PHASE CHANGE-TYPE OPTICAL RECORDING MEDIUM AND PROCESS FOR MANUFACTURING THE SAME

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a phase change-type optical recording medium in which recording of information is made utilizing phase change by light, and a process for manufacturing the same.

2. Description of the Related Art

A phase change-type optical recording medium utilizes, to recording and erasing of information, a reversible structural change or a phase change between amorphous and crystal states or phases of a recording layer derived from difference of thermal history of heating and cooling by light or laser beam application. More specifically, a portion of a recording layer is melted and rapidly cooled to make it amorphous for recording, and is kept at a temperature higher than the crystallization temperature of the recording layer for a certain time period to make it crystalline for erasing. It is estimated that the temperature of the recording layer of GeSbTe, as a typical example, becomes to about 600°C when being recorded and to more than about 170°C when being erased. Reading or reproduction of a signal is done by using a difference of reflectivity between the amorphous and crystal phases. The phase change-type optical recording medium has a high information processing speed as well as a high recording capacity. Also, the phase change-type optical recording system has an advantage of low cost since the structure of a drive such as an optical head is simpler than a drive for a magneto-optical recording medium.

In a typical phase change-type optical recording medium, the crystal phase of a recording layer is used as the erase state of information, and a high

laser power is applied to melt and rapidly cool the recording layer to make it amorphous and to use the amorphous phase of a recording layer as the record state of information. Since recording layers of phase change-type optical recording media are amorphous as-deposited, i.e., immediately after it is deposited, for example, by sputtering, media including a recording layer are entirely annealed to make the recording layer crystalline, i.e., the erase state. The entire annealing is carried out, for example, by application of a laser beam having, for example, a width of 1 - 2 μm and a length of 100 μm at about 1W to a recording layer of a recording medium usually with a plurality passes. This annealing is called as "initial-crystallization", "post-crystallization", or simply "initialization".

A typical manufacturing process of a phase change-type optical recording medium comprises injection molding of a plastic substrate, sputtering for depositing a stack of layers including a recording layer, optionally coating an organic protective layer on the stack of layers, initial-crystallization, assembling with a casing, inspecting and shipping, in this order. Two discs comprising a 0.6 mm-thick substrate and a stack of layers including a recording layer are bonded to each other, when a double-sided recording medium, for example, as of a DVD-RAM disc, is manufactured. In this case, the two discs are usually bonded to each other with an adhesive after an organic protective layer is coated, but the organic protective layer is sometime eliminated.

A phase change-type optical recording medium has a basic recording layer structure comprising a lower dielectric layer, a recording layer, an upper dielectric layer and a reflective layer, which layers are formed by sputtering or other thin film depositing method. "Rapid cooling structure phase change-type optical disc using $ZnS-SiO_2$ dielectric" (Denshi Johou Tsushin Gakkai

Technical Research Review, CPM 90-35, July 27, 1990, pp43 - 48) shows the structure of a typical phase change-type optical recording medium which is commercially used. This structure comprises a polycarbonate substrate (usually a thickness of 0.6 mm or 1.2 mm)/a lower dielectric layer ($ZnS \cdot SiO_2$)/a recording layer (GeSbTe)/an upper dielectric layer ($ZnS \cdot SiO_2$)/a reflective layer (Al alloy)/an adhesive layer. A focused laser beam for initial-crystallization, writing and reading is usually applied to the recording layer through the plastic substrate.

The investigation of layer-side-beam-incident type medium in which a focused laser beam is applied to a recording layer through the stack of layers side, and not through a substrate, for initial-crystallization, writing and reading has started recently. This type of medium usually has a structure in which the layers are formed on a substrate in the order reversed to the above-mentioned usual order, i.e., in the order of a substrate/a reflective layer/a lower dielectric layer/a recording layer/an upper dielectric layer. A proposed structure of an optical head for this type medium is similar to a head of a hard disc that is, a flying head in which an objective lens is mounted on a slider since an objective lens should be very close to the surface of a medium.

The above-mentioned literature also describes that commercial phase change-type optical recording media use a chalcogene alloy such as GeSbTe and AgInSbTe for a recording layer. A dielectric layer used comprises a ZnS-based layer such as $ZnS \cdot SiO_2$ or a nitride-based layer such as GeN. A reflective layer used comprises an Al alloy, Au, an Ag alloy, etc.

The initial-crystallization of a phase change-type optical recording medium is carried out using a specialized initial-crystallization apparatus equipped with a high power optical head emitting a high power

laser beam. Specifically, a disc is being rotated while an optical beam focused on the plane of a recording layer is moved in the radial direction to effect the initial-crystallization to the entire surface of a disc. This initial-crystallization involves two problems as below:

1) An initial-crystallization apparatus is expensive and an initial-crystallization treatment requires a long time period. Usually, an initial-crystallization treatment takes several tens of seconds per disc, typically 40 to 120 seconds, which is significantly longer than a cycle time of injection molding of a plastic substrate and sputtering, each taking about ten and several seconds. As a result, a number of expensive initial-crystallization apparatus are required in one commercial manufacture line for manufacturing phase change-type optical recording media.

2) A recording layer tends to have un-uniform crystal state, more specifically un-uniform crystal grain size. Particularly, as the initial-crystallization is carried out at a higher power for a higher production rate, the un-uniformity of the crystal grains becomes larger. Although the measurable phenomenon is a variation of reflectivity of a medium or disc in one rotation of a medium, the phenomenon is considered to have a relation with the un-uniform crystal grain size. A medium with this type of variation after the initial-crystallization treatment has a large variation in timing of detecting a reproduction signal (large jitter), and has a severe deterioration after repetition of overwrite (increase in jitter), which are critical disadvantages of a recording medium. Upon investigation by the present inventors, the variation of reflectivity of a medium in a rotation of a medium should be not more than 7%. The variation of reflectivity of a medium in a rotation of a medium can be measured by the amplitude of reproduction signals (SUM signal) using an electrical characteristic evaluating apparatus.

If the initial-crystallization is carried out at a lower speed or is repeated at a lower power, a recording layer with excellent initial-crystallization state of uniform crystal grain size can be obtained. However, this causes a decrease in productivity and/or significant increase in investment for manufacturing apparatus, specifically initial-crystallization apparatus, which is very disadvantageous.

The above problems have been noticed when mass production was intended and the object of the present invention is to solve the above problems and attain increase both in quality and productivity and to provide a high quality and in-expensive phase change-type optical recording medium.

SUMMARY OF THE INVENTION

The above and other objects have been attained in accordance with the present invention by providing the following:

(1) A phase change-type optical recording medium in which recording of information is made utilizing phase change by light, comprising:

substrate;

a first dielectric layer on said substrate;

a phase change-type optical recording layer made of GeSbTe wherein the molar ratio of Sb:Te is less than 0.6 on said first dielectric layer;

a second dielectric layer on said phase change-type optical recording layer; and

a reflective layer either on the second dielectric layer or between said substrate and said first dielectric layer;

wherein an intermediate layer is further disposed between said first dielectric layer and said phase change-type optical recording layer and/or between said phase change-type optical recording layer and said second dielectric layer, said intermediate layer being a

single layer of Sb_2Te_3 or GeTe or a laminate layer of Sb_2Te_3 and GeTe, said intermediate layer being in direct contact with said phase change-type optical recording layer.

(2) The phase change-type optical recording medium according to (1), wherein said intermediate layer is disposed between said first dielectric layer and said phase change-type optical recording layer, and said phase change-type optical recording layer is in the as-deposited state without an initial-crystallization treatment.

(3) The phase change-type optical recording medium according to (1) or (2), wherein said intermediate layer is disposed between said first dielectric layer and said phase change-type optical recording layer, and said optical recording medium having said phase change-type optical recording layer in the as-deposited state without an initial-crystallization treatment has a reflectivity R_d satisfying the following formula:

$$| R_d - R_a | \div | R_c - R_a | \geqq 0.5$$

where R_d stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the as-deposited state without an initial-crystallization treatment, R_a stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the amorphous state used for writing, and R_c stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the crystal state used for erasing. In the above formula and in the specification, $| R |$ means the absolute value of R.

(4) The phase change-type optical recording medium according to (1) - (3), wherein said phase change-type optical recording medium has not more than 7% of a variation from a median of reflectivity, in a rotation of said medium, when said phase change-type optical

recording layer is in the crystal state.

(5) The phase change-type optical recording medium according to (1) - (4), wherein said phase change-type optical recording layer of GeSbTe has an atomic ratio of Ge:Sb:Te of about 1:2:4 or about 2:2:5.

(6) The phase change-type optical recording medium according to (1) - (5), wherein said intermediate layer is a layer of Sb_2Te_3.

(7) The phase change-type optical recording medium according to (1) - (6), wherein said intermediate layer is an intermetallic compound layer or a laminated layer of two or more intermetallic compounds.

(8) The phase change-type optical recording medium according to (1) - (7), wherein said recording medium has a first reflectivity for writing and a second reflectivity higher than said first reflectivity for erasing, and said first reflectivity is attained when said phase change-type optical recording layer is amorphous.

(9) The phase change-type optical recording medium according to (1) - (7), wherein said recording medium has a first reflectivity for writing and a second reflectivity lower than said first reflectivity for erasing, and said first reflectivity is attained when said phase change-type optical recording layer is amorphous.

(10) The phase change-type optical recording medium according to (1) - (9), wherein said first and second dielectric layers are made of at least one selected from the group consisting of SiO_2, ZnS, Si_3N_4, and a combination of SiO_2 and ZnS, and said recording medium further comprises a substrate of a polycarbonate resin and a reflecting layer of an aluminum alloy.

(11) A process for manufacturing a phase change-type optical recording medium in which recording of information is made utilizing phase change by light, comprising the steps of:

providing a substrate;

forming a first dielectric layer on said substrate;

depositing a phase change-type optical recording layer made of GeSbTe wherein the molar ratio of Sb:Te is less than 0.6 on said first dielectric layer;

forming a second dielectric layer on said phase change-type optical recording layer;

forming a reflective layer either on the second dielectric layer or between said substrate and said first dielectric layer;

wherein said process further comprises a step of depositing an intermediate layer between said first dielectric layer and said phase change-type optical recording layer and/or between said phase change-type optical recording layer and said second dielectric layer, said intermediate layer being made in direct contact with said phase change-type optical recording layer, said intermediate layer being a single layer of Sb_2Te_3 or GeTe or a laminated layer of Sb_2Te_3 and GeTe.

(12) The process according to (11), wherein said intermediate layer is deposited on said first dielectric layer, and said optical recording medium having said phase change-type optical recording layer in the as-deposited state without an initial-crystallization treatment has a reflectivity R_d satisfying the following formula:

$$| R_d - R_a | \div | R_c - R_a | \geq 0.5$$

where R_d stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the as-deposited state without an initial-crystallization treatment, R_a stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the amorphous state used for writing, and R_c stands for the reflectivity of said optical recording medium having the

phase change-type optical recording layer in the crystal state used for erasing.

(13) The process according to (11) or (12), further comprising a step of initial-crystallization treating said recording medium.

(14) The process according to (11) - (12), wherein said phase change-type optical recording layer of GeSbTe has an atomic ratio of Ge:Sb:Te of about 1:2:4 or about 2:2:5.

(15) The process according to (12) - (14), wherein said intermediate layer is a layer of Sb_2Te_3.

(16) The process according to (11) - (15), wherein said intermediate layer deposited is an intermetallic compound layer or a laminated layer of two or more intermetallic compounds.

(17) The process according to (11) - (16), wherein said intermediate layer is deposited between said first dielectric layer and said phase change-type optical recording layer.

(18) The process according to (11) - (17), wherein said intermediate layer is deposited between said phase change-type optical recording layer and said second dielectric layer.

(19) The process according to (11) - (19), wherein said phase change-type optical recording medium is manufactured in a manufacturing line comprising at least one apparatus for depositing at least said phase change-type optical recording layer and at least one apparatus for initial-crystallization treatment, and said line includes said initial-crystallization treatment apparatus in number equal to or less than said deposition apparatus.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1 to 3 are cross sectional views of examples of a phase change-type optical recording medium according to the present invention.

Fig. 4 schematically shows the line for

manufacturing a phase change-type optical recording medium.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Briefly, in accordance with the present invention, it was found that by providing, between a phase change-type optical recording layer made of GeSbTe wherein the molar ratio of Sb:Te is less than 0.6 and a dielectric layer contiguous to the recording layer, an intermediate layer of Sb_2Te_3 or GeTe, which may be a laminated layer of Sb_2Te_3 and GeTe, in direct contact with the recording layer, the obtained phase change-type optical recording medium may have a reflectivity equal or close to that of crystal state of the recording layer without an initial-crystallization treatment or with a short time initial-crystallization treatment. In accordance with the present invention, initial-crystallization treatment may be eliminated. Alternatively, initial-crystallization treatment of a recording layer may be conducted to obtain a uniform initial-crystallization, if necessary or desired, but this treatment is far easier or shorter in comparison with a phase change-type optical recording medium without an intermediate layer of the present invention. The phase change-type optical recording medium having the above construction of the present invention does not have disadvantages derived form the additional intermediate layer and may have very high productivity and high quality as a phase change-type optical recording medium. Thus, in accordance with the present invention, both a high quality of a phase change-type optical recording medium and a significantly improved productivity are attained.

The obtainable reflectivity, without initial-crystallization treatment, of a medium having an as-deposited phase change-type optical recording layer, in accordance with the present invention, can be the reflectivity R_d which satisfies the following formula:

preferably

$$\gamma = | R_d - R_a | \div | R_c - R_a | \geqq 0.5$$

more preferably

$$\gamma = | R_d - R_a | \div | R_c - R_a | \geqq 0.7$$

further preferably

$$\gamma = | R_d - R_a | \div | R_c - R_a | \geqq 0.9$$

where R_d stands for the reflectivity of the recording medium having the phase change-type optical recording layer in the as-deposited state without an initial-crystallization treatment, R_a stands for the reflectivity of the recording medium having the phase change-type optical recording layer in the amorphous phase used for writing or recording, and R_c stands for the reflectivity of the recording medium having the phase change-type optical recording layer in the crystal state used for erasing.

Although a crystal state of a recording layer of GeSbTe is used for erasing and an amorphous phase is used for recording, the reflectivity of a recording medium having a phase change-type optical recording layer can be controlled to be both higher and lower in a medium having a recording layer of crystal state, than in a medium having a recording layer of amorphous state, by changing the construction of the layers other than the recording layer. In either case, therefore, the relationship of the reflectivity between media having the crystal and amorphous states of a recording layer of the present invention can satisfy the above formula.

As a result, a medium having an as-deposited recording layer without initial-crystallization treatment of the present invention can be used as a ready usable final product supplied to the users, without any initial-crystallization treatment, or with an initial-crystallization treatment which is far shorter in time period and/or uses a lower power than a conventional one. For example, a time period of initial-crystallization treatment of a 5-inch medium or disc of not more than

60 second, with a laser beam having a power of 1 W, can be attained.

Furthermore, a medium having a recording layer with or without initial-crystallization treatment of the present invention is advantageous in that the medium can have a variation, in a rotation of the medium, of the reflectivity not more than 7%, more preferably not more than 6%. This uniform reflectivity of a medium indicates uniform crystal grain size of a recording layer.

The phase change-type optical recording layer of the present invention is made of GeSbTe wherein the molar ratio of Sb:Te is less than 0.6, more preferably not more than about 0.5. This phase change-type optical recording material allows to provide excellent performance and characteristics as a phase change-type optical recording medium. If the molar ratio of Sb:Te is not less than 0.6, a phase change-type optical recording medium having the recording layer has a large jitter of reproduction signal since the recorded marks may have undesired shapes. Examples of preferred GeSbTe are $GeSb_2Te_4$ and $Ge_2Sb_2Te_5$. The atomic ratio of Ge:Sb:Te of the above preferred GeSbTe is preferably within ±5%, more preferably within ±3% from the stoichiometric ratio of 1:2:4 or 2:2:5. These GeSbTe materials are preferable since they allow a good repeated overwrite characteristic and a high speed erase. Further, these materials preferably have a composition of an intermetallic compound of $(GeTe)(Sb_2Te_3)$ or $(GeTe)_2(Sb_2Te_3)$ and have a high affinity with an intermetallic compound of GeTe and Sb_2Te_3, which therefore can be more easily crystallized when deposited on an intermediate layer of GeTe or Sb_2Te_3.

The thickness of the phase change-type optical recording layer is preferably in a range of 12 to 50 nm. If it is less than 12 nm, the repetition durability is lowered. If it is more than 50 nm, the recording sensitivity decreases and the signal to noise ratio (S/N

ratio) also decreases.

The intermediate layer of the present invention is a layer of GeTe or Sb_2Te_3, or a laminated layer of GeTe and Sb_2Te_3. The GeTe and Sb_2Te_3 are advantageous since they do not contain any element other than the constituent elements of GeSbTe and, therefore, they do not disadvantageously change the composition of the recording layer and have affinity with the GeSbTe of the recording layer. Further, since GeTe and Sb_2Te_3 are intermetallic compounds, they can be easily crystallized when they are deposited or sputtered, by which crystallization of a recording layer of GeSbTe in direct contact with the intermediate layer is accelerated.

From the above reasons, the GeTe or Sb_2Te_3 of the intermediate layer preferably has a composition equal or close to an intermetallic compound, i.e., preferably within ±5%, more preferably within ±3% from the stoichiometric ratio of 1:1 of GeTe or 2:3 of Sb_2Te_3.

The intermediate layer may be a laminated layer of GeTe and Sb_2Te_3. It is possible to make the composition of the intermediate layer similar to that of the recording layer by using the laminated layer or a combination of two intermediate layers on and under the recording layer.

The intermediate layer may be formed between the lower dielectric layer and the recording layer and/or between the recording layer and the upper dielectric layer, with the intermediate layer being in direct contact with the recording layer. It is preferable that an intermediate layer is first formed and the recording layer is then deposited on the intermediate layer, i.e., it is formed between the lower dielectric layer and the recording layer, since in this case the first deposited intermediate layer, which is preferably crystalline at least to some extent, accelerates crystallization of the recording layer when it is deposited.

If initial-crystallization treatment is adopted, an

intermediate layer on the recording layer or between the recording layer and the upper dielectric layer is also effective. Of course, this initial-crystallization treatment can be shorter in time period or can use a lower power than a conventional case or a medium without an intermediate layer. It is also possible that a combination of two intermediate layers formed both on and under the recording layer is regulated to have a specific average composition, for example, the same composition as the recording layer.

The formation method of the intermediate layer of the present invention is not particularly limited, and includes vacuum evaporation, sputtering, ion beam sputtering, CVD, etc. The same process as used for forming the other layers such as the recording layer and dielectric layers is preferred from the viewpoint of continuity of the manufacturing process, and sputtering is particularly preferable from the viewpoints of adhesion with the underlying layer, control of an alloy composition, uniform layer thickness distribution, uniform composition distribution, etc. The deposition conditions including deposition rate and sputtering gas pressure may be suitably selected considering the productivity and internal stress of the deposited layer.

The thickness of the intermediate layer is preferably in a range of 1/40 to 1/4, more preferably 1/20 to 1/5 based on the thickness of the recording layer. If the thickness of the intermediate layer is less than 1/40 of the thickness of the recording layer, it is not easy to deposit a crystalline intermediate layer by sputtering or other method and therefore the effect of the intermediate layer may not appear. If the thickness of the intermediate layer is more than 1/4 of the thickness of the recording layer, the intermediate layer may possibly be melted and mixed with the recording layer to disadvantageously change the composition of the recording layer, resulting in deterioration of

characteristics, such as recording sensitivity, by repeated overwrite.

The substrate of a medium in the present invention may be any known substrate used for a phase change-type optical recording medium, for example, a transparent substrate of polycarbonate, polyolefin resin or glass. A preferable example is an injection molded polycarbonate disc having a thickness of about 0.6 to 2.0 mm and a diameter of about 60 to 120 mm. The transparency of the substrate is not essential if a laser beam need not pass through the substrate.

The first and second dielectric layers or lower and upper dielectric layers used in the present invention may be any dielectric layer transparent to a laser used and preferably has heat resistance and a high refractive index. For example, oxides, nitrides, sulfides, carbides and fluorides of metals, and composites thereof may be used. Specifically, silicon oxide, indium oxide, tantalum oxide, aluminum oxide, silicon nitride, aluminum nitride, titanium nitride, zinc sulfide, magnesium fluoride, aluminum fluoride, silicon carbide, and composites thereof can be mentioned, although it is not limited to these. Particularly preferred is a transparent dielectric having a refractive index of near 2.1, for example, $ZnS \cdot SiO_2$ which is obtained by sputtering a mixed target comprising ZnS (e.g., 80 mol%) and SiO_2 (e.g., 20 mol%) in an argon gas.

The thickness of the dielectric layers is different between the lower and upper dielectric layers and depends on the medium construction and the refractive index. However, a range of 10 to 150 nm is generally preferred.

The dielectric layer may be formed by a known method including vacuum evaporation, sputtering, ion beam sputtering, CVD, etc. However, it is preferable that all the layers of a recording medium are formed using a same method for the continuity of the manufacturing process.

The reflective layer used in the preset invention

can be disposed on the second or upper dielectric layer or between the substrate and the first or lower dielectric layer, depending on the side of incidence of a laser beam. A preferred example of the reflective layer is an Al alloy with a few or several % of Ti or Cr. Alternatively, a thin Au layer, for example, is used when a medium is to have a construction in which the light adsorption of the crystal phase of the recording layer should be greater than the light adsorption of the amorphous phase of the recording layer.

An organic protective layer may be optionally provided on the top of the medium.

Any additional layers, for example, a heat insulating layer or an adhesive layer, may be included in the medium of the present invention if desired as long as the features and advantages of the present invention are not lost.

Figs. 1 to 3 show examples of the constructions of a phase change-type optical recording medium of the present invention. In Fig. 1, the medium comprises a transparent substrate 1, and on the substrate 1, a lower dielectric layer 2, an intermediate layer 3, a recording layer 4, an upper dielectric layer 5, a reflective layer 6 and an organic protective layer 7 are deposited in this order. A laser beam is incident on the backside of the substrate 1 and focused on the recording layer 4.

In Fig. 2, the medium comprises a transparent substrate 1, and on the substrate 1, a heat insulating layer 8, a reflective layer 6', a lower dielectric layer 2, an intermediate layer 3, a recording layer 4, and an upper dielectric layer 5 are deposited in this order. A laser beam is incident on the side of the upper dielectric layer 5 and focused on the recording layer 4. This is a layer-side-beam-incident phase-change type optical recording medium.

As described before, the reflectivity of a medium can be controlled by the layer construction such that the

medium having a recording layer in the crystal state has a reflectivity higher or lower than the same medium having the same recording layer in the amorphous state. If the reflectivity of a medium having a recording layer in the crystal state is higher than in the amorphous state, this medium is called as "high-to-low type" (from erase state to record state). If the reflectivity of a medium having a recording layer in the crystal phase is lower than in the amorphous phase, this medium is called as "low-to-high type".

In Fig. 3, the medium is a double-sided recording medium. Two media or discs comprising a transparent substrate 1, a lower dielectric layer 2, an intermediate layer 3, a recording layer 4, an upper dielectric layer 5, a reflective layer 6 and an organic protective layer 7, as shown in Fig. 1, are bonded with each other with an adhesive layer 9 being applied between the two organic protective layers 7.

As explained before, the medium thus manufactured may have a reflectivity R_d which satisfies the formula: $\gamma = |R_d - R_a| \div |R_c - R_a| \geq 0.5$, more preferably $|R_d - R_a| \div |R_c - R_a| \geq 0.7$, $|R_d - R_a| \div |R_c - R_a| \geq 0.9$, even without initial-crystallization treatment. Therefore, the medium of the present invention may be supplied to the users as a ready usable finished product without any initial-crystallization treatment. Alternatively, the initial-crystallization treatment of the medium can be effected in a very short time period or with a significantly lower power in comparison with a conventional medium without an intermediate layer, to complete the initial-crystallization. It is noted that in a conventional medium without an intermediate layer, an initial-crystallization treatment is essential and it requires a long time, about 3 minutes for a typical example of a 120 mm disc, and/or repeated treatments.

The initial-crystallization treatment of the present

invention may be effected using a commercially available specific initial-crystallization apparatus. For example, a laser beam having a width of 1 to 2 μm and a length of about 100 μm with a power of about 1 Watt is scanned on the recording layer. The scan can be only one pass in the present invention. The initial-crystallization treatment is carried out by keeping the recording layer at a temperature higher than the crystallization temperature thereof for a certain time period. The time period for the initial-crystallization treatment can be, for example, not more than 60 seconds in the present invention.

As a result of short time period for initial-crystallization treatment, it is possible in the present invention that only one, or sometimes less than one, initial-crystallization apparatus is arranged in one line of manufacturing a phase change-type optical recording medium including only one series of sputtering apparatus for the layers. Fig. 4 shows this type of manufacturing line, in which 11 denotes a sputtering apparatus, 12 a coating apparatus and 13 an initial-crystallization apparatus.

The reflectivity of a medium of the present invention can be measured by a spectrometer or an spin-stand-type electric characteristic evaluation apparatus. The amorphous and crystal states or the write and erase states can be easily determined by the reflectivity of the medium.

By measuring the reflectivity of a medium with varying the wavelength, it can be determined which of the crystal and amorphous states the recording layer of the medium is. The crystal and amorphous states can be determined by the reflectivity at a single wavelength, but it can be more easily and surely determined by the pattern of distribution of the reflectivity depending on the wavelength.

The variation of the reflectivity of a medium, in a rotation of a medium, can be determined using an electric characteristic evaluation apparatus having an optical head to measure the variation of the amount of the laser light returned from the medium when a reading or reproducing laser beam is applied and the medium is rotated. It was found that even when the amount of the returned laser light is within the standard range, for example ISO standard range, for the medium, if the above variation of the reflectivity is large, the medium had disadvantageously deteriorated in durability against repeated overwrite, which was considered to be caused by a large variation of the crystal size in the recording layer.

EXAMPLES

(Example 1 and Comparative Example 1)

On one surface of a plastic substrate having a thickness of 1.2 mm, a lower dielectric layer, an intermediate layer, a recording layer, an upper dielectric layer, a reflective layer and an organic protective layer in this order were formed to manufacture a phase change-type optical recording medium of Example 1. As a recording medium of Comparative Example 1, a phase change-type optical recording medium without an intermediate layer was manufactured which had a construction comprising, on one surface of a plastic substrate having a thickness of 1.2 mm, a lower dielectric layer, a recording layer, an upper dielectric layer, a reflective layer and an organic protective layer in this order.

Two kinds of plastic substrates of a polycarbonate disc having a diameter of 120 mm and an inner diameter of 15 mm were used for each of Example 1 and Comparative Example 1. One of the two substrates was a substrate having a plane surface for measuring the reflectivity of the medium by a spectrometer. The other one of the two substrates was a substrate produced by injection molding

to provide continuous servo spiral grooves in an area having radius of 24 to 58 mm, for measuring the distribution of the reflectivity by an electric characteristic evaluation apparatus. The depth of the groove was 70 nm, the track pitch was 1.48 μm, and the widths of the groove and land were about 0.74 μm.

On the grooved surface of the substrate and on the plane surface of the substrate, the 95 nm thick lower dielectric layer, the 2 nm intermediate layer thick (only in Example 1), the 18 nm thick recording layer of GeSbTe, the 16 nm thick upper dielectric layer, the 150 nm thick reflectivity layer and the 3 μm thick organic protective layer were formed in this order. In Comparative Example 1, the recording layer was a 20 nm thick GeSbTe alloy layer and the intermediate layer was eliminated.

The recording layer was an GeSbTe alloy layer with an atomic ratio of Ge:Sb:Te = 1:2:4 and the intermediate layer was a SbTe layer with an atomic ratio of Sb:Te = 2:3.

The lower and upper dielectric layers were a $ZnS:SiO_2$ layer obtained by sputtering a target of $ZnS:SiO_2$ = 80 mol%:20 mol%. The reflective layer was an AlCr alloy layer with an atomic ratio of Al:Cr = 97:3.

All the layers were formed on the substrate by magnetron sputtering.

The sputtering apparatus used was a magnetron sputtering apparatus (ANELVA SPF-430H type) in which the holder for a substrate was modified so as to set a plurality of substrates thereto. This apparatus allowed three targets to be set in a vacuum chamber to sputter three kinds of layers in the row. In Example 1, the target exchange was effected, after the 95 nm-thick lower dielectric layer, the 2 nm-thick intermediate layer, the 18 nm-thick GeSbTe recording layer and the 16 nm-thick upper dielectric layer were deposited sequentially. The two substrates were set in the vacuum chamber, which was

evacuated to 8×10^{-5} Pa and an Ar gas was introduced at a flow rate of 75 SCCM and the orifice of a main valve was regulated to attain a pressure of 0.8 Pa. The targets used were a GeSbTe alloy, a $ZnS \cdot SiO_2$ sintered body, a SbTe alloy, and the AlCr alloy, each target having a diameter of 101 mm and a thickness of 5 mm. The substrate was set in a plane above the target at a distance of about 120 mm and the substrate, while being self-rotated, was further rotated around a center located on the central axis of the target at a radius of 100 mm.

The powers applied were a 500W radio frequency power for sputtering the $ZnS \cdot SiO_2$ sintered body, a 400W direct current power for sputtering the AlCr target, and a 50W direct current power for sputtering the SbTe and GeSbTe targets. The deposition rates were 23.3 nm/min for the $ZnS \cdot SiO_2$ layer, 10.2 nm/min for the AlCr layer, 21.1 nm/min for the SbTe layer, and 20.5 nm/min for the GeSbTe layer.

On the AlCr layer, a ultra-violet curable phenol novolak epoxy acrylate resin was coated and cured by irradiation with UV rays to obtain a phase change-type optical recording medium having an organic protective layer.

As shown in Table 1, the medium of Example 1 had a reflectivity of 35% at a wavelength of 680 nm, immediately after the sputtering was completed, i.e., at the stage of removal of the medium or the substrate with the deposited layers from the vacuum chamber. It was also confirmed by the distribution of the reflectivity on the wavelength that the recording layer was crystalline.

On the other hand, as shown in Table 1, the medium of Comparative Example 1 had a low reflectivity of 6% and the recording layer was amorphous when the medium was removed from the vacuum chamber, and the reflectivity of the medium increased to 35% by initial-crystallization treatment.

The measurement of the reflectivity was carried out at a location with a radius of 35 mm of the medium. The reflectivity was measured by an optical fiber-type spectrometer (Device name: Photal, manufactured by Hodaka electronics).

The initial-crystallization apparatus was a bulk eraser apparatus (LK101A type, manufactured by Shibasoku). The optical head used emitted a laser beam having a power of about 1W on the surface of the disc, a wavelength of 810 nm, an NA (numerical aperture of objective lens) of 0.34 and a spot size of 125 μm (long axis) × 1.27 μm (short axis), and was set to have the long axis at an angle of 30° inclined from the radial direction of the disc. The initial-crystallization treatment was effected by rotating the disc at a constant linear speed of 5 m/sec and moving the optical head at a feed speed of 86 μm/rotation (i.e., the optical head moves 86 μm per one rotation of the disc), while the power was set to 65% (i.e., about 650 mW) of the maximum power. The scan was only one pass on the disc.

The variation of the reflectivity of the grooved medium was evaluated on a circle with a radius of 35 mm. The evaluation was made by an electric characteristic evaluation apparatus (DDU-1000 type, manufactured by Pulstech Industries). The variation of the reflectivity was determined by measuring, with an osciloscope, the reflectivity of a medium for one circle. The variation of the reflectivity of the medium of Example 1 was 6% from the median reflectivity but that of Comparative Example 1 was 12%, disadvantageously exceeding the reference value of 7%.

It was confirmed that the manufacturing process, specifically the initial-crystallization process, can be shortened and the recording medium has excellent performance in accordance with the present invention.

(Examples 2 to 6)

The media as shown in Table 1 were manufactured. The substrate, the method for manufacturing the medium, the thicknesses of the layers, and the methods for evaluation were the same as in Example 1. The GeTe layer with an atomic ratio of Ge:Te = 1:1 was formed by sputtering a GeTe alloy target, the sputtering conditions were the same as the SbTe, and the sputtering rate was then 13.6 nm/min.

The same evaluation as in Example 1 was conducted. The results are shown in Table 1.

In Table 1, γ represents $| R_d - R_a | \div | R_c - R_a |$.

In Examples 2 to 4, the difference of the reflectivity between before and after the initial-crystallization was low, only 3 to 12%.

Table 1

	Com. Ex. 1	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6
Lower intermediate layer	None	Sb_2Te_3	Ge_1Te_1	Sb_2Te_3	Ge_1Te_1	None	None
Recording layer	$GeSb_2Te_4$	$GeSb_2Te_4$	$GeSb_2Te_4$	$Ge_2Sb_2Te_5$	$Ge_2Sb_2Te_5$	$GeSb_2Te_4$	$Ge_2Sb_2Te_5$
Upper intermediate layer	None	None	None	None	None	Sb_2Te_3	Sb_2Te_3
Initial-crystallization	Done	No	Done	Done	Done	Done	Done
Reflectivity before initial-crystallization (Rd)	6%	35%	29%	32%	25%	7%	8%
Reflectivity after initial-crystallization	35%	-	36%	35%	37%	35%	36%
Reflectivity of amorphous state (R_a)	6	6	6	7	7	7	8
Reflectivity of crystal state (R_c)	35	35	36	35	37	35	36
γ	~0	1.0	0.77	0.89	0.60	~0	~0
Variation of reflectivity	12%	6%	5%	5%	6%	6%	5%

(Example 7 and Comparative Example 2)

A layer-side-beam-incident phase-change type optical recording medium of Example 7 was manufactured with a construction of a heat insulating layer, a reflective layer, a lower dielectric layer, an intermediate layer, a recording layer and an upper dielectric layer in this order on a plastic substrate 1.2 mm thick. A layer-side-beam-incident phase-change type optical recording medium of Comparative Example 2 did not have an intermediate layer, that is, the construction comprised a heat insulating layer, a reflective layer, a lower dielectric layer, a recording layer and an upper dielectric layer in this order on a plastic substrate 1.2 mm thick.

Two kinds of plastic substrates of a polycarbonate disc having a diameter of 120 mm and an inner diameter of 15 mm were used for each of Example 7 and Comparative Example 2. One of the two substrates was a substrate having a plane surface for measuring the reflectivity of the medium by a spectrometer. The other one of the two substrates was a substrate produced by injection molding to provide continuous servo spiral grooves in an area having a radius of 24 to 58 mm, for measuring the reflectivity by an electric characteristic evaluation apparatus. The depth of the groove was 70 nm, the track pitch was 1.10 μm, and the widths of the groove and land were about 0.55 μm.

On the recording or groove surface of the substrate and on the plane surface of the substrate, the 100 nm thick heat insulating layer, the 150 nm thick reflective layer, the 20 nm thick lower dielectric layer, the 2 nm thick intermediate layer (only in Example 7), the 18 nm thick recording layer of GeSbTe, and the 95 nm thick upper dielectric layer were formed in this order. In Comparative Example 2, the recording layer was a 20 nm thick GeSbTe alloy layer and the intermediate layer was eliminated.

The recording layer was an GeSbTe alloy layer with an atomic ratio of Ge:Sb:Te = 1:2:4 and the intermediate layer was a SbTe layer with an atomic ratio of Sb:Te = 2:3.

The heat insulating layer and lower and upper dielectric layers were a $ZnS \cdot SiO_2$ layer obtained by sputtering a target of $ZnS:SiO_2$ = 80 mol%:20 mol%. The reflective layer was an AlCr alloy layer with an atomic ratio of Al:Cr = 97:3.

All the inorganic layers were formed on the substrate by magnetron sputtering.

The sputtering apparatus used was a magnetron sputtering apparatus (ANELVA SPF-430H type) in which the holder for a substrate was modified so as to set a plurality of substrates thereto. This apparatus allowed three targets to be set in a vacuum chamber to sputter three kinds of layers sequentially. In Example 7, after the 100 nm thick heat insulating layer and the 150 nm thick AlCr reflective layer were deposited, the target exchange was effected to further deposit the 20 nm thick lower dielectric layer, the 2 nm-thick SbTe intermediate layer, the 18 nm-thick GeSbTe recording layer and the 95 nm-thick upper dielectric layer sequentially. The two substrates were set in the vacuum chamber, which was evacuated to 8×10^{-5} Pa and an Ar gas was introduced at a flow rate of 75 SCCM and the orifice of a main valve was regulated to attain a pressure of 0.8 Pa. The targets used were a GeSbTe alloy, a $ZnS \cdot SiO_2$ sintered body, a SbTe alloy, and an AlCr alloy, each target having a diameter of 101 mm and a thickness of 5 mm. The substrate was set in a plane above the target at a distance of about 120 mm from the target surface and the substrate, while being self-rotated, was further rotated around a center located on the axis passing through the center of the target at a radius of 100 mm.

The powers applied were a 500W radio frequency power

for sputtering the $ZnS \cdot SiO_2$ sintered body, a 400W direct current power for sputtering the AlCr target, and a 50W direct current power for sputtering the SbTe and GeSbTe targets. The deposition rates were 23.3 nm/min for the $ZnS \cdot SiO_2$ layer, 10.2 nm/min for the AlCr layer, 21.1 nm/min for the SbTe layer, and 20.5 nm/min for the GeSbTe layer.

As shown in Table 2, the medium of Example 7 had a reflectivity of 39% at a wavelength of 680 nm, immediately after the sputtering was completed, i.e., at the stage of removal of the medium or the substrate with the deposited layers from the vacuum chamber. It was also confirmed by the distribution of the reflectivity on the wavelength that the recording layer was crystalline.

On the other hand, as shown in Table 2, the medium of Comparative Example 2 had a low reflectivity of 11% and the recording layer was amorphous when the median was removed from the vacuum chamber, but the reflectivity of the medium increased to 38% by conventional initial-crystallization treatment.

The measurement of the reflectivity was carried out at a location with a radius of 35 mm of the medium. The reflectivity was measured by an optical fiber-type spectrometer (Device name: Photal, manufactured by Hodaka electronics).

The initial-crystallization apparatus was a bulk eraser apparatus (LK101A type, manufactured by Shibasoku). The optical head used emitted a laser beam having a power of about 1W on the surface of the disc, a wavelength of 810 nm, an NA (numerical aperture of objective lens) of 0.34 and a spot size of 125 μm (long axis) × 1.27 μm (short axis), and was set to have the longitudinal axis at an angle of 30° inclined from the radial direction of the disc. The initial-crystallization treatment was effected by rotating the

disc at a constant linear speed of 5 m/sec and moving the optical head at a feed speed of 86 μm/rotation (i.e., the optical head moves 86 μm per one rotation of the disc), while the power was set to 65% of the maximum power, i.e., about 650 mW. The scan of the laser beam in this Example was one pass on the disc in contrast to a plurality of passes in the conventional initial-crystallization treatment.

The variation of the reflectivity of the grooved medium was evaluated on a circle with a radius of 35 mm. The evaluation was made by an electric characteristic evaluation apparatus (DDU-1000 type, manufactured by Pulstech Industries). The variation of the reflectivity was determined by measuring the reflectivity of a medium for one circle. The variation of the reflectivity of the medium of Example 7 was 5% from the median reflectivity but that of Comparative Example 2 was 11%, disadvantageously exceeding the reference value of 7%.

It was confirmed that the manufacturing process, specifically the initial-crystallization process, can be shortened and that the recording medium had excellent performance in accordance with the present invention.

(Examples 8 to 12)

The media as shown in Table 2 were manufactured. The substrate, the method for manufacturing the medium, the thicknesses of the layers, and the methods for evaluation were the same as in Example 7. The GeTe layer with an atomic ratio of Ge:Te = 1:1 was formed by sputtering a GeTe alloy target, the sputtering conditions were the same as the SbTe, and the sputtering rate was then 13.6 nm/min.

The same evaluation as in Example 7 was conducted. The results are shown in Table 2.

In Table 2, γ represents $| R_d - R_a | \div | R_c - R_a |$.

In Examples 8 to 10, the difference of the reflectivity between before and after the initial-

crystallization was low, only 2 to 12%.

Table 2

	Com. Ex. 2	Ex. 7	Ex. 8	Ex. 9	Ex. 10	Ex. 11	Ex. 12
Lower intermediate layer	None	Sb_2Te_3	Ge_1Te_1	Sb_2Te_3	Ge_1Te_1	None	None
Recording layer	$Ge_1Sb_2Te_4$	$Ge_1Sb_2Te_4$	$Ge_1Sb_2Te_4$	$Ge_2Sb_2Te_5$	$Ge_2Sb_2Te_5$	$Ge_1Sb_2Te_4$	$Ge_2Sb_2Te_5$
Upper intermediate layer	None	None	None	None	None	Sb_2Te_3	Sb_2Te_3
Initial-crystallization	Done	No	Done	Done	Done	Done	Done
Reflectivity before initial-crystallization (Rd)	11%	39%	37%	28%	28%	10%	9%
Reflectivity after initial-crystallization	38%	-	39%	38%	40%	39%	38%
Reflectivity of amorphous state (R_a)	11	11	10	10	10	10	9
Reflectivity of crystal state (R_c)	38	39	39	38	40	39	38
γ	~0	~1.0	0.93	0.64	0.60	~0	~0
Variation of reflectivity	11%	5%	6%	6%	5%	6%	6%

* C L M S *

CLAIMS

1. A phase change-type optical recording medium in which recording of information is made utilizing phase change by light, comprising:

a substrate;

a first dielectric layer on said substrate;

a phase change-type optical recording layer made of GeSbTe wherein the molar ratio of Sb:Te is less than 0.6 on said first dielectric layer;

a second dielectric layer on said phase change-type optical recording layer; and

a reflective layer either on the second dielectric layer or between said substrate and said first dielectric layer;

wherein an intermediate layer is further disposed between said first dielectric layer and said phase change-type optical recording layer and/or between said phase change-type optical recording layer and said second dielectric layer, said intermediate layer being a single layer of Sb_2Te_3 or GeTe or a laminate layer of Sb_2Te_3 and GeTe, said intermediate layer being in direct contact with said phase change-type optical recording layer.

2. The phase change-type optical recording medium according to claim 1, wherein said intermediate layer is disposed between said first dielectric layer and said phase change-type optical recording layer, and said phase change-type optical recording layer is in the as-deposited state without an initial-crystallization treatment.

3. The phase change-type optical recording medium according to claim 1, wherein said intermediate layer is disposed between said first dielectric layer and said phase change-type optical recording layer, and said optical recording medium having said phase change-type optical recording layer in the as-deposited state without

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an initial-crystallization treatment has a reflectivity R_d satisfying the following formula:

$$| R_d - R_a | \div | R_c - R_a | \geq 0.5$$

where R_d stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the as-deposited state without an initial-crystallization treatment, R_a stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the amorphous state used for writing, and R_c stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the crystal state used for erasing.

4. The phase change-type optical recording medium according to claim 1, wherein said phase change-type optical recording medium has not more than 7% of a variation from a median of reflectivity, in a rotation of said medium, when said phase change-type optical recording layer is in the crystal state.

5. The phase change-type optical recording medium according to claim 1, wherein said phase change-type optical recording layer of GeSbTe has an atomic ratio of Ge:Sb:Te of about 1:2:4 or about 2:2:5.

6. The phase change-type optical recording medium according to claim 5, wherein said intermediate layer is a layer of Sb_2Te_3.

7. The phase change-type optical recording medium according to claim 1, wherein said intermediate layer is an intermetallic compound layer or a laminated layer of two or more intermetallic compounds.

8. The phase change-type optical recording medium according to claim 1, wherein said recording medium has a first reflectivity for writing and a second reflectivity higher than said first reflectivity for erasing, and said first reflectivity is attained when said phase change-type optical recording layer is amorphous.

9. The phase change-type optical recording medium according to claim 1, wherein said recording medium has a first reflectivity for writing and a second reflectivity lower than said first reflectivity for erasing, and said first reflectivity is attained when said phase change-type optical recording layer is amorphous.

10. The phase change-type optical recording medium according to claim 1, wherein said first and second dielectric layers are made of at least one selected from the group consisting of SiO_2, ZnS, Si_3N_4, and a combination of SiO_2 and ZnS, and said recording medium further comprises a substrate of a polycarbonate resin and a reflecting layer of an aluminum alloy.

11. A process for manufacturing a phase change-type optical recording medium in which recording of information is made utilizing phase change by light, comprising the steps of:

providing a substrate;

forming a first dielectric layer on said substrate;

depositing a phase change-type optical recording layer made of GeSbTe wherein the molar ratio of Sb:Te is less than 0.6 on said first dielectric layer;

forming a second dielectric layer on said phase change-type optical recording layer;

forming a reflective layer either on the second dielectric layer or between said substrate and said first dielectric layer;

wherein said process further comprises a step of depositing an intermediate layer between said first dielectric layer and said phase change-type optical recording layer and/or between said phase change-type optical recording layer and said second dielectric layer, said intermediate layer being made in direct contact with said phase change-type optical recording layer, said intermediate layer being a single layer of Sb_2Te_3 or GeTe or a laminated layer of Sb_2Te_3 and GeTe.

12. The process according to claim 11, wherein said intermediate layer is deposited on said first dielectric layer, and said optical recording medium having said phase change-type optical recording layer in the as-deposited state without an initial-crystallization treatment has a reflectivity R_d satisfying the following formula:

$$| R_d - R_a | \div | R_c - R_a | \geqq 0.5$$

where R_d stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the as-deposited state without an initial-crystallization treatment, R_a stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the amorphous state used for writing, and R_c stands for the reflectivity of said optical recording medium having the phase change-type optical recording layer in the crystal state used for erasing.

13. The process according to claim 11, further comprising a step of initial-crystallization treating said recording medium.

14. The process according to claim 11, wherein said phase change-type optical recording layer of GeSbTe has an atomic ratio of Ge:Sb:Te of about 1:2:4 or about 2:2:5.

15. The process according to claim 14, wherein said intermediate layer is a layer of Sb_2Te_3.

16. The process according to claim 11, wherein said intermediate layer deposited is an intermetallic compound layer or a laminated layer of two or more intermetallic compounds.

17. The process according to claim 11, wherein said intermediate layer is deposited between said first dielectric layer and said phase change-type optical recording layer.

18. The process according to claim 13, wherein said

intermediate layer is deposited between said phase change-type optical recording layer and said second dielectric layer.

19. The process according to claim 13, wherein said phase change-type optical recording medium is manufactured in a manufacturing line comprising at least one apparatus for depositing at least said phase change-type optical recording layer and at least one apparatus for initial-crystallization treatment, and said line includes said initial-crystallization treatment apparatus in number equal to or less than said deposition apparatus.