

Title of the Invention

Magnetic recording medium and manufacturing method therefor

5 Technical field of the invention

The present invention relates to a method for manufacturing a magnetic recording medium used in a device such as an external memory device or a hard disk drive of a computer, and also relates to magnetic recording medium
10 produced by such a method.

Background of the invention

Demand for recording density of the magnetic recording medium used in
15 a hard disk is continuously rising from year to year. To meet this rigorous demand for high recording density, high coercive force and low noise of a magnetic thin film is critical. Accordingly, various composition and structure of a magnetic layer, material of a non-magnetic under-layer, and methods for lamination have been proposed.

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Japanese Patent No. 2806443 provides a magnetic recording medium with high coercive force by controlling oxygen concentration of a metallic under-layer and/or a ferromagnetic layer at 100 wt ppm or less in a magnetic recording medium having a ferromagnetic metal layer that is formed directly
25 or via an under-layer on a surface of a substrate. The ferromagnetic metal layer used here is composed of a cobalt-base alloy and the material for the metallic under-layer listed here are chromium, titanium, tungsten and alloy of these metals.

30 Recently, a magnetic layer commonly called a granular magnetic layer has been proposed that has a structure composed of magnetic grains and non-

magnetic non-metallic substance such as oxide or nitride, surrounding the grains.

Japanese Unexamined Patent Application Publication No. H8-255342,
5 for example, discloses a method for attaining low noise by forming a granular recording layer in which ferromagnetic grains are dispersed in a non-magnetic film, by a procedure comprising steps of sequentially depositing a non-magnetic film, a ferromagnetic film and a non-magnetic film on a non-magnetic substrate, and heat-treating the laminate. For a magnetic layer in
10 this technology, cobalt or an alloy containing cobalt as a main component is used. For the non-magnetic film, metal, oxide, nitride, carbon or carbide is used. US Patent No. 5,679,473 discloses that a granular recording film in which each magnetic grain is surrounded by a non-magnetic oxide and separated with each other can be formed by means of RF (radio frequency)
15 sputtering using a CoNiPt target containing an oxide, such as SiO_2 , and high coercive force H_c and low noise are achieved by such a recording film.

The low noise is considered to be achieved by the following reason. Since each of the magnetic grains in this granular magnetic film is physically
20 separated by a grain boundary of non-magnetic non-metallic phase, magnetic interaction between the magnetic grains is reduced and formation of the magnetic domain wall with a zigzag shape at the transition region of a recording bit is suppressed.

25 Noises of a recording medium are caused by fluctuation of magnetization due to magnetic interaction between magnetic grains that constitute the medium, and the size of the grain. In order to maintain high signal-to-noise ratio SNR keeping up with enhancement of the recording density, it is necessary to hold the number of magnetic grains per bit cell to be greater than
30 a certain value; in other words, minimization of the size of the magnetic grain is required. However, in the situation where large exchange interaction arises between the magnetic grains, the minimization of magnetic grains frequently

does not necessarily mean minimization of a unit of reversed magnetization. Therefore, it is also needed to suppress the exchange interaction between the grains for minimizing the unit of reversed magnetization itself that is represented by an activation magnetic moment. Further in the minimization, the magnetic grain itself must have a relatively large value of energy of magnetic anisotropy so that a superparamagnetic state does not arise and the magnetic characteristic essential for high-resolution recording, which means a large H_c/M_r value, can be obtained. The objective aimed at by the granular structure, in which magnetic grains having high energy of magnetic anisotropy are dispersed in a non-magnetic matrix, is that the above-described every rigorous requirements are met for attaining high SNR.

In the conventionally used Co-Cr alloy magnetic film, chromium is segregated from a cobalt alloy magnetic grain towards a grain boundary by deposition at high temperature, so as to reduce magnetic interaction between the magnetic grains. On the other hand, in the granular magnetic layer, since the grain boundary phase is composed of a non-magnetic non-metallic substance, the segregation occurs easier than the conventional chromium. Consequently, isolation of magnetic grains is easily enhanced. In the conventional Co-Cr alloy magnetic layer, heating the substrate over 200°C is essential for enough segregation of chromium when laminating the layer, and in the method of above-mentioned Japanese Patent No. 2806443, heating the substrate up to a temperature between 60 to 150°C was necessary, while the granular magnetic layer has the advantage that the non-magnetic non-metallic substance segregates even in lamination without heating.

Problem to be solved by the invention

However, a magnetic recording medium having a granular magnetic layer requires addition of relatively large amount of platinum to the cobalt alloy to attain desired magnetic characteristics, in particular, high coercive force H_c . Specifically, to attain coercive force H_c of $2,800$ Oe, as high as 16

at% of expensive platinum is needed, while in the conventional CoCr metallic magnetic film, only about 8 at% of platinum is to be added for obtaining the same value of H_c . With rising recording density in recent years, high H_c over 3,000 Oe is demanded, which leads to more addition of the expensive platinum. This goes against the trend to a lower price, and raises a problem from the viewpoint of a manufacturing cost. Moreover, increased platinum content increases media noise. Thus, control of granular magnetic layer is also necessary from the viewpoint of reduction of the media noise.

The present invention provides a method for manufacturing a magnetic recording medium having granular magnetic layer meeting these requirements, namely exhibiting high coercive force, low cost and low noise. The invention also provides a magnetic recording medium manufactured by such a method.

Means to solve the problem

The inventors of the present invention have made rigorous studies for achieving high coercive force, low cost and low noise in a magnetic recording medium having a granular magnetic layer, and found that high coercive force and low media noise are achieved without increasing the content of expensive platinum when ultimate pressure of the sputtering apparatus is improved and the sputtering is performed under a clean atmosphere.

Specifically, a method of the present invention for manufacturing a magnetic recording medium comprises steps of:

forming a non-magnetic under-layer on a non-magnetic substrate by sputtering under an atmosphere in which partial pressure of H_2O is 2×10^{-10} Torr or lower,

forming a non-magnetic intermediate layer on the under-layer by sputtering under an atmosphere in which partial pressure of H_2O is 2×10^{-10} Torr or lower,

forming a magnetic layer comprising ferromagnetic grains and non-magnetic grain boundaries surrounding the grains on the intermediate layer by sputtering under an atmosphere in which partial pressure of H_2O is 2×10^{-10} Torr or lower,

- 5 forming a protective layer on the magnetic layer, and
 forming a liquid lubricant layer on the protective layer.

Advantageously, the non-magnetic intermediate layer is made of a metal selected from the group consisting of Ti, Cr, Zr, Hf, Ti alloy, Cr alloy, Zr alloy
10 and Hf alloy and has a crystal structure of hexagonal closest packing.

Advantageously, the intermediate layer has a thickness of from 0.5 nm to 20 nm

- 15 Advantageously, the non-magnetic grain boundary in the magnetic layer is composed of oxide or nitride of at least one element selected from the group consisting of Mg, Al, Si, Ti, Cr, Mn, Co, Zr, Ta, W and. Hf.

Advantageously, the non-magnetic under-layer is composed of chromium
20 or chromium alloy, and the non-magnetic substrate is composed of crystallized glass, chemically strengthened glass or plastic.

Advantageously, in the manufacturing method, the step for forming the under-layer, the step for forming the intermediate layer, the step for forming
25 the magnetic layer, the step for forming the protective layer, and the step for forming the liquid lubricant layer are conducted without heating the non-magnetic substrate in advance.

The present invention also provides a magnetic recording medium
30 manufactured by the method described above.

Brief description of the drawings

Fig. 1

- 5 A schematic cross-sectional view of a magnetic recording medium obtained by a manufacturing method according to the present invention.

Fig. 2

- 10 A graph showing dependence of coercive force H_c on the product $Br \delta$ of remanent magnetic flux density Br and film thickness δ of the magnetic layer of the magnetic recording media produced in Example 1 and Comparative Example 1.

Fig. 3

- 15 A graph showing dependence of coercive force H_c on the product $Br \delta$ of remanent magnetic flux density Br and film thickness δ of the magnetic layer of the magnetic recording media produced in Example 2 and Comparative Example 1.

20 Fig. 4

- A graph showing the dependence of signal-to-noise ratio SNR on the track recording density of the magnetic recording medium produced in Example 1, Example 2, and Comparative Example 1.

- 25 Aspects of some preferred embodiments of the invention

- Now, aspects of some preferred embodiments of the invention will be described in detail referring to Fig. 1, which is a schematic cross-sectional view of a magnetic recording medium as an example of embodiments of the invention. The magnetic recording medium illustrated in Fig. 1 comprises
30 non-magnetic under-layer 2, non-magnetic intermediate layer 3, magnetic

layer 4 and protective layer 5 that are sequentially formed on non-magnetic substrate 1, and further comprises liquid lubricant layer 6 on this laminate.

Non-magnetic substrate 1 may be made of NiP-plated aluminum alloy, strengthened glass, or crystallized glass as in the conventional magnetic recording medium. In addition, a substrate made by injection-molding polycarbonate, polyolefin or other resins may also be used since heating the substrate may not be executed in the manufacturing process of the invention.

On this substrate 1, a non-magnetic under-layer is formed by sputtering method. For the sputtering condition in this process, it is preferable to lower the ultimate pressure of the sputter chamber and make the partial pressure of H_2O to be 2×10^{-10} Torr or lower, to establish a clean atmosphere.

Non-magnetic under-layer 2 may be composed of non-magnetic material including NiAl and Cr. Chromium or chromium alloy is preferably used for the under-layer. The preferable chromium alloy includes CrMo, CrTi, CrV and CrW. Thickness of the under-layer 2 is preferably in the range from 5 nm to 50 nm.

On this under-layer 2, a non-magnetic intermediate layer 3 is formed by a sputtering method. For the sputtering condition in this process, it is preferable to lower the ultimate pressure of the sputter chamber and make the partial pressure of H_2O to be 2×10^{-10} Torr or lower, to establish a clean atmosphere.

The intermediate layer 3 is composed of a material selected from the group consisting of Ti, Cr, Zr, Hf, Ti alloy, Cr alloy, Zr alloy and Hf alloy and has a crystal structure of hexagonal closest-packing. The intermediate layer 3 getters oxygen from the under-layer 2 and has a metallic surface that contains essentially no oxygen, to improve the surface condition for forming a granular magnetic layer in the next step. Therefore, the state of initial growth of the

granular magnetic layer formed on this intermediate layer is modified, and the quantity of the platinum retained in the homogeneously grown ferromagnetic grains increases, resulting in readily achieving high coercive force.

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Thickness of the intermediate layer 3 is preferably in the range from 0.5 nm to 20 nm.

10 On this intermediate layer 3, a magnetic layer 4 is formed by a sputtering method. For the sputtering condition in this process, it is preferable to lower the ultimate pressure of the sputter chamber and make the partial pressure of H_2O to be 2×10^{-10} Torr or lower, to establish a clean atmosphere.

15 The magnetic layer 4 is a so-called granular magnetic layer that comprises ferromagnetic grains and non-magnetic grain boundaries surrounding the grains, the non-magnetic grain boundary being composed of oxide or nitride of a metal or silicon. Such structure may be produced, for example, by a sputtering method under the sputtering condition described
20 above using a target of ferromagnetic metal containing the oxide that composes the grain boundary.

For the material composing the ferromagnetic crystal, CoPt alloy is preferably used. In particular, addition of an element selected from the group
25 consisting of Cr, Ni and Ta to the CoPt alloy is favorable to reduce media noise. For the material composing the non-magnetic grain boundary, oxide or nitride of at least one element selected from the group consisting of Mg, Al, Si, Ti, Cr, Mn, Co, Zr, Ta, W and Hf is particularly favorable to form a stable granular structure. Thickness of the magnetic layer is necessary to be such a
30 value that provides enough head reproduction output when reproducing a record.

On this magnetic layer 4, a protective layer 5 is formed by sputtering method, for example. The protective layer 5 is a thin film composed mainly of carbon. On this protective layer 5, a liquid lubricant layer 6 is formed. The liquid lubricant layer 6 may be made of perfluoropolyether lubricant.

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Thus, a magnetic recording medium according to the present invention is formed. A magnetic recording medium produced by the manufacturing method according to the present invention allows to achieve high coercive force and low media noise even without the step for heating the substrate, the step being needed in the conventional manufacturing process. This simplification of manufacturing process and, in addition, the possibility to employ an inexpensive plastic substrate permits reduction of a manufacturing cost.

15 Examples

The following shows some examples of embodiments of the present invention. However, the scope of the present invention should not be limited by the specific examples.

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Example 1

A plurality of chemically strengthened glass substrates with smooth surface, N-10 glass substrates manufactured by Hoya Corp., was used for the substrates of Example 1. After precision cleaning, the set of substrates was introduced into a sputtering apparatus under the condition of partial pressure of H_2O at 3×10^{-11} Torr. On each of the substrates, a non-magnetic under-layer 2 having thickness of 15 nm was formed of Cr-20 at% Mo by a dc magnetron sputtering method under an argon gas pressure of 5 mTorr. On each of the under-layers 2, a non-magnetic intermediate layer 3 having thickness of 10 nm was formed of Co-40 at% Cr by a dc magnetron sputtering method under an argon gas pressure of 5 mTorr. On each of the intermediate

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layers 3, a granular magnetic layer having varied thickness from 12 nm to 28 nm, corresponding to the product $Br \delta$ of remanent magnetic flux density Br and film thickness δ in the range from 55 to 130 G μ m, was formed by an RF sputtering method using a target of Co-12 at% Cr-12 at% Pt containing 10 mol% of SiO₂ under an argon gas pressure of 3 mTorr. On each of the granular magnetic layers, a carbon protective layer 5 having thickness of 10 nm was formed by a sputtering method. Then, the set of the obtained laminates was taken out from the vacuum chamber. On each of the protective layer 5, a liquid lubricant layer 6 having thickness of 1.5 nm was formed by applying liquid lubricant. Thus, a set of magnetic recording media with a structure as shown in Fig. 1 was produced.

In this manufacturing process, heating of the substrate prior to lamination was not conducted.

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On each of the obtained magnetic recording media, coercive force H_c was measured using a vibrating sample magnetometer VSM. Fig. 2 shows dependence of the coercive force H_c on the product $Br \delta$ of remanent magnetic flux density Br and film thickness δ . On the magnetic recording medium having thickness of 15 nm, which corresponds to the $Br \delta$ of 70 G μ m, signal-to-noise ratio SNR was measured by using a GMR head on a spinning stand tester. Fig. 4 shows dependence of the signal-to-noise ratio SNR on the track recording density kFCI.

25 Comparative Example 1

A set of magnetic recording media as shown in Fig. 1 was produced in the same manner as in Example 1 except that under-layer 2, intermediate layer 3 and magnetic layer 4 were formed in the sputtering apparatus under the partial pressure of H₂O at 4×10^{-10} Torr.

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Coercive force H_c was measured on each of the obtained magnetic recording medium in the same manner as in Example 1. The dependence of the H_c on the $Br \delta$ is shown in Fig. 2 and Fig. 3. The signal-to-noise ratio SNR was measured in the same manner as in Example 1 on the magnetic recording medium of this Comparative Example having thickness of 15 nm, which corresponding to the $Br \delta$ of 70 G μ m that generates equal output to that of a medium of Example 1 having thickness of 15 nm. The result is shown in Fig. 4.

10 Example 2

A set of magnetic recording media as shown in Fig. 1 was produced in the same manner as in Example 1 except that the granular magnetic layer was formed using a target of Co-12 at% Cr-10 at% Pt containing 10 mol% of SiO_2 , in which the platinum content was decreased by 2 at% as compared with Example 1 and Comparative Example 1..

The coercive force H_c was measured on each of the obtained magnetic recording medium in the same manner as in Example 1. Fig. 3 shows the dependence of the H_c on the $Br \delta$. The signal-to-noise ratio SNR was measured on the magnetic recording medium of this example having thickness of 14 nm, which corresponds to the $Br \delta$ of 70 G μ m and generates equal output to that of a medium of Example 1 having thickness of 15 nm. The result is shown in Fig 4.

As is apparent from Fig. 2, dependence of coercive force H_c on thickness of the magnetic layer shifts to higher H_c side by decreasing the partial pressure of H_2O . The coercive force H_c in the case of the partial pressure of H_2O of 3×10^{-11} Torr and the magnetic layer thickness of 15 nm, that is in a case of a specimen of Example 1, was 3,000 Oe, while H_c in the case of the partial pressure of H_2O of 4×10^{-10} Torr and the magnetic layer thickness of 15

nm, that is in a case of a specimen of Comparative Example 1, was 2,500 Oe. Thus, coercive force Hc was enhanced by 500 Oe. The values of the product Br δ of remanent magnetic flux density and film thickness for the both media were the same and equal to 70 G μ m.

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As is apparent from Fig. 3, even in the case where the platinum content was decreased by 2 at% to the value of 10 at% as the specimens of Example 2, the similar Hc values were attained to the case of H₂O partial pressure of 4×10^{-10} Torr and platinum content of 12 at% by virtue of lowering of H₂O partial pressure.

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The dependence of signal-to-noise ratio SNR on track recording density shown in Fig. 4 indicates that the most favorable SNR characteristics was obtained in the case of lowered H₂O partial pressure and reduced platinum content as the specimens of Example 2.

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Advantageous Effect of the invention

As described so far, by improving ultimate pressure of the sputtering apparatus and performing sputtering under a clean atmosphere according to the present invention, high coercive force is achieved and, as a result, the platinum content may be reduced. The media noise characteristic is excellent in a magnetic recording medium manufactured by applying these technologies. These effects bring about reduction of manufacturing cost and improvement of the media characteristics.

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More favorable effect is obtained when the non-magnetic intermediate layer is formed of substance selected from the group consisting of Ti, Cr, Zr, Hf, Ti alloy, Cr alloy, Zr alloy and Hf alloy, and has a crystal structure of hexagonal closest-packing.

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Since high coercive force is achieved by employing the method and the composition according to the invention, heating of the substrate is not needed anymore. Consequently, simplification and cost reduction of the manufacturing process is achieved and further, plastics with less cost may be
5 used for the substrate as well as conventional aluminum and glass substrates.

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Claims

- 1 A method for manufacturing a magnetic recording medium comprising steps of:
- 5 laminating a non-magnetic under-layer on a non-magnetic substrate by sputtering in an atmosphere in which partial pressure of H_2O is 2×10^{-10} Torr or less,
- laminating a non-magnetic intermediate layer on said under-layer by sputtering in an atmosphere in which partial pressure of H_2O is 2×10^{-10} Torr
- 10 or less,
- laminating a magnetic layer on said intermediate layer by sputtering in an atmosphere in which partial pressure of H_2O is 2×10^{-10} Torr or less, said magnetic layer comprising ferromagnetic grains and grain boundaries surrounding said grains,
- 15 laminating said protective layer on said magnetic layer, and laminating said liquid lubricant layer on said protective layer.
- 2 A method for manufacturing a magnetic recording medium according to claim 1, wherein said intermediate layer is made of a metal selected from the
- 20 group consisting of Ti, Cr, Zr, Hf, Ti alloy, Cr alloy, Zr alloy and Hf alloy and has a crystal structure of hexagonal closest packing.
- 3 A method for manufacturing a magnetic recording medium according to claim 1, wherein said intermediate layer has a thickness of from 0.5 nm to 20
- 25 nm
- 4 A method for manufacturing a magnetic recording medium according to claim 1, wherein said non-magnetic grain boundary is composed of oxide or nitride of at least one element selected from the group consisting of Mg, Al, Si,
- 30 Ti, Cr, Mn, Co, Zr, Ta, W and Hf.



- 5 A method for manufacturing a magnetic recording medium according to claim 1, wherein said under-layer is composed of chromium or chromium alloy.
- 6 A method for manufacturing a magnetic recording medium according to claim 1, wherein said substrate is composed of a material selected from the group consisting of crystallized glass, chemically strengthened glass and plastic.
- 7 A method for manufacturing a magnetic recording medium according to claim 1, wherein said step for forming said under-layer, said step for forming said intermediate layer, said step for forming said magnetic layer, said step for forming said protective layer, and said step for forming said liquid lubricant layer are conducted without heating said substrate in advance.
- 8 A magnetic recording medium manufactured by a method according to claim 1.