

MAGNETIC RECORDING MEDIUM AND MANUFACTURING METHOD THEREOF

TECHNICAL FIELD OF THE INVENTION

The present invention relates to a magnetic recording medium and a manufacturing method thereof and, more particularly, to a hard-disk magnetic recording medium constituting a hard-disk device and a method of manufacturing a protective film and lubricating layer thereof.

PRIOR ART

Hard-disk devices, which are major external recording devices for computers, are rapidly increasing in recording density and transfer rate and decreasing in size with the progress of multimedia. The higher recording density of the magnetic recording medium – a main component of hard-disk devices – has made it necessary to reduce the head flying height and make the protective film and lubricating layer thinner. Additionally, the medium's rotational speed has been increased as a result of the higher transfer rate. This requires that the tribological mechanical strength be maintained for the magnetic recording medium in conjunction with the enhancement of its recording density.

The magnetic recording medium, a component that magnetically records information, is successively laminated with an undercoat film, magnetic film, and protective film on a substrate, and further coated with a lubricant.

Normally, the substrate is made of an Al alloy, with the surface thereof protected by an NiP-plated layer. Further, a glass substrate is used if improved shock resistance is required.

The magnetic film for recording information is made of a Co-based ferromagnetic substance, with a Cr undercoat film applied for enhanced magnetic properties.

The magnetic film is further coated with diamond-like carbon (DLC), a hard carbon-based protective film that offers excellent lubricity and high wear resistance for

protection purposes. Normally, the carbon protective film is formed by the sputter method, as with the Cr undercoat film and the magnetic film, or by the plasma CVD method using hydrocarbon gas as a raw material.

Perfluoropolyether (PFPE) is commonly used as the lubricating layer applied on top of the protective film. The lubricating layer is formed by dipping or spin coating by diluting perfluoropolyether with a solvent. The lubricating layer is approximately one to several nm in thickness. This thickness is approximately the same as or severalfold of that of the one molecule layer of lubricant. The thickness of one molecule layer, which is dependent on the quantity of molecules in the lubricant, is approximately twice the molecular radius of gyration (e.g., refer to H. Tani, IEEE Trans. On Magn., 35, 5. (1999)). This has been confirmed by atomic-force microscopy and measured to be roughly 1 nm for 2000 g/mol and roughly 1.5 nm for 4000 g/mol in the case of PFPE Z-dol.

The lubricating layer on top of the protective film is divided into two types. One of them is a layer (bonded lubricating layer) combined with (chemically adsorbed to) the protective film, whereas the other is an uncombined layer (mobile lubricating layer). Experimentally, the lubricating layer, which remains unremoved after rinsing thereof with a solvent such as fluorocarbon, is the bonded lubricating layer, whereas that removed is the mobile lubricating layer. Having the effect of repairing the lubricating film shaved by sliding, the mobile lubricating layer has a considerable impact on the sliding property.

PROBLEM SOLVED BY THE INVENTION

However, the thick mobile lubricating layer has resulted in problems including adhering of the layer to the head, affecting the head flying height and stiction between the magnetic recording medium and the head, stopping rotation of the magnetic recording medium.

Moreover, because the magnetic recording medium rotates at a high speed, the mobile lubricating layer moves toward the outer perimeter (spinoff phenomenon). This movement results in the area deprived of the mobile lubricating layer becoming easily worn and the

area on the outer-perimeter side with accumulated lubricant readily adhering to the head. A spinoff phenomenon-free bonded lubricating layer has been hitherto provided to suppress wear in the event that the mobile lubricating layer is worn away (e.g., refer to Japanese Unexamined Patent Application Publication No. 11-172268). For this reason, it has been impossible to make the lubricating layer thinner than a given thickness.

In light of the above, it is an object of the present invention to provide a magnetic recording medium with ability for a higher transfer rate and higher recording density, and with an increased resistance to the spinoff phenomenon caused by high speed rotation; and a manufacturing method thereof.

MEANS FOR SOLVING THE PROBLEM

To achieve such an object, a magnetic recording medium according to the present invention is successively laminated with at least a magnetic film, protective film, and lubricating layer on a non-magnetic substrate, in which 90% or more of the area of said lubricating layer is not chemically adsorbed to said protective film, and in which said lubricating layer is an average of one molecule layer or less in thickness.

It is preferable if a surface of said protective film is at least fluorine-added or fluorine-terminated.

It is further preferred that the contact angle of the surface of said protective film with respect to water be 90 degrees or more.

It is also preferred that at least part of the surface of said protective film be a fluorine-added amorphous carbon-based protective film.

Moreover, a method of manufacturing a magnetic recording medium according to the present invention comprises the steps of forming a magnetic film on a non-magnetic substrate, forming a protective film on top of said magnetic film and forming a lubricating

layer with an average thickness of one molecule layer or less on top of said protective film so as to ensure that 90% or more of the area of said lubricating layer is not chemically adsorbed to said protective film.

The method further preferably comprises the step of fluorine-terminating the surface of said formed protective film by decomposition of a carbon fluoride-based gas.

It is also preferred that the step of forming said protective film comprises a plasma CVD method using hydrocarbon gas to which carbon fluoride-based gas has been added as a raw material.

It is also preferred that the step of forming said protective film comprises a reactive sputter method using carbon as a target material in a sputter gas to which carbon fluoride-based gas has been added.

EMBODIMENTS OF THE INVENTION

Embodiments of the present invention will be described below in detail.

In the manufacture of the magnetic recording medium according to the present embodiments, at least a magnetic film, protective film, and lubricating film are successively laminated on top of a non-magnetic substrate. Here, as the aforementioned conventional method can be used for the steps of forming the magnetic film on the non-magnetic substrate and forming the protective film on top of the magnetic film, a description thereof will be omitted.

Next, prior to lamination of the lubricating layer, the protective-film surface is covered with fluorine (fluorination), followed by the formation of a mobile lubricating layer of one molecule layer or less in thickness, thus forming a lubricating layer substantially free of a bonded lubricating layer. For fluorination, any of the following methods can be adopted:

- 1) The protective-film surface is fluorine-terminated by decomposition of a carbon fluoride-based gas such as CF₄ (tetrafluoromethane) or C₂F₆ (hexafluoroethane) using plasma, UV irradiation, etc.
- 2) A fluorine-added amorphous carbon-based film is used for all or part of the surface of the protective film. For this, a fluorine-added amorphous carbon-based protective film is formed by the plasma CVD method using hydrocarbon gas to which carbon fluoride-based gas such as CF₄ or C₂F₆ has been added as a raw material.
- 3) A fluorine-added amorphous carbon-based film is used for all or part of the surface of the protective film. For this, the protective film is formed by the reactive sputter method using carbon as a target material in a sputter gas (e.g., Ar) to which carbon fluoride-based gas such as CF₄ or C₂F₆ has been added.

The present invention is therefore characterized in that a mobile lubricating layer of one molecule layer or less is provided without forming a bonded lubricating layer on the fluorinated surface of the protective film, unlike the prior art (Japanese Unexamined Patent Application Publication No. 5-174354, for example).

Of the bonded and mobile lubricating layers, the mobile lubricating layer contributes considerably to the sliding property. In the conventional method of using the bonded and mobile lubricating layers to comprise the lubricating layer, the mobile lubricating layer moves to the outer-perimeter side due to the spinoff phenomenon as a result of rotation of the magnetic recording medium, resulting in reduced thickness of the mobile lubricating layer. In contrast, the present invention prevents chemical adsorption of the lubricant by a method including fluorine termination of the protective-film surface, thus providing a mobile lubricating layer of one molecule or less in thickness, without forming a bonded lubricating layer. The mobile lubricating layer of one molecule layer or less thus provided is free of the spinoff phenomenon, and this is presumed to be due to the fact that the protective-film surface and the lubricant both contain carbon fluoride. Therefore, such a configuration is effective in preventing the spinoff phenomenon and reducing the thickness of the lubricating layer.

Here, the thickness of the one molecule layer has been determined experimentally to be the saturation value obtained when increasing the thickness of the bonded lubricating layer in the lubricating layer by heat treatment or UV irradiation, and the maximum thickness of the bonded lubricating layer in the lubricating layer applied by the vapor deposition method (e.g., refer to Japanese Unexamined Patent Application Publication No. 2002-324310).

In the case of Fomblin Z-dol used as lubricant in the embodiments described below, the thickness of the one molecule layer, calculated from the maximum thickness of the bonded lubricating layer applied by the vacuum vapor deposition method, was found to be approximately 1.4 nm to 1.5 nm (refer to Japanese Unexamined Patent Application Publication No. 2002-324310). For a sample obtained by thermally treating a thick lubricating layer (4 nm) applied by the dip method, the thickness of the one molecule layer, measured from the maximum thickness of the bonded lubricating layer, was found to be approximately 1.4 nm.

The fact that no bonded lubricating layer is formed indicates that the lubricating layer is substantially made of the mobile lubricating layer. Here, the term “substantially” does not mean that all of the lubricating layer constituting the lubricating layer must have fluidity, and it suffices for the percentage of lubricant having fluidity to be 90% or more. It is preferred, however, that the percentage thereof be 95% or more.

Embodiments of the present invention will be described below.

EMBODIMENTS

Embodiment 1

In the present embodiment, a method of fluorine-terminating the protective-film surface by the plasma CVD method will be described. A magnetic disk 65 mm in diameter was used as the substrate for the experiment. An NiP film, Cr undercoat film, CoCrTaPt magnetic film, and nitrogen-added amorphous carbon protective film were laminated in succession on top of

the Al substrate for use as a sample. Fluorine termination of the protective-film surface was conducted by the ECR (electron cyclotron resonance) plasma CVD method (refer to Japanese Unexamined Patent Application Publication No. 2000-144429). The manufacturing conditions were as follows.

- Pressure reached: 1.3×10^{-4} Pa or less
- Microwave: 200 W output, 2.45 GHz
- Magnetic field: 1.5 kG
- Reactive gas: Freon CF₄
- Reaction pressure: 0.7 Pa
- Gas flowrate: 20 sccm
- Substrate temperature: Room temperature

A lubricating layer of 0.5 nm to 2.5 nm was applied on top thereof. The lubricant used was Fomblin Z-dol made by Ausimont. The layer was formed by the dip method, with thermal treatment (100°C) provided for approximately one hour. The sample was subjected to a spinoff test in which the sample was rotated at high speed (10,000 revolutions/min) for 10 days. The thicknesses of the mobile and bonded lubricating layers were determined before and after the spinoff test. Here, the lubricating-layer thicknesses were measured by infrared spectroscopy (IR). As the lubricant contains CF bond, infrared absorption resulting from CF vibration appears near 1270 cm^{-1} , thus enabling determination of the lubricating-layer thicknesses from the amount of absorbed infrared radiation. The thickness measurements were calculated from the difference in absorption between before and after application of the lubricating layer.

Of the lubricating layers, the part that was rinsed with the fluorocarbon solvent was regarded as the mobile lubricating layer, whereas that which remained unreduced was regarded as the bonded lubricating layer. It is to be noted, however, that because the bonded-lubricating-layer thickness remains unchanged before and after the experiment, the post-experiment thickness was used. More specifically:

- (1) Measurement was conducted by IR prior to application of the lubricating film.
- (2) Measurement was similarly performed following the application of the lubricating film and prior to the spinoff test, and the total lubricating-layer thickness before the spinoff test was determined from the difference from (1).
- (3) Measurement was similarly performed following the spinoff test, and the total lubricating-layer thickness after the spinoff test was determined from the difference from (2).
- (4) Then, measurement was similarly performed following a 5-min ultrasonic cleaning in the fluorocarbon solvent, and the bonded-lubricating-layer thickness was determined from the difference from (1).
- (5) The bonded-lubricating-layer thickness was subtracted from the total lubricating-layer thickness before the spinoff test for use as the mobile-lubricating-layer thickness before the spinoff test.
- (6) The bonded-lubricating-layer thickness was subtracted from the total lubricating-layer thickness after the spinoff test for use as the mobile-lubricating-layer thickness after the spinoff test.

The properties of the fluorine-terminated surface will be described in embodiment 2. The spinoff-test results are shown in Table 1. The bonded lubricating layer was hardly formed due to fluorine termination of the protective film. When the mobile-lubricating-layer thickness before the spinoff test was less than 1 nm, the layer barely span off, remaining unmoved even after the spinoff test. When the layer thickness was 1.5 nm or more, 1.2 nm of the mobile lubricating layer remained. The value, smaller than the thickness of the one molecule layer of Z-dol (approx. 1.4 nm), is close thereto, and it is clear that an approximately one molecule layer of the mobile lubricating layer remains. Therefore, when the average mobile-lubricating-layer thickness is greater than that of the one molecule layer, the film thickness is reduced to approximately that of the one molecule layer by the spinoff test. On the other hand, when the average thickness is less than that of the one molecule layer, the film thickness remains basically unchanged by the spinoff test.

Fluorine termination of the protective-film surface made it possible to almost completely

eliminate the bonded lubricating layer, whereas keeping the mobile lubricating layer an average of one molecule or less in thickness enabled nearly complete elimination of layer thickness reduction in the 10-day spinoff test.

Table 1

Sample	No. 1	No. 2	No. 3	No. 4
Mobile-lubricating-layer thickness before spinoff test [nm]	0.5	1	1.5	2.5
Mobile-lubricating-layer thickness after spinoff test [nm]	0.4	0.9	1.2	1.2
Bonded-lubricating-layer thickness [nm]	0	0	0	0

Comparative Example 1

For comparison with embodiment 1, a similar test was conducted on a magnetic disk with its protective-film surface not fluorine-terminated. A magnetic disk 65 mm in diameter was used as the substrate for the experiment. An NiP film, Cr undercoat film, CoCrTaPt magnetic film, and nitrogen-added amorphous carbon protective film were laminated in succession on top of the Al substrate for use as a sample. A lubricating layer of 0.5 nm to 2.5 nm was applied on top thereof. The lubricant used was Fomblin Z-dol made by Ausimont. The layer was formed by the dip method, with thermal treatment (100°C) provided for approximately one hour. The sample was subjected to a spinoff test in which the sample was rotated at high speed (10,000 revolutions/min) for 10 days. The thicknesses of the mobile and bonded lubricating layers were determined before and after the spinoff test.

The spinoff-test results are shown in Table 2. A bonded lubricating layer was found to be formed on top of the protective film, with the mobile lubricating layer thinned by the spinoff test. Even when the mobile lubricating layer was reduced to a thickness of the one molecule layer or less, the majority thereof disappeared in the 10-day spinoff test.

Table 2

Sample	No. 5	No. 6	No. 7	No. 8
Mobile-lubricating-layer thickness before spinoff test [nm]	0.4	0.8	1.2	2.1
Mobile-lubricating-layer thickness after spinoff test [nm]	0.1	0.15	0.25	0.3
Bonded-lubricating-layer thickness [nm]	0.15	0.2	0.3	0.4

Embodiment 2

A description will be given of a method of making a protective film with a fluorine-added surface by forming a second protective film constituted by a fluorine-added amorphous carbon film, by the plasma CVD method, on top of a first protective film formed in advance. A fluorine-added amorphous carbon film (a-CFH) was formed instead of fluorine-terminating the protective-film surface by the ECR (electron cyclotron resonance) plasma CVD method as shown in embodiment 1. The manufacturing conditions were the same as in embodiment 1, except that the reactive gas was a mixed gas of ethylene C₂H₆ and freon CF₄ (CF₄ percentage: 70%, 80%).

The contact angle of the protective film with respect to water is shown in Table 3. Here, a freon gas percentage of 100% in the reactive gas represents the condition in embodiment 1, whereas a CF gas percentage of 0% in the reactive gas indicates the condition in comparative example 1. In plasma treatment using 100% freon, the protective film was successfully formed except for slight etching of the film. As for the sample plasma-treated (fluorine-terminated) using freon-added gas or that on which a fluorine-added amorphous carbon film was formed, fluorine was detected by photo-electron spectroscopy from the surface, indicating that the surface had been fluorinated. The findings also showed that the water contact angle was large, at 90 degrees or more. From the results, it is apparent that the surface is fluorinated.

Table 3

Fluorination	Yes			No
CF gas percentage in reactive gas [%]	100	80	70	0
a-CFH film-forming rate [nm/s]	-0.1	0.01	0.17	0.8
Water contact angle [deg]	102	107	105	72

On top thereof, 1 nm to 2.5 nm of Fomblin Z-dol was applied as a lubricating layer. These samples were rotated at high speed (10,000 revolutions/min) for approximately 10 days. The measured thicknesses of the mobile and bonded lubricating layers before and after the spinoff test are shown in Table 4. As for the sample with a formed fluorine-added amorphous carbon film (freon gas percentage: 70%, 80%), a bonded lubricating layer was hardly formed. As with embodiment 1, the spinoff-test results show that when the average thickness of the mobile lubricating layer was greater than that of the one molecule layer, the film thickness was reduced to approximately that of the one molecule layer. On the other hand, when the average thickness was less than that of the one molecule layer, the film thickness remained roughly unchanged by the spinoff test.

Table 4

Sample	No. 9	No. 10	No. 11	No. 12
CF gas percentage in reactive gas [%]	80	80	70	70
Mobile-lubricating-layer thickness before spinoff test [nm]	1.0	2.5	1.0	2.5
Mobile-lubricating-layer thickness after spinoff test [nm]	0.9	1.3	0.7	1.2
Bonded-lubricating-layer thickness [nm]	0	0	0.05	0.1

Thus, fluorine termination of the protective-film surface or formation of a fluorine-added amorphous carbon film thereon almost completely eliminates the formation of a bonded lubricating layer on the surface. Further, when the average mobile-lubricating-layer

thickness is greater than that of the one molecule layer, the film thickness decreases to that of the one molecule layer over the 10-day spinoff test, whereas when the average thickness is less than that of the one molecule layer, the film thickness remains basically unchanged. Therefore, keeping the mobile lubricating layer one molecule or less in thickness suppresses spinoff, forming a lubricating layer made up of a mobile lubricating layer alone – the type of lubricating layer that considerably contributes to wear resistance. Against a backdrop of the declining head flying height with an increase in the recording density, the present invention is effective for obtaining a thin lubricating layer.

As for the fluorination method, it is apparent that fluorine termination of the protective-film surface by the decomposition of a mixed carbon fluoride-based gas such as CF₄ or C₂F₆ and another gas in plasma, or the formation of a fluorine-added amorphous carbon film on the surface, is effective. Alternatively, the plasma process may be replaced, for example, by UV irradiation. It may also be possible to form the film by the reactive sputter method using a sputter gas such as Ar to which carbon fluoride-based gas such as CF₄ or C₂F₆ has been added.

It has been experimentally confirmed that it is not necessary that all of the lubricant be a mobile layer, and that the effect of the invention can be produced as long as the percentage thereof is 90% or more.

ADVANTAGEOUS EFFECT OF THE INVENTION

As described above, it is possible according to the present invention to implement a magnetic recording medium that is resistant to the spinoff phenomenon caused by high speed rotation and has a thin lubricating layer suitable for higher recording density.

CLAIMS

1. A magnetic recording medium successively laminated with at least a magnetic film, protective film, and lubricating layer on a non-magnetic substrate, wherein 90% or more of the area of said lubricating layer is not chemically adsorbed to said protective film, and wherein said lubricating layer is, on average, one molecule layer or less in thickness.

2. The magnetic recording medium according to claim 1, wherein a surface of said protective film is at least fluorine-added or fluorine-terminated.

3. The magnetic recording medium according to claim 1, wherein the contact angle of a surface of said protective film with respect to water is 90 degrees or more.

4. The magnetic recording medium according to claim 1, wherein at least a part of a surface of said protective film is a fluorine-added amorphous carbon-based protective film.

5. A method of manufacturing a magnetic recording medium, comprising the following steps:

forming a magnetic film on a non-magnetic substrate;

forming a protective film on top of said magnetic film; and

forming a lubricating layer with an average thickness of one molecule layer or less on top of said protective film so as to ensure that 90% or more of the area of said lubricating layer is not chemically adsorbed to said protective film.

6. The method of manufacturing a magnetic recording medium according to claim 5, further comprising the step of fluorine-terminating the surface of said formed protective film by decomposition of a carbon fluoride-based gas.

7. The method of manufacturing a magnetic recording medium according to claim 5, wherein the step of forming said protective film comprises a plasma CVD method using

hydrocarbon gas to which carbon fluoride-based gas is added as a raw material.

8. The method of manufacturing a magnetic recording medium according to claim 5, wherein the step of forming said protective film comprises a reactive sputter method using carbon as a target material in a sputter gas to which carbon fluoride-based gas has been added.