amorphous ferromagnetic pinned layer.

26. The method according to claim 25, wherein the
second crystalline ferromagnetic pinned layer of the
10 said ferromagnetic pinned layer is formed using at
least one of Co, Ni, Fe and B.

27. The method according to claim 25, wherein the
first amorphous ferromagnetic pinned layer of the
15 said ferromagnetic pinned layer is ternary alloy
containing Co, Fe and B.

28. The method according to claim 25, wherein the
first amorphous ferromagnetic pinned layer of the
20 ferromagnetic pinned layer is formed with the
thickness between 0.5 nm and 2 nm.

29. The method according to claim 25, wherein the
second crystalline ferromagnetic pinned layer of the
25 said ferromagnetic pinned layer is formed with the
thickness between 1 nm and 4 nm.

30. The method according to claim 1, further comprising;

a process of the crystallization of the first amorphous ferromagnetic layer and grain growth of the tunnel barrier layer which is amorphous or microcrystalline with poor (001) out-of-plane texture.

31. The method according to claim 30, wherein the process of the crystallization of the first amorphous ferromagnetic layer and the preferred grain growth of the said tunnel barrier layer is carried out through vacuum annealing, and vacuum annealing condition is 300 °C ~ 400 °C, 1 - 4 hours under magnetic field of 3 - 10 kOe.

15

32. The method according to claim 30, wherein the crystallization of the first amorphous ferromagnetic layer and the preferred grain growth of the tunnel barrier layer is realized using the second crystalline ferromagnetic layer, which is the PGGP seed layer, as adjacent crystallization or grain growth seed layer during annealing, thus eventually overall (001) out-of-plane texture of the first layer and tunnel barrier layer is achieved.

25

33. A method of manufacturing a magnetic tunnel junction device, the method comprising:
a first layer deposition step of depositing a first layer which contains ferromagnetic material, which
5 comprises
a first step of forming a first amorphous ferromagnetic layer, and
a second step of forming a second crystalline layer on the first amorphous ferromagnetic layer;
10 a tunnel barrier layer deposition step of depositing a tunnel barrier layer which is amorphous or microcrystalline with poor (001) out-of-plane texture, and
a process of crystallizing of the first layer and
15 grain growth of the tunnel barrier layer.

34. A method of manufacturing a magnetic tunnel junction device, the method comprising:
a first layer deposition step of depositing a first
20 layer which contains ferromagnetic material, which comprises
a first step of forming a first amorphous ferromagnetic layer, and
a second step of forming a second crystalline
25 ferromagnetic layer on the first amorphous ferromagnetic layer;
a tunnel barrier layer deposition step of depositing

a tunnel barrier layer which consists of metal-oxide
onto the lower ferromagnetic layer, wherein the
tunnel barrier layer deposition step comprises
a metal layer formation step of forming a metal layer
5 onto the second ferromagnetic layer,
a process step of performing an oxidation process
through the metal layer to form a metal-oxide layer;
and
a process of crystallizing or preferred grain growth
10 of the first layer and the tunnel barrier layer.

35. A method of manufacturing a magnetic tunnel
junction device, the method comprising:
a first layer deposition step of depositing a first
layer which contains ferromagnetic material, which
15 comprises:
a first step of forming a first amorphous
ferromagnetic layer, and
a second step of forming a second crystalline
ferromagnetic layer on the first amorphous
20 ferromagnetic layer;
a tunnel barrier layer deposition step of depositing
a tunnel barrier layer which consists of metal-oxide
onto the lower ferromagnetic layer, wherein the
tunnel barrier layer deposition step comprises:
25 a metal-oxide layer formation step of forming a
partly or fully oxidized metal-oxide layer on the
second ferromagnetic layer,

a process step of performing an oxidation process through the metal oxide layer to form a fully oxidized metal-oxide layer; and
a process of crystallizing or preferred grain growth
5 of the first layer and the tunnel barrier layer.

36.A method of manufacturing a magnetic tunnel junction device, the method comprising:
a free layer deposition step of depositing a free layer which contains ferromagnetic material;
10 a reference layer deposition step of depositing a reference layer which contains ferromagnetic material;
a tunnel barrier layer deposition step of depositing a tunnel barrier layer between the free layer and
15 reference layer;
a non-magnetic spacer layer deposition step of depositing a non-magnetic spacer layer which contacts the reference layer ;and
a ferromagnetic pinned layer deposition step of
20 depositing a ferromagnetic pinned layer which contacts the non-magnetic spacer layer,
wherein the ferromagnetic pinned layer deposition step comprises:
a crystalline ferromagnetic pinned layer formation
25 step of forming a crystalline ferromagnetic pinned layer which contacts the non-magnetic spacer layer,
and

an amorphous ferromagnetic pinned layer formation step of forming an amorphous ferromagnetic pinned layer which contacts the crystalline ferromagnetic pinned layer.

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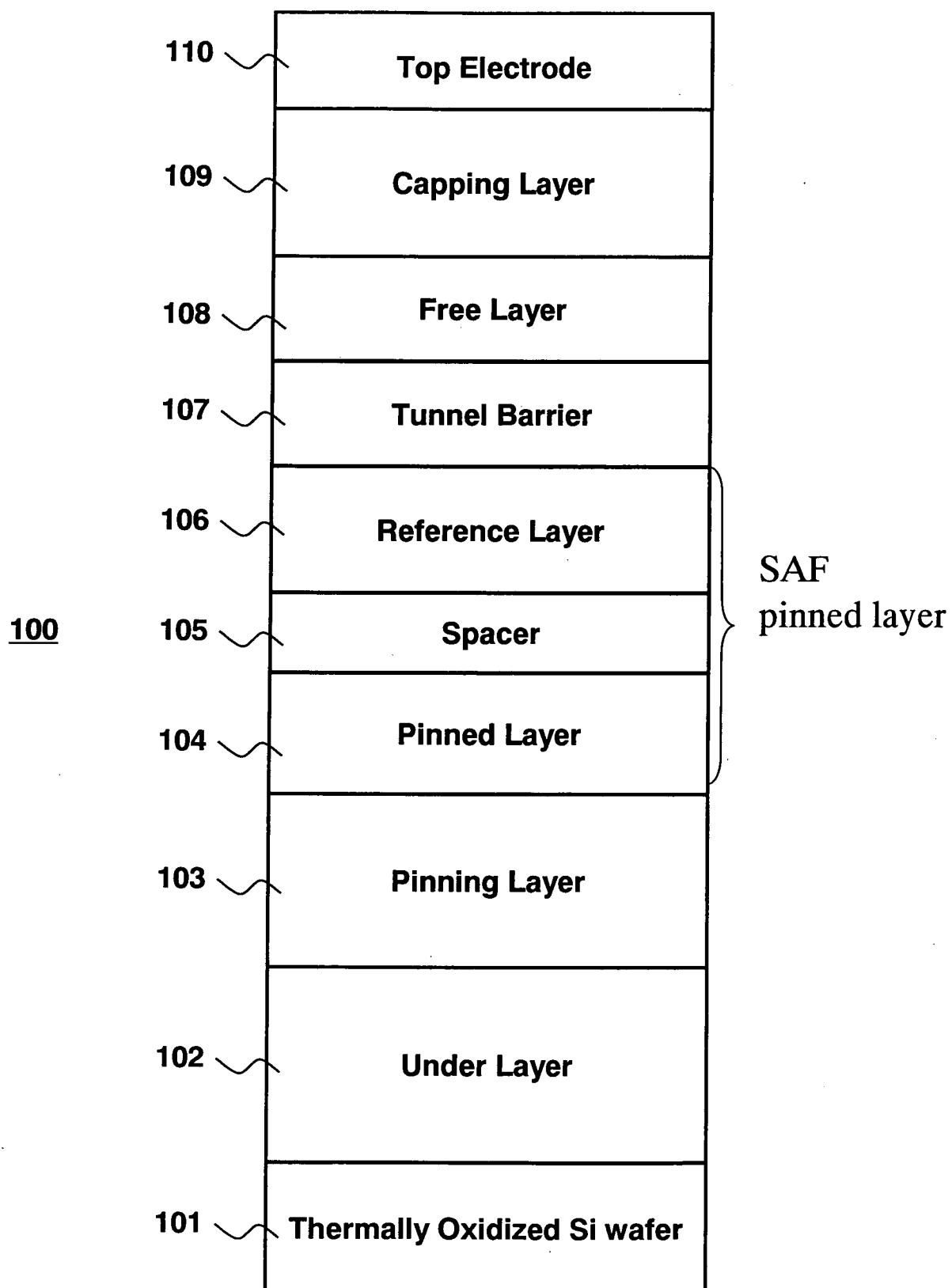
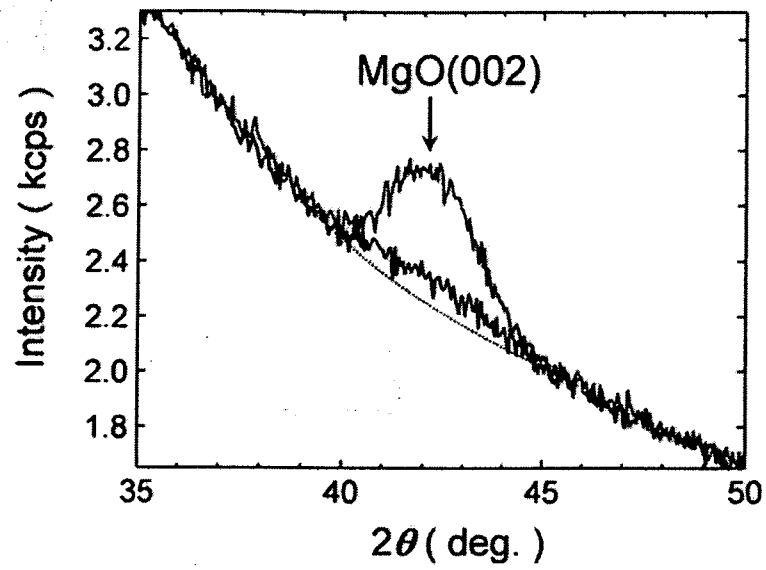
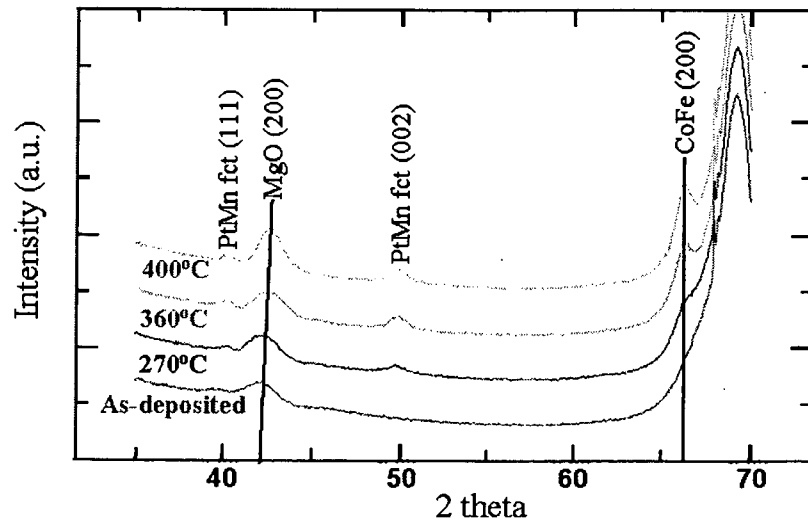


Fig. 1

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**Fig.2A****Fig.2B**

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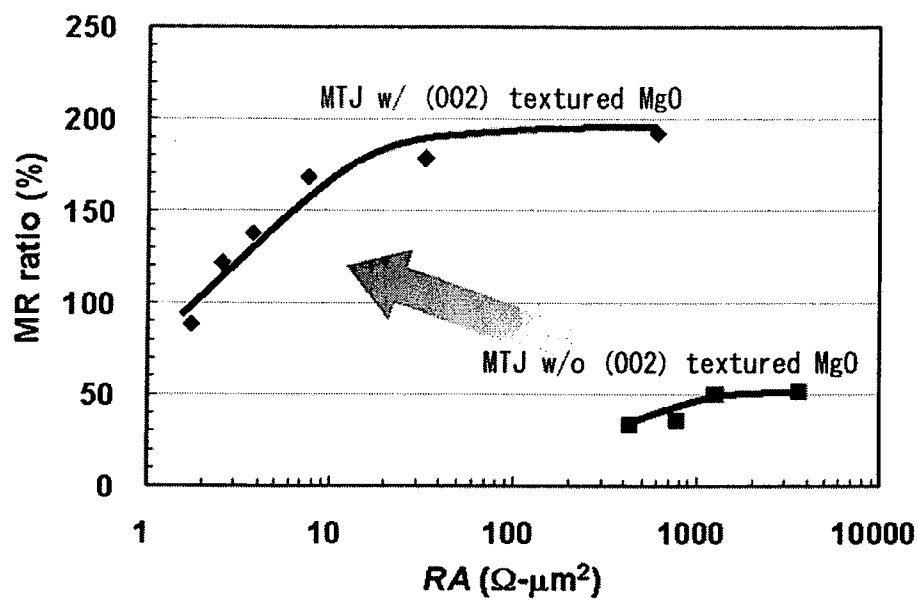


Fig.2C

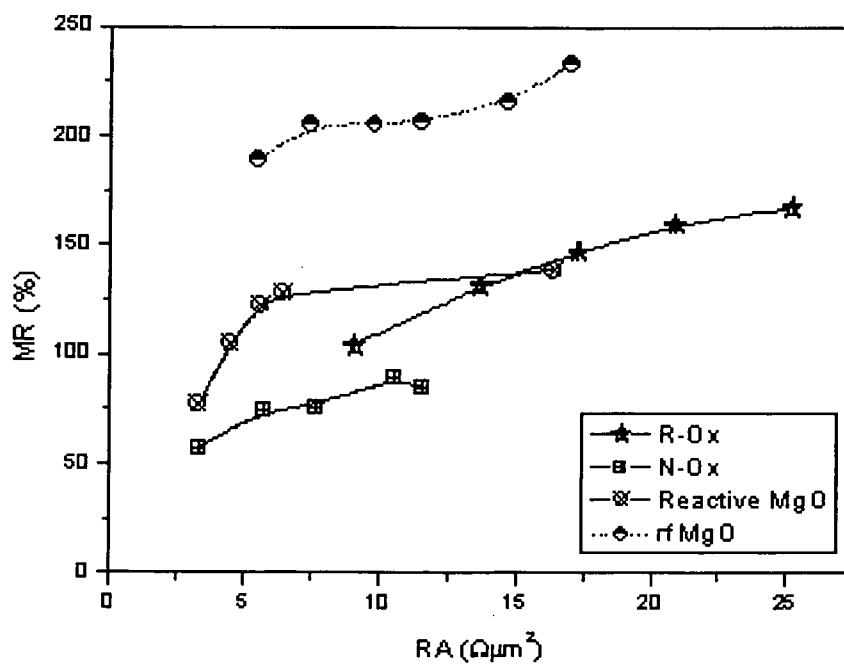


Fig. 3

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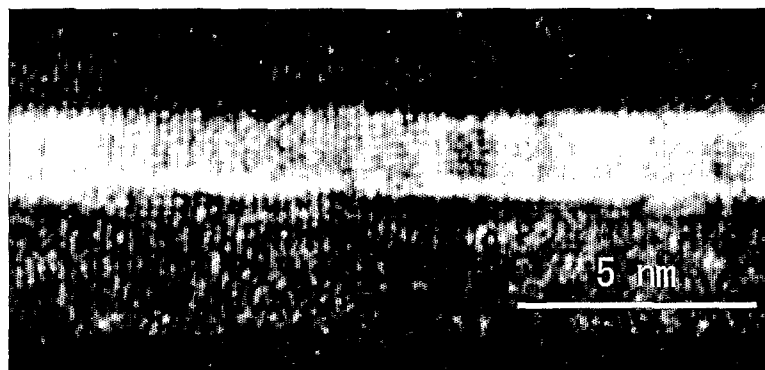


Fig.4A

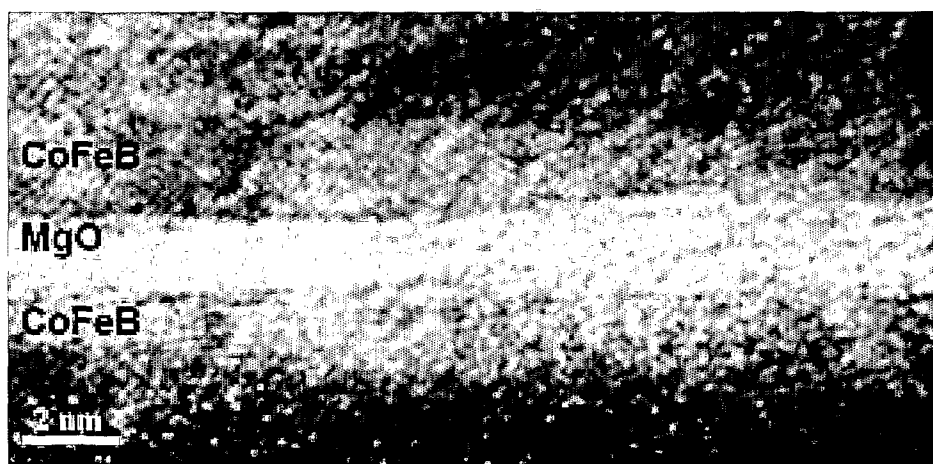
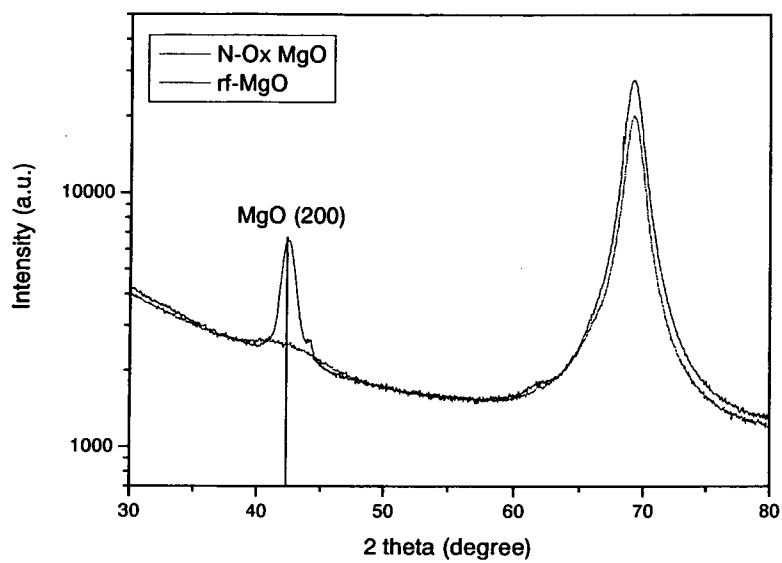


Fig.4B

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**Fig.4C**

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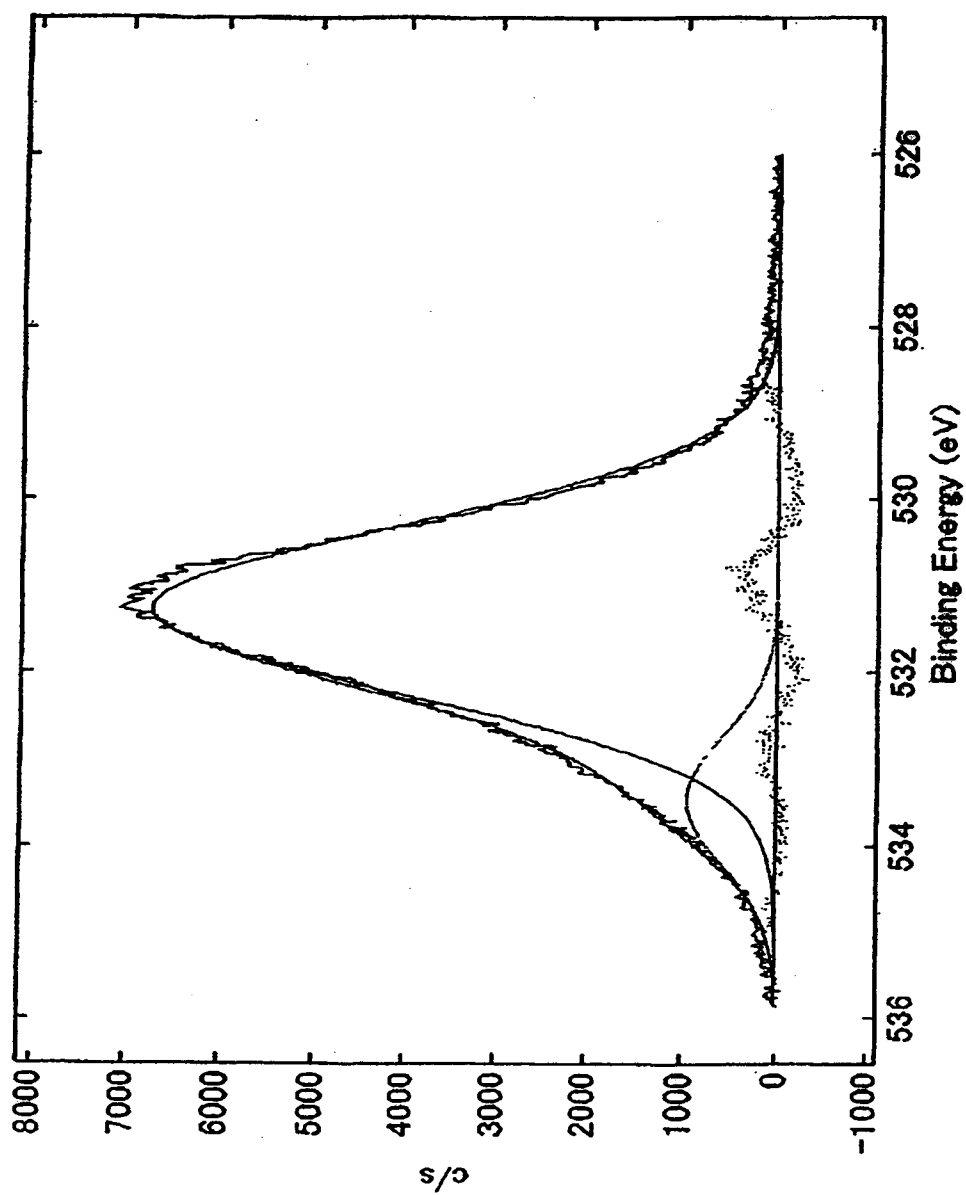


Fig.4D

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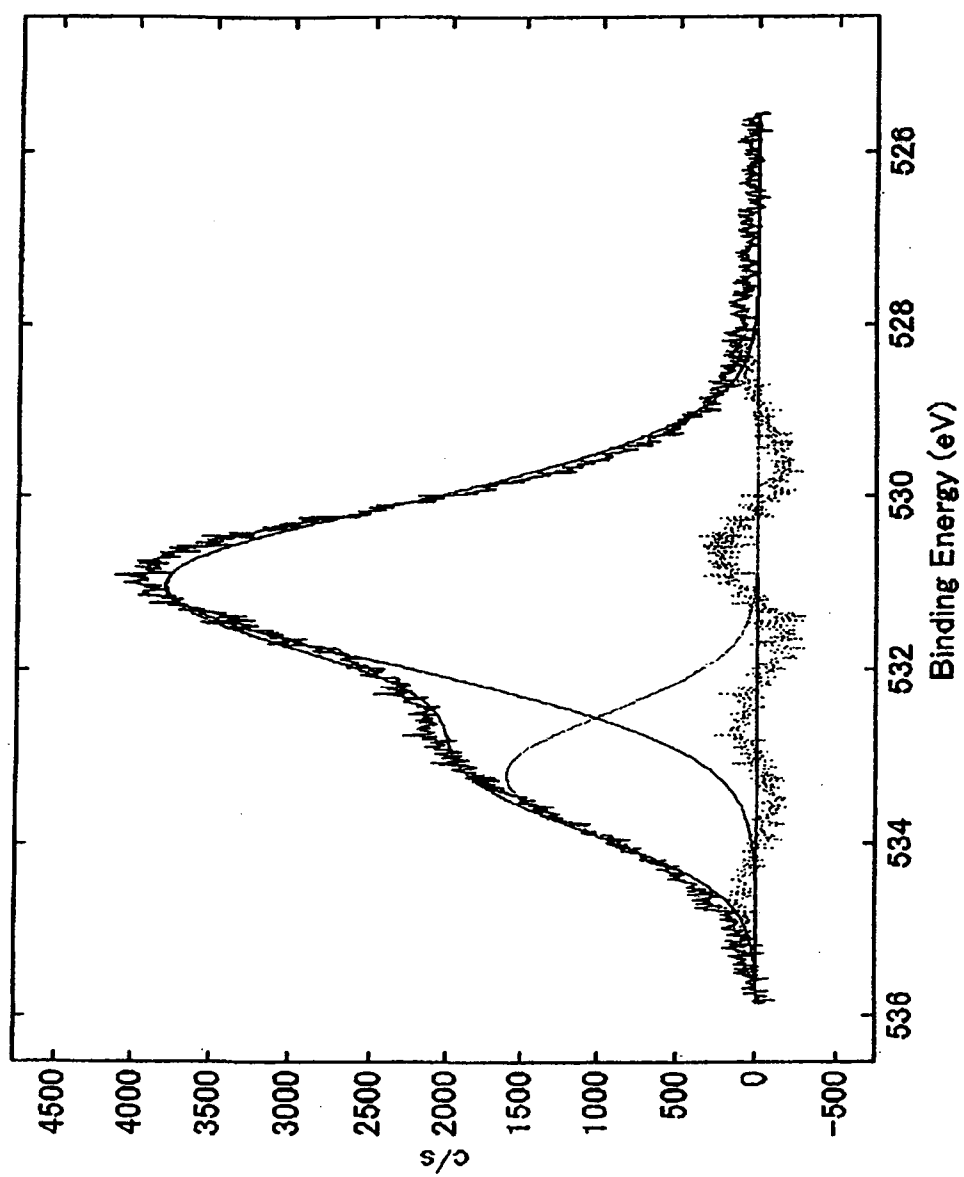
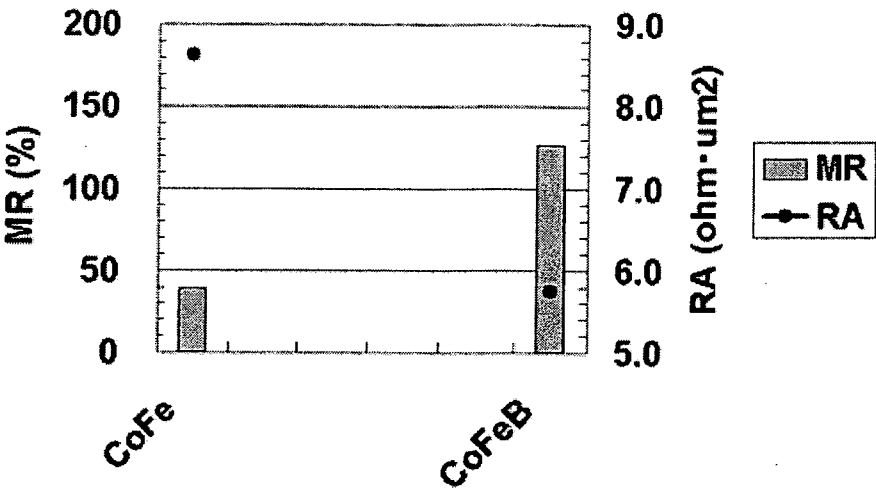


Fig.4E



Reference layer
Fig.5A

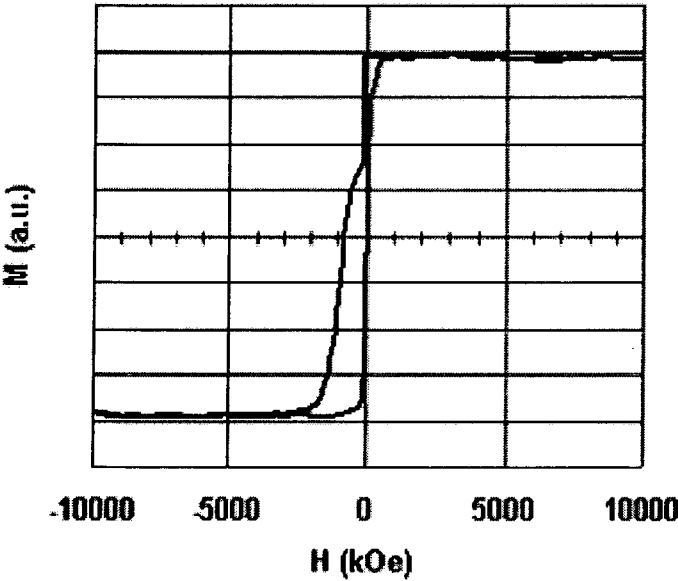


Fig.5B

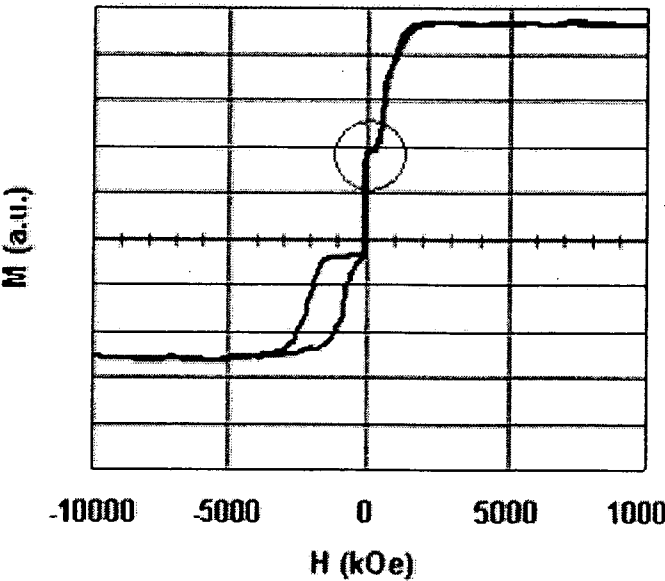
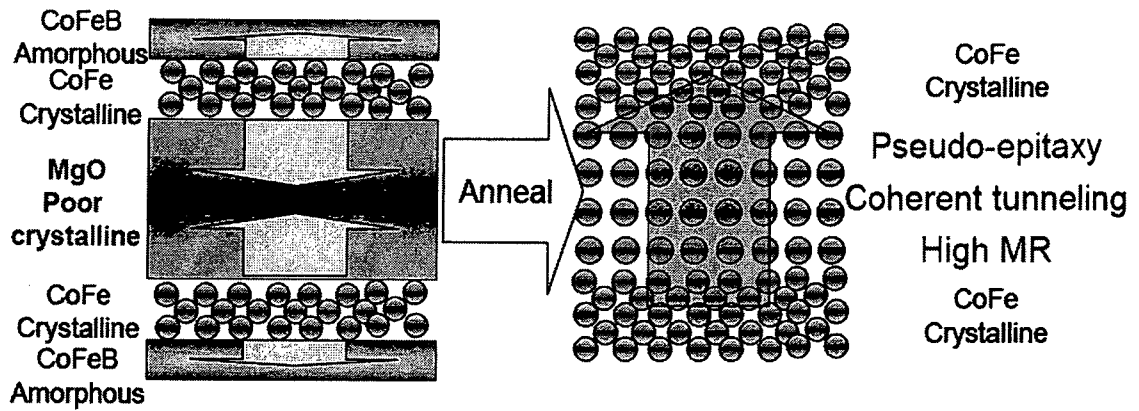
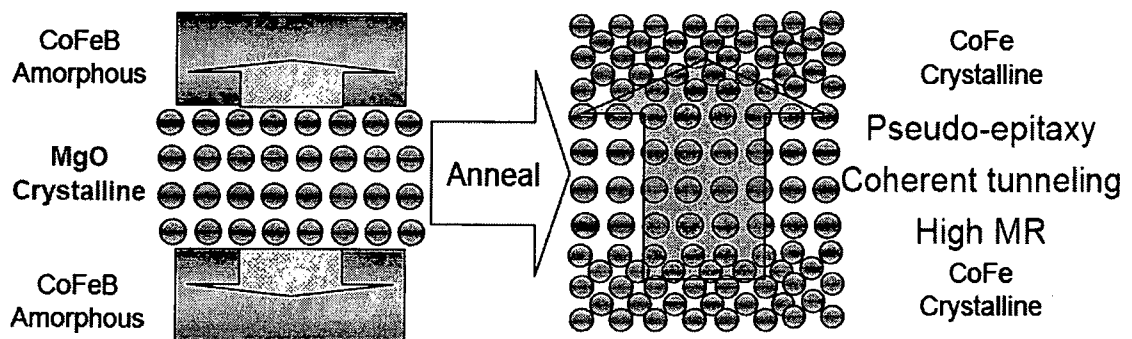


Fig.5C

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**Fig.6A****Fig.6B**

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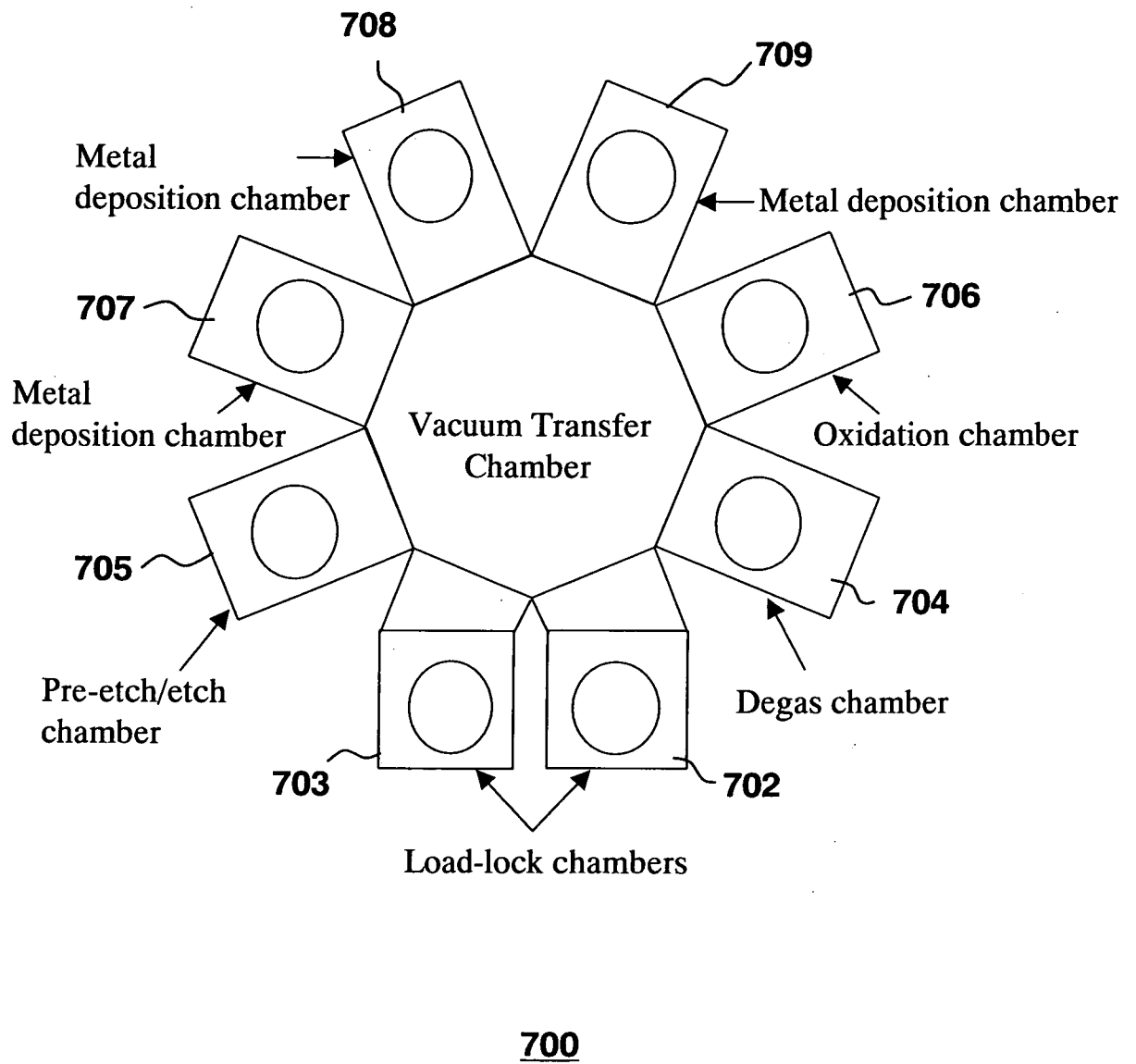


Fig. 7

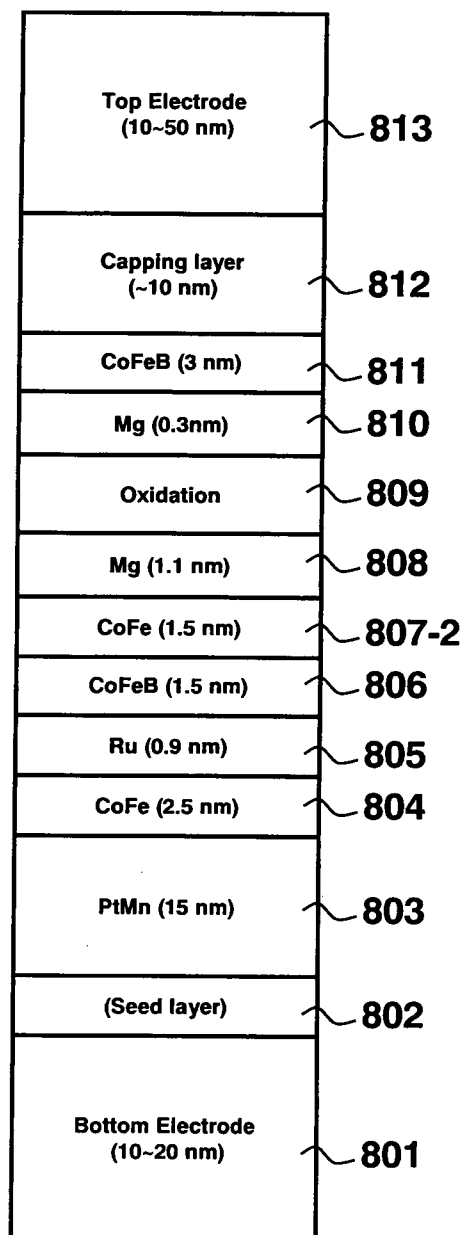


Fig.8A

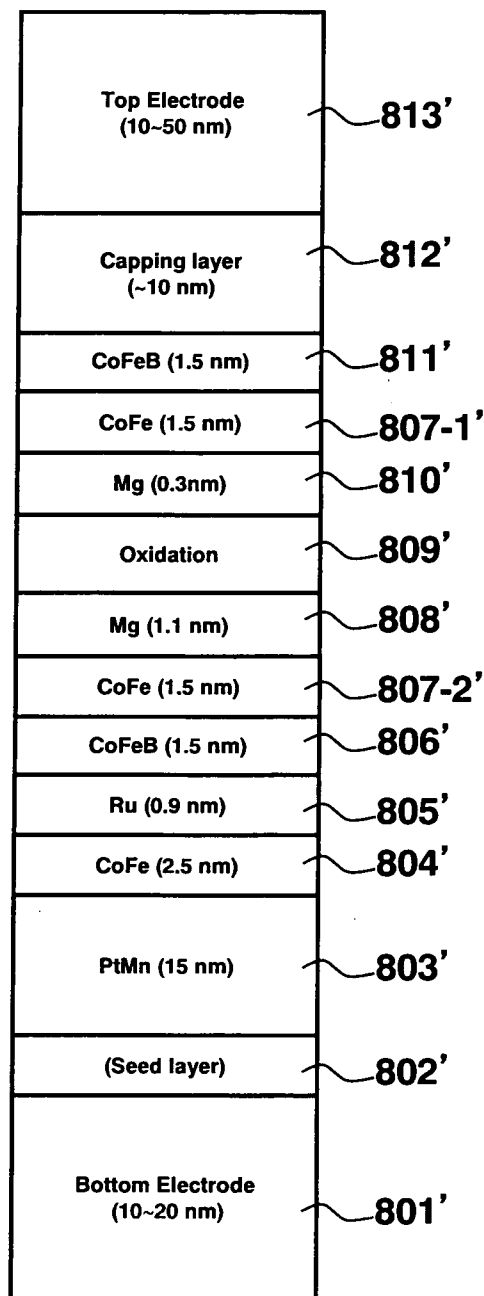


Fig.8B

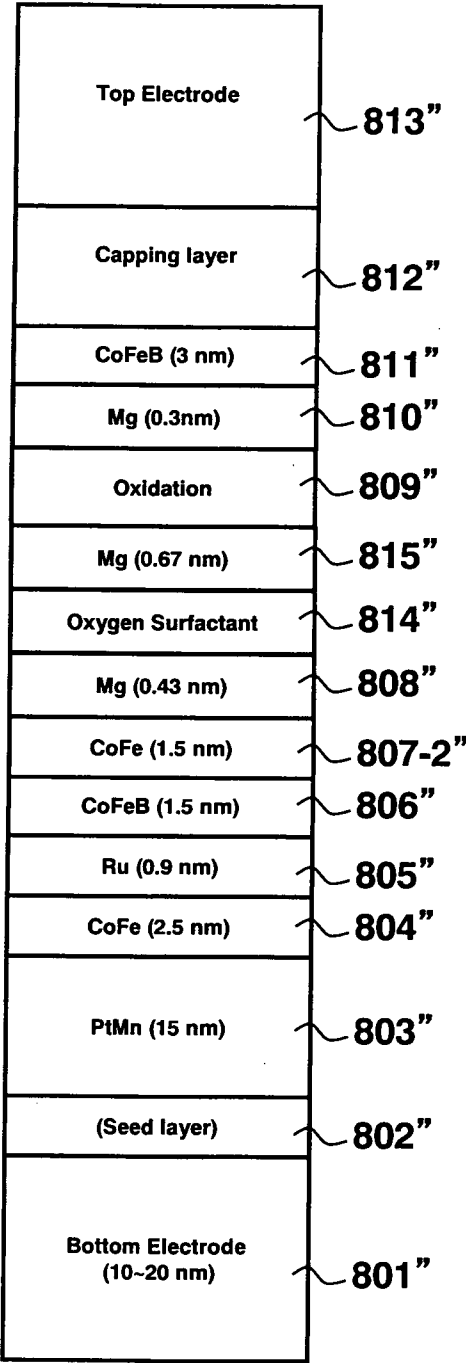


Fig.8C

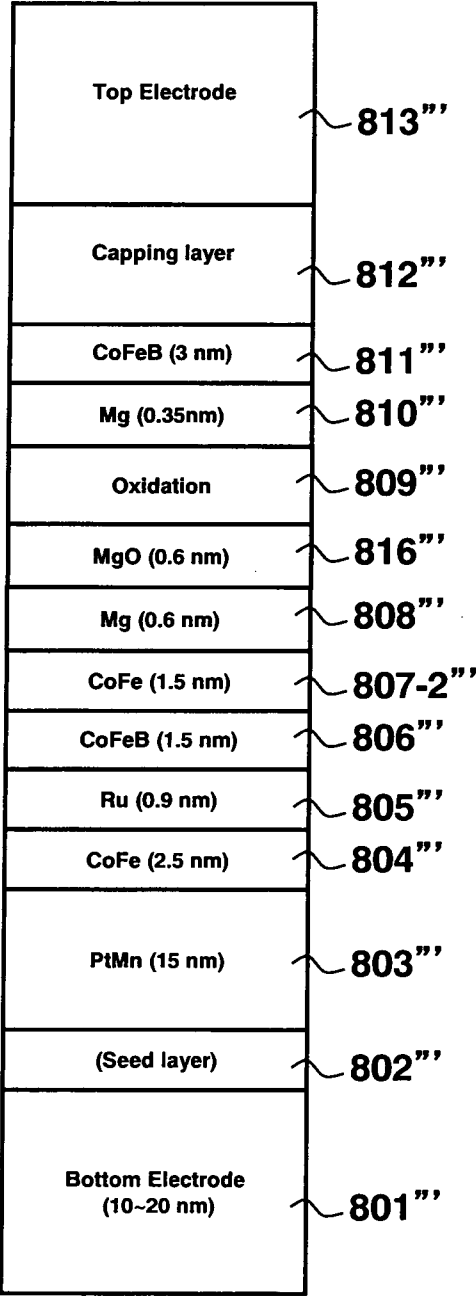


Fig.8D

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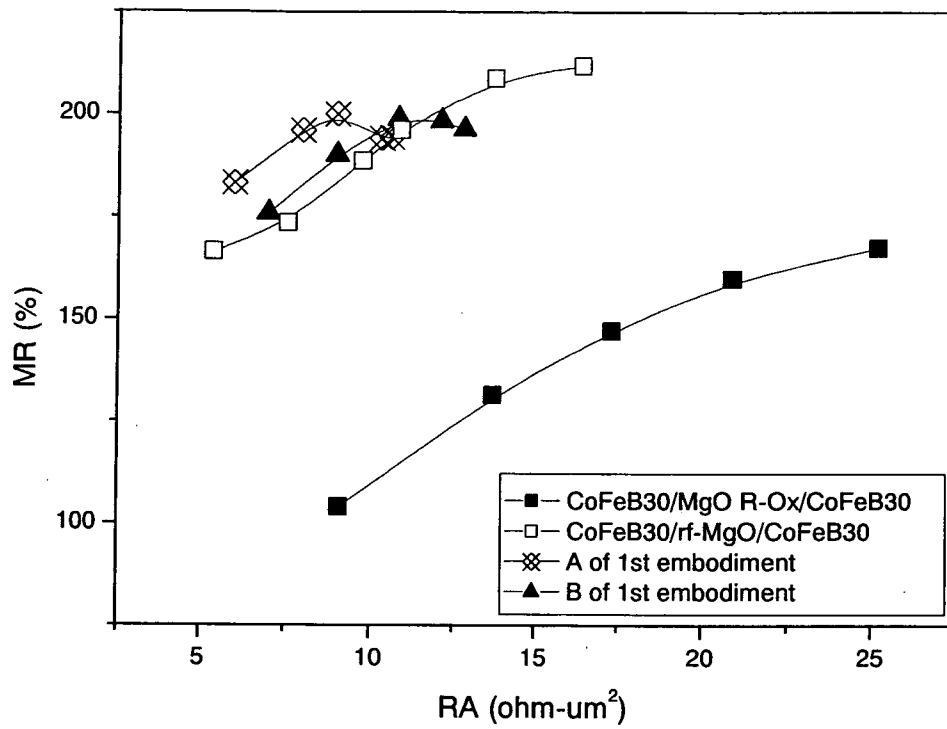


Fig.9A

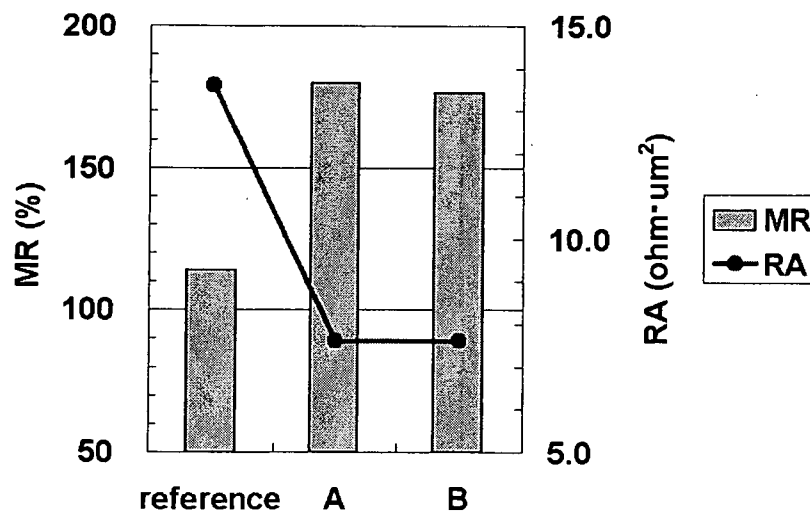


Fig.9B

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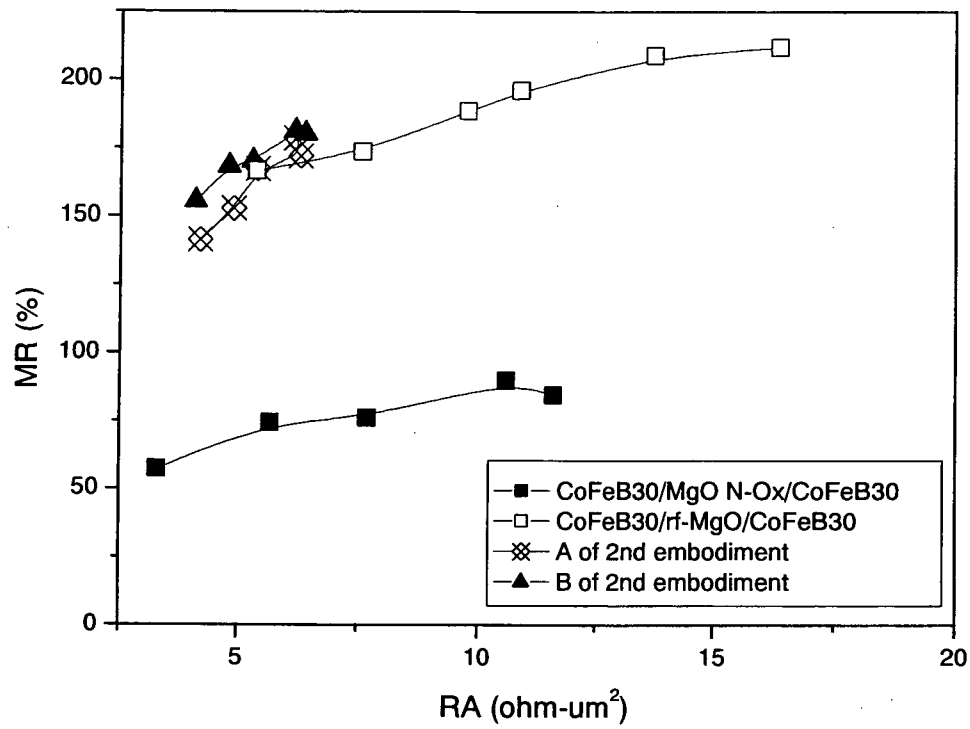


Fig.10A

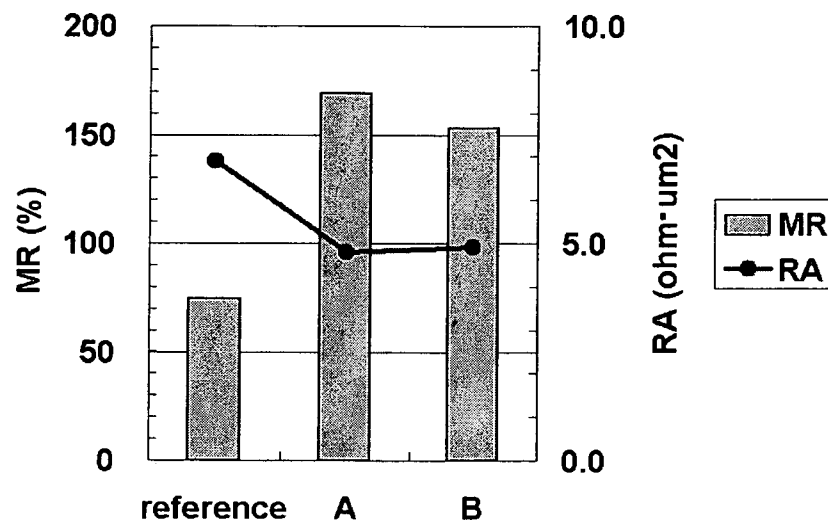


Fig.10B

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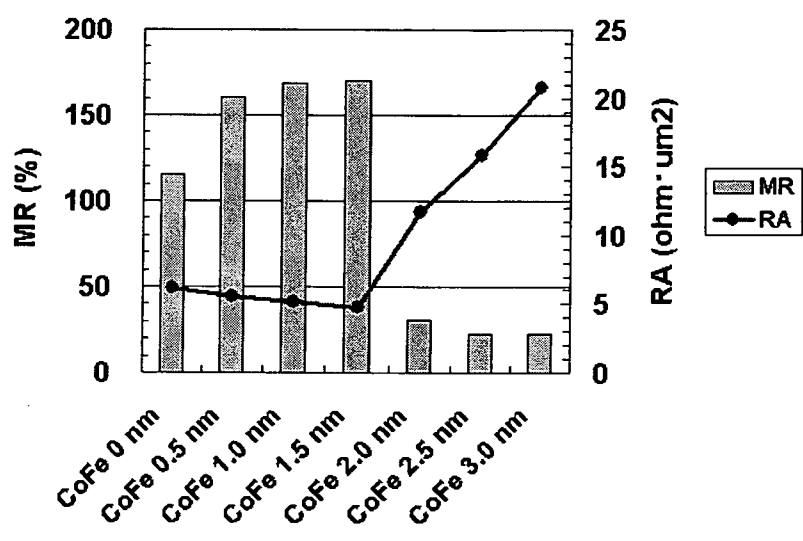


Fig. 11

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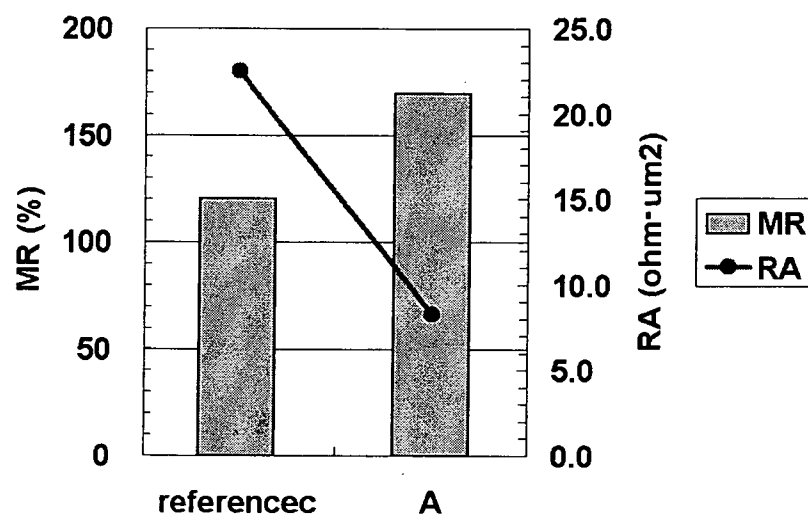


Fig. 12

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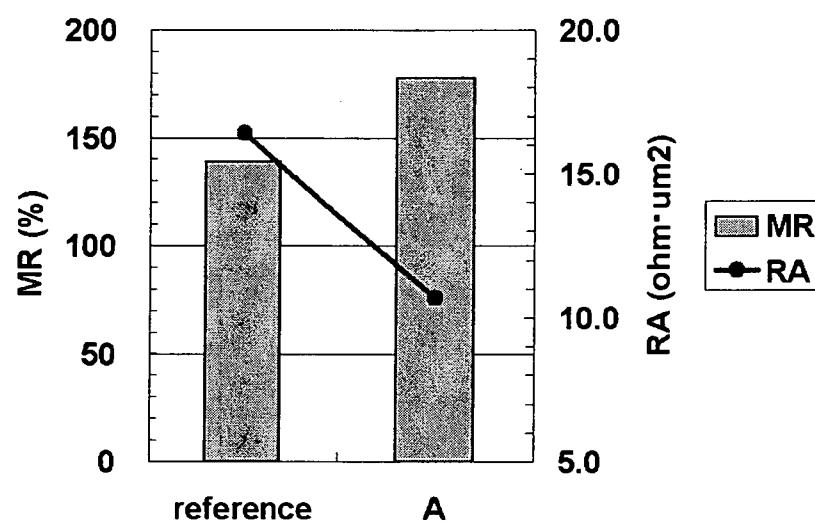


Fig. 13

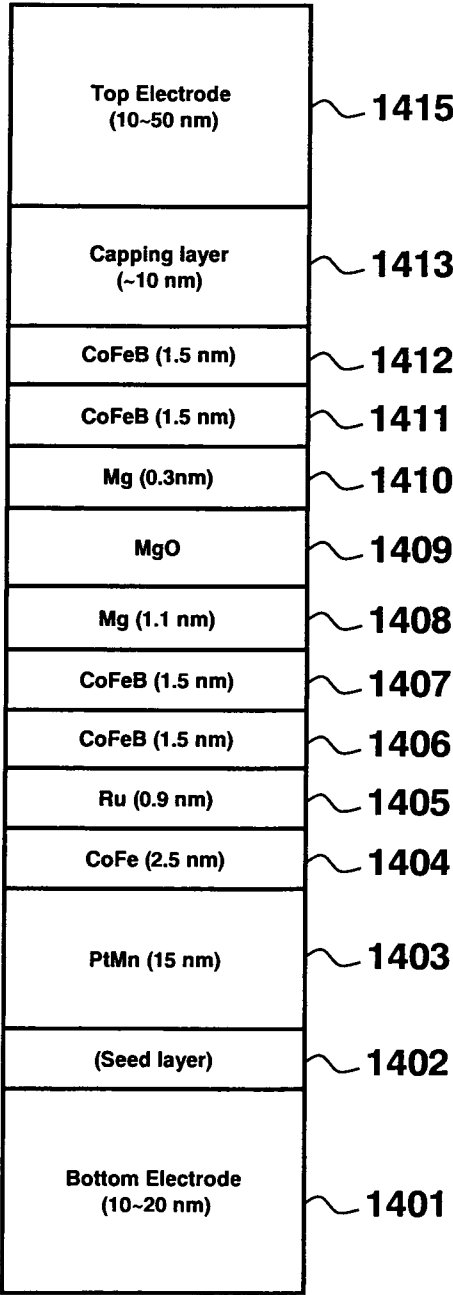


Fig. 14

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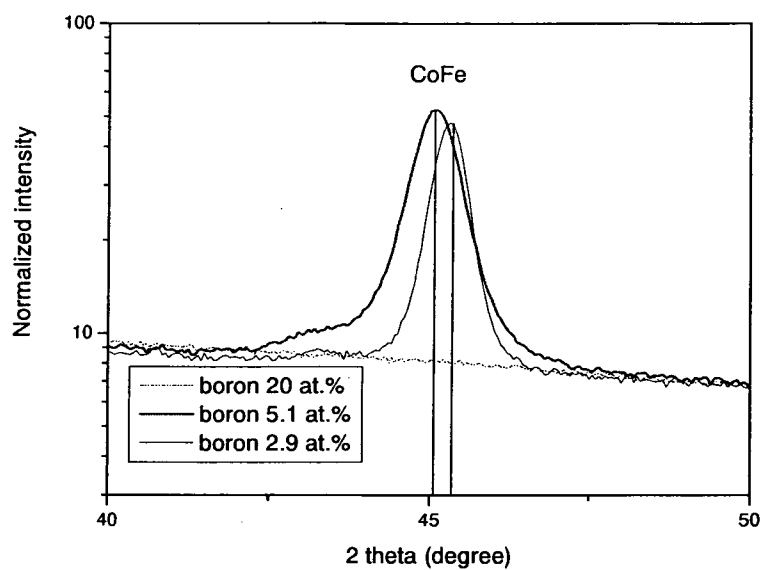


Fig.15A

Boron content	2 theta	FWHM*	Resistivity ($\mu\Omega\text{-cm}$)
2.9 at. %	45.35	0.593	20.59
5.1 at. %	45.02	0.820	43.16
20 at. %	No peak	N/A	111.47

*FWHM : Full Width at Half Maximum

Fig.15B

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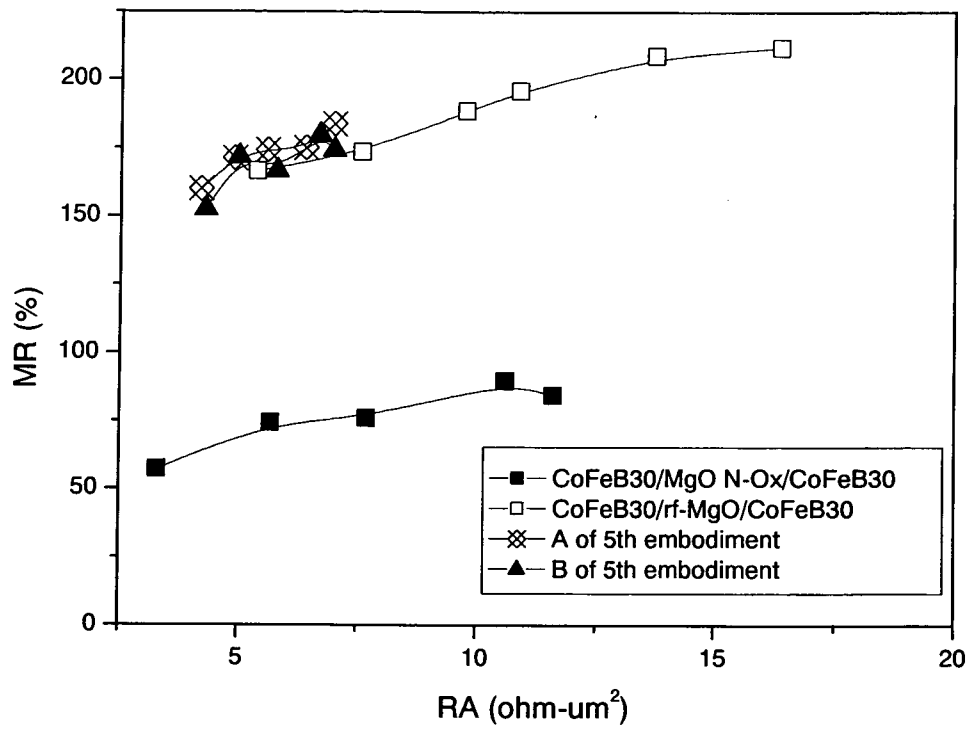


Fig.16A

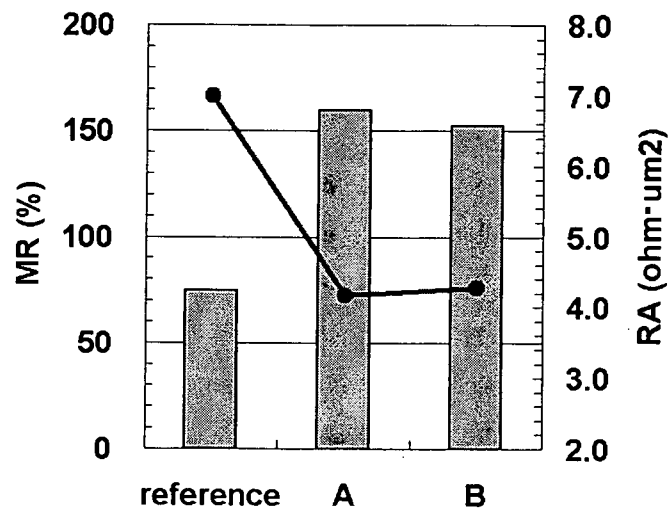


Fig.16B

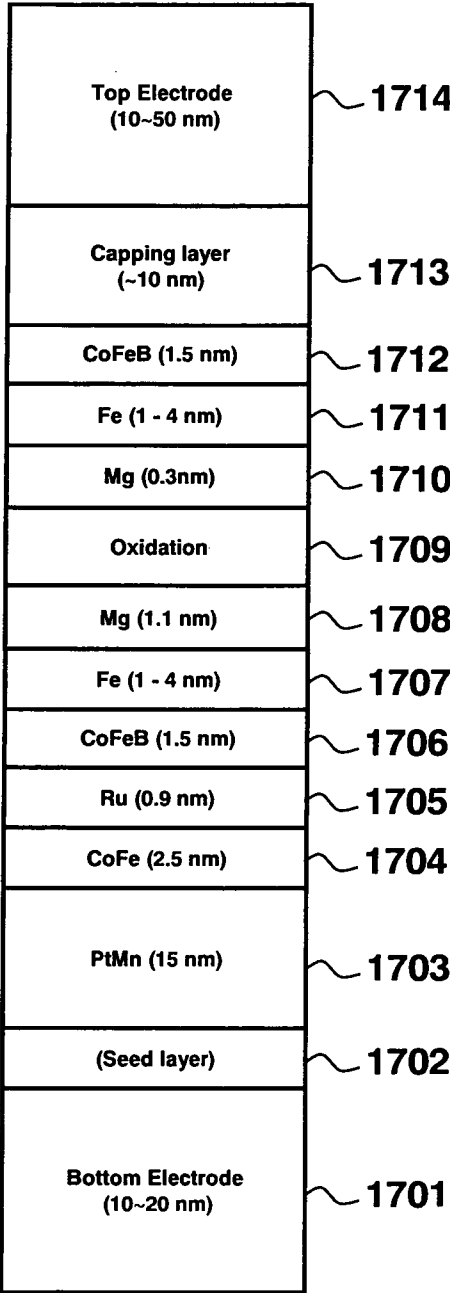


Fig. 17

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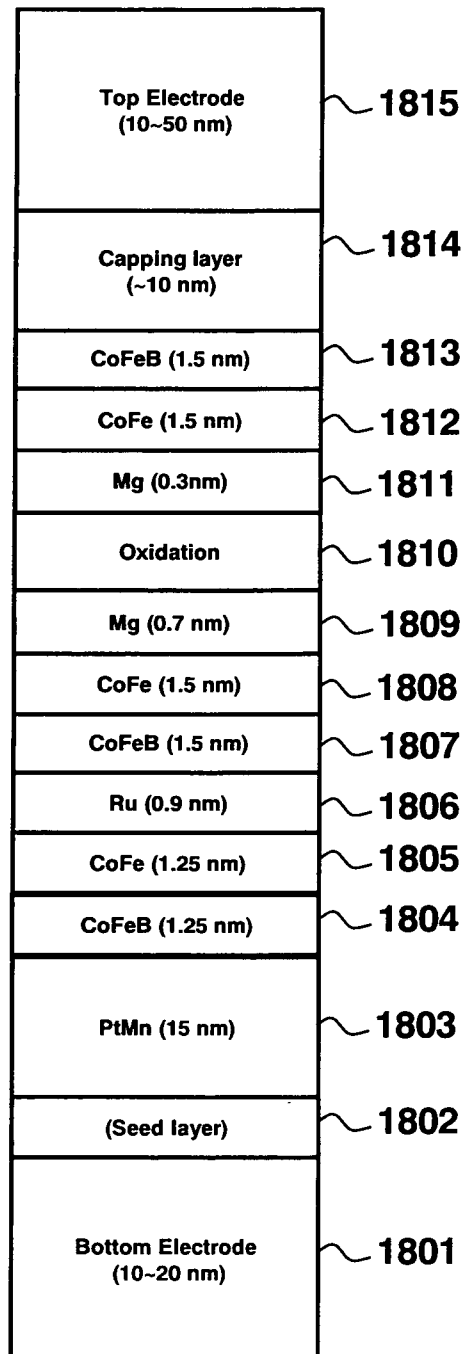


Fig. 18

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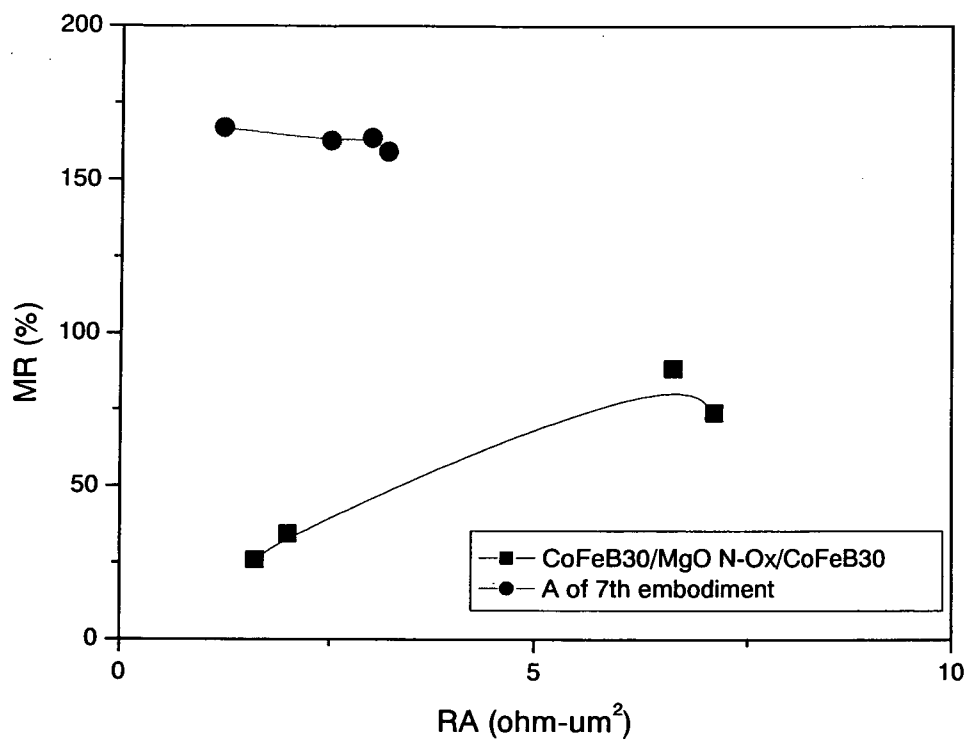


Fig. 19

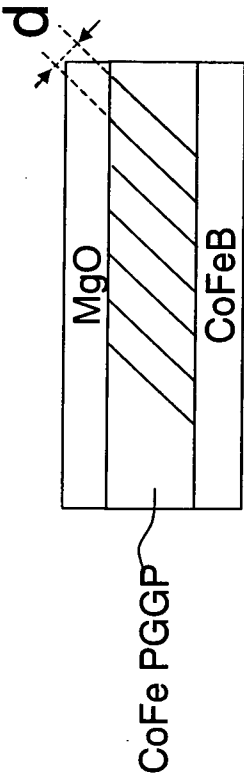
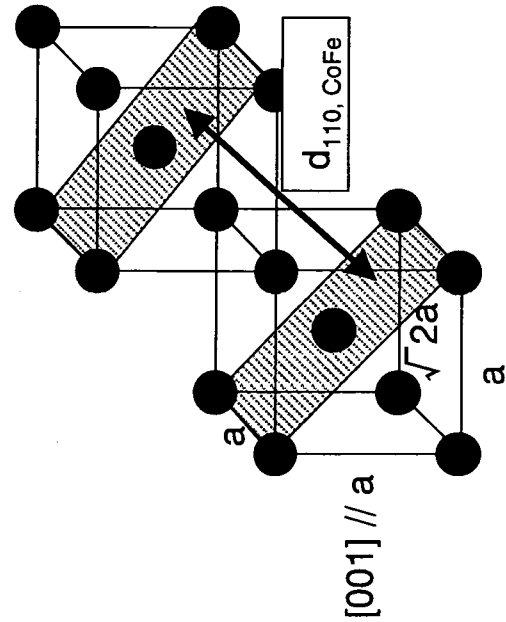
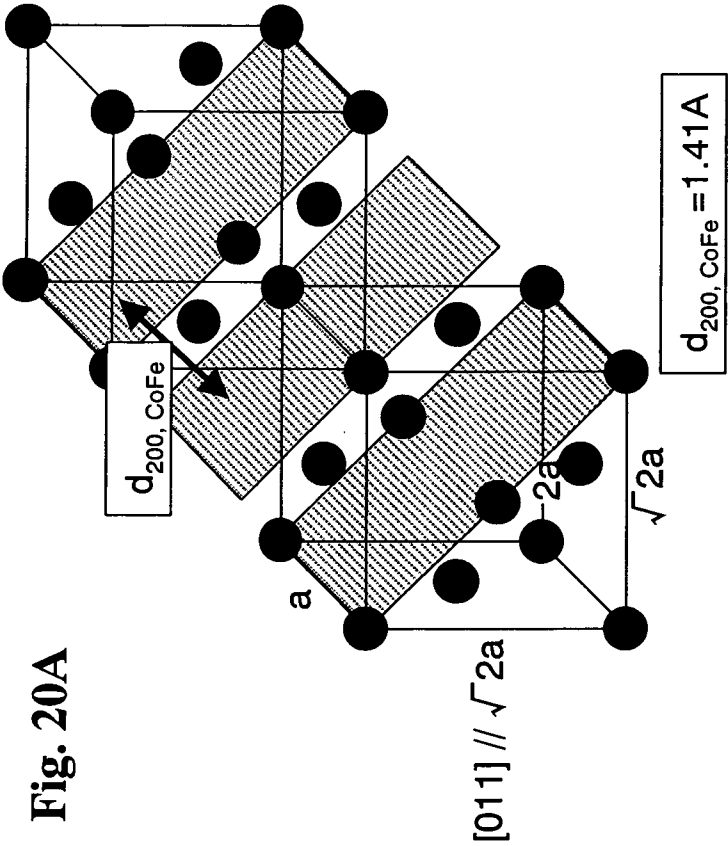


Fig. 20A



$d_{110, \text{CoFe}} = 2.02\text{\AA}$

Fig. 20B



$d_{200, \text{CoFe}} = 1.41\text{\AA}$

Fig. 20C

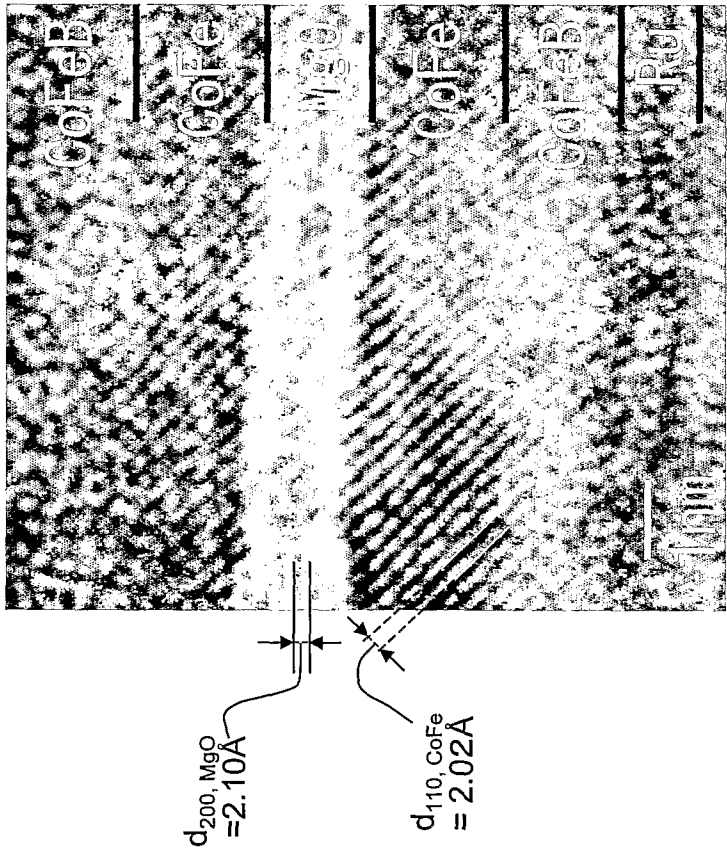


Fig. 21

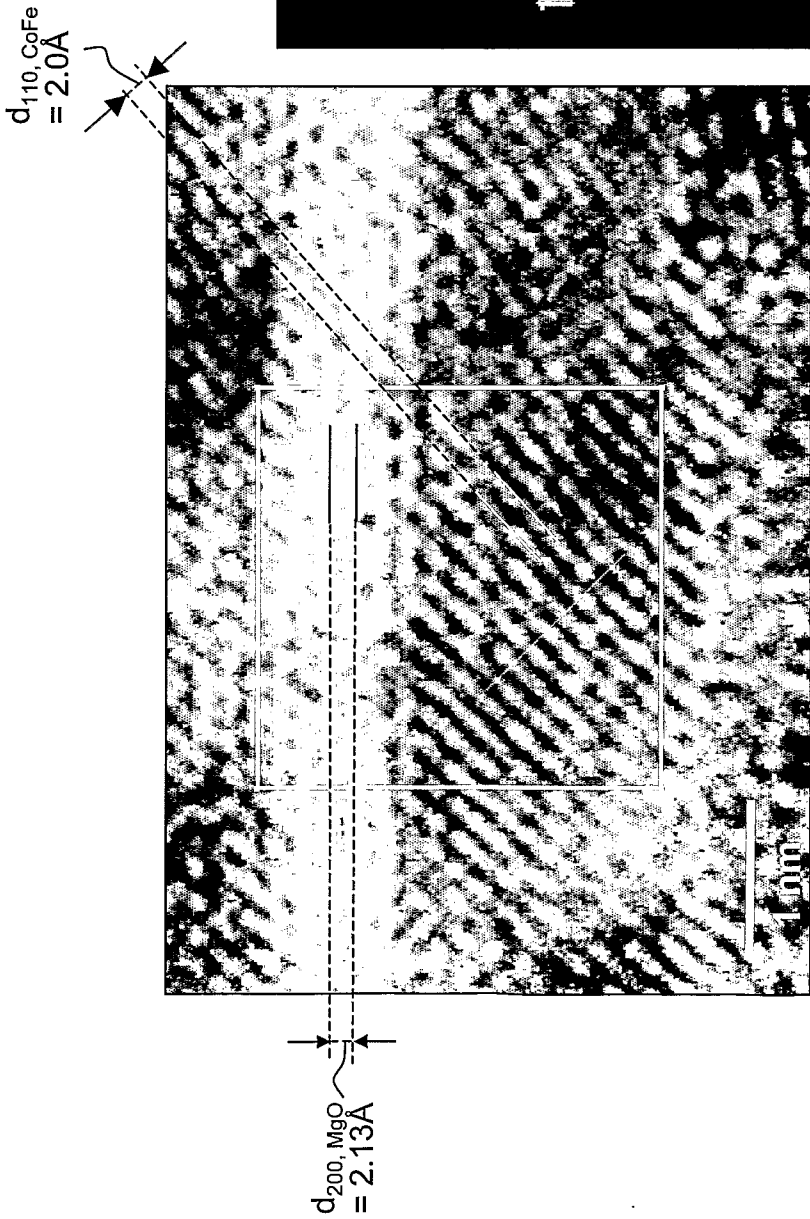


Fig. 22A

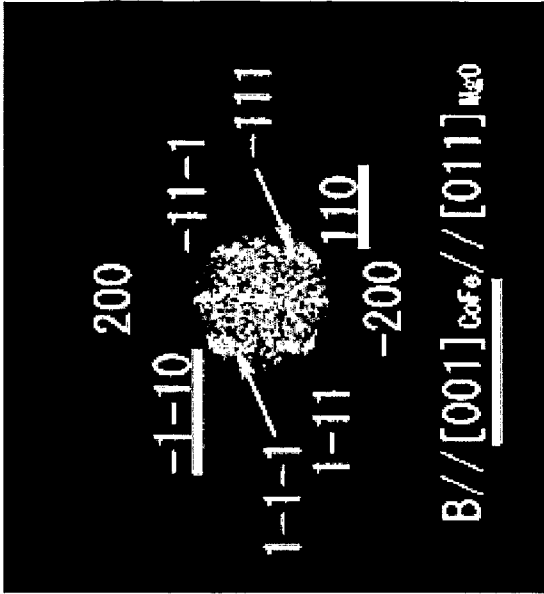


Fig. 22B

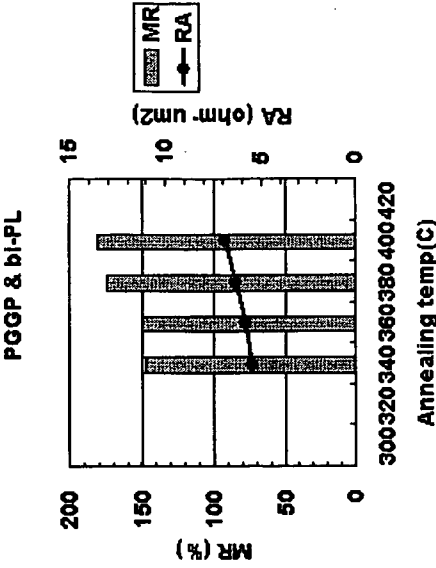


Fig.23C

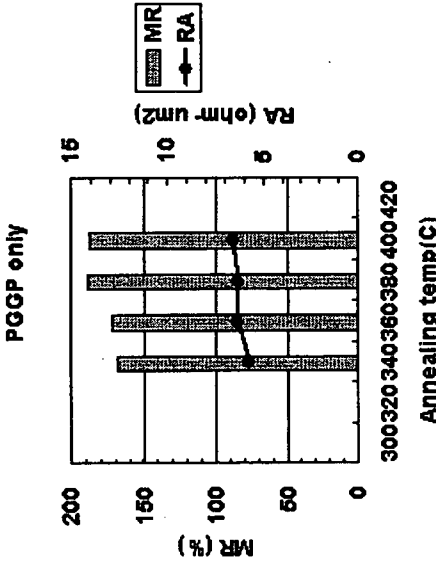


Fig.23B

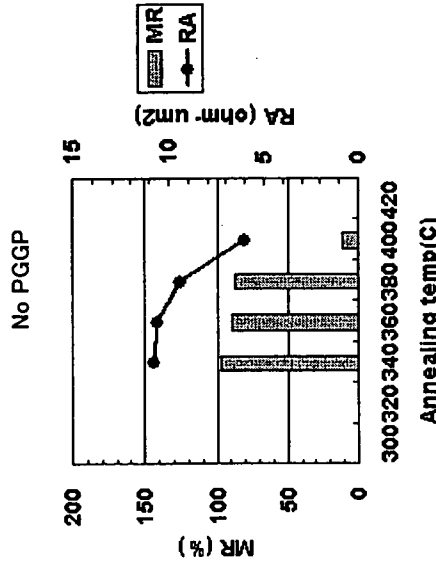


Fig.23A

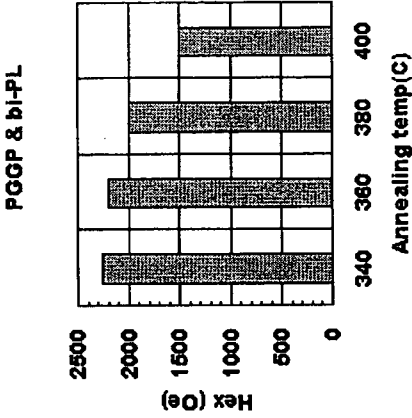


Fig.23F

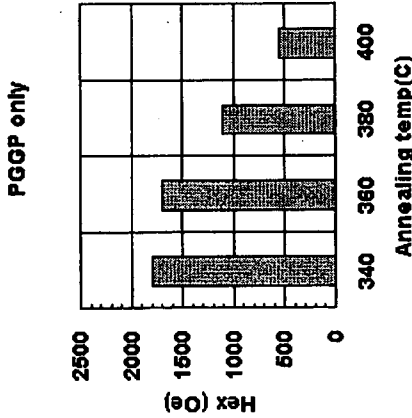


Fig.23E

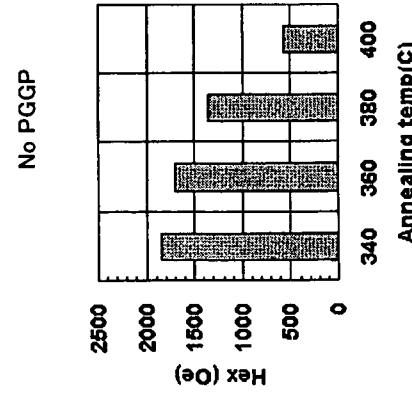


Fig.23D

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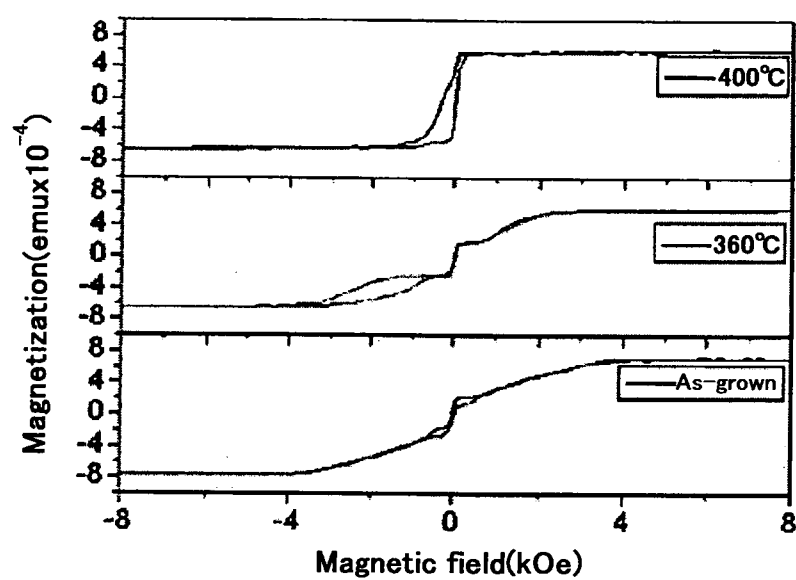
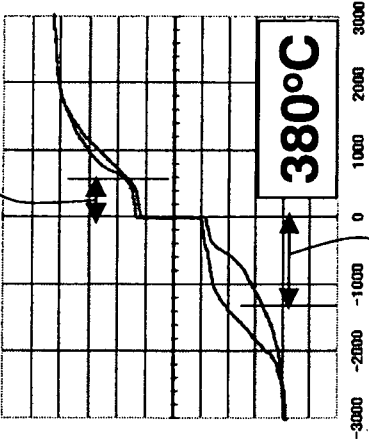


Fig. 24

SAF plateau



H_{ex}

Fig. 25A

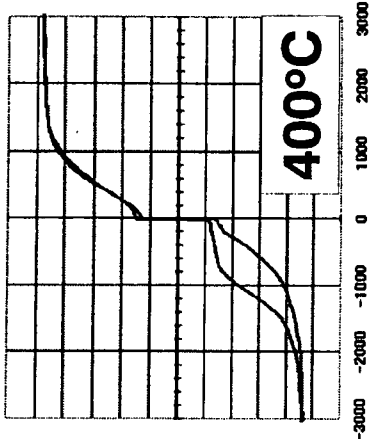


Fig. 25B

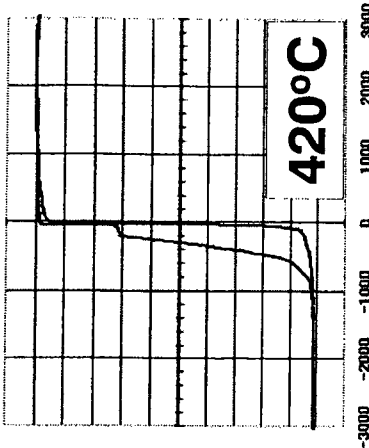


Fig. 25C

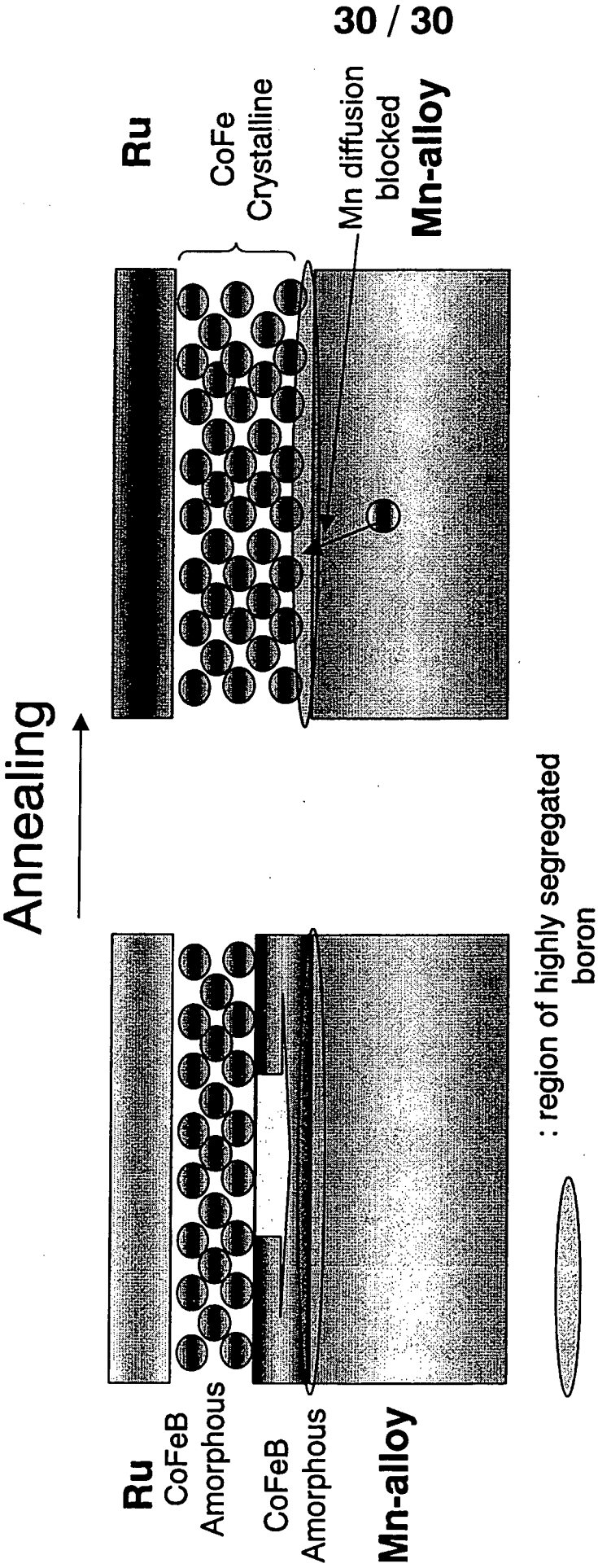


Fig. 26

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/058948

A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. H01L43/12 (2006.01) i, G11B5/39 (2006.01) i, H01L21/8246 (2006.01) i,
H01L27/105 (2006.01) i, H01L43/08 (2006.01) i, H01L43/10 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int.Cl. H01L43/12, G11B5/39, H01L21/8246, H01L27/105, H01L43/08, H01L43/10

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Published examined utility model applications of Japan 1922-1996
Published unexamined utility model applications of Japan 1971-2009
Registered utility model specifications of Japan 1996-2009
Published registered utility model applications of Japan 1994-2009

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2008-507854 A (freescall semiconductor incorporated) 2008.03.13, a whole document	1-4, 7, 8, 15-17, 20-23
Y	& US 2006/0017081 A1 & WO 2006/023018 A2	5, 6, 9-14, 18, 19, 24, 30, 32-35
A		25-29, 31, 36
Y	JP 2007-150265 A (TOSHIBA CORPORATION) 2007.06.14, a whole document	5, 6, 9-14, 18, 19, 30, 32-35
A	& US 2007/0096229 A1	1-4, 7, 8, 15-17, 20-29, 31, 36
Y	JP 2008-166533 A (TDK CORPORATION) 2008.07.17, a whole document	9-11
A	& US 2008/0160326 A1	1-8, 12-36



Further documents are listed in the continuation of Box C.



See patent family annex.

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“&” document member of the same patent family

Date of the actual completion of the international search

13.08.2009

Date of mailing of the international search report

25.08.2009

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2009/058948

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y A	JP 2007-165786 A (TOSHIBA CORPORATION) 2007.06.28, a whole document (No Family)	12-14 1-11, 15-36
Y A	JP 2006-210391 A (Japan Science and Technology Agency) 2006.08.10, a whole document & US 2006/0176735 A1	18, 19, 30, 32-35 1-17, 20-29, 31, 36
Y A	JP 2005-085821 A (TOSHIBA CORPORATION) 2005.03.31, a whole document (No Family)	24 1-23, 25-36
A	JP 2008-091484 A (TOSHIBA CORPORATION) 2008.04.17, a whole document (No Family)	1-36