Special Issue New Thin Film Multilayered Systems for Recordable Optical Disc Memory Compatible with CD and DVD

Research Report

Noise Reduction and Improvement of Reflectance in the Dielectric/Metal Thin Film Multilayered Recordable Optical Disc Memory

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Abstract

We have developed a new type of recordable optical disc memory using an inorganic thin film multilayered system: substrate/GeS_2/ZnS-SiO_2/Ge-doped Sn-Bi. The recording mechanism utilized in the system is based on a redox reaction between GeS_2 and Sn-Bi. Insertion of the ZnS-SiO_2 layer suppressed the reaction between GeS_2 layer and Ge-doped Sn-Bi layer during the deposition processes, and improved the reflectance of the disc. Use of Sn-57wt.%Bi eutectic alloy resulted in fine crystalline grains and reduced the white noise level of the disc in playing with the drive. The Ge doping into Sn-Bi alloy improved durability of the disc. The disc employing the newly developed multilayered system could be used for recording with commercially available CD-R drives and could be played with CD-ROM drives. It had a monotonous dependence of reflectance on wavelength over a wide range and showed rather high reflectance at both the wavelengths used in CD and DVD drives.

Keywords: Recordable optical disc, Compact disc, Thin film, Barrier layer, Reflectance, Eutectic alloy, Durability, Grain size, Redox reaction, GeS_2

1. Introduction

The recordable optical disc, CD-R,[1] on which users can record data but cannot erase them, is widely used for image data storage and archival use, etc. due to its low cost and compatibility with CD-ROM drives. However, CD-R cannot be played with the DVD system equipped only with 650 nm laser diode, because CD-R does not have enough reflectance to be played at a wavelength of 650 nm.[2] This is because the organic dye used in its recording layer is designed to have a specific feature[2] around the recording and playing wavelength of 780 nm in its optical absorption spectrum.

We have proposed a new type of recordable optical disc memory having an inorganic thin film multilayered system.[3] The principle of the recording mechanism is utilization of an interlayer exothermic chemical reaction between a transparent inorganic dielectric layer and a highly reflective metal layer triggered by a recording laser irradiation.[4] The reaction decreases both the transmittance of the dielectric layer and the reflectance of the metal layer, resulting in the formation of recording pits with low reflectance.[5] Monotonous dependence of reflectance on wavelength in a wide range from 400 nm to 800 nm is expected in this inorganic disc memory, because there is no specific optical absorption feature like that found in the organic dye. Therefore, recording on and playing the disc would be possible at various wavelengths.

Under the above-mentioned principle, we have developed a multilayered disc (substrate/GeS_2 /metal with a low melting point such as indium (In)) which has enough recording sensitivity comparable to that of CD-R as reported in our previous report.[4] However, this disc had two serious disadvantages: low reflectance even before recording, and high white noise level compared with CD-R, resulting in unsuccessful recording with CD-R drives and unsuccessful playing with CD-ROM drives. In this study, we found the origin of these disadvantages and solutions to realize a new disc that can be used for recording with CD-R drives and can be played with CD-ROM drives.

2. Experimental

2. 1 Sample preparation

Disc samples of multilayered structure (substrate/GeS_2/metal with a low melting point) were fabricated by successive sputter-deposition on a pre-grooved polycarbonate disc in the previously reported method.[4] Materials of the metal were In, indium-silver (In-3wt.%Ag),[6] and tin-bismuth (Sn-57wt.%Bi)[7] eutectic alloys as shown **Fig. 1**. The GeS_2 layer thickness was 140-180 nm, and the metal layer thickness was 40-60 nm. Finally, organic resin curable by ultraviolet light irradiation was spin-coated on the metal layer

2. 2 Method to test recordability of the disc

The recordability of the disc samples was evaluated in the previously reported procedure.[4] *CNR* is defined as the ratio of carrier signal to noise level when recorded data on a disc are played. Reflectance and *CNR* of discs were measured using a spectrum analyzer and a dynamic tester equipped with a 780 nm laser diode and an objective lens of numerical aperture 0.53. A rectangular pulse signal (duty ratio of 50%, frequency of 400 kHz), which roughly corresponded to an 11T signal of CD system,[8] was used to modulate the laser power incident onto the rotating disc at a constant linear velocity of 2.8 m/s. The minimum recording laser power is defined as the laser power necessary to obtain a *CNR* over 47 dB. The laser power to record the signal was varied from 2 mW to 12 mW,

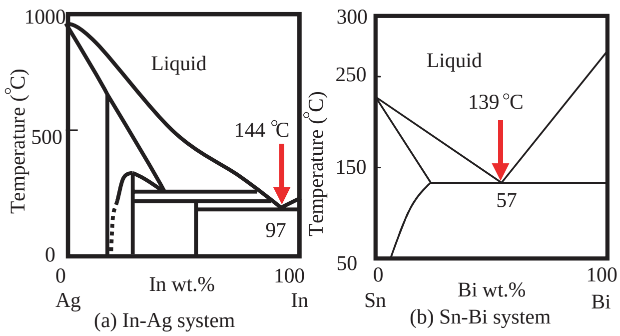

Fig. 1 Binary alloy phase diagrams.
(a) Indium - Silver (In-Ag) alloy[6]
(b) Tin - Bismuth (Sn-Bi) alloy[7]
Arrows indicate the eutectic temperature and composition.

whereas the laser power to play was set to be 0.8 mW. The durability of the discs was tested by checking if they could be used for recording with CD-R drives and played with the CD-ROM drives before and after storage in an oven at 70 °C and relative humidity of 50% for 96 hours. The reflectances of the discs before and after the durability test were also measured.

3. Results and discussion

3. 1 Improvement of the reflectance by insertion of the barrier layer

Reflectance of the disc with the structure of substrate/GeS_2/In before recording was much lower than that of the disc using single layer of In (substrate/In). The origin of the low reflectance of the disc (substrate/GeS_2/In) is considered to be the undesirable reaction between GeS_2 and In during the deposition process. The following reaction occurs easily during the deposition of In on the GeS_2 layer,

$$GeS_2 + In \rightarrow GeS + InS, \cdots\cdots\cdots\cdots (1)$$

because the calculated heat of reaction (Q : + 50 kcal /mol) according to the reported data[9] is positive when GeS_2 reacts with In. Since the reaction product was not metallic but colored dark gray, reflectance of the disc decreased.

In order to solve this problem, we inserted a barrier layer between the GeS_2 layer and the metal layer to suppress the undesirable reaction, as shown in **Fig. 2**. ZnS-SiO_2 was chosen for this barrier layer, since the calculated Q (-65 kcal/mol) for reaction between ZnS-SiO_2 and In is negative at temperatures between 300 K and 1000 K, showing ZnS-SiO_2 does not spontaneously react with In. Changing the thickness from 1 nm to 5 nm, the barrier layer was deposited on the GeS_2 layer by sputter-deposition.

Figure 3 shows the dependence of the reflectance before recording and the minimum recording laser power on the thickness of the sputter-deposited ZnS-SiO_2 barrier layer in the structure of substrate /GeS_2/ZnS-SiO_2/In. While the minimum recording laser power increased monotonously with the barrier layer thickness, the reflectance showed the maximum around 1-2 nm; that is, the optimal value for the present system. Insertion of the ZnS-SiO_2 barrier layer contributed to getting out of the trade-off relation between the reflectance before recording and the recording laser power, as shown in **Fig. 4**. The resultant new write-once discs could be used for recording with CD-R drives, and they could be played with plural different CD-ROM drives. However, there are some CD-ROM drives which could not play these discs.

3. 2 Improvement of CNR by employing eutectic alloy

Although sufficient reflectance was obtained by insertion of a ZnS-SiO_2 barrier layer, the noise level of the disc having the structure of substrate /GeS_2/ZnS-SiO_2/In was found to be higher than that of CD-R. To find the reason for the higher noise

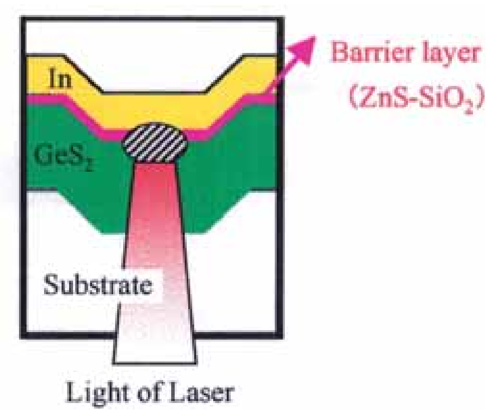

Fig. 2 Schematic illustration of the disc memory with a barrier layer of ZnS-SiO_2 inserted between the GeS_2 and the In layers.

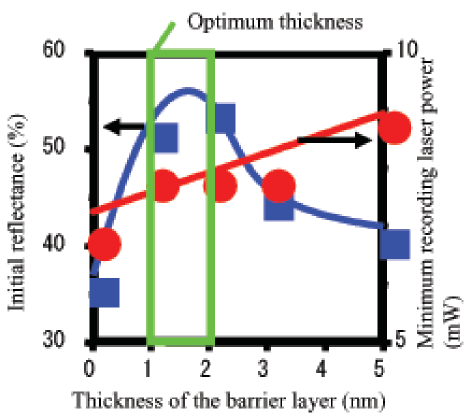

Fig. 3 Dependence of the reflectance and the minimum recording laser power on the thickness of the barrier layer of the disc employing substrate/ GeS_2/ZnS-SiO_2/In. Lines are guide to eye.

level, the recording pits and their surroundings were observed by transmission electron microscopy (TEM). **Figure 5**(a) shows the TEM images of recording pits of the disc having the structure of substrate/GeS_2/ZnS-SiO_2/In. The crystalline grains in the In layer were not small as compared with the laser beam diameter (approximately 1 μm) or the recording pits. The large grains of In layer cause the scattering of laser light, resulting in the increase of white noise level.

The use of eutectic alloys with low melting temperatures may lead to a reduction in crystalline grain size, since phase separation of each metal constituting a eutectic alloy at the eutectic temperature causes an increase in the number of crystalline nuclei. In-3wt.%Ag and Sn-57wt.%Bi eutectic alloys were examined as the metal layer materials. While In-Ag disc gave almost the same noise level as an In disc, an Sn-Bi disc gave a lower noise level than In disc. These results were supported by TEM observation of the smaller crystalline grain size in the Sn-Bi layer shown in Fig. 5(b) than in the In layer shown in Fig. 5(a). The edges of the recording pits of the Sn-Bi disc were clear and their forms were not distorted so much as those of the In disc. **Figure 6** shows the signal patterns and the *CNR* values at the minimum recording laser power of 8 mW for the discs having the structure of substrate/ GeS_2/ZnS-SiO_2/ (In or Sn-Bi). The modulated pattern of the Sn-Bi disc was closer to the rectangular signal of the incident laser than that of the In disc, whereas the reflectance before recording of the Sn-Bi disc was almost the same as that of the In disc.

This resulted in the improvement of the *CNR* of the Sn-Bi disc in comparison with the In disc. Therefore, Sn-Bi alloy was selected as the metal for the disc having the structure: substrate/GeS_2/ZnS-SiO_2/metal.

3. 3 Improvement of durability by doping Ge into the Sn-Bi layer

Sn-Bi alloy was found to be effective for noise reduction. Since Sn-Bi is an alloy used for a soft solder, it is known that Sn-Bi is easily oxidized.[10] This may lead to poor durability of the disc. Doping of oxygen-gettering material may improve the durability. The durability of Sn-Bi solder was also reported to be improved by doping Ge.[10] Following

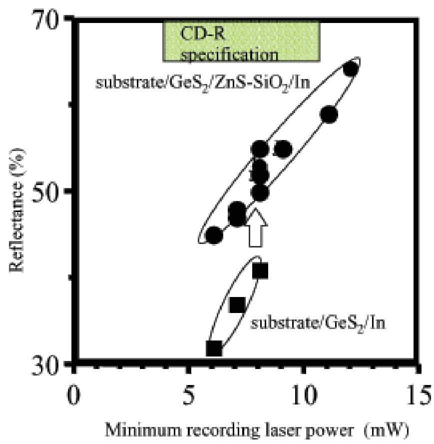

Fig. 4 Relation between the reflectance before recording and the minimum recording laser power of the discs employing substrate/GeS_2/ZnS-SiO_2/In and substrate/GeS_2/In.

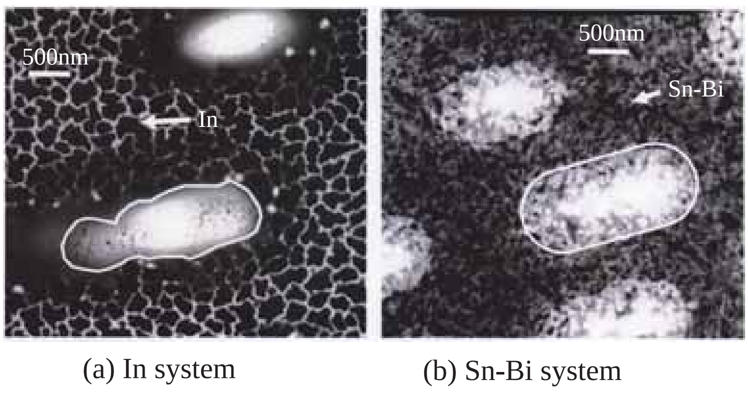

Fig. 5 Transmission electron microscope (TEM) images of the recording pits on the discs using substrate/GeS_2/ZnS-SiO_2/(In or Sn-Bi). Arrows indicate the crystalline grains of the metal layers.

this result, doping of 1 mol.% Ge into Sn-Bi alloy was also adapted in order to improve the durability of the substrate/GeS_2/ZnS-SiO_2/Sn-Bi disc.

Table 1 shows the change in reflectance of the substrate/GeS_2/ZnS-SiO_2/metals (In or Sn-Bi or Ge-doped Sn-Bi) after storage at 70 °C and 95% R.H. for 96 hrs. Among the three, the In disc showed the largest change in reflectance. After the durability test, the In disc could not be played with any of the CD-ROM drives. The Sn-Bi disc could be played with only limited number of CD-ROM drives used in the examination. The Ge-doped Sn-Bi disc showed the smallest change in reflectance, and could be played with all of the CD-ROM drives used. Thus, Ge doping into Sn-Bi was effective for improvement of disc durability, although whether or not it depressed the oxidation of Sn-Bi is unclear.

Table 1 Performance of the disc memory with (substrate/GeS_2/ZnS-SiO_2/metals) multi-layer systems after durability test of 70 °C, 50%R.H., 96 hrs.

Metals	Change of reflectance (%)	Ability of playing with CD-ROM drives
In	24	No good
Sn-Bi	8	Moderate
Ge-doped Sn-Bi	5	Good

3. 4 Comparison of spectral reflectance of the newly developed multilayered optical disc with that of conventional CD-R

The spectral reflectance of the newly developed (substrate/GeS_2/ZnS-SiO_2/Ge-doped Sn-Bi) multilayered optical disc is shown in **Fig. 7** along with that of CD-R. The newly developed disc shows monotonous dependence of reflectance on wavelength over a wide range and showed high reflectances at two different wavelengths for the CD system and the DVD system.

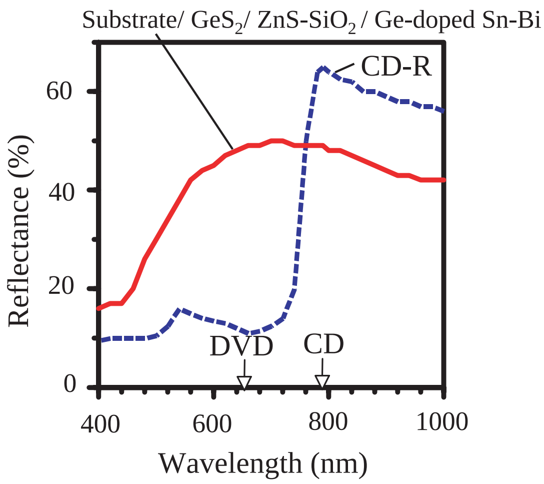

Fig. 7 Reflectance spectra of the disc memory using substrate/GeS_2/ZnS-SiO_2/Ge-doped Sn-Bi and CD-R. Arrows indicate the wavelength of CD system and DVD system.

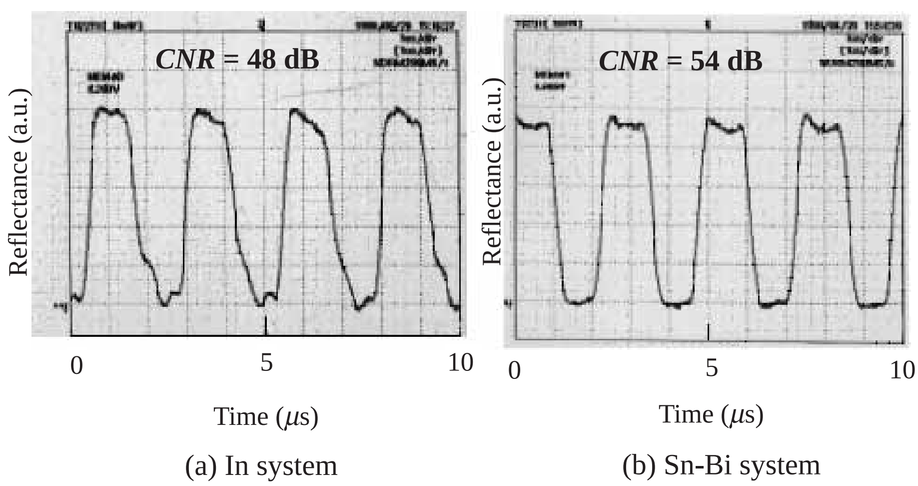

Fig. 6 Signal patterns and *CNR* values of the disc memory using substrate/GeS_2/ZnS-SiO_2/ (In or Sn-Bi).

4. Conclusion

Insertion of the barrier layer ($ZnS\text{-}SiO_2$) improved the reflectance of the GeS_2/metal thin film multilayered optical disc memory. This effect is due to the suppression of reaction during the deposition of the GeS_2 layer and the metal layer. The crystalline grain size became small by employing Sn-57wt.%Bi eutectic alloy, resulting in a reduction in the noise level. The durability of the disc was improved by doping Ge into Sn-Bi alloy.

We have realized a new type of recordable optical disc memory using the (substrate/GeS_2/$ZnS\text{-}SiO_2$ /Ge-doped Sn-Bi) multilayered system. The disc memory could be used for recording with CD-R drives and could be played with CD-ROM drives. Recording and played were possible after the durability test carried out at 70 °C and 50%R.H. for 96 hrs.

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