This Sheet Has Been Replaced



9901378-1
IPOS Copy - for reference only

TITLE OF THE INVENTION:

MAGNETIC RECORDING MEDIUM AND PROCESS FOR PRODUCING THE SAME

BACKGROUND OF THE INVENTION:

The present invention relates to a magnetic recording medium and a process for producing the magnetic recording medium, and more particularly, to a magnetic recording medium suitably applicable to existent magnetic recording systems using a ring-type magnetic head and capable of using a plastic substrate for providing a magnetic recording medium for high-density recording. Still more particularly, the present invention relates to a magnetic recording medium having an excellent stability independent of change in passage of time caused by a high coercive force, e.g., coercive force of not less than 2,000 Oe, even when the cobalt content is as low as possible, e.g., cobalt content at a molar ratio of cobalt to iron of not more than 0.06:1, and a large output in a high frequency range, and being free from the distortion in reproduction waveform, and a process for producing such a magnetic recording medium in industrially and economically advantageous manner.

In recent years, in magnetic recording apparatuses such as a hard disc drive, there has been a remarkable tendency that information devices or systems used therefor are miniaturized and required to have a high reliability. In association with such a recent tendency, in order to deal with

a large capacity data, there has been an increasing demand for providing magnetic recording media on which information can be stored with a high density.

In order to fulfill such requirements, the magnetic recording media have been strongly required to have an excellent stability independent of change in passage of time and a coercive force as high as possible.

As magnetic recording media having a high coercive force, there have been widely known those comprising a substrate and a magnetic thin film formed on the substrate.

The magnetic thin films which have been already put into practice, are generally classified into oxide thin films composed of maghemite, etc. (refer to "Technical Report of Electronic Telecommunication Institute", published by Electronic Telecommunication Institute, (1981) MR81-20, pp. 5 to 12), and alloy thin films composed of Co-Cr alloy or the like.

The magnetic oxide thin films composed of maghemite are excellent in oxidation resistance or corrosion resistance because maghemite is iron oxide. Therefore, the magnetic oxide thin films composed of maghemite can show an excellent stability independent of change in passage of time, and less change in magnetic properties with passage of time. However, the coercive force of the magnetic oxide thin films composed of maghemite is as low as at most about 700 Oe.

Whereas, the alloy thin films have a coercive force as

This Sheet Has Been Replaced



high as not less than about 2,000 Oe. However, metal materials themselves in the alloy thin films tend to be readily oxidized, so that the stability independent of change in passage of time is deteriorated.

In order to prevent magnetic properties of these alloy thin films from being deteriorated due to the oxidation, the surfaces of the alloy thin films have been coated with a protective film, e.g., a carbon film having usually a thickness of about 100 to about 200 Å. However, in such a case, a whole thickness of the resultant magnetic recording medium becomes increased by the thickness of the carbon film, the loss due to the magnetic spacing (distance between a magnetic head and a magnetic recording layer) becomes large, resulting in incompetence of which disables the magnetic recording medium to be applied to high-density recording.

In consequence, it has been attempted to enhance the coercive force and saturation magnetization of the above-mentioned magnetic oxide thin films composed of maghemite which are excellent in oxidation resistance, corrosion resistance and stability independent of change in passage of time, by incorporating cobalt or the like into the maghemite thin film. The maghemite thin films containing cobalt, etc., have been already put into practice (Japanese Patent Publications (KOKOKU) Nos. 51-4086(1976) and 5-63925(1993), "CERAMICS", published by Japan Ceramics Institute (1986), Vol. 24, No. 1, pp. 21-24, and the like).

This Sheet Has Been Replaced



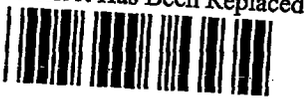
In the cobalt-containing maghemite thin films, the more the cobalt content, the higher the coercive force thereof becomes. However, with the increase in the cobalt content, the stability independent of change in passage of time of the magnetic maghemite thin films tend to be deteriorated by adverse influences of heat or the like.

Thus, at the present time, there has been a strong demand for providing magnetic recording media for high-density recording which are suitable for use in current magnetic recording systems equipped with a ring-type magnetic head. For this reason, various kinds of magnetic recording media as mentioned above have been extensively developed. Among them, the magnetic oxide thin films composed of maghemite having excellent oxidation resistance and corrosion resistance have been considered to be most useful, so that it have been more strongly demanded to improve properties of these magnetic oxide thin films composed of maghemite.

That is, as described above, the cobalt-containing maghemite thin films have been strongly required not only to show a high coercive force and a high saturation magnetization, but also to exhibit a less noise and a large output in a high frequency region.

Meanwhile, the cobalt-containing maghemite film has been produced on a substrate by a sputtering method or the like. The production process generally requires a temperature as high as not less than about 300°C. As a result, there arises

This Sheet Has Been Replaced



a problem that only aluminum discs, aluminum alloy discs or the like which can withstand a temperature as high as not less than 300°C, are usable in the process. The conventional production processes in which the temperature as high as not less than 300°C is required, have such a problem that it becomes difficult to produce the cobalt-containing maghemite film in industrially and economically useful manner.

As conventional methods for producing the cobalt-containing maghemite thin film, there are known (1) a method of sputtering an Fe-Co alloy target in a mixed gas atmosphere composed of argon and oxygen to form a cobalt-containing hematite thin film on a substrate, reducing the hematite thin film in a hydrogen atmosphere at a temperature as high as 230 to 320°C so as to transform the hematite thin film into a cobalt-containing magnetite thin film, and then oxidizing the obtained cobalt-containing magnetite thin film at a temperature of 290 to 330°C; (2) a method of sputtering sintered magnetite containing cobalt as a target to form a cobalt-containing magnetite thin film on a substrate, and then oxidizing the obtained cobalt-containing magnetite thin film at a temperature as high as not less than 320°C; (3) a method of forming a cobalt-containing maghemite thin film directly on a substrate by decomposing a vapor of metal chelate, metal carbonyl or ferrocenes containing iron and M_x (wherein M represents at least one element selected from the group consisting of Co, Cu, Rh, Ru, Os, Ti, V and Nb, and x is 0.01

This Sheet Has Been Replaced



to 0.1), and an oxygen gas in a pressure-reduced plasma which is highly-densified by applying a magnetic field thereto (Japanese Patent Application Laid-Open (KOKAI) No. 3-78114(1991)); or the like.

At the present time, as magnetic recording media for high-density recording which are suitable for use in current magnetic recording systems using a ring-type magnetic head, there have been demanded magnetic recording media having an excellent stability independent of change in passage of time and a high coercive force, and exhibiting a large output in a high frequency region, and further it has been demanded to produce these magnetic recording media in industrially and economically advantageous manner without limitation to materials for substrates thereof. However, there have not been provided yet such magnetic recording media satisfying all of the above-mentioned requirements.

However, the conventional Co-containing maghemite thin films are still unsatisfactory in magnetic properties, especially cannot exhibit a high coercive force. When it is attempted to obtain a high coercive force, especially not less than 2,000 Oe, it is necessary to incorporate a large amount of cobalt thereinto, e.g., cobalt content at a molar ratio of cobalt to iron of more than 0.06:1. However, in such a case, the Co-containing maghemite thin film tends to be deteriorated in magnetic properties with passage of time by adverse influences of heat or the like. Further, the cobalt-

This Sheet Has Been Replaced



containing maghemite thin films have a problem that the output in a high frequency region is not larger for high-density recording.

In the above-mentioned methods (1) and (2) of producing a cobalt-containing maghemite thin film, since these methods require a temperature as high as not less than 290°C, a material usable for the substrate is restricted. Therefore, these conventional methods are industrially and economically disadvantageous.

In the above-mentioned method (3) of producing a cobalt-containing maghemite thin film, since the maghemite thin film can be formed on a substrate maintained at a temperature as low as about 50°C, there can be used substrates composed of a plastic material having a low heat resistance, such as polyesters, polystyrene terephthalate, polyamides or the like. However, the coercive force value of the obtained magnetic recording media is about 1,700 Oe at most.

As a result of the present inventors' earnest studies, it has been found that by forming a cobalt-containing magnetite thin film containing cobalt at a molar ratio of Co to Fe of not more than 0.06:1 , on a plastic substrate by conducting a reactive sputtering in a mixed gas atmosphere composed of oxygen and a rare gas at a substrate temperature of less than 240°C using a cobalt-containing iron alloy as a target, and then oxidizing the obtained cobalt-containing magnetite thin film in a plasma-activated oxygen atmosphere containing a rare

This Sheet Has Been Replaced



gas at a substrate temperature of less than 240°C to transform the cobalt-containing magnetite thin film into a cobalt-containing maghemite thin film, a magnetic recording medium comprising a magnetic iron oxide thin film, which is capable of having a high coercive force even when the cobalt content is low, exhibits a large output in a high frequency region, can be produced in industrially and economically advantageous manner without limitation to a material for the substrate thereof. The present invention has been attained on the basis of the finding.

SUMMARY OF THE INVENTION

It is an object of the present invention to provide a magnetic recording medium comprising a cobalt-containing maghemite thin film, which has a high coercive force even when the cobalt content is as low as possible and exhibits a large output in a high frequency region, and which can be produced in industrially and economically advantageous manner without limitation to a material for the substrate thereof.

To accomplish the aims, in a first aspect of the present invention, there is provided a magnetic recording medium having a coercive force of not less than 2,000 Oe, comprising a plastic substrate, and a cobalt-containing maghemite thin film formed on the substrate, containing cobalt at a molar ratio of cobalt to iron of not more than 0.06:1, and having either a spacing of a plane (311) of not more than 2.510Å, a spacing of a plane (222) of not more than 2.415Å or a spacing

This Sheet Has Been Replaced



of a plane (220) of not more than 2.950Å.

In a second aspect of the present invention, there is provided a process for producing a magnetic recording medium comprising:

forming a cobalt-containing magnetite thin film containing cobalt at a molar ratio of Co to Fe of not more than 0.06:1, on a plastic substrate by reactive sputtering a cobalt-containing iron alloy target at a substrate temperature of less than 240°C in a mixed gas atmosphere containing oxygen and a rare gas; and

oxidizing the obtained cobalt-containing magnetite thin film in a plasma-activated oxygen atmosphere containing a rare gas at a substrate temperature of less than 240°C, thereby converting the cobalt-containing magnetite thin film into a cobalt-containing maghemite thin film.

DETAILED DESCRIPTION OF THE INVENTION

First, the magnetic recording medium according to the present invention is described.

The magnetic recording medium according to the present invention comprises a plastic substrate and a cobalt-containing maghemite thin film formed on the plastic substrate.

The plastic substrate used in the present invention may be composed of resins having a thermal deformation temperature of not more than 240°C. Examples of the resins may include so-called heat-resistant resins such as polyimides, polysulfones, polyarylates, polyphenylene sulfides (PPS),

This Sheet Has Been Replaced



polyether ether ketones (PEEK), poly-p-vinyl phenol resins (PVP polymers), polyamides, polyethylene naphthalate (PEN), polyethylene terephthlate (PET), polyformaldehyde (e.g., "Delurin" produced by du Pont Corp.) polyethylene tetrafluoride, polyethylene trifluoride chloride, polystyrene, methacrylates, polycarbonates (PC) or the like. Meanwhile, the "thermal deformation temperature" means a temperature measured, for example, according to ASTM D-648.

The cobalt-containing maghemite thin film has a thickness of usually 0.005 to 1.0 μm, preferably 0.006 to 0.5 μm, more preferably 0.007 to 0.3 μm. When the thickness of the cobalt-containing maghemite thin film is less than 0.005 μm, it is difficult to obtain a magnetic recording medium comprising a cobalt-containing maghemite thin film having a coercive force of not less than 2,000 Oe. On the other hand, when the thickness of the cobalt-containing maghemite thin film is more than 1.0 μm, it is difficult to uniformly magnetize the obtained cobalt-containing maghemite thin film up to a deep portion thereof when signals are recorded thereon, thereby failing to obtain good recording and reproduction characteristics.

In the present invention, the maghemite is represented by the general formula of γ-Fe_2O_3, but may contain a slight amount of Fe^{2+}.

The cobalt content in the cobalt-containing maghemite thin film at a molar ratio of Co to Fe is usually not more

This Sheet Has Been Replaced



than 0.06:1, preferably 0.03:1 to 0.06:1. When the molar ratio is less than 0.03:1, it may be difficult to obtain a magnetic recording medium having a coercive force as high as not less than 2,000 Oe. On the other hand, when the molar ratio is more than 0.06:1, it is difficult to obtain a magnetic recording medium having an excellent stability independent of change in passage of time.

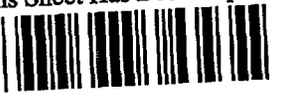
The cobalt-containing maghemite thin film may further contain at least one element selected from the group consisting of Mn, Ni, Cu, Ti and Zn in order to improve various properties thereof, in such an amount that the molar ratio of these elements to Fe is usually about 0.005:1 to about 0.04:1. Even in this case, the aimed effects of the present invention can be obtained similarly.

The cobalt-containing maghemite thin film according to the present invention has either a spacing of a plane (311) of not more than 2.510 Å, a spacing of a plane (222) of not more than 2.415 Å or a spacing of a plane (220) of not more than 2.950 Å.

In this case, if any one spacing condition is satisfied, it is not required to satisfy the other two spacing conditions.

When all of the above-mentioned three spacing conditions concerning the planes (311), (222) and (220) are not satisfied, it is not possible to obtain a magnetic recording medium having a high coercive force. Further, such a magnetic recording medium cannot exhibit a sufficiently large output in

This Sheet Has Been Replaced



a high frequency region.

There is a close relationship between the spacing of the plane (311), the plane (222) or the plane (220) and the coercive force of the cobalt-containing maghemite thin film. In the case where the molar ratio of Co to Fe is the same, there is a tendency that the smaller the spacing, the higher the coercive force becomes.

The spacing of the plane (311) is usually not more than 2.510 Å, preferably not more than 2.509 Å, more preferably not more than 2.506 Å. The lower limit of the spacing of the plane (311) is preferably 2.490 Å.

The spacing of the plane (222) is usually not more than 2.415 Å, preferably not more than 2.400 Å, more preferably not more than 2.398 Å. The lower limit of the spacing of the plane (222) is preferably 2.385 Å.

The spacing of the plane (220) is usually not more than 2.950 Å, preferably not more than 2.943 Å, more preferably not more than 2.940 Å. The lower limit of the spacing of the plane (220) is preferably 2.920 Å.

The magnetic recording medium according to the present invention, has a saturation magnetization (value of magnetization at an applied magnetic field of 15 kOe) of usually 230 to 350 emu/cm^3, preferably 240 to 300 emu/cm^3, and a coercive force (value of coercive force at an applied magnetic field of 15 kOe)of usually not less than 2,000 Oe, preferably not less than 2,200 Oe, more preferably not less

This Sheet Has Been Replaced



than 2,400 Oe. In the present invention, especially when the molar ratio of Co to Fe is 0.04:1, such magnetic recording medium has a coercive force as high as about 3,200 Oe.

Incidentally, the upper limit of the coercive force of the magnetic recording medium according to the present invention, represents a value measured at an applied magnetic field of 15 kOe which is an upper limit value of the coercive force measurable by "vibration sample-type magnetometer VSM"

In addition, the magnetic recording medium according to the present invention, exhibits a recording property (S_{p-p}/N_{rms}) of preferably not less than 40 dB, more preferably not less than 41 dB. Further, the recording density when the reproduced output is one half of a reproduced output obtained at a recording density of 1kFRPI (flux reversals per inch), is preferably not less than 120 kFRPI, more preferably not less than 130 kFRPI, and the di-pulse ratio thereof is 0.

Next, the process for producing the magnetic recording medium according to the present invention, is described.

The magnetic recording medium according to the present invention may be produced by forming a cobalt-containing magnetite thin film which is deposited on the substrate by a so-called sputtering method using Co-containing iron alloy as a target while introducing a mixed gas composed of oxygen and a rare gas, and controlling an oxygen flow rate (CCM) and a deposition speed (nm/min) of the cobalt-containing magnetite;

This Sheet Has Been Replaced



and then oxidizing the obtained cobalt-containing magnetite thin film to transform the magnetite thin film into a cobalt-containing maghemite thin film.

In order to obtain the aimed magnetic recording medium according to the present invention, it is important to control the oxygen flow rate (CCM) in the mixed gas relative to the deposition speed (nm/min) of the cobalt-containing magnetite.

The oxygen flow rate (CCM) in the mixed gas relative to the deposition speed (nm/min) of the cobalt-containing magnetite, is varied depending upon various conditions for obtaining the cobalt-containing magnetite thin film oxidizing the Co-containing iron alloy target, for example, kind and structure of apparatus used, a total gas pressure, a substrate temperature, an area of the target to be sputtered or the like.

However, as a result of many experiments conducted, it has been recognized that there is a tendency that the less the oxygen flow rate (CCM) in the mixed gas relative to the deposition speed (nm/min) of the cobalt-containing magnetite, the smaller the spacing of each of the planes (311), (222) and (220) of the obtained cobalt-containing maghemite thin film becomes.

Accordingly, by conducting various experiments to obtain the oxygen flow rate (CCM) in the mixed gas relative to the deposition speed (nm/min) of the cobalt-containing magnetite at which the spacing of each of planes (311), (222) and (220) becomes smaller than that of the bulk, the deposition speed

This Sheet Has Been Replaced



(nm/min) of the cobalt-containing magnetite and the oxygen flow rate can be respectively controlled so as to be smaller than that of the bulk.

In order to obtain such a cobalt-containing maghemite thin film having a smaller spacing of plane than that of bulk, in accordance with the experiments conducted, as described in Examples and Comparative Examples hereinafter, when the deposition speed of the cobalt-containing magnetite is 3.5 nm/min and a whole flow rate of the mixed gas is about 10 CCM, the oxygen flow rate is usually not more than 0.35 CCM, preferably not more than 0.27 CCM, more preferably not more than 0.25 CCM. The lower limit of the oxygen flow rate is usually 0.13 CCM. When the oxygen flow rate is more than 0.35 CCM, it is difficult to obtain such a cobalt-containing maghemite thin film that the spacing of either the plane (311), the plane (222) or the plane (220) is smaller than that of bulk. Further, hematite tends to be produced in the obtained cobalt-containing maghemite thin film, so that the saturation magnetization value thereof tends to be reduced. On the other hand, when the oxygen flow rate is less than 0.13 CCM, metal iron (Fe) or wustite (FeO) tends to be produced in the obtained cobalt-containing maghemite thin film, resulting in decrease in coercive force thereof.

As the rare gases used in the present invention, there may be exemplified helium, neon, argon, krypton, xenon, radon or the like. In the consideration of the sputtering rate and

This Sheet Has Been Replaced



economy, argon is preferable among these rare gases.

The cobalt-containing magnetite may be deposited at a substrate temperature of usually less than 240°C. In the consideration of the heat-resistance of plastic materials used for the substrate, the deposition temperature is preferably not more than 200°C, more preferably not more than 180°C. The lower limit of the deposition temperature is preferably -196°C.

The time required for depositing the cobalt-containing magnetite may be represented by the value obtained by dividing the thickness of deposited film by the deposition speed.

The cobalt-containing magnetite thin film is then oxidized into a cobalt-containing maghemite thin film. At this time, it is important that the oxidation is conducted at a substrate temperature of less than 240°C in a plasma-activated oxygen atmosphere containing a rare gas.

As the method of irradiating the plasma-activated oxygen ions, there may be exemplified a method using an ECR microplasma. In addition, the irradiation condition includes an ashing mode and an etching mode. In general, in the ashing mode, an ion beam emitted from a plasma-generating chamber is irradiated onto a substrate while maintaining the ionized state. Therefore, the ashing mode is suitably used for surface-modification treatments. On the other hand, in the etching mode, the ion beam emitted from the plasma-generating chamber neutralizes a space charge using a neutralizer, so that the intensity and amount of the ion beam are increased.

This Sheet Has Been Replaced



Therefore, the etching mode is effective to conduct an etching treatment.

The ion acceleration voltage is preferably -500 to 0 V, more preferably -300 to -100 V. When the ion acceleration voltage is less than -500 V, the thin film may suffer from etching, so that the film thickness becomes decrease or uneven. When the ion acceleration voltage is more than 0 V, the plasma-activated oxygen ion is not irradiated because the electron is emitted. In the present invention, it has been recognized that under such a condition that the thin film remains unremoved, for example, the ion acceleration voltage of less than -500 V, a similar oxidation-accelerating effect can be obtained by any of the irradiation modes.

In order to increase the amount of plasma generated, it is important to incorporate a rare gas (such as He, Ne, Ar, Kr, Xe or Rn) into a process gas (oxygen) for the purpose of acceleration of the reaction. In the consideration of the effect of accelerating the oxidation of the cobalt-containing magnetite, helium and neon are preferable. As to the amount of the rare gas contained, the percentage of flow rate of the rare gas to that of oxygen is preferably 1 to 90 %, more preferably 2 to 75 %, still more preferably 3 to 60 %. When the rare gas is contained in the above-specified range, the oxygen can be effectively excited.

When the percentage of the rare gas flow rate to the

This Sheet Has Been Replaced



oxygen flow rate is less than 1 %, it is difficult to effectively produce an activated oxygen. On the other hand, when the percentage of the rare gas flow rate to the oxygen flow rate is more than 90 %, the amount of oxygen required for the oxidation of the cobalt-containing magnetite may be comparatively reduced, so that the oxidation reaction takes a long period of time. The oxidation temperature is less than 240°C. In the consideration of heat resistance of the plastic substrate and productivity, the oxidation temperature is preferably not more than 200°C, more preferably not more than 180°C. The lower limit of the oxidation temperature is preferably -196°C.

The important point of the present invention lies in such a fact that in the case where the cobalt-containing maghemite thin film formed on the substrate contain cobalt at a molar ratio of cobalt to iron of not more than 0.06:1, and is adjusted so that either the spacing of plane (311) of not more than 2.510 Å, the spacing of plane (222) of not more than 2.415 Å or the spacing of plane (220) of not more than 2.950 Å can be satisfied, the obtained magnetic recording medium has an excellent stability independent of change in passage of time caused by low cobalt content and a higher coercive force, and can exhibit a large output in a high frequency region.

The reason why the magnetic recording medium having such excellent properties can be obtained, is considered as follows. That is, due to the fact that the aimed magnetic recording

This Sheet Has Been Replaced



medium cannot be obtained in any of the cases where the cobalt-containing maghemite thin film satisfies the specified spacing but the cobalt content thereof is out of the specified range, and where the specified cobalt content is satisfied but the cobalt-containing maghemite thin film does not satisfy the specified spacing, the technical advantages of the present invention have been attained by a synergistic effect based on the specified cobalt content and the specified spacing in the cobalt-containing maghemite thin film.

As to the spacing of the respective planes of the cobalt-containing maghemite thin film according to the present invention, even though the same heating temperature is used to transform the cobalt-containing magnetite thin film into the cobalt-containing maghemite thin film, the spacing of each of the planes (311), (222) and (220) is changed by varying the oxygen flow rate upon production of the cobalt-containing magnetite thin film. Due to this fact, it can be recognized that the change of the spacing is not caused by the difference in thermal expansion coefficient between the substrate and the cobalt-containing maghemite thin film upon the heat treatment, but is caused by reduction in spacing of the cobalt-containing maghemite thin film itself.

The reason why the oxidation temperature can be reduced to the temperature as low as less than 240°C, is considered as follows. That is, since the cobalt-containing magnetite thin film of the present invention cannot be oxidized merely by

This Sheet Has Been Replaced



heat-treating the film at a substrate temperature of less than 240°C in an atmospheric air, as shown in Comparative Examples hereinafter, it is considered that the oxidation temperature can be reduced to less than 240°C by irradiating a plasma-activated oxygen ions containing a rare gas onto the cobalt-containing magnetite thin film.

The magnetic recording medium according to the present invention can have a higher coercive force even if the cobalt content is as low as possible, can exhibit a large output in a high frequency region, and can be, therefore, suitably used as magnetic recording media for high-density recording in current magnetic recording systems using a ring-type magnetic head.

In addition, in the magnetic recording medium according to the present invention, since the heat-treating temperature used for oxidizing the cobalt-containing magnetite thin film into the cobalt-containing maghemite thin film, is as low as less than 240°C, raw materials for the substrate is not required to have a heat resistance, so that plastic materials can be used therefor, resulting in a good productivity and industrial and economical advantages.

EXAMPLES

The present invention is described in more detail by Examples and Comparative Examples, but the Examples are only illustrative and, therefore, not intended to limit the scope of the present invention.

(1) The oxidation of the cobalt-containing magnetite thin

This Sheet Has Been Replaced



film into the cobalt-containing maghemite thin film was determined by observing change in surface resistivity of the thin film which is one of indices thereof.

That is, the surface resistivity of the cobalt-containing magnetite thin film was in the range of 0.001 to 0.5 MΩ, while the surface resistivity of the cobalt-containing maghemite thin film was raised from 1 to 100 MΩ. and varied thereover. The surface resistivity was measured by an Insulation Tester DM-1527 (manufactured by Sanwa Denki Keiki Co., Ltd.) by setting the distance between two probes to 10 mm.

(2) The magnetostatic properties such as coercive force and saturation magnetization of the magnetic recording medium, are expressed by values measured by "Vibration Sample Magnetometer VSM" (manufactured by TOEI KOGYO CO., LTD.).

(3) The X-ray diffraction patterns of the thin films are measured by "X-Ray Diffractometer RAD-IIA" (manufactured by RIGAKU DENKI CO., LTD.).

The measuring conditions of the X-ray diffraction patterns are as follow:

lamp used: Fe; lamp voltage: 40 kV; lamp current: 25 mA; sampling width of goniometer: 0.010°; scanning speed: 1.000°/min; light-emitting (divergent) slit: 1°; scattering slit: 1°; light-receiving slit: 0.30 mm.

The region covering a diffraction angle (2θ) of 30.00° to

This Sheet Has Been Replaced



60.00° was measured under the above-mentioned conditions.

(4) The recording properties such as a reproduced output or di-pulse of the magnetic recording medium are evaluated as follows.

That is, after a magnetic film was formed on the substrate and then the surface of the magnetic film was coated with a perfluoropolyether-based lubricant "FOMBLIN Z DOL" (tradename: produced by AUSIMONT K. K.), an MIG head for VCR having a gap length of about 0.2 μm and a track width of 21 μm was run on the obtained magnetic recording medium while contacting therewith. The respective recording properties were evaluated by using "Recording and Reproduction Tester M-84V" (manufactured by FUJITSU AUTOMATION CO., LTD.).

Specifically, the noise value (Nrms) was analyzed by "Spectrum Analyzer TR4171" (manufactured by ADVANTEST CO., LTD.) at a velocity of 3.0 m/s.

The reproduced output (Sp-p) and di-pulse ratio were analyzed by "Oscilloscope VP5514A" (manufactured by PANASONIC CO., LTD.) at a velocity of 3.0 m/s.

Example 1:

Using a high frequency sputtering apparatus SH-250H-T06 (manufactured by NIPPON VACUUM CO., LTD.), a cobalt-containing iron alloy target (Fe containing Co of 4wt.%) was reactive-sputtered by adjusting a distance between a polyimide substrate and the target to 80 mm, at a substrate temperature

This Sheet Has Been Replaced



of 200°C in a mixed gas atmosphere composed of argon and oxygen at an oxygen flow rate of 0.18 CCM under an oxygen partial pressure of 0.155 mTorr and a total pressure of 9 mTorr, thereby depositing a cobalt-containing magnetite thin film having a thickness of 60 nm and containing cobalt at a molar ratio of Co to Fe of 0.04:1, on the substrate at a deposition speed of 4.3 nm/min. The obtained cobalt-containing magnetite thin film had a surface resistivity of 0.06 MΩ. Incidentally, the electric power applied was 300 W.

The obtained cobalt-containing magnetite thin film was oxidized by irradiating with plasma-activated oxygen ions under a total gas pressure of 3×10^{-4} Torr in an oxygen atmosphere containing helium (percentage of helium gas flow rate to oxygen flow rate: 50 %) at a substrate temperature of 150°C, at a microwave power of 100 W, at an ion acceleration voltage of -150 V for 30 minutes by using an Electron Cyclotron Resonance (ECR)-type ion shower apparatus "EIS-200ER" (manufactured by ELIONIX CO., LTD.), thereby producing a magnetic recording medium. The obtained thin film had a surface resistivity of 70 MΩ, and was, therefore, determined to be a cobalt-containing maghemite thin film.

The cobalt-containing maghemite film had a thickness of 60 nm. As a result of the measurement of X-ray diffraction pattern, diffraction peaks of the plane (311) having a spacing of 2.505 Å and the plane (222) having a spacing of 2.412 Å,

This Sheet Has Been Replaced



were observed.

The magnetostatic property of the obtained magnetic recording medium was measured, so that it was determined that the coercive force thereof was 2,200 Oe and the saturation magnetization thereof was 275 emu/cm^3.

The recording properties of the obtained magnetic recording medium were measured, so that it was determined that the S_{p-p}/N_{rms} obtained when a 100 kFRPI signal was recorded, was 40 dB, and the half-voltage density D_{50} (recording density when the reproduced output was one half of a reproduced output obtained at a recording density of 1 kFRPI) was 130 kFRPI.

In addition, the isolated reproduced waveform of the magnetic recording medium obtained when a 1 kFRPI signal was recorded, was observed by the oscilloscope, so that it was determined that the waveform exhibited a unimodal pulse shape corresponding to a di-pulse ratio of 0. The obtained magnetic recording medium was a longitudinal recording medium.

Examples 2 to 5 and Comparative Examples 1 to 3:

The same procedure defined in Example 1 was conducted except that kind of plastic substrate, substrate temperature, oxygen flow rate and deposition speed upon production of the cobalt-containing magnetite thin film, and substrate temperature, kind of the rare gas, percentage of rare gas flow rate to oxygen flow rate and irradiation time upon oxidation of the magnetite thin film were varied, thereby obtaining

This Sheet Has Been Replaced



magnetic recording media.

The production conditions and various properties are shown in Tables 1 and 2.

Incidentally, in Comparative Example 3, the cobalt-containing magnetite thin film was treated in an atmospheric air instead of the plasma-activated oxygen atmosphere containing the rare gas. However, the cobalt-containing magnetite thin film was not oxidized and remained as magnetite even after the treatment.

This Sheet Has Been Replaced



Table 1

Examples and Comparative Examples	Production of cobalt-containing magnetite thin film			
	Substrate used	Substrate temperature (°C)	Oxygen flow rate (CCM)	Deposition speed (nm/min)
Example 2	PC	80	0.22	3.3
Example 3	Polyamide	100	0.22	3.3
Example 4	Polyimide	150	0.21	3.3
Example 5	Polyimide	200	0.15	4.0
Comparative Example 1	PC	80	0.36	3.3
Comparative Example 2	PC	80	0.22	3.4
Comparative Example 3	Polyimide	200	0.22	3.3

This Sheet Has Been Replaced

Table 1 (continued)

Examples and Comparative Examples	Cobalt-containing magnetite thin film	
	Surface resistivity (MΩ)	Cobalt content (molar ratio of Co:Fe)
Example 2	0.06	0.04:1
Example 3	0.05	0.06:1
Example 4	0.15	0.03:1
Example 5	0.19	0.04:1
Comparative Example 1	0.007	0.04:1
Comparative Example 2	0.05	0:1
Comparative Example 3	0.10	0.04:1

This Sheet Has Been Replaced

Table 1 (continued)

Examples and Comparative Examples	Oxidation treatment			
	Substrate temperature (°C)	Kind of rare gas	Percentage of rare gas flow rate to oxygen flow rate (%)	Irradiation time
Example 2	130	He	50	30 min.
Example 3	180	He	50	1 min.
Example 4	200	He	50	5 sec.
Example 5	200	He	30	5 sec.
Comparative Example 1	130	He	60	30 min.
Comparative Example 2	180	He	50	30 min.
Comparative Example 3	200	-	0	5 sec.

This Sheet Has Been Replaced



Table 2

Examples and Comparative Examples	Magnetic thin film		
	Kind	Cobalt content (molar ratio of Co:Fe)	Thickness (nm)
Example 2	cobalt-containing maghemite	0.04:1	80
Example 3	cobalt-containing maghemite	0.06:1	60
Example 4	cobalt-containing maghemite	0.03:1	20
Example 5	cobalt-containing maghemite	0.04:1	20
Comparative Example 1	cobalt-containing maghemite	0.04:1	80
Comparative Example 2	cobalt-containing maghemite	0:1	60
Comparative Example 3	cobalt-containing magnetite	0.04:1	20

This Sheet Has Been Replaced



Table 2 (continued)

Examples and Comparative Examples	Magnetic thin film			
	Surface resistivity (MΩ)	Spacing		
		Plane (311) (Å)	Plane (222) (Å)	Plane (220) (Å)
Example 2	50	2.505	-	-
Example 3	12	2.508	-	2.938
Example 4	11	2.506	2.400	-
Example 5	10	2.502	2.399	-
Comparative Example 1	5	2.530	2.423	-
Comparative Example 2	11	2.508	-	-
Comparative Example 3	0.10	2.505	-	-

This Sheet Has Been Replaced



Table 2 (continued)

Examples and Comparative Examples	Magnetic thin film				
	Saturation magneti-zation (emu/cm^3)	Coercive force (Oe)	S_{p-p} /N_{rms} (dB)	D_{50} (kFRPI)	Di-pulse ratio
Example 2	267	2,890	45	135	0
Example 3	289	3,390	46	138	0
Example 4	252	2,540	43	142	0
Example 5	273	3,620	42	140	0
Comparative Example 1	310	810	38	100	0
Comparative Example 2	260	420	38	98	0
Comparative Example 3	285	580	43	88	0

This Sheet Has Been Replaced





WHAT IS CLAIMED IS:

1. A magnetic recording medium comprising:

a plastic substrate; and

a cobalt-containing maghemite thin film formed on said substrate, containing cobalt at a molar ratio of cobalt to iron of not more than 0.06:1, and having either a spacing of a plane (311) of not more than 2.510Å, a spacing of a plane (222) of not more than 2.415Å or a spacing of a plane (220) of not more than 2.950Å,

and having a coercive force of not less than 2,000 Oe.

2. A magnetic recording medium according to claim 1, wherein the molar ratio of cobalt to iron in said cobalt-containing maghemite thin film is 0.03:1 to 0.06:1, and the coercive force is not less than 2,200 Oe.

3. A magnetic recording medium according to claim 1, which further contains at least one element selected from the group consisting of Mn, Ni, Cu, Ti and Zn in such an amount that the molar ratio of said element to iron is 0.005:1 to 0.04:1.

4. A magnetic recording medium according to claim 1, wherein the spacing of the plane (311) is 2.490 to 2.509 Å, the spacing of the plane (222) is 2.385 to 2.400 Å, and the spacing of the plane (220) is 2.920 to 2.943 Å.

This Sheet Has Been Replaced



* C L M S *

5. A magnetic recording medium according to claim 1, which further has a recording property of not less than 40 dB, and a recording density when the reproduced output is one half of a reproduced output obtained at a recording density of 1kFRPI, of not less than 120k FRPI .

6. A process for producing a magnetic recording medium as set forth in claim 1, comprising:

forming a cobalt-containing magnetite thin film containing cobalt at a molar ratio of Co to Fe of not more than 0.06:1, on a plastic substrate by reactive sputtering a cobalt-containing iron alloy target at a substrate temperature of less than 240°C in a mixed gas atmosphere containing oxygen and a rare gas; and

oxidizing the obtained cobalt-containing magnetite thin film in a plasma-activated oxygen atmosphere containing a rare gas at a substrate temperature of less than 240°C, thereby converting the cobalt-containing magnetite thin film into a cobalt-containing maghemite thin film.

This Sheet Has Been Replaced