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Description

[0001] The present invention relates to a method for optically recording information on an optical information recording medium and the optical information recording medium having optically readable pits thereby formed.

[0002] Conventional optical information recording media of such type have a recording layer of e.g. a metal such as Te, Bi or Mn or a dye such as cyanine, merocyanine or phthalocyanine, and they are designed to record data in such a manner that when irradiated with a laser beam, such recording layer is deformed, sublimed, evaporated or modified to form pits. With optical information recording media having such recording layer, it is common to form a space behind the recording layer to facilitate the deformation, sublimation, evaporation or modification of the recording layer for the formation of the pits. A typical example is a laminated structure so-called an air sandwich structure wherein a pair of substrates are laminated with a space therebetween.

[0003] With the optical information recording media of this type, a writing laser beam is irradiated through a transparent substrate to form optically readable pits in the recording layer. For reproducing the recorded data, a reading laser beam having a less power than the writing laser beam is irradiated through the substrate, and the contrast between the light reflected from the pits and the light reflected from non-pitted portion, is read as an electrical signal.

[0004] On the other hand, optical information recording media of so-called ROM (read only memory) type wherein data are already recorded, and no further data are recordable or the recorded data are no longer erasable or rewritable, are widely practically employed in the sound recording and information treating fields. Optical information recording media of this type have no such a recording layer as described above. Pits corresponding to data to be reproduced are already formed on a substrate of e.g. polycarbonate by e.g. press molding, a reflective layer of a metal such as Au, Ag, Cu or Al is formed thereon, and a protective layer is further provided thereon.

[0005] The most typical optical information recording medium of this ROM type is a compact disc so-called CD which is widely used in the sound recording and information treating fields. The specification for recording and read-out signals for this CD is standardized, and the reproducing or play back apparatus for CD in accordance with the standards is widely available as compact disc players (CD players).

[0006] Therefore, it is strongly desired that the above-mentioned optical information recording media follow the same standards as the widely prevailing standards for CD, so that they are interchangeable with already prevailing CD and-can be played back by CD players for reproduction of recorded information.

[0007] However, conventional optical information recording media of the above mentioned type have a recording layer which is not present in CD, and they are designed to form pits in the recording layer and not in the substrate (see e.g. IBM TDB, vol. 25, No. 118, April 1983, p. 5940, 5941). Further, in some cases, a space is provided to facilitate the formation of pits in this recording layer. Consequently, the read-out signals are naturally different from those of CD due to differences in e.g. the reflectance of the laser beam and the degree of modulation of the read-out signals. In particular, the pits formed in the recording layer by the laser beam are not so distinct as pits mechanically formed by e.g. press molding, whereby it has been difficult to obtain a high degree of modulation. Therefore, it has been difficult for the conventional optical information recording media to meet the above-mentioned standards for CD, and it has been difficult to provide an optical disc playable by conventional CD players.

[0008] EP-A-0 019 329 describes a recording medium according to the preamble of claim 1, whereby a pit is formed only in a relatively thin dye layer; US-A-4 398 203 describes a recording medium whereby a dye is not adjacent to the substrate, but rather to an absorptive metal interlayer; JP-A-1982-60543 describes a recording medium, whereby an absorptive dye layer in not provided between a reflective layer and a substrate; and for all then recording media the possibility of forming a pit extending into the substrate so as to stably meet a CD standard is not reported.

[0009] Therefore, it is an object of the present invention to provide an optical information recording medium which is capable of providing read-out signals having a high degree of modulation to meet the CD standards.

[0010] The present invention is based on a discovery that optically readable pits can be formed directly on the substrate by a laser beam by means a laser beam absorptive layer which functions as a means to form such pits, whereby it is possible to obtain a recordable optical disc which meets the CD standards.

[0011] The present invention provides a method for optically recording information on an optical information medium according to claim 1.

[0012] The present invention also provides an optical information recording medium according to claim 3.

[0013] For the purpose of the present invention, the term "optically readable pits" or "pits" generally includes optically readable or detectable marks of all kinds.

[0014] With this optical information recording medium, when the light absorptive dye layer is irradiated with a laser beam, it generates heat upon absorption of the laser beam and at the same time, the surface of the substrate adjacent to the absorption layer and the absorption layer or additionally a layer adjacent to the absorption layer undergo melting, evaporation, sublimation, reaction, decomposition or modification. When the laser beam is applied in a focused state to the light absorptive layer, energy is locally generated. The impact of such energy reaches the surface of the layers adjacent to the light absorptive layer, whereby said layers are locally de-

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formed to form optically modified portions (optically readable pits).

[0015] At the pitted portions, the surface of the layers of the substrate adjacent to the light absorptive layer is locally deformed, whereby there is a phase difference between the pitted portions and the non-pitted portion, and the incident laser beam is scattered so that there will be a substantial difference in the quantity of the reflected laser beam. Therefore, it is possible to obtain a high degree of modulation for the read-out signals.

[0016] Here, the above function is generally equal irrespective of the shape of the deformation of said layers whether the deformation consists in protuberances toward the light absorptive layer, waves or dents. In addition to the above deformation, the pitted portions may include optically modified portions where the optical properties are different locally in said layers. Spaces may be formed at the interfacial portion between the light absorptive layer and the adjacent layer, or fine bubbles may be dispersed in the light absorptive layer at the pitted potions, whereby the reflectance of the laser beam will be substantially different between the pitted portions and the non-pitted portion due to such functions as the phase difference, absorption and scattering of the laser beam thereby caused, and it is possible to obtain a high degree of modulation of the read-out signals.

[0017] Likewise, when the deformed portions of said layers have optical properties different from the rest of said layers, there will be a substantial difference in the optical conditions, particularly in the reflectance of the laser beam, between the pitted portions and the non-pitted portion due to such functions as the phase difference, absorption and scattering of the incident laser beam at the optically modified portions, and it is thereby possible to obtain a high degree of modulation of the read-out signals as mentioned above.

[0018] Thus, the optically modified portions formed on said layers are different from those formed in the conventional recording layer, and they rather resemble pits of CD which are preformed on a substrate surface by e. g. press molding. In the optically writable information recording medium of such a structure, a reflective layer can be provided on the light absorptive layer in close contact therewith. Thus, also from the configuration point of view, the optical information recording medium of the present invention is similar to CD. It is particularly significant that it is thereby possible to readily obtain an optically writable information recording medium, particularly a write-once type recordable optical disc, which meets the CD standards with respect to the reflectance of the reading laser beam, the degree of modulation of the read-out signals and the block error rate.

[0019] Now, the preferred embodiments of the present invention will be described with reference to the drawings, in which:

Figure 1 is a partially cross-sectional diagrammatical perspective view illustrating an embodiment of the structure of the optical information recording medium of the present invention.

Figure 2 is a partially enlarged cross-sectional view taken along the track of the information recording medium of Figure 1 prior to optical recording.

Figure 3 is a partially enlarged cross-sectional view taken along the track of the optical information recording medium of Figure 1 after the optical recording.

Figure 4 is a partially enlarged cross-sectional view taken along the track of another embodiment of the optical information recording medium of the present invention prior to optical recording.

Figure 5 is a partially enlarged cross-sectional view taken along the track of the same embodiment after the optical recording.

Figure 6 is a partially enlarged cross-sectional view taken along the track of a still another embodiment of the optical information recording medium of the present invention prior to optical recording.

Figure 7 is a partially enlarged cross-sectional view taken along the track of the embodiment of Figure 6 after the optical recording.

Figure 8 is a partially enlarged cross-sectional view taken along the track of a further embodiment of the present invention prior to optical recording.

Figure 9 is a partially enlarged cross-sectional view of the embodiment of Figure 8 after the optical recording.

Figure 10 is a partially enlarged cross-sectional view taken along the track of a still further embodiment of the optical recording medium of the present invention prior to optical recording.

Figure 11 is a partially enlarged cross-sectional view taken along the track of the embodiment of Figure 10 after the optical recording.

Figure 12 is a graph showing the relation between an optical parameter represented by the formula $\rho = n_{abs}d_{abs}/\lambda$ where n_{abs} is the real part of the complex refractive index of the light absorptive layer of the optical disc, d_{abs} is the thickness of the light absorptive layer and λ is the wavelength of the reading laser beam and the reflectance of the reading laser beam.

Figure 13 is a graph showing the relation between the imaginary part k_{abs} of the complex refractive index of the light absorptive layer of the optical disc and the reflectance of the reading laser beam.

Figure 14 is a partially enlarged diagrammatical perspective view of the surface of the light transmitting substrate of the optical information recording medium of the present invention after optical recording.

Figures 15(a) and (b) are graphs showing the relation between the moving distance of a tip or probe along the track and the height of the pit or protuberance when the surface of the transparent substrate of Figure 14 was observed by STM (scanning tun-

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neling microscope).

Figures 16 to 19 are partially enlarged cross-sectional views taken along the tracks of various embodiments of the pits of the optical information recording media.

[0020] Figures 1 to 11 diagrammatically illustrate various structures of the optical information recording medium of the present invention. In these Figures, reference numeral 1 indicates a light transmitting substrate, numeral 2 indicates a light absorptive layer overlaying the substrate, and numeral 3 indicates a light reflective layer overlaying the light absorptive layer. Reference numeral 4 indicates a protective layer.

[0021] The light transmitting substrate 1 is made of a material having high transparency to laser beams and is usually made of a resin having excellent impact strength such as a polycarbonate, an acrylate resin or an epoxy resin. However, the substrate may be made of any other material so long as it is transparent to writing and reading laser beams and as at least the surface of the substrate adjacent to the light absorptive layer is deformable by energy generated by the light absorptive layer upon absorption of the writing laser beam, to form optically readable pits. In this respect, the substrate or at least the surface layer thereof preferably has a heat distortion temperature within a range of from 85 to 200°C, more preferably from 90 to 150°C, as measured in accordance with ASTM D648 under a load of 4.6 kg/cm^2 and/or a Rockwell hardness within a range of from M200 to M75, more preferably from M105 to M80, as measured in accordance with ASTM D785. When the heat distortion temperature or the Rockwell hardness of the substrate is within the above-mentioned range, the energy generated by the light absorptive layer 2 upon absorption of the writing laser beam can effectively be absorbed by the local deformation of the surface layer of the substrate 1 so that no substantial strain will remain in the formed pits, whereby the stability of the recorded data will be secured. If the heat deformation temperature or the hardness is too low, the formed pits tend to easily be deformed by heat or external force, whereby the stability will be poor. On the other hand, if the heat distortion temperature or the hardness is too high, the energy generated by the light absorptive layer 2 can hardly be absorbed in the form of deformation of the substrate 1, and it is difficult to form distinct pits 5, whereby it will be difficult to obtain read-out signals having a high degree of modulation.

[0022] The thickness of the substrate 1 is not critical, but it is usually within a range of from 1.1 to 1.5 mm.

[0023] The light absorptive layer 2 is a layer which absorbs a laser beam entered through the light transmitting substrate 1, whereupon it generates heat and at the same time undergoes melting, evaporation, sublimation, reaction, decomposition or modification. It is formed usually by spin coating a dye material such as a cyanine dye on the substrate 1 or on an inter-layer 6 formed on the substrate 1.

[0024] The thickness of the light absorptive layer 2 is usually within a range offrom 20 to 500 nm, preferably from 100 to 300 nm.

[0025] The light reflective layer 3 is usually made of a metal such as gold, silver, copper, aluminum or an alloy thereof. The thickness of the light reflective layer 3 is usually within a range of from 30 to 150 nm, preferably from 40 to 130 nm.

[0026] The protective layer 4 is made of a resin excellent in the impact resistance like the light transmitting substrate 1 and is most commonly formed by coating a ultraviolet curable resin by spin coating, followed by irradiation with ultraviolet rays for curing. As other materials, an epoxy resin, an acrylate resin and a silicone hard coat resin may usually be used. It is also possible to employ a resilient material such as a urethane resin to obtain a cushion effect.

[0027] The thickness of the protective layer 4 is not critical and is usually within a range of from 3 to 30 μm, preferably from 5 to 15 μm.

[0028] As shown in Figures 4 to 7, an inter-layer 6 such as a resin layer or a solvent resistant layer may be disposed between the substrate 1 and the light absorptive layer 2. As shown in Figures 5 and 7, such an inter-layer 6 deforms by the energy generated by the light absorptive layer 2 upon absorption of the writing laser beam to form optically modified pits 5. If such an inter-layer 6 is sufficiently thick, pits 5 will be formed therein as shown in Figure 5, whereby the inter-layer serves as the surface layer of the substrate 1. If the inter-layer 6 is relatively thin, i.e. has a thickness of at most 30 nm, not only the inter-layer 6 but also the substrate 1 will be deformed as shown in Figure 7. When such an inter-layer 6 is not present, the surface layer of the substrate 1 will be deformed as shown in Figure 3 to form optically modified pits 5.

[0029] The inter-layer 6 preferably has a heat distortion temperature within a range of from 50 to 150°C, more preferably from 85 to 140°C, as measured in accordance with ASTM D648 under a load of 4.6 kg/cm^2 and/or a Rockwell hardness within a range of from M100 to M50, more preferably from M95 to M75, as measured in accordance with ASTM D785. The heat distortion temperature and the Rockwell hardness of the inter-layer 6 within the above ranges are preferred for the same reasons as mentioned with respect to the heat distortion temperature and the Rockwell hardness of the substrate 1. The inter-layer 6 may be made of a resin such as an acrylate resin, a vinyl chloride resin, a vinylidene chloride resin, a polystyrene resin, a polyester resin, a polyurethane resin, a cellulose resin or a silicone resin. However, any other resin may be employed so long as it satisfies the above-mentioned properties for the inter-layer 6.

[0030] The thickness of the inter-layer is usually within a range of from 2 nm to 500 μm, preferably from 10 to 200 nm.

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[0031] Further, a hard layer 16 less heat-deformable than the substrate may be disposed between the light absorptive layer 2 and the light reflective layer 3 as shown in Figures 8 and 9, or on the light reflective layer 3 as shown in Figures 10 and 11. The hard layer 16 is made of a material less heat-deformable than the substrate and preferably has a Rockwell hardness of at least M100, as measured in accordance with ASTM D785 and/or a heat distortion temperature of at least 100°C, more preferably at least 130°C, as measured in accordance with ASTM D648 under a load of 4.6 kg/cm^2.

[0032] Each of Figures 2, 4, 6, 8 and 10 illustrates a state prior to optical recording by a laser beam. Each of Figures 3, 5, 7, 9 and 11 illustrates a state after the optical recording. Namely, when a laser beam 7 from an optical pickup 8 is irradiated in a focused state to the light absorptive layer 2, the surface layer of the substrate 1 is locally deformed by the energy generated at the light absorptive layer 2, to form optically modified pits 5, as diagrammatically illustrated in these Figures.

[0033] In the optical information recording medium of the present invention, it is preferred that an optical parameter represented by $\rho = n_{abs}d_{abs}/\lambda$ where n_{abs} is the real part of the complex refractive index of the light absorptive layer, d_{abs} is the thickness of the light absorptive layer and λ is the wavelength of a reading laser beam, is $0.05 \leqq \rho \leqq 0.6$, and the imaginary part k_{abs} of the complex refractive index of the light absorptive layer is at most 0.3. Figure 12 is a graph showing the relation between the optical parameter $p = n_{abs}d_{abs}/\lambda$ where n_{abs} is the real part of the complex refractive index of the light absorptive layer 2 of the optical disc, d_{abs} is the thickness of the light absorptive layer 2 and λ is the wavelength of a reading laser beam and the reflectance of light entered through the substrate, when a semiconductor laser beam having a wavelength λ of 780 nm was used as the reading laser beam, with respect to two examples of the optical disc. Further, Figure 13 shows the reflectance when the imaginary part k_{abs} was changed from a value close to 0 to a value of 2.0 by changing the light transmittance of the light absorptive layer while maintaining the real part of the complex refractive index to a constant level of $n_{abs} = 2.4$, with respect to an optical disc wherein a gold film was used as the light reflective layer. From these Figures, it is evident that when the optical parameter of $\rho = n_{abs}d_{abs}/\lambda$ and the imaginary part k_{abs} satisfy the above-mentioned conditions, a high reflectance is obtainable, whereby it is readily possible to secure the standard properties stipulated in the CD standards i.e. the reflectance of at least 70%.

[0034] Figure 14 diagrammatically illustrates the surface of the light transmitting substrate 1 of the optical information recording medium of the present invention having the protective layer 4, the light reflective layer 3 and the light absorptive layer 2 removed after optical recording. Namely, in order to form pits 5 along a pregroove 9 which is a tracking guide groove formed on the surface of the substrate 1, a focused laser beam modulated by EFM signals was irradiated to the light absorptive layer 2 along the pregroove 9, and then the protective layer 4 and the light reflective layer 3 were peeled off from the substrate 1. Thereafter, the light absorptive layer 2 was also removed from the surface of the substrate 1.

[0035] Further, the surface of the light transmitting substrate 1 was observed along the pregroove 9 by STM (Scanning Tunneling Microscope). The results are shown in Figures 15(a) and (b). In these Figures, the abscissa indicates the moving distance of a tip (probe) 10 along the pregroove 9 i.e. in the tracking direction, and the ordinate indicates the height of the surface of the substrate 1: Figure 15(a) illustrates a case where the length of a pit is relatively short at a level of 10,000 Å, whereby it is evident that a clear deformation in the form of a protuberance with a height of about 200 Å is formed. Likewise, Figure 15(b) illustrates a case where the length of a pit is relatively long at a level of 40,000 Å, whereby a deformation in the form of a protuberance with a height of about 200 Å is observed, but the protuberance has two peaks with a slightly lower portion at the center. Thus, in a preferred embodiment, optically readable pits are formed in the pregroove 9 as a tracking guide groove formed on the deformable surface layer of the substrate 1.

[0036] Figures 16 to 19 diagrammatically illustrate the states of the pits 5 formed by irradiation with a laser beam.

[0037] Figures 16(a) to (d) diagrammatically illustrate the state in which a deformation 14 is formed on the substrate 1 adjacent to the light absorptive layer 2 by the irradiation of the light absorptive layer 2 with a focused laser beam 7.

[0038] More specifically, Figure 16(a) diagrammatically illustrates a case wherein when the light absorptive layer 2 has been irradiated with a focused laser beam, the components constituting the layer 2 undergo melting and decomposition and at the same time, the interfacial side of the light transmitting substrate 1 adjacent to the light absorptive layer 2 softens, whereby the components of the light absorptive layer 2 diffuse or flow into the substrate 1 to form a deformation 14. In many cases, at the deformed portion, the components of the light absorptive layer 2 are locally mixed and partially chemically reacted with the material constituting the light transmitting substrate 1 to form an optically modified portion 12 having optical properties differentfrom the light absorptive layer 2 or the light transmitting substrate 1. For example, when the light absorptive layer 2 is formed with a cyanine dye, and the light transmitting substrate 1 is formed with a polycarbonate, the optical properties of the optically modified portion 12 shows values slightly different from the transmitting substrate 1.

[0039] It is usual that when a laser beam is irradiated to a light absorptive layer 2 to form a pit 5, the material constituting the light absorptive layer 2 locally under-

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goes heat generation, melting and decomposition at that portion, whereby the optical properties of the light absorptive layer 2 will also be locally changed. In some cases, such a phenomenon is accompanied with formation of a space 10 between the light absorptive layer 2 and the light reflective layer 3, or formation of bubbles 11 in the light absorptive layer 2, which may remain after cooling.

[0040] Such a space 10 is likely to form particularly when the layer adjacent on the incident light side of the light absorptive layer 2, such as the surface layer of the substrate 1 is relatively heat-deformable as compared with the layer behind the light absorptive layer 2, such as the light reflective layer 3 or the protective layer 4, and the layer behind the light absorptive layer 2 has poor adhesion to the light absorptive layer 2 as compared with the adjacent layer on the incident light side. With such an optical information recording medium, when a laser beam 7 is irradiated to the light absorptive layer 2, energy is generated in the light absorptive layer 2 and the substrate 1 is deformed at 14, as mentioned above, and at the same time a gas is generated in the light absorptive layer 2, whereby a space 10 will be formed between the light absorptive layer 2 and the adjacent light reflective layer 3 having poor adhesive properties, and the gas tends to remain in the space 10. The gas generated in the interior of the light absorptive layer 2 may remain as bubbles 11.

[0041] Figures 16(c) and (d) illustrate other shapes of the deformation 14 on the transparent substrate 1. Figure 16(c) illustrates a deformation 14 in the form of a protuberance with its top separated to form two peaks, whereas Figure 16(d) illustartes a deformation 14 of a waveform wherein protuberances and dents are alternately repeated. In these cases, the above-mentioned space 10, bubbles 11 or optically modified portion 12 may also be formed.

[0042] Figures 17(a) to (c) diagrammatically illustrate a case wherein the deformation 14 of the light transmitting substrate 1 adjacent to the light absorptive layer 2 at the portion of the pit 5 is in the form of a dent or recess relative to the light absorptive layer 2.

[0043] Figure 17(a) illustrates a case where a space 10 is formed at the boundary of the light absorptive layer 2 and the light reflective layer 3, and Figure 17(b) illustrates a case wherein at the same time as the formation of the space 10, fine bubbles 11 are dispersed in the light absorptive layer 2, and further the decomposed components of a light absorptive layer 2 diffuse into the light transmitting substrate 1 formed with a deformation 14 so that the decomposed components and the components constituting the light transmitting substrate 1 are mixed and partly chemically reacted to form an optically modified portion 12. Further, Figure 17(c) illustrates a case wherein at the same time as the formation of the above-mentioned space 10, another space 10 is formed between the substrate 1 and the light absorptive layer 2.

[0044] Figures 18(a) to (d) illustrate a case wherein deformations 14 and 14' at the pit 5 reach both layers adjacent to the light absorptive layer 2. Such a pit is likely to be formed in a case where the heat distortion temperature or the hardness is substantially the same as between the two layers sandwiching the light absorptive layer 2, such as the substrate 1 and the light reflective layer 3 or the protective layer 4.

[0045] Figure 18(a) illustrates a case wherein a space 10' is formed between the light absorptive layer 2 and the substrate 1 at the pit 5, Figure 18(b) illustrates a case wherein spaces 10 and 10' are formed between the light absorptive layer 2 and the adjacent substrate 1 and between the light absorptive layer 2 and the adjacent light reflective layer 3, and Figure 18(c) illustrates a case wherein fine bubbles 11 are dispersed in the light absorptive layer 2. Figure 18(d) illustrates a state in which the deformations 14 and 14' are both in the form of protuberances towards the light absorptive layer 2.

[0046] Further, Figures 19(a) and (b) illustrate a case wherein an optically modified portion 13 having optical properties different from other portions is formed at the pit 5 in a layer on the incident light side relative to the light absorptive layer 2. This modified portion 13 is always located on the side from which the laser beam 7 enters. In many cases, the modified portion extends to the interior of the light absorptive layer 2. In such a case, a deformation 14 may be observed in the layer adjacent to the light absorptive layer 2, but due to the presence of the optically modified portion 13, it is usual that the deformation is not distinct.

[0047] Figure 19(a) illustrates a state wherein an optically modified portion 13 is formed on the surface of e. g. the substrate 1 adjacent to the light absorptive layer 2, and Figure 19(b) illustrates a state in which the optical properties gradually change in a thickness direction from substrate 1 to the light absorptive layer 2.

[0048] Such modifications of layers are brought about by the decomposition, reaction or mutual diffusion of the light absorptive layer 2 and another layer caused by the heat generated in the light absorptive layer 2 by the irradiation with a laser beam 7. Thus, such pits 5 are formed when the light absorptive layer 2 and the adjacent layer are made of materials having such functions.

[0049] In the optical information recording medium of the present invention, a layer behind the light absorptive layer 2 relative to the light transmitting substrate 1, such as the light reflective layer 3 or the protective layer 4, is preferably made of a material having a heat distortion temperature and a hardness higher than the layer on which pits 5 are formed. By forming the layer behind the absorptive layer 2 with a hard material, the block error rate of recorded signals can effectively be reduced whereby it is readily possible to meet the standard requirement of BLER (block error rate) being not higher then 3×10^{-2} as prescribed in the CD standards.

[0050] Now, the present invention will be described in further detail with reference to Examples. However, i

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should be understood that the present invention is by no means restricted to such specific Examples.

EXAMPLE 1

[0051] A polycarbonate substrate 1 having a thickness of 1.2 mm, an outer diameter of 120 mm and an inner diameter of 15 mm and having a spiral pregroove formed on its surface with a width of 0.8 μm, a depth of 0.08 μm and a pitch of 1.6 μm, was formed by injection molding. This polycarbonate substrate 1 had a Rockwell hardness (ASTM D785) of M75 which corresponds to HB of the pencil hardness and a heat distortion temperature (ASTM D648) of 121°C under a load of 4.6 kg/cm^2.

[0052] As an organic dye to form the light absorptive layer 2, 0.65 g of 1,1'-dibutyl-3,3,3',3'-tetramethyl-4,5,4',5'-dibenzoindodicarbocyanine perchlorate (product number NK3219, manufactured by Nippon Kanko Shikiso Kenkyusho) was dissolved in 10 mℓ of a diacetone alcohol solvent, and the solution was coated on the surface of the substrate 1 by spin coating to form a light absorptive layer 2 of a light sensitive dye film having a thickness of 130 nm. The optical parameter $\rho = n_{abs}d_{abs}/\lambda$ where n_{abs} is the real part of the complex refractive index of the light absorptive layer 2, d_{abs} is the thickness of the layer and λ is the wavelength of a read-out laser beam, was 0.45, and the imaginary part k_{abs} of the complex refractive index was 0.05.

[0053] Then, a gold film having a thickness of 80 nm was formed by sputtering on the entire surface of the region covered by the diameter of from 45 to 118 mm of this disc, to form a light reflective layer 3. Further, on this light reflective layer 3, an ultraviolet curable resin was spin-coated and then cured by irradiation with ultraviolet rays, to form a protective layer 4 having a thickness of 10 μm. After the curing, this protective layer 4 had a Rockwell hardness (ASTM D785) of M90 and a heat distortion temperature (ASTM D648) of 135°C under a load of 4.6 kg/cm^2.

[0054] To the optical disc thus obtained, a semiconductor laser having a wavelength of 780 nm was irradiated at a linear speed of 1.2 m/sec at a recording power of 6.0 mW, to record EFM signals. Then, this optical disc was played back by a commercially available CD player (Aurex XR-V73, wavelength of the reading laser beam λ = 780 nm), whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.68, I_3/I_{top} was 0.35, and the block error rate BLER was 1.2 x 10^{-2}.

[0055] The CD standards prescribe that the reflectance is at least 70%, I_{11}/I_{top} is at least 0.6, I_3/I_{top} is from 0.3 to 0.7, and the block error rate BLER is not higher than 3 x 10^{-2}. The optical disc of this example meets this standards.

[0056] Further, after the recording, the protective layer 4 and the light reflective layer 3 of the optical disc were peeled off, and the exposed surface of the light absorptive layer 2 was inspected, whereby linear fine irregularities were observed which appeared to represent the outline profile of pits. Further, the light absorptive layer 2 was washed off with a solvent, and the surface of the substrate 1 was inspected, whereby formation of optically modified pits 5 was confirmed.

[0057] The layered structure of this optical disc is diagrammatically illustrated in Figure 2, and the same structure after the optical recording is diagrammatically illustrated in Figure 3.

[0058] The surface of the light transmitting substrate 1 was observed by STM (Scanning Tunneling Microscope), whereby the pitted portion was found to be deformed in the form of protuberances. Further, the recorded portion and the non-recorded portion of the substrate 1 were measured by a spectrophotometer, whereby at the recorded portion, peaks other than the peaks observed with the resin of the non-recorded portion, were observed.

EXAMPLE 2

[0059] An optical disc was prepared in the same manner as in Example 1 except that an epoxy resin was spin-coated to form a hard layer having a thickness of 100 nm between the light absorptive layer 2 and the light reflective layer 3 in Example 1. After the curing, this epoxy resin had a Rockwell hardness (ASTM D785) of M90 and a heat distortion temperature (ASTM D648) of 135°C under a load of 4.6 kg/cm^2.

[0060] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 1. Then, this optical disc was played back by the commercially available CD player, whereby the reflectance of the semiconductor laser beam and the read-out signal output characteristics were the same as in Example 1, and the block error rate BLER was 3.0 x 10^{-3}. The surface of the substrate 1 of the optical disc after the recording was inspected in the same manner as in Example 1 to confirm the formation of pits 5. Namely, from the observation of the surface of the substrate 1 by STM, a deformation 14 in the form of a protuberance was observed. This protuberance had two peaks with a slightly low portion at the center.

EXAMPLE 3

[0061] An optical disc was prepared in the same manner as in Example 1 except that between the light absorptive layer 2 and the light reflective layer 3 in Example 1, a hard layer of a silicone acrylate resin having a thickness of 100 nm was formed by spin coating on the light absorptive layer 2 and a binding layer of an epoxy resin having a thickness of 20 nm was formed by spin coating on the upper surface of this hard layer. After curing, this silicone acryate resin layer had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 100°C under a load of 4.6 kg/cm^2.

[0062] To the optical disc thus obtained, EFM signals

were recorded with a recording power of 7.0 mW in the same manner as in Example 1. Then, this optical disc was played back by the same CD player (Aurex XR-V73) as used in Example 1 with a semiconductor laser beam having wavelength of 780 nm, whereby the reflectance of the semiconductor laser beam was 75%, I_{11}/I_{top} was 0.63, I_3/I_{top} was 0.35, and the block error rate BLER was 2.5×10^{-3}. Further, the surface of the substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1, to confirm the formation of pits 5 as in Example 1.

EXAMPLE 4

[0063] An optical disc was prepared in the same manner as in Example 1 except that in Example 1, a film of an alloy of gold and antimony in a ratio of 9:1 was formed by vacuum vapor deposition as a light reflective layer 3 on the light absorptive layer 2, and on this reflective layer 3, a protective layer 4 of a ultraviolet curable resin was formed with a binding layer of an epoxy resin having a thickness of 20 nm interposed therebetween. The above light reflective layer 3 had a hardness of at least H as pencil hardness.

[0064] To the optical disc thus obtained, EFM signals were recorded with a recording power of 6.2 mW in the same manner as in Example 1. Then, this optical disc was played back by the same CD player as used in Example 1, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.62, I_3/I_{top} was 0.32, and the block error rate BLER was 3.5×10^{-3}. Further, the surface of the substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1, to confirm the formation of pits 5 as in Example 1.

EXAMPLE 5

[0065] An optical disc was prepared in the same manner as in Example 1 except that in Example 1, an ultraviolet curable type hard coat resin was spin-coated on the incident light side of the polycarbonate substrate 1 to form a substrate protective layer having a thickness of 1 μm, the light absorptive layer 2 was formed on the side having the pregroove, and on this light absorptive layer 2, a film of an alloy of gold and iridium in a ratio of 3:1 was formed by sputtering as a light reflective layer 3. The light reflective layer 3 had a hardness of at least 5H as pencil hardness.

[0066] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 1. Then, this optical disc was played back by the same CD player as used in Example 1, whereby the reflectance of the semiconductor laser beam was 70%, I_{11}/I_{top} was 0.62, I_3/I_{top} was 0.37, and the block error rate BLER was 3.7×10^{-3}. Further, the surface of the substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1, to confirm the formation of pits 5 as in Example 1.

EXAMPLE 6

[0067] An optical disc was prepared in the same manner as in Example 1 except that in Example 1, the light reflective layer 3 was formed by a silver layer having a thickness of 60 nm, and a silicone hard coating agent was spin-coated thereon, heated and cured to form a hard protective layer 4 having a thickness of 3 μm. The protective layer 4 had a hardness of at least of HB as pencil hardness.

[0068] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 1. Then, this optical disc was played back by the same CD player as used in Example 1, whereby the reflectance of the semiconductor laser beam was 71%, I_{11}/I_{top} was 0.63, I_3/I_{top} was 0.35, and the block error rate BLER was 2.8×10^{-3}. Further, the surface of the substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1, to confirm the formation of pits 5 as in Example 1.

EXAMPLE 7

[0069] An optical disc was prepared in the same manner as in Example 1 except that in Example 1, a polysulfide-incorporated epoxy resin diluted with diglycidyl ether was spin-coated to form a binding layer of 30 nm on the light reflective layer 3 formed by vacuum vapor deposition of a gold film having a thickness of 50 nm, and a silicone hard coating agent was spin-coated on the binding layer, heated and cured to form a hard protective layer 4 having a thickness of 3 μm.

[0070] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 1. Then, this optical disc was played back by the same CD player as used in Example 1, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.65, I_3/I_{top} was 0.35, and the block error rate BLER was 2.5×10^{-3}. Further, the surface of the substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1, to confirm the formation of pits 5 as in Example 1.

EXAMPLE 8

[0071] An optical disc was prepared in the same manner as in Example 1 except that in Example 1, the light absorptive layer was formed by using 1,1'-dibutyl-3,3,3',3'-tetramethyl-5,5'-diethoxyindodicarbocyani ne perchlorate, a hard layer of an epoxy resin having a thickness of 100 nm was formed on the light reflective layer 3, an ultraviolet curable resin was formed thereon in a thickness of 10 μm and then the protective layer 4 was formed.

[0072] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 1

Then, this optical disc was played back by the same CD player as used in Example 1, whereby the reflectance of the semiconductor laser beam was 74%, I_{11}/I_{top} was 0.68, I_3/I_{top} was 0.34, and the block error rate BLER was 8.3 x 10^{-3}. Further, the surface of the substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1, to confirm the formation of pits 5 as in Example 1.

EXAMPLE 9

[0073] On the surface of the same polycarbonate substrate 1 as used in Example 1, an acrylate resin dissolved in diisobutyl ketone was spin-coated to form an inter-layer 6 having a thickness of 40 nm. This inter-layer 6 had a Rockwell hardness (ASTM D785) of M85 and a heat distortion temperature (ASTM D648) of 100°C under a load of 4.6 kg/cm^2.

[0074] As an organic dye to form the light absorptive layer 2, 0.6 g of 1,1'-dipropyl-3,3,3',3'-tetramethyl-5,5'-dimethoxyindodicarbocyanine iodide was dissolved in 10 mℓ of an isopropyl alcohol solvent. The solution was coated on the surface of the above substrate 1 by spin coating to form a light absorptive layer 2 of a light sensitive dye film having a thickness of 120 nm. The optical parameter of $\rho = n_{abs}d_{abs}/\lambda$ where n_{abs} is the real part of the complex refractive index of this light absorptive layer 2, d_{abs} is the thickness of the layer and λ is the wavelength of a reading laser beam, was 0.41, and the imaginary part k_{abs} of the complex refractive index was 0.02.

[0075] Then, a silicone acrylate resin dissolved in cyclohexane was spin-coated thereon to form a silicone acrylate resin layer having a thickness of 100 nm, a pencil hardness of 2H and a heat distortion temperature (ASTM D648) of 120°C under a load of 4.6 kg/cm^2. Then, a gold film having a thickness of 50 nm was formed by sputtering to form a light reflective layer 3. Further, an ultraviolet curable resin was spin-coated on this light reflective layer 3 and cured by irradiation with ultraviolet rays to form a protective layer 4 having a thickness of 10 μm. After curing, this protective layer 4 had a Rockwell hardness (ASTM D785) of M90, a heat distortion temperature (ASTM D648) was 135°C under a load of 4.6 kg/cm^2.

[0076] To the optical disc thus obtained, a semiconductor laser beam having wavelength of 780 nm was irradiated at a linear speed of 1.2 m/sec with a recording power of 7.5 mW to record EFM signals. Then, this optical disc was played back by the same CD player as used in Example 1, whereby the reflectance of the semiconductor laser beam was 74%, I_{11}/I_{top} was 0.62, I_3/I_{top} was 0.31, and the block error rate BLER was 4.0 x 10^{-3}.

[0077] Further, the protective layer 4 and the light reflective layer 3 of the optical disc after recording were peeled off, and the light absorptive layer 2 was washed off with a solvent, and the surface of the inter-layer 6 was inspected to confirm the formation of pits 5.

EXAMPLE 10

[0078] An optical disc was prepared in the same manner as in Example 9 except that in Example 9, a silicone coating agent was spin-coated on the inter-layer 6 to form a silicate layer having a thickness of 0.01 μm, and the light absorptive layer 2 was formed thereon.

[0079] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.8 mW in the same manner as in Example 9. Then, this optical disc was played back by the same CD player as used in Example 9, whereby the reflectance of the semiconductor laser beam was 73%, I_{11}/I_{top} was 0.62, I_3/I_{top} was 0.31, and the block error rate BLER was 3.4 x 10^{-3}. Further, the surface of the inter-layer 6 of the optical disc after recording was inspected in the same manner as in Example 9, to confirm the formation of pits 5.

EXAMPLE 11

[0080] An optical disc was prepared in the same manner as in Example 9 except that in Example 9, a glass substrate was used as the substrate 1, and an isocyanate resin dissolved with a solvent mixture of toluene and methyl ethyl ketone in a ratio of 1:1, was spin-coated on the reflective layer to form a binding layer having a thickness of 20 nm.

[0081] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.2 mW in the same manner as in Example 9. Then, this optical disc was played back by the same CD player as used in Example 9, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.65, I_3/I_{top} was 0.33, and the block error rate BLER was 3.6 x 10^{-3}. Further, the surface of the inter-layer 6 of the optical disc after recording was inspected in the same manner as in Example 9, to confirm the formation of pits 5.

EXAMPLE 12

[0082] An optical disc was prepared in the same manner as in Example 9 except that in Example 9, a silicone coating agent was spin-coated on the inter-layer 6 to form a silicate layer having a thickness of 0.01 μm, and the light absorptive layer 2 was formed thereon, and polybutadiene was spin-coated on the reflective layer to form a binding layer having a thickness of 20 nm.

[0083] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.2 mW in the same manner as in Example 9. Then, this optical disc was played back by the same CD player as in Example 9, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.66, I_3/I_{top} was 0.35, and the block error rate BLER was 3.5 x 10^{-3}. Further, the surface of the inter-layer 6 of the optical disc after recording was inspected in the same manner as in Example 9, to confirm the formation of pits 5.

EXAMPLE 13

[0084] An optical disc was prepared in the same manner as in Example 9 except that in Example 9, the thickness of the inter-layer 6 was changed to 20 nm, no silicone acrylate resin layer was provided, and a film of an alloy of iridium and gold in a ratio of 1:9 was formed by sputtering as the reflective layer 3. The alloy layer had a pencil hardness of 2H.

[0085] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.0 mW in the same manner as in Example 9. Then, this optical disc was played back by the same CD player as used in Example 9, whereby the reflectance of the semi-conductor laser beam was 71%, I_{11}/I_{top} was 0.63, I_3/I_{top} was 0.32, and the block error rate BLER was 3.3×10^{-3}. Further, the surface of the inter-layer 6 of the optical disc after recording was inspected in the same manner as in Example 9, to confirm the formation of pits 5. The pits 5 reached to the surface of the substrate since the thickness of the inter-layer 6 was thin.

[0086] The layered structure of this optical disc is diagrammatically illustrated in Figure 6, and the same structure after optical recording is diagrammatically illustrated in Figure 7.

EXAMPLE 14

[0087] An optical disc was prepared in the same manner as in Example 9 except that in Example 9, a silicone coating agent was spin-coated on the inter-layer 6 to form a silicate layer having a thickness of 0.01 μm, the light absorptive layer 2 was formed thereon, no silicone acrylate resin layer was formed, and a film of an alloy of iridium and gold in a ratio of 1:9 was formed by sputtering as the reflective layer 3.

[0088] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.8 mW in the same manner as in Example 9. Then, this optical disc was played back by the same CD player as used in Example 9, whereby the reflectance of the semiconductor laser beam was 71%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.32, and the block error rate BLER was 2.8×10^{-3}. Further, the surface of the inter-layer 6 of the optical disc after recording was inspected in the same manner as in Example 9, to confirm the formation of pits 5.

EXAMPLE 15

[0089] An optical disc was prepared in the same manner as in Example 9 except that in Example 9, no silicone acrylate resin layer was formed, a film of an alloy of iridum and gold in a ratio of 1:9 was formed by sputtering as the reflective layer 3, and polyisoprene was spin-coated on the light reflective layer to form a binding layer having a thickness of 20 nm and the protective layer 4 of an ultraviolet curable resin was formed thereon.

[0090] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.4 mW in the same manner as in Example 9. Then, this optical disc was played back by the same CD player as used in Example 9, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.32, and the block error rate BLER was 4.1×10^{-3}. Further, the surface of the inter-layer 6 of the optical disc after recording was inspected in the same manner as in Example 9, to confirm the formation of pits 5.

EXAMPLE 16

[0091] An optical disc was prepared in the same manner as in Example 9 except that in Example 9, no silicone acrylate resin layer was formed, a copper film having a thickness of 50 nm was formed as the reflective layer 3, and a bisphenol curable type epoxy resin diluted in a diglycidyl ether solvent was spin-coated to form an epoxy resin layer having a thickness of 10 μm as the protective layer 4. The protective layer had a Rockwell hardness (ASTM D785) of M110 and thus had a function as a hard layer.

[0092] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.0 mW in the same manner as in Example 9. Then, this optical disc was played back by the same CD player as used in Example 9, whereby the reflectance of the semiconductor laser beam was 75%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.33, and the block error rate BLER was 2.9×10^{-3}. Further, the surface of the inter-layer 6 of the optical disc after recording was inspected in the same manner as in Example 9, to confirm the formation of pits 5.

EXAMPLE 17

[0093] An optical disc was prepared in the same manner as in Example 9 except that in Example 9, a silicone coating agent was spin-coated on the inter-layer 6 to form a silicate layer having a thickness of 0.01 μm, the light absorptive layer 2 was formed thereon, no silicone acrylate resin layer was formed, a copper film having a thickness of 50 nm was formed as the light reflective layer 3, and a bisphenol curable type epoxy resin diluted with a diglycidyl ether solvent was spin-coated to form an epoxy resin layer having a thickness of 10 μm as the protective layer 4.

[0094] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.0 mW in the same manner as in Example 9. Then, this optical disc was played back by the same CD player as used in Example 9, whereby the reflectance of the semi-conductor laser beam was 74%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.33, and the block error rate BLER was 3.5×10^{-3}. Further, the surface of the inter-layer 6 of the optical disc after recording was inspected in the same manner as in Example 9, to confirm the formation of pits 5.

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EXAMPLE 18

[0095] An optical disc was prepared in the same manner as in Example 9 except that in Example 9, no silicone acrylate layer was formed, a copper film having a thickness of 50 nm was formed by vacuum vapor deposition as the light reflective layer 3, a polyvinyl acetate resin dissolved with a solvent mixture of toluene and methyl ethyl ketone in a ratio of 6:4, was spin-coated on the light reflective layer to form a binding layer having a thickness of 20 nm, the protective layer 4 was formed thereon, and a bisphenol curable type epoxy resin diluted with a diglycidyl ether solvent was spin-coated to form an epoxy resin layer having a thickness of 10 μm as the protective layer 4.

[0096] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.4 mW in the same manner as in Example 9. Then, this optical disc was played back by the same CD player as used in Example 9, whereby the reflectance of the semiconductor laser beam was 74%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.33, and the block error rate BLER was 3.6×10^{-3}. Further, the surface of the inter-layer 6 of the optical disc after recording was inspected in the same manner as in Example 9, to confirm the formation of pits 5.

EXAMPLE 19

[0097] A polycarbonate disc (Panlite, tradename, manufactured by Tenjin Kasei K.K.) having a thickness of 1.2 mm, an outer diameter of 120 mm and an inner diameter of 15 mm and having a spiral pregroove 8 with a width of 0.8 μm, a depth of 0.08 μm and a pitch of 1.6 μm in a region covered by the diameter of from 46 to 117 mm of the disc, formed by injection molding, was used as the light transmitting substrate 1. This polycarbonate substrate 1 had a Rockwell hardness (ASTM D785) of M75 and a heat distortion temperature (ASTM D648) of 135°C under a load of 4.6 kg/cm^2. As an organic dye to form the light absorptive layer 2, 0.65 g of 1,1'-dibutyl-3,3,3',3'-tetramethyl-4,5,4',5'-di-benzoindodicarbocyanine perchlorate (product number NK3219, manufactured by Nippon Kanko Shikiso K.K.) was dissolved in 10 mℓ of a diacetone alcohol solvent. This solution was coated by spin coating on the surface of the substrate 1 to form a light absorptive layer 2 having a thickness of 130 nm.

[0098] Then, a silver film having a thickness of 50 nm was formed by sputtering over the entire surface of a region covered by the diameter of from 45 to 118 mm of this disc, to form a light reflective layer 3. Further, on this light reflective layer 3, an ultraviolet curable resin was spin-coated and cured by irradiation with ultraviolet rays to form a protective layer 4 having a thickness of 10 μm. After the curing of the ultraviolet ray curable resin, this protective layer 4 had a Rockwell hardness (ASTM D785) of M90 and a heat distortion temperature (ASTM D648) of 150°C under a load of 4.6 kg/cm^2.

[0099] To the optical disc thus obtained, a semiconductor laser beam having a wavelength of 780 nm was irradiated at a linear speed of 1.2 m/sec with a recording power of 6.0 mW to record EFM signals. Then, this optical disc was played back by a commercially available CD player (Aurex XR-V73, wavelength of the reading laser beam λ = 780 nm), whereby I_{11}/I_{top} obtained from the eye pattern of the read-out signals was 0.63, and I_3/I_{top} was 0.32.

[0100] The CD standards prescribe that I_{11}/I_{top} is at least 0.6, and I_3/I_{top} is from 0.3 to 0.7. Thus, the optical disc of this example meets the standards.

[0101] Further, protective layer 4 and the light reflective layer 3 of the optical disc were peeled off after recording, and the surface of the light absorptive layer 2 was inspected, whereby linear fine irregularities were observed which appeared to represent the outline profile of pits. Further, the light absorptive layer 2 was washed off with a solvent, and the surface of the substrate 1 was inspected, whereby optically modified pits 5 in the form of protuberances were observed.

EXAMPLE 20

[0102] An optical disc was prepared in the same manner as in Example 19 except that in Example 19, a polycarbonate disc (Iupilon, tradename, manufactured by Mitsubishi Gas Kagaku K.K.) having a thickness of 1.2 mm, and outer diameter of 120 mm, an inner diameter of 15 mm, a Rockwell hardness (ASTM D785) of M75 and a heat distortion temperature (ASTM D648) of 132°C under a load of 4.6 kg/cm^2 and having a spiral prepit 8 for CD format signals formed with a width of 0.6 μm, a depth of 0.8 μm and a pitch of 1.6 μm in a range of the diameter of from 46 to 80 mm of the disc and a spiral pregroove 9 formed outside thereof with a width of 0.8 μm, a depth of 0.08 μm and a pitch of 1.6 μm in a range of the diameter of from 80 to 117 mm of the disc, which was formed by injection molding, was used as the light transmitting substrate 1, a gold film was used as the light reflective layer 3, and an epoxy resin layer having a thickness of 2 μm was formed by spin coating between this light reflective layer 3 and the protective layer 4 made of the ultraviolet curable resin. The epoxy resin layer had a Rockwell hardness (ASTM D785) of M90 and a heat distortion temperature (ASTM D648) of 140°C under a load of 4.6 kg/cm^2. The inside range of the diameter of from 46 to 80 mm of this optical disc is a so-called ROM (read only memory) region, and the outside range of the diameter of from 80 to 117 mm is a recordable region.

[0103] To the recordable region of the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 19. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.62, and I_3/I_{top} was 0.32.

[0104] Further, the surface of the substrate 1 of the optical disc after recording was inspected in the same

manner as in Example 19, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 21

[0105] An optical disc was prepared in the same manner as in Example 19 except that in Example 19, a polystyrene disc having a Rockwell hardness (ASTM D785) of M80 and a heat distortion temperature (ASTM D648) of 89°C under a load of 4.6 kg/cm^2, was used as the light transmitting substrate 1, the pregroove on the disc was subjected to webling of 22.11 kHz with an amplitude of 30 nm, a silicone acrylate resin layer having a thickness of 40 nm was formed by spin coating between the light absorptive layer 2 and the light reflective layer 3, and an epoxy resin layer having a thickness of 10 nm was formed by spin coating between this layer and the light absorptive layer, and a gold film was formed as the light reflective layer 3. The silicone acrylate resin layer had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 200°C under a load of 4.6 kg/cm^2.

[0106] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 19. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.63, and I_3/I_{top} Was 0.33.

[0107] Further, the surface of the substrate 1 of the optical disc after recording was inspected in the same manner as in Example 19, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 22

[0108] As the light transmitting substrate 1, the same polycarbonate disc as used in Example 19 was employed.

[0109] On this light transmitting substrate 1, an acrylate resin was spin-coated to form an inter-layer in a thickness of 70 nm. Then, as an organic dye to form the light absorptive layer 2, 0.65 g of 1,1'-dipropyl-3,3,3',3'-tetramethyl-5,5'-dimethoxyindodicarbocya nine iodide was dissolved in 10 mℓ of a diacetone alcohol solvent, and the solution was coated by spin coating on the inter-layer 6 on the substrate 1, to form a light absorptive layer 2 having a thickness of 90 nm. The inter-layer 6 had a heat deformation temperature (ASTM D648) of 100°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M85.

[0110] Then, a silicone acrylate resin was formed by spin coating in a thickness of 50 nm on the above light absorptive layer 2. Then, a gold film having a thickness of 50 nm was formed by sputtering on the entire surface of a region of the diameter of from 45 to 118 mm of the disc, to form a light reflective layer 3. Further, an ultraviolet curable resin was spin-coated on this light reflective layer 3 and cured by irradiation with ultraviolet rays to form a protective layer 4 having a thickness of 10μm.

[0111] To the optical disc thus obtained, a semiconductor laser beam having a wavelength of 780 nm was irradiated at a linear speed of 1.2 m/sec with a recording power of 6.0 mW to record EFM signals. Then, this optical disc was played back by the commercially available CD player (Aurex XR-V73, wavelength of the reading laser beam λ = 780 nm), whereby I_{11}/I_{top} obtained from the eye pattern of the read-out signals, was 0.63, and I_3/I_{top} was 0.32.

[0112] The CD standards prescribe that I_{11}/I_{top} is at least 0.6, and I_3/I_{top} is from 0.3 to 0.7. Thus, the optical disc of this example satisfies the standards.

[0113] Further, the protective layer 4, the light reflective layer 3 and the light absorptive layer 2 of this optical disc were peeled off after recording, and the surface of the inter-layer 6 was inspected, whereby formation of optically modified pits 5 in the form of protuberances was confirmed.

EXAMPLE 23

[0114] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with a vinyl chloride copolymer having a heat distortion temperature (ASTM D648) of 80°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M95, in a thickness of 60 nm.

[0115] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.66, and I_3/I_{top} Was 0.35.

[0116] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 24

[0117] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with an acrylate resin having a heat distortion temperature (ASTM D648) of 90°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M100, the thickness of the light absorptive layer 2 was changed to 130 nm, no silicone acrylate resin layer was formed between the light absorptive layer 2 and the light reflective layer 3, and the light reflective layer 3 was formed with a film of an alloy of gold and iridium in a ratio of 9:1.

[0118] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.63, and I_3/I_{top} was 0.32.

[0119] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits

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5 in the form of protuberances.

EXAMPLE 25

[0120] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with a vinylidene chloride copolymer having a heat distortion temperature (ASTM D648) of 66°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M60, in a thickness of 60 nm.

[0121] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.67, and I_3/I_{top} was 0.36.

[0122] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 26

[0123] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with polystyrene having a heat deformation temperature (ASTM D648) of 85°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M70.

[0124] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.65, and I_3/I_{top} was 0.34.

[0125] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 27

[0126] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with a polyvinyl acetate having a heat distortion temperature (ASTM D648) of 55°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M70 in a thickness of 60 nm, and isocyanate was spin-coated on the silicone acrylate resin layer in a thickness of 10 nm.

[0127] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.66, and I_3/I_{top} was 0.32.

[0128] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 28

[0129] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with a polyester having a heat distortion temperature (ASTM D648) of 70°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M70, as the organic dye to form the light absorptive layer 2, 1,1'-dibutyl-3,3,3',3'-tetramethyl-4,5,4', 5'-dibenzoindodicarbocyanine perchlorate was used, a silicone resin was coated on the light absorptive layer 2 instead of the silicone acrylate resin, and a bisphenol curable type epoxy resin layer was formed on the light reflective layer 3 in a thickness of 20 nm.

[0130] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.61, and I_3/I_{top} was 0.31.

[0131] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 29

[0132] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with a polyurethane resin having a heat distortion temperature (ASTM D648) of 50°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M60 in a thickness of 50 nm, a silicone resin was spin-coated on this inter-layer 6 in a thickness of 15 nm for solvent resistant treatment, then a light absorptive layer 2 having a thickness of 130 nm was formed by using 1,1'-dibutyl-3,3,3',3'-tetramethyl-4,5,4', 5'-dibenzoindodicarbocyanine perchlorate, no silicone acrylate resin was coated between the light absorptive layer 2 and the light reflective layer 3, and the light reflective layer 3 was formed with a film of an alloy of gold and iridium in a ratio of 9:1.

[0133] To the optical disc thus prepared, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.66, and I_3/I_{top} was 0.33.

[0134] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 30

[0135] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with a polyurethane resin having a heat distortion temperature (ASTM D648) of 50°C under a load of 4.6 kg/cm^2 and a Rockwell hardness

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(ASTM D785) of M60, a silicone coating agent was spin-coated on this interlayer 6 in a thickness of 15 nm for solvent resistant treatment, and then a light absorptive layer 2 was formed by using 1,1'-dibutyl-3,3,3',3'-tetramethyl-4,5,4',5'-dibenzoindodicarboc yanine perchlorate, and a silicone resin was formed on this light absorptive layer 2 instead of the silicone acrylate resin, a polysulfide-incorporated epoxy resin was coated on the light reflective layer 3 in a thickness of 20 nm, and the protective layer 4 was formed thereon.

[0136] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.66, and I_3/I_{top} was 0.33.

[0137] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 31

[0138] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with a cellulose resin having a heat distortion temperature (ASTM D648) of 60°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M100, as an organic dye to form the light absorptive layer 2, 1,1'-dibutyl-3,3,3',3'-tetramethyl-4,5,4',5'-dibenzoindodicarbocyanine perchlorate was employed, and a silicone resin was coated on the light absorptive layer 2 instead of the silicone acrylate resin.

[0139] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.65, and I_3/I_{top} was 0.32.

[0140] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 32

[0141] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with an urethane thermoplastic resin having a heat distortion temperature (ASTM D648) of 50°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M30 in a thickness of 50 nm, a silicone coating agent was spin-coated on this inter-layer 6 in a thickness of 15 nm for solvent resistant treatment, and then a light absorptive layer 2 was formed by using 1,1'-dibutyl-3,3,3',3'-tetramethyl-4,5,4',5'-dibenzoindodicarbocyanine perchlorate, and a silicone resin was coated instead of the silicone acrylate resin.

[0142] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.67, and I_3/I_{top} was 0.34.

[0143] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 33

[0144] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with an acrylic resin having a heat distortion temperature (ASTM D648) of 70°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M90, a light absorptive layer2 having a thickness of 130 nm was formed by using 1,1'-dipropyl-5,7,5',7'-dimethoxyindodicarbocyanine fluoroborate as an organic dye, the light reflective layer 3 was formed by a copper film, and the protective layer 4 was formed with a silicone hard coating agent in a thickness of 5 μm.

[0145] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.63, and I_3/I_{top} was 0.32.

[0146] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

EXAMPLE 34

[0147] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with a polyurethane resin having a heat distortion temperature (ASTM D648) of 50°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M60, 1,1'-dipropyl-5,7,5',7'-dimethoxyindodicarbocyanine fluoroborate was used as an organic dye for the light absorptive layer 2, a SiO_2 film having a thickness of 30 nm was formed on the light absorptive layer 2 by sputtering, the light reflective layer 3 was formed with a copper film, an epoxy resin was spin-coated on the light reflective layer 3 in a thickness of 20 nm, and the protective layer 4 was formed thereon with a silicone hard coating agent in a thickness of 5 μm.

[0148] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.66, and I_3/I_{top} was 0.33.

[0149] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

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EXAMPLE 35

[0150] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, a glass disc was used as the light transmitting substrate 1, the inter-layer 6 was formed with an acrylate resin having a heat distortion temperature (ASTM D648) of 70°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M90 and having a pregroove formed by a photo polymerization method, a light absorptive layer 2 having a thickness of 130 nm was formed by using 1,1'-dipropyl 5,7,5',7'-dimethoxyindodicarbocyanine fluoroborate as an organic dye to form the light absorptive layer 2, the light reflective layer 3 was formed by a copper film, and the protective layer 4 was formed with a silicone hard coating agent in a thickness of 5 μm.

[0151] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.63, and I_3/I_{top} was 0.32.

[0152] Further, the surface of the inter-layer 6 after recording was inspected in the same manner as in Example 22, to confirm the formation of optically modified pits 5 in the form of protuberances.

COMPARATIVE EXAMPLE 1

[0153] An optical disc was prepared in the same manner as in Example 22 except that in Example 22, the interlayer 6 was formed with a silicone resin having a heat distortion temperature (ASTM D648) of 180°C under a load of 4.6 kg/cm^2 and a Rockwell hardness (ASTM D785) of M100.

[0154] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 22. Then, this optical disc was played back by the commercially available CD player, whereby I_{11}/I_{top} was 0.28, and I_3/I_{top} was 0.05.

[0155] Thus, this disc does not satisfy the CD format.

EXAMPLE 36

[0156] A polycarbonate substrate 1 of a disc shape having a thickness of 1.2 mm, an outer diameter of 120 mm and an inner diameter of 15 mm and having a spiral pregroove formed with a width of 0.8 μm, a depth of 0.08 μm and a pitch of 1.6 μm in a range of the diameter of from 46 to 117 mm of the disc, was formed by injection molding. This polycarbonate substrate 1 had a Rockwell hardness (ASTM D785) of M75 and a heat distortion temperature (ASTM D648) of 132°C.

[0157] As an organic dye to form the light absorptive layer, 0.65 g of 1,1'-dibutyl-3,3,3',3'-tetramethyl-4,5,4', 5'-dibenzoindodicarbocyanine perchlorate (product number NK3219, manufactured by Nippon Kanko Shikiso K.K.) was dissolved in 10 mℓ of a diacetone alcohol solvent. The solution was coated on the surface of the substrate 1 by spin coating to form a light absorptive layer 2 having a thickness of 130 nm.

[0158] Then, a gold film having a thickness of 50 nm was formed by sputtering on the entire surface in a region of the diameter of from 45 to 118 nm of this disc, to form a light reflective layer 3. Further, an ultraviolet curable resin was spin-coated on this light reflective layer 3 and cured by irradiation with ultraviolet rays, to form a protective layer 4 having a thickness of 10 μm. After curing, this protective layer had a Rockwell hardness (ASTM D785) of M90 and a heat distortion temperature (ASTM D648) of 150°C.

[0159] To the recordable region 7 of the optical disc thus obtained, a semiconductor laser beam having a wavelength of 780 nm was irradiated at a linear speed of 1.2 m/sec with a recording power of 6.0 mW to record EFM signals. Then, this optical disc was played back by a commercially available CD player (Aurex XR-V73, wavelength of the reading laser beam λ = 780 nm), whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.65, and I_3/I_{top} was 0.35, and the block error rate BLER was 3.4 x 10^{-3}.

[0160] The CD standards prescribe that the reflectance is at least 70%, I_{11}/I_{top} is at least 0.6, I_3/I_{top} is from 0.3 to 0.7, and the block error rate BLER is not higher than 3 x 10^{-2}. The optical disc of this reference meets the standards.

[0161] Further, the protective layer 4 and the light reflective layer 4 of the optical disc were peeled off after recording, and the light absorptive layer 2 was washed off with a solvent, and the surface of the light transmitting substrate 1 was observed by STM (Scanning Tunneling Microscope) whereby deformation in the form of protuberances was observed at the pitted portion. Further, the recorded portion and the non-recorded portion of the substrate 1 were measured by a spectro photometer, whereby at the recorded portion, peaks other than the peaks of the resin observed at the non-recorded portion, were observed.

[0162] This example illustrates the case where the protective layer 4 was utilized as a hard layer.

EXAMPLE 37

[0163] On a polycarbonate substrate (Panlite, manufactured by Teijin Kagaku) having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as described above, a silicone acrylate layer having a thickness of 50 nm was formed thereon as a hard layer 6, a silver layer having a thickness of 50 nm was formed thereon by vacuum vapor deposition as a light reflective layer 3, and the same protective layer 4 as in Example 36 was formed thereon. The above substrate had a Rockwell hardness (ASTM D785) of M75 and a heat distortion temperature (ASTM D648) of 135°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 200°C.

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[0164] To this optical disc, data were recorded in the same manner as in Example 36, and then reproduced, whereby the reflectance of the semiconductor laser beam was 71%, I_{11}/I_{top} was 0.63, I_3/I_{top} was 0.33, and the block error rate BLER was 3.5×10^{-3}.

[0165] Further, the surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM (Scanning Tunneling Microscope) in the same manner as in Example 36, whereby deformation in the form of protuberances was observed at the pitted portion. The center portion of this deformation was slightly low, and the deformation 6 was found to have two peaks, as illustrated in Figure 15(b).

EXAMPLE 38

[0166] On a polycarbonate substrate (lupilon, manufactured by Mitsubishi Gas Kagaku) having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as above, an epoxy resin layer having a thickness of 50 nm was formed thereon as a hard layer 6, a gold film having a thickness of 50 nm was formed by vacuum vapor deposition thereon as a light reflective layer 3, and the same protective layer 4 as in Example 36 was formed thereon. The substrate had a Rockwell hardness (ASTM D785) of M75 and a heat distortion temperature (ASTM D648) of 132°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M90 and a heat distortion temperature (ASTM D648) of 140°C.

[0167] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.62, I_3/I_{top} was 0.32, and the block error rate BLER was 2.4×10^{-3}.

EXAMPLE 39

[0168] On a polystyrene substrate having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as above, an acrylate resin layer having a thickness of 50 nm was formed thereon as a hard layer 6, an epoxy resin was spin-coated thereon to improve the bonding properties, then a gold film having a thickness of 50 nm was formed by vacuum vapor deposition as the light reflective layer 3, and the same protective layer 4 as in Example 36 was formed thereon. The substrate had a Rockwell hardness (ASTM D785) of M80 and a heat distortion temperature (ASTM D648) of 89°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 100°C.

[0169] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.62, I_3/I_{top} was 0.31, and the block error rate BLER was 7.0×10^{-3}.

EXAMPLE 40

[0170] On a polymethyl methacrylate substrate having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as described above, then a polyester resin layer having a thickness of 50 nm was formed thereon as a hard layer 6, a gold layer having a thickness of 50 nm was formed thereon as a light reflective layer 3 by vacuum vapor deposition, an epoxy resin was further spin-coated thereon to improve the bonding properties, and then the same protective layer 4 as in Example 36 was formed. The substrate had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 110°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M110 and a heat distortion temperature (ASTM D648) of 115°C.

[0171] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.34, and the block error rate BLER was 8.0×10^{-3}.

EXAMPLE 41

[0172] On a polyolefin substrate having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as in Example 36 by using 1,1'-dibutyl-3,3,3',3'-tetramethyl-5,5'-diethoxyindodicarbocyanine perchlorate, then a silicone acrylate resin layer having a thickness of 50 nm was formed thereon as the hard layer 6, and a gold film having a thickness of 50 nm was formed thereon as the light reflective layer 3 by vacuum vapor deposition, an epoxy resin was spin-coated thereon to improve the bonding properties, and then the same protective layer 4 as in Example 36 was formed. The substrate had a Rockwell hardness (ASTM D785) of M75 and a heat distortion temperature (ASTM D648) of 140°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 200°C.

[0173] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 74%, I_{11}/I_{top} was 0.61, I_3/I_{top} was 0.33, and the block error rate BLER was 2.3×10^{-3}.

EXAMPLE 42

[0174] On an epoxy resin substrate having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as in Example 36 by using 1,1'-dibutyl-3,3,3',3'-tetramethyl-5,5'-diethoxyindodicarbocyanine perchlorate, and a silicone resin layer having a thickness of 50 nm was formed thereon as the hard layer 6, an aluminum film having a thickness of 50 nm was formed thereon as the light reflective

layer 3 by vacuum vapor deposition, and the same protective layer 4 as in Example 36 was formed thereon. The substrate had a Rockwell hardness (ASTM D785) of M90 and a heat distortion temperature (ASTM D648) of 135°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 180°C.

[0175] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 73%, I_{11}/I_{top} was 0.61, I_3/I_{top} was 0.30, and the block error rate BLER was 2.0×10^{-3}.

EXAMPLE 43

[0176] On a polycarbonate substrate (Panlite, manufactured by Teijin Kagaku) having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as described above, a silver film having a thickness of 50 nm was formed thereon as the light reflective layer 3 by vacuum vapor deposition, a silicone acrylate layer having a thickness of 50 nm was formed thereon as the hard layer 6, and the same protective layer 4 as in Example 36 was formed thereon. The substrate had a Rockwell hardness (ASTM D785) of M75 and a heat distortion temperature (ASTM D648) of 135°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 200°C.

[0177] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 71%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.34, and the block error rate BLER was 3.7×10^{-3}.

EXAMPLE 44

[0178] On a polycarbonate substrate (Iupilon, manufactured by Mitsubishi Gas Kagaku) having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as described above, a gold film having a thickness of 50 nm was formed thereon as the light reflective layer 3 by vacuum vapor deposition, and an epoxy resin layer having a thickness of 50 nm was formed thereon as the hard layer 6 which also served as a protective layer. The substrate had a Rockwell hardness (ASTM D785) of M75 and a heat deformation temperature (ASTM D648) of 135°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M90 and a heat distortion temperature (ASTM D648) of 140°C.

[0179] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.63, I_3/I_{top} was 0.33, and the block error rate BLER was 2.7×10^{-3}.

EXAMPLE 45

[0180] On a polystyrene substrate having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as described above, a gold film having a thickness of 50 nm was formed thereon as the light reflective layer 3 by vacuum vapor deposition, and an acrylate resin layer having a thickness of 50 nm was formed thereon as the hard layer 6 which served also as a protective layer. The substrate had a Rockwell hardness (ASTM D785) of M80 and a heat deformation temperature (ASTM D648) of 89°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 100°C.

[0181] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.63, I_3/I_{top} was 0.32, and the block error rate BLER was 7.1×10^{-3}.

EXAMPLE 46

[0182] On a polymethyl methacrylate substrate having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as described above, then, a gold film having a thickness of 50 nm was formed thereon as the light reflective layer 3 by vacuum vapor deposition, and an epoxy resin was spin-coated thereon to improve the bonding properties, and a polyester resin layer having a thickness of 50 nm was formed as the hard layer 6 which served also as a protective layer. The substrate had a Rockwell hardness (ASTM D785) of M100 and a heat deformation temperature (ASTM D648) of 110°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M110 and a heat distortion temperature (ASTM D648) of 115°C.

[0183] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.65, I_3/I_{top} was 0.34, and the block error rate BLER was 8.3×10^{-3}.

EXAMPLE 47

[0184] On a polyolefin substrate having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as in Example 36 by using 1,1'-dibutyl-3,3,3',3'-tetramethyl-5,5'-diethoxyindodicarbocyanine perchlorate, then a gold film having a thickness of 50 nm was formed thereon as the light reflective layer 3 by vacuum vapor deposition, an epoxy resin was spin coated thereon to improve the bonding properties, and a silicone acrylate resin layer having a thickness of 50 nm was formed thereon as the hard layer 6 which served also as a protective layer. The substrate had a Rockwell hardness (ASTM D785) of

M75 and a heat distortion temperature (ASTM D648) of 140°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 200°C.

[0185] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 71%, I_{11}/I_{top} was 0.62, I_3/I_{top} was 0.34, and the block error rate BLER was 2.4×10^{-3}.

EXAMPLE 48

[0186] On an epoxy resin substrate having the same shape and pregroove as in Example 36, a light absorptive layer 2 was formed in the same manner as in Example 36 by using 1,1'-dibutyl-3,3,3',3'-tetramethyl-5,5'-diethoxyindodicarbocyanine perchlorate, then an aluminum film having a thickness of 50 nm was formed thereon as the light reflective layer 3 by vacuum vapor deposition, and a silicone resin layer having a thickness of 50 nm was formed as the hard layer 6 which served also as a protective layer. The substrate had a Rockwell hardness (ASTM D785) of M90 and a heat distortion temperature (ASTM D648) of 135°C. Whereas, the above hard layer 6 had a Rockwell hardness (ASTM D785) of M100 and a heat distortion temperature (ASTM D648) of 180°C.

[0187] To this optical disc, data were recorded in the same manner as in Example 36 and then reproduced, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.62, I_3/I_{top} was 0.32, and the block error rate BLER was 2.1×10^{-3}.

COMPARATIVE EXAMPLE 2

[0188] An optical disc was prepared in the same manner as in Example 36 except that in Example 36, the protective layer 4 made of the ultraviolet curable resin was formed to have a Rockwell hardness (ASTM D785) of M60 and a heat distortion temperature (ASTM D648) of 90°C under a load of 4.6 kg/cm^2 after curing.

[0189] To this optical disc, a semiconductor laser beam having a wavelength of 780 nm was irradiated at a linear speed of 1.2 m/sec to record EFM signals in the same manner as in Example 36, whereby no adequately distinct pits were observed on the substrate 1. Then, this optical disc was played back by the same CD player as used in Example 36, whereby the reflectance of the optical disc was 71%, I_{11}/I_{top} was 0.7, I_3/I_{top} was 0.37, but the block error rate BLER was 1.5×10^{-1} and thus failed to meet the CD standards.

EXAMPLE 49

[0190] An optical disc was prepared in the same manner as in Example 1 except that in Example 1, an ultraviolet curable hard coating resin was spin-coated on the incident light side of the polycarbonate substrate 1 to form a substrate protective layer having a thickness of 1 μm.

[0191] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 1. Then, this optical disc was played back by the same CD player as in Example 1, whereby the reflectance of the semiconductor laser beam was 70%, I_{11}/I_{top} was 0.62, I_3/I_{top} was 0.37, and the block error rate BLER was 1.3×10^{-2}.

[0192] The surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1, to confirm the formation of pits 5 as in Example 1.

EXAMPLE 50

[0193] An optical disc was prepared in the same manner as in Example 1 except that in Example 1 a polybutadiene resin dissolved in cyclohexane was spin-coated to form a polybutadiene resin layer having a thickness of 10 nm between the light absorptive layer 2 and the light reflective layer 3.

[0194] To the optical disc thus obtained, EFM signals were recorded in the same manner as in Example 1. Then, this optical disc was played back by the same CD player as in Example 1, whereby the reflectance of the semiconductor laser beam was 72%, I_{11}/I_{top} was 0.65, I_3/I_{top} was 0.35, and the block error rate BLER was 8.6×10^{-3}.

[0195] Further, the surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1, to confirm the formation of pits 5 as in Example 1.

EXAMPLE 51

[0196] A polycarbonate substrate 1 having a thickness of 1.2 mm, an outer diameter of 120 mm and an inner diameter of 15 mm and having a spiral pregroove 8 formed on its surface with a width of 0.8 μm, depth of 0.08 μm and a pitch of 1.6 μm, was injection-molded. As an organic dye to form the light absorptive layer 2, 0.5 g of 1,1'-dipropyl-3,3,3',3'-tetramethyl-5,5'-diethoxyindodicarbocyanine perchlorate was dissovled in 10 mℓ of an isopropyl alcohol solvent. The solution was spin-coated on the surface of this substrate 1, to form a light absorptive layer 2 having a thickness of 100 nm. Further, a SiO_2 film was formed thereon by sputtering in a thickness of 40 nm.

[0197] Then, a gold film having a thickness of 50 nm was formed by sputtering on the entire surface of a region of the diameter of from 45 to 118 nm of this disc, to form a light reflective layer 3. Further, on this light reflective layer 3, a urethane resin dissolved in methyl ethyl ketone was spin-coated in a thickness of 100 nm to form a shock absorbing layer, and an ultraviolet curable resin was spin-coated thereon and cured by irradiation of ultraviolet rays to form a protective layer 4 hav-

ing a thickness of 10 μm.

[0198] To the optical disc thus obtained, a semiconductor laser beam having a wavelength of 780 nm was irradiated at a linear speed of 1.2 m/sec with a recording power of 6.8 mW to record EFM signals. Then, this optical disc was played back by a commercially available CD player (Aurex XR-V73, wavelength of the reading laser beam λ = 780 nm), whereby the reflectance of the semiconductor laser beam was 77%, I_{11}/I_{top} was 0.66, I_3/I_{top} was 0.36, and the block error rate BLER was 3.5×10^{-3}.

[0199] Further, the surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1 to confirm the formation of pits 5 as in Example 2.

EXAMPLE 52

[0200] An optical disc was prepared in the same manner as in Example 51 except that in Example 51, the SiO_2 film was formed by LPD method, and a dioxane solvent was used as the solvent for the coating agent for forming the light absorptive layer 2.

[0201] To the optical disc thus obtained, EFM signals were recorded with a power of 7.2 mW in the same manner as in Example 51. Then, this optical disc was played back by the same CD player as in Example 51, whereby the reflectance of the semiconductor laser beam was 77%, I_{11}/I_{top} was 0.66, I_3/I_{top} was 0.35, and the block error rate BLER was 4.0×10^{-3}.

[0202] Further, the surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1 to confirm the formation of pits 5 as in Example 1.

EXAMPLE 53

[0203] An optical disc was prepared in the same manner as in Example 51 except that in Example 51, instead of the SiO_2 film, an epoxy resin dissolved in diglycicyl ether was spin-coated to form an epoxy resin layer having a thickness of 40 nm, a thin layer of an alloy of gold and titanium in a ratio of 9:1 was formed as the light reflective layer 3, and a polybutadiene resin dissolved in cyclohexane was spin-coated to form a polybutadiene resin layer having a thickness of 10 nm between the light absorptive layer 2 and the light reflective layer 3.

[0204] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.0 mW in the same manner as in Example 51. Then, this optical disc was played back by the same CD player as in Example 51, whereby the reflectance of the semiconductor laser beam was 74%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.33, and the block error rate BLER was 2.5×10^{-3}.

[0205] Further, the surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1 to confirm the formation of pits 5 as in Example 1.

EXAMPLE 54

[0206] An optical disc was prepared in the same manner as in Example 51 except that in Example 51, instead of the SiO_2 film, an epoxy resin dissolved in diglycicyl ether was spin-coated to form an epoxy resin layer having a thickness of 40 nm, a thin layer of an alloy of gold and titanium in a ratio of 9:1 was formed as the light reflective layer 3, and a polybutadiene resin dissolved in cyclohexane was spin-coated to form a polybutadiene resin layer having a thickness of 10 nm between the light absorptive layer 2 and the light reflective layer 3, and a bisphenol curable type epoxy resin was spin-coated in a thickness of 20 nm between the light reflective layer and the protective layer 4 to improve the adhesion therebetween.

[0207] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.2 mW in the same manner as in Example 51. Then, this optical disc was played back by the same CD player as in Example 51, whereby the reflectance of the semiconductor laser beam was 74%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.33, and the block error rate BLER was 3.0×10^{-3}.

[0208] Further, the surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1 to confirm the formation of pits 5 as in Example 1.

EXAMPLE 55

[0209] An optical disc was prepared in the same manner as in Example 51 except that in Example 51, instead of the SiO_2 film, an epoxy resin dissolved in diglycicyl ether was spin-coated to form an epoxy resin layer having a thickness of 40 nm, a polybutadiene resin dissolved in cyclohexane was spin-coated to form a polybutadiene resin layer having a thickness of 10 nm between this epoxy resin layer and the light reflective layer 3, and the thickness of the protective layer was changed to 5 μm.

[0210] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.2 mW in the same manner as in Example 51. Then, this optical disc was played back by the same CD player as in Example 51, whereby the reflectance of the semiconductor laser beam was 74%, I_{11}/I_{top} was 0.64, I_3/I_{top} was 0.32, and the block error rate BLER was 3.3×10^{-3}.

[0211] Further, the surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1 to confirm the formation of pits 5 as in Example 1.

EXAMPLE 56

[0212] An optical disc was prepared in the same manner as in Example 51 except that in Example 51, no SiO_2 film was formed, a polybutadiene resin dissolved in cyclohexane was spin-coated to form a polybutadiene res-

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in layer having a thickness of 10 nm between the light absorptive layer 2 and the light reflective layer 3, a bisphenol curable type epoxy resin was spin-coated in a thickness of 20 nm between the light reflective layer and the protective layer 4 to improve the adhesion therebetween, and the thickness of the protective layer was changed to 5 μm.

[0213] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.2 mW in the same manner as in Example 51. Then, this optical disc was played back by the same CD player as in Example 51, whereby the reflectance of the semiconductor laser beam was 74%, I_{11}/I_{top} was 0.63, I_3/I_{top} was 0.32, and the block error rate BLER was 2.8×10^{-3}.

[0214] Further, the surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1 to confirm the formation of pits 5 as in Example 1.

EXAMPLE 57

[0215] An optical disc was prepared in the same manner as in Example 51 except that in Example 51, no SiO_2 film was formed.

[0216] To the optical disc thus obtained, EFM signals were recorded with a recording power of 7.2 mW in the same manner as in Example 51. Then, this optical disc was played back by the same CD player as in Example 51, whereby the reflectance of the semiconductor laser beam was 77%, I_{11}/I_{top} was 0.66, I_3/I_{top} was 0.35, and the block error rate BLER was 1.0×10^{-2}.

[0217] Further, the surface of the light transmitting substrate 1 of the optical disc after recording was inspected by STM in the same manner as in Example 1 to confirm the formation of pits 5 as in Example 1.

[0218] As described in the foregoing, according to the optical information recording medium of the present invention, it is possible to form pits optically similar to CD by irradiation with a laser beam, and at the same time, the reflective layer is provided behind the light absorptive layer in close contact therewith, whereby it is possible to take a layered structure similar to CD. Thus, according to the present invention, a recordable optical information recording medium which meets the CD format, can readily be obtained.

Claims

1. A method for optically recording information on an optical information recording medium, the medium comprising

   (i) a light transmitting substrate (1),
   (ii) a light absorptive dye layer (2) overlaying the substrate it) to absorb a laser beam (7), and
   (iii) a light reflective layer (3) overlaying the light absorptive layer (2), the method comprising energizing the light absorptive layer (2) by the energy of a laser beam (7) entered through the light transmitting substrate (1), to form optically readable pits **characterized in that**

   said optically readable pits are formed either

   (a) in the surface of the substrate (1) adjacent to the absorptive layer (2) and in the absorptive layer (2), or
   (b) in the surface of the substrate (1) adjacent to the absorptive layer (2), in the absorptive layer (2), and additionally in an additional inter-layer (6) disposed between the substrate (1) and the light absorptive layer (2),

   all said layers having a suitable heat distortion and/or a suitable hardness.

2. The method according to claim 1, wherein the light absorptive layer (2) is melted and decomposed upon absorption of the laser beam (7), and said layers are locally deformed by the melting and the decomposition of the light absorptive layer (2), to form optically readable pits in said layers.

3. An optical information recording medium comprising

   (i) a light transmitting substrate (1),
   (ii) a light absorptive dye layer (2) overlaying the substrate (1) to absorb a laser beam (7) to form optically readable pits, and
   (iii) a light reflective layer (3) overlaying the light absorptive layer,

   characterized in that said optically readable pits are formed either

   (a) in the surface of the substrate (1) adjacent to the absorptive layer (2) and in the absorptive layer (2), or
   (b) in the surface of the substrate (1) adjacent to the absorptive layer (2), in the absorptive layer (2), and additionally in an addtional inter-layer (6) disposed between the substrate (1) and the light absorptive layer (2),

   all said layers having a suitable heat distortion and/or a suitable hardness.

4. The optical information recording medium according to claim 3, wherein the deformation of the surface layer consists in protuberances towards the light absorptive layer.

5. The optical information recording medium according to claim 3 or 4, wherein the deformed portions

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of said layers have optical properties different from the rest of said layers.

6. The optical information recording medium according to claim 3, 4 or 5, wherein the deformed portions of layers adjacent to the absorptive layer contain decomposed components of the light absorptive layer diffused therein.

7. The optical information recording medium according to any one of claims 3 to 6, wherein the surface of the substrate or the additional layer has a tracking guide groove, and the optically readable pits are formed in the guide groove.