Research Report

Interface Reaction between a Metal Mirror Layer and a Dielectric Transparent Layer Triggered by Laser Irradiation for a New Recording Mechanism

Tatsuo Fukano, Naohiko Kato, Yasuhiko Takeda, Akihiro Takeichi, Tomoyoshi Motohiro

Abstract

A new optical recording mechanism based on an interface reaction in thin film multi-layered systems was proposed. Its three basic concepts are (1) use of an interface exothermic redox reaction between a high reflective metal mirror layer and an inorganic dielectric transparent layer triggered by a recording laser irradiation and maintained by the exothermic heat of reaction, (2) reduction by thermal dissipation and enhancement of reactivity by simultaneous melting of the metal mirror layer at the recording laser irradiation, (3) disuse of poisonous materials. The performance of this new recording mechanism for write-once type optical disc memories was studied. Sufficient sensitivity was obtained with the interface reaction between the transparent GeS_2 layer and the highly reflective, low-melting In or Sn-57wt.%Bi eutectic alloy layer. The resultant systems showed monotonous wavelength dependences of the reflectance in contrast to specific optical absorption features of the organic dyes in conventional CD-R and DVD-R. This feature allows potential application to a write-once type disc memory compatible with CD (780 nm) and DVD (635 nm).

Keywords: Optical memory, Redox reaction, Exothermic reaction, Melting, Inorganic material, Metal, Multilayer, GeS_2, In, Sn, Bi

1. Introduction

The recording layer used in commercially available optical disc memories of the write-once type (CD-R or DVD-R) consists of an organic dye layer and a metal mirror layer. When a CD-R is irradiated by a recording laser, the recording pits are formed by decomposition or degeneration of the dye succeeded by deformation of the metal reflective layer, resulting in reflectance decrease.

The organic dye is designed to have a specific spectral absorption feature around the recording and playing wavelength so as to have an appropriate recording sensitivity. Therefore, digital data information recorded on a CD-R can not be read with commercially available DVD drives using only a 635-nm laser, or with next generation DVD drives using 405-nm lasers.

To get rid of this inconvenience, we propose a concept of the recording mechanism for a new write-once type optical disc memory, that is, the use of an interface exothermic redox reaction between a mirror layer and an inorganic dielectric transparent layer triggered by a recording laser irradiation and maintained by the exothermic heat of reaction. The reaction decreases both the reflectance of the metal layer and the transmittance of the dielectric layer, resulting in the formation of recording pits with low reflectance. **Figure 1** shows the schematic diagram of this concept of the recording mechanism and the stack structure for the new write-once type optical disc memory.

This structure is not to give a specific spectral absorption feature like the organic dye, but rather to give a monotonous spectral reflectance which enables recording and playing over a wide wavelength range.

To be playable with CD-ROM drive, optical disc memories are requested to have reflectance as high as 65%. However, the selection of a metal for the mirror layer is not a simple problem. Drude theorem based on a free electron model for metals supports Hargen-Rubens relation between reflectance R and electric conductivity σ in the wavelength range used for an optical disc as follows:

$$R \sim 1\text{-}2\{\,\omega\ /(2\pi\sigma)\}^{1/2},$$

where ω stands for frequency of light. Therefore, to obtain high reflectance, metals with high electric conductivity have to be chosen.

The Wiedemann-Franz law tells the relation between thermal conductivity K and electric conductivity σ; K is proportional to σ as follows:

$$K / \sigma = \pi^2 \,(k_{\mathrm{B}} / e)^2\, T / 3,$$

where k_{B}, e and T stand for Boltzmann constant, elementary electric charge, and temperature, respectively.

Therefore, the two established relations lead to the fact that metals of high reflectance generally possess high thermal conductivity.

High thermal dissipation due to high thermal conductivity of a metal layer leads to insufficient temperature rise of a recording layer during a recording laser irradiation to trigger the interface exothermic redox reaction between the transparent layer and the mirror layer. Therefore, the recording layer using high reflectance metal leads to low recording sensitivity.

To overcome this ineludible relation between the R and K of metal, the second concept was introduced; that is, utilization of both the reduction of thermal dissipation[1)] and enhancement[2)] of reactivity by instantaneous melting of the metal mirror layer during the recording laser irradiation. Thermal conductivity of not a few metals decreases as much as 50 % when they melt as shown for the typical

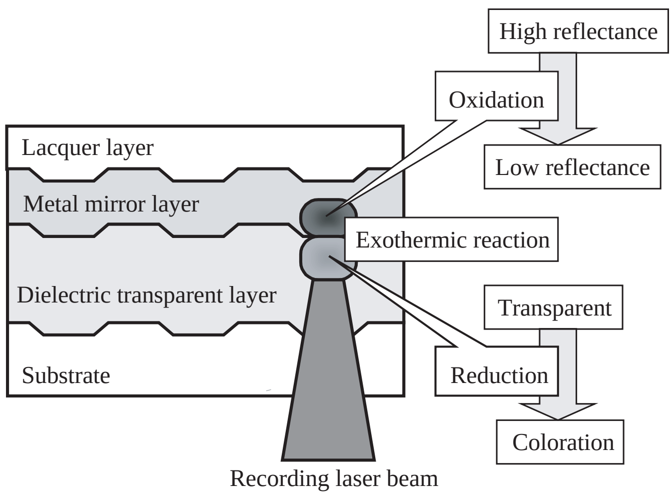


Fig. 1 Schematic diagram of the new principal concept of recording mechanism and the multi-layered structure for the new optical disc memory.

case in **Fig. 2.**[1)]

Therefore, a recording layer with high reflectance and high recording sensitivity can be realized if a highly reflective metal with a low melting point is employed.

In conventional CD-R and DVD-R, or in their production process, poisonous materials such as Sb, Te, Pb or organic solvents are used which environmental. Therefore, the third concept proposed is disuse of poisonous materials.

In the present work, the new thin film multi-layered systems based on the three concepts were developed for a new write-once type optical disc memory.

2. Experimental

2. 1 Materials for the new thin film multi-layered systems

Starting from a WO_3/Al system, various combinations of transparent oxide / metal have been examined. However, recording sensitivity could not be sufficiently lowered, the details of which will be described elsewhere.

As for sulfide, transparent and stable materials are limited practically to GeS_2 and ZnS. The GeS_2 and ZnS thin films with the high transmittance could be easily fabricated using the conventional sputter deposition.

Combinations between these dielectric materials and metals were tested for the recording layers of optical disc memories of the write-once type. In (melting point: 157°C) and Sn-57wt.%Bi eutectic alloy (melting point: 139°C) were selected as highly reflective metals with low melting points. Ag, Al, Au, Cu, 50vol.%Ag-Al alloy, 50vol.%Cu-Al alloy and 69vol.%Mg-Al alloy were also used for highly reflective metals with relatively high melting points for comparison.

2. 2 Stack structure of the new thin film multi-layered system

The thicknesses of the transparent layers were set so that the maximums in reflectance spectra due to optical interference effect come around 780 nm. The thicknesses of the mirror layers were adjusted to several tens of nanometers.

2. 3 Construction of a sputter-coating apparatus for fabricating 120-mm optical disc memories

Figure 3 shows a sputter-coating newly designed for laboratory stage of coating on 120-mm optical disc substrates. The rotary and revolutionary motion of disc substrates as well as a relatively large cathode-substrate distance of 150 mm makes it possible to attain a thickness uniformity of < ±5 %. Three RF-magnetron cathodes with 4-inch sputtering targets are equipped in the vacuum chamber to enable coating three layers at most without breaking

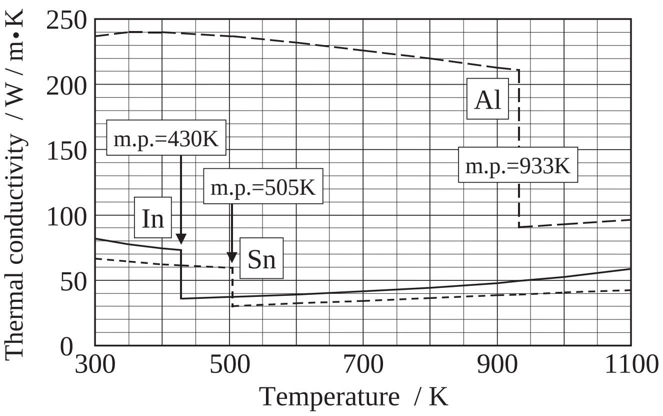


Fig. 2 Thermal conductivity versus temperature of several kinds of metals.[1)]
—— : In, ---- : Sn, – – : Al.

Fig. 3 Photograph of new sputter-coating apparatus with 3 RF-magnetron 4 inch-cathodes in a vacuum chamber (right).

the vacuum.

2. 4 Coating conditions

The sputter-deposition conditions of the thin film multi-layered systems were as follows. The vacuum chamber was evacuated to 1×10^{-3} Pa and then Ar gas was introduced up to 3×10^{-3} Pa for sputtering. The polycarbonate disc substrate of 120 mm has a pre-groove for tracking. A lacquer layer was spin-coated on the recording layer and then UV-hardened to protect the recording layer.

2. 5 Method of testing recordability: reflectance, modulation, carrier-to-noise ratio

Recordability of the disc samples was studied by measuring the reflectance, the modulation and the carrier (carrier signal of digital information) to noise ratio (*CNR*). The reflectance spectrum was measured with a spectrophotometer. The modulation (*Mod*) is defined as follows:

$Mod = \{R(bef)-R(aft)\}/R(bef)$,

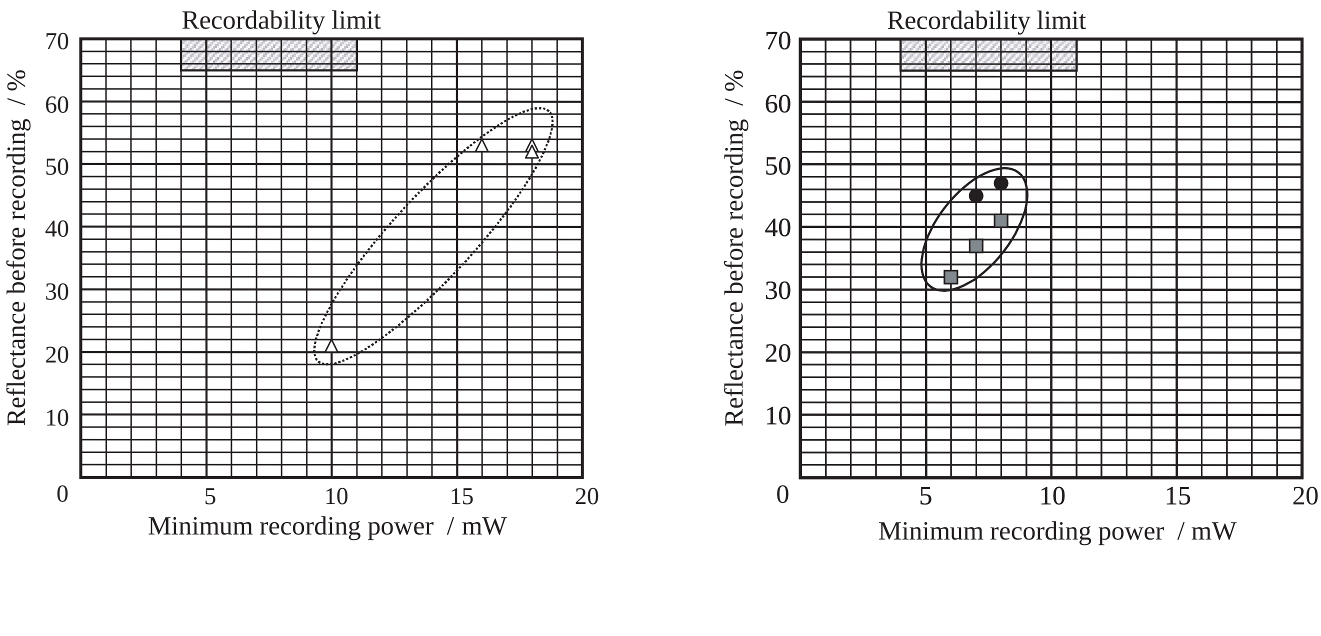
where $R(bef)$ and $R(aft)$ stand for the reflectances of the disc samples before and after recording, respectively. *CNR* was measured by a write-read analyzer system (model OMS-2000, Nakamichi) for optical discs. The intensity of the laser beam is defined as the laser beam power at the recording spot on the disc sample.

The digital data was recorded on the rotating disc samples at a constant linear velocity of 2.8 m/sec with the recording laser of a wavelength: 780 nm focused by an objective lens of NA (numerical aperture): 0.53. The recording laser was modulated at 400 kHz to form a rectangular wave of 50% duty ratio with its power varied from 0 to 19 mW. The reading laser power was 0.6 mW, much smaller than the recording laser power.

3. Results and discussion

3. 1 Metals of relatively high melting points

Alloy films were formed by co-deposition using two different pure metal targets. The compositions



(a) In the case of using Au, Cu, 50vol.%Ag-Al or 50vol.%Cu-Al as a metal with a rather high melting point for a mirror layer.

(b) In the case of using In or Sn-57wt.%Bi as a metal with a low melting point for a mirror layer.

Fig. 4 Reflectance before recording versus minimum recording power of disc samples using combinations of the transparent GeS_2 layer and a mirror layer of several kinds of reflective metals.
△ : Au, Cu , 50vol.%Ag-Al and 50vol.%CuAl, ■ : In, ● : Sn-57wt.%Bi as metals for a mirror layer.

were estimated from each deposition rate.

The disc samples using ZnS with any kinds of metals showed no change of the reflectance, modulation nor *CNR* at a recording laser power up to 19 mW. The disc samples using GeS_2 and Ag, Al or Mg-Al alloy showed no change, either. When Au, Cu, Ag-Al alloy or Cu-Al alloy layer with a thickness between 50 nm and 70 nm was used with a GeS_2 layer with a thickness of about 194 nm, increases in *CNR* of the disc samples were observed with increasing recording power. In these cases, the recording power dependence of *CNR* of the disc samples showed a plateau or a broad peak with its maximum value being far below 47 dB: the lowest *CNR* level acceptable for the write-once type optical disc memories. In this case, the minimum recording power was defined as the lowest recording power at which the largest *CNR* was obtained.

Figure 4(a) shows the relation between reflectance before recording and the minimum recording power of the disc samples with which the *CNR* increase were observed. The extent of recordability limit is defined by the minimum reflectance.[3] Both the reflectance and *CNR* of these disc samples were, however, lower than the values of the recordability limit. It was confirmed that the reactivities between GeS_2 and these metals with relatively high melting points (~ 650°C-1085°C) were low.

3. 2 Metal of low melting points

The effect of the metals with low melting points on the improvement of the reactivity between the GeS_2 transparent layer and the metal mirror layer was examined.

Disc samples using combinations of the transparent GeS_2 layer with a thickness of about 180 nm and a mirror In layer or a mirror Sn-Bi layer with a thickness between 40 nm and 60 nm were estimated. In this case, the minimum recording power was defined as the lowest power of the recording laser beam at which digital data could be recorded on the write-once type optical disc memories with *CNR*s larger than 47 dB. In contrast to the case of metals with relatively high melting points, the *CNR*s of these disc samples reached 47 dB at recording laser powers of less than 19 mW.

The minimum recording powers of these disc samples were improved to reach the extent of recordability limit by the use of In or Sn-Bi, as shown in Fig. 4(b). Their reflectances were, however, still lower than the required level.

The reflectances of the disc samples using In were significantly lower than the value estimated from that of a single In layer with the same thickness used for the mirror layers. It was suggested that the decrease in reflectance of GeS_2/In was caused by an unexpected interface reaction between the GeS_2 layer and the In layer during the sputtering depositions of In on the GeS_2 layer. In was found to be too active to be utilized for the mirror layer.

4. Conclusion

A new optical recording mechanism based on an interface reaction in thin film multi-layered systems was proposed in order to get rid of the inconvenience that digital data recorded on a commercially available CD-R could not be read with commercially available DVD drives equipped with only a 650-nm laser or the next generation DVD drives equipped with 405-nm lasers. Its basic concept is to utilize the interface exothermic redox reaction between the GeS_2 transparent layer and the reflective In or Sn-Bi mirror layer with low melting points triggered by the recording laser irradiation. Using these systems, digital data could be recorded on the disk samples having *CNR*s larger than 47 dB at recording laser powers of less than 10 mW. These systems had high recording sensitivities, as well as monotonous wavelength dependence of the reflectance. These features allow potential application to a write-once type disc memory compatible with CD (780 nm) and DVD (635 nm).

Acknowledgements

This work was carried out in collaboration with ITS Engineering Department 2 and Corporate R&D Department of Denso Corporation.

References

1) Touloukian, Y. S., et al. : Thermal Conductivity, (1970), IFI/PLENUM
2) Motoki, Y., et al. : *Seramikku Kogaku Handobukku* (in Japanese), (1989), Gihodosyuppan
3) Nakajima, H., et al. : *CD Famiri* (in Japanese), (1996), Ohmusya

(Report received on July 24, 2003)

Tatsuo Fukano
Year of birth : 1960
Division : Research-Domain 34
Research fields : Solid state physics, Inorganic material science, Optical science
Academic society : Jpn. Soc. Appl. Phys., Ceram. Soc. Jpn., Electrochem. Soc. Jpn.
Awards : 38th Annu. R&D 100 Award, 2000

Naohiko Kato
Year of birth : 1965
Division : Research-Domain 34
Research fields : Photo-functional interfaces, Solar energy materials
Academic society : Jpn. Soc. Appl. Phys., Chem. Soc. Jpn.
Awards : 38th Annu. R&D 100 Award, 2000

Yasuhiko Takeda
Year of birth : 1965
Division : Research-Domain 34
Research fields : Optical properties of inorganic materials
Academic degree : Dr. Eng.
Academic society : Jpn. Soc. Appl. Phys., Opt. Soc. Jpn.
Awards : 38th Annu. R&D 100 Award, 2000

Akihiro Takeichi
Year of birth : 1967
Division : Research-Domain 34
Research fields : Solid state physics, Optical measurement
Academic society : Jpn. Soc. Appl. Phys., Laser Soc. Jpn.
Awards : 38th Annu. R&D 100 Award, 2000

Tomoyoshi Motohiro
Year of birth : 1953
Division : Research-Domain 34
Research fields : Thin films and surface science, Solar energy materials, Renewable energy and new energy resources
Academic degree : Dr. Eng.
Academic society : Surf. Sci. Soc. Jpn., Soc. for Sci. on Form, Jpn. Soc. Appl. Phys., Opt. Soc. Jpn., MRS
Awards : 38th Annu. R&D 100 Award, 2000