

TITLE OF THE INVENTION

SPUTTERING TARGET MEMBER, SPUTTERING TARGET ASSEMBLY, AND
METHOD FOR FORMING FILM

FIELD OF THE INVENTION

[0001] In one embodiment, the present invention relates to a sputtering target member for a magnetic recording layer. In another embodiment, the invention relates to a sputtering target assembly comprising such a sputtering target member. In yet another embodiment, the present invention relates to a method for forming a film using such a sputtering target member.

BACKGROUND OF THE INVENTION

[0002] In the field of magnetic recording, typified by hard disk drives, materials based on ferromagnetic metals such as Co, Fe, or Ni are used as materials for magnetic thin films which are responsible for recording. For example, in the recording layer of a hard disk that uses the perpendicular magnetic recording method that has been put into practical use in recent years, composite materials in which non-magnetic particles such as oxide particles and carbon particles are dispersed in a Co-Pt ferromagnetic alloy containing Co as a main component are often used. The recording layer may have a finer

granular structure in which magnetic particles are magnetically separated by non-magnetic particles, thereby increasing the amount of recording per unit area.

[0003] Due to its high productivity, magnetic thin films are often manufactured by sputtering a sputtering target containing the above-mentioned materials using a magnetron sputtering device. Therefore, technological development of sputtering targets for forming magnetic thin films has been made from various viewpoints.

[0004] Patent Literature 1 (Japanese Patent Application Publication No. 2013-37730) discloses a sputtering target in which a metal (magnetic metal, noble metal) constituting an $L1_0$ type ordered alloy of Fe-Pt and carbon are mixed.

In this literature, in order to suppress the expansion of the head spacing of the magnetic recording medium and improve the recording density, there is described a method for manufacturing a perpendicular magnetic recording medium, comprising:

(1) forming on a non-magnetic substrate a magnetic recording layer consisting of crystal grains of an ordered alloy and a grain boundary layer

made of carbon, and a protective layer precursor consisting of carbon and existing on the magnetic recording layer; and

(2) irradiating the protective layer precursor with hydrocarbon ions generated by plasma discharge against a hydrocarbon gas to transform the protective layer precursor into a protective layer,

the method characterized in that the hydrocarbon ions have an energy of 300 eV or more when reaching the protective layer precursor.

[0005] Patent Literature 2 (WO 2014/132746) discloses a Fe-Pt-C sputtering target comprising Fe, Pt and C, characterized in that the Fe-Pt-C sputtering target has a structure in which C primary particles containing inevitable impurities are dispersed so as not to come into contact with each other in a Fe-Pt alloy phase containing 33 at% or more and 60 at% or less of Pt with the remainder being Fe and inevitable impurities. According to Patent Literature 2, this Fe-Pt-C sputtering target has fewer particles.

[0006] Patent Literature 3 (Japanese Patent Application Publication No. 2018-172770) discloses a ferromagnetic material sputtering target, comprising a total of 70 mol% or more of metallic Co and metallic Pt at a molar ratio of Co:Pt = X:100-X ($59 \leq X < 100$), and 0 mol% or more and 20 mol% or less of

metal Cr, wherein the ferromagnetic material sputtering target comprises a Co particle phase containing 90 mol% or more of metallic Co and having an average particle size of 30 to 300 μm , and a Co-Pt alloy particle phase containing a total of 70 mol% or more of metallic Co and metallic Pt and having an average particle size of 7 μm or less under the conditions that the molar ratio is Co:Pt = Y:100-Y ($20 \leq Y \leq 60.5$). Patent Literature 3 also discloses containing a total of 25 mol% or less of one or more non-magnetic materials selected from the group consisting of carbon, oxides, nitrides, carbides, and carbonitrides. This ferromagnetic material sputtering target is described to have a high leakage magnetic flux and can suppress the generation of particles during sputtering by adopting a method of coarsening the Co phase while making the Co-Pt alloy phase finer.

[0007] Patent Literature 4 (WO 2012/081340) proposes adding 10 wtppm or more of B (boron) in addition to SiO_2 in a sputtering target for a magnetic recording film. It is described that by suppressing the formation of cristobalite, which causes the generation of particles during sputtering, it is possible to suppress microcracks in the target and generation of particles during sputtering, and to shorten the burn-in time.

PRIOR ART

[0008] Patent Literature

[Patent Literature 1] Japanese Patent Application Publication No. 2013-37730

[Patent Literature 2] WO 2014/132746

[Patent Literature 3] Japanese Patent Application Publication No. 2018-172770

[Patent Literature 4] WO 2012/081340

SUMMARY OF THE INVENTION

[0009] In recent years, when forming a magnetic recording layer, the substrate is sometimes heated in advance (for example, to about 200 °C). The main purpose is to improve the crystallinity of the magnetic particles, but as a side effect, the oxide particles may diffuse toward the magnetic particles, which may deteriorate the magnetic properties after film formation. Therefore, it is conceivable to use carbon as a grain boundary material that is stable even at a high temperature. However, simply adding carbon increases the number of particles during sputtering and greatly reduces the yield. Although it is possible to reduce particles by employing the techniques described in the above-mentioned prior art literatures, there is a limitation. Therefore, if particles can be reduced by a different approach than these, it would be useful from the

perspective of increasing the number of technological options and expanding the possibilities for further technological development.

[0010] Therefore, in one embodiment of the present invention, an object is to provide a sputtering target member for a magnetic recording layer that can suppress the generation of particles from a different perspective from the above-mentioned prior art. In another embodiment of the present invention, an object is to provide a sputtering target assembly comprising such a sputtering target member. In yet another embodiment of the present invention, an object is to provide a method for forming a film using such a sputtering target member.

[0011] The inventors of the present invention made extensive studies to solve the above problems, and found that using a Co-Pt sputtering target member with a higher carbide ratio is effective in suppressing particles. The present invention was completed based on the above findings, and is exemplified as below.

[0012]

[1]

A sputtering target member for a magnetic recording layer, comprising 10 to 70 mol% of Co, 5 to 30 mol% of Pt, 1.5 to 10 mol% of carbide, and a total of 0 to 30 mol% of one or more non-magnetic materials selected from carbon, oxides, nitrides, and carbonitrides.

[2]

The sputtering target member for a magnetic recording layer according to [1], wherein a molar ratio of the carbide to a total of the carbon and the carbide is 0.25 or more.

[3]

The sputtering target member for a magnetic recording layer according to [1] or [2], wherein the carbide comprises one or more selected from B_4C , Cr_3C_2 , and TiC .

[4]

The sputtering target member for a magnetic recording layer according to [3], comprising a total of 1.5 to 10 mol% of one or more selected from B_4C , Cr_3C_2 , and TiC .

[5]

The sputtering target for a magnetic recording layer according to any one of [1] to [4], comprising a total of 30 mol% or less of one or more metal elements selected from Cr, Ru, B, Ti, Si, and Mn.

[6]

The sputtering target member for a magnetic recording layer according to any one of [1] to [5], wherein a relative density is 90% or more.

[7]

A sputtering target assembly, comprising the sputtering target member for a magnetic recording layer according to any one of [1] to [6], and a backing tube or a backing plate bonded to the sputtering target member.

[8]

A method for forming a film, comprising sputtering the sputtering target member for a magnetic recording layer according to any one of [1] to [6].

[0013] According to an embodiment of the present invention, since carbide is stable even at a high temperature, it is possible to suppress the influence on magnetic properties after film formation, and at the same time, it is possible to obtain the significant effect of reducing particles during sputtering.

DETAILED DESCRIPTION OF THE INVENTION

[0014] (1. Sputtering target member)

(1-1. Composition)

In one embodiment according to the present invention, the sputtering target member comprises 10 to 70 mol% of Co, 5 to 30 mol% of Pt, 1.5 to 10 mol% of carbide, and a total of 0 to 30 mol% of one or more non-magnetic materials selected from carbon, oxides, nitrides, and carbonitrides. This composition has a high proportion of carbide in the entire sputtering target member, which contributes to suppression of particles during sputtering.

[0015] From the viewpoint of forming a magnetic recording layer, the concentration of Co in the sputtering target member is preferably 10 to 70 mol%. The concentration of Co may be adjusted as appropriate depending on the required magnetic properties of the magnetic recording layer, and typically it can be 20 to 70 mol%, more typically it can be 30 to 70 mol%, even more

typically it can be 40 to 60 mol%. In addition, the Co considered here is metallic Co existing alone or forming an alloy with other metals such as Pt.

[0016] From the viewpoint of forming a magnetic recording layer, the concentration of Pt in the sputtering target member is preferably 5 to 30 mol%. The concentration of Pt may be adjusted as appropriate depending on the required magnetic properties of the magnetic recording layer, and typically it can be 5 to 25 mol%, more typically it can be 10 to 25 mol%, even more typically it can be 10 to 20 mol%. In addition, the Pt considered here is metallic Pt existing alone or forming an alloy with other metals such as Co.

[0017] The concentration of carbide in the sputtering target member is preferably 1.5 to 10 mol%. From the viewpoint of increasing the particle suppression effect during sputtering, the lower limit of the carbide concentration is 1.5 mol% or more, preferably 1.8 mol% or more, and more preferably 2.0 mol% or more. However, if the concentration of carbide is too high, the effect of suppressing particles will decrease, so the upper limit of the concentration of carbide is 10 mol% or less, preferably 8.0 mol% or less, and more preferably 6.0 mol% or less.

[0018] The sputtering target member may contain one type of carbide, or may contain two or more types of carbide. Examples of the carbide include carbides of one or more elements selected from B, Ca, Cr, Nb, Si, Ta, Ti, W and Zr. Among these, one or more selected from B_4C , Cr_3C_2 and TiC are preferred, one or two selected from B_4C and Cr_3C_2 are more preferred, and B_4C is even more preferred.

[0019] Therefore, in a preferred embodiment, the sputtering target member comprises a total of 1.5 to 10 mol%, preferably 1.8 to 8.0 mol%, and more preferably 2.0 to 6.0 mol% of one or more selected from B_4C , Cr_3C_2 and TiC.

In a more preferred embodiment, the sputtering target member comprises a total of 1.5 to 10 mol%, preferably 1.8 to 8.0 mol%, and more preferably 2.0 to 6.0 mol% of one or two selected from B_4C and Cr_3C_2 .

In an even more preferred embodiment, the sputtering target member comprises 1.5 to 10 mol%, preferably 1.8 to 8.0 mol%, and more preferably 2.0 to 6.0 mol% of B_4C .

[0020] From the viewpoint of adjusting the magnetic properties of the magnetic recording layer, a non-magnetic material other than carbide may be

added to the sputtering target member. Specifically, one or more non-magnetic materials selected from carbon, oxides, nitrides, and carbonitrides may be contained in a total amount of 0 to 30 mol%, preferably in an amount of 0 to 25 mol%, and more preferably in an amount of 0 to 20 mol%.

As examples of oxides, mention can be made to oxides of one or more elements selected from Al, B, Ba, Be, Ca, Ce, Co, Cr, Dy, Er, Eu, Ga, Gd, Ho, Li, Mg, Mn, Nb, Nd, Pr, Sc, Si, Sm, Sr, Ta, Tb, Ti, V, Y, Zn and Zr. Among the oxides, oxides of one or more elements selected from B, Co, Cr, Si, and Ti are preferred.

As examples of nitrides, mention can be made to nitrides of one or more elements selected from Al, B, Ca, Nb, Si, Ta, Ti, and Zr.

As examples of carbonitrides, mention can be made to carbonitrides of one or more elements selected from Ti, Cr, V, and Zr.

[0021] From the viewpoint of effectively suppressing particles during sputtering, the molar ratio of carbide to the total of carbon and carbide in the sputtering target member is preferably 0.25 or more, more preferably 0.4 or more, even more preferably 0.6 or more, even more preferably 0.8 or more, and most preferably 1.0.

[0022] The sputtering target may contain, as a third element, one or more metal elements selected from Cr, Ru, B, Ti, Si, and Mn in a total amount of 30 mol% or less, and for example, in an amount of 0.01 to 20 mol%, and typically in an amount of 0.05 to 10 mol%. These metals are added as necessary to improve the characteristics of the magnetic recording layer. The formulation ratio can be adjusted variously within the above range, and in any case, the properties as an effective magnetic recording layer can be maintained. In addition, in the present invention, element B is also treated as a metal. If the above-mentioned third elements exist as a carbide, oxide, nitride, or carbonitride rather than as a single metal or alloy, they are treated as the above-mentioned non-magnetic materials rather than as the third elements as defined herein.

[0023] (1-2. Relative density)

In one embodiment according to the present invention, the sputtering target member preferably has a relative density of 90% or more, more preferably 95% or more. The relative density can be, for example, 90% to 100%. In this way, a uniform thin film can be produced with less occurrence of abnormal discharge (arcing) during film formation. As used herein, the relative

density is a value obtained by dividing the actually measured density of the sputtering target member by the calculated density (also referred to as the theoretical density). The actual density is measured by the Archimedes method. The calculated density is the density when it is assumed that the constituent components of the raw material powder of the target member are mixed without diffusing or reacting with each other, and is calculated by the following formula.

Formula: Calculated density = Σ (molecular weight of constituent components of raw material powder $\times$ molar concentration of constituent components of raw material powder) / Σ (molecular weight of constituent components of raw material powder $\times$ molar concentration of constituent components of raw material powder / literature value density of constituent components of raw material powder).

Here, Σ means calculating the sum of all constituent components other than impurities of the target member.

[0024] The sputtering target member may be bonded to a substrate such as a backing plate or a backing tube, if necessary, and mounted in a sputtering apparatus as a sputtering target assembly. The sputtering target member may

also be mounted on a sputtering apparatus as a sputtering target without using a substrate.

[0025] (2. Manufacturing method)

The sputtering target member according to the present invention can be manufactured using a powder sintering method, for example, by the following method.

[0026] First, raw material powder is prepared according to the composition of the intended sputtering target member. As the raw material powder, for example, in addition to Co powder, Pt powder, and carbide powder, mention can be made to powder of one or more non-magnetic materials selected from carbon powder, oxide powder, nitride powder, and carbonitride powder. Furthermore, one or more metal powders selected from Cr, Ru, B, Ti, Si, and Mn may be prepared.

[0027] The purity of the raw material powder is preferably 90 mol% or more, more preferably 95 mol% or more, and even more preferably 99.9 mol% or more. In a typical embodiment, the raw powder does not contain anything other than the indicated component and inevitable impurities.

[0028] In order to realize a uniform structure, the upper limit of the median diameter (D50) of each raw material powder is preferably 200 μm or less, more preferably 100 μm or less, even more preferably 50 μm or less, and even more preferably 10 μm or less. Further, for the reason of preventing oxidation of the raw material powder, the lower limit of the median diameter of the raw material powder is preferably 0.1 μm or more, more preferably 0.3 μm or more, and even more preferably 0.5 μm or more. The median diameter can be adjusted by crushing or sieving.

[0029] Next, the prepared raw material powder is weighed so as to have a desired composition, and mixed using a known method such as a ball mill, which also serves as pulverization, to obtain a mixed powder. At this time, it is desirable to suppress oxidation of the raw material powder as much as possible by enclosing an inert gas in the pulverization vessel. Examples of the inert gas include Ar and N_2 gas.

[0030] In order to realize a uniform structure, the upper limit of the median diameter (D50) of the mixed powder is preferably 20 μm or less, more preferably 10 μm or less, and even more preferably 5 μm or less, respectively. Further, for the reason of preventing oxidation of the mixed powder, the lower

limit of the median diameter of the mixed powder is preferably 0.1 μm or more, more preferably 0.3 μm or more, and even more preferably 0.5 μm or more.

[0031] In the present invention, the median diameter of each raw material powder and the mixed powder means the particle diameter (D50) at an accumulated value of 50% on a volume basis in a particle diameter distribution determined by a laser diffraction / scattering method. In the Examples, a particle diameter distribution analyzer model LA-920 manufactured by Horiba, Ltd. was used and measurement was performed by dispersing the powder in an ethanol solvent. For the refractive index, the value of metal cobalt was used.

[0032] The mixed powder thus obtained is molded and sintered by a hot pressing method in a vacuum atmosphere or an inert gas atmosphere. In addition to the hot pressing method, various pressure sintering methods such as a plasma discharge sintering method can be used. In particular, hot isostatic pressing (HIP) is effective in increasing the density of sintered bodies, and it is preferable to carry out the hot pressing method and hot isostatic pressing (HIP) in this order from the viewpoint of improving the density of the sintered body.

[0033] In order to prevent coarsening of crystal grains, the upper limit of the holding temperature during the sintering is preferably 1500 $^{\circ}\text{C}$ or less, more

preferably 1400 °C or lower, and even more preferably 1200 °C or lower, although it may also depend on the composition of the target. In addition, to avoid a decrease in the density of the sintered body, the lower limit of the holding temperature during sintering is preferably 600 °C or higher, more preferably 650 °C or higher, and even more preferably 700 °C or higher.

[0034] The lower limit of the press pressure during the sintering is preferably 10 MPa or more, more preferably 15 MPa or more, and even more preferably 20 MPa or more to promote sintering. In addition, the upper limit of the press pressure during the sintering is preferably 70 MPa or less, more preferably 50 MPa or less, and even more preferably 40 MPa or less, considering the strength of the die.

[0035] The lower limit of the sintering time is preferably 0.1 hours or more, more preferably 0.2 hours or more, and even more preferably 0.5 hours or more, to improve the density of the sintered body. Further, the upper limit of the sintering time is preferably 10 hours or less, more preferably 5 hours or less, and even more preferably 2 hours or less, to prevent coarsening of crystal grains.

[0036] A sputtering target member according to an embodiment of the present invention can be manufactured by molding the obtained sintered body into a desired shape using a lathe or the like. The shape of the target is not particularly limited, but examples thereof include a flat plate shape (including a disk shape and a rectangular plate shape) and a cylindrical shape. In one embodiment, the sputtering target member according to the present invention is particularly useful as a sputtering target member used for forming a magnetic recording layer having a granular structure.

[0037] (3. Method for forming film)

In one embodiment according to the present invention, there is provided a method for forming a film, comprising a step of sputtering using the sputtering target member as described above. The sputtering conditions can be set as appropriate.

EXAMPLES

[0038] Examples of the present invention are shown below along with comparative examples, but the examples and Comparative Examples are provided to better understand the present invention and its advantages, and are not intended to limit the present invention.

[0039] (1. Preparation of sputtering target member)

The following powders were prepared as raw material powders. All of them were highly pure products with a purity of 99.9% by mass or more, and do not contain anything other than the indicated components and inevitable impurities. The median diameter of these powders was adjusted appropriately by sieving.

Co powder: median diameter (D50) = 3.3 μm

Pt powder: median diameter (D50) = 21.8 μm

Cr powder: median diameter (D50) = 2.7 μm

B powder: median diameter (D50) = 3.9 μm

C powder: median diameter (D50) = 25.5 μm

B₄C powder: median diameter (D50) = 0.5 μm

Cr₃C₂ powder: median diameter (D50) = 1.2 μm

TiC powder: median diameter (D50) = 5.1 μm

B₂O₃ powder: median diameter (D50) = 0.5 μm

TiO₂ powder: median diameter (D50) = 0.9 μm

CoO powder: median diameter (D50) = 2.1 μm

[0040] Next, each of the above-mentioned raw material powders was pulverized while being mixed using a ball mill with zirconia balls as a pulverizing medium so as to have the molar ratio described in the raw material composition column of Table 1 according to the test number. The median diameter (D50) of all of the obtained mixed powders was approximately 0.5 to 5.0 μm. Next, the obtained mixed powder was filled into a carbon mold, and sintered by hot pressing in a vacuum atmosphere and hot isostatic pressing (HIP) in an Ar atmosphere. Hot pressing was carried out at a holding temperature of 800 to 1100 °C and a pressing pressure of 20 to 30 MPa for 1 to 2 hours. The hot isostatic pressing (HIP) after the hot pressing was performed for densification. Thereafter, the sintered body after HIP was ground using a general-purpose lathe and a surface grinder to obtain a disc-shaped sputtering target member with a diameter of 180 mm and a thickness of 5 mm.

[0041] (2. Relative density)

The relative density of each sputtering target member obtained by the above procedure was measured according to the method described above

(relative density = actually measured density / theoretical density × 100%). The results are shown in Table 1.

[0042]

Table 1-1

Test Number	Raw material composition (mol%)										
	Co	Cr	Pt	B	B ₂ O ₃	TiO ₂	CoO	C	B ₄ C	TiC	Cr ₃ C ₂
Example 1	53	5	20	-	5	5	10		2		
Example 2										2	
Comparative Example 1								2			
Example 3	60	10	20	5							5
Example 4								3			2
Comparative Example 2								4			1
Comparative Example 3								5			

[0043]

Table 1-2 (Continuation of Table 1)

Test Number	Carbide molar ratio to total non-magnetic material	Carbide molar ratio to total carbon and carbide	Carbide concentration relative to entire raw material (mol%)	Relative density
Example 1	0.09	1	2	94%
Example 2	0.09	1	2	100%
Comparative Example 1	0	0	0	100%
Example 3	1	1	5	95%
Example 4	0.4	0.4	2	94%
Comparative Example 2	0.2	0.2	1	94%
Comparative Example 3	0	0	0	99%

[0044] (3. Number of particles)

Each sputtering target member obtained by the above procedure was mounted on a magnetron sputtering device (C-3010 sputtering system manufactured by Canon Anelva Co., Ltd.), and sputtering was performed. The sputtering conditions were an input power of 1 kW, an Ar gas pressure of 1.7 Pa. After performing pre-sputtering for a total of 2 hours, a film was formed on a 4-inch diameter silicon substrate for 20 seconds. Then, the number of particles with a particle diameter of 0.07 μm or more adhering to the substrate was measured using a surface foreign matter inspection device (Candela CS920 manufactured by KLA-Tencor). The results are shown in Table 2.

[0045]

Table 2

Test Number	Number of particles detected
Example 1	60
Example 2	1500
Comparative Example 1	2100
Example 3	300
Example 4	4000
Comparative Example 2	15000
Comparative Example 3	20000

[0046] Comparing Example 1, Example 2, and Comparative Example 1, which had the same composition except for carbon and carbide, they all had a common molar concentration of C source of 2 mol %. However, compared to

Comparative Example 1 in which only carbon was used as a C source, the number of particles was smaller in Examples 1 and 2 in which only carbide was used as a C source. Comparing Example 1 and Example 2, it can be seen that the number of particles was drastically reduced by using B_4C as a carbide.

[0047] Comparing Example 3, Example 4, Comparative Example 2, and Comparative Example 3, which had the same composition except for carbon and carbide, they had a common molar concentration of C source of 5 mol%. However, compared to Comparative Example 3 in which only carbon was used as a C source, the number of particles was smaller in Comparative Example 2, Example 3, and Example 4 in which carbide was used as the C source. Comparing Comparative Example 2, Example 3, and Example 4, it can be seen that the number of particles decreased as the carbide content increased. Furthermore, compared to Comparative Example 2, in which the carbide concentration was less than 1.5 mol%, the reduction in the number of particles in Examples 3 and 4, in which the carbide concentration was 1.5 mol% or more, was remarkable.

CLAIMS

1. A sputtering target member for a magnetic recording layer, comprising 10 to 70 mol% of Co, 5 to 30 mol% of Pt, 1.5 to 10 mol% of carbide, and a total of 0 to 30 mol% of one or more non-magnetic materials selected from carbon, oxides, nitrides, and carbonitrides, wherein a molar ratio of the carbide to a total of the carbon and the carbide is 0.25 or more.
2. The sputtering target member for a magnetic recording layer according to claim 1, wherein a molar ratio of the carbide to a total of the carbon and the carbide is 0.4 or more.
3. The sputtering target member for a magnetic recording layer according to claim 1 or 2, wherein the carbide comprises one or more selected from B_4C , Cr_3C_2 , and TiC .
4. The sputtering target member for a magnetic recording layer according to claim 3, comprising a total of 1.5 to 10 mol% of one or more selected from B_4C , Cr_3C_2 , and TiC .

5. The sputtering target for a magnetic recording layer according to any one of claims 1 to 4, comprising a total of 30 mol% or less of one or more metal elements selected from Cr, Ru, B, Ti, Si, and Mn.
6. The sputtering target member for a magnetic recording layer according to any one of claims 1 to 5, wherein a relative density is 90% or more.
7. A sputtering target assembly, comprising the sputtering target member for a magnetic recording layer according to any one of claims 1 to 6, and a backing tube or a backing plate bonded to the sputtering target member.
8. A method for forming a film, comprising sputtering the sputtering target member for a magnetic recording layer according to any one of claims 1 to 6.